Chemical Characterization of Secondary Organic Aerosol Constituents from Isoprene Ozonolysis in the Presence of Acidic Aerosol

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HIGHLIGHTS

- Acidified sulfate aerosol enhances production of SOA from isoprene ozonolysis.
- Isoprene ozonolysis in the presence of acidic aerosol yields 2-methyltetrols.
- Unique organosulfates (OSs) are characterized from isoprene ozonolysis.
- 2-Methyltetrols and OSs may originate from heterogeneous reaction of peroxides.
- Isoprene ozonolysis yields on average 14% of isoprene-derived OSs in field samples.

KEYWORDS

SOA, ozonolysis, isoprene, organosulfates, 2-methyltetrols

ABSTRACT

Isoprene is the most abundant non-methane hydrocarbon emitted into Earth's atmosphere and is predominantly derived from terrestrial vegetation. Prior studies have focused largely on the hydroxyl (OH) radical-initiated oxidation of isoprene and have demonstrated that highly oxidized compounds, such as isoprene-derived epoxides, enhance the formation of secondary organic aerosol (SOA) through heterogeneous (multiphase) reactions on acidified sulfate aerosol. However, studies on the impact of acidified sulfate aerosol on SOA formation from isoprene ozonolysis are lacking and the current work systematically examines this reaction. SOA was generated in an indoor smog chamber from isoprene ozonolysis under dark conditions in the presence of non-acidified or acidified sulfate seed aerosol. The effect of OH radicals on SOA chemical composition was investigated using diethyl ether as an OH radical scavenger. Aerosols were collected and chemically characterized by ultra performance liquid chromatography/electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS) and gas chromatography/electron impact ionization-mass spectrometry (GC/EI-MS). Analysis revealed the formation of highly oxidized compounds, including organosulfates (OSs) and 2-methylterols, which were significantly enhanced in the presence of acidified sulfate seed aerosol. OSs identified in the chamber experiments were also observed and quantified in summertime fine aerosol collected from two rural locations in the southeastern United States during the 2013 Southern Oxidant and Aerosol Study (SOAS).

1. INTRODUCTION

The largest mass fraction of fine particulate matter ($PM_{2.5}$, aerosol with aerodynamic diameters $\leq$ 2.5 μm) is generally organic, dominated by secondary organic aerosol (SOA) formed from the gas-phase oxidation of volatile organic compounds (VOCs). Although SOA contributes a large portion (20–90%) of the total $PM_{2.5}$ mass, for the most part current models under-predict SOA mass (Kroll and Seinfeld, 2008; Hallquist et al., 2009). Biogenic VOCs (BVOCs), such as isoprene and monoterpenes, are typically the most abundant SOA precursors, especially in regions of dense terrestrial vegetation (Guenther et al., 2006).

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is the most abundant non-methane hydrocarbon emitted into the troposphere with emissions exceeding 500 Tg yr^{-1} (Guenther et al., 2006). The principal atmospheric degradation pathway of isoprene is oxidation by hydroxyl (OH) radical (Atkinson, 1997; Edney et al., 2005; Kroll et al., 2006), which along with oxidation by nitrate (NO_3) radical and ozone (O_3), accounts for up to 50% of the SOA budget (Henze and Seinfeld, 2006). Before 2004, SOA formation from atmospheric oxidation of isoprene was considered insignificant (Kamens et al., 1982; Pandis et al., 1991) because of the low molecular weight and high volatility of its known oxidation products and as a consequence, isoprene was not included in SOA models. However, the identification by Claeys and coworkers of 2-methyltetrols (Claeys et al., 2004a) and C_5-alkene triols (Wang et al., 2005) in ambient $PM_{2.5}$ collected in the Amazon caused a re-examination of the potential for isoprene oxidation to yield SOA. Since the 2-methyltetrols and C_5-alkene triols contain the isoprene skeleton, isoprene was proposed as their source, although the mechanisms and environmental conditions leading to these products as well as the formation of isoprene SOA were not evident. Research over the last decade has established that relative humidity (RH) (Nguyen et al., 2011), levels of nitrogen oxides (NO_x) (Kroll et al., 2006; Chan et al., 2010) and aerosol acidity (Surratt et al., 2007a, b) have pronounced effects on isoprene SOA formation. Recent

