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Title: Organosulfates in Atlanta, Georgia: Anthropogenic influences on biogenic secondary organic aerosol formation

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Response to Referee #1 Comments

Anonymous Referee # 1, General Comments: *“The manuscript presents new measurements focusing on occurrence of organosulfates in aerosol samples collected in the city of Atlanta, USA. A detailed chemical analysis is reported, while the study would benefit from a more thorough discussion of relation to atmospheric parameters and broader implications for other regions. Such a discussion should cover influence of air mass transport from precursor source areas.”*

Authors' response to anonymous referee # 1, general comments: We thank the referee for his/her thoughtful comments and suggestions to improve the manuscript. As suggested and as detailed in the following responses to specific comments, we have improved our comparison of organosulfate abundance and composition in urban Atlanta to rural Centreville. New insights to the importance of NO_x in the urban environment are gained from this comparison, although we are cautious not to extrapolate our findings to other regions. Instead, we encourage future studies to determine the consistency of these findings at other urban rural pairs.

Anonymous Referee # 1, Specific comments on Abstract (page 1 line 26): *“I suggest to briefly explain the formation mechanisms of organosulfate, as this knowledge is needed to understand your point here. The abstract would also benefit from an introduction in the first sentences to put the work into context for the general reader.”*

Authors' response to anonymous referee # 1, specific comments on abstract (page 1 line 26): We thank the referee for this suggestion and have added the following text to the abstract at page 1, line 1: “Organosulfates are secondary organic aerosol (SOA) products that form from reactions of volatile organic compounds (VOC), such as isoprene, in the presence of sulfate that is primarily emitted by fossil fuel combustion.”

At line 26, we have revised the text to read: “. The greatest enhancement in concentration was observed for 2-methylglyceric acid sulfate whose formation is enhanced in the presence of nitrogen oxides (NO and NO₂; NO_x) and is a tracer for isoprene high-NO_x SOA.”

Anonymous Referee # 1, Specific Comments on Introduction: *“The introduction needs a more thorough presentation of state of the art and previous studies of organosulfates in aerosols.”*

Authors' response to anonymous referee # 1, specific comments on introduction: We thank the reviewer for this suggestion and have provided additional discussion as detailed in our response to referee #1's specific comments on introduction.

Page 2 Line 2: *"Suggest to rephrase to "Organosulfates are components of atmospheric secondary organic aerosol..."*.

Page 2, lines 2-3 originally read: *"Atmospheric organosulfates are components of secondary organic aerosol (SOA) that contain a sulfate ester functional group."*

This text has been revised to read: *"Organosulfates are components of atmospheric secondary organic aerosol (SOA) that contain a sulfate ester functional group."*

Page 2, line 3: *"Organosulfates have been detected all around the world". Please be more specific and include references."*

Page 2, line 3 originally read: *"Organosulfates have been detected all around the world and are estimated to contribute up to 5-9% of PM2.5 OA in the Southeastern US (Tolocka and Turpin, 2012)."*

This text has been revised to read: *"This class of compounds has been detected in ambient aerosols around the world, including rural, urban, forested, and coastal sites in the United States (US), China, and/or Europe (Hansen et al., 2014; He et al., 2014; Kristensen and Glasius, 2011; Lin et al., 2012; Stone et al., 2012; Ma et al., 2014). In the Southeastern US, organosulfates are estimated to contribute up to 5-9% of PM2.5 organic aerosol (Tolocka and Turpin, 2012)."*

Page 2, line 6: *"VOC are in the gasphase while sulfate radicals are in the particle phase."*

Authors' response to referee's specific comment on page 2, line 6: We thank the referee for pointing this out. We have corrected this sentence in the revised manuscript as shown below.

Page 2, line 6 originally read: *"Alternatively, they form by the sulfate radical-initiated oxidation of volatile organic compounds (VOC) (Nozière et al., 2010; Schindelka et al., 2013)...."*

This text is revised to read: *"Alternatively, they form by reaction of oxidized volatile organic compounds (VOC) with sulfate radicals (Nozière et al., 2010; Schindelka et al., 2013)..."*

Page 2, line 8: *"largely biogenic" - there have been many studies of biogenic precursors, and fewer of anthropogenic so this statement may not be correct because we have not yet investigated all precursors of organosulfates."*

Authors' response to referee's specific comment on page 2, line 8: We agree with referee's comment. We have revised this text and the text at page 2, lines 15-17 as follows.

Page 2, lines 7-9 originally read: *"Precursors of organosulfates are largely biogenic VOC such as isoprene, monoterpenes, sesquiterpenes, 2-methyl-3-butene-2-ol (MBO), and green leaf volatiles (Zhang et al., 2012; Surratt et al., 2008; Chan et al., 2011; Iinuma et al., 2009; Shalamzari et al., 2014)."*

This text is revised to read: “Biogenic VOC precursors of organosulfates include isoprene, monoterpenes, sesquiterpenes, 2-methyl-3-butene-2-ol (MBO), and green leaf volatiles (Zhang et al., 2012; Surratt et al., 2008; Chan et al., 2011; Iinuma et al., 2009; Shalamzari et al., 2014).”

page 2, lines 15-17 originally read: “*Since fossil fuel combustion is the major source of sulfate aerosols in the atmosphere (Wuebbles and Jain, 2001; Hidy et al., 2014; Carlton et al., 2010), organosulfates are tracers of anthropogenically influenced biogenic SOA (Hettiyadura et al., 2018).*”

This text is revised to read: “Since fossil fuel combustion is the major source of sulfate aerosols in the atmosphere (Wuebbles and Jain, 2001; Hidy et al., 2014; Carlton et al., 2010), biogenic VOC derived organosulfates are useful as tracers of anthropogenically influenced biogenic SOA (Hettiyadura et al., 2018).”

Page 2, line 14: “*The influence of anthropogenic VOC has been established in e.g. Asian studies.*”

Authors’ response to referee’s specific comment on page 2, line 14: We thank the referee for indicating this. We have removed this phrase from the text below.

Page 2, line 12-14 originally read: “*Organosulfates have also been observed in diesel and biodiesel emissions (Blair et al., 2017) and in SOA produced from anthropogenic VOC (i.e. naphthalene, methylnaphthalene) (Riva et al., 2015) and long chain n-alkanes (Riva et al., 2016a), although the significance of these sources to ambient organosulfates has not yet been established.*”

This text has been revised to read: “Organosulfates have also been detected among the SOA generated from diesel and biodiesel fuel emissions (Blair et al., 2017) and in SOA produced from aromatic VOC such as naphthalene and methylnaphthalene (Riva et al., 2015) as well as long chain *n*-alkanes (Riva et al., 2016a).”

Anonymous Referee # 1, Specific comments on Experimental Section (page 4, line 30): “*What do you mean by “30% of the measurement”? Of the value?*”

Authors’ response to anonymous referee # 1, specific comments on experimental section (page 4, line 30): For the organosulfates that did not have authentic standards, the analytical uncertainty was estimated as 30% of their concentration value. We have revised the text to make it clear as shown below.

Page 4, line 30 originally read: “*For methyltetrol sulfate and the other organosulfates that did not have standards, 30% of the measurement was used as an estimate of the analytical uncertainty (Hettiyadura et al., 2018).*”

This text has been revised to read: “For methyltetrol sulfate and the other organosulfates that did not have authentic standards, the analytical uncertainty was estimated as 30% of their concentration values (Hettiyadura et al., 2018).”

Anonymous Referee # 1 General Comments on Results and Discussion: *“All headlines include the words “in Atlanta”. I suggest to leave this out and only specify the comparison with Centreville in that specific headline.”*

Authors’ response to anonymous referee # 1, general comment on results and discussion: We thank the referee for this suggestion. We have revised the sub-headings of the manuscript accordingly.

Figure 2: *“The time series in Figure 2 would benefit from showing time series of relevant pollution indicators.”*

Authors’ response to anonymous referee # 1, specific comment on Figure 2: We thank the reviewer for the suggestion, however we prefer to maintain Figure 2 as a presentation of the organosulfate measurements that were made in this study. Other pollution indicators, such as NO_x were not measured at the Georgia Tech sampling site and instead were drawn from measurement archives at a nearby monitoring station. Further, NO_x and sulfate only weakly correlate with the organosulfates shown in Figure 2 (Table S4 and Sect. 3.8, page 11, lines 1-5), which is consistent with their consistently high levels in urban Atlanta, GA. Therefore, we respectfully disagree that Figure 2 would benefit from additional data.

Page 6, line 14: *““many species” - can you be more specific e.g. “many other organosulfate species originating from xxx””*

The text in page 6, line 14 originally read: *“These results indicate that organosulfates in Atlanta during August 2015 were dominated by methyltetrol sulfate, with minor contributions from many species.”*

This text has been revised to read: *“These results indicate that organosulfates in Atlanta during August 2015 were dominated by methyltetrol sulfate, with minor contributions from many other organosulfate species derived from isoprene, monoterpenes, and anthropogenic sources.”*

Page 6, line 19-20: *“Please describe more clearly what you mean by these relative intensities (in the mass spectra, I assume?) of organosulfate and sulphonate species.”*

Page 6, line 19-20 originally read: *“Major species were defined in one of two ways: 1) having a minimum relative intensity ($\geq 1.0\%$ for m/z 97, $>12\%$ for m/z 96, $>5\%$ for m/z 81, and $>3\%$ for m/z 80 in any of the three samples) or...”*

This text has been revised to read: *“Major organosulfur compounds were defined in one of two ways: 1) having a minimum relative intensity in the MS/MS spectra ($\geq 1.0\%$ for precursors to m/z 97, $>12\%$ for m/z 96, $>5\%$ for m/z 81, and $>3\%$ for m/z 80 in any of the three samples) or...”*

Page 7, line 21: *“As all readers might not be familiar with HILIC, I suggest to explain this reasoning in more details.”*

Authors' response to referee's specific comment on page 7, line 21: As suggested by the reviewer, the HILIC method used in this study is further described at page 4 line 11 and reasoning has been further explained at page 6, lines 20-22.

The text at page 7, line 21 originally read: *"The organosulfate with m/z 274 has multiple isomers, while only the two isomers retaining greater than 4 min are considered to be major ones (Sect. 3.2 and Fig. 3o)."*

This text has been revised to read: *"The organosulfate with m/z 274 has multiple isomers, while only the two isomers retaining greater than 4 min are considered to be major ones as described in section 3.2 (Fig. 3o)."*

Following text is added to page 4 line 11: *"Briefly, the acetonitrile rich mobile phase was held at 100% from 0 to 2 minutes, and then decreased to 85% from 2 to 4 minutes and held constant at 85% until 11 minutes."*

Text at page 6, lines 20-22 originally read: *"...or 2) by retaining more than four minutes on the HILIC column that results in a lower relative response due to changing mobile phase conditions, despite high ambient concentrations (Hettiyadura et al., 2017)."*

This text has been revised to read: *"...or 2) by retaining more than four minutes. Despite the observation that organosulfates eluting after four minutes often have higher concentrations than early-eluting species, their MS response is observed to be lower because of the increased water content of the mobile phase (20%) that does not de-solvate as efficiently as acetonitrile in the ESI source (Hettiyadura et al., 2017)."*

Page 7: *"The first paragraph contains a lot of information and I suggest to divide into at least two paragraphs to improve readability."*

Authors' response to referee's specific comment on page 7: According to the referee's suggestion we have divided the first paragraph on page 7 into two paragraphs as shown below.

