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Qualitative and Quantitative Analysis of Atmospheric Organosulfates in Centreville, Alabama

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Abstract. Organosulfates are components of secondary organic aerosols (SOA) that form from oxidation of biogenic volatile organic compounds (VOC) in the presence of sulfate. In this study, the composition and abundance of organosulfates were determined in fine particulate matter ($PM_{2.5}$) collected from Centreville, AL from 07-11 July 2013 during Southern Oxidant and Aerosol Study (SOAS). Six organosulfates were quantified using hydrophilic interaction liquid chromatography (HILIC) with triple quadrupole mass spectrometry (TQD) against standard compounds. Among these, the three most abundant species were glycolic acid sulfate (2.4 – 27.3 ng m^{-3}), lactic acid sulfate (1.4 – 22.1 ng m^{-3}) and hydroxyacetone sulfate (0.5 – 8.7 ng m^{-3}). Positive filter sampling artifacts associated with these organosulfates due to gas adsorption and reaction of their VOC precursors with sulfuric acid were found to be negligible (at $\leq$ 7.3 % of their measured concentrations). Together, the quantified organosulfates accounted for < 0.3 % of organic carbon mass in $PM_{2.5}$. To gain insight to other organosulfates in $PM_{2.5}$ from Centreville, semi-quantitative and qualitative analysis were employed by way of monitoring of precursors to the bisulfate anion (a characteristic product ion of organosulfates) by HILIC-TQD and determining their molecular formulas and fragmentation by high-resolution time-of-flight (ToF) mass spectrometry. The major organosulfate signal across all samples corresponded to 2-methyltetrol sulfate, which accounted for 42 – 62 % of the total bisulfate ion signal. Most of the ten most prevalent organosulfate were associated with biogenic VOC precursors (i.e. isoprene, monoterpenes, and 2-methyl-3-buten-2-ol [MBO]). While a small number of molecules dominated the total organosulfate signal, a large number of minor species were also present. This study provides insights to the major organosulfate species in the Southeastern US, as measured by tandem mass spectrometry, that should be targets for future standard development and quantitative analysis.

1 Introduction

Atmospheric particulate matter (PM) adversely affects human health and climate (Anderson et al., 2011; Kim et al., 2015; Rosenfeld et al., 2014; Levy et al., 2013). A significant fraction of PM is comprised of secondary organic aerosols (SOA) (Zhang et al., 2011) that form from reactions of volatile organic compounds (VOC) yielding semi-volatile products that partition to the aerosol phase. Among SOA products are organosulfates, which are produced in the presence of sulfate aerosol and are particularly enhanced under acidic conditions (Surratt et al., 2007b; Surratt et al., 2010; Surratt et al., 2008; Surratt et al., 2007a). Important precursors to organosulfates have been identified through a combination of field and laboratory studies, and include biogenic VOC such as isoprene (Surratt et al., 2007b), monoterpenes (Iinuma et al., 2009), sesquiterpenes (Chan et al., 2011), 2-methyl-3-buten-2-ol (MBO) (Zhang et al., 2012a) and 3-Z-hexenal (Shalamzari et al., 2014). Sulfate in the atmosphere is generated by the oxidation of SO_2 that is primarily emitted by fossil fuel combustion (Wuebbles and Jain, 2001; Chin and Jacob, 1996). Thus, organosulfates may be useful markers of anthropogenically influenced biogenic SOA.

$PM_{2.5}$ mass in the Southeastern (SE) US is dominated by sulfate and organic PM (Attwood et al., 2014) and is highly acidic with pH ranging from 0.5-2 in summer and 1-3 in winter (Guo et al., 2015). SOA accounts for a significant fraction of organic $PM_{2.5}$ in SE US (Lee et al., 2010) and suggested to derive primarily from isoprene (Ying et al., 2015). Together, high sulfate, isoprene, and aerosol acidity make the atmosphere in the SE US subject to anthropogenic influences on biogenic SOA formation (Weber et al., 2007; Goldstein et al., 2009; Watson et al., 2015). The Southern Oxidant and Aerosol Study (SOAS) which took place in 01 June–15 July of 2013 was focused on studying the SOA formation in SE US and their impacts on air quality and climate. The ground site discussed in this paper was situated in Centreville, AL, a long-standing rural air quality monitoring station that is part of the Southeastern Aerosol and Research Characterization (SEARCH) network.

Organosulfates have been widely identified throughout the SE US. Their overall contribution to $PM_{2.5}$ organic mass is estimated to have an upper limit of 5-10 % in SE US (Tolocka and Turpin, 2012), suggesting that organosulfates may contribute significantly to organic aerosol mass in this region. A limited, but growing number of organosulfates have been accurately quantified against authentic standards. Among them are most abundant organosulfate has been 2-methyltetrol sulfate, followed by 2-methylglyceric acid sulfate, glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate during SOAS 2013 in Birmingham, AL (Rattanavaraha et al., 2016), Look Rock, TN (Budisulistiorini et al., 2015; Riva et al., 2016) and Centreville, AL (Hettiyadura et al., 2015; Riva et al., 2016). These measurements indicate an important role for isoprene as a precursor to organosulfates in the SE US. The quantification of organosulfates is currently limited by very few atmospherically relevant standards being commercially available, requiring the development of standards by synthesis (Olson et al., 2011; Staudt et al., 2014; Hettiyadura et al., 2015). In the absence of authentic standards, surrogate standards are commonly instead, but can lead to significant and often uncharacterized biases that result from differences in (-) ESI ionization efficiencies (Staudt et al., 2014). With organosulfate quantification in its infancy, it remains important to develop authentic standards to extend quantification of this class of compounds.