studies show that increased aerosol acidity is a key variable in enhancing SOA formation through the acid-catalyzed reactive uptake and multiphase chemistry of the OH radical-initiated oxidation products of isoprene, particularly the isomeric isoprene epoxydiols (IEPOX) (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012; Gaston et al., 2014). Acid-catalyzed particle-phase reactions of IEPOX have been shown to yield the 2-methyltetrols and C_5-alkene triols as well as IEPOX-derived dimers observed in the Amazonian $PM_{2.5}$ (Surratt et al., 2010; Lin et al., 2012). Epoxides generated by OH radical oxidation of isoprene have also been shown to explain the formation known organosulfates (OSs) and oligomers measured in ambient $PM_{2.5}$ samples (Surratt et al., 2007a, 2008; Lin et al., 2014). Although research over the last decade has focused principally on OH radical-initiated oxidation of isoprene, some work has also demonstrated significant SOA formation from the NO_3 radical-initiated oxidation of isoprene (Ng et al., 2008).

The contribution of isoprene ozonolysis to the SOA budget had been concluded to be negligible (Hasson et al., 2001; Kleindienst et al. 2007; Sato et al., 2013) on the basis of a large number of studies reporting only volatile and semivolatile products, such as methyl vinyl ketone (MVK), methacrolein (MACR) or low molecular weight acids. However, the potential importance of isoprene ozonolysis as a pathway for SOA formation is supported by recent studies documenting the formation of highly oxidized products, including oligomers, in both gas and particulate phases (Nguyen et al., 2010; Inomata et al., 2014). Initial formation of isoprene primary ozonides leads to stabilized Criegee intermediates (sCIs), which can react to form OH radicals, undergo further oxidation or condense to form higher molecular weight products. The total yield of sCIs, including CH_2OO radical and higher molecular weight fragments, was determined to be 0.26 (Hasson et al., 2001), and the yield of OH radicals to be 0.25 - 0.27 (Atkinson et al., 1992). Formation of highly oxidized compounds, such as oligomeric hydroperoxides identified in recent studies (Nguyen et al., 2010; Inomata et al.,

2014), was proposed by the reaction of sCIs with organic ozonolysis products (e.g. carboxylic acids) of isoprene. Multiphase reactions of the oxidized products could thus make significant contributions to the yield of SOA from isoprene ozonolysis. With the exception of reports by Jang et al. (2002) and Czoschke et al. (2003), effects of varying composition and acidity of sulfate aerosols and the presence of OH scavengers on SOA generated from isoprene ozonolysis have not been systematically investigated, nor have efforts have been reported to identify products unique to isoprene ozonolysis in ambient $PM_{2.5}$ samples collected from isoprene-rich areas.

In this study we investigate isoprene ozonolysis in the presence of sulfate seed aerosol of varying acidity and composition with a focus on the formation of OSs and highly oxidized compounds. Because of the high yield of OH radicals from isoprene ozonolysis, experiments were performed both in the presence and absence of an OH radical scavenger in order to identify SOA constituents derived directly from ozonolysis. Filters collected from indoor smog chamber experiments were analyzed by ultra performance liquid chromatography/ electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS) and gas chromatography/electron impact mass spectrometry (GC/EI-MS). $PM_{2.5}$ samples collected from ground sites at Look Rock, TN, and Centerville, AL, during the 2013 Southern Oxidant and Aerosol Study (SOAS) were also analyzed to identify OSs present in both field and chamber studies and quantify their contribution to ambient $PM_{2.5}$. Comparison of lab and field data supports the potential importance of isoprene ozonolysis in the isoprene-derived SOA budget.

