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

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Received and published: 04 August 2016

Anonymous Referee # 1, Summary and Recommendation: “*This manuscript summarizes quantitative and semi-quantitative data obtained for organosulfates chemically characterized from $PM_{2.5}$ 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 $PM_{2.5}$ (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 $PM_{2.5}$ (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 $PM_{2.5}$ (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 NO_x oxidation products of isoprene (Bates et al., 2016; Krechmer et al., 2015)), as well as MVK and isoprene nitrates (ISOPN) that are high NO_x 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 NO_x (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 NO_x 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/$PM_{2.5}$ 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 $PM_{2.5}$ and less than 0.3 % of OC (Table 1). Meanwhile, organosulfates are estimated to contribute 1-2 % of $PM_{2.5}$ 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 MS^2 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 MS^2? 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 MS^2 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 MS^2 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, $C_5H_{10}NSO_9^-$ (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; $C_{10}H_{16}NSO_{10}^-$ (342.0495), $C_{10}H_{16}NSO_8^-$ (310.0597 (Ma et al., 2014; Surratt et al., 2008)) and $C_{10}H_{16}NSO_7^-$ (294.0647) (Table S1 and Fig. S4). The nitro-oxy organosulfate $C_{10}H_{16}NSO_7^-$ (294.0647) accounted for 25 % of the total *m/z* 96 signal in $PM_{2.5}$ 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 $C_4H_7SO_4^-$ (151.0065), $C_3H_5SO_4^-$ (136.9909) and $C_5H_8NO_8S^-$ (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 $PM_{2.5}$ 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 ($PM_{2.5}$; particles ≤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 $PM_{2.5}$ 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.*”

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 $PM_{2.5}$. 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.*"

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

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Received and published: 04 August 2016

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* $PM_{2.5}$*, (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 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 $PM_{2.5}$ (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 $PM_{2.5}$ (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 $PM_{2.5}$ (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 NO_x oxidation products of isoprene (Bates et al., 2016; Krechmer et al., 2015)), as well as MVK and isoprene nitrates (ISOPN) that are high NO_x 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 NO_x (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 NO_x 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 $PM_{2.5}$ and less than 0.3 % of OC (Table 1). Meanwhile, organosulfates are estimated to contribute 1-2 % of $PM_{2.5}$ 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 MS^2 organosulfate signals are qualitatively and semi-quantitatively examined in Sect. 3.3."

The text will be 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 $C_5H_{11}SO_7^-$ (215.0225), $C_5H_9SO_7^-$ (213.0069), $C_3H_5SO_5^-$ (152.9858) and isoprene ozonolysis products $C_4H_7SO_6^-$ (182.9963) and $C_5H_{11}SO_6^-$ (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 ($C_5H_9SO_6^-$) 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 (≥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 NO_x 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 $HSO_3^{-\cdot}$ (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 NO_x conditions (Zhang et al., 2012a) and $C_4H_7O_4^-$ (119.0341, -0.3) whose mass spectrum matched that of 2-methylglyceric acid sulfate (Fig S5). An isoprene-derived nitro-oxy organosulfate, $C_5H_{10}NSO_9^-$ (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, $C_3H_5SO_5^-$ (152.9858) and $C_3H_7SO_5^-$ (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 $C_7H_{11}SO_7^-$ (239.0225; Fig. 3d) and $C_{10}H_{16}NSO_{10}^-$ (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 $C_{10}H_{17}SO_7^-$ (281.0695; observed in 90 % of the samples analyzed) $C_{10}H_{17}SO_8^-$ (297.0644), $C_7H_{11}SO_6^-$ (223.0276) and $C_{10}H_{15}SO_7^-$ (279.0538) (Table S2 and Fig. S2 and S3). Monoterpene-derived nitro-oxy organosulfates were particularly responsive to precursors of *m/z* 96; $C_{10}H_{16}NSO_{10}^-$ - (342.0495), $C_{10}H_{16}NSO_8^-$ (310.0597) and $C_{10}H_{16}NSO_7^-$ (294.0647) (Table S1 and Fig. S4). The nitro-oxy organosulfate $C_{10}H_{16}NSO_7^-$ (294.0647) accounted for 25 % of the total *m/z* 96 signal in $PM_{2.5}$ 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 $C_4H_7SO_4^-$ (151.0065), $C_3H_5SO_4^-$ (136.9909) and $C_5H_8NO_8S^-$ (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 $C_{12}H_{25}SO_4^-$ (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 ($C_5H_{11}SO_7^-$; 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, $C_5H_9SO_7^-$ (213.0069) and $C_5H_7SO_7^-$ (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 $C_4H_7SO_6^-$ (182.9963) in Centreville, AL. Likewise, $C_{10}H_{16}NSO_{10}^-$ (342.0495) and $C_7H_{11}SO_7^-$ (239.0225) are expected to be among abundant monoterpene derived organosulfates in Centreville, AL. Similar to Riva et al. (2016), $C_5H_{11}SO_6^-$ (199.0276) is relatively abundant in Centreville, but further experiments are need to identify its origin. Because of their relatively strong MS^2 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 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?*"

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 counteracting 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 ($PM_{2.5}$; particles ≤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.*”

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.*”

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 $PM_{2.5}$ 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 (Q_B) and sulfuric acid impregnated back-up QFF (Q_B-H_2SO_4; H_2SO_4 - 8.65 μg cm^{-2}) collected in series behind front QFF (Q_F) that collected $PM_{2.5}$ (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 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* H_2O *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 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 $PM_{2.5}$ 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 $PM_{2.5}$ 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*"

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*"

Introduction, Page 3, Line 9 originally read: "Thus MS^2 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 MS^2 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*"

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"?*"

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.*"

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: "*MS^2 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 MS^2 of precursor ions in the response to technical comment 4.

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Qualitative and Quantitative Analysis of Atmospheric Organosulfates in Centreville, Alabama

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Abstract. Organosulfates are components of secondary organic aerosols (SOA) that form from oxidation of ~~biogenic~~ volatile organic compounds (VOC) in the presence of sulfate. In this study, the composition and abundance of organosulfates were determined in fine particulate matter ($PM_{2.5}$) collected from Centreville, AL ~~from 07-11 July 2013~~ during the Southern Oxidant and Aerosol Study (SOAS) in 2013. Six organosulfates were quantified using hydrophilic interaction liquid chromatography (HILIC) with triple quadrupole mass spectrometry (TQD) against authentic standards~~ compounds~~. Among these, the three most abundant species were glycolic acid sulfate (0.5 – 52.5 ng m^{-3})~~(2.4 – 27.3 ng m^{-3})~~, lactic acid sulfate (0.5 – 36.7 ng m^{-3})~~(1.4 – 22.1 ng m^{-3})~~ and hydroxyacetone sulfate (0.5 – 14.3 ng m^{-3})~~(0.5 – 8.7 ng m^{-3})~~. These three species were strongly inter-correlated, suggesting similar precursors and/or formation pathways. Further correlations with sulfate, isoprene and isoprene oxidation products indicate important roles for these precursors in organosulfate formation in Centreville. Positive filter sampling artifacts associated with these organosulfates due to gas adsorption ~~and~~ or reaction of gas phase~~their VOC~~ precursors of organosulfates with sulfuric acid were assessed for a subset of samples and ~~found to be negligible (at ≤~~ were less than 7.~~3~~ 8 % of their ~~measured~~ $PM_{2.5}$ concentrations~~)~~. Together, the quantified organosulfates accounted for < 0.3 % of organic carbon mass in $PM_{2.5}$. To gain insights to other organosulfates in $PM_{2.5}$ collected from Centreville, semi-quantitative ~~and qualitative~~ analysis ~~were~~ was employed by way of monitoring of ~~precursors to the bisulfate anion (a~~ characteristic product ions of organosulfates (HSO_4^- at *m/z* 97 and $SO_4^{\cdot -}$ at *m/z* 96) and evaluating relative signal strength~~)~~ by HILIC-TQD. ~~and determining their molecular~~ Molecular formulas~~ and fragmentation by~~ of organosulfates were determined by high-resolution time-of-flight (ToF) mass spectrometry. The major organosulfate signal across all samples corresponded to 2-methyltetrol sulfates, which accounted for 42 – 62 % of the total bisulfate ion signal. Whereas, glycolic acid sulfate, the most abundant organosulfate quantified in this study, was 0.13 - 0.57 % of the total

bisulfate ion signal. Precursors of *m/z* 96 mainly consisted of nitro-oxy organosulfates. ~~Most~~ Nine of the ten strongest~~of the ten most prevalent~~ organosulfate signals were associated with biogenic VOC precursors (i.e. isoprene, monoterpenes, and 2-methyl-3-buten-2-ol [MBO]). While a small number of molecules dominated the total organosulfate signal, a large number of minor species were also present. This study provides insights to the major organosulfate species in the Southeastern US, as measured by tandem mass spectrometry~~,~~ that should be targets for future standard development and quantitative analysis.

