# Organosulfates in the Midwestern United States: Abundance, composition and stability

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*Research Paper*

# Organosulfates in the Midwestern United States: abundance, composition and stability

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**Environmental context.** Organosulfates in the atmosphere are an indicator that particulate matter has formed from gases in the presence of anthropogenic pollution. By characterising organosulfates in atmospheric fine particulate matter from the Midwestern USA, we found that organosulfates account for a significant fraction of organic carbon and that they are associated with both plant-derived and anthropogenic gases. Our results demonstrate that anthropogenic pollution significantly influences atmospheric particle concentrations and composition.

**Abstract.** Organosulfates are components of secondary organic aerosol resulting from the oxidation of volatile organic compounds in the presence of acidic sulfate. This study characterises organosulfates in the Midwestern United States for the first time. In fine particulate matter ($PM_{2.5}$) collected in Iowa City, IA, in September 2017, organosulfates were analysed using liquid chromatography coupled to high-resolution and tandem mass spectrometry (MS) to identify and quantify (or semi-quantify) major species. Among the 22 identified species, methyltetrol sulfate ($m/z$ 215; $C_5H_{11}SO_7^-$) had the largest contribution to the bisulfate ($m/z$ 97) product ion, as determined by precursor-ion MS/MS (59.5 % of signal), followed by ten other isoprene-derived organosulfates (15.2 %), seven monoterpene-derived organosulfates (5.6 %), three anthropogenic organosulfates (4.3 %) and one species of unknown origin (0.6 %). Among the quantified species were hydroxyacetone sulfate ($4.8 \pm 1.1$ ng m$^{-3}$), glycolic acid sulfate ($21.0 \pm 1.5$ ng m$^{-3}$), 2-methylgyceric acid sulfate ($15.1 \pm 0.8$ ng m$^{-3}$), $C_5H_7SO_7^-$ ($m/z$ 211; $17.9 \pm 0.9$ ng m$^{-3}$), $C_5H_9SO_7^-$ ($m/z$ 213; $16.0 \pm 1.0$ ng m$^{-3}$), and methyltetrol sulfate ($214 \pm 8$ ng m$^{-3}$); together, these species accounted for 4.4 % of organic carbon. To further validate the measurement of organic species in PM using filter samples, the stability of organosulfates on filters frozen at $-20\,°C$ was evaluated over the course of 1 year. The stored samples revealed no degradation of organosulfates, indicating their stability on filters stored frozen for extended periods of time. This study provides new insight into the abundance and identity of organosulfates in the Midwestern US and demonstrates that isoprene-derived organosulfates, in particular, are a significant contributor to $PM_{2.5}$ organic carbon.

**Additional keywords:** atmospheric aerosols, chemical composition, isoprene, $PM_{2.5}$, secondary organic aerosol.

## Introduction

Atmospheric fine particulate matter ($PM_{2.5}$; particles ≤2.5 μm in aerodynamic diameter) influences the Earth's climate through direct and indirect radiative forcing (Novakov and Penner 1993; Hansen et al. 1997; Jacobson et al. 2000; Ramanathan et al. 2001) and adversely affects human health by causing inflammation of the respiratory system, morbidity and, in some cases, premature death (Brunekreef and Holgate 2002; Kampa and Castanas 2008; Valavanidis et al. 2008). A large fraction of $PM_{2.5}$ is organic and can enter the atmosphere directly (from primary sources) or form in the atmosphere as secondary organic aerosol (SOA) through the oxidation of volatile organic compounds (VOCs) and subsequent partitioning to the aerosol phase (Turpin and Lim 2001; Hallquist et al. 2009). Chamber studies have demonstrated that the formation of SOA increases in the presence of acidic sulfate (Surratt et al. 2007; Surratt et al. 2008); however, the impact of SOA formation on the atmospheric organic carbon (OC) budget remains unclear, with estimates of global SOA production ranging from 13 to 121 Tg year$^{-1}$ (Tsigaridis et al. 2014).

Organosulfates are a portion of SOA formed from the oxidation of VOCs in the presence of sulfate and are estimated to account for as much as 5–10 % of the organic mass across the continental US (Tolocka and Turpin 2012). Organosulfates are ubiquitous, being detected at many sites globally, including in megacities, and urban, rural and remote environments (Surratt et al. 2008; Iinuma et al. 2009; Kristensen and Glasius 2011; Olson et al. 2011; Stone et al. 2012; Hansen et al. 2014; Meade et al. 2016; Hettiyadura et al. 2017; Wang et al. 2018). They are primarily formed through the acid-catalysed reactive uptake of gas-phase epoxides onto sulfate aerosol (Surratt et al. 2010), but have also been found to form by the nucleophilic substitution of organic nitrate by sulfate (Darer et al. 2011) and through the oxidation of VOCs via sulfate radical anions (Nozière et al. 2010; Schindelka et al. 2013). Through a combination of chamber experiments and field studies, organosulfates have been shown to form mainly from biogenic precursors that include isoprene (Surratt et al. 2007), monoterpenes (Iinuma et al. 2009), sesquiterpenes (Chan et al. 2011), 2-methyl-3-buten-2-ol (MBO) (Zhang et al. 2012) and 3-$Z$-hexenal (Shalamzari et al. 2014).

With sulfate primarily resulting from fossil fuel combustion (Carlton et al. 2010), organosulfates are unique tracers for biogenic SOA influenced by anthropogenic emissions.

The composition and abundance of organosulfates have yet to be studied in the Midwestern US. This region is recognised as being affected by biogenic SOA and anthropogenic sulfate (Lewandowski et al. 2008; Stone et al. 2009; Jayarathne et al. 2016). At our study site in Iowa City, IA, PM$_{2.5}$ mass in late summer (27 August to 23 September 2011) was demonstrated to be largely composed of OC (22 %), ammonium (14 %) and sulfate (13 %) (Jayarathne et al. 2016). Primary sources including vegetative detritus, biomass burning, diesel engines, gasoline engines and coal combustion were estimated to account for 34 % of OC. The majority of the remaining OC was attributed to secondary sources, although only 3 and 4 % of OC was attributed to isoprene and monoterpene SOA respectively by the SOA-tracer method (Jayarathne et al. 2016). Notably, these SOA estimates do not account for organosulfates and thus the total impact of SOA is expectedly larger. Peak levels of biogenic SOA concentrations coincided with elevated levels of PM, sulfate and southerly winds (Jayarathne et al. 2016), and are expected to contain organosulfates.

The chemical analysis of organosulfates often involves collecting PM on filters and subjecting them to chemical analysis by techniques such as Fourier-transform infrared spectroscopy (Maria et al. 2003; Hawkins and Russell 2010) or mass spectrometry (MS) coupled with reversed-phase chromatography (Surratt et al. 2008; Kristensen and Glasius 2011; Rattanavaraha et al. 2016; Riva et al. 2016a), hydrophilic interaction liquid chromatography (HILIC) (Hettiyadura et al. 2015; Cui et al. 2018; Spolnik et al. 2018), or capillary electrophoresis (Yassine et al. 2012). Filter sample collection is subject to both positive and negative sampling artefacts (Turpin et al. 2000). Previous work has shown that organosulfates are capable of forming on filters from β-pinene oxide (Kristensen et al. 2016). Positive sampling artefacts due to gas-phase adsorption were shown to be negligible (i.e. within the analytical measurement uncertainty) in Centreville, AL, owing to the low volatility and gas-phase concentrations of organosulfates (Hettiyadura et al. 2017). In addition, the formation of organosulfates on filters through acid-catalysed reactions with sulfate was determined to be negligible (Hettiyadura et al. 2017). A recurring concern with respect to chemical analysis of PM filter samples is the stability of material on filters after collection. In the present study, we test the assumption that organosulfates are stable on filters after sample collection when those filters are stored frozen in the dark.

The present study characterises atmospheric organosulfates in PM$_{2.5}$ in the Midwestern US for the first time. Our measurements in Iowa City provide the first insight into the contribution of organosulfates to OC in this region. PM$_{2.5}$ at our suburban study site was previously characterised in the late summer as being influenced by secondary reactions, as indicated by ammonium sulfate and SOA tracers associated with isoprene and monoterpenes that are characteristic of the Midwestern US more broadly (Jayarathne et al. 2016). Regional transport is a major contributor to PM$_{2.5}$ loadings in the Midwestern US, particularly from southerly air masses that coincide with elevated levels of ammonium sulfate and SOA tracers (Jayarathne et al. 2016). Notably, two sites in Iowa City separated by 8 km had significant differences in their levels of organic molecular markers for primary and secondary sources, indicating local influences on primary and secondary organic PM$_{2.5}$ (Jayarathne et al. 2016). Hence, our measurements represent a site-specific case study

that is expected reveal trends in the relative abundance of organosulfates relevant to the Midwestern US more broadly, while their absolute concentrations are expected to vary across study sites, with air masses, and by season.