2. EXPERIMENTAL SECTION

2.1 Smog Chamber Experiments. Ten experiments were performed in the indoor environmental smog chamber at the University of North Carolina. The experimental setup and

119 analysis techniques used in this work were described in detail previously (Lin et al., 2012;
120 Zhang et al., 2012). Briefly, experiments were carried out under dark and dry conditions (3.3
121 ± 0.25%, RH) at 296 ± 1 K in a 10-m^3 Teflon chamber. Experimental conditions are
122 summarized in Table 1. Prior to each experiment, the chamber was flushed continuously with
123 clean air for ~ 24 hours until the particle mass concentration was < 0.01 μg m^{-3} to ensure that
124 there were no pre-existing aerosol particles prior to injection of isoprene. Aerosol size
125 distributions were continuously measured using a differential mobility analyzer (DMA, BMI
126 model 2002) coupled to a mixing condensation particle counter (MCPC, BMI model 1710) in
127 order to monitor aerosol number, surface area, and volume concentration within the chamber.
128 Chamber flushing also reduced O_3 and VOC concentrations below the detection limit (< 1
129 ppb for ozone and isoprene). Temperature and RH in the chamber were continuously
130 monitored using a dew point meter (Omega Engineering Inc.).
131 A known quantity of isoprene (Sigma-Aldrich, 99%) was introduced into the chamber
132 by passing a heated nitrogen (N_2) stream through a heated glass manifold. In some
133 experiments, diethyl ether was injected by the same procedure to serve as an OH scavenger.
134 Concentrations of isoprene and diethyl ether were measured every 10 minutes using an online
135 gas chromatography/flame ionization detector (GC-FID, Model CP-3800, Varian), which was
136 calibrated using multiple injections of isoprene and diethyl ether. Approximately 100 ppb of
137 isoprene was injected for each experiment, while 3.5 ppm of diethyl ether was introduced in
138 the experiments performed in the presence of OH scavenger. Approximately 1 hour after
139 isoprene injection, 120–150 ppb of O_3 was introduced into the chamber using an O_3 generator
140 (Model L21, Pacific ozone). O_3 concentration was monitored over the course of experiments
141 using an UV photometric analyzer (Model 49P, Thermo-Environmental).
142 Non-acidified or acidified ammonium or magnesium sulfate seed aerosols were
143 introduced two hours after O_3 injection. Non-acidified seed aerosol was generated from 0.06

144 M magnesium sulfate ($MgSO_4$) or ammonium sulfate ($(NH_4)_2SO_4$) (aq) solutions and
145 acidified seed aerosol from 0.06 M $MgSO_4$ (aq) or $(NH_4)_2SO_4$ (aq) + 0.06 M H_2SO_4 (aq)
146 solutions. Once aerosol volume concentrations stabilized (~1 hour after reaction), aerosols
147 were collected onto 47-mm diameter Teflon filters (1.0-μm pore size, Tisch Environmental,
148 EPA $PM_{2.5}$ membrane) for two hours at a sampling flow rate of 25 L min^{-1} to characterize
149 particle-phase reaction products.

150 **2.2 Ambient $PM_{2.5}$ Collection.** $PM_{2.5}$ samples were collected during the 2013 SOAS
151 campaign from 1 June to 15 July 2013 at Centerville, AL (CTR), and from 1 June to 17 July
152 2013 at Look Rock, TN (LRK). Both sites are strongly influenced by isoprene emissions
153 (Guenther et al., 2006), and isoprene oxidation appears to be one of the main SOA
154 contributors (Budisulistiorini et al., 2015; Xu et al., 2015). At each site, $PM_{2.5}$ samples were
155 collected onto pre-baked 8 × 10 in Tissuquartz™ Filters (Pall Life Sciences) with high-
156 volume $PM_{2.5}$ air samplers (Tisch Environmental) operated at 1 m^3 min^{-1} using two sampling
157 protocols described in detail elsewhere (Budisulistiorini et al. 2015). A total of 118 filters
158 from CTR and 123 filters from LRK were analyzed to evaluate the contributions of OSs
159 identified from isoprene ozonolysis on the isoprene-derived SOA budget.

160 **2.3 Aerosol-Phase Chemical Characterization.** Chemical characterization of SOA
161 from isoprene ozonolysis was performed by UPLC/ESI-HR-Q-TOFMS (6520 Series, Agilent)
162 operated in the negative ion mode and by GC/EI-MS (Hewlett-Packard, 5890 Series II).
163 Operating conditions have been described in detail in elsewhere (Lin et al., 2012). Filters
164 collected from smog chamber experiments were extracted with 22 mL of high-purity
165 methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich) by sonication for 45 min. The
166 methanol extracts were blown dry under a gentle N_2 (g) stream at ambient temperature. Dried
167 extracts were reconstituted in 2 mL methanol, divided into two equal portions and then blown
168 dry.