1 Introduction

Atmospheric fine particulate matter ($PM_{2.5}$; particles ≤2.5 µm in aerodynamic diameter) adversely affects human health (Valavanidis et al., 2008; Anderson et al., 2011; Kim et al., 2015~~; Rosenfeld et al., 2014; Levy et al., 2013~~) and influences the Earth's climate via direct and indirect radiative forcing (Novakov and Penner, 1993; Haywood and Boucher, 2000). A significant fraction of $PM_{2.5}$ organic matter is ~~comprised of~~ secondary in ~~organic aerosols (SOA)~~origin (Zhang et al., 2011), and forms by atmospheric oxidation ~~that form from~~ reactions of volatile organic compounds (VOC) and partitioning of reaction products ~~yielding semi-volatile products that partition~~ to the aerosol phase (Hallquist et al., 2009). Among secondary organic aerosols (SOA) ~~products~~ are organosulfates, which are mainly produced from acid-catalyzed particle-phase reactions ~~in the presence~~ of gaseous oxidation products such as epoxides (Lin et al., 2012) and hydroperoxides (Mutzel et al., 2015) with 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; Liao et al., 2015). Important precursors to organosulfates have been identified through a combination of field and laboratory studies, and include biogenic VOC such as isoprene (Surratt et al., 2007b), monoterpenes (Iinuma et al., 2009), sesquiterpenes (Chan et al., 2011), 2-methyl-3-buten-2-ol (MBO) (Zhang et al., 2012a) and 3-Z-hexenal (Shalamzari et al., 2014). ~~Sulfate in the atmosphere is generated by the oxidation of~~ SO_2 ~~that is primarily emitted by fossil fuel combustion (Wuebbles and Jain, 2001; Chin and Jacob, 1996).~~ Thus, organosulfates may be useful markers for sulfate-~~of anthropogenically~~ influenced biogenic SOA.

$PM_{2.5}$ mass in the Southeastern (SE) US is dominated by sulfate and organic matter~~PM~~ (Attwood et al., 2014) and is highly acidic with pH ranging from 0.5-2 in summer and 1-3 in winter (Guo et al., 2015). SOA accounts for a significant fraction of organic $PM_{2.5}$ in SE US (Lee et al., 2010) and is expected~~suggested~~ to derive primarily from isoprene (Ying et al., 2015). Together, high ~~sulfate,~~ isoprene, sulfate and aerosol acidity make ~~the atmosphere in~~ the SE US prime for the formation of sulfate-influenced biogenic SOA, including organosulfates. ~~subject to anthropogenic influences on biogenic SOA formation (Weber et al., 2007; Goldstein et al., 2009; Watson et al., 2015).~~ The Southern Oxidant and Aerosol Study (SOAS) which took place in 01 June–15 July of 2013 was focused on studying the SOA formation in the SE US and ~~their~~ its impact~~s~~ on air quality and climate. The ground site discussed in this paper was situated in Centreville, AL, a rural, forested site which is mainly characterized by high isoprene emissions and to a lesser extent by other biogenic VOC such as monoterpenes, and is affected by anthropogenic pollutants from nearby cities such as Montgomery, Birmingham and Tuscaloosa (Hagerman et al., 1997), thus an ideal location for studying organosulfates derived from biogenic VOC. ~~, a long-standing rural air quality monitoring station that is part of the Southeastern Aerosol and Research Characterization (SEARCH) network.~~

The o~~O~~rganosulfate~~s have been widely identified throughout the SE US. Their overall~~ contribution to $PM_{2.5}$ organic mass is estimated to have an upper limit of 5.0 -~~10~~ 9.3 % in the SE US (Tolocka and Turpin, 2012), suggesting that organosulfates ~~may~~ contribute significantly to organic aerosol mass in this region. A limited, but growing number of organosulfates have been accurately quantified against authentic standards. The most abundant organosulfates to be

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previously quantified, during SOAS 2013, using authentic standards include ~~Among them are most abundant organosulfate has been~~ 2-methyltetrol sulfate (Budisulistiorini et al., 2015; Rattanavaraha et al., 2016), ~~followed by~~ 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)~~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)~~. ~~These measurements indicate an important role for isoprene as a precursor to organosulfates in the SE US.~~ The quantification of organosulfates is currently limited by very few atmospherically relevant standards being commercially available, requiring the development of standards by synthesis (Olson et al., 2011; Staudt et al., 2014; Hettiyadura et al., 2015; Rattanavaraha et al., 2016). In the absence of authentic standards, surrogate standards are commonly ~~instead~~used, but can lead to significant and often uncharacterized biases that result from differences in negative electrospray ionization ((-) ESI) ~~ionization~~ efficiencies (Staudt et al., 2014). Authentic standards are thus required for accurate quantification and determination of their contributions to PM mass.

~~With organosulfate quantification in its infancy, it remains important to develop authentic standards to extend quantification of this class of compounds.~~

~~In order to accurately determine organosulfate contribution to PM mass and constrain anthropogenic influences on biogenic SOA formation, an improved understanding of organosulfate concentrations and composition is needed. Mass spectrometry (MS) in the negative electrospray ionization mode ((-) ESI) is widely used to detect organosulfates (Iinuma et al., 2007; Gómez-González et al., 2008; Altieri et al., 2009; Reemtsma et al., 2006; Romero and Oehme, 2005). The bisulfate anion is identified as a characteristic fragment ion of organosulfates (Gómez-González et al., 2008; Romero and Oehme, 2005). Thus~~ ~~MS^2 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. Offline MS detection of organosulfates is often coupled with liquid chromatography (LC). Reverse phase LC-MS methods are suitable for separation of aromatic and monoterpene derived organosulfates that contain hydrophobic moieties (e.g. aromatic rings or long alkyl chains) (Stone et al., 2012), but do not retain carboxy- and polyhydroxy-organosulfates that instead co-elute with sulfate and other organic compounds. Hydrophilic interaction liquid chromatography (HILIC) has been demonstrated to have complementary selectivity to reversed phase separation and is preferred for retention of carboxyl-containing organosulfates (Hettiyadura et al., 2015).~~

~~Relevant to the quantification of organosulfates is the potential for artifacts during sampling and analysis. Gas phase compounds can adsorb on to quartz fiber filters (QFF) during sampling giving rise to positive filter sampling artifacts (Zhu et al., 2012; Turpin et al., 2000; Turpin et al., 1994). This may be important to quantitative analysis of organosulfates that have been observed in the gas phase such as glycolic acid sulfate (Ehn et al., 2010). In addition, a recent study that assessed sampling artifacts has shown formation of organosulfates on β-pinene oxide (a gas phase oxidized product of monoterpene) adsorbed QFF suggesting that organosulfates can also form from further oxidation and sulfation of adsorbed gases during~~

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~~sampling (Kristensen et al., 2016). Thus characterizing the extent of artifacts in ambient sampling is needed to ensure accurate measurements of organosulfates.~~

Mechanistic studies have revealed pathways by which organosulfates form and have been reviewed elsewhere (Hallquist et al., 2009; Surratt et al., 2010; Ervens et al., 2011; Darer et al., 2011; Riva et al., 2015). Here, we focus on organosulfates that have been ~~The following description focuses on species~~ quantified against authentic standards in the SE US during SOAS. 2-Methyltetrol sulfates ~~and 2-methylglyceric acid sulfate~~ primarily form ~~from~~ by acid-catalyzed nucleophilic addition of sulfate to isoprene epoxydiols~~epoxides~~ (IEPOX) (Surratt et al., 2010). They may also form ~~In addition, 2-methyltetrol sulfates can form from~~ by nucleophilic substitution of nitrate in organonitrates with sulfate ~~from the corresponding organonitrates~~ (Darer et al., 2011) and ~~from~~ isoprene ozonolysis in the presence of acidified sulfate seed aerosol (Riva et al., 2016). 2-~~methylglyceric~~ Methylglyceric acid sulfate forms from either methacrylic acid epoxide (Lin et al., 2013b) or hydroxymethyl-methyl-α-lactone (isoprene oxidation products), similarly to 2-methyltetrol sulfates, in the presence of sulfate under high NO_x conditions (Nguyen et al., 2015). ~~Formation of g~~Glycolic acid sulfate ~~has been observed~~ f~~ro~~orms more efficiently from glycolic acid relative to ~~reactive uptake of~~ glyoxal in the presence of acidic sulfate (Liao et al., 2015), while both precursors have ~~.to neutral or acidic sulfate aerosol upon irradiation (Galloway et al., 2009). Lactic acid sulfate is also suggested to form from similar pathways from methylglyoxal (Shalamzari et al., 2013). Glycolic acid and Gglyoxal and methylglyoxal have form from both~~ biogenic and anthropogenic ~~precursors~~origins (Liao et al., 2015; Fu et al., 2008). ~~precursors, although isoprene is their major source. There is also evidence for formation of l~~Lactic acid sulfate and hydroxyacetone sulfate can form ~~from~~via isoprene photo-oxidation in the presence of acidic sulfate (Surratt et al., 2008), while ~~. L~~lactic acid sulfate ~~can also forms~~may also derive from 2-E-pentenal, a photolysis product of 3-Z-hexenal (Shalamzari et al., 2015). In addition, ~~Organosulfates may also form from~~ sulfate ~~radical~~ radical-induced oxidation can form organosulfates ~~in the presence of an acidified sulfate radical precursor~~under acidic conditions~~, by which 2-methylterol sulfate forms from isoprene while other products form from isoprene oxidation products; for example,~~ ; following this pathway, methyl vinyl ketone (MVK) can generate 2-methylglyceric acid sulfate, glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate while methacrolein (MACR) ~~is a precursor to~~can form 2-methylglyceric acid sulfate and hydroxyacetone sulfate (Schindelka et al., 2013; Nozière et al., 2010). Alternatively, hydroxyacetone sulfate can form from isoprene ozonolysis in the presence of acidified sulfate seed aerosol (Riva et al., 2016). Organosulfate product distributions are thus expected to depend on precursor gas concentrations, acidity, and oxidant concentrations. ~~Prior mechanistic studies have revealed multiple pathways for biogenic organosulfates to form, which depend on the availability of reactants in the ambient atmosphere.~~