The 1st paragraph on page 7 originally read:

"The strongest organosulfate signals are attributed to species associated with isoprene SOA. Methyltetrol sulfate (m/z 215), the most abundant organosulfate observed, is produced from the acid catalyzed nucleophilic addition of sulfate to IEPOX ring (Surratt et al., 2010). Organosulfates with m/z 211 (sulfate esters of methyl dihydroxylactone) and 213 (sulfate esters of cyclic methyl trihydroxylaldehyde hemiacetal), of the next-highest abundance, have been observed during photo-oxidation of isoprene (Surratt et al., 2008) and are suggested to derive from oxidation of primary alcohols in methyltetrol sulfates (Hettiyadura et al., 2015). In addition, 14 other major organosulfates identified are known to derive from isoprene and isoprene oxidation products (Table 1). Many of these organosulfates have been identified as SOA products from diesel and biodiesel fuel emissions (e.g., 2-methylglyceric acid sulfate, lactic acid sulfate, hydroxyacetone sulfate, m/z 167, 183, 197, 211, 213, 237, 239, and 253) (Blair et al., 2017), monoterpenes (m/z 239 and 253) (Surratt et al., 2008), and/or MBO (199; C₅H₁₁SO₆) (Zhang et al.,

2012). However, their moderate to strong correlations with methyltetrol sulfate (Table S1) and 2-methyltetrols (Table S2) suggest that they are mainly derived from isoprene. 2-Methylglyceric acid sulfate correlated significantly with 2-methylglyceric acid ($r=0.608$, $p\text{-value}=0.001$, Table S2); both of these compounds are tracers for isoprene high- NO_x SOA, and are formed by the acid-catalyzed nucleophilic addition of sulfate and water, respectively, to methacrylic acid epoxide (MAE) or hydroxymethyl-methyl- α -lactone (HMML) (Lin et al., 2013). The organosulfate with m/z 260 is a nitrooxy-organosulfate that derives from photooxidation of isoprene under high- NO_x conditions (Surratt et al., 2008; Gómez-González et al., 2008). Two isomers of m/z 260 were identified in this study, while up to four isomers of m/z 260 were reported in Centreville (Surratt et al., 2008). The m/z 260 also correlated moderately with methyltetrol sulfate ($r=0.539$, $p\text{-value}=0.005$, Table S1), supporting its formation from isoprene. The organosulfate with m/z 274 is also a nitrooxy organosulfate that is derived from isoprene photooxidation under high- NO_x conditions (Nestorowicz et al., in review). The organosulfate with m/z 274 has multiple isomers, while only the two isomers retaining greater than 4 min are considered to be major ones (Sect. 3.2 and Fig. 3o). Their longer retention times (5.6 and 5.8 min), three additional oxygen atoms, and one unit of unsaturation suggest the presence of a carboxylic acid functional group and a hydroxyl group. Plausible structures for these two organosulfates are diastereomers of 2-carboxy-3-hydroxy-4-(nitrooxy)butan-2-yl sulfate (Table 1), which could form by the oxidation of a primary hydroxyl group in 1,3-dihydroxy-2-methyl-4-(nitrooxy)butan-2-yl sulfate (an isomer of m/z 260, $\text{C}_5\text{H}_{10}\text{SO}_9^-$, proposed by Darer et al. (2011)) to a carboxylic acid. The strong correlation of these two signals at m/z 274 with the less-oxidized isoprene nitrooxy-organosulfate (m/z 260) ($r=0.860$, $p\text{-value}<0.001$, Table S1), supports this prediction. Overall, these results indicate that isoprene is the major precursor of the most abundant organosulfates in this study.”

This text has been revised to read:

“The strongest organosulfate signals observed in m/z 97, 80, and 81 precursor ion scans are associated with isoprene (Figure 1 and Table 1). Methyltetrol sulfate (m/z 215), the most abundant organosulfate observed, is produced from the acid catalyzed nucleophilic addition of sulfate to IEPOX ring (Surratt et al., 2010). Organosulfates with m/z 211 (hydroxy-methyl-tetrahydrofuranone sulfates) and 213 (dihydroxy-methyl-tetrahydrofuranyl sulfates), of the next-highest abundance, have been observed during photo-oxidation of isoprene (Surratt et al., 2008) and are suggested to derive from oxidation of primary alcohols in methyltetrol sulfates (Hettiyadura et al., 2015). In addition, 14 other major organosulfates identified are known to derive from isoprene and isoprene oxidation products (Table 1). Many of these organosulfates have also been identified as SOA products from diesel and biodiesel fuel emissions (e.g., 2-methylglyceric acid sulfate, lactic acid sulfate, hydroxyacetone sulfate, m/z 167, 183, 197, 211, 213, 237, 239, and 253) (Blair et al., 2017), monoterpenes (m/z 239 and 253) (Surratt et al., 2008), and/or MBO (199; $\text{C}_5\text{H}_{11}\text{SO}_6^-$) (Zhang et al., 2012). However, their moderate to strong correlations with methyltetrol sulfate (Table S1) and 2-methyltetrols (Table S2) suggest that they are mainly derived from isoprene.

Among the major organosulfate signals are those associated with isoprene oxidation under high- NO_x conditions such as 2-methylglyceric acid sulfate, m/z 260 and 274. 2-Methylglyceric acid sulfate is a tracer for isoprene high- NO_x SOA that is formed by the acid-catalyzed nucleophilic addition of sulfate to methacrylic acid epoxide (MAE) and/or hydroxymethyl-methyl- α -lactone (HMML) (Lin et al., 2013). The organosulfate with m/z 260 is a nitrooxy-organosulfate that derives from photooxidation of isoprene under high- NO_x conditions (Surratt et al., 2008; Gómez-González et al., 2008). Two isomers of m/z 260

were identified in this study, while up to four isomers of m/z 260 were reported in Centreville (Surratt et al., 2008). The m/z 260 also correlated moderately with methyltetrol sulfate ($r=0.539$, $p\text{-value}=0.005$, Table S1), supporting its formation from isoprene. The organosulfate with m/z 274 is also a nitrooxy organosulfate that is derived from isoprene photooxidation under high- NO_x conditions (Nestorowicz et al., in review). The organosulfate with m/z 274 has multiple isomers, while only the two isomers retaining greater than 4 min are considered to be major ones (Sect. 3.2 and Fig. 3o). Their longer retention times (5.6 and 5.8 min), three additional oxygen atoms, and one unit of unsaturation suggest the presence of a carboxylic acid functional group and a hydroxyl group. Plausible structures for these two organosulfates are diastereomers of 2-carboxy-3-hydroxy-4-(nitrooxy)butan-2-yl sulfate (Table 1), which could form by the oxidation of a primary hydroxyl group in 1,3-dihydroxy-2-methyl-4-(nitrooxy)butan-2-yl sulfate (an isomer of m/z 260, $\text{C}_5\text{H}_{10}\text{SO}_9^-$, proposed by Darer et al. (2011)) to a carboxylic acid. The strong correlation of these two signals at m/z 274 with the less-oxidized isoprene nitrooxy-organosulfate (m/z 260) ($r=0.860$, $p\text{-value}<0.001$, Table S1) supports this prediction. Overall, these results indicate that isoprene is the major precursor of the most abundant organosulfates observed in this study."

Page 7, line 2: *"Which "signal" do you refer to?"*

Authors' response to referee's specific comment on page 7, line 2: We thank the referee for indicating this. The majority of the strongest organosulfate signals observed in m/z 97, 80, and 81 are attributed to isoprene. We have added this to the revised manuscript as shown in the authors' response to referee's specific comment on page 7.

Page 7, lines 4-5: *"Please check that all compounds names are written correctly - it seems that spaces are missing in some names."*

Authors' response to referee's specific comment on page 7, lines 4-5: We have revised the nomenclature of m/z 213 and 211 according to Hettiyadura et al. (2015) as shown in the authors' response to referee's specific comment on page 7.

Page 7, line 8: *"Suggest to rephrase to "have also been identified as.."*

Authors' response to referee's specific comment on page 7, line 8: We have revised this sentence according to referee's comment in the authors' response to referee's specific comment on page 7.

Page 7, line 16: nitooxy -> nitrooxy

Authors' response to referee's specific comment on page 7, line 8: We thank the referee for pointing out this typo. We have corrected it in the revised manuscript as shown in the authors' response to referee's specific comment on page 7.

Page 7, line 30: *"Please explain how "isoprene-derived organic aerosol" was identified and quantified. Using AMS data?"*

Authors' response to referee's specific comment on page 7, line 30: IEPOX-OA was determined using a multilinear engine (ME-2) by analyzing PM₁ OA mass spectra collected using ACSM. We have added this to the text in the revised manuscript as shown below.

The text at page 7, line 30 originally read: *"IEPOX-derived OA accounted for 29% (3.3 $\mu\text{g m}^{-3}$) of PM₁ OA at the nearby JST monitoring site in summer 2014, while the measured IEPOX-OA tracers (2-methyltetrols, C₅-alkene triols, and 3-methyl-hydrofuran-3,4-diols) in PM_{2.5} (averaged 391.7 ng m⁻³) accounted for 3% of PM₁ OA (RattanaVaraha et al., 2017), assuming negligible differences between PM₁ and PM_{2.5}."*

This text has been revised to read: "By factor analysis of aerosol chemical speciation data (using multilinear engine [ME-2]), IEPOX-derived OA was estimated to account for 29% (3.3 $\mu\text{g m}^{-3}$) of PM₁ (submicron particulate matter) OA at the nearby JST monitoring site in summer 2014, while the IEPOX-OA tracers measured in PM_{2.5} (2-methyltetrols, C₅-alkene triols, and 3-methyl-hydrofuran-3,4-diols) accounted for 3% of PM₁ OA (RattanaVaraha et al., 2017), assuming negligible differences between PM₁ and PM_{2.5}."

Page 8, line 32: *"The dodecyl sulfate from surfactants is not covered well by the title of the section."*

Authors' response to referee's specific comment on page 8, line 32: We thank the referee for indicating this error. We have revised this subheading as "Organosulfates derived from anthropogenic sources"

Page 9, line 24: *"It is not so clear which organosulfates are detected for the first time ever and which are detected for the first time in Atlanta."*

Authors' response to referee's specific comment on page 9, line 24: We recognize that a clarification is needed for this sub-heading. This section discusses the organosulfates that has been identified in Atlanta, but have not been detected in laboratory studies. The focus of this sub section is to give insights to their structures based on their elemental composition and retention times, and precursors based on their correlations with other organosulfates. We have revised the sub-heading of this section as "Additional organosulfates observed in ambient aerosol" to match with its contents. Also, the first paragraph of this section has been revised accordingly.

Text at page 9, line 25-30 originally read: *"Three major organosulfates observed at m/z 155 (C₃H₇SO₄⁻), 165, and 242 have not been previously reported in laboratory smog chamber experiments. They were detected in the PM_{2.5} collected from Centreville during summer 2013 (Hettiyadura et al., 2017). The m/z 155 in Atlanta correlated with most of the isoprene-derived organosulfates (Table S1), suggesting that it was derived from isoprene. Insight into the chemical composition, structure, and origins of m/z 165 and 242 are presented in the following paragraphs."*

This text has been revised to read: "Three organosulfates that have not been previously reported in laboratory smog chamber experiments were detected among the major organosulfate signals: m/z 155 (C₃H₇SO₄⁻), 165, and 242. These signals were previously detected in PM_{2.5} in Centreville, AL (Hettiyadura et al., 2017), while new insights to their possible precursors and structures are gained here. The species

with m/z 155 was previously identified as a mono-hydroxy propyl sulfate (Hettiyadura et al., 2017); in Atlanta, it correlated with most of the isoprene-derived organosulfates (Table S1), suggesting that it was derived from isoprene.”

Page 10, lines 15-16: *“This would need additional laboratory studies to confirm.”*

Authors’ response to referee’s specific comment on page 10, lines 15-16: We agree with the referee’s comment. We have revised this text to include this as shown below.

Text at page 10, line 15-16 originally read: “As this nitrooxy organosulfate is expected to derive from m/z 260, it may useful as a tracer for isoprene SOA formed under high-NO_x conditions and provide insights into atmospheric aging of isoprene-derived SOA.”

This text has been revised to read: “As m/z 242 nitrooxy organosulfate is expected to derive from m/z 260, it may provide insight to the atmospheric aging of isoprene-derived SOA, although further evaluation is needed.”

Page 10, Section 3.8: *“Please make it more clear that you are comparing samples collected in different years. Differences in levels are thus heavily affected by differences in meteorology affecting isoprene emissions, transport and mixing of biogenic and anthropogenic pollutants.”*

Authors’ response to referee’s specific comment on page 10, 3.8: Following text is revised to clearly indicate the different years of sample collection at the two sites and its consequences.

Text at page 10, lines 18-20 originally read: *“To better understand the extent of which anthropogenic pollutants influence biogenic SOA formation in urban Atlanta during summer, the concentrations of the major organosulfates were compared to those measured in rural Centreville, AL during summer 2013 analyzed by similar methodology (Hettiyadura et al., 2017; Hidy et al., 2014).”*

This text has been revised to read: “To better understand the extent of which anthropogenic pollutants influence biogenic SOA formation in urban Atlanta during August 2015, the concentrations of the major organosulfates were compared with those measured in rural Centreville, AL during summer 2013 by similar methodology (Hettiyadura et al., 2017; Hidy et al., 2014).

Text at page 10, lines 23-25 originally read: *“Since the absolute concentrations of these organosulfates can vary with time due to changes in meteorology and other factors influencing their formation, their relative contributions to PM_{2.5} OC were compared across the two sites (Table 2).”*

This text has been revised to read: “Since the absolute concentrations of these organosulfates vary with time due to changes in meteorology, which affects isoprene emissions, transport and mixing of biogenic and anthropogenic pollutants, their relative contributions to PM_{2.5} OC were compared across the two sites (Table 2).”