For UPLC/ESI-HR-QTOFMS analysis, one of the dried extracts was reconstituted with 150 μL of a 50:50 (v/v) solvent mixture of methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich) and high-purity water (Milli-Q, 18.2 MΩ). 5 μL aliquots were injected onto the UPLC column (Waters ACQUITY UPLC HSS T3 column, 2.1 × 100 mm, 1.8 μm particle size) and eluted at a flow rate of 0.3 mL min^{-1} with a solvent mixture of methanol containing 0.1% acetic acid (LC-MS CHROMASOLV-grade, Sigma-Aldrich) and water containing 0.1 % acetic acid (LC-MS CHROMASOLV-grade, Sigma-Aldrich). OSs were characterized by high-resolution mass spectra to determine the composition of SOA constituents and structural information was obtained through acquisition of high-resolution tandem mass spectra (MS^2) at a collision energy of 15 V. A mixture of 2-methyltetrol sulfate esters ($C_5H_{11}O_7S^-$) (Budisulistiorini et al., 2015) and 2-oxopropyl sulfate (hydroxyacetone sulfate ester; $C_3H_5O_5S^-$; SI Figures S1, S2) were synthesized in-house as authentic standards. Propyl sulfate ($C_3H_7O_4S^-$; electronic grade, City Chemical LLC) and 3-pinanol-2-hydrogen sulfate ($C_9H_{13}O_6S^-$; synthesized standard from Marianne Glasius's group) served as surrogate standards to quantify the remaining OSs.

The second portion of dried filter extract was trimethylsilylated by addition of 100 μL BSTFA + trimethylchlorosilane (99:1 (v/v), Supleco) and 50 μL pyridine (Sigma-Aldrich, 98%, anhydrous). The mixture was heated for 1 h at 70 °C and analyzed within 24 hours following trimethylsilylation. Analyses were performed by GC/EI-MS at 70 eV (Hewlett 5890 Packard Series II Gas Chromatograph interfaced to a HP 5971A Series Mass Selective Detector, Econo-CapTM-ECTM-5 column, 30 m × 0.25 mm × 0.25 μm). 2-Methyltetrols were quantified using the authentic standard (Budisulistiorini et al., 2015).

Filters collected from field studies were extracted using the protocol described above; however, prior to drying, extracts were filtered through 0.2-μm PTFE syringe filters (Pall Life Science, Acrodisc) to remove insoluble particles or quartz filter fibers.

3. RESULTS AND DISCUSSION

3.1 OS formation. In addition to four sulfate esters previously reported from photooxidation of isoprene under low- or high-NO_x conditions (Surratt et al., 2008) (Table 1), 12 products unique to ozonolysis were identified and quantified (Table 2).

Negative ion UPLC/ESI-HR-QTOFMS analysis of filter extracts provides excellent sensitivity for the detection of OSs, which yield intense $[M–H]^-$ ions (Surratt et al., 2008; Hansen et al., 2014) and show characteristic product ions at *m/z* 80 ($SO_3^{\bullet/-}$), 81 (HSO_3^-) or 97 (HSO_4^-) in MS^2 spectra. Accurate mass measurements of parent and major product ions, number of isomers/isobars for each parent mass, MS^2 spectra and proposed structures are given in Figure 1 and Supporting Information (SI; Figures S3 and S4 and Table S1). 2-Methyltetrol sulfate esters (isomers not specified) and 2-oxopropyl sulfate were identified by comparison with the authentic standards; other structures have been tentatively assigned based on accurate mass measurements of parent and product ions and comparison of MS^2 fragmentation patterns with those of structurally similar OSs available in the literature such as the OSs at *m/z* 169, 213, and 215 (Surratt et al., 2007a; Gomez-Gonzalez et al., 2008), the OS at *m/z* 199 (Zhang et al., 2012), and the OS at *m/z* 183 (Safi Shalamzari et al., 2013). Figures 1a–f illustrate the assignment of structures for the major OSs identified in both laboratory-generated and ambient SOA.