~~In order to accurately determine organosulfate contribution to PM mass and constrain anthropogenic influences on biogenic SOA formation, an improved understanding of organosulfate concentrations and composition is needed.~~ Mass spectrometry (MS) ~~in the negative electrospray ionization mode (~~with (-) ESI~~)~~ is widely used to detect organosulfates (Iinuma et al., 2007; Gómez-González et al., 2008; Altieri et al., 2009; Reemtsma et al., 2006; Romero and Oehme, 2005). The bisulfate anion (HSO_4^- at *m/z* 97) and sulfate radical ($SO_4^{\cdot-}$ at *m/z* 96) is identified as a characteristic fragment ion of

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organosulfates (Gómez-González et al., 2008; Romero and Oehme, 2005; Surratt et al., 2008). Tandem mass spectrometry (~~Thus~~ MS^2), in which precursors to these ions ~~of precursors to bisulfate ion (which scan all the precursors of a common product ion)~~ can be used as a means of identifying organosulfates and ~~for~~ semi-quantifying them ~~ication of organosulfates~~ in the absence of authentic standards (Stone et al., 2009)~~,~~. The inherent~~;~~ ~~however there are some~~ limitations of this approach to semi-quantitation are~~which have been~~ discussed in Sect. 3.3. Offline MS detection of organosulfates is often coupled with liquid chromatography (LC). Reverse phase LC-MS methods are suitable for separation of aromatic and monoterpene derived organosulfates that contain hydrophobic moieties (e.g. aromatic rings or long alkyl chains) (Stone et al., 2012), but do not retain carboxy- and polyhydroxy-organosulfates that instead co-elute with sulfate and other organic compounds. Hydrophilic interaction liquid chromatography (HILIC) has been demonstrated to have complementary selectivity to reversed phase separation and is preferred for retention of carboxyl-containing organosulfates (Hettiyadura et al., 2015).

Filter-based aerosol measurements are subject to sampling artifacts, such as g~~Relevant to the quantification of organosulfates is the potential for artifacts during sampling and analysis. G~~as ~~phase compounds can~~ adsorbption on to quartz fiber filters (QFF) during sampling ~~giving rise to positive filter sampling artifacts~~ (Zhu et al., 2012; Turpin et al., 2000; Turpin et al., 1994). ~~This may be important to quantitative analysis of organosulfates that have been observed in the gas phase such as glycolic acid sulfate (Ehn et al., 2010). In addition, a~~A recent study demonstrated ~~that assessed sampling artifacts has shown~~ formation of organosulfates ~~on~~from β-pinene oxide (a gas phase monoterpene oxidation~~oxidized~~ product ~~of monoterpene~~) adsorbed onto QFF, suggesting that organosulfates can also form ~~from further oxidation and sulfation of adsorbed gases~~ on QFF during sampling (Kristensen et al., 2016). Thus, characterizing the extent of artifacts in ambient sampling is needed to ensure accurate measurements of organosulfates.

The central objectives of this study include; i) quantification of select organosulfates in $PM_{2.5}$ collected from Centreville, AL from 13 June – 13 ~~07-11~~ July~~,~~ 2013 during SOAS against authentic standards ~~by HILIC coupled to a triple quadrupole mass spectrometry (TQD) methodology developed by Hettiyadura et al. (2015)~~, ii) assessment of correlations of select organosulfates with co-located measurements such as sulfate, aerosol water, aerosol acidity and potential VOC precursors, iii) evaluation~~assessment~~ of the extent of positive filter sampling artifacts associated with select ~~these~~ organosulfates ~~due to gas adsorption and reaction of their VOC precursors with sulfuric acid,~~ and ~~iii~~iv) identification of the major organosulfates in Centreville, AL using semi-quantitative MS^2. For the latter two objectives a smaller subset of samples collected from 07 – 11 July 2013 were analyzed~~,~~ and the extent to which these samples represent the typical conditions observed during SOAS is discussed in Sect. 3.2 and 3.3. ~~The third objective is complementary to that of Riva et al. (2016), who focused on identifying and semi-quantifying isoprene-derived organosulfates in Centreville during SOAS, particularly those that form through ozonolysis reactions.~~ Through these efforts we expand the understanding of organosulfates ~~concentrations~~ in Centreville, AL during SOAS 2013 and constrain the extent to which positive filter sampling artifacts affect quantitation. In addition, the major organosulfates identified during this study provide new insights to the organosulfates that should be targets for future standard development.

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2 Materials and methods

2.1 Chemicals and reagents

Methyl sulfate (sodium salt, 99 %, Acros Organics) and ethyl sulfate (sodium salt, 96.31 %, Sigma-Aldrich) standards were purchased. Benzyl sulfate (70.1 %) sodium salt was synthesized as described in Estillore et al. (2016). Hydroxyacetone sulfate and glycolic acid sulfate (potassium salts, > 95 %) were synthesized according to the method described in Hettiyadura et al. (2015). Lactic acid sulfate (24.9 %) was synthesized as described in Olson et al. (2011). Ultra-pure water was prepared on site (Thermo, Barnsted EasyPure-II; ~~> ~~18.2 MΩ cm resistivity, with OC < 40 µg/L). Other reagents included acetonitrile (Optima^{TM}, Fisher Scientific), ammonium acetate (≥ 99 %, Fluka, Sigma Aldrich) and ammonium hydroxide (Optima, Fisher Scientific).

2.2 $PM_{2.5}$ samples

$PM_{2.5}$ ~~S~~samples were collected from 13 June – 13 July, 2013 following the ~~on the basis of~~ daytime (8:00-19:00 LT) and nighttime (20:00-7:00 LT) schedule. $PM_{2.5}$ ~~samples were~~was collected ~~in duplicate~~ using two co-located medium-volume samplers (Teflon coated aluminum cyclone, ~~2.5 µm cut off, 92 lpm,~~ URG-3000B, URG Corporation~~; Fig. S1~~) on pre-baked (550 °C for 18 h) QFF (90 mm diameter, Pall Life Sciences). For the study of sampling artifacts during 07 - 11 July 2013, samplers were equipped with back-up QFF as described in section 2.3. ~~Samples were collected on the basis of daytime (8:00-19:00 LT) and nighttime (20:00-7:00 LT) schedule.~~ One field blank was collected for every five $PM_{2.5}$ samples following the same procedure, ~~but~~ without passing air through the filters. All filter samples collected were stored in Al-foil (pre-baked at 550 °C for 5.5 h) lined petri dishes and were kept frozen (-20.0 °C) under dark conditions until extracted.

2.3 Positive filter sampling artifacts

Positive filter sampling artifacts associated with ~~lactic acid sulfate,~~ glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate from 07-11 July 2013 were assessed using filter samples collected on bare back-up QFF (Q_B) and sulfuric acid impregnated back-up QFF ($Q_{B\text{-}H_2SO_4}$; H_2SO_4 - 8.65 µg cm^{-2}) collected in series behind front QFF (Q_F) that collected $PM_{2.5}$~~,~~ (Fig. S1). Q_B were used to assess positive filter sampling artifacts due to gas adsorption on QFF, while $Q_{B\text{-}H_2SO_4}$ were used to assess positive filter sampling artifacts due to gas adsorption and reactions of gas phase precursors of organosulfates ~~VOC~~ with sulfuric acid during sample collection. Positive filter sampling artifacts (% $f_{\text{artifacts}}$) were calculated as the percent of organosulfate (X) on Q_B or $Q_{B\text{-}H_2SO_4}$ relative to Q_F, according to Eq. (1):

$$\%f_{artifacts} = \left(\frac{[\mathrm{X}\ (\mathrm{ng\ m^{-3}})]_{\text{back up filter}}}{[\mathrm{X}\ (\mathrm{ng\ m^{-3}})]_{\text{front filter}}}\right) \times 100\% \qquad (1)$$

2.4 Sample preparation

Filter samples collected were prepared for the chemical analysis as described in Hettiyadura et al. (2015). Briefly, portions of filters (~ 15 cm^2) were extracted by sonication (20 min, 60 sonics min^{-1}, 5510, Branson) with acetonitrile and ultra-pure water (95:5, 10 mL), filtered through polypropylene membrane syringe filters (0.45 µm pore size, Puradisc^{TM}25PP, Whatman$^{®}$), and reduced the volume to 500 µL under a stream of ultra-high purity nitrogen gas (≤ 5 psi) at 50 °C using an evaporation system (Turbovap$^{®}$ LV, Caliper Life Sciences). Then the extracts were transferred to LC vials (1.5 mL, Agilent) and evaporated to dryness under a very light stream of ultra-high purity nitrogen gas at 50 °C using a microscale nitrogen evaporation system (Reacti-Therm III TS 18824 and Reacti-Vap I 18825, Thermo Scientific) and then reconstituted in 300 µL acetonitrile: ultra-pure water (95:5).