Our study centers around three primary objectives. First, we identify the major organosulfate MS signals and quantify (or semi-quantify) these species in PM$_{2.5}$ collected in Iowa City, IA. Second, we compare our observations in the upper Midwestern US with prior field measurements to gain insight into how their absolute and relative concentrations compare with other regions in the US and other continents. Third, we evaluate the integrity of organosulfate compounds during extended periods of storage following sample collection. This work provides the first chemical characterisation of organosulfates in the upper Midwestern US and the first investigation of their stability on archived filter substrates. The measurements presented in this study provide new insight into the chemical nature and sources of organosulfates and SOA in an understudied region.

## Experimental

### Chemicals and reagents

Standards for methyl sulfate and ethyl sulfate were purchased from Sigma–Aldrich. Standards for glycolic acid sulfate, hydroxyacetone sulfate, acetoin sulfate and benzyl sulfate were synthesised as potassium salts (>95 % purity) as described in Hettiyadura et al. (2015). Ultrapure water was generated on site (Thermo, Barnsted EasyPure-II; >18.2 MΩ cm resistivity, OC <40 μg L$^{-1}$). Acetonitrile (Optima, Fisher Scientific), ammonium acetate (≥99 %, Sigma–Aldrich) and ammonium hydroxide (Optima, Fisher Scientific) were used as received.

### PM$_{2.5}$ sample collection

Two PM$_{2.5}$ samples were collected on prebaked (550 °C for 18 h) quartz fibre filters (QFFs; 90-mm diameter, Pall Life Science) from 16 to 20 September 2017 at the University of Iowa Air Monitoring Site (IA-AMS; 41.6647N, 91.5845W), which is surrounded by woods, agricultural fields and a parking lot. Measured by a local outdoor monitor managed by the Environmental Protection Agency, the temperature ranged from 12 to 33 °C with predominate southerly winds. The 5-day sampling time, rather than a 24-h sample, was preferred to amass a relatively large amount of PM$_{2.5}$ on a single filter so that subsamples of that filter could be extracted and analysed over the course of 1 year to evaluate organosulfate stability on filters. PM$_{2.5}$ was collected using two medium-volume air samplers (3000B, URG Corporation) affixed to a platform 1 m above the ground and equipped with a cyclone operating at a flow rate of 90 L min$^{-1}$. PM$_{2.5}$ mass, measured using a federal reference method at a local Environmental Protection Agency Air Monitoring site (41.6572N, 91.5035W) 8 km east of our sampling site, averaged 8.56 ± 4.03 μg m$^{-3}$ during the study period. Following collection, QFFs were stored in aluminium foil (prebaked at 550 °C for 5.5 h)-lined Petri dishes and transported to the laboratory for immediate analysis and subsequent storage at −20 °C.

### Extraction of organosulfates

As described in Hettiyadura et al. (2015), subsamples of the QFFs were extracted via sonication in 10 mL acetonitrile and ultrapure water (95 : 5 v/v) for 20 min. The extracts were filtered through a polypropylene membrane syringe filter (0.45-μm pore size; Puradisc, Whatman), evaporated to dryness under ultrahigh purity nitrogen at 50 °C (Turbovap LV, Capiler Life

Sciences; Reacti-Vap I 18825, Thermo Scientific), and reconstituted to a final volume of 300 μL using 95 : 5 (v/v) acetonitrile : ultrapure water. This extraction protocol efficiently recovered a range of organosulfates, including methyl sulfate (102 %), ethyl sulfate (96 %), benzyl sulfate (111 %), acetoin sulfate (96 %), hydroxyacetone sulfate (105 %) and glycolic acid sulfate (90 %). An initial extraction was carried out immediately following sample collection where a 2.56-cm$^2$ punch of each filter was analysed to evaluate organosulfate loadings on each filter and develop the experimental plan. Following the initial extraction, three 0.78-cm$^2$ punches were extracted from each filter 2, 8, 29, 83, 180, 251 and 364 days after collection, giving a total of six samples at each time period. Filters were removed from storage at −20 °C immediately before sub-sampling and replaced immediately after.

### Separation and quantitation

Using the optimised conditions described in Hettiyadura et al. (2015), an ultraperformance liquid chromatograph (UPLC) interfaced to a triple quadrupole mass spectrometer (TQD) with negative electrospray ionisation ((–)ESI) operating in multiple reaction monitoring (MRM) mode was used to quantify organosulfates. Separation was achieved using an ethylene-bridged hybrid amide (BEH-amide) column (2.1 × 100 mm, 1.7-μm particle size; Acquity UPLC Waters). The eluents, delivered as a gradient outlined by Hettiyadura et al. (2015), included an organic eluent of ammonium acetate buffer (10 mM, pH 9) in acetonitrile and ultrapure water (95 : 5 v/v) and an aqueous eluent of ammonium acetate buffer (10 mM, pH 9) in ultrapure water. Data were acquired and analysed using *MassLynx* and *QuanLynx* software (Waters Inc., Version 4.1).

### Qualitative analysis of organosulfates

Organosulfate species were defined as species that fragmented to a bisulfate anion (*m/z* 97) or a sulfate radical anion (*m/z* 96) using HILIC-TQD in precursor ion mode scanning masses ranging from 100 to 400 Da. The organosulfates identified in the precursor ion scans were further characterised using UPLC coupled with (–)ESI time-of-flight mass spectrometry (TOF-MS) (Bruker Daltonics MicrOTOF) to determine their monoisotopic mass and elemental composition. The working resolution for the TOF-MS was 9000. Data were acquired and analysed using *MassLynx* and *Quanlynx* software (Waters Inc., Version 4.1), and molecular formulae were assigned considering both odd and even electron states, $C_{0-20}$, $H_{0-50}$, $N_{0-10}$, $O_{0-10}$, $S_{0-6}$, and a maximum error of 5 mDa.

### Measurement of organic carbon

OC was measured on a 1.0-cm$^2$ PM$_{2.5}$ subsample using a thermal-optical analyser (Sunset Laboratory) according to the Aerosol Characterisation Experiment-Asia base case protocol (Schauer et al. 2003).

### Statistical analysis

Differences in means were assessed by a two-sample *t*-test using *Minitab* software and were considered significant if $P < 0.05$, corresponding to the 95 % confidence interval.

## Results and discussion

### Identification of major organosulfates in Iowa City

Organosulfates exhibit characteristic product ions under (–)ESI conditions: the bisulfate anion (HSO$_4^-$ at *m/z* 97), the sulfate radical anion (SO$_4^{-\bullet}$ at *m/z* 96), the bisulfate anion (HSO$_3^-$ at *m/z* 81) and the bisulfite radical anion (SO$_3^{-\bullet}$ at *m/z* 80) (Attygalle et al. 2001; Gómez-González et al. 2008; Surratt et al. 2008). In the present study, precursors to the bisulfate anion and sulfate radical were used to identify organosulfates in ambient PM$_{2.5}$ collected in Iowa City, IA. The bisulfate ion forms by syn-elimination and is the predominant sulfur-containing fragment ion for organosulfates with sp$^3$-hybridised carbon atoms in the α and β positions from the sulfate group and an abstractable proton in the β position (Attygalle et al. 2001). When a proton cannot be abstracted from the β position, it may be abstracted from carbon atoms more distant from the sulfate group (Attygalle et al. 2001). Bisulfate is the major sulfate-containing product for many organosulfates observed in atmospheric aerosols, such as hydroxyacetone sulfate and methyltetrol sulfate. The sulfate radical anion forms from the homolytic cleavage of the C–O bond associated with the sulfate group and is the major sulfur-containing product ion for allylic and benzylic organosulfates, such as benzyl sulfate, that stabilise the radical by resonance (Attygalle et al. 2001). The sulfate radical anion is also the predominant sulfur-containing fragment ion for nitro-oxy organosulfates observed in atmospheric aerosols. The bisulfite anion (*m/z* 81) and sulfite radical anion (*m/z* 80) are also observed in MS/MS spectra from organosulfates, but results from their precursor ion scans are largely redundant with those from the bisulfate anion (*m/z* 97) and sulfate radical anion (*m/z* 96) (Hettiyadura et al. 2019). Consequently, precursors to the bisulfite anion and sulfite radical anion were not measured in the present study.