In order to accurately determine organosulfate contribution to PM mass and constrain anthropogenic influences on biogenic SOA formation, an improved understanding of organosulfate concentrations and composition is needed. Mass spectrometry (MS) in the negative electrospray ionization mode ((-) ESI) is widely used to detect organosulfates (Iinuma et al., 2007; Gómez-González et al., 2008; Altieri et al., 2009; Reemtsma et al., 2006; Romero and Oehme, 2005). The bisulfate anion is identified as a characteristic fragment ion of organosulfates (Gómez-González et al., 2008; Romero and Oehme, 2005). Thus MS^2 of precursors to bisulfate ion can be used for semi-quantification of organosulfates in the absence of authentic standards (Stone et al., 2009), however there are some limitations which have been discussed in Sect. 3.3. Offline MS detection of organosulfates is often coupled with liquid chromatography (LC). Reverse phase LC-MS methods are suitable for separation of aromatic and monoterpene derived organosulfates that contain hydrophobic moieties (e.g. aromatic rings or long alkyl chains) (Stone et al., 2012), but do not retain carboxy- and polyhydroxy-organosulfates that instead co-elute with sulfate and other organic compounds. Hydrophilic interaction liquid chromatography (HILIC) has been demonstrated to have complementary selectivity to reversed phase separation and is preferred for retention of carboxyl-containing organosulfates (Hettiyadura et al., 2015).

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

Mechanistic studies have revealed pathways by which organosulfates form and have been reviewed elsewhere (Hallquist et al., 2009; Surratt et al., 2010; Ervens et al., 2011; Darer et al., 2011; Riva et al., 2015). The following description focuses on species quantified against authentic standards. 2-Methyltetrol sulfates and 2-methylglyceric acid sulfate primarily form from acid-catalyzed nucleophilic addition of sulfate to isoprene epoxides (IEPOX) (Surratt et al., 2010) and methacrylic acid epoxide (an isoprene oxidation product) (Lin et al., 2013), respectively. In addition, 2-methyltetrol sulfates can form from nucleophilic substitution of nitrate with sulfate from the corresponding organonitrates (Darer et al., 2011) and from isoprene ozonolysis in the presence of acidified sulfate seed aerosol (Riva et al., 2016). Formation of glycolic acid sulfate has been observed from reactive uptake of glyoxal to neutral or acidic sulfate aerosol upon irradiation (Galloway et al., 2009). Lactic acid sulfate is also suggested to form from similar pathways from methylglyoxal (Shalamzari et al., 2013). Glyoxal and methylglyoxal have both biogenic and anthropogenic precursors, although isoprene is their major source (Fu et al., 2008). There is also evidence for formation of lactic acid sulfate from 2-E-pentenal, a photolysis product of 3-Z-hexenal (Shalamzari et al., 2015). Organosulfates may also form from sulfate radical induced oxidation in the presence of an acidified sulfate radical precursor, by which 2-methylterol sulfate forms from isoprene while other products form from isoprene oxidation products; for example, methyl vinyl ketone (MVK) can generate 2-methylglyceric acid sulfate, glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate while methacrolein (MACR) is a precursor to 2-methylglyceric acid sulfate and hydroxyacetone sulfate (Schindelka et al., 2013; Nozière et al., 2010). Alternatively, hydroxyacetone sulfate can form from isoprene ozonolysis in the presence of acidified sulfate seed aerosol (Riva et al., 2016). Prior mechanistic studies have revealed multiple pathways for biogenic organosulfates to form, which depend on the availability of reactants in the ambient atmosphere.

The central objectives of this study include i) quantification of select organosulfates in $PM_{2.5}$ collected from Centreville, AL from 07-11 July, 2013 during SOAS against authentic standards by HILIC coupled to a triple quadrupole mass spectrometry (TQD) methodology developed by Hettiyadura et al. (2015), ii) assessment of positive filter sampling artifacts associated with these organosulfates due to gas adsorption and reaction of their VOC precursors with sulfuric acid, and iii) identification of major organosulfates in Centreville, AL. The third objective is complementary to that of Riva et al. (2016), who focused on identifying and semi-quantifying isoprene-derived organosulfates in Centreville during SOAS, particularly those that form through ozonolysis reactions. Through these efforts we expand the understanding of organosulfate concentrations in Centreville, AL during SOAS 2013 and constrain the extent to which filter sampling artifacts affect quantitation. In addition, the major organosulfates identified during this study provide new insights to the organosulfates that should be targets for future standard development.

2 Materials and methods

2.1 Chemicals and reagents

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

2.2 $PM_{2.5}$ samples

$PM_{2.5}$ samples were collected in duplicate using two medium-volume samplers (aluminum cyclone, 2.5 µm cut-off, 92 lpm, URG-3000B, URG Corporation; Fig. S1) on pre-baked (550 °C for 18 h) QFF (90 mm diameter, Pall Life Sciences). Samples were collected on the basis of daytime (8:00-19:00 LT) and nighttime (20:00-7:00 LT) schedule. One field blank was collected for every five $PM_{2.5}$ samples following the same procedure, but without passing air through the filters. All filter samples collected were stored in Al-foil (pre-baked at 550 °C for 5.5 h) lined petri dishes and were kept frozen (-20.0 °C) under dark conditions until extracted.