Page 11, lines 1-5: *"I suggest to specify that you measure inorganic sulfate as opposed to total sulfate measured by AMS."*

Text at page 11, line 1-2 originally read: *"The correlations of sulfate with most of the organosulfates were weak or negligible in Atlanta (Table S4), but were moderate to strong in Centreville ($r = 0.5-0.8$) (Table S6 in Hettiyadura et al. (2018))."*

This text has been revised to read: *"The correlations of inorganic sulfate with most of the organosulfates were weak or negligible in Atlanta (Table S4), but were moderate to strong in Centreville ($r = 0.5-0.8$) (Table S6 in Hettiyadura et al. (2018))."*

Page 11, line 17: *"Can other species or photochemical processes related to NO_x be ruled out?"*

Authors' response to referee's specific comment on page 11, line 17: No, other processes of isoprene-derived organosulfate formation such as by ozonolysis cannot be ruled out. We have added this to the page 11, line 17 as indicated below.

Following text has been added to page 11, line 17: *"However, organosulfate formation from ozonolysis cannot be ruled out (Riva et al., 2016b)."*

Page 11, line 19: *"I suggest to compare your results with some of the previous results obtained during SOAS."*

The text at page 11, line 18-19 originally read: *"Together, these results suggest a greater influence of NO_x on isoprene-SOA formation in Atlanta compared to Centreville in summer."*

This text has been revised to read: *"While these findings are consistent with other studies that indicate a substantial influence of anthropogenic SO₂ and NO_x on biogenic SOA formation in the Southeastern US during summer (Rattanavaraha et al., 2016; Xu et al., 2015a), this study provides evidence for a greater influence of NO_x on isoprene-SOA formation in urban Atlanta, GA compared to rural Centreville, AL in summer."*

Page 11, line 22: *"Do you mean standard synthesis (instead of development)?"*

Authors' response to referee's specific comment on page 11, line 22: Yes, we have corrected this in the revised text as indicated below.

Text at page 11, line 21-22 originally read: *"This study provides insights to the major organosulfate species that should be targets for future measurements and standard development."*

This text has been revised to read: *"This study provides insights to the major organosulfate species that should be targets for future measurements and standard synthesis."*

Page 11, line 23: *"Suggestion: "Of these, a standard for methyltetrol sulfate was synthesized"*

-> *"Of these, only a standard for methyltetrol sulfate was previously synthesized".*

Authors' response to referee's specific comment on page 11, line 23: We thank the referee for his/her suggestion. We have revised this text accordingly as shown below.

Text at page 11, line 23-24 originally read: *"Of these, a standard for methyltetrol sulfate was synthesized (Budisulistiorini et al., 2015; Bondy et al., 2018)."*

This text has been revised to read: *"Of these, only a standard for methyltetrol sulfate was previously synthesized (Budisulistiorini et al., 2015; Bondy et al., 2018)."*

Page 12, line 15: *"I suggest to divide this into two sentences to indicate more clearly which data are in the SI and which are being published elsewhere."*

Authors' response to referee's specific comment on page 12, line 15: We have divided this sentence into two, according to the referee's suggestion as shown below.

Text at page 12, line 15 originally read: *"Organosulfate measurements are given in Table S5 and other PM_{2.5} measurements used in this study will be published soon elsewhere (Al-Naiema et al., in preparation)."*

This text has been revised to read: *"Organosulfate measurements are given in Table S5. Other PM_{2.5} measurements such as OC, inorganic sulfate, and SOA measured using GC-MS are provided elsewhere (Al-Naiema et al., in preparation)."*

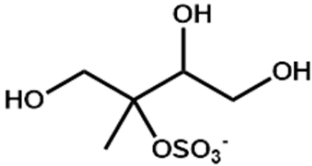
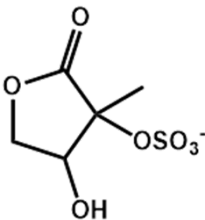
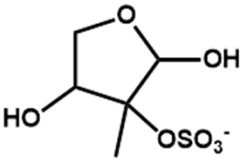
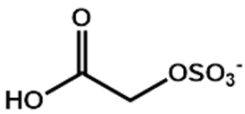
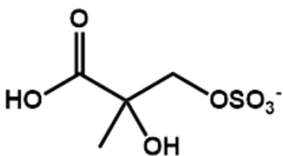
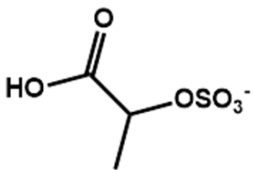
Table 1: *"Please check that the resolution of molecular structures is adequate."*

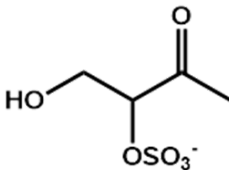
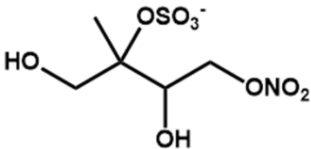
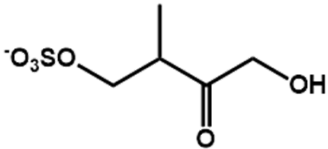
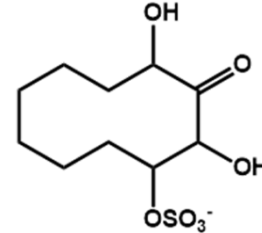
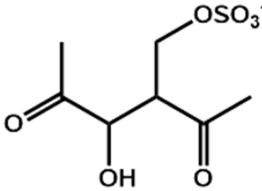
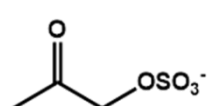
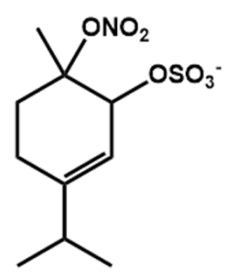
Authors' response to referee's specific comment on Table 1: We thank the referee for indicating this. We have replaced the structures in Table 1 with high resolution images as shown below.

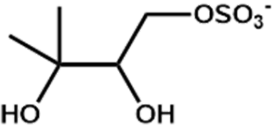
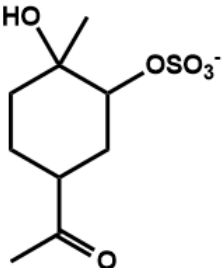
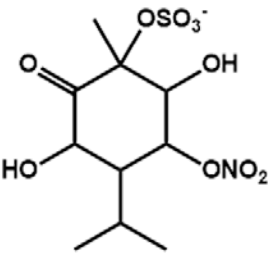
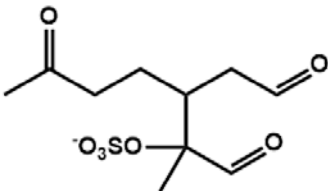
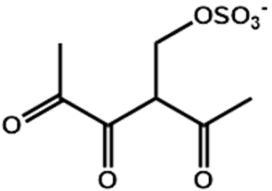
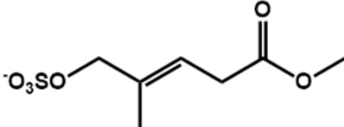
Table 2: *"The number of significant figures should indicate the uncertainty for each number and does not have to be the same for all levels of concentrations. The number of significant figures should thus be reduced for the highest concentrations."*

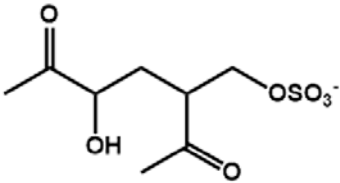
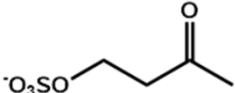
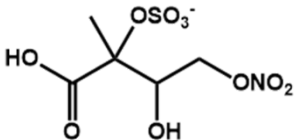
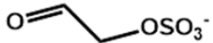
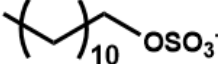
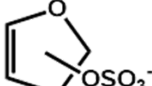
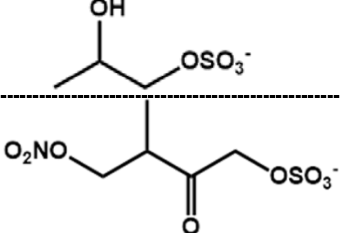
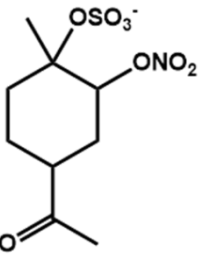
Authors' response to referee's specific comment on Table 2: We have revised the significant figures in both Tables 1 and 2 according to the referee's comment.

Revised Table 1. The major organosulfates identified using HILIC-TQ in daily PM_{2.5} samples collected from Atlanta, GA in August 2015, indicating nominal mass-to-charge ratio (m/z), chemical formula and monoisotopic mass (at 0.01 Da) determined from HILIC-ToF, proposed structure (with a star indicating many isomers, although only one is shown), and potential VOC precursors, and their average ambient concentrations with one standard deviation (SD). For these organosulfates the median and the maximum error in the observed mass is 1.7 and 7.5 mDa, respectively. Organosulfates are ordered in the table from greatest to least abundance.

m/z [M-H] ⁻	Formula [M-H] ⁻	Monoisotopic mass [M-H] ⁻	Proposed structure	Precursor(s)	Average (SD) (ng m ⁻³)
215	C ₅ H ₁₁ SO ₇ ⁻	215.0225 (Methyltetrol sulfate)	1* 	Isoprene ²⁻⁵	1792 (1085)
211	C ₅ H ₇ SO ₇ ⁻	210.9912	6* 	Isoprene ²	131 (82) ⁷
213	C ₅ H ₉ SO ₇ ⁻	213.0069	6* 	Isoprene ²⁻³	114 (79) ⁷
155	C ₂ H ₃ SO ₆ ⁻	154.9650 (Glycolic acid sulfate)	6-8 	Isoprene, ^{2,4-5} MVK ^{4,9}	58.5 (40.2)
199	C ₄ H ₇ SO ₇ ⁻	198.9912	2 	Isoprene, ²⁻⁵ MVK and MACR ^{4,9}	53.0 (42.3) ¹⁰
169	C ₃ H ₅ SO ₆ ⁻	168.9807 (Lactic acid sulfate)	6-8 	Isoprene, ^{2-3,5} 3- <i>E</i> -hexenal, 3- <i>Z</i> -hezenal, and]2- <i>E</i> -pentenal, ¹¹ MVK ⁴	38.4 (24.2)

183	C ₄ H ₇ SO ₆ ⁻	182.9963	12*		Isoprene, ³ MACR and MVK ⁹	23.4 (14.9) ¹³
260	C ₅ H ₁₀ NSO ₉ ⁻	260.0076	14*		Isoprene ^{2, 5}	18.7 (11.2) ⁷
197	C ₅ H ₉ SO ₆ ⁻	197.0120	3*		Isoprene ³	13.3 (6.1) ¹³
281	C ₁₀ H ₁₇ SO ₇ ⁻	281.0695	15*		Monoterpenes, ² pinene ⁴	12.1 (7.8) ¹³
239	C ₇ H ₁₁ SO ₇ ⁻	239.0225	4*		Limonene, ² MVK and MACR ⁴	11.5 (6.1) ¹³
209	C ₆ H ₉ SO ₆ ⁻	209.0120	*Not identified DBE 2.5		Diesel and biodiesel fuel ¹⁶	10.2 (6.3) ¹³
153	C ₃ H ₅ SO ₅ ⁻	152.9858 (Hydroxyacetone sulfate)	2		Isoprene, ²⁻³ MACR and MVK ⁹	10.1 (6.0)
294	C ₁₀ H ₁₆ NSO ₇ ⁻	294.0647	2*		α-Pinene, terpinolene, and α-terpinene, ² β-pinene ^{2, 17}	9.0 (7.1) ¹⁸

199	$C_5H_{11}SO_6^-$	199.0276	19*		Isoprene, ³ MBO ¹⁹	8.4 (5.4) ¹³
251	$C_9H_{15}SO_6^-$	251.0589	2*		Limonene, ² β -caryophylline ²⁰	8.0 (3.3) ¹³
195	$C_5H_7SO_6^-$	194.9963	*Not identified DBE 2.5		Diesel and biodiesel fuel ¹⁶	7.6 (4.5) ¹³
342	$C_{10}H_{16}NSO_{10}^-$	342.0495	21		α -Pinene and α -terpinene, ² β -pinene, ^{2, 17}	7.1 (3.9) ¹³
279	$C_{10}H_{15}SO_7^-$	279.0538	2*		Monoterpenes, ² pinene ⁴	7.1 (3.2) ¹³
237	$C_7H_9SO_7^-$	237.0069	4*		MVK ⁴	6.6 (3.2) ¹³
223	$C_7H_{11}SO_6^-$	223.0276	21*		α -Pinene ²	6.3 (2.8) ¹³