Major organosulfates were defined as the organosulfate species that exhibited either: (1) a contribution ≥0.5 % to the precursor to the *m/z* 97 signal; (2) a contribution ≥1.0 % to the precursor to the *m/z* 96 signal; or (3) a retention time (T$_R$) greater than 4 min on the HILIC column. The selection criteria were utilised to focus our attention on organosulfates of high atmospheric abundance and maximise instrument sensitivity by limiting the number of ions monitored. In addition to the species with a significant contribution to the precursor ion signal, organosulfates eluting after 4 min were also selected for analysis because despite having a high atmospheric abundance, these compounds have a low instrumental response owing to the mobile phase gradient shifting from acetonitrile to aqueous, which decreases mobile phase desolvation and ionisation efficiency (Hettiyadura et al. 2017). The MS signals corresponding to the major organosulfate species are labelled in Fig. 1 and are the focus of the ensuing discussion, although many additional minor signals were observed. The strongest signals were observed in the precursor to *m/z* 97 scans owing to the greater stability of the bisulfate anion compared with the sulfate radical anion; for example, the precursor to the *m/z* 96 signal was only 1.9 % of the precursor to the *m/z* 97 signal. Using product ion signals to evaluate the relative abundance of organosulfates relies on the assumption that each organosulfate has an equal ability to form fragment ions. As discussed in Hettiyadura et al. (2017), this approach does not account for differing ionisation efficiencies or fragmentation patterns that may introduce positive or negative biases. Nonetheless, it provides a means of evaluating the presence of organosulfates by their relative signal strengths in the absence of quantification standards for each species. The major organosulfates observed are summarised in Table 1 along with their calculated monoisotopic mass, molecular formula determined using HILIC-TOF, molecular structures and expected precursor(s) based on previous chamber
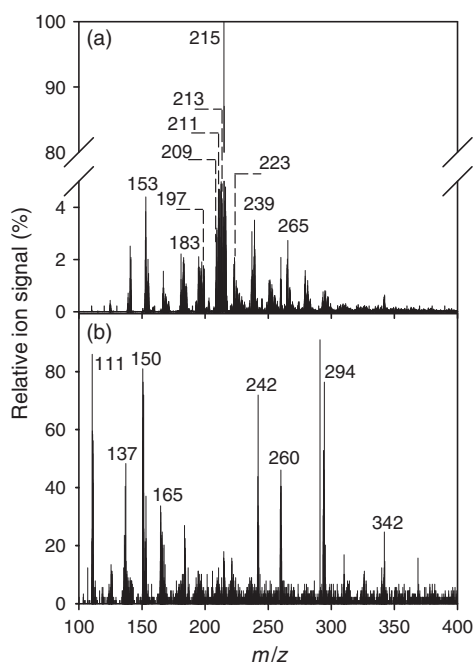
**Fig. 1.** Mass spectra corresponding to precursor ion scans of (a) bisulfate anion ($m/z$ 97), and (b) sulfate ion radical ($m/z$ 96). The maximum absolute signal for each precursor ion scan was 55 600 au and 218 au respectively, reflecting a much stronger signals for the $m/z$ 97 product ion compared with $m/z$ 96. The organosulfates observed by each precursor ion scan type are influenced by their chemical structures and fragmentation pathways, discussed in the section *Identification of major organosulfates in Iowa City.*

experiments and field work, and relative contribution to precursor ion signals.

*Organosulfates derived from isoprene*

Isoprene-related organosulfates accounted for 11 of the 22 major organosulfates and accounted for 74.8 % of the bisulfate ion signal. Methyltetrol sulfate ($C_5H_{11}SO_7^-$; $m/z$ 215), formed via acid-catalysed nucleophilic addition of sulfate to isoprene epoxydiols (IEPOX) (Surratt et al. 2010), was the most abundant organosulfate and accounted for 59.5 % of the bisulfate ion signal. Four isomers of methyltetrol sulfate that corresponded to secondary diastereomers ($T_R$ of 1.40 and 1.72) and tertiary diastereomers (2.76 and 3.44) (Cui et al. 2018) were baseline-resolved. Sulfate esters of cyclic methyltrihydroxyaldehyde hemiacetal ($C_5H_9SO_7^-$; $m/z$ 213) and of methydihydroxylactone ($C_5H_7SO_7^-$; $m/z$ 211), with tentatively identified structures (Hettiyadura et al. 2015), were the next strongest signals and contributed 5.5 and 4.2 % to the bisulfate ion signal respectively. These organosulfur species result from the photooxidation of isoprene (Surratt et al. 2008) and have also been suggested to result from further oxidation of methyltetrol sulfates (Hettiyadura et al. 2015). Smaller contributions (≤1.1 %) from numerous other organosulfates ($m/z$ 183, 153 and 197) and a nitro-oxy organosulfate ($m/z$ 260) that primarily result from the atmospheric processing of isoprene were also identified (Table 1) (Surratt et al. 2008; Riva et al. 2016a).

The organosulfates eluting after 4 min on the HILIC column included glycolic acid sulfate ($C_2H_3SO_6^-$; $m/z$ 155), 2-methylglyceric acid sulfate ($C_4H_7SO_7^-$; $m/z$ 199) and lactic acid sulfate ($C_3H_5SO_6^-$; $m/z$ 169), and together accounted for 1.0 % of the bisulfate anion signal and were also associated with isoprene.

Glycolic acid sulfate has been shown to form from both glyoxal and more efficiently from glycolic acid (Liao et al. 2015). Although both have biogenic and anthropogenic sources, glycolic acid sulfate is primarily associated with the oxidation of isoprene (Nozière et al. 2010; Liao et al. 2015). Lactic acid sulfate has been reported to form via isoprene photooxidation (Surratt et al. 2008) and isoprene ozonolysis (Riva et al. 2016a) whereas 2-methylglyceric acid sulfate forms from isoprene photooxidation under high $NO_x$ conditions (Nguyen et al. 2015). In total, these species indicate that isoprene is the major precursor to organosulfates.
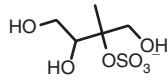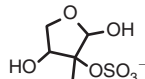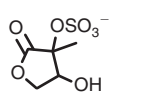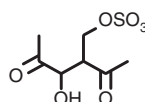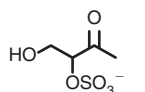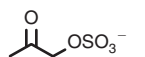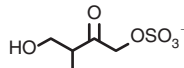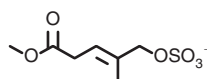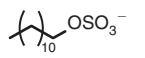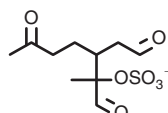
*Terpene-derived organosulfates*

Terpenes contributed to SOA to a lesser extent, with seven organosulfur compounds associated with terpene oxidation identified among the top 22 signals and a total contribution of 5.6 % to the bisu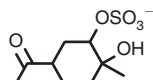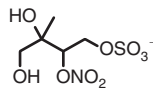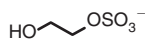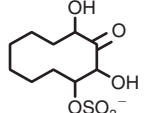lfate ion signal. The most abundant signal among the organosulfates derived from terpenes corresponded to a species with the chemical formula $C_7H_{11}SO_7^-$ ($m/z$ 239), which has been reported as a product of limonene photooxidation (Surratt et al. 2008). Other products of limonene oxidation corresponded to $C_9H_{15}SO_7^-$ ($m/z$ 267) and $C_9H_{15}SO_6^-$ ($m/z$ 251) (Surratt et al. 2008). Although $C_9H_{15}SO_6^-$ may also arise from the photooxidation of β-caryophyllene (Chan et al. 2011), it has been suggested to form primarily from limonene in previous field measurements (Hettiyadura et al. 2019). Additional organosulfates with $m/z$ 223 ($C_7H_{11}SO_6^-$), $m/z$ 237 ($C_8H_{13}SO_6^-$), $m/z$ 279 ($C_{10}H_{15}SO_7^-$) and $m/z$ 281 ($C_{10}H_{17}SO_7^-$) have been identified as SOA products of α-pinene oxidation as well as the oxidation of other monoterpenes in the presence of $NO_x$ and sulfate (Surratt et al. 2008). Two monoterpene-derived nitro-oxy organosulfates, $C_{10}H_{16}NSO_7^-$ ($m/z$ 294) and $C_{10}H_{16}NSO_{10}^-$ ($m/z$ 342), were two of the eight strongest signals in the precursor to the $m/z$ 96 scan (Fig. 1b and Table S1, Supplementary Material). These organosulfates have been shown to result from numerous monoterpenes in the presence of $NO_x$ (Surratt et al. 2008). The observed organosulfates associated with monoterpenes highlight the role of $NO_x$ on monoterpene SOA formation.
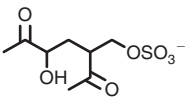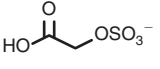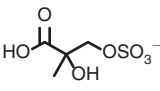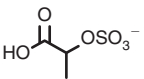
*Anthropogenic organosulfates*

Although organosulfate compounds are inherently influenced by anthropogenic emissions owing to their sulfate moiety, some organosulfates have been associated with anthropogenic VOC or primary emissions. Three such compounds were detected and collectively accounted for 4.3 % of the bisulfate anion signal. Two of these are associated with the photooxidation of cyclohexene (Liu et al. 2017), a common solvent used in industry, and include $C_6H_9SO_6^-$ ($m/z$ 209), which had the fourth strongest signal, and $C_6H_9SO_7^-$ ($m/z$ 225). Dodecyl sulfate ($C_{12}H_{25}SO_4^-$; $m/z$ 265), a common surfactant in detergents and wastewater treatment (Hettiyadura et al. 2017), was likely emitted from primary source. Its relatively large contribution to the bisulfate anion signal is likely influenced by efficient ionisation of surfactants in electrospray ionisation (Cortés-Francisco and Caixach 2013). Additional anthropogenic organosulfates were identified in the precursor to the $m/z$ 96 scan (Fig. 1b and Table S1, Supplementary Material): $C_4H_7SO_4^-$ ($m/z$ 151) and $C_3H_5SO_4^-$ ($m/z$ 137), which have been identified as oxidation products of diesel emissions (Blair et al. 2017), and $C_6H_9SO_6^-$ ($m/z$ 165), which is derived from the oxidation of cyclohexene (Liu et al. 2017). These observations indicate that anthropogenic organosulfates are among the strongest organosulfate signals, but with lower signal strength compared with biogenic organosulfates.