2.3 Positive filter sampling artifacts

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

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

2.4 Sample preparation

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

2.5 Chemical analysis

2.5.1 $PM_{2.5}$ and Organic carbon (OC)

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

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

2.5.2 Quantification of organosulfates using HILIC-TQD

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

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

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

2.5.3 Qualitative analysis of major organosulfates in Centreville, AL

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

3 Results and discussion

3.1 Quantification of organosulfates in Centreville, AL

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

Levels of glycolic acid sulfate and lactic acid sulfate were markedly higher in the SE US during SOAS compared to other regions during summer. The glycolic acid sulfate and lactic acid sulfate quantified in this study ranged from 2.4 - 27.3 ng m^{-3} and 1.4 - 22.1 ng m^{-3}, respectively (Table 1). At the nearby Birmingham, AL which is an industrial and residential site even higher glycolic acid sulfate concentrations (75.2 ng m^{-3}) were reported from 01 June – 15 July, 2013 during SOAS (Rattanavaraha et al., 2016) with a mean concentration of 26.2 ng m^{-3}. These levels are significantly higher than the levels of glycolic acid sulfate and lactic acid sulfate reported previously in Bakersfield, CA (an urban site) from 16-18 June, 2010 which were 4.5 – 5.4 ng m^{-3} and 0.6 – 0.7 ng m^{-3}, respectively (Olson et al., 2011). Together, these data indicate higher levels of these organosulfates in the SE compared to the Southwestern US during summer, but are limited by the very few measurements of organosulfates reported in the literature.

The total contribution of the organosulfates quantified using authentic standards accounted for less than 0.5 % of $PM_{2.5}$ and less than 0.3 % of OC (Table 1). Meanwhile, organosulfates are estimated to contribute 1-2 % of $PM_{2.5}$ and 5-10 % OC in Eastern US (Shakya and Peltier, 2015). Therefore, the organosulfates quantified against authentic standards account for a minority of the total organosulfates, while other organosulfates likely comprise the majority of this class of compounds in Centreville, AL (as discussed in Sect. 3.3).

3.2 Positive filter sampling artifacts for select organosulfates

The positive filter sampling artifacts associated with the three most abundant organosulfates quantified in Sect. 3.1 (glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate, respectively) were assessed. The potential for these organosulfates in the gas phase to form positive sampling artifacts by adsorption onto QFF was assessed by parallel analysis of Q_F and Q_B. Of the ten Q_B analyzed to assess positive filter sampling artifacts due to gas adsorption, only three contained detectable levels of glycolic acid sulfate and one contained detectable levels of lactic acid sulfate (Table 2). Maxima for both species occurred in the nighttime sample collected on 09 July and were 1.1 ± 0.3 % (0.30 ± 0.06 ng m^{-3}) and 0.8 ± 0.4 % (0.15 ± 0.07 ng m^{-3}) respectively. Meanwhile, hydroxyacetone sulfate was below the instrument detection limit in all Q_B analyzed, such that the upper limit of the positive artifact was estimated as 1.3 %. From 07-11 July 2013, the 09 July had the highest $PM_{2.5}$ loadings, temperature, solar radiation (data available at

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http://esrl.noaa.gov/csd/groups/csd7/measurements/2013senex/Ground/DataDownload/) and quantified organosulfate concentrations (Fig. 1) for both the daytime and nighttime sampling periods. Consequently, it is expected that the maximum gas phase concentrations of glycolic acid sulfate and lactic acid sulfate also occurred on this day, which would have led to the observed positive sampling artifacts due to gas adsorption. The positive filter sampling artifacts associated with these three organosulfates from gas adsorption were only detected sporadically and at very low levels (~ 1%) that fell within the propagated analytical uncertainty.

In a prior study by Kristensen et al. (2016) at an urban site in Copenhagen, Denmark and a forested site in Hyytiälä, Finland, the abovementioned organosulfates were not detected in the gas phase via analysis of denuder samples collected upstream of Teflon filters on which these organosulfates were detected. The very minor influence of gas-phase glycolic acid sulfate and lactic acid sulfate in Centreville may be promoted by the higher organosulfate concentrations in the SE US, as well as the higher acidity (Gao et al. 2015) that can promote partitioning of acidic species like organosulfates to the gas phase, and possibly temperature.

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

The extent of on-filter reactions to form glycolic acid sulfate, lactic acid sulfate, and hydroxyacetone sulfate appears to be site-specific. In a prior study in Hyytiälä, Finland, Kristensen et al. (2016) attributed the majority of organosulfates detected on high-volume filter samples collected to on-filter oxidation and sulfation reactions forming organosulfates with *m/z* corresponding to glycolic acid sulfate, lactic acid sulfate, and hydroxyacetone sulfate. However, for samples collected in

Copenhagen, only 5 % of the daytime average concentrations and 14 % of the nighttime average concentrations of the glycolic acid sulfate was attributed to on-filter reactions, similar to this study, while lactic acid sulfate and hydroxyacetone sulfate concentrations appear to have been subjected to negative sampling artifacts. With varying extents of organosulfate sampling artifacts reported across sampling sites, it is recommended that sampling artifacts be evaluated at future field study sites.

3.3 Major organosulfates in Centreville, AL

Because the quantified organosulfates accounted for a small fraction of OC, other major organosulfate species in Centreville, AL were identified using ions that fragmented to bisulfate anion (*m/z* 97). The ability of an organosulfate to contribute to the bisulfate ion signal depends on its individual (-) ESI ionization efficiency, MS^2 fragmentation patterns, and mass concentration. Absolute quantitation requires instrument calibration as discussed in Sect. 1; however, this is not possible for the vast majority of atmospheric organosulfates, because standards are not commercially available. In the following data analysis, it is assumed that organosulfates have an equal ability to form the bisulfate anion, so that semi-quantitative insight may be gained to their relative abundance in ambient aerosol. This approach is limited by the fact that differing ionization efficiencies and fragmentation patterns have not been controlled and may introduce positive or negative biases. Consequently, the following ranking should not be considered as an accurate measure of relative abundance, but a best estimate in the absence of authentic standards.