253	$C_8H_{13}SO_7^-$	253.0382	9*		α -Terpinene, ² MVK and MACR ^{4, 9}	6.3 (2.7) ¹³
167	$C_4H_7SO_5^-$	167.0014	9*		MACR and MVK ⁹	4.2 (1.8) ¹³
274	$C_5H_8NSO_{10}^-$	273.9869	*		Isoprene ²²	2.9 (1.2) ¹⁰
151	$C_4H_7SO_4^-$	151.0065	Not identified DBE 1.5		Diesel ¹⁶	2.7 (1.9) ¹⁸
139	$C_2H_3SO_5^-$	138.9701	2*		Isoprene ²	2.4 (1.1) ²³
265	$C_{12}H_{25}SO_4^-$	265.1474	24		Diesel and biodiesel fuel ¹⁶	2.3 (1.5) ¹³
165	$C_4H_5SO_5^-$	164.9858	*		Unknown	2.0 (1.4) ¹⁸
137	$C_3H_5SO_4^-$	136.9909	*Not identified DBE 1.5		Diesel ¹⁶	1.8 (0.8) ²³
155	$C_3H_7SO_5^-$	155.0014	24		Unknown ²⁴	1.6 (0.9) ¹³
242	$C_5H_8NSO_8^-$	241.9971			Unknown	0.5 (0.4) ¹⁸
296	$C_9H_{14}NSO_8^-$	296.0440	2		Limonene ²	0.5 (0.2) ²³

Methylvinyl ketone (MVK), methacrolein (MACR), 2-methyl-3-buten-2-ol (MBO), double bond equivalence (DBE); ¹Surratt et al. (2010), ²Surratt et al. (2008), ³Riva et al. (2016b), ⁴Nozière et al. (2010), ⁵Gómez-González et al. (2008), ⁶Hettiyadura et al. (2015), ⁷quantified using a response factor of *m/z* 97 of the 2-methyltetrol sulfate standard detected in a previous experiment, ⁸Olson et al. (2011), ⁹Schindelka et al. (2013), ¹⁰quantified against *m/z* 97 of glycolic acid sulfate standard, ¹¹Shalamzari et al. (2016), ¹²Shalamzari et al. (2013), ¹³quantified against *m/z* 97 of hydroxyacetone sulfate standard, ¹⁴Darer et al. (2011), ¹⁵Riva et al. (2016a), ¹⁶Blair et al. (2017), ¹⁷Iinuma et al. (2007), ¹⁸quantified against *m/z* 96 of methyl sulfate standard, ¹⁹Zhang et al. (2012), ²⁰Chan et al. (2011), ²¹Yassine et al. (2012), ²²Nestorowicz et al. (in review), ²³quantified against *m/z* 80 of hydroxyacetone sulfate standard, ²⁴Hettiyadura et al. (2017).

Revised Table 2. Comparison of organosulfates quantified or semi-quantified in Centreville, AL from 13 June to 13 July, 2013 and in Atlanta, GA in August 2015. Standard deviations are given in parenthesis.

Organosulfate	Atlanta, GA		Centreville, AL ¹	
	Average (ng m ⁻³)	%OC	Average (ng m ⁻³)	%OC
Hydroxyacetone sulfate (<i>m/z</i> 153) ²	10.1 (6.0)	0.06 (0.03)	5.8 (3.1)	0.05 (0.04)
Glycolic acid sulfate (<i>m/z</i> 155) ²	58.5 (40.2)	0.24 (0.14)	20.6 (14.3)	0.10 (0.08)
C ₃ H ₇ SO ₅ ⁻ (<i>m/z</i> 155) ³	1.6 (0.9)	0.01 (0.01)	1.1 (0.8)	0.01 (0.01)
Lactic acid sulfate (<i>m/z</i> 169) ²	38.4 (24.2)	0.20 (0.11)	16.5 (10.3)	0.12 (0.10)
C ₄ H ₇ SO ₆ ⁻ (<i>m/z</i> 183) ³	23.4 (14.9)	0.15 (0.07)	9.4 (5.8)	0.09 (0.08)
C ₄ H ₇ SO ₇ ⁻ (<i>m/z</i> 199) ⁴	53.0 (42.3)	0.32 (0.22)	8.4 (9.0)	0.07 (0.09)
C ₅ H ₁₁ SO ₆ ⁻ (<i>m/z</i> 199) ³	8.4 (5.4)	0.06 (0.03)	2.6 (2.2)	0.03 (0.03)
C ₅ H ₇ SO ₇ ⁻ (<i>m/z</i> 211) ⁵	131 (82)	0.93 (0.48)	35.3 (25.6)	0.33 (0.31)
C ₅ H ₉ SO ₇ ⁻ (<i>m/z</i> 213) ⁵	114 (79)	0.80 (0.48)	31.6 (22.5)	0.30 (0.26)
Methyltetrol sulfate (<i>m/z</i> 215) ²	1792 (1085)	12.6 (6.3)	668 (515)	6.06 (5.49)
C ₇ H ₁₁ SO ₇ ⁻ (<i>m/z</i> 239) ³	11.5 (6.1)	0.10 (0.04)	7.0 (3.9)	0.09 (0.07)
C ₁₀ H ₁₆ NSO ₁₀ ⁻ (<i>m/z</i> 342) ³	7.1 (3.9)	0.07 (0.04)	5.7 (5.7)	0.08 (0.10)
<i>Sum</i>	2249	15.5	812	7.3

¹Published in Hettiyadura et al. (2018), ²quantified against authentic standards or response factors detected in a previous experiment, ³semi-quantified against hydroxyacetone sulfate, ⁴semi-quantified against glycolic acid sulfate, ⁵semi-quantified against methyltetrol sulfate or using its response factor.

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Response to Referee #2 Comments

Anonymous Referee # 2, General Comments: *“The study examines the influence of anthropogenic emissions to formation of organosulfates in an urban site in the Southeastern United States (SE-US). This is achieved by quantifying the major organosulfates from ambient measurements and comparing the identified compounds with those from laboratory experiment and a rural site in the SE-US, and other tracers measurements. The study reveals an enhanced formation of isoprene-derived organosulfate concentration, particularly the 2-methylglyceric acid sulfate which is known to be a tracer for high-NO_x isoprene-derived secondary organic aerosol (SOA) formation mechanism. The general objective is clear and the methods are well executed. There are some minor errors in the manuscript and some clarifications needed. Overall, I recommend accepting this manuscript for publication after corrections as detailed in the following.”*

Authors' response to anonymous referee # 2, general comments: We thank the referee for his/her careful review of our manuscript and for correcting the technical errors. We have made corrections to the manuscript according to the referee's comments in a point by point form as shown below.

Anonymous Referee # 2, Technical Comments 1: *“Define abbreviations at their first appearance when you are using them repeatedly, such as: GA (Pg 1 Ln 12), AL (Pg 1 Ln 22)”*

Page 1, lines 11-12 originally read: *“This study examines the anthropogenic influence on biogenic organosulfate formation at an urban site in Atlanta, GA in the Southeastern United States.”*

This text has been revised to read: *“This study examines the anthropogenic influence on biogenic organosulfate formation at an urban site in Atlanta, Georgia (GA) in the Southeastern United States (US).”*

Page 1, lines 21-22 originally read: *“Organosulfate species and concentrations in Atlanta were compared to those in a rural forested site in Centreville, AL during summer 2013, which were also dominated by isoprene-derived organosulfates.”*

This text has been revised to read: *“Organosulfate species and concentrations in Atlanta were compared to those in a rural forested site in Centreville, Alabama (AL) during summer 2013, which were also dominated by isoprene-derived organosulfates.”*

Anonymous Referee # 2, Technical Comments 2: *“Pg 1 Ln 11: add (US) after Southeastern United States”*

Authors' response to anonymous referee # 2, technical comments 2: This technical error has been corrected in the respond to anonymous referee #2, technical comment 1 at page 1, line 11.

Anonymous Referee # 2, Technical Comments 3: *“Pg 7 Lns 12-15: It is said here that the correlation between 2-methylglyceric acid sulfate with 2-methylglyceric acid is significant at $r = 0.608$. Based on description in Section 2.7, this correlation values is classified to be moderate. The use of “significant” is ambiguous, as it may be inferred as “strong”. I recommend being consistent with the classification and description throughout the text.”*

Authors' response to anonymous referee # 2, technical comments 3: We agree with the referee's comment on using a consistent terminology to indicate the strengths of the correlations. However, this sentence is no longer in the revised text as it has been removed in the authors response to referee #1, specific comment on page 7.

Anonymous Referee # 2, Technical Comments 4: *“Pg 11 Ln 30: insert “an authentic” before standard development.”*

Page 11, lines 28- 30 originally reads: *“Given the ubiquity and high abundance of m/z 211 and 213 in the Southeastern US and other locations (Hettiyadura et al., 2017; Spolnik et al., 2018), they should be the next highest priorities for standard development.”*

This text is revised to read: *“Given the ubiquity and high abundance of m/z 211 and 213 in the Southeastern US and other locations (Hettiyadura et al., 2017; Spolnik et al., 2018), they should be the next highest priorities for authentic standard development.”*

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Organosulfates in Atlanta, Georgia: Anthropogenic influences on biogenic secondary organic aerosol formation

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Abstract

Organosulfates are secondary organic aerosol (SOA) products that form from reactions of volatile organic compounds (VOC), such as isoprene, in the presence of sulfate that is primarily emitted by fossil fuel combustion. This study examines the anthropogenic influence on biogenic organosulfate formation at an urban site in Atlanta, Georgia (GA) in the Southeastern United States (US). Organosulfates were analyzed in fine particulate matter (PM_{2.5}) collected during August 2015 in Atlanta using hydrophilic interaction liquid chromatography (HILIC), tandem mass spectrometry (MS/MS), and high-resolution time-of-flight (ToF) mass spectrometry. By their MS/MS response, 32 major organosulfate species were identified, selected species were quantified, and other species were semi-quantified using surrogate standards. Organosulfates accounted for 16.5% of PM_{2.5} organic carbon (OC). Isoprene-derived organosulfates were the most abundant, dominated by methyltetrol sulfate which accounted for 12.6% of PM_{2.5} OC. Together, the isoprene-derived organosulfates accounted for the majority of the isoprene-derived ~~secondary organic aerosols~~ (SOA) that had been previously observed in Atlanta, but had not been identified at the molecular level. Other major species included seven monoterpene-derived organosulfates, five diesel and/or biodiesel-derived organosulfates, and three new organosulfates that are also expected to derive from isoprene. Organosulfate species and concentrations in Atlanta were compared to those in a rural forested site in Centreville, Alabama (AL) during summer 2013, which were also dominated by isoprene-derived organosulfates. In Atlanta, isoprene-derived organosulfate concentrations were two to six times higher and accounted for twice as much OC. The greatest enhancement in concentration was observed for 2-methylglyceric acid sulfate whose formation is enhanced in the presence of nitrogen oxides (NO and NO₂; NO_x) and is, a tracer for isoprene high-NO_x SOA. The isoprene-derived organosulfates indicated a stronger influence of NO_x in Atlanta compared to Centreville. Overall, these results suggest that SOA in the Southeastern US can be reduced by controlling NO_x and SO₂ emissions from fossil fuel combustion. This study gives insights into the major organosulfate species that should be targets for future measurements in urban environments and standard development.

1 Introduction

Organosulfates are components of atmospheric secondary organic aerosol (SOA) that contain a sulfate ester functional group. This class of compounds has been detected in ambient aerosols around the world, including collected from rural, urban, forested, and coastal sites in the United States (US), China, and/or Europe (Hansen et al., 2014; He et al., 2014; Kristensen and Glasius, 2011; Lin et al., 2012; Stone et al., 2012; Ma et al., 2014). all-around-the-world In the Southeastern US, organosulfates are estimated to contribute up to 5-9% of PM_{2.5} organic aerosol OA in the Southeastern US (Tolocka and Turpin, 2012). Organosulfates primarily form by the reactive uptake of gas-phase epoxides on acidic sulfate particles (Surratt et al., 2010; Lin et al., 2013). Alternatively, they form by the reaction of oxidized volatile organic compounds (VOC) with sulfate radicals-initiated-oxidation-of-volatile-organic-compounds-(VOC) (Nozière et al., 2010; Schindelka et al., 2013) and nucleophilic substitution of nitrate groups by sulfate (Darer et al., 2011; Hu et al., 2011). Precursors-Biogenic VOC precursors of organosulfates are largely biogenic VOC such as include isoprene, monoterpenes, sesquiterpenes, 2-methyl-3-butene-2-ol (MBO), and green leaf volatiles (Zhang et al., 2012; Surratt et al., 2008; Chan et al., 2011; Iinuma et al., 2009; Shalamzari et al., 2014). Since fossil fuel combustion is the major source of sulfate aerosols in the atmosphere (Wuebbles and Jain, 2001; Hidy et al., 2014; Carlton et al., 2010), biogenic VOC derived organosulfates are useful as tracers of anthropogenically influenced biogenic SOA (Hettiyadura et al., 2018). Organosulfates have also been observed-detected in among the SOA generated from diesel and biodiesel fuel emissions (Blair et al., 2017) and in SOA produced from anthropogenic-aromatic VOC (i.e. such as naphthalene and; methyl-naphthalene) (Riva et al., 2015) and-as well as long chain n-alkanes (Riva et al., 2016a). , although the significance of these sources to ambient organosulfates has not yet been established.