2.5 Chemical analysis

2.5.1 ~~PM$_{2.5}$ and~~ Organic carbon (OC)

~~PM$_{2.5}$ mass was measured every five minutes using a Tapered Element Oscillating Microbalance (TEOM, Thermo Scientific, R & P model 1400a/b) according to the method described in Edgerton et al. (2006). These data are available at http://esrl.noaa.gov/csd/groups/csd7/measurements/2013senex/Ground/DataDownload/. The TEOM was operated at 30 °C with a main flow of 3 lpm and an auxiliary flow of 13.7 lpm. The relative humidity was maintained < 20 %. PM$_{2.5}$ measured were averaged based on filter sample collection times.~~

OC mass was measured on 1.0 cm^2 punches of PM$_{2.5}$ sampled on Q$_F$ using a thermal-optical analyzer (Sunset Laboratory, Forest Grove, OR, USA) according to the Aerosol Characterization Experiment (ACE)-Asia protocol described in Schauer et al. (2003).

2.5.2 Co-located measurements during SOAS

PM$_{2.5}$, sulfate, aerosol acidity, aerosol water, isoprene, MACR, MVK, glyoxal, formaldehyde, isoprene hydroxyl nitrates (ISOPN), isoprene hydroxyl hydroperoxide (ISOPOOH) and IEPOX measured during SOAS from 13 June – 13 July 2013 were averaged across sample collection time. The methods used for quantification of each of these were published elsewhere:~~;~~ PM$_{2.5}$ and sulfate (Edgerton et al., 2006), aerosol acidity and aerosol water (Guo et al., 2015), isoprene, MACR and MVK (Goldan et al., 2004), glyoxal (Huisman et al., 2008), formaldehyde (Hottle et al., 2009; DiGangi et al., 2011), ISOPN (Crounse et al., 2006), ISOPOOH and IEPOX (St. Clair et al., 2016).

2.5.~~2~~ 3 Quantification of organosulfates using HILIC-TQD

Organosulfates were quantified using HILIC-TQD following Hettiyadura et al., (2015). Briefly, an ultra-performance liquid chromatography (UPLC; ACQUITY UPLC H-Class, Waters, Milford, MA, USA) with (-) ESI TQD

(AQCUITY, Waters) was employed in multiple reaction monitoring (MRM) mode. Optimized MS conditions (cone voltages and collision energies) used for each analyte in MRM mode were given in Hettiyadura et al. (2015). Organosulfates were separated using HILIC on an ethylene bridged hybrid amide (BEH-amide) column (2.1 × 100 mm, 1.7 µm particle size; AQCUITY UPLC Waters) using an acetonitrile rich eluent with 10 mM ammonium acetate buffered to pH 9 by adjustment with ammonium hydroxide. The aqueous portion of the eluent was held at 5 % for two minutes, then increased to ~19 % over two minutes and held constant until 11 minutes before column re-equilibration. The instrument was calibrated daily with a freshly-prepared seven point calibration standard series (0.500-500. µg L^{-1}). Data were acquired and processed using MassLynx software (version 4.1). All measurements were field blank subtracted.

The analytical uncertainty in organosulfate concentrations were calculated from the total relative uncertainty (% e_T) propagated according to Eq. (2), accounting for the relative errors in air volume (% e_V, 5 %), extraction efficiency (% e_E; which represents the difference in the observed and expected responses of quality control samples to which known amounts of analytes were added), and the relative error in instrumental analysis (% e_I; which is propagated from the instrument limit of detection and relative standard deviation of each organosulfate reported in Hettiyadura et al., 2015). For measurements requiring sample dilution, an additional error term (% e_D) was propagated considering the errors in initial and final volumes.

$$\%\,e_T = \sqrt{(\%\,e_V^2 + \%\,e_E^2 + \%\,e_I^2 + \%\,e_D^2)} \qquad (2)$$

2.5.~~3~~ 4 Qualitative analysis of major organosulfates in Centreville, AL

Major organosulfates in Centreville, AL were operationally defined as ions that fragmented to bisulfate anion (*m/z* 97) and sulfate radical (*m/z* 96) using HILIC-TQD in precursor ion mode across the ~~. In both precursor ion scans MS^2 data were collected in the~~ mass range 100-400 Da. For the precursors of *m/z* 97 ~~using~~ a cone voltage of 28 V and a collision energy of 16 eV were used. For the precursors of *m/z* 96 a cone voltage of 42 V and a collision energy of 20 eV were used~~.~~. The identified organosulfates underwent further characterization using UPLC (ACQUITY UPLC, Waters; Milford, MA, USA) coupled with (-) ESI time-of-flight mass spectrometry (TOF-MS) (Bruker Daltonics MicrOTOF). HILIC separation was performed as described previously (Sect. 2.5.2.), with a different capillary voltage of 2.8 kV, a sampling cone voltage of 30 V and a desolvation gas flow rate of 600 L h^{-1}. Data were collected in the mass range 100–400 Da in full scan mode. A peptide, Val-Tyr-Val (*m/z* 378.2029, Sigma-Aldrich), was used for continuous MS mass calibration. Molecular formulas were assigned considering the presence of $C_{0\text{-}500}$, $H_{0\text{-}100}$, $N_{0\text{-}5}$, $O_{0\text{-}50}$, $S_{0\text{-}2}$, odd and even electron state, and a maximum error of 6 mDa.

3 Results and discussion

3.1 Quantification of organosulfates in Centreville, AL

The ambient concentrations of the ~~four most abundant~~ organosulfates quantified against authentic standards in $PM_{2.5}$ collected from Centreville, AL from 13 June – 13 ~~07–11~~ July 2013 ~~for daytime and nighttime periods~~ are summarized in Table 1, and the three most abundant species are shown in Fig. 1 along with $PM_{2.5}$, OC and sulfate concentrations~~and summarized in Table 1~~. Glycolic acid sulfate was the most abundant organosulfate followed by ~~and~~ lactic acid sulfate, ~~are the most abundant organosulfates quantified followed by~~ hydroxyacetone sulfate~~ then~~, methyl sulfate, ethyl sulfate (detected only in 18 samples) and benzyl sulfate (detected only in 1 sample). ~~Benzyl sulfate was detected only in one daytime sample which was collected on 09 July at a concentration of 0.17 ± 0.08 ng m^{-3}. Ethyl sulfate was below instrument limit of detection (< 0.06 ng m^{-3}) in all ten samples analyzed.~~

~~Levels of glycolic acid sulfate and lactic acid sulfate were markedly higher in the SE US during SOAS compared to other regions during summer. The g~~Glycolic acid sulfate and lactic acid sulfate quantified in this study ranged from 0.5 – 52.5 ng m^{-3} ~~2.4 – 27.3 ng m^{-3}~~ and 0.5 – 36.7 ng m^{-3}~~1.4 – 22.1 ng m^{-3}~~, respectively (Table 1). At the nearby Birmingham, AL site during SOAS, similar organosulfate concentrations were reported: ~~which is an industrial and residential site even higher~~ glycolic acid sulfate averaged 26.2 ng m^{-3} and had a maximum value of ~~concentrations (~~75.2 ng m^{-3} while lactic acid sulfate (quantified using propyl sulfate as the surrogate standard) averaged 2.7 ng m^{-3} with a maximum value of 10.5 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}~~. These levels are significantly higher than the levels of glycolic acid sulfate and lactic acid sulfate reported previously in Bakersfield, CA (an urban site) from 16-18 June, 2010 ~~which were~~at 4.5 – 5.4 ng m^{-3} and 0.6 – 0.7 ng m^{-3}, respectively (Olson et al., 2011). T~~ogether, t~~hese data indicate higher levels of these organosulfates in the SE compared to the Southwestern US (California) during summer, but are limited by ~~the very~~ few measurements of organosulfates ~~reported~~ in the literature.