D

**Table 1.  Organosulfates identified in Iowa City, IA from the precursor to the *m/z* 97 scan**

Summarised for each compound is the calculated monoisotopic mass, formula determined by TOF-MS, proposed structure, VOC precursor(s) with reference to prior studies, HILIC retention time for major peaks, *m/z* error (mDa), and percentage contribution to the precursor ion signal

| Calculated mass [M − H]⁻ | Formula | Proposed structure | VOC precursor(s) | $T_R$ (min) | Error (mDa) | Contribution to precursor ion signal (%) |
|---|---|---|---|---|---|---|
| 215.0225 | $C_5H_{11}SO_7^-$ 2-methyltetrol sulfate | A  | Isoprene[A,B] | 1.40 1.72 2.76 3.44 | −0.6 0.7 −0.6 0.5 | 59.5 |
| 213.0069 | $C_5H_9SO_7^-$ | C  | Isoprene[B] | 1.11 1.49 2.14 | 0.2 0.4 −0.4 | 5.5 |
| 210.9912 | $C_5H_7SO_7^-$ | C  | Isoprene[B] | 0.54 0.71 0.87 | 1.0 1.1 1.3 | 4.2 |
| 209.0120 | $C_6H_9SO_6^-$ | Unknown | Cyclohexene[D] | 0.55 | 0.6 | 3.0 |
| 239.0225 | $C_7H_{11}SO_7^-$ | E  | Limonene[B] MVK/MACR[E–F] | 0.75 | 0.8 | 1.4 |
| 182.9963 | $C_4H_7SO_6^-$ | G  | Isoprene[H] MVK/MACR[I] | 1.03 | 0.8 | 1.1 |
| 152.9858 | $C_3H_5SO_5^-$ Hydroxyacetone sulfate | B  | Isoprene[B] MVK/MACR[I] | 0.70 | 1.0 | 1.1 |
| 197.0120 | $C_5H_9SO_6^-$ | H  | Isoprene[H] | 0.91 | 1.1 | 1.0 |
| 223.0276 | $C_7H_{11}SO_6^-$ | J  | α-Pinene[B] | 0.65 | 2.5 | 0.9 |
| 265.1474 | $C_{12}H_{25}SO_4^-$ Dodecyl sulfate | K  | Anthropogenic[K] | 0.53 | 0.6 | 0.8 |
| 237.0433 | $C_8H_{13}SO_6^-$ | Unknown | α-Pinene[B] | 0.67 | 1.0 | 0.8 |
| 279.0538 | $C_{10}H_{15}SO_7^-$ | B  | α-Pinene[B,E] Monoterpenes[B] Dodecane and cyclododecane[L] | 0.80 | 1.3 | 0.7 |
| 251.0589 | $C_9H_{15}SO_6^-$ | B  | Limonene[B] β-Caryophyllene[M] | 0.59 | 1.3 | 0.6 |
| 260.0076 | $C_5H_{10}NSO_9^-$ | N  | Isoprene[B] | 0.65 | 1.1 | 0.6 |
| 140.9858 | $C_2H_5SO_5^-$ | O  | Numerous sources | 1.79 | 0.9 | 0.6 |
| 281.0695 | $C_{10}H_{17}SO_7^-$ | D  | α-pinene[B,E] Limonene[B] | 0.59 | 0.3 | 0.6 |

(*Continued*)

E

**Table 1.  (Continued)**

| Calculated mass $[M - H]^-$ | Formula | Proposed structure | VOC precursor(s) | $T_R$ (min) | Error (mDa) | Contribution to precursor ion signal (%) |
|---|---|---|---|---|---|---|
| 267.0538 | $C_9H_{15}SO_7^-$ | Unknown | Limonene[B,P] $\alpha$-Pinene[P] | 0.76 | 1.3 | 0.5 |
| 225.0069 | $C_6H_9SO_7^-$ | Unknown | Cyclohexene[D] | 0.79 | 1.3 | 0.5 |
| 253.0382 | $C_8H_{13}SO_7^-$ | [I]  | $\alpha$-Terpinene[B] MVK/MACR[E] | 0.82 | 1.4 | 0.5 |
| 154.9650 | $C_2H_3SO_6^-$ Glycolic acid sulfate | [Q]  | Isoprene[B] | 7.46 | 1.2 | 0.5 |
| 198.9912 | $C_4H_7SO_7^-$ 2-methylglyceric acid sulfate | [B]  | Isoprene[B] (high $NO_x$) | 7.74 | 0.7 | 0.4 |
| 169.9807 | $C_3H_5SO_6^-$ Lactic acid sulfate | [Q]  | Isoprene[B,H] | 0.80 | 1.3 | 0.7 |

[A]Surratt et al. (2010); [B]Surratt et al. (2008); [C]Hettiyadura et al. (2015); [D]Liu et al. (2017); [E]Nozière et al. (2010); [F]Methylvinyl ketone (MVK) methacrolein (MACR); [G]Shalamzari et al. (2014); [H]Riva et al. (2016a); [I]Schindelka et al. (2013); [J]Yassine et al. (2012); [K]Hettiyadura et al. (2017); [L]Riva et al. (2016b); [M]Chan et al. (2011); [N]Darer et al. (2011); [O]Kwong et al. (2018); [P]Ye et al. (2018); [Q]Olson et al. (2011).

*Organosulfates from unknown sources*

An organosulfate with the formula $C_2H_5SO_5^-$ (m/z 141) was tentatively identified as 2-hydroxyethyl sulfate and accounted for 0.6 % of the bisulfate ion signal. This compound has been shown to form through the oxidation of ethyl sulfate (Kwong et al. 2018); however, given the low atmospheric concentration of ethyl sulfate (0.08 ng m$^{-3}$), we propose this organosulfate could also result from the oxidation of ethylene through the reactive uptake of ethylene oxide via acid-catalysed ring opening and subsequent nucleophilic addition of sulfate. The sources of atmospheric ethylene are both biogenic and anthropogenic, and include vegetation (Goldstein et al. 1996), marine water (Gist and Lewis 2006), biomass burning (Lewis et al. 2013), vehicle exhaust (Wang et al. 2013) and industrial processes (Na et al. 2001). Therefore, this organosulfate cannot be tied to a specific source, but is likely to be associated with emissions from biomass burning and vehicle exhaust in Iowa City based on previous source apportionment modelling (Jayarathne et al. 2016).

*Quantitation and semi-quantitation of organosulfates*

The concentrations of organosulfates with the strongest MS/MS signals are listed in Table 2, with additional notable species reported in Table S2 (Supplementary Material). For species quantified against authentic standards, methyl sulfate and ethyl sulfate were low in concentration (0.7 $\pm$ 0.2 ng m$^{-3}$ and 0.08 $\pm$ 0.02 ng m$^{-3}$) and accounted for 0.01 and 0.001 % of OC respectively. Benzyl sulfate and acetoin sulfate were below the limit of detection (<0.1 ng m$^{-3}$). These results are consistent with those reported by Hettiyadura et al. (2017) for Centreville, AL, in which methyl sulfate only accounted for 0.007 % of OC whereas ethyl sulfate and benzyl sulfate were consistently below detection limits.