Atlanta, Georgia (GA) is the 9th most populous metropolitan area in the US with a population in 2017 of 5.9 million (U.S. Census Bureau). Here, organic aerosols account for 68-70% of PM_{2.5} during summer (RattanaVaraha et al., 2017; Al-Naiema et al., in preparation) the majority of which is secondary in origin (50-65%) and is strongly influenced by isoprene SOA (Weber et al., 2007). For example, isoprene dihydroxy epoxides (IEPOX) contributed 29-38% of fine OA (RattanaVaraha et al., 2017; Budisulistiorini et al., 2016; Xu et al., 2015a) and total isoprene-derived OA contributed to 27% of PM_{2.5} organic carbon (OC) (Al-Naiema et al., in preparation). The diurnal variation of IEPOX-OA in Atlanta, GA was temporally consistent with isoprene emissions from plants, suggesting that the IEPOX-OA form locally rather than being transported from surrounding forested sites (Xu et al., 2015b). In Atlanta, sulfate is the second largest component of PM_{2.5} and accounted for 15-21% of PM_{2.5} mass (RattanaVaraha et al., 2017; Al-Naiema et al., in preparation). The aerosol acidity (average pH 1.4 ± 0.7) and the aerosol water content (averaging $8.4 \pm 4.8 \mu\text{g m}^{-3}$) in Atlanta peaks during summer (RattanaVaraha et al., 2017), similar to other locations in the Southeastern US (Guo et al., 2015). Previous studies have demonstrated that the biogenic SOA formation in the Southeastern US is enhanced by sulfate, NO_x, and O₃, which are mainly coming from fossil fuel combustion, particularly during summer when the biogenic emissions are high (Goldstein et al., 2009; Gao et al., 2006; Xu et al., 2015a; Carlton et al., 2010).

Field Code Changed

This study examines the anthropogenic influence on organosulfate formation during summer at an urban site in Atlanta in the Southeastern US. Our specific objectives include 1) identification and quantification of major organosulfate species in Atlanta, GA during August 2015 using hydrophilic interaction liquid chromatography (HILIC), tandem mass spectrometry (MS/MS), and high-resolution time-of-flight mass spectrometry (ToF-MS), 2) evaluation of the factors that influence organosulfate formation *via* comparison of observed species to SOA chamber experiments and correlations of organosulfates with SOA tracers, other PM_{2.5} constituents, gas-phase reactive species, and meteorological conditions, and 3) comparison of these results with the major organosulfates identified and quantified in Centreville, [Alabama \(AL\)](#) during summer 2013 (Hettiyadura et al., 2017; Hettiyadura et al., 2018) to better understand the extent to which anthropogenic pollutants affect biogenic organosulfate formation across an urban and rural pair in the Southeastern US during summer. This study provides insights into the composition, abundance, sources, and formation pathways of organosulfates, which are useful as tracers for anthropogenically-influenced SOA.

2 Materials and methods

2.1 Chemicals and reagents

Hydroxyacetone sulfate and glycolic acid sulfate (potassium salts, > 95% purity) were synthesized according to Hettiyadura et al. (2015); lactic acid sulfate (24.9% purity) was synthesized according to Olson et al. (2011); 2-methyltetrol sulfate was synthesized according to Budisulistiorini et al. (2015) and Bondy et al. (2018). Ultra-pure water was prepared on site (Thermo, Barnsted EasyPure-II; 18.2 MΩ-cm resistivity, with total organic carbon (OC) < 40 µg L⁻¹). Other reagents include acetonitrile (Optima™, Fisher Scientific), ammonium acetate (≥ 99 %, Fluka, Sigma Aldrich) and ammonium hydroxide (Optima, Fisher Scientific).

2.2 PM_{2.5} sample collection

PM_{2.5} samples were collected in Atlanta, GA from 29 July to 27 August in 2015. A medium volume sampler (3000B, URG Corp.) operated at a flow rate of 90 L min⁻¹ was used to collect PM_{2.5} on pre-baked (550 °C for 18 hours) quartz fiber filters (90 mm, Pallflex® Tissuquartz™, Pall life science). The PM_{2.5} sampler was placed on the roof top of the School of Earth and Atmospheric Sciences building at the Georgia Institute of Technology (33°46'44.2" N, 84°23'46.2" W; height ~30-40 m). A detailed description of the sampling site is provided by Verma et al. (2014). Samples were collected daily from 1:30 p.m. to 12:30 p.m. next day (local time). One filter blank was collected for every five PM_{2.5} samples. Samples from 29 July, 03, 11, and 19 August were not ~~analysed-analyzed~~ for organosulfates as the filters were used for a different purpose. The collected samples were placed in aluminium-lined (pre-baked at 550 °C for 18 hours) Petri dishes, sealed with Teflon tape, and stored at -20 °C until extracted.

2.3 Extraction of organosulfates

Organosulfates were extracted according to the method described in Hettiyadura et al. (2015) that has been demonstrated to efficiently recover 83-121% of organosulfates with aliphatic, aromatic, carbonyl, hydroxyl, and carboxyl acid groups. Briefly, sub-samples of filters (averaging ~3 cm²) were extracted with 10.0 mL of acetonitrile and ultra-pure water (95:5, by volume) for 20 minutes by ultra-sonication (5510, Branson). The sample extracts were filtered using polypropylene membrane syringe filter disks (0.45 µm pore size, Puradisc™25 PP, Whatman®). The extracts were evaporated to dryness under ultra-high purity nitrogen gas at 50 °C (Turbovap®LV, Caliper Life Sciences, Reacti-Therm III TS 18824, and Reacti-Vap I 18825, Thermo Scientific). Dried extracts were reconstituted in 600 µL of acetonitrile and ultra-pure water (95:5 by volume).

2.4 Quantification of organosulfates

Organosulfates were quantified using HILIC coupled with negative electrospray ionization tandem mass spectrometry (ESI(-)-MS/MS) on an ultra-performance liquid chromatography system (UPLC, ACQUITY UPLC H-Class, Waters) coupled with a triple quadrupole (TQ) mass spectrometer (ACQUITY, Waters). The separation of organosulfates was performed on an ethylene-bridged hybrid amide column using an acetonitrile rich mobile phase (acetonitrile and ultra-pure water; 95: 5) and an aqueous mobile phase (ultra-pure water; 100%). Both mobile phases were buffered at pH 9 with 10 mM ammonium acetate and ammonium hydroxide. Organosulfates were eluted using a stepwise gradient as described in Hettiyadura et al. (2015). Briefly, the acetonitrile rich mobile phase was held at 100% from 0 to 2 minutes, and then decreased to 85% from 2 to 4 minutes and held constant at 85% until 11 minutes. Targeted analysis was performed in multiple reaction monitoring mode. Hydroxyacetone sulfate and glycolic acid sulfate were quantified using authentic standards. Lactic acid sulfate and methyltetrol sulfate were quantified using their response factors determined previously using authentic standards. Notably, these prior experiments had response factors (determined as the slope of the calibration curve) for glycolic acid sulfate and hydroxyacetone sulfate that were within 10% of the current experiments, indicating that instrument performance and ionization were consistent within 10%. The optimized ESI(-)-MS/MS conditions used for each of these organosulfates are given in Hettiyadura et al. (2015) and Hettiyadura et al. (2018), respectively.

Semi-quantitation of other organosulfates was based upon the MS/MS response of authentic standards and matched to the sulfur-containing fragment ions observed. For semi-quantitation of organosulfates that fragmented to the bisulfate anion (m/z 97, Fig. 1a), m/z 211, 213, and 260 the response factor of 2-methyltetrol sulfate was used, other organosulfates eluting prior to four minutes hydroxyacetone sulfate was used, and those retaining more than four minutes glycolic acid sulfate was used. For the semi-quantitation of organosulfates that fragmented only to the sulfate radical anion (m/z 96, Fig. 1b), methyl sulfate was used. Organosulfates with m/z 137, 139 and 296 that fragmented to the sulfite radical anion (m/z 80, Fig. 1d) hydroxyacetone sulfate was used. The cone voltage and collision energy used for the organosulfates that were semi-quantified using surrogate standards were same as the ESI(-)-MS conditions used for corresponding precursor ion scans (given in Sect.

2.5.1). The uncertainty of the organosulfate concentrations were calculated accounting for relative errors in air volume, extraction efficiency and instrumental analysis according to the method described in Hettiyadura et al. (2017). The relative error in the instrument analysis was propagated using the limit of detection and the relative standard deviation for each organosulfate standard given in Hettiyadura et al. (2015). For methyltetrol sulfate and the other organosulfates that did not have authentic standards, the analytical uncertainty was estimated as 30% of the measurement was used as an estimate of the analytical uncertainty their concentration values (Hettiyadura et al., 2018). This uncertainty does not account for any bias introduced by the use of a surrogate standard, which can be only evaluated by using an authentic standard. All data were acquired and analyzed using MassLynx and QuanLynx softwares (Waters Inc., version 4.1).

2.5 Qualitative analysis of organosulfates

2.5.1 Precursor ion scans

Sample analysis was performed on the UPLC-TQ in precursor ion mode as described in Hettiyadura et al. (2017). Briefly, a cone voltage and a collision energy of 28 V and 16 eV were used for the m/z 97 precursor ion scan and 42 V and 20 eV were used for the m/z 96 precursor ion scan. In addition, precursor ion scans of m/z 81 (bisulfite anion) and m/z 80 were used to identify organosulfates that did not fragment into m/z 97 or 96, for which a cone voltage of 34 V and a collision energy of 18 eV were used. A mass range of 100-400 Da was used in all precursor ion scans. The data were acquired and analysed using MassLynx and QuanLynx software packages (Waters Inc., version 4.1).

2.5.2 Chemical characterization and structure elucidation

PM extracts were also analyzed by a UPLC-ToF mass spectrometer (Bruker Daltonics MicroTOF) to determine the elemental composition and structural information of the major sulfur- containing species. The ESI(-) conditions included a capillary voltage of 2.6 kV, a cone voltage of 30 V, and a desolvation gas flow rate of 600 L h⁻¹. Other ESI(-) conditions used were the same as in Hettiyadura et al. (2015). Data were collected in a mass range 100-400 Da. A peptide, Val-Tyr-Val (m/z 378.2029, Sigma-Aldrich), was used as the lock mass to correct for any instrument drift. Molecular formulas were assigned considering both odd and even electron states, C₁₋₂₅, H₀₋₅₀, O₃₋₂₀, S₁₋₂, N₀₋₅, and a maximum error of 10 mDa. The data were acquired and analyzed using MassLynx software (Water, version 4.1) and elemental composition tool (Water Inc., version 4.0).

2.6 Collocated measurements

Percent contributions of organosulfates to PM_{2.5} OC were compared to determine the relative abundances of the major organosulfates in Atlanta and Centreville. OC in the PM_{2.5} samples were measured on 1 cm² filter punches using a thermal-optical analyzer (Sunset laboratory) according to Schauer et al. (2003). Filter-based measurements of other PM_{2.5} components, gas-phase measurements, and meteorological conditions were used in correlation analysis to provide insight to precursors and

formation pathways of organosulfates. Isoprene SOA tracers (2-methylthreitol, 2-methylerythritols, 2-methylglyceric acid, cis-2-methyl-1,3,4-trihydroxy-1-butadiene, 3-methyl-2,3,4-trihydroxy-1-butene, and trans-2-methyl-1,3,4-trihydroxy-1-butene), cis-pinonic acid, β -caryophyllinic acid, meso-erythritol, 2,3-dihydroxy-4-oxopentanoic acid, aromatic dicarboxylic acids (phthalic acid, terephthalic acid, isophthalic acid, and 4-methylphthalic acid), and mononitroaromatic compounds (4-nitrophenol, 2-methyl-4-nitrophenol, 4-methyl-2-nitrophenol, 4-nitrocatechol, 3-methyl-6-nitrocatechol, and 3-methyl-5-nitrocatechol) were measured by gas chromatography (GC)-MS according to the methods described in Al-Naiema and Stone (2017). Sulfate was measured by ion chromatography following Jayarathne et al. (2014). The hourly-based measurements of O_3 , NO_x (nitrogen oxides such as, NO and NO_2), and solar radiation were obtained from the Southeastern Aerosol and Research Characterization network monitoring site at Jefferson Street (JST) located 2 km west of the sampling site and were averaged across the sample collection time. Detailed descriptions of their quantification methods are described in Hansen et al. (2003).