The limitations of this approach can be illustrated by the comparison of the semi-quantitative behavior of glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate in their formation of the bisulfate anion and their absolute quantitation. For the 10 July 2013 daytime sample, the relative contribution to bisulfate ion signal was highest for hydroxyacetone sulfate (1.10 %), then glycolic acid sulfate (0.57 %) and lactic acid sulfate (0.23 %) respectively, while their absolute concentrations followed the opposite trend: lactic acid sulfate (15 ± 1 ng m^{-3}), glycolic acid sulfate (14 ± 3 ng m^{-3}) and hydroxyacetone sulfate (5.8 ± 0.3 ng m^{-3}). This comparison indicates that there is a positive bias in the bisulfate ion signal towards early-eluting organosulfates, which results from the use of a mobile phase gradient in UPLC. Acetonitrile has a higher vapor pressure than water and more readily desolvates in the mass spectrometer, leading to higher signals. When hydroxyacetone sulfate elutes (t_R 0.69 min), the mobile phase is 95 % acetonitrile and 5 % water, compared to ~81 % acetonitrile and ~19 % water when glycolic acid sulfate (t_R 7.82 min) and lactic acid sulfate (t_R 7.54 min) elute. Consequently, organosulfates retained longer on the BEH-amide column during HILIC gradient separation, such as organosulfates containing carboxyl and multiple hydroxyl groups are expected to be under-represented in this semi-quantitative analysis. Nonetheless, it is a valuable endeavor to gain semi-quantitative information on major organosulfate signals in order to guide future developments of authentic standards that will ultimately provide for absolute quantitation.

A mass spectrum of the precursor ions to *m/z* 97 integrated over the entire HILIC separation (0-11 min) for the 10 July daytime sample with the ten strongest signals marked is shown in Fig. 2. Each nominal *m/z* in Fig. 2 corresponded to a single monoisotopic mass as determined from HILIC-TOF, except for *m/z* 155 and 199, which are discussed in detail below.

Table 3 ranks these ten organosulfate signals in order of decreasing relative contribution to the total bisulfate product ion signal and summarizes their *m/z*, molecular formulae determined from HILIC-TOF, expected precursor(s) based on prior field and SOA chamber studies, and proposed molecular structures with consideration of results from prior studies, double bond equivalences, and functional groups.

The dominant precursor to the bisulfate ion signal in the daytime 10 July sample was $C_5H_{11}SO_7^-$ (215.0225), which accounted for 43 % of the signal. This MS^2 signal corresponds to 2-methyltetrol sulfate, a major isoprene SOA product. HILIC chromatography resolved six, baseline resolved peaks of $C_5H_{11}SO_7^-$ (Fig. 3a) with retention times consistent with those reported by Hettiyadura et al. (2015). The dominance of *m/z* 215 to *m/z* 97 is consistent with this being the most abundant organosulfate quantified against an authentic standard in Look Rock, TN (Budisulistiorini et al., 2015) and in Birmingham, AL (Rattanavaraha et al., 2016) during SOAS 2013. As discussed in Sect. 1, 2-methyltetrol sulfates predominantly form by the acid catalyzed nucleophilic addition of sulfate to IEPOX (Surratt et al., 2010). Based on the structures of β- and δ-IEPOX (Paulot et al., 2009), it is possible that the resulting 2-methyltetrol sulfate include the sulfate moiety at primary, secondary or tertiary positions.

2-Methyltetrol organosulfates were tentatively identified as primary, secondary, or tertiary by their relative acid hydrolysis rates (as discussed in the SI and shown in Fig. S2). The fastest *m/z* 215 peaks to hydrolyze (i.e. least stable) were tentatively identified as tertiary, the next to hydrolyze (i.e. intermediate stability) as secondary, and the most stable were as primary, with assignments based upon their enthalpy of hydrolysis and neutral hydrolysis lifetime reported by Darer et al. (2011) and Hu et al. (2011). Accordingly, the first two peaks were tentatively assigned as diastereomers of the tertiary conformation, the middle two peaks as diastereomers of the secondary conformation, and the last two peaks as diastereomers of primary 2-methyltetrol sulfate (Fig. 3a and Fig. S2). The relative contribution of these peaks to the bisulfate anion signal in order of elution were 23.9 %, 10.5 %, 23.4 %, 41.0 %, 0.8 %, and 0.4 %. With a negative bias in peak area for late-eluting peaks, due to the desolvation effect, these percentages are expected to underestimate the contribution from primary organosulfates. These results suggest that 2-methyltetrol sulfates have appreciable contributions from primary, secondary, and tertiary organosulfates. Confirmation of the configuration and their absolute quantitation would be made possible through synthesized standards.

The organosulfate with the second greatest contribution to the bisulfate ion signal (4.91 %) was $C_5H_9SO_7^-$ (213.0069). It consists of multiple isomers that are not fully baseline resolved (Fig. 3b). Organosulfates with this formula have been reported in chamber experiments involving isoprene photo-oxidation in the presence of acidic sulfate under NO_x free conditions (Surratt et al., 2008); these conditions are generally characteristic of Centreville, AL. Recently an organosulfate with the same elemental composition was identified among the organosulfates form from isoprene ozonolysis (Riva et al., 2016). Structurally, $C_5H_9SO_7^-$ is closely related to 2-methyltetrol sulfate, with one increasing unit of unsaturation. The short retention time (< 3 min) indicates the absence of carboxyl group and has been proposed to result from the oxidation of a primary hydroxyl group in a 2-methyltetrol sulfate followed by subsequent ring closing (Hettiyadura et al. 2015), although this has not been confirmed. The absence of a carboxyl group excludes the structures proposed by

Gómez-González et al. (2008) for *m/z* 213. Organosulfates with the same elemental composition were identified in other field studies, in Denmark (Nguyen et al., 2014; Kristensen and Glasius, 2011) and particularly in SE US (Surratt et al., 2008; Riva et al., 2016), making it ubiquitous in the atmosphere.