The total contribution of the organosulfates quantified using authentic standards ~~accounted for~~was less than ~~0.5 % of $PM_{2.5}$ and less than~~ 0.3 % of OC (Table 1). Meanwhile, ~~organosulfates are~~the estimated upper bound contribution of organosulfates to organic matter (OM) is 5.0 – 9.3 % in the SE US (Tolocka and Turpin, 2012). ~~to contribute 1-2 % of $PM_{2.5}$ and 5-10 % OC in Eastern US (Shakya and Peltier, 2015).~~ 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 ~~(with a~~ mean concentration of 207.1 ng m^{-3} and were estimated to account for 3.7% ~~)~~ ~~and~~while 2-methylglyceric acid sulfate ~~(with~~had a mean concentration of 10.2 ng m^{-3} and accounted for 0.2% of OM, ~~) in Centreville during SOAS 2013 account for 3.7 % and 0.2 % of OM, respectivel~~y ~~(~~considering the average OC concentration of 3.07 ug m^{-3} and an OM/OC ratio of 1.8~~)~~. Together, ~~Therefore,~~ the organosulfates quantified against authentic standards in Centreville accounts for 4.7 % of OM. Additional species that contribute significantly to MS^2 organosulfate signals are qualitatively and semi-quantitatively examined in Sect. 3.3. ~~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).~~

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 ~~show~~had higher correlations with formaldehyde, MACR and glyoxal relative to isoprene, ISOPOOH and IEPOX ~~(isoprene~~that are low NO_x oxidation products of isoprene (Bates et al., 2016; Krechmer et al., 2015)), as well as MVK and isoprene nitrates (ISOPN) that are ~~-(an isoprene~~ high NO_x 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 NO_x (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 NO_x 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 ~~is their~~ limit~~ing~~ ~~factor~~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 ~~this~~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.

3.2 Positive filter sampling artifacts for select organosulfates

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 $PM_{2.5}$ (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 concentrations from 13 June – 13 July 2013: $PM_{2.5}$ (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. The potential for these organosulfates in the gas phase to form positive sampling artifacts by adsorption onto QFF was assessed by parallel

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analysis of Q_F and Q_B. Of the ten Q_B analyzed to assess positive filter sampling artifacts due to gas adsorption, only three contained detectable levels of glycolic acid sulfate and one contained detectable levels of lactic acid sulfate (Table ~~2~~3). Maxima ~~for both species~~ occurred in the 09 July nighttime sample ~~collected on 09 July~~ with the backup filter containing 2.2 ± 0.8 % ~~and were 1.1 ± 0.3 %~~ (0.30 ± 0.06 ng m^{-3}) of the $PM_{2.5}$ glycolic acid sulfate concentration and 1.1 ± 0.5 % ~~0.8 ± 0.4 %~~ (0.15 ± 0.07 ng m^{-3}) of the $PM_{2.5}$ lactic acid sulfate concentration~~respectively~~. Meanwhile, hydroxyacetone sulfate was below the instrument detection limit in all Q_B analyzed, and an ~~such that the~~ upper limit of the positive artifact was estimated as 3.2 %~~1.3 %~~. The positive filter sampling artifacts associated with these three organosulfates from gas adsorption were only detected sporadically and at very low levels (~ ~~1~~3 %) that fell within the propagated analytical uncertainty and were considered to be negligible. ~~From 07-11 July 2013, the 09 July had the highest $PM_{2.5}$ loadings, temperature, solar radiation (data available at http://esrl.noaa.gov/csd/groups/csd7/measurements/2013senex/Ground/DataDownload/) and quantified organosulfate concentrations (Fig. 1) for both the daytime and nighttime sampling periods. Consequently, it is expected that the maximum gas phase concentrations of glycolic acid sulfate and lactic acid sulfate also occurred on this day, which would have led to the observed positive sampling artifacts due to gas adsorption. The positive filter sampling artifacts associated with these three organosulfates from gas adsorption were only detected sporadically and at very low levels (~ 1%) that fell within the propagated analytical uncertainty.~~

~~In a prior study by~~These results are consistent with those of Kristensen et al. (2016) who did not observe these three organosulfates in the denuder samples collected upstream of Teflon filters on which these organosulfates were detected. Because the greatest sampling artifacts were observed on 09 July when $PM_{2.5}$ and OC loadings were greatest (Fig. 1), the extent of artifacts may be even greater on days with higher $PM_{2.5}$ and OC loadings. ~~at an urban site in Copenhagen, Denmark and a forested site in Hyytiälä, Finland, the abovementioned organosulfates were not detected in the gas phase via analysis of denuder samples collected upstream of Teflon filters on which these organosulfates were detected. 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 (Gao et al. 2015) that can promote partitioning of acidic species like organosulfates to the gas phase, and possibly temperature.~~

The potential for glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate to form on QFF by acid catalyzed heterogeneous reactions ~~were~~ was assessed by the parallel analysis of Q_F with $Q_{B\text{-}H_2SO_4}$, in which the $Q_{B\text{-}H_2SO_4}$ filters were loaded with approximately twice the amount of sulfate that was expected to be collected on 90 mm QFF (with a total sampling area of 50.3 cm^2) over 11 hours of sampling at a flow rate of 92 lpm, based on an average $PM_{2.5}$ sulfate concentration of 4.11 ± 0.55 μg m^{-3} in Centreville, AL (Edgerton et al., 2005). The organosulfates detected on $Q_{B\text{-}H_2SO_4}$ (maximum concentration, % $f_{artifacts}$) was highest for glycolic acid sulfate (0.8 ± 0.2 ng m^{-3}, 5.7 ± 2.1 %~~2.9 % ± 0.6 %~~), then lactic acid sulfate (0.43 ± 0.08 ng m^{-3}, 3.7 ± 0.8 %~~4.9 % ± 1.0 %~~) followed by hydroxyacetone sulfate (0.18 ± 0.05 ng m^{-3}, 4.7 ± 1.2 %~~7.3 % ± 1.9 %~~). Concentrations of organosulfates formed on the $Q_{B\text{-}H_2SO_4}$ filters followed the same trend as their $PM_{2.5}$ concentrations (section 3.1), while the % $f_{artifacts}$ was relatively consistent across the detected organosulfates. Organosulfates were more frequently detected on the $Q_{B\text{-}H_2SO_4}$ compared to the Q_B and at higher concentrations (Table ~~2~~3), indicating that in addition to adsorption of organosulfates in the gas phase, organosulfate formation may occur on QFF by adsorption and reaction of gas-phase precursors of organosulfates~~VOC~~ with H_2SO_4. The maximum extent of the sulfuric acid-enhanced artifact formation was 4.5 – 7.8 % ~~2.9-7.3 %~~ (Table ~~2~~3), ~~indicating that the extent of the artifact formation enhanced by acidic sulfate on filters~~which is greater than gas adsorption alone, but is overall relatively low ~~in Centreville~~. ~~This is consistent with the aerosol in Centreville being sufficiently acidic and containing high sulfate levels such that SOA formation is limited by neither of these factors (Xu et al., 2015).~~ Because the positive filter sampling artifacts were detected sporadically and only accounted for a minor fraction of the total organosulfate concentration that fell within the analytical uncertainty, the $PM_{2.5}$ organosulfate concentrations reported in section 3.1 were not corrected for positive filter sampling artifacts.

The extent of on-filter reactions to form glycolic acid sulfate, lactic acid sulfate, and hydroxyacetone sulfate appears to be site-specific. In a prior study in Hyytiälä, Finland, Kristensen et al. (2016) attributed the majority of organosulfates detected on high-volume filter samples ~~collected~~ to on-filter oxidation and sulfation reactions, including ~~forming organosulfates with~~ *m/z* corresponding to glycolic acid sulfate, lactic acid sulfate, and hydroxyacetone sulfate. However, for samples collected in Copenhagen, only 5 % of the daytime average concentrations and 14 % of the nighttime average concentrations of the glycolic acid sulfate was attributed to on-filter reactions, similar to this study, while lactic acid sulfate and hydroxyacetone sulfate were reported to have negative sampling artifacts (Kristensen et al., 2016), which could result from degradation during sampling, sample preparation, or analysis ~~concentrations appear to have been subjected to negative sampling artifacts~~. With varying extents of organosulfate sampling artifacts reported across sampling sites, it is recommended that sampling artifacts be evaluated at future field study sites.

3.3 Major organosulfates in Centreville, AL

A semi-quantitative analysis was conducted to identify the organosulfate species strongest MS^2 signals. Organosulfates were evaluated as precursor ions of ~~Because the quantified organosulfates accounted for a small fraction of OC, other major organosulfate species in Centreville, AL were identified using ions that fragmented to~~ the bisulfate anion (HSO_4^- at *m/z* 97) and sulfate ion radical ($SO_4^{-\bullet}$ at *m/z* 96) that are characteristic of this group of compounds (Gómez-González et al., 2008; Riva et al., 2016; Surratt et al., 2008). This analysis was applied to samples collected from 07 – 11 July, 2013, with a focus on the 10 July daytime sample with levels of $PM_{2.5}$ (7.01 ± 0.80 $\mu g\ m^{-3}$), OC (2.63 ± 0.21 $\mu g\ m^{-3}$), sulfate (1.06 ± 0.17 $\mu g\ m^{-3}$) and organosulfates (Fig. 1) near to the study average (Sect. 3.2 and Table 1).