2.7 Correlation analysis

Pearson's correlation coefficients were assessed using a statistical analysis software (IBM® SPSS® statistics, version 25). Correlations were interpreted as very strong (0.9-1.0), strong (0.7-0.9), moderate (0.5-0.7), weak (0.3-0.5), or negligible (0.0-0.3) (Hinkle et al., 2003). The correlations were considered as statistically significant at the 95% confidence.

3 Results and Discussion

3.1 Quantitative analysis of organosulfates in Atlanta

Quantitative information about the organosulfates observed in Atlanta are summarized in Table 1, with time series of select species shown in Figure 2. Methyltetrol sulfate is the most abundant quantified organosulfate, contributing 12.6% of $PM_{2.5}$ OC, followed by m/z 211 (0.93%), 213 (0.80%), glycolic acid sulfate (0.24%), 2-methylglyceric acid sulfate (0.32%), and lactic acid sulfate (0.20%) (Table 2). The remaining 26 organosulfates were estimated to contribute 1% of $PM_{2.5}$ OC. Altogether, the 32 measured organosulfates in Table 1 account for 16.5% of $PM_{2.5}$ OC. These results indicate that organosulfates in Atlanta during August 2015 were dominated by methyltetrol sulfate, with minor contributions from many other organosulfate species derived from isoprene, monoterpenes, and anthropogenic sources.

3.2 Qualitative analysis of major organosulfates in Atlanta

Organosulfates were identified by precursors to m/z 97 (HSO_4^-), 96 (SO_4^-), 81 (HSO_3^-), and 80 (SO_3^-) in three $PM_{2.5}$ samples collected on 30-31 July and 01 August in 2015. Results were similar for all three samples, therefore the results obtained only for 30 July sample is shown in Figure 1. Major species-organosulfur compounds were defined in one of two ways: 1) having a minimum relative intensity in the MS/MS spectra ($\geq 1.0\%$ for precursors to m/z 97, $>12\%$ for m/z 96, $>5\%$ for m/z 81, and $>3\%$ for m/z 80 in any of the three samples) or 2) by retaining more than four minutes. Despite the observation that organosulfates eluting after four minutes often have higher concentrations than early-eluting species, their MS response

is observed to be lower because of the increased water content of the mobile phase (>20%) that does not de-solvate as efficiently as acetonitrile in the ESI source (Hettiyadura et al., 2017). The absolute MS signal for precursors to m/z 97 was 52, 10, and 8 times greater than m/z 96, 81, and 80, respectively; however, due to differing ionization efficiencies and stabilities among these fragment ions, the strength of the MS signal is not indicative of the relative concentrations of species that form these fragments. Table 1 summarizes the major organosulfates' elemental composition, monoisotopic mass, proposed or known structures and precursor gases. Of the major organosulfates, 26 of the 32 consisted of C, H, O, and S, while 6 of 32 consisted of C, H, O, S, and N. Structures were proposed based on elemental composition, double bond equivalence (DBE), retention time, and prior studies.

3.3 Isoprene-derived organosulfates in Atlanta.

The strongest organosulfate signals observed in m/z 97, 80, and 81 precursor ion scans are attributed to species associated with isoprene SOA (Fig. 1 and Table 1). Methyltetrol sulfate (m/z 215), the most abundant organosulfate observed, is produced from the acid catalyzed nucleophilic addition of sulfate to IEPOX ring (Surratt et al., 2010). Organosulfates with m/z 211 (hydroxy-methyl-tetrahydrofuranone sulfates-esters-of-methyl-dihydroxylactone) and 213 (dihydroxy-methyl-tetrahydrofuranyl sulfates-esters-of-cyclic-methyl-trihydroxyaldehyde-hemiacetal), of the next-highest abundance, have been observed during photo-oxidation of isoprene (Surratt et al., 2008) and are suggested to derive from oxidation of primary alcohols in methyltetrol sulfates (Hettiyadura et al., 2015). In addition, 14 other major organosulfates identified are known to derive from isoprene and isoprene oxidation products (Table 1). Many of these organosulfates have also been identified as SOA products from diesel and biodiesel fuel emissions (e.g., 2-methylglyceric acid sulfate, lactic acid sulfate, hydroxyacetone sulfate, m/z 167, 183, 197, 211, 213, 237, 239, and 253) (Blair et al., 2017), monoterpenes (m/z 239 and 253) (Surratt et al., 2008), and/or MBO (199; $C_5H_{11}SO_6^-$) (Zhang et al., 2012). However, their moderate to strong correlations with methyltetrol sulfate (Table S1) and 2-methyltetrols (Table S2) suggest that they are mainly derived from isoprene.

Among the major organosulfate signals are those associated with isoprene oxidation under high- NO_x conditions such as 2-methylglyceric acid sulfate, m/z 260 and 274. 2-Methylglyceric acid sulfate correlated significantly with 2-methylglyceric acid ($r=0.608$, p -value=0.001, Table S2); both of these compounds are known tracers for isoprene high- NO_x SOA that, and are formed by the acid-catalyzed nucleophilic addition of sulfate and water, respectively, to methacrylic acid epoxide (MAE) and/or hydroxymethyl-methyl- α -lactone (HMML) (Lin et al., 2013). The organosulfate with m/z 260 is a nitrooxy-organosulfate that derives from photooxidation of isoprene under high- NO_x conditions (Surratt et al., 2008; Gómez-González et al., 2008). Two isomers of m/z 260 were identified in this study, while up to four isomers of m/z 260 were reported in Centreville (Surratt et al., 2008). The m/z 260 also correlated moderately with methyltetrol sulfate ($r=0.539$, p -value=0.005, Table S1), supporting its formation from isoprene. The organosulfate with m/z 274 is also a nitrooxy organosulfate that is derived from isoprene photooxidation under high- NO_x conditions (Nestorowicz et al., in review). The organosulfate with m/z 274 has multiple isomers, while only the two isomers retaining greater than 4 min are considered to be major ones (as described in Section 3.2 and Fig. 3o). Their longer retention times (5.6 and 5.8 min), three additional oxygen atoms, and one unit

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of unsaturation suggest the presence of a carboxylic acid functional group and a hydroxyl group. Plausible structures for these two organosulfates are diastereomers of 2-carboxy-3-hydroxy-4-(nitrooxy)butan-2-yl sulfate (Table 1), which could form by the oxidation of a primary hydroxyl group in 1,3-dihydroxy-2-methyl-4-(nitrooxy)butan-2-yl sulfate (an isomer of m/z 260, $C_5H_{10}SO_9$, proposed by Darer et al. (2011)) to a carboxylic acid. The strong correlation of these two signals at m/z 274 with the less-oxidized isoprene nitrooxy-organosulfate (m/z 260) ($r=0.860$, $p\text{-value}<0.001$, Table S1); supports this prediction. Overall, these results indicate that isoprene is the major precursor of the most abundant organosulfates in this study.

Isoprene-derived organosulfates explain a significant fraction of isoprene-derived organic aerosol observed in Atlanta that had not previously been identified on a molecular level. By factor analysis of aerosol chemical speciation data (using multilinear engine [ME-2]), IEPOX-derived OA was estimated to accounted for 29% ($3.3 \mu\text{g m}^{-3}$) of PM_{10} (submicron particulate matter) OA at the nearby JST monitoring site in summer 2014, while the measured-IEPOX-OA tracers measured in $PM_{2.5}$ (2-methyltetrols, C_5 -alkene triols, and 3-methyl-hydrofuran-3,4-diols) in $PM_{2.5}$ (averaged 391.7 ng m^{-3}) accounted for 3% of PM_{10} OA (RattanaVaraha et al., 2017), assuming negligible differences between PM_{10} and $PM_{2.5}$. The remaining IEPOX-derived OA corresponded to 10-18% of PM_{10} OC (considering an OM:OC ratio of 2.05 ± 0.57) (Xu et al., 2017), and is comparable to the contribution of isoprene-derived organosulfates to $PM_{2.5}$ OC in this study (15.7%). Additionally, the isoprene-derived organosulfates observed in this study account for more than half of the $PM_{2.5}$ secondary organic carbon coming from isoprene, which is estimated as 27% following the SOA tracer method (Al-Naiema et al., in preparation; Kleindienst et al., 2007). These results indicate that more than half of the isoprene-derived OA in Atlanta during summer is comprised by organosulfates, mainly methyltetrol sulfate.

3.4 Monoterpene-derived organosulfates in Atlanta

Seven of the 32 major organosulfates identified in Atlanta (Table 1) were previously detected among the SOA produced from monoterpenes in the presence of NO_x and acidic sulfate seed aerosols (Surratt et al., 2008). Of these, nitrooxy-organosulfates at m/z 342, 294, and 296 are derived from monoterpenes either by photooxidation in the presence of NO_x or from nitrate radical-initiated oxidation (Surratt et al., 2008; Iinuma et al., 2007). The estimated contribution of these seven monoterpene-derived organosulfates is 0.5% of $PM_{2.5}$ OC. However, the accuracy of this estimate is limited by the lack of authentic standards for monoterpene organosulfates and the large differences in molecular structure between the monoterpene organosulfates and the standards utilized in this study. The absence of significant correlations among nitrooxy-organosulfates with other organosulfates (Table S1) and biogenic SOA tracers that predominantly derive from photooxidation reactions (Table S2) suggest that these nitrooxy-organosulfates likely formed by nitrate radical-initiated oxidation. Organosulfates with m/z 223, 279, and 281 have been identified as SOA products of α -pinene, as well as from other monoterpenes (m/z 279 and 281), in the presence of NO_x and highly acidic sulfate seed aerosol (Surratt et al., 2008). The organosulfate with m/z 251 has been identified in SOA from the photooxidation of β -caryophyllene (a sesquiterpene) and limonene (a monoterpene) in the presence of NO_x and sulfate seed aerosols (Chan et al., 2011; Surratt et al., 2008). These species did not correlate with β -caryophyllinic acid (Table S2), an SOA tracer for β -caryophyllene formed under high- NO_x conditions (Jaoui et al., 2007), suggesting that m/z

251 mainly forms from monoterpenes. Organosulfates with the same m/z were also detected among the organosulfates generated from diesel and biodiesel fuel emissions (Blair et al., 2017) and photooxidation of n -alkanes such as decaline (m/z 281) and cyclodecane (m/z 279 and 281) (Riva et al., 2016a), but these species are expected to be biogenic in nature due to dominance of biogenic VOC in Atlanta during summer (Geron et al., 1995; Al-Naiema et al., in preparation; Rattanavaraha et al., 2017).

3.5 Organosulfates derived from diesel and/or biodiesel fuel emissions anthropogenic sources

Five organosulfates that were previously reported only in photooxidation of diesel and/or biodiesel fuel in the presence of SO_2 were identified among the 32 major organosulfates. These include m/z 137 and 151 that were generated from diesel fuel emissions and m/z 195, 209, and 265 that were generated from both diesel and biodiesel emissions (Blair et al., 2017). The organosulfate with m/z 265 corresponds to dodecyl sulfate, a widely used surfactant in detergents that can also come from wastewater treatment plants (Hettiyadura et al., 2017). The concentrations of m/z 209 and 195 are at least 3 times higher compared to other organosulfates derived from diesel and/or biodiesel emissions in this study (Table 1). These organosulfates (m/z 209 and 195) were also detected with a high abundance in urban Shanghai and Los Angeles (Tao et al., 2014). The organosulfates with m/z 209 and 195 are homologs, differing by one methylene. Both compounds have two units of unsaturation and two additional oxygen atoms. Further, their retention times, which were less than a minute, suggest that they do not contain a carboxylic acid group, but may contain two carbonyl groups (Fig. S3). Additional work is required to determine the position of carbonyl and sulfate groups in these compounds. As m/z 209 and 195 are highly abundant in other urban locations and are only known to derive from diesel and/or biodiesel fuel, they may be useful as tracers for SOA derived from diesel and biodiesel emissions.