Additional organosulfates were semi-quantified using surrogate standards. Two anthropogenic organosulfates, dodecyl sulfate (m/z 265) and $C_6H_9SO_6^-$ (m/z 209), averaged 1.4 $\pm$ 0.3 ng m$^{-3}$ and 8.3 $\pm$ 0.4 ng m$^{-3}$ respectively. In comparison with Atlanta, GA, these two organosulfates had comparable atmospheric concentrations (Hettiyadura et al. 2019), but contributed ~1.75× more to OC in Iowa City. Four monoterpene-derived organosulfates ($C_7H_{11}SO_7^-$, $C_7H_{11}SO_6^-$, $C_8H_{13}SO_6^-$ and $C_{10}H_{15}SO_7^-$) had a total concentration of 6.4 $\pm$ 0.6 ng m$^{-3}$. Relative to other studies, these four organosulfates had significantly higher concentrations than in Towson, MD (~14× higher) (Meade et al. 2016) and a much lower concentration than in Atlanta, GA (~5× lower) (Hettiyadura et al. 2019). Additionally, the concentration of $C_7H_{11}SO_7^-$ (m/z 239) was ~4× lower in Iowa City when compared with Centreville, AL (Hettiyadura et al. 2018). In comparison with the isoprene-derived organosulfates quantified in Iowa City (Table 2), the four most abundant monoterpene-derived organosulfates were much lower in their estimated concentrations (~45× lower) and their contribution to OC (~44× lower). Hydroxyethyl sulfate was estimated to have an ambient concentration of 2.9 $\pm$ 0.2 ng m$^{-3}$ and accounted for 0.03 % of OC in Iowa City. Together, these additional organosulfates further support that organosulfate formation in Iowa City is largely isoprene-related with minor contributions from monoterpenes and anthropogenic sources.

*Comparison of major organosulfates with previous work*

The major organosulfates identified in this study are consistent with those observed in previous studies. Methyltetrol sulfate (m/z 215) was the most abundant organosulfate in Iowa City and is the most common organosulfate observed in ambient samples worldwide (Meade et al. 2016; Rattanavaraha et al. 2016; Hettiyadura et al. 2018; Cui et al. 2018; Wang et al. 2018). In comparison with studies utilising similar methodology (Hettiyadura et al. 2017, 2019), the major organosulfates

**Table 2.** Summary of organosulfates quantified in $PM_{2.5}$ as mean with standard deviation (s.d.) and percentage of organic carbon (%OC) in the present and prior studies

| Location (GPS) | Date | m/z 153 $C_3H_5SO_5^-$ mean ± s.d. (%OC) | m/z 155 $C_2H_3SO_6^-$ mean ± s.d. (%OC) | m/z 199 $C_4H_7SO_7^-$ mean ± s.d. (%OC) | m/z 211 $C_5H_7SO_7^-$ mean ± s.d. (%OC) | m/z 213 $C_5H_9SO_7^-$ mean ± s.d. (%OC) | m/z 215 $C_5H_{11}SO_7^-$ mean ± s.d. (%OC) | Reference |
|---|---|---|---|---|---|---|---|---|
| Iowa City, IA[A] (41.665N, 91.585W) | 9/16/17–9/20/17 | 4.8 ± 1.1 (0.07) | 19.5 ± 2.1 (0.17) | 15.1 ± 0.8 (0.21) | 17.9 ± 0.9 (0.29) | 16.0 ± 1.0 (0.26) | 214 ± 8 (3.40) | Present study |
| Centreville, AL[B] (32.902N, 87.250W) | 6/13/13–7/13/13 | 5.8 ± 3.1 (0.05) | 20.6 ± 14.3 (0.10) | 8.4 ± 9.0 (0.07) | 35.3 ± 25.6 (0.33) | 31.6 ± 22.5 (0.30) | 668 ± 515 (6.06) | Hettiyadura et al. (2017) |
| Atlanta, GA[C] (33.779N, 84.396W) | 7/29/15–8/27/15 | 10.1 ± 6.0 (0.06) | 58.5 ± 40.2 (0.24) | 53.0 ± 42.3 (0.22) | 130.6 ± 81.9 (0.93) | 114.3 ± 78.9 (0.80) | 1792 ± 1085 (12.55) | Hettiyadura et al. (2019) |
| Look Rock, TN[D] (35.633N, 83.942W) | 6/1/13–7/17/13 | NR[E] | NR | NR | NR | NR | 2330 (12.9) | Cui et al. (2018) |
| Birmingham, AL[F] (33.553N, 86.815W) | 6/1/13–7/16/13 | NR | 26.2 (0.06) | 7.2 (0.02) | 1.4 (0.01) | NR | 164.5 (0.64) | Rattanavaraha et al. (2016) |
| Towson, MD[G] (39.392N, 76.610W) | 8/29/12–8/30/12 | 0.8 ± 0.4 (0.002) | NR | 1.3 ± 0.7 (0.003) | NR | 1.1 ± 0.7 (0.003) | 14.1 ± 13.0 (0.04) | Meade et al. (2016) |
| Changping, China[H] (40.140N, 116.110E) | 5/20/16–6/3/16 | 2.2 (0.01) | 19.5 (0.04) | 3.6 (0.01) | 5.9 (0.02) | NR | 5.3 (0.02) | Wang et al. (2018) |
| Silkeborg, Denmark[I,J] (56.182N, 9.580E) | 4/15/08–5/14/08 | NR | NR | NR | NR | 0.02 ± 0.02 (NR) | 0.01 ± 0.02 (NR) | Kristensen and Glasius (2011) |
| HCAB, Denmark[I,K] (55.633N, 12.567E) | 5/19/11–6/22/11 | 6.6 ± 6.0 (NR) | 5.3 ± 3.8 (NR) | 7.1 ± 6.7 (NR) | 7.4 ± 6.0 (NR) | 5.1 ± 4.5 (NR) | 5.0 ± 6.8 (NR) | Nguyen et al. (2014) |

[A] m/z 153 and 155 quantified with synthesised standards, m/z 199 quantified using glycolic acid sulfate as a surrogate standard, m/z 211, 213, and 215 quantified using hydroxyacetone sulfate as a surrogate standard; [B] m/z 153, 155, and 215 quantified with synthesised standards, m/z 199 quantified using glycolic acid sulfate as a surrogate standard, m/z 211 and 213 quantified using hydroxyacetone sulfate as a surrogate standard; [C] m/z 153 and 155 quantified with synthesised standards, m/z 199 quantified using glycolic acid sulfate as a surrogate standard, m/z 211 and 213 quantified using hydroxyacetone sulfate as a surrogate standard, m/z 215 quantified using a response factor; [D] m/z 215 quantified with a synthesised standard; [E] Not reported; [F] m/z 155, 199, and 215 quantified with synthesised standards, m/z 211 quantified using propyl sulfate as a surrogate standard; [G] m/z 153, 199, 213 and 215 quantified using glycolic sulfate ester as a surrogate standard; [H] m/z 155 quantified with a synthesised standard, m/z 199, 211 and 215 quantified using glycolic acid sulfate as a surrogate standard; [K] m/z 153, 155, 199, 211, 213 and 215 quantified using camphor sulfonic acid as a surrogate standard; [I] $PM_1$; [J] m/z 213 and 215 quantified using D-mannose sulfate as a surrogate standard.

G
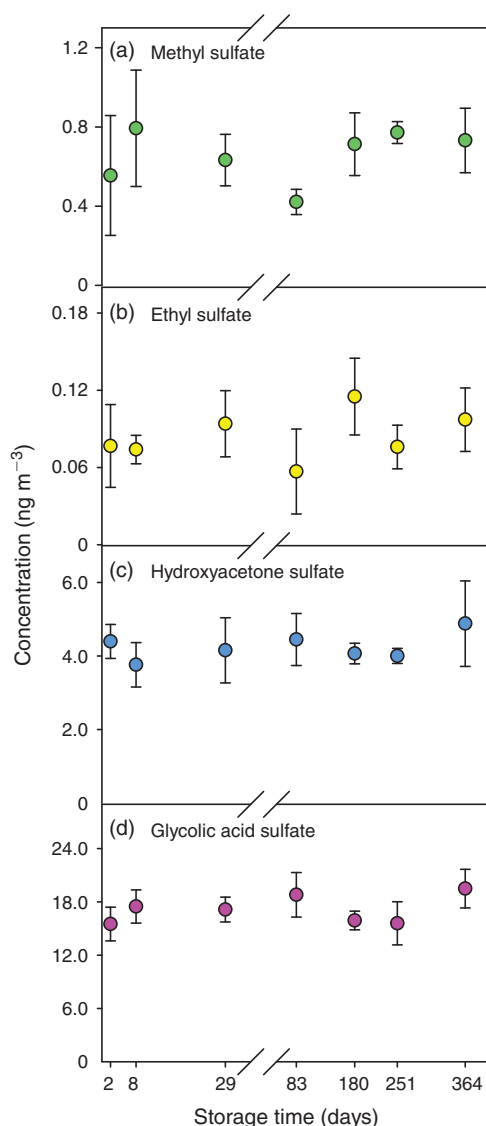
**Fig. 2.** Concentrations of (a) methyl sulfate, (b) ethyl sulfate, (c) hydroxyacetone sulfate, and (d) glycolic acid sulfate at each time period. Error bars represent the 95 % confidence interval where $n = 5$ for Days 2 and 251 and $n = 6$ for Days 8, 29, 83, 180, 361.

identified via their contribution to the bisulfate anion signal are largely similar, with $m/z$ 215 the largest, followed by $C_5H_9SO_7^-$ ($m/z$ 213) and $C_5H_7SO_7^-$ ($m/z$ 211). In addition, our observations in Iowa City suggest that the primary precursor of organosulfates in the Midwestern US is isoprene with minor contributions from other biogenic and anthropogenic precursors.