The organosulfate with the third greatest contribution to the bisulfate ion signal (4.27 %) was $C_5H_7SO_7^-$ (210.9912). This organosulfate is among the most abundant organosulfates semi-quantified by Rattanavaraha et al. (2016) in Birmingham, AL during SOAS 2013. It has four constitutional isomers and/ or diasteriomers that are not fully baseline resolved (Fig. 3c). Its relatively short retention time (< 3 min) indicates the absence of a carboxyl group (Hettiyadura et al. 2015). Consequently, the carboxylic acid-bearing structure proposed by Shalamzari et al. (2014) may be excluded. This organosulfate is related to 2-methyltetrol sulfate by two units of unsaturation and has been suggested to form by oxidation of 2-methyltetrol sulfate and inter-molecular ring closing (Hettiyadura et al., 2015). In prior work, only one of four organosulfate peaks with $C_5H_7SO_7^-$ in ambient $PM_{2.5}$ collected from SEARCH sites matched the isoprene chamber experiment, leading Surratt et al. (2008) to suggest that this species may have other VOC precursors. Organosulfates with the same elemental composition were also detected at four sites in South Asia (Stone et al., 2012), indicating that this particular organosulfate is also ubiquitous in ambient aerosol. Future research with respect to this molecule should include identifying its VOC precursors and synthesizing authentic standards to determine their absolute abundance in the atmosphere.

The fourth greatest contributor to the bisulfate ion signal (1.81 %) was $C_7H_{11}SO_7^-$ (239.0225), which has multiple isomers that are not baseline resolved (Fig. 3d). Formation of $C_7H_{11}SO_7^-$ has been observed during oxidation of limonene, a monoterpene, in the presence of oxidants, NO_x and acidic sulfate (Surratt et al., 2008). Another laboratory study suggested that this organosulfate form from oligomerization of MVK and MACR, the two major first generation oxidation products of isoprene, *via* sulfate radical induced oxidation pathway (Nozière et al., 2010). With the $C_7H_{11}SO_7^-$ organosulfate being one of the dominant organosulfates in the atmosphere, this is a prime target for standard development; however a better understanding of its structure is needed to guide this effort.

The fifth greatest contributor to the bisulfate ion signal (1.73 %) was $C_4H_7SO_6^-$ (182.9963). The MS^2 chromatogram (Fig. 3e) reveals multiple constitutional isomers that were not fully baseline resolved. The MS^2 spectra (Fig. S3) obtained for the dominant peak that eluted at 0.91 included the following peaks (by chemical formula, observed mass, and error in mDa); $HSO_3^{-\cdot}$ (80.9642, -0.4), HSO_4^- (96.9593, -0.3), $C_3H_5SO_5^-$ (152.9856, -0.2) and $C_4H_5SO_5^-$ (164.9859, 0.1). The MS^2 fragments reported for the synthesized hydroxybutan-3-one-2-sulfate standard in Shalamzari et al. (2013) matched the observed signals, indicating that this is the likely structure. Chamber studies have pointed towards isoprene (Riva et al., 2016) and its oxidation products such as MVK and MACR for formation of $C_4H_7SO_6^-$ (Schindelka et al., 2013). The plausible formation pathways of this organosulfate were reviewed in Riva et al. (2016), which include sulfate radical induced oxidation (Schindelka et al., 2013), acid catalyzed ring opening of oxiranes (Iinuma et al., 2009; Surratt et al., 2010) , or sulfate addition to alkenes and aldehydes (Liggio and Li, 2006; Surratt et al., 2007a). This organosulfate has also been identified in $PM_{2.5}$ collected from Centreville, AL and Look rock, TN during SOAS 2013 (Riva et al., 2016). Thus future studies should focus on confirming the structure of the major isomer of $C_4H_7SO_6^-$ against a hydroxybutan-3-one-2-sulfate standard, which may also be used for absolute quantification.

The sixth greatest contributor to the bisulfate ion signal (1.49 %) was a nitrooxy organosulfate with the formula $C_{10}H_{16}NSO_{10}^-$ (342.0495). The HILIC chromatogram shows two co-eluting peaks that eluted less than 1 minute (Fig. 3f). Organosulfates with the same elemental composition have been observed to form from monoterpenes in the presence of NO_x under highly acidic conditions (Surratt et al., 2008). Further, this organosulfate has been previously identified in the ambient aerosol at a forested site in Germany (Iinuma et al., 2007) and in the SE US (Gao et al., 2006; Surratt et al., 2008). Prior studies have identified up to ten isomers of this organosulfate in SE US using reversed phase chromatography (Surratt et al., 2008). Thus, further characterization and quantification of this organosulfate should proceed with reversed phase chromatography, which affords better separation of the $C_{10}H_{16}NSO_{10}^-$ isomers.