Two isobaric parent ions with the composition $C_4H_7O_6S^-$ (*m/z* 183) in Figure 1a and b lose bisulfate (*m/z* 97) as the base peak fragment ion and can thus be identified as OSs with a labile proton β to the sulfate group; proposed fragmentation schemes for these two isomers can be found in Figures S3a and S3b. An OS with this composition has been reported in ambient $PM_{2.5}$ (Safi Shalamzari et al., 2013), and was assigned as the O^3-sulfate ester of 3,4-dihydroxybutan-2-one based by comparison of its MS^2 spectrum with the MS^2 spectrum of a synthetic mixture of the O^3- + O^4-sulfate esters of 3,4-dihydroxybutan-2-one. While these

data were acquired on an Orbitrap mass spectrometer and a QTOFMS was employed in this study, the key product ions at *m/z* 165 [M − H_2O], 153 [M − CH_2O] and 97 [HSO_4^-] are common to both analyses and in accord with monosulfated 3,4-diol isomers of of 3,4-dihydroxybutan-2-one. In Figure 1b, an additional product ion appears in the MS^2 spectrum of the late-eluting peak at *m/z* 85 [M − H_2SO_4]. Loss of H_2SO_4 as a neutral fragment to give 3-oxobut-1-en-1-olate, a homolog of the known, stable enolate of malondialdehyde, would be favored by the O^3-sulfate ester (Figure S3b). In addition, the loss of formaldehyde to give the product ion at *m/z* 153 is also favored. The favorability of both fragmentation pathways by the O^3-ester might be expected to result in reduced parent ion intensity relative to the O^4-ester at a given collisional energy, as is observed in the MS^2 spectrum (Figure 1b). On this basis O^3- and O^4-sulfate ester structural assignments have been made for the late- and early-eluting products, respectively.

Regarding a possible source of the *m/z* 183 isomers, the epoxide of MVK (1-oxiran-2-yl-ethan-1-one) has been proposed as the precursor (Safi Shalamzari et al. 2013). The oxirane is unlikely to be a product of gas-phase ozonolysis of MVK (Neeb et al., 1998). However, uptake onto sulfate aerosols of gas-phase organic peroxides from the reaction of sCIs with carboxylic acids (Nguyen et al., 2010; Inomata et al., 2014) is a potential source of aerosol phase oxidants either by oxidation of sulfate to $SO_4^{-/\bullet}$ or via generation of H_2O_2 (Chen et al., 2008). An *m/z* 183 product has been identified from sulfate radical oxidation of MVK in bulk aqueous solution (Schindelka et al., 2013), suggesting aerosol-phase oxidation by $SO_4^{-/\bullet}$ is possible. Hence, aerosol-phase oxidation by $SO_4^{-/\bullet}$ or acid-catalyzed ring opening of peroxide-generated oxiranes (Iinuma et al., 2009; Surratt et al., 2010) are plausible routes to *m/z* 183 and other OSs. Sulfate addition to alkenes or aldehyde groups under strong acid conditions (Liggio et al., 2006; Surratt et al., 2007a) could also be considered as an alternative pathway to some products.

Two ions were identified at *m/z* 197 ($C_5H_9O_6S^-$). OSs with this nominal mass have been tentatively identified as sulfate esters of C_5-alkene triols from uptake of isoprene oxidation products onto acidified sulfate aerosol (Surratt et al., 2007a). However, molecular compositions were not verified by accurate mass measurements and MS^2 spectra were not reported. MS^2 spectra of products at *m/z* 197 observed in our ozonolysis experiment (Figures 1c, d; Figures S3c, d) are consistent with a tentative assignment as isomeric sulfate esters of the alkene triol 1,4-dihydroxy-3-methylbutan-2-one. The early eluting sulfate is assigned the structure 4-hydroxy-2-methyl-3-oxobutyl sulfate based on the loss of the neutral fragment $C_2H_4O_2$ (2-hydroxyacetaldehyde) to give a product ion at *m/z* 137 ($C_3H_5O_4S^-$) (Figure S3c), and the late-eluting isomer is assigned as the 2-oxo sulfate based on the loss of 60 mass units (C_3H_8O) to give a product ion at *m/z* 139 ($C_2H_3O_5S^-$) (Figure S3d). Prominent ions are present for bisulfate (*m/z* 97), $SO_3^{-/\bullet}$ (*m/z* 80) and loss of formaldehyde (*m/z* 167) in MS^2 spectra of both early- and late-eluting isomers, consistent with the proposed OS structures.