The concentrations of six major organosulfates, along with their contribution to OC, were compared with prior field studies to gain insight into how anthropogenic pollutants influence SOA formation in Iowa City. The six organosulfates selected for comparison are isoprene-related SOA products (Table 2) that accounted for 4.4 % of OC in Iowa City, and contributed 70.9 % to the bisulfate anion signal. Although methyltetrol sulfate was found to have a much lower ambient concentration in Iowa City compared with Centreville, AL ($\sim$3× lower), Atlanta, GA ($\sim$8× lower), and Look Rock, TN ($\sim$10× lower) (Hettiyadura et al. 2018, 2019; Cui et al. 2018), it had higher concentrations compared with Birmingham, AL ($\sim$1.3× higher), Towson, MD

($\sim$15× higher), and Changping, China ($\sim$40× higher) (Meade et al. 2016; Rattanavaraha et al. 2016; Wang et al. 2018).

The absolute concentrations of these organosulfates are lower in Iowa City than in most sites in the Southeastern US, and this may arise from differences in meteorology, variations in mixing ratios of VOC precursors, and other factors that influence organosulfate formation. On a relative scale, the six organosulfates in Table 2 contributed 4.4 % of OC in Iowa City, and this was slightly less than their OC contribution in Centreville (7.0 %) and significantly less than the contribution observed in Atlanta (14.8 %). This finding demonstrates that isoprene-derived organosulfates make a sizeable contribution to OC in the Midwestern US similar to the Southeastern US.

### Organosulfate stability on filter substrates

The concentrations of methyl sulfate, ethyl sulfate, hydroxyacetone sulfate and glycolic acid sulfate within one year of collection were within 31, 35, 15 and 26 % of their initial concentrations measured 48 h after collection respectively (Fig. 2). No significant concentration differences were observed over the 1-year study stability study ($P > 0.05$; Table S2, Supplementary Material), with one exception. Glycolic acid sulfate measured at the 1-year mark was significantly higher than the concentration measured initially ($P = 0.01$). The 25 % increase in glycolic acid concentration and concurrent (but not significant) increases in other organosulfates (Fig. 2) occurred immediately after major instrument maintenance that increased MS/MS signals by a factor of 2. Hence, the increasing glycolic acid sulfate response is expected to be due to instrumental maintenance and not a change in its concentration on the stored filters. Additionally, the MS/MS responses of methyltetrol sulfate, $C_5H_9SO_7^-$ ($m/z$ 213), and $C_5H_7SO_7^-$ ($m/z$ 211) relative to that of hydroxyacetone sulfate were within 35 % of their initial values, suggesting neither loss nor formation on filters during storage. From this, we conclude that organosulfates with a range of alkyl, carboxylate and hydroxyl functional groups are stable post collection when stored frozen. Additionally, these species are expected to remain stable for periods even longer than considered here as any changes would be expected to occur within the first year of storage.

### Summary and implications

For the first time, we demonstrate that organosulfates are significant components of ambient $PM_{2.5}$ OC in the Midwestern US. These compounds account for additional OC that was previously uncharacterised by gas chromatography MS methods and unapportioned by chemical mass balance source apportionment modelling described in Jayarathne et al. (2016). Although the upper Midwestern US is not often considered to be heavily influenced by isoprene SOA, the contribution of organosulfates to OC was within a factor of 2–3 when compared with the contributions observed in the Southeastern US.

Iowa City was similar to sites throughout the Southeastern US in that the three most abundant organosulfates corresponded to methyltetrol sulfate, $C_5H_9SO_7^-$ ($m/z$ 213) and $C_5H_7SO_7^-$ ($m/z$ 211). However, four methyltetrol sulfate isomers were detected in Iowa City, corresponding to secondary and tertiary diastereomers, whereas six isomers were reported in Centreville (Hettiyadura et al. 2017) and Atlanta (Hettiyadura et al. 2019), and included additional primary diastereomers that are unique products of δ-IEPOX oxidation (Cui et al. 2018). The absence of the primary diastereomers in Iowa City suggests that organosulfate

formation in Midwestern US may primarily result from β-IEPOX whereas the Southeastern US appears to have influence from both δ-IEPOX and β-IEPOX.

Multiple isomers of $C_5H_9SO_7^-$ ($m/z$ 213) and $C_5H_7SO_7^-$ ($m/z$ 211) have also been reported (Hettiyadura et al. 2015; Spolnik et al. 2018), and given their high abundance in numerous locations, they should be the next priority for standard development so that differences SOA formation across regions can be further explored. The identification of other major organosulfates is useful from the perspective of guiding standard development to support more accurate quantitation of this class of compounds. Moreover, the knowledge that organosulfates are stable on filters stored over the course of 1 year, and expectedly longer, indicates that archived samples may be analysed as new methods of analysis and standards emerge. Future work should continue to expand organosulfate analysis in understudied regions to enhance our understanding of how anthropogenic emissions influence biogenic SOA formation.

## Supplementary material

The supplementary material includes a table summarising the organosulfates identified in the precursor to $m/z$ 96 scan (Table S1), the concentrations and OC contributions of additional organosulfates measured in Iowa City (Table S2) and the statistical results from the organosulfate stability study (Table S3).

## Conflicts of Interests

The authors declare no conflicts of interest.

## Acknowledgements

## References

Attygalle AB, Garcãa-Rubio S, Ta J, Meinwald J (2001). Collisionally induced dissociation mass spectra of organic sulfate anions. *Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry* 498–506. doi:10.1039/B009019K

Blair SL, Macmillan AC, Drozd GT, Goldstein AH, Chu RK, Paša-Tolić L, Shaw JB, Tolić N, Lin P, Laskin J, Laskin A, Nizkorodov SA (2017). Molecular characterization of organosulfur compounds in biodiesel and diesel fuel secondary organic aerosol. *Environmental Science & Technology* 51, 119–127. doi:10.1021/ACS.EST.6B03304

Brunekreef B, Holgate ST (2002). Air pollution and health. *Lancet* 360, 1233–1242. doi:10.1016/S0140-6736(02)11274-8

Carlton AG, Pinder RW, Bhave PV, Pouliot GA (2010). To what extent can biogenic SOA be controlled? *Environmental Science & Technology* 44, 3376–3380. doi:10.1021/ES903506B

Chan MN, Surratt JD, Chan AWH, Schilling K, Offenberg JH, Lewandowski M, Edney EO, Kleindienst TE, Jaoui M, Edgerton ES, Tanner RL, Shaw SL, Zheng M, Knipping EM, Seinfeld JH (2011). Influence of aerosol acidity on the chemical composition of secondary organic aerosol from β-caryophyllene. *Atmospheric Chemistry and Physics* 11, 1735–1751. doi:10.5194/ACP-11-1735-2011

Cortés-Francisco N, Caixach J (2013). Molecular characterization of dissolved organic matter through a desalination process by high-resolution mass spectrometry. *Environmental Science & Technology* 47, 9619–9627. doi:10.1021/ES4000388

Cui T, Zeng Z, Dos Santos EO, Zhang Z, Chen Y, Zhang Y, Rose CA, Budisulistiorini SH, Collins LB, Bodnar WM, De Souza RF, Martin ST, Machado CMD, Turpin BJ, Gold A, Ault AP, Surratt JD (2018). Development of a hydrophilic interaction liquid chromatography (HILIC) method for the chemical characterization of water-soluble isoprene epoxydiol (IEPOX)-derived secondary organic aerosol. *Environmental Science. Processes & Impacts* 20, 1524–1536. doi:10.1039/C8EM00308D

Darer AI, Cole-Filipiak NC, O'Connor AE, Elrod MJ (2011). Formation and stability of atmospherically relevant isoprene-derived organosulfates and organonitrates. *Environmental Science & Technology* 45, 1895–1902. doi:10.1021/ES103797Z

Gist N, Lewis AC (2006). Seasonal variations of dissolved alkenes in coastal waters. *Marine Chemistry* 100, 1–10. doi:10.1016/J.MARCHEM.2005.10.004