The seventh greatest contributor to the bisulfate ion signal (1.27 %) was $C_3H_5SO_5^-$ (152.9858). The HILIC column resolved one major and two minor peaks (Fig. 3g). The major peak of $C_3H_5SO_5^-$ (t_R 0.69 min) accounted for 87 % of the total *m/z* 153 signal and was identified as hydroxyacetone sulfate (Sect. 3.1) against the authentic standard. The two minor peaks observed for $C_3H_5SO_5^-$ have low abundance and likely contain an aldehyde functional group based on their retention time (<5 min) and one unit of unsaturation. Thus, hydroxyacetone sulfate is expected to be the major organosulfate with *m/z* 153 in Centreville.

The eighth greatest contributor to the bisulfate ion signal (1.03 %) was $C_5H_{11}SO_6^-$ (199.0276). Chromatographically, two peaks were baseline resolved (Fig. 3h) with retention times of 1.05 and 1.89 min and relatively equal peak areas, suggesting similar atmospheric abundance. Organosulfates with the same elemental composition were previously identified as products of SOA formed from MBO in the presence of oxidants and sulfate under low NO_x conditions (Zhang et al., 2012a). In addition to MBO, formation of $C_5H_{11}SO_6^-$ was identified among the organosulfates form from isoprene ozonolysis in the presence of acidic sulfate (Riva et al., 2016). This organosulfate was also detected in aerosol samples collected from SE US during SOAS 2013 (Riva et al., 2016). Another organosulfate with the nominal *m/z* 199 corresponding to a different formula—$C_4H_7SO_7^-$—was identified. It had a minor contribution to bisulfate ion signal (0.29 %) and a longer retention time (8.3 min; Fig. S4). The longer retention time suggested the presence of a carboxyl functional group. With a similar bisulfate ion contribution to glycolic acid sulfate and lactic acid sulfate, $C_4H_7SO_7^-$ is likely to have atmospheric abundances in the same range as these species (section 3.1). The MS^2 fragments obtained for $C_4H_7SO_7^-$ (Fig. S5) included the following peaks (by chemical formula, observed mass, and error in mDa): HSO_4^- (96.9592, -0.4), and $C_4H_7O_4^-$ (119.0341, -0.3) which was formed from the neutral loss of SO_3 (*m/z* 80). The MS^2 spectrum matched that of 2-methylglyceric acid sulfate, an isoprene derived organosulfate (section 1), reported by Gómez-González et al. (2008) making this the likely structure, although the position of the sulfate group has yet to be confirmed.

The ninth greatest contributor to the bisulfate ion signal (0.98 %) was $C_{12}H_{25}SO_4^-$ (265.1474) that is consistent with dodecyl sulfate (a.k.a. lauryl sulfate). Sodium dodecyl sulfate is the most common surfactant use in manufacture of cleaning and hygiene products. A single peak with a very short retention time is consistent with a largely aliphatic structure (Fig. 3i).

Anionic surfactants including dodecyl sulfate have been observed in aerosol generated from waste water (Radke, 2005) and in coastal sea spray aerosol (Cochran et al., 2016). While sea spray was observed to impact the Centreville site on some days during SOAS (Allen et al., 2015), it was not a major source on the dates discussed herein, pointing towards waste water as a possible origin.

The tenth greatest contributor to the bisulfate ion signal (0.62 %) was $C_3H_7SO_5^-$ (155.0014). It consist of two overlapping peaks eluted at 1.23 and 1.31 min (Fig. 3j). HILIC-TOF results indicated the absence of any unsaturation (DBE=0.5), thus that the non-sulfate oxygen is likely a hydroxyl group. Glycolic acid sulfate, also has the nominal *m/z* 155 with formula $C_2H_3SO_6^-$, and made a sizeable contribution to the bisulfate anion signal (0.57%). A second isomer with the formula $C_2H_3SO_6^-$ eluted at 0.54 min, but only a minor contributor of the bisulfate ion signal (0.03 %; Fig. S6). As late-eluting organosulfates have a negative bias due to mobile phase gradient, glycolic acid sulfate is most likely the most abundant organosulfate with *m/z* 155 in the atmosphere.

Parallel semi-quantitative analysis of organosulfates in 10 July nighttime sample (Fig. S7) and other daytime and nighttime samples collected from 07-11 July 2013 (Fig. S8) revealed many similarities to the 10 July daytime sample. Among the similarities was the dominance of the 2-methyltetrol sulfate signal (*m/z* 215) that accounted for 42–62 % of the bisulfate product ion signal. Other major organosulfate signals that were consistently observed (≥90% of the 10 samples) included *m/z* 153, 183, 211, 213 and 239. With all of these organosulfates associated with isoprene, data suggest that isoprene chemistry dominates the formation of organosulfates in Centreville. While *m/z* 281 ($C_{10}H_{17}SO_7^-$; Table S1) was not among the ten highest contributors to the bisulfate anion signal in the 10 July daytime sample, it was among the highest signals of all other samples analyzed (Fig. S7 and S8). An organosulfate with this elemental composition was previously identified in an SOA chamber experiment involving monoterpenes and in ambient aerosol in Centreville and Birmingham, AL, and Atlanta, GA (Surratt et al., 2008). In addition, other monoterpene-derived organosulfates with *m/z* 297 ($C_{10}H_{17}SO_8^-$), 223 ($C_7H_{11}SO_6^-$) and 279 ($C_{10}H_{15}SO_7^-$) (Surratt et al., 2008) were sporadically detected among the highest organosulfate signals. Because of their frequent detection and specificity to monoterpene-derived organosulfates, these organosulfate may be useful tracers for monoterpene-derived SOA.