The ability of an organosulfate to contribute to the bisulfate ion signal depends on its individual (-) ESI ionization efficiency, MS^2 fragmentation patterns, and mass concentration. Absolute quantitation requires instrument calibration as discussed in Sect. 1; however, this is not possible for the vast majority of atmospheric organosulfates, because standards are not commercially available. In the following data analysis, it is assumed that organosulfates have an equal ability to form the bisulfate anion/sulfate ion radical, so that semi-quantitative insight may be gained to their relative abundance in ambient aerosol. This approach is limited by the fact that differing ionization efficiencies and fragmentation patterns have not been controlled and may introduce positive or negative biases. Consequently, the ~~following~~ ranking in Table 4 should not be considered as an accurate measure of relative abundance, but a best estimate in the absence of authentic standards.

The limitations of this approach ~~can be~~is illustrated by the comparison of the semi-quantitative behavior of glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate in their formation of the bisulfate anion and their absolute quantitation. For the 10 July 2013 daytime sample, the relative contribution to bisulfate ion signal was highest for hydroxyacetone sulfate (1.10 %), then glycolic acid sulfate (0.57 %) and lactic acid sulfate (0.23 %) respectively, while ~~their~~ absolute concentrations ~~followed the opposite trend:~~ of glycolic acid sulfate (14 ± 5 ng m^{-3}) and lactic acid sulfate (~~15~~ 13 ± ~~1~~ 2 ng m^{-3}~~),~~) were greater than ~~glycolic acid sulfate (14 ± 3 ng m^{-3}) and~~ hydroxyacetone sulfate (~~5.8~~8.5 ± 0.3 ng m^{-3}) (Fig. 1). ~~This~~ The ~~comparison indicates that there is a positive~~ negative bias in the bisulfate ion signal towards ~~early~~later-eluting organosulfates~~, which~~ results from the ~~use of a~~ mobile phase gradient used in UPLC; w~~. :~~ ~~Acetonitrile has a higher vapor pressure than water and more readily desolvates in the mass spectrometer, leading to higher signals. W~~hen hydroxyacetone sulfate elutes (t_R 0.69 min), the mobile phase is 95: 5 % acetonitrile and ~~5 %~~ water~~,~~ compared to an average of ~~∼~~81: 19 % acetonitrile and ~~∼19 %~~ water when glycolic acid sulfate (t_R 7.82 min) and lactic acid sulfate (t_R 7.54 min) elute. Acetonitrile has a higher vapor pressure than water and more ~~, thus~~ ~~and more~~ readily desolvates in the ~~mass spectrometer, leading to higher signals~~ionization source. When increases the water content of the eluent, the signal of later-eluting ions is lower. ~~will decrease due to suppress of desolvation of ions. This indicates the importance of using authentic standards to calibrate the instrument, thus quantification.~~ 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. Nonetheless, it is a valuable endeavor to gain semi-quantitative information on major organosulfate signals in order to guide future developments of authentic standards that will ultimately ~~provide for~~enables absolute quantitation.

A mass spectrum of the precursor ions to *m/z* 97 integrated over the entire HILIC separation (0-11 min) for the 10 July daytime sample with the ten strongest signals marked is shown in Fig. 2. Each nominal *m/z* in Fig. 2 corresponded to a single monoisotopic mass as determined from HILIC-TOF, except for *m/z* 155 and 199 (as discussed in the Supporting Information)~~, which are discussed in detail below~~. Table ~~3~~ 4 ranks these ten organosulfate signals in order of decreasing relative contribution to the total bisulfate ~~product~~ ion signal and summarizes their *m/z*, molecular formulae determined from HILIC-TOF, expected precursor(s) based on prior field and SOA chamber studies, and proposed molecular structures with consideration of results from prior studies, double bond equivalences, ~~and~~ functional groups, and HILIC retention time. ~~Parallel semi-quantitative analysis of organosulfates in~~ The 10 July nighttime ~~sample~~ (Fig. S~~7~~2) and other daytime and nighttime samples collected from 07-11 July 2013 (Fig. S~~8~~3) ~~revealed many similarities to the 10 July daytime sample.~~ were analyzed in an analogous way. Because some organosulfates do not fragment to *m/z* 97, precursors of the *m/z* 96 was analyzed (Fig. S4, Table S1), although ~~;~~ its signal was only 2% of the MS^2 response of *m/z* 97.

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 (≥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 NO_x 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 $HSO_3^{-\cdot}$ (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 NO_x conditions (Zhang et al., 2012a) and $C_4H_7O_4^-$ (119.0341, -0.3) whose mass spectrum matched that of 2-methylglyceric acid sulfate (Fig S5). An isoprene-derived nitro-oxy organosulfate, $C_5H_{10}NSO_9^-$ (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, $C_3H_5SO_5^-$ (152.9858) and $C_3H_7SO_5^-$ (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 ~~derived from monoterpenes in the presence of acidic sulfate were also among the strongest signals: The fourth greatest contributor to the bisulfate ion signal (1.81 %) was~~ $C_7H_{11}SO_7^-$ (239.0225~~), which has multiple isomers that are not baseline resolved (~~; Fig. 3d)~~.~~ ~~Formation of $C_7H_{11}SO_7^-$ has been observed during oxidation of limonene, a monoterpene, in the presence of oxidants, NO_x and acidic sulfate (Surratt et al., 2008). Another laboratory study suggested that this organosulfate form from oligomerization of MVK and MACR, the two major first generation oxidation products of isoprene, *via* sulfate radical induced oxidation pathway (Nozière et al., 2010). With the $C_7H_{11}SO_7^-$ organosulfate~~

~~being one of the dominant organosulfates in the atmosphere, this is a prime target for standard development; however a better understanding of its structure is needed to guide this effort.~~

~~The sixth greatest contributor to the bisulfate ion signal (1.49 %) was a nitrooxy organosulfate with the formula~~ and $C_{10}H_{16}NSO_{10}^-$ (342.0495~~). The HILIC chromatogram shows two co-eluting peaks that eluted less than 1 minute (~~; Fig. 3f)~~.~~ were also among the strongest signals and have been associated with monoterpene SOA formed in the presence of acidic sulfate ~~Organosulfates with the same elemental composition have been observed to form from monoterpenes in the presence of NO_x under highly acidic conditions~~ (Surratt et al., 2008). ~~Further, this organosulfate has been previously identified in the ambient aerosol at a forested site in Germany (Iinuma et al., 2007) and in the SE US (Gao et al., 2006; Surratt et al., 2008). Prior studies have identified up to ten isomers of this organosulfate in SE US using reversed phase chromatography (Surratt et al., 2008). Thus, further characterization and quantification of this organosulfate should proceed with reversed phase chromatography, which affords better separation of the $C_{10}H_{16}NSO_{10}^-$ isomers.~~Other monoterpene derived organosulfates identified from bisulfate ion signal include ~~While *m/z* 281 (~~$C_{10}H_{17}SO_7^-$ (281.0695; observed in 90 % of the samples analyzed) ~~Table S1) was not among the ten highest contributors to the bisulfate anion signal in the 10 July daytime sample, it was among the highest signals of all other samples analyzed (Fig. S7 and S8). An organosulfate with this elemental composition was previously identified in an SOA chamber experiment involving monoterpenes and in ambient aerosol in Centreville and Birmingham, AL, and Atlanta, GA (Surratt et al., 2008). In addition, other monoterpene-derived organosulfates with *m/z* 297 (~~$C_{10}H_{17}SO_8^-$ (297.0644), ~~223 (~~$C_7H_{11}SO_6^-$ (223.0276) and ~~279 (~~$C_{10}H_{15}SO_7^-$ (279.0538) (Table S2 and Fig. S2 and S3). ~~(Surratt et al., 2008) were sporadically detected among the highest organosulfate signals. Because of their frequent detection and specificity to monoterpene-derived organosulfates, these organosulfate may be useful tracers for monoterpene-derived SOA.~~ Monoterpene-derived nitro-oxy organosulfates were particularly responsive to precursors of *m/z* 96; $C_{10}H_{16}NSO_{10}^-$ ~~-~~(342.0495), $C_{10}H_{16}NSO_8^-$ (310.0597~~ (Ma et al., 2014; Surratt et al., 2008)~~) and $C_{10}H_{16}NSO_7^-$ (294.0647) (Table S1 and Fig. S4). The nitro-oxy organosulfate $C_{10}H_{16}NSO_7^-$ (294.0647) accounted for 25 % of the total *m/z* 96 signal in $PM_{2.5}$ 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 $C_4H_7SO_4^-$ (151.0065), $C_3H_5SO_4^-$ (136.9909) and $C_5H_8NO_8S^-$ (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 ~~The ninth greatest contributor to the bisulfate ion signal (0.98 %) was~~ $C_{12}H_{25}SO_4^-$ (265.1474; Fig. 3i) ~~that~~ is consistent with dodecyl sulfate (a.k.a. lauryl sulfate),~~. Sodium dodecyl sulfate is~~ 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~~ (Fig. 3i)~~. 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 ~~(n=10)~~ analyzed (Fig. 2, ~~S7~~ S2 and ~~S8~~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. ~~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.~~

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 $C_5H_{11}SO_7^-$ (215.0225), $C_5H_9SO_7^-$ (213.0069), $C_3H_5SO_5^-$ (152.9858) and isoprene ozonolysis products $C_4H_7SO_6^-$ (182.9963) and $C_5H_{11}SO_6^-$ (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 ($C_5H_9SO_6^-$) 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.