Goldstein AH, Fan SM, Goulden ML, Munger JW, Wofsy SC (1996). Emissions of ethene, propene, and 1-butene by a midlatitude forest. *Journal of Geophysical Research, D, Atmospheres* 101, 9149–9157. doi:10.1029/96JD00334

Gómez-González Y, Surratt JD, Cuyckens F, Szmigielski R, Vermeylen R, Jaoui M, Lewandowski M, Offenberg JH, Kleindienst TE, Edney EO, Blockhuys F, Van Alsenoy C, Maenhaut W, Claeys M (2008). Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(−) electrospray ionization mass spectrometry. *Journal of Mass Spectrometry* 43, 371–382. doi:10.1002/JMS.1329

Hallquist M, Wenger JC, Baltensperger U, Rudich Y, Simpson D, Claeys M, Dommen J, Donahue NM, George C, Goldstein AH, Hamilton JF, Herrmann H, Hoffmann T, Iinuma Y, Jang M, Jenkin ME, Jimenez JL, Kiendler-Scharr A, Maenhaut W, McFiggans G, Mentel TF, Monod A, Prévôt ASH, Seinfeld JH, Surratt JD, Szmigielski R, Wildt J (2009). The formation, properties and impact of secondary organic aerosol: Current and emerging issues. *Atmospheric Chemistry and Physics* 9, 5155–5236. doi:10.5194/ACP-9-5155-2009

Hansen AMK, Kristensen K, Nguyen QT, Zare A, Cozzi F, Nøjgaard JK, Skov H, Brandt J, Christensen JH, Ström J, Tunved P, Krejci R, Glasius M (2014). Organosulfates and organic acids in Arctic aerosols: Speciation, annual variation and concentration levels. *Atmospheric Chemistry and Physics* 14, 7807–7823. doi:10.5194/ACP-14-7807-2014

Hansen J, Sato M, Ruedy R (1997). Radiative forcing and climate response. *Journal of Geophysical Research, D, Atmospheres* 102, 6831–6864. doi:10.1029/96JD03436

Hawkins LN, Russell LM (2010). Oxidation of ketone groups in transported biomass burning aerosol from the 2008 Northern California Lightning Series fires. *Atmospheric Environment* 44, 4142–4154. doi:10.1016/J.ATMOSENV.2010.07.036

Hettiyadura APS, Stone EA, Kundu S, Baker Z, Geddes E, Richards K, Humphry T (2015). Determination of atmospheric organosulfates using HILIC chromatography with MS detection. *Atmospheric Measurement Techniques* 8, 2347–2358. doi:10.5194/AMT-8-2347-2015

Hettiyadura APS, Jayarathne T, Baumann K, Goldstein AH, De Gouw JA, Koss A, Keutsch FN, Skog K, Stone EA (2017). Qualitative and quantitative analysis of atmospheric organosulfates in Centreville, Alabama. *Atmospheric Chemistry and Physics* 17, 1343–1359. doi:10.5194/ACP-17-1343-2017

Hettiyadura APS, Xu L, Jayarathne T, Skog K, Guo H, Weber RJ, Nenes A, Keutsch FN, Ng NL, Stone EA (2018). Source apportionment of organic carbon in Centreville, AL using organosulfates in organic tracer-based positive matrix factorization. *Atmospheric Environment* 186, 74–88. doi:10.1016/J.ATMOSENV.2018.05.007

Hettiyadura APS, Al-Naiema IM, Hughes DD, Fang T, Stone EA (2019). Organosulfates in Atlanta, Georgia: anthropogenic influences on biogenic secondary organic aerosol formation. *Atmospheric Chemistry and Physics* 19, 3191–3206. doi:10.5194/ACP-19-3191-2019

Iinuma Y, Boge O, Kahnt A, Herrmann H (2009). Laboratory chamber studies on the formation of organosulfates from reactive uptake of monoterpene oxides. *Physical Chemistry Chemical Physics* 11, 7985–7997. doi:10.1039/B904025K

Jacobson MC, Hansson H-C, Noone KJ, Charlson RJ (2000). Organic atmospheric aerosols: Review and state of the science. *Reviews of Geophysics* 38, 267–294. doi:10.1029/1998RG000045

Jayarathne T, Rathnayake CM, Stone EA (2016). Local source impacts on primary and secondary aerosols in the Midwestern United States. *Atmospheric Environment* 130, 74–83. doi:10.1016/J.ATMOSENV.2015.09.058

Kampa M, Castanas E (2008). Human health effects of air pollution. *Environmental Pollution* **151**, 362–367. doi:10.1016/J.ENVPOL.2007.06.012

Kristensen K, Glasius M (2011). Organosulfates and oxidation products from biogenic hydrocarbons in fine aerosols from a forest in north-west Europe during spring. *Atmospheric Environment* **45**, 4546–4556. doi:10.1016/J.ATMOSENV.2011.05.063

Kristensen K, Bilde M, Aalto PP, Petäjä T, Glasius M (2016). Denuder/filter sampling of organic acids and organosulfates at urban and boreal forest sites: Gas/particle distribution and possible sampling artefacts. *Atmospheric Environment* **130**, 36–53. doi:10.1016/J.ATMOSENV.2015.10.046

Kwong KC, Chim MM, Davies JF, Wilson KR, Chan MN (2018). Importance of sulfate radical anion formation and chemistry in heterogeneous OH oxidation of sodium methyl sulfate, the smallest organosulfate. *Atmospheric Chemistry and Physics* **18**, 2809–2820. doi:10.5194/ACP-18-2809-2018

Lewandowski M, Jaoui M, Offenberg JH, Kleindienst TE, Edney EO, Sheesley RJ, Schauer JJ (2008). Primary and secondary contributions to ambient PM in the Midwestern United States. *Environmental Science & Technology* **42**, 3303–3309. doi:10.1021/ES0720412

Lewis AC, Evans MJ, Hopkins JR, Punjabi S, Read KA, Purvis RM, Andrews SJ, Moller SJ, Carpenter LJ, Lee JD, Rickard AR, Palmer PI, Parrington M (2013). The influence of biomass burning on the global distribution of selected non-methane organic compounds. *Atmospheric Chemistry and Physics* **13**, 851–867. doi:10.5194/ACP-13-851-2013

Liao J, Froyd KD, Murphy DM, Keutsch FN, Yu G, Wennberg PO, St. Clair JM, Crounse JD, Wisthaler A, Mikoviny T, Jimenez JL, Campuzano-Jost P, Day DA, Hu W, Ryerson TB, Pollack IB, Peischl J, Anderson BE, Ziemba LD, Blake DR, Meinardi S, Diskin G (2015). Airborne measurements of organosulfates over the continental U.S. *Journal of Geophysical Research, D, Atmospheres* **120**, 2990–3005. doi:10.1002/2014JD022378

Liu S, Jia L, Xu Y, Tsona NT, Ge S, Du L (2017). Photooxidation of cyclohexene in the presence of $SO_2$: SOA yield and chemical composition. *Atmospheric Chemistry and Physics* **17**, 13329–13343. doi:10.5194/ACP-17-13329-2017

Maria SF, Russell LM, Turpin BJ, Porcja RJ, Campos TL, Weber RJ, Huebert BJ (2003). Source signatures of carbon monoxide and organic functional groups in Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) submicron aerosol types. *Journal of Geophysical Research, D, Atmospheres* **108**, 8637. doi:10.1029/2003JD003703

Meade LE, Riva M, Blomberg MZ, Brock AK, Qualters EM, Siejack RA, Ramakrishnan K, Surratt JD, Kautzman KE (2016). Seasonal variations of fine particulate organosulfates derived from biogenic and anthropogenic hydrocarbons in the mid-Atlantic United States. *Atmospheric Environment* **145**, 405–414. doi:10.1016/J.ATMOSENV.2016.09.028

Na K, Kim YP, Moon KC, Moon I, Fung K (2001). Concentrations of volatile organic compounds in an industrial area of Korea. *Atmospheric Environment* **35**, 2747–2756. doi:10.1016/S1352-2310(00)00313-7

Nguyen Q, Christensen MK, Cozzi F, Zare A, Hansen AMK, Kristensen K, Tulinius TE, Madsen H, Christensen JH, Brandt J (2014). Understanding the anthropogenic influence on formation of biogenic secondary organic aerosols in Denmark via analysis of organosulfates and related oxidation products. *Atmospheric Chemistry and Physics* **14**, 8961–8981. doi:10.5194/ACP-14-8961-2014

Nguyen TB, Bates KH, Crounse JD, Schwantes RH, Zhang X, Kjaergaard HG, Surratt JD, Lin P, Laskin A, Seinfeld JH, Wennberg PO (2015). Mechanism of the hydroxyl radical oxidation of methacryloyl peroxynitrate (MPAN) and its pathway toward secondary organic aerosol formation in the atmosphere. *Physical Chemistry Chemical Physics* **17**, 17914–17926. doi:10.1039/C5CP02001H