Together, the ten highest organosulfate signals in each sample (n=10) analyzed (Fig. 2, S7 and S8) contributed 58-78 % of the total bisulfate ion signal, with the tenth greatest intensity signal accounting for 0.25 to 1.12 % of the total bisulfate ion signal. From the remaining organosulfate signal, we estimate a minimum of ~20-200 other minor organosulfates are present in Centreville, AL. In summary, a few highly abundant organosulfate species (e.g. 2-methyltetrol sulfate) dominate the bisulfate ion signal, while a relatively large number of minor organosulfate species are present in Centreville during the summer. Future efforts at standard development should focus on organosulfates that are expected to have high abundance, frequently detected in ambient aerosol, and/or have high specificity to VOC precursors.

4 Conclusions

The three most abundant organosulfates quantified using authentic standards in $PM_{2.5}$ collected from Centreville, AL from 07-11 July, 2013 were glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate respectively. Positive filter sampling artifacts associated with these three organosulfates due to gas adsorption were negligible ($\%f < 1.3\%$). Sulfuric acid enhanced the positive filter sampling artifacts associated with these organosulfates, but were relatively small ($\%f \leq 7.3\%$). Thus the organosulfates quantified using $PM_{2.5}$ sampled on QFF in Centreville, AL during SOAS 2013 can be used without a significant positive bias. Because, positive filter sampling artifacts associated with organosulfates are likely site specific, it is important to assess sampling artifacts at new study sites. The organosulfates quantified against authentic standards accounted for a small fraction of the $PM_{2.5}$ and organic carbon mass. The precursor ion scan to the bisulfate anion fragment (*m/z* 97) was used semi-quantitatively to assess major organosulfate species in ambient aerosol in the SE US. From the ten strongest responding ions identified, 2-methyltetrol sulfate accounted for nearly half of the total bisulfate ion signal in all samples analyzed. By comparison to chamber studies, it is seen that the ten major organosulfates identified derive mainly from biogenic VOC, mainly isoprene, and to a lesser extent monoterpenes and MBO. Many of the major organosulfate signals observed are consistent with those reported by Riva et al. (2016) for Centreville during SOAS and thus reinforce their conclusions that ozonolysis and photochemical reactions of isoprene influence the organosulfate levels and composition in Centreville. Further, our semi-quantitative analysis shows that in Centreville, AL the organosulfates that fragment to the bisulfate product ion were dominated by few major species among large number of minor species. This study also provides insights for the major organosulfate species in SE US that should be targets for future organosulfate standard development.

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Figure 1: Concentrations of organosulfates in $PM_{2.5}$ at Centreville, AL on 07-11 July 2013 on the basis of day (D; 08:00-19:00 LT) and night (N; 20:00-07:00 LT). All species were quantified against authentic standards. Error bars represent the analytical uncertainty.

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

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

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

Organosulfate	**Concentration (ng m^{-3})**		**Mean contribution (%)**	
	Range	**Mean**	**$PM_{2.5}$**	**OC**
glycolic acid sulfate	2.4 – 27.3	12.0 ± 7.9	0.2 ± 0.1	0.09 ± 0.05
lactic acid sulfate	1.4 – 22.1	9.9 ± 7.0	0.17 ± 0.08	0.10 ± 0.05
hydroxyacetone sulfate	0.5 – 8.7	3.3 ± 2.4	0.06 ± 0.03	0.04 ± 0.02
methyl sulfate	0.2 – 1.0	0.6 ± 0.3	0.010 ± 0.004	0.003 ± 0.002

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

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

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

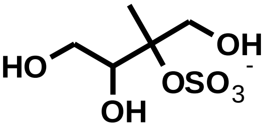
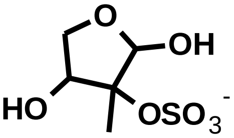
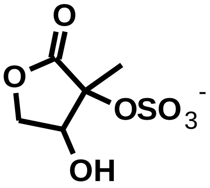
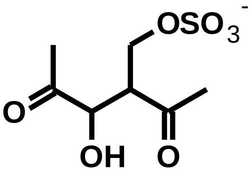
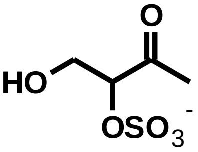
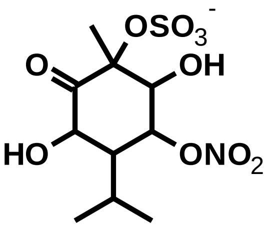
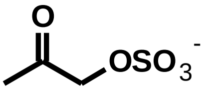
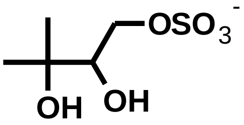
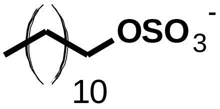
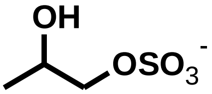
Rank	**[M-H]$^-$**		**Structure**	**VOC precursor(s)**	**t_R (min)**	**Error (mDa)**	**Contribution to total bisulfate signal (%)**	
	Formula	**Mass**					**by peak**	**total**
1	$C_5H_{11}SO_7^-$	215.0225	 (Surratt et al., 2010)	Isoprene (Surratt et al., 2007a; Surratt et al., 2007b; Surratt et al.,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

Table 3: (Cont.)

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

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

Figure 1.