An ion at *m/z* 199 with composition $C_5H_{11}O_7S^-$ (Figure 1e) has been observed as a component of SOA generated by the reactive uptake of oxidation products of 2-methyl-3-buten-2-ol (MBO) on both acidified and neutral ammonium sulfate aerosols (Zhang et al., 2012) and tentatively identified as 2,3-dihydroxy-3-methylbutyl sulfate. Bisulfate is the only significant product ion in the MS^2, which is identical to the MS^2 spectrum obtained from the ozonolysis experiment in this study (Figure 1e). Since terminal hydroxymethylene groups in possible isobaric structures would be expected to result in MS^2 pathways yielding more complex fragmentation patterns, the structural assignment 2,3-dihydroxy-3-methylbutyl sulfate is tentatively made for this ozonolysis product. The parent ion at *m/z* 215 ($C_5H_{11}O_7S^-$) has been identified as a 2-methyltetrol sulfate isomer (or isomer mixture) by comparison of the retention time and MS^2 spectrum with the authentic standard mixture. Its MS^2 spectrum is characterized by loss of bisulfate as the only significant fragmentation (Figures 1f, S3f).

All the parent ions of products in Tables 1 and 2 show an intense product ion at *m/z* 97, characteristic of sulfate esters with a labile proton in proximity to the sulfate group. Two ions are present at *m/z* 153 with composition $C_3H_5O_5S^-$. MS^2 spectra of earlier- and later-eluting products are presented in Figures S4a and S4b, respectively. Products with this composition, tentatively identified as the sulfate ester of hydroxyacetone (2-oxopropyl sulfate), a known oxidation product of isoprene, have been observed in SOA from uptake of isoprene oxidation products onto acidic sulfate seed aerosol (Surratt et al., 2007a) and from bisulfate radical oxidation of isoprene in bulk solution (Schindelka et al., 2013). The later-eluting product was identified as 2-oxopropyl sulfate by matching retention time and MS^2 with an authentic sample. The MS^2 of the earlier-eluting product was identical (Figures S4a1, 4a2), yielding product ions for loss of bisulfate, bisulfite and SO_3 and therefore not informative regarding structural identification. The tautomer of 2-oxopropyl sulfate, 1-oxopropan-2-yl sulfate, is a possible isobaric structure.

Only one of two ions at *m/z* 169 ($C_3H_5O_6S^-$) was present in sufficient abundance for acquisition of an MS^2 spectrum. The MS^2 is not consistent with the MS^2 reported for an authentic sample of the known lactic acid sulfate (Olson et al., 2011; Safi Shalamzari et al., 2013). Although the published spectrum was acquired on an instrument equipped with an ion trap source and complete correspondence to QTOFMS in this study might not be assumed, the product ions in the MS^2 spectra in this study (Figure S4b) are incompatible with the lactic acid derivative. A potential candidate for *m/z* 169 isomers observed here are the sulfate esters of glyceraldehyde (2,3-dihydroxypropanal), which is a known product from isoprene oxidation (Fang et al. 2012) and has been previously identified in $PM_{2.5}$ samples collected from isoprene rich-regions (Surratt et al. 2008). The fragmentation pattern in Figure S4b is consistent with a mixture of isomeric glyceraldehyde sulfate esters. The product ion at *m/z* 137 ($C_2HO_5S^-$), can be rationalized as the sulfate ester of hydroxy ketene. In the absence of

294 MS^2 data for both parent ions, however, an alternative explanation for one of the parent ions
295 would be the sulfate ester of dihydroxyacetone (Paulot et al., 2009), which could also give the
296 observed MS^2 (Figure S4b).