Novakov T, Penner JE (1993). Large contribution of organic aerosols to cloud-condensation-nuclei concentrations. *Nature* **365**, 823. doi:10.1038/365823A0

Nozière B, Ekström S, Alsberg T, Holmström S (2010). Radical-initiated formation of organosulfates and surfactants in atmospheric aerosols. *Geophysical Research Letters* **37**, L05806. doi:10.1029/2009GL041683

Olson CN, Galloway MM, Yu G, Hedman CJ, Lockett MR, Yoon T, Stone EA, Smith LM, Keutsch FN (2011). Hydroxycarboxylic acid-derived organosulfates: Synthesis, stability, and quantification in ambient aerosol. *Environmental Science & Technology* **45**, 6468–6474. doi:10.1021/ES201039P

Ramanathan V, Crutzen PJ, Kiehl JT, Rosenfeld D (2001). Aerosols, climate, and the hydrological cycle. *Science* **294**, 2119–2124. doi:10.1126/SCIENCE.1064034

Rattanavaraha W, Chu K, Budisulistiorini SH, Riva M, Lin YH, Edgerton ES, Baumann K, Shaw SL, Guo H, King L, Weber RJ, Neff ME, Stone EA, Offenberg JH, Zhang Z, Gold A, Surratt JD (2016). Assessing the impact of anthropogenic pollution on isoprene-derived secondary organic aerosol formation in $PM_{2.5}$ collected from the Birmingham, Alabama, ground site during the 2013 Southern Oxidant and Aerosol Study. *Atmospheric Chemistry and Physics* **16**, 4897–4914. doi:10.5194/ACP-16-4897-2016

Riva M, Budisulistiorini SH, Zhang Z, Gold A, Surratt JD (2016a). Chemical characterization of secondary organic aerosol constituents from isoprene ozonolysis in the presence of acidic aerosol. *Atmospheric Environment* **130**, 5–13. doi:10.1016/J.ATMOSENV.2015.06.027

Riva M, Da Silva Barbosa T, Lin YH, Stone EA, Gold A, Surratt JD (2016b). Chemical characterization of organosulfates in secondary organic aerosol derived from the photooxidation of alkanes. *Atmospheric Chemistry and Physics* **16**, 11001–11018. doi:10.5194/ACP-16-11001-2016

Schauer JJ, Mader BT, Deminter JT, Heidemann G, Bae MS, Seinfeld JH, Flagan RC, Cary RA, Smith D, Huebert BJ, Bertram T, Howell S, Kline JT, Quinn P, Bates T, Turpin B, Lim HJ, Yu JZ, Yang H, Keywood MD (2003). ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon. *Environmental Science & Technology* **37**, 993–1001. doi:10.1021/ES020622F

Schindelka J, Iinuma Y, Hoffmann D, Herrmann H (2013). Sulfate radical-initiated formation of isoprene-derived organosulfates in atmospheric aerosols. *Faraday Discussions* **165**, 237–259. doi:10.1039/C3FD00042G

Shalamzari MS, Kahnt A, Vermeylen R, Kleindienst TE, Lewandowski M, Cuyckens F, Maenhaut W, Claeys M (2014). Characterization of polar organosulfates in secondary organic aerosol from the green leaf volatile 3-Z-hexenal. *Environmental Science & Technology* **48**, 12671–12678. doi:10.1021/ES503226B

Spolnik G, Wach P, Rudzinski KJ, Skotak K, Danikiewicz W, Szmigielski R (2018). Improved UHPLC-MS/MS methods for analysis of isoprene-derived organosulfates. *Analytical Chemistry* **90**, 3416–3423. doi:10.1021/ACS.ANALCHEM.7B05060

Stone EA, Hedman CJ, Sheesley RJ, Shafer MM, Schauer JJ (2009). Investigating the chemical nature of humic-like substances (HULIS) in North American atmospheric aerosols by liquid chromatography tandem mass spectrometry. *Atmospheric Environment* **43**, 4205–4213. doi:10.1016/J.ATMOSENV.2009.05.030

Stone EA, Yang L, Yu LE, Rupakheti M (2012). Characterization of organosulfates in atmospheric aerosols at four Asian locations. *Atmospheric Environment* **47**, 323–329. doi:10.1016/J.ATMOSENV.2011.10.058

Surratt JD, Lewandowski M, Offenberg JH, Jaoui M, Kleindienst TE, Edney EO, Seinfeld JH (2007). Effect of acidity on secondary organic aerosol formation from isoprene. *Environmental Science & Technology* **41**, 5363–5369. doi:10.1021/ES0704176

Surratt JD, Gómez-González Y, Chan AWH, Vermeylen R, Shahgholi M, Kleindienst TE, Edney EO, Offenberg JH, Lewandowski M, Jaoui M, Maenhaut W, Claeys M, Flagan RC, Seinfeld JH (2008). Organosulfate formation in biogenic secondary organic aerosol. *Journal of Physical Chemistry* **112**, 8345–8378. doi:10.1021/JP802310P

Surratt JD, Chan AWH, Eddingsaas NC, Chan M, Loza CL, Kwan AJ, Hersey SP, Flagan RC, Wennberg PO, Seinfeld JH (2010). Reactive intermediates revealed in secondary organic aerosol formation from isoprene. *Proceedings of the National Academy of Sciences of the United States of America* **107**, 6640–6645. doi:10.1073/PNAS.0911114107

Tolocka MP, Turpin B (2012). Contribution of organosulfur compounds to organic aerosol mass. *Environmental Science & Technology* **46**, 7978–7983. doi:10.1021/ES300651V

Tsigaridis K, Daskalakis N, Kanakidou M, Adams P, Artaxo P, Bahadur R, Balkanski Y, Bauer S, Bellouin N, Benedetti A (2014). The AeroCom evaluation and intercomparison of organic aerosol in global models. *Atmospheric Chemistry and Physics* **14**, 10845–10895. doi:10.5194/ACP-14-10845-2014

Turpin BJ, Lim H-J (2001). Species contributions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* **35**, 602–610. doi:10.1080/02786820119445

Turpin BJ, Saxena P, Andrews E (2000). Measuring and simulating particulate organics in the atmosphere: Problems and prospects. *Atmospheric Environment* **34**, 2983–3013. doi:10.1016/S1352-2310(99)00501-4

Valavanidis A, Fiotakis K, Vlachogianni T (2008). Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. *Journal of Environmental Science and Health Part C* **26**, 339–362. doi:10.1080/10590500802494538

Wang J, Jin L, Gao J, Shi J, Zhao Y, Liu S, Jin T, Bai Z, Wu CY (2013). Investigation of speciated VOC in gasoline vehicular exhaust under ECE and EUDC test cycles. *The Science of the Total Environment* **445–446**, 110–116. doi:10.1016/J.SCITOTENV.2012.12.044

Wang Y, Hu M, Guo S, Wang Y, Zheng J, Yang Y, Zhu W, Tang R, Li X, Liu Y (2018). The secondary formation of organosulfates under interactions between biogenic emissions and anthropogenic pollutants in summer in Beijing. *Atmospheric Chemistry and Physics* **18**, 10693–10713. doi:10.5194/ACP-18-10693-2018

Yassine MM, Dabek-Zlotorzynska E, Harir M, Schmitt-Kopplin P (2012). Identification of weak and strong organic acids in atmospheric aerosols by capillary electrophoresis/mass spectrometry and ultra-high-resolution Fourier transform ion cyclotron resonance mass spectrometry. *Analytical Chemistry* **84**, 6586–6594. doi:10.1021/AC300798G

Ye J, Abbatt JPD, Chan AWH (2018). Novel pathway of $SO_2$ oxidation in the atmosphere: Reactions with monoterpene ozonolysis intermediates and secondary organic aerosol. *Atmospheric Chemistry and Physics* **18**, 5549–5565. doi:10.5194/ACP-18-5549-2018

Zhang H, Worton DR, Lewandowski M, Ortega J, Rubitschun CL, Park J-H, Kristensen K, Campuzano-Jost P, Day DA, Jimenez JL, Jaoui M, Offenberg JH, Kleindienst TE, Gilman J, Kuster WC, De Gouw J, Park C, Schade GW, Frossard AA, Russell L, Kaser L, Jud W, Hansel A, Cappellin L, Karl T, Glasius M, Guenther A, Goldstein AH, Seinfeld JH, Gold A, Kamens RM, Surratt JD (2012). Organosulfates as tracers for secondary organic aerosol (SOA) formation from 2-methyl-3-buten-2-ol (MBO) in the atmosphere. *Environmental Science & Technology* **46**, 9437–9446. doi:10.1021/ES301648Z

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