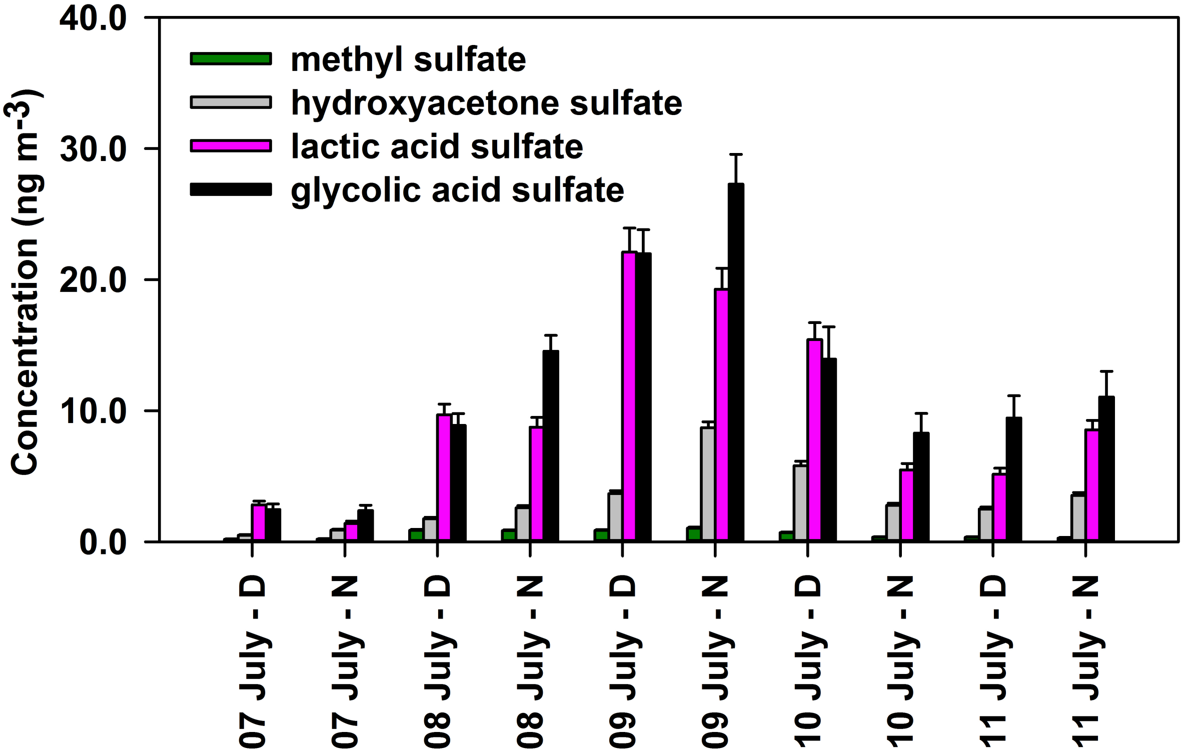

40.0
30.0
20.0
10.0
0.0
Concentration (ng m-3)
methyl sulfate
hydroxyacetone sulfate
lactic acid sulfate
glycolic acid sulfate
07 July - D
07 July - N
08 July - D
08 July - N
09 July - D
09 July - N
10 July - D
10 July - N
11 July - D
11 July - N

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Figure 2.

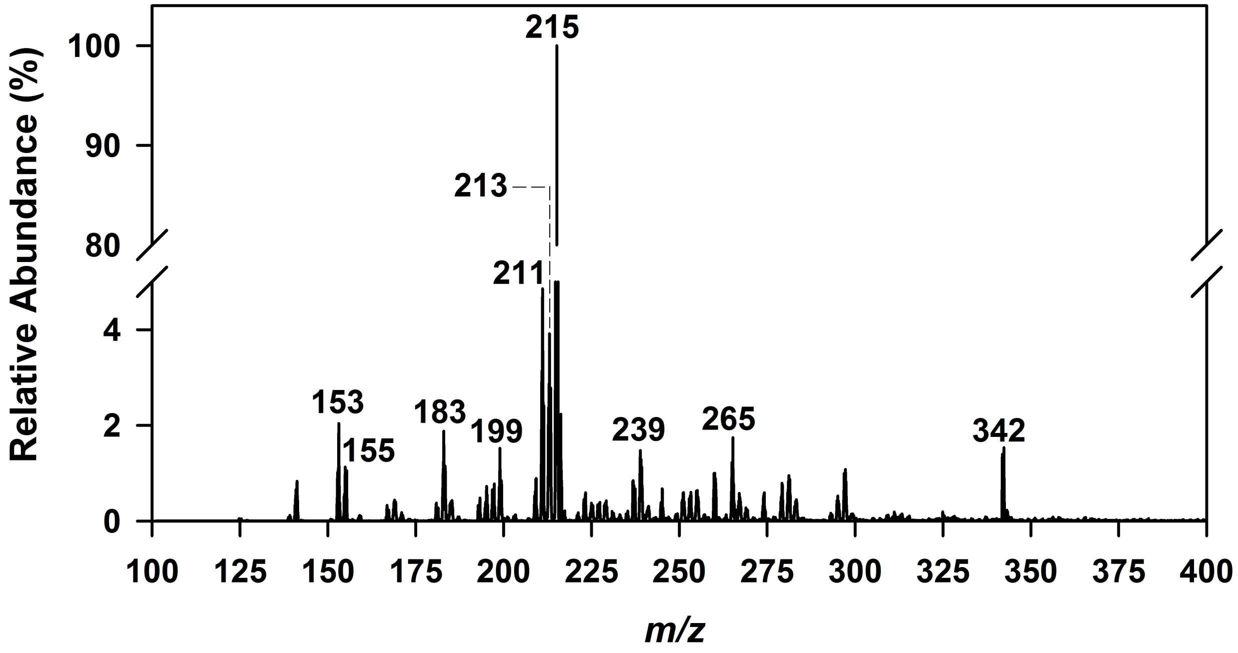

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Figure 3.