3.6 Aromatic organosulfates in Atlanta

Aromatic sulfur-containing compounds were not detected among the major organosulfate species (Table 1), although some were observed by ToF MS. Two sulfur-containing compounds had large DBEs indicating aromatic groups: m/z 185 (t_R 1.06 min, $\text{C}_7\text{H}_5\text{SO}_4^-$, DBE 5.5, error 3.7 mDa) and 201 (t_R 7.56 and 8.17 min, $\text{C}_7\text{H}_5\text{SO}_5^-$, DBE 5.5, error 3.5 mDa). The MS data matched the molecular formula reported by Riva et al. (2015), who detected m/z 185 in naphthalene and 2-methylnaphthalene photooxidation experiments and identified it as formylbenzenesulfonate by MS fragmentation. Riva et al. (2015) also reported m/z 201 in SOA generated by the photooxidation of 2-methylnaphthalene and identified it as 4-sulfobenzoic acid using an authentic standard. In the Atlanta $\text{PM}_{2.5}$, two isomers of m/z 201, likely conformational isomers of 4-sulfobenzoic acid, are observed. The presence of a carboxylic acid group in m/z 201 is evident by the retention time > 7 minutes in the HILIC method (Hettiyadura et al., 2015). None of the aromatic organosulfates reported in Staudt et al. (2014) (phenyl sulfates and benzyl sulfates) were detected in ToF MS. This may be due to the lower retention times and higher detection limits for aromatic organosulfates in HILIC compared to reversed-phase LC (Hettiyadura et al., 2015). These results

suggest that aromatic organosulfates have low PM_{2.5} concentrations in comparison to biogenic organosulfates in Atlanta during the summertime.

3.7 ~~New~~ ~~Other major~~ Additional organosulfates observed in ambient aerosol organosulfates identified in Atlanta

Three ~~major~~ organosulfates ~~observed at m/z 155 ($C_3H_7SO_4^-$), 165, and 242 that~~ have not been previously reported in laboratory smog chamber experiments ~~were detected among the major organosulfate signals: m/z 155 ($C_3H_7SO_4^-$), 165, and 242. They~~ These signals were previously also detected in the PM_{2.5} collected from Centreville, AL during summer 2013 (Hettiyadura et al., 2017), while new insights to their possible precursors and structures are gained here. Of these, ~~the~~ The species with m/z 155 was previously identified as a mono-hydroxy propyl sulfate and was among the ten major organosulfate signals identified in Centreville (Hettiyadura et al., 2017); in Atlanta, ~~The m/z 155 in Atlanta~~ correlated with most of the isoprene-derived organosulfates (Table S1), suggesting that it was derived from isoprene. ~~Insight into the chemical composition, structure, and origins of m/z 165 and 242 are presented in the following paragraphs.~~

The organosulfate at m/z 165 has an elemental composition of $C_4H_5SO_5^-$, indicating the presence of sulfate, an additional oxygenated functional group, and two DBEs. The ToF chromatograms (Fig. 3d) indicate two isomers of m/z 165 that eluted ~~<in less than~~ 2 min. While both isomers were fragmented into m/z 80, only the first isomer fragmented into m/z 96, which was quantified. Its elemental composition and DBE suggest a dihydrofuran ring structure (Table 1). The strong correlations of m/z 165 with methyltetrol sulfate ($r=0.720$, p -value <0.001 ; Table S1) and 2-methyltetrols ($r=0.670$ and 0.768 , p -value <0.001 ; Table S2) suggest that it ~~is~~ also derived from isoprene.

The organosulfate at m/z 242 has an elemental composition of $C_5H_8NSO_8^-$, indicating the presence of sulfate, nitrooxy, an oxygen-containing functional groups, and two DBEs. Its short retention time of 0.5 min (Fig. 3k) suggests that it contains a carbonyl group as organosulfates with hydroxyl and carboxylate groups retain more than 1 and 4 minutes, respectively (Hettiyadura et al., 2015; Hettiyadura et al., 2017). A possible formation pathway for this nitrooxy-organosulfate can be loss of a water molecule from 2,3-dihydroxy-3-methyl-4-(nitrooxy)butyl sulfate (an isomer of m/z 260, $C_5H_{10}SO_9^-$, proposed by Gómez-González et al. (2008)) forming an enol that tautomerizes to ~~its stable~~ a carbonyl forming resulting in 3-methyl-4-(nitrooxy)-2-oxobutyl sulfate (Table 1). Only a few atmospherically relevant isoprene-derived nitrooxy organosulfates have been identified in previous studies. These include m/z 244, 260, 274, and 305 that are derived from isoprene photooxidation under high-NO_x conditions (Surratt et al., 2008; Gómez-González et al., 2012). It is expected that m/z 242 is an additional nitrooxy organosulfate that has not been previously identified in isoprene photooxidation experiments. As ~~this nitrooxy-organosulfate m/z 242 nitrooxy organosulfate~~ is expected to derive from m/z 260, ~~it may useful as a tracer for isoprene SOA formed under high-NO_x conditions and will~~ may provide insights into the atmospheric aging of isoprene-derived SOA, ~~although, however this require further work to confirm~~ evaluation is needed.

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3.8 Comparison of major organosulfates in Atlanta and Centreville

To better understand the extent of which anthropogenic pollutants influence biogenic SOA formation in urban Atlanta during ~~summer~~ August 2015, the concentrations of the major organosulfates were compared to those measured in rural Centreville, AL during summer 2013 analyzed by similar methodology (Hettiyadura et al., 2017; Hidy et al., 2014). Although the major organosulfates identified in both sites were similar and mainly derived from isoprene, their concentrations were two to six times higher in Atlanta than in Centreville, with greatest enhancement obtained for 2-methylglyceric acid sulfate (Table 2). Since the absolute concentrations of these organosulfates ~~can~~ vary with time due to changes in meteorology, ~~which affects isoprene emissions, transport and mixing of biogenic and anthropogenic pollutants and other factors influencing their formation~~, their relative contributions to PM_{2.5} OC were compared across the two sites (Table 2). In total, 12 organosulfates quantified or semi-quantified in both studies contributed 7% of PM_{2.5} OC in Centreville, and 16% in Atlanta. These 12 organosulfates accounted for 95% of the total organosulfate mass in Atlanta and 58-78% of the total bisulfate ion signal in Centreville (Hettiyadura et al., 2017), indicating that these were the dominant species at both sites. Similarly, the IEPOX-OA in Atlanta during August 2012 (31% of PM₁ OA) was ~two times greater than IEPOX-OA in Centreville in summer 2013 (18% of PM₁ OA) (Xu et al., 2015a; Xu et al., 2015b). Overall, these results suggest isoprene SOA is two times higher in Atlanta compared to Centreville during summer.

Correlations of major organosulfate species were examined at both Atlanta and Centreville sites to gain insight to their sources and formation pathways. Organosulfates at both sites show moderate to strong correlations with isoprene, isoprene oxidation products, and/or isoprene SOA tracers (Table S2; Table S6 in Hettiyadura et al. (2018)), supporting that they mainly derive from isoprene. The correlations of ~~inorganic~~ sulfate with most of the organosulfates were weak or negligible in Atlanta (Table S4), but were moderate to strong in Centreville ($r = 0.5-0.8$) (Table S6 in Hettiyadura et al. (2018)). This is likely due to the consistently high levels of sulfate observed in urban Atlanta (ranging $0.82 - 3.24 \mu\text{g m}^{-3}$, averaging $1.70 \pm 0.58 \mu\text{g m}^{-3}$) compared to more variable sulfate concentrations in rural Centreville (ranging $0.42 - 4.17 \mu\text{g m}^{-3}$, averaging $1.78 \pm 0.81 \mu\text{g m}^{-3}$) (Hettiyadura et al., 2017). Overall these results suggest isoprene and sulfate are important factors influencing the organosulfate formation in both urban Atlanta and rural Centreville.

Isoprene-derived organosulfates indicated a stronger influence of NO_x on their formation in Atlanta compared to Centreville. A NO_x influence is evident by the elevated levels of high-NO_x isoprene oxidation products such as 2-methylglyceric acid sulfate, which was six times higher in Atlanta than in Centreville, and the isoprene-derived nitrooxy organosulfate at m/z 260 being the 8th strongest organosulfate signal in Atlanta. These results are consistent with the average NO_x concentration in urban Atlanta in August 2015 (10.5 ppb) that was 15 times greater than the average NO_x concentration in rural Centreville during summer 2013 (0.7 ppb) (SOAS, 2013). Methyltetrol sulfate, the most abundant organosulfate at both sites, is thus expected to derive from low-NO_x oxidation pathway in Centreville as described in Surratt et al. (2010) and by high-NO_x oxidation pathway in Atlanta as described in Jacobs et al. (2014). The moderate and strong correlations obtained for isoprene-derived organosulfates with high-NO_x SOA products (Table S3) such as meso-erythritol (Angove et al., 2006)

and nitroaromatic compounds (Al-Naiema and Stone, 2017), as well as with ozone (Table S4) that is formed by the photochemical reactions of NO_x and VOC (Blanchard et al., 2014), also support that NO_x play a key role in isoprene-derived organosulfate formation in Atlanta. However, organosulfate formation from ozonolysis (Riva et al., 2016b) cannot be ruled out. Together While these findings are consistent with other studies that indicate a substantial influence of anthropogenic SO₂ and NO_x on biogenic SOA formation in the Southeastern US during summer (RattanaVaraha et al., 2016; Xu et al., 2015a), this study provides evidence for, these results suggest a greater influence of NO_x on isoprene-SOA formation in urban Atlanta, GA compared to rural Centreville, AL in summer.

4 Implications and future work

This study provides insights to the major organosulfate species that should be targets for future measurements and standard development/synthesis. The three most abundant organosulfates measured in both Atlanta and Centreville include methyltetrol sulfate, *m/z* 211, and 213. Of these, only a standard for methyltetrol sulfate was previously synthesized (Budisulistiorini et al., 2015; Bondy et al., 2018). Six isomers of methyltetrol sulfates were baseline resolved in the PM_{2.5} samples collected from Centreville and Atlanta. Based on their stability to acid hydrolysis, these were tentatively identified as diastereomer pairs of methyltetrol sulfates with the sulfate group attached to primary (highest stability), secondary (intermediate stability), and tertiary (lowest stability) carbons (Hettiyadura et al., 2017). Development of authentic standards for quantification of the three methyltetrol diastereomer pairs thus will give insights to atmospheric aging and lifetime of this compound. Given the ubiquity and high abundance of *m/z* 211 and 213 in the Southeastern US and other locations (Hettiyadura et al., 2017; Spolnik et al., 2018), they should be the next highest priorities for authentic standard development. The *m/z* 211 and 213 also have multiple isomers as described by Hettiyadura et al. (2015) and Spolnik et al. (2018). Further, this study reveals isoprene-derived organosulfates such as 2-methylglyceric acid sulfate and *m/z* 260 are useful in distinguishing SOA formed under high-NO_x conditions in urban environments.

While isoprene was the major precursor to organosulfates at both Atlanta and Centreville, the comparison of these two datasets reveals different anthropogenic influences on biogenic SOA formation (Sect. 3.8). In particular, NO_x had a stronger influence on organosulfate formation in Atlanta and sulfate having a stronger influence on organosulfate formation in Centreville. Future studies should focus on comparing the major organosulfate species in other urban and rural locations in the Southeastern US to determine if these trends are ubiquitous across urban-rural landscapes and to better understand the anthropogenic influences on biogenic SOA formation. While high levels of isoprene-derived organosulfates detected in the Southeastern US during summer coincide with high isoprene emissions from plants, high levels of aromatic organosulfates and nitrooxy organosulfates detected in fall and winter coincide with high levels of biomass burning (Ma et al., 2014; He et al., 2014). Thus, longer-term measurements of organosulfates spanning an annual cycle are needed to further evaluate the sources and concentrations of organosulfates in the atmosphere.

5 Data availability

Organosulfate measurements are given in Table S5, and other PM_{2.5} measurements [such as OC, inorganic sulfate, and SOA measured using GC-MS are provided](#) elsewhere (Al-Naiema et al., *in preparation*).

6 Disclaimer

- Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation (NSF).

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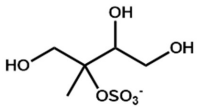
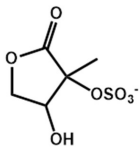
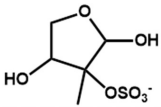
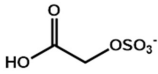
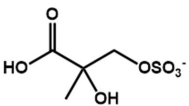
Figure Captions

Figure 1. Precursors of a) bisulfate ion (m/z 97), b) sulfate ion radical (m/z 96), c) bisulfite ion (m/z 81), and d) sulfite ion radical (m/z 80) identified from a sample collected on 30 July 2015 in Atlanta. Blue indicates nominal m/z of the major organosulfate species that were identified from the precursor m/z 97 scan. Red indicates nominal m/z of the major organosulfate species that were identified from the precursor m/z 96, 81 and 80 scans.