3.4 Tentative identification of 2-methyltetrol sulfate isomers

HILIC chromatography resolved six, baseline resolved peaks of 2-methyltetrol sulfates ($C_5H_{11}SO_7^-$~~-~~; ~~(~~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-~~M~~methyltetrol ~~organo~~sulfates were tentatively identified by their relative acid hydrolysis rates as primary (most stable), secondary (intermediate stability), or tertiary (least stable; ~~by their relative acid hydrolysis rates (~~as discussed in the SI and shown in Fig. S~~2~~9). ~~The fastest *m/z* 215 peaks to hydrolyze (i.e. least stable) were tentatively identified as tertiary, the next to hydrolyze (i.e. intermediate stability) as secondary, and the most stable were as primary, with~~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 ~~tentatively~~ 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. S~~2~~9). 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, ~~due to the desolvation effect,~~ these percentages are expected to underestimate the contribution from primary organosulfates. With this knowledge, we expect ~~These results suggest~~ 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.

4 Conclusions

The three most abundant organosulfates quantified using authentic standards in $PM_{2.5}$ collected from Centreville, AL from 13 June – 13 ~~07-11~~ July, 2013 were glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate respectively. Their ambient concentrations correlated with sulfate and biogenic VOC precursors, particularly isoprene and its oxidation products, indicating their importance in organosulfate formation in the SE US. Positive filter sampling artifacts associated with these three organosulfates due to gas adsorption were negligible (%*f* < ~~1.3~~3 ~~%).~~ %), while ~~Sulfuric~~ sulfuric acid enhanced the positive filter sampling artifacts ~~associated with these organosulfates~~, but were relatively small (%*f* ~~≤~~ ≤ 7.~~3~~8 %). Thus the organosulfates quantified using $PM_{2.5}$ sampled on QFF in Centreville, AL during SOAS 2013 considered to have negligible to minor ~~can be used without a significant~~ positive ~~bias~~ filter sampling artifacts. ~~Because, positive filter sampling artifacts associated with organosulfates are likely site specific, it is important to assess sampling artifacts at new study sites. The organosulfates quantified against authentic standards in this study accounted for a small fraction of the $PM_{2.5}$ and organic carbon mass (< 0.3 %).~~

The precursor ion scan ~~to~~ of the bisulfate anion ~~fragment~~ (*m/z* 97) and sulfate ion radical (*m/z* 96) were ~~was~~ used semi-quantitatively to ~~assess~~ identify major organosulfate species in ambient aerosol in the ~~SE US~~Centreville, AL. From the ten strongest responding ions identified, 2-methyltetrol sulfates accounted for nearly half of the total bisulfate ion signal in all samples analyzed. By comparison to chamber studies, ~~it is seen that~~ the ~~ten~~ major organosulfates identified in this study derive mainly from biogenic VOC, mainly isoprene, and to a lesser extent monoterpenes and MBO. ~~Many~~ Five of the ten major organosulfates ~~signals~~ identified from the bisulfate ion signal ~~observed~~ are consistent with those reported by Riva et al. (2016) ~~for~~ in Centreville during SOAS and thus reinforce their conclusions that ozonolysis and photochemical reactions of isoprene influence the organosulfate levels and composition in Centreville. The organosulfates in Centreville, AL ~~Further, our semi-quantitative analysis shows that in Centreville, AL the organosulfates that fragment to the bisulfate product ion~~ were dominated by few major species among large number of minor species. Even in areas heavily influenced by biogenic SOA, like Centreville, organosulfates may have primary sources, such as dodecyl sulfate ($C_4H_7SO_6^-$; 265.1474) that is expected to originate from wastewater.

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:

~~The ratios of bisulfate ion signals to the absolute concentrations of hydroxyacetone sulfate and glycolic acid sulfate, and hydroxyacetone sulfate and lactic acid sulfate were differ by a factor of 3 and 7, respectively, indicating the importance of using authentic standards for quantification of organosulfates. However, in the absence of authentic standards, precursors of bisulfate ion provides a way to determine the relative abundances of organosulfates giving This study also provides insights for to the major organosulfate species in the 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, $C_5H_9SO_7^-$ (213.0069) and $C_5H_7SO_7^-$ (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 $C_4H_7SO_6^-$ (182.9963) in Centreville, AL. Likewise, $C_{10}H_{16}NSO_{10}^-$ (342.0495) and $C_7H_{11}SO_7^-$ (239.0225) are expected to be among abundant monoterpene derived organosulfates in Centreville, AL. Similar to Riva et al. (2016), $C_5H_{11}SO_6^-$ (199.0276) is relatively abundant in Centreville, but further experiments are need to identify its origin. Because of their relatively strong MS^2 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.

5 Data availability

The SOAS research data used in this publication are available at http://esrl.noaa.gov/csd/groups/csd7/measurements/2013senex/Ground/DataDownload/.

Acknowledgements

The authors would like to thank E. Geddes, K. Richards, and T. Humphrey at Truman State University for synthesizing standards of benzyl sulfate, hydroxyacetone sulfate, and glycolic acid sulfate; S. Staudt at University of Wisconsin, Madison for synthesizing the lactic acid sulfate standard; L. Teesch and V. Parcell for their assistance in University of Iowa High Resolution Mass Spectrometry Facility (HRMSF); Ruikun Xin for his assistance in data processing; Eric Edgerton at Atmospheric Research & Analysis for providing $PM_{2.5}$ and sulfate measured in Centreville, AL during SOAS 2013; R. Weber, H. Guo and A. Nenes at Georgia Institute of Technology for providing aerosol acidity and aerosol water measured during SOAS 2013; P. Wennberg, T. Nguyen, J. St. Clair at California Institute of Technology for access to IEPOX, ISPOOH and ISOPN measurements; and A. Carlton from Rutgers University and J. Jimenez from University of Colorado, Boulder for organizing the SOAS component of Southeast Atmosphere Study. We would also like to thank US EPA Science To Achieve Results (STAR) program (grant number 83540101) for funding this research.

~~The authors would like to thank E. Geddes, K. Richards, and T. Humphrey at Truman State University for synthesizing standards of benzyl sulfate, hydroxyacetone sulfate, and glycolic acid sulfate; S. Staudt and F. Keutsch at University of Wisconsin, Madison (now at Harvard University) for synthesizing the lactic acid sulfate standard; L. Teesch and V. Parcell for their assistance in University of Iowa High Resolution Mass Spectrometry Facility (HRMSF); Ruikun Xin at University of Iowa (now at Carnegie Mellon University) for his assistance in data processing; Eric Edgerton at Atmospheric Research & Analysis for collecting providing PM~~$_{2.5}$ ~~and meteorological data fromsulfate measured in Centreville, AL during SOAS 2013; R. Weber, H. Guo and A. Nenes at Earth and Atmospheric Science, Georgia Institute of Technology for providing aerosol acidity and aerosol water measured during SOAS 2013; P. Wennberg at California Institute of Technology, T. Nguyen (now at University of California, Davis) and J. St. Clair (now at University of Maryland, Baltimore County) for providing us the IEPOX, ISPOOH and ISOPN measurements in Centreville, AL during SOAS 2013 and A. Carlton from Rutgers University, and A. Goldstein from University of California, Berkeley, J. Jimenez from University of Colorado, Boulder and Joost deGouw from the National Oceanic and Atmospheric Administration for organizing the SOAS component of Southeast Atmosphere Study. We would also like to thank US EPA Science To Achieve Results (STAR) program (grant number 83540101) for funding this research.~~

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Figure 1: Concentrations of glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate quantified against authentic standards, and $PM_{2.5}$, organic carbon (OC) and sulfate (SO_4^{2-}) measured ~~organosulfates in $PM_{2.5}$~~ at Centreville, AL during SOAS from 13 June – 13 ~~on 07-11~~ July 2013 on the basis of day (D; 08:00-19:00 LT) and night (N; 20:00-07:00 LT). ~~All species were quantified against authentic standards.~~ Error bars represent the analytical uncertainty.

Figure 2: The ~~integrated~~ mass spectrum of precursors ~~to~~ of *m/z* 97 (HSO_4^-) ~~mass spectrum~~ for the daytime sample collected on 10 July 2013 collected by HILIC-TQD. The ten labeled *m/z* correspond to the deprotonated ions ($[M-H]^-$) of organosulfates with the greatest intensity.

Figure 3: Extracted chromatograms for the ten major organosulfates (monoisotopic mass ± 0.01 Da) in the daytime sample collected on 10 July 2013 as determined by HILIC-TOF.

Table 1: Concentration (range and mean ± one standard deviation) of each organosulfate quantified against authentic standards from 13 June – 13~~07–11~~ July 2013 in Centreville, AL and their mean contribution (%) to $PM_{2.5}$ and OC (± one standard deviation).

Organosulfate	**Concentration (ng m^{-3})**		**Mean contribution (%)**	
	Range	**Mean**	**$PM_{2.5}$**	**OC**
glycolic acid sulfate	0.5 – 52.5~~2.4 – 27.3~~	20.6 ± 14.3~~12.0 ± 7.9~~	0.2 ± 0.1	0.09 ± 0.~~05~~04
lactic acid sulfate	0.5 – 36.7~~1.4 – 22.1~~	16.5 ± 10.3~~9.9 ± 7.0~~	0.2 ± 0.1~~0.17 ± 0.08~~	0.10 ± 0.05
hydroxyacetone sulfate	0.5 – 14.3~~0.5 – 8.7~~	5.8 ± 3.1~~3.3 ± 2.4~~	0.~~06~~ 08 ± 0.03	0.04 ± 0.02
methyl sulfate	0.2 – 9.3~~0.2 – 1.0~~	1.8 ± 2.4~~0.6 ± 0.3~~	0.~~010~~ 03 ± 0.0~~0~~4	0.~~003~~ 007 ± 0.~~002~~008

Table 2: Correlations of hydroxyacetone sulfate, lactic acid sulfate and glycolic acid sulfate with each other and co-located measurements: ~~$PM_{2.5}$,~~ isoprene, formaldehyde, glyoxal, high NOx isoprene oxidation products ~~such~~including ~~as~~ isoprene hydroxyl nitrates (ISOPN), methacrolein (MACR), methylvinyl ketone (MVK), ~~glyoxal, formaldehyde,~~ low NOx isoprene oxidation products ~~such as~~including 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 ≤ 0.05)~~.

~~VOC precursor/PM constituent~~Co-located measurement	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
Isoprene	59	0.44	0.40	0.45
Formaldehyde	60	0.73	0.76	0.69
Glyoxal	60	0.59	0.64	0.56
ISOPN	42	0.32	0.40	0.30
MACR~~Formaldehyde~~	59~~60~~	0.67~~0.73~~	0.67~~0.76~~	0.59~~0.69~~
MVK~~Sulfate~~	59~~60~~	0.30~~0.69~~	0.43~~0.74~~	0.35~~0.63~~
ISOPOOH~~MACR~~	38~~59~~	0.52~~0.67~~	0.48~~0.67~~	0.32~~0.59~~
IEPOX~~Glyoxal~~	38~~60~~	0.40~~0.59~~	0.41~~0.64~~	0.14~~0.56~~
~~ISOPOOH~~	~~38~~	~~0.52~~	~~0.48~~	~~0.32~~
~~Isoprene~~	~~59~~	~~0.44~~	~~0.40~~	~~0.45~~
~~MVK~~	~~59~~	~~0.30~~	~~0.43~~	~~0.35~~
Sulfate~~ISOPN~~	60~~42~~	0.69~~0.32~~	0.74~~0.40~~	0.63~~0.30~~
~~IEPOX~~	~~38~~	~~0.40~~	~~0.41~~	~~0.14~~
Aerosol water	56	0.32	0.26	0.33

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Aerosol acidity	49	-0.14	0.13	0.20

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Table ~~2~~3: Positive filter sampling artifacts associated with the three most abundant organosulfates quantified in Centreville, AL from 07-11 July 2013 due to gas adsorption alone and gas adsorption and reaction of VOC precursors of organosulfates with sulfuric acid. Given in the table are frequency of detection (FOD, n = 10) and positive filter sampling artifacts as a fraction of their PM$_{2.5}$ concentrations (%*f*).

Organosulfate	**Artifacts by gas adsorption**		**Artifacts by gas adsorption and reaction of VOC precursors of organosulfates with sulfuric acid**	
	FOD (%)	$\%f_{\text{artifacts}}$ **(max)**	**FOD (%)**	$\%f_{\text{artifacts}}$ **(max)**
glycolic acid sulfate	30	2.2 ± 0.8~~1.1 ± 0.3~~	60	5.7 ± 2.1~~2.9 ± 0.6~~
lactic acid sulfate	10	1.1 ± 0.5~~0.8 ± 0.4~~	20	3.7 ± 0.8~~4.9 ± 1.0~~
hydroxyacetone sulfate	0	-	40	4.7 ± 1.2~~7.3 ± 1.9~~

Table ~~3~~4: The ten organosulfates with the strongest contributions to the bisulfate product ion signal in Centreville, AL for the daytime sample collected on 10 July 2013. The ten organosulfates were ranked in the order of the greatest contribution to the bisulfate product ion signal. Summarized for each signal are formula determined using high resolution ToF MS, the calculated monoisotopic mass ([M-H$^-$]~~$^-$~~), proposed structure (with reference to the article proposing the structure), VOC precursor(s) indicated by SOA chamber studies, retention time(s) (t_R) on the BEH-amide column during HILIC gradient separation (solvent peak at 0.38 min), error in *m/z* (mDa) for each peak, and the relative contribution of each peak and the total peak area to the total bisulfate product ion signal. Many organosulfates are likely to have multiple isomers, although only one isomer is shown.

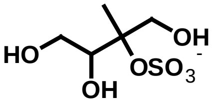
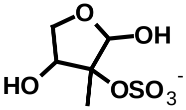
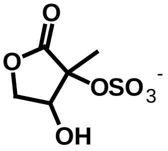
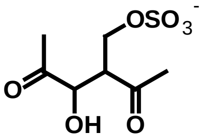
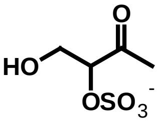
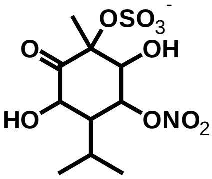
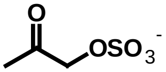
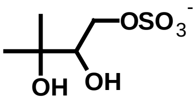
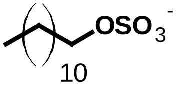
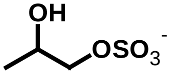
Rank	**[M-H]$^-$**		**Structure**	**VOC precursor(s)**	**t_R (min)**	**Error (mDa)**	**Contribution to total bisulfate signal (%)**	
	Formula	**Mass**					**by peak**	**total**
1	$C_5H_{11}SO_7^-$	215.0225	 (Surratt et al., 2010)	Isoprene (Surratt et al., 2007a; Surratt et al., 2007b; Surratt et al., 2010)	1.40 1.74 2.87 3.65 4.49 4.83	-0.6 0.5 -0.3 -1.7 -0.2 0.1	10.35 4.53 10.12 17.75 0.35 0.17	43.27
2	$C_5H_9SO_7^-$	213.0069	 (Hettiyadura et al., 2015)	Isoprene (Surratt et al., 2008)	1.10 1.29 1.4 – 1.65 1.80 1.9 – 2.8	-0.4 0.5 1.2 0.7 1.4	0.47 0.17 0.22 0.62 3.44	4.91
3	$C_5H_7SO_7^-$	210.9912	 (Hettiyadura et al., 2015)	Isoprene (Surratt et al., 2008)	0.56 0.67 0.74 0.85	-1.5 -1.4 0.9 -1.4	0.42 1.63 0.63 1.59	4.27
4	$C_7H_{11}SO_7^-$	239.0225	 (Nozière et al., 2010)	Limonene (Surratt et al., 2008) ~~Methyl vinyl ketone and methacrolein~~ ~~(Nozière et al., 2010)~~	0.58 0.67 0.74 0.80 0.91 1.00	4.5 -0.4 -1.4 0.5 -0.8 -1.2	0.05 0.33 0.36 0.25 0.16 0.65	1.81
5	$C_4H_7SO_6^-$	182.9963	 (Shalamzari et al., 2013)	Isoprene (Riva et al., 2016) Methyl vinyl ketone and methacrolein (Schindelka et al., 2013)	0.67 0.83 0.91 1.00 1.23	1.2 1.0 -0.6 -1.8 -0.1	0.05 0.20 1.02 0.22 0.25	1.73

Table ~~3~~4: (Cont.)

Rank	$[M-H]^-$		Structure	VOC precursor(s)	t_R (min)	Error (mDa)	Contribution to total bisulfate signal (%)	
	Formula	Mass					by peak	total
6	$C_{10}H_{16}NSO_{10}^-$	342.0495	 (Yassine et al., 2012, supporting information)	α-terpinene and α and β-pinene (Surratt et al., 2008)	0.54 0.61	0.3 0.7	1.13 0.36	1.49
7	$C_3H_5SO_5^-$	152.9858	 (Surratt et al., 2010)	Isoprene (Surratt et al., 2008)	0.69[a] 0.91 4.34	-1.1 -1.2 -0.7	1.10 0.12 0.05	1.27
8	$C_5H_{11}SO_6^-$	199.0276	 (Zhang et al., 2012b)	MBO (Nozière et al., 2010) Isoprene (Riva et al., 2016)	1.05 1.89	-0.9 0.8	0.46 0.57	1.03
9	$C_{12}H_{25}SO_4^-$	265.1474		Anthropogenic	0.54	0.0	0.98	0.98
10	$C_3H_7SO_5^-$	155.0014		Unknown	1.23 1.31	-0.5 -0.7	0.32 0.30	0.62

[a] structure was confirmed using a synthesized authentic standard of hydroxyacetone sulfate