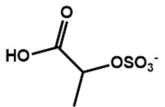
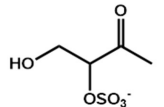
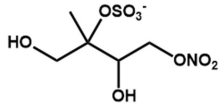
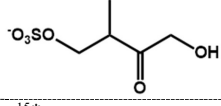
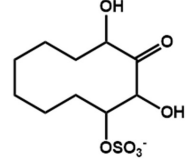
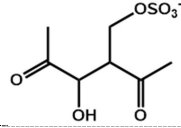
Figure 2. Time series of seven major organosulfate species quantified in August 2015 in Atlanta. Samples that were not analyzed (because they were used for a different purpose) are marked with a star.

Figure 3. Extracted chromatograms of 19 major organosulfate species obtained from a $PM_{2.5}$ sample collected in Atlanta using HR-ToF (at 0.01 Da error). Extracted chromatograms of the remaining 13 major organosulfate species are shown in Hettiyadura et al. (2017) for a $PM_{2.5}$ sample collected in Centreville. MS data, structures, and VOC precursors of these organosulfates are given in Table 1.

Table 1. The major organosulfates identified using HILIC-TQ in daily PM_{2.5} samples collected from Atlanta, GA in August 2015, indicating nominal mass-to-charge ratio (m/z), chemical formula and monoisotopic mass (at 0.01 Da) determined from HILIC-ToF, proposed structure (with a star indicating many isomers, although only one is shown), and potential VOC precursors, and their average ambient concentrations with one standard deviation (SD). For these organosulfates the median and the maximum error in the observed mass is 1.7 and 7.5 mDa, respectively. Organosulfates are ordered in the table from greatest to least abundance.

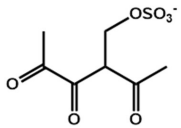
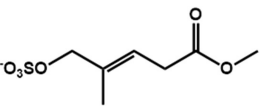
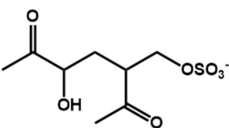
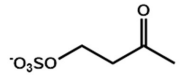
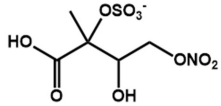
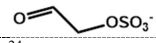
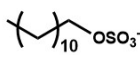
m/z [M-H] ⁻	Formula [M-H] ⁻	Monoisotopic mass [M-H] ⁻	Proposed structure	Precursor(s)	Average (SD) (ng m ⁻³)
215	C ₅ H ₁₁ SO ₇ ⁻	215.0225 (Methyltetrol sulfate)	1* 	Isoprene ²⁻⁵	1792 (1085)
211	C ₅ H ₇ SO ₇ ⁻	210.9912	6* 	Isoprene ²	131 (82) ⁷
213	C ₅ H ₉ SO ₇ ⁻	213.0069	6* 	Isoprene ²⁻³	114 (79) ⁷
155	C ₂ H ₃ SO ₆ ⁻	154.9650 (Glycolic acid sulfate)	6-8 	Isoprene, ^{2, 4-5} MVK ^{4, 9}	58.5 (40.2)
199	C ₄ H ₇ SO ₇ ⁻	198.9912	2 	Isoprene, ²⁻⁵ MVK and MACR ^{4, 9}	53.0 (42.3) ¹⁰

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169	C ₃ H ₅ SO ₆ ⁻	168.9807 (Lactic acid sulfate)	6-8 	Isoprene, ^{2,3,5} 3- <i>E</i> -hexenal, 3- <i>Z</i> -hexenal, and]2- <i>E</i> -pentenal, ¹¹ MVK ⁴	38.4 (24.2)
183	C ₄ H ₇ SO ₆ ⁻	182.9963	12* 	Isoprene, ³ MACR and MVK ⁹	23.4 (14.9) ¹³
260	C ₅ H ₁₀ NSO ₉ ⁻	260.0076	14* 	Isoprene ^{2,5}	18.7 (11.2) ⁷
197	C ₅ H ₉ SO ₆ ⁻	197.0120	3* 	Isoprene ³	13.3 (6.1) ¹³
281	C ₁₀ H ₁₇ SO ₇ ⁻	281.0695	15* 	Monoterpenes, ² pinene ⁴	12.1 (7.8) ¹³
239	C ₇ H ₁₁ SO ₇ ⁻	239.0225	4* 	Limonene, ² MVK and MACR ⁴	11.5 (6.1) ¹³
209	C ₆ H ₉ SO ₆ ⁻	209.0120	*Not identified DBE 2.5	Diesel and biodiesel fuel ¹⁶	10.2 (6.3) ¹³

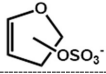
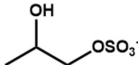
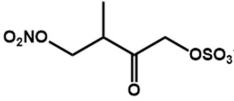
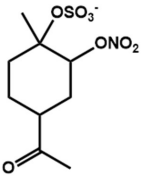
153	C ₃ H ₅ SO ₃ ⁻	152.9858	²		Isoprene, ^{2,3} MACR and MVK ⁹	10.1 (6.0)
294	C ₁₀ H ₁₆ NSO ₇ ⁻	294.0647	^{2*}		α-Pinene, terpinolene, and α-terpinene, ² β-pinene ^{2, 17}	9.0 (7.1) ¹⁸
199	C ₅ H ₁₁ SO ₆ ⁻	199.0276	^{19*}		Isoprene, ³ MBO ¹⁹	8.4 (5.4) ¹³
251	C ₉ H ₁₅ SO ₆ ⁻	251.0589	^{2*}		Limonene, ² β-caryophylline ²⁰	8.0 (3.3) ¹³
195	C ₅ H ₇ SO ₆ ⁻	194.9963	*Not identified DBE 2.5		Diesel and biodiesel fuel ¹⁶	7.6 (4.5) ¹³
342	C ₁₀ H ₁₆ NSO ₁₀ ⁻	342.0495	²¹		α-Pinene and α-terpinene, ² β-pinene, ^{2, 17}	7.1 (3.9) ¹³
279	C ₁₀ H ₁₅ SO ₇ ⁻	279.0538	^{2*}		Monoterpenes, ² pinene ⁴	7.1 (3.2) ¹³

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237	C ₇ H ₉ SO ₇ ⁻	237.0069	4*	MVK ⁴	6.6 (3.2) ¹³
					
223	C ₇ H ₁₁ SO ₆ ⁻	223.0276	21*	α-Pinene ²	6.3 (2.8) ¹³
					
253	C ₈ H ₁₃ SO ₇ ⁻	253.0382	9*	α-Terpinene, ² MVK and MACR ^{4,9}	6.3 (2.7) ¹³
					
167	C ₄ H ₇ SO ₅ ⁻	167.0014	9*	MACR and MVK ⁹	4.2 (1.8) ¹³
					
274	C ₅ H ₈ NSO ₁₀ ⁻	273.9869	*	Isoprene ²²	2.9 (1.2) ¹⁰
					
151	C ₄ H ₇ SO ₄ ⁻	151.0065	Not identified DBE 1.5	Diesel ¹⁶	2.7 (1.9) ¹⁸
139	C ₂ H ₃ SO ₅ ⁻	138.9701	2*	Isoprene ²	2.4 (1.1) ²³
					
265	C ₁₂ H ₂₅ SO ₄ ⁻	265.1474	24	Diesel and biodiesel fuel ¹⁶	2.3 (1.5) ¹³
					

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165	C ₄ H ₅ SO ₃ ⁻	164.9858	*	Unknown	2.0 (1.4) ¹⁸
					
137	C ₃ H ₅ SO ₄ ⁻	136.9909	*Not identified	Diesel ¹⁶	1.8 (0.8) ²³
			DBE 1.5		
155	C ₃ H ₇ SO ₃ ⁻	155.0014	²⁴	Unknown ²⁴	1.6 (0.9) ¹³
					
242	C ₅ H ₈ NSO ₈ ⁻	241.9971		Unknown	0.5 (0.4) ¹⁸
					
296	C ₉ H ₁₄ NSO ₈ ⁻	296.0440	²	Limonene ²	0.5 (0.2) ²³
					

Methylvinyl ketone (MVK), methacrolein (MACR), 2-methyl-3-buten-2-ol (MBO), double bond equivalence (DBE); ¹Surratt et al. (2010), ²Surratt et al. (2008), ³Riva et al. (2016b), ⁴Nozière et al. (2010), ⁵Gómez-González et al. (2008), ⁶Hettiyadura et al. (2015), ⁷quantified using a response factor of *m/z* 97 of the 2-methyltetrol sulfate standard detected in a previous experiment, ⁸Olson et al. (2011), ⁹Schindelka et al. (2013), ¹⁰quantified against *m/z* 97 of glycolic acid sulfate standard, ¹¹Shalamzari et al. (2016), ¹²Shalamzari et al. (2013), ¹³quantified against *m/z* 97 of hydroxyacetone sulfate standard, ¹⁴Darer et al. (2011), ¹⁵Riva et al. (2016a), ¹⁶Blair et al. (2017), ¹⁷Linuma et al. (2007), ¹⁸quantified against *m/z* 96 of methyl sulfate standard, ¹⁹Zhang et al. (2012), ²⁰Chan et al. (2011), ²¹Yassine et al. (2012), ²²Nestorowicz et al. (in review), ²³quantified against *m/z* 80 of hydroxyacetone sulfate standard, ²⁴Hettiyadura et al. (2017).

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Table 2. Comparison of organosulfates quantified or semi-quantified in Centreville, AL from 13 June to 13 July, 2013 and in Atlanta, GA in August 2015. Standard deviations are given in parenthesis.

Organosulfate	Atlanta, GA		Centreville, AL ¹	
	Average (ng m ⁻³)	%OC	Average (ng m ⁻³)	%OC
Hydroxyacetone sulfate (<i>m/z</i> 153) ²	10.1 (6.0)	0.06 (0.03)	5.8 (3.1)	0.05 (0.04)
Glycolic acid sulfate (<i>m/z</i> 155) ²	58.5 (40.2)	0.24 (0.14)	20.6 (14.3)	0.10 (0.08)
C ₃ H ₇ SO ₅ ⁻ (<i>m/z</i> 155) ³	1.6 (0.9)	0.01 (0.01)	1.1 (0.8)	0.01 (0.01)
Lactic acid sulfate (<i>m/z</i> 169) ²	38.4 (24.2)	0.20 (0.11)	16.5 (10.3)	0.12 (0.10)
C ₄ H ₇ SO ₆ ⁻ (<i>m/z</i> 183) ³	23.4 (14.9)	0.15 (0.07)	9.4 (5.8)	0.09 (0.08)
C ₄ H ₇ SO ₇ ⁻ (<i>m/z</i> 199) ⁴	53.0 (42.3)	0.32 (0.22)	8.4 (9.0)	0.07 (0.09)
C ₅ H ₁₁ SO ₆ ⁻ (<i>m/z</i> 199) ³	8.4 (5.4)	0.06 (0.03)	2.6 (2.2)	0.03 (0.03)
C ₅ H ₇ SO ₇ ⁻ (<i>m/z</i> 211) ⁵	1310.6 (821.9)	0.93 (0.48)	35.3 (25.6)	0.33 (0.31)
C ₅ H ₉ SO ₇ ⁻ (<i>m/z</i> 213) ⁵	114.3 (798.9)	0.80 (0.48)	31.6 (22.5)	0.30 (0.26)
Methyltetrol sulfate (<i>m/z</i> 215) ²	17921.7 (10854.7)	12.655 (6.325)	668.2 (515.4)	6.06 (5.49)
C ₇ H ₁₁ SO ₇ ⁻ (<i>m/z</i> 239) ³	11.5 (6.1)	0.10 (0.04)	7.0 (3.9)	0.09 (0.07)
C ₁₀ H ₁₆ NSO ₁₀ ⁻ (<i>m/z</i> 342) ³	7.1 (3.9)	0.07 (0.04)	5.7 (5.7)	0.08 (0.10)
<i>Sum</i>	22498.6	15.5	812.1	7.3

¹Published in Hettiyadura et al. (2018), ²quantified against authentic standards or response factors detected in a previous experiment, ³semi-quantified against hydroxyacetone sulfate, ⁴semi-quantified against glycolic acid sulfate, ⁵semi-quantified against 2-methyltetrol sulfate or using its response factor.