297 Parent ions at *m/z* 179 ($C_5H_7O_5S^-$) and 181 ($C_5H_9O_5S^-$) from isoprene oxidation have not
298 been previously reported. The composition of the parent ion at *m/z* 179 indicates retention of
299 the isoprene carbon skeleton. The MS^2 spectrum (Figure S4c) is characterized by product ions
300 HSO_4^-, HSO_3^- and $C_4H_7O_4S^-$ [(M – CO)]. The bisulfite product ion is characteristic of a
301 labile proton α to the sulfate substituent, while bisulfate product ion indicates a labile proton
302 accessible 2 or more carbons removed and the loss of CO indicates a terminal carbonyl group.
303 The isomeric structures 4-oxo-3-(or 2-)methyl-but-2-ene sulfate, sulfate esters of the reported
304 isoprene oxidation products 4-hydroxy-2-(or 3-)-methylbut-2-enal (Baker et al., 2005), are
305 compatible with the MS^2 data and hence are proposed as possible structures of the ion at *m/z*
306 179. The bisulfate product ion and the loss of formaldehyde in MS^2 spectrum of the parent ion
307 at *m/z* 181 (Figure S4d) suggest that a labile proton 2 or more carbons removed from the
308 sulfate substituent and a terminal hydroxymethyl group are structural features. Sulfate esters
309 of the known 1,4-, 1,2-, and 3,4-dihydroxy oxidation products of isoprene might yield the
310 observed MS^2 trace. However, bisulfite is not present in the MS^2 spectrum, thus the O^2-sulfate
311 ester of 1,2-dihydroxy-2-methylbutene best explains the data (Figure S4d) and is suggested as
312 the structure of the parent ion.

313 Parent ions at *m/z* 213 having the composition $C_5H_9O_7S^-$ have been detected in ambient
314 SOA collected at K-puszta, Hungary (Gómez-González et al., 2008) and in chamber studies
315 of isoprene photooxidation (Surratt et al., 2008). Based on analysis of MS^2 and MS^3 data, the
316 compounds observed at K-puszta were assigned as sulfate esters of 4,5-dihydroxypentanoic
317 acid from fatty acid oxidation and 2,3-dihydroxypentanoic acid, a photoproduct of plant leaf
318 volatiles (Gómez-González et al., 2008). The isoprene-derived OSs at *m/z* 213 were not

assigned structures and no full-scan or MS^2 mass spectra were given (Surratt et al., 2008). The MS^2 spectrum acquired in this study (Figure S4e) is characterized by product ions at *m/z* 183 (M – CH_2O), 139 (M – $C_3H_6O_2$), and 97 (bisulfate), which are not compatible with either of the pentanoic acid derivatives reported by Gómez-González et al. (2008). A product retaining the isoprene carbon skeleton, 3,4-dihydroxy-3-methyl-2-oxobutylsulfate, could be anticipated to lose formaldehyde and hydroxyacetone as neutral fragments (Figure S4e) and this structure is tentatively assigned to the isoprene-derived OS.

Seven parent ions with 6 or more carbons not previously reported from isoprene ozonolysis were observed (Table 2). The products were mainly observed in experiments using acidified $MgSO_4$ seed aerosol (Table 2) and the low intensity of the parent ions precluded acquisition of MS^2 data. Formation of oligomers and their OS derivatives in the presence of $MgSO_4$ seed aerosol has been previously reported and potential involvements of Mg^{2+} have been discussed (Lin et al., 2014); specifically, $MgSO_4$ aerosols do not effloresce at low-RH conditions and instead form gel-like chain structures of contact ion pairs (Chan et al., 2000). We tentatively propose that this phase state (gel-like chain structures) of $MgSO_4$ allows transient moieties to be held in close proximity to each other by coordination to Mg^{2+} ions in the gel-like aerosol structure. Future work is needed to more fully resolve the effect of $MgSO_4$ seed aerosol. Consistent with previous work (Surratt et al., 2007b), acidity enhanced the formation of all OSs (Figure 2).

The products in Table 1 at *m/z* 153 ($C_3H_5O_5S^-$), 169 ($C_3H_5O_6S^-$), 213 ($C_5H_9O_7S^-$) and 215 ($C_5H_{11}O_7S^-$), which have been observed during OH radical-initiated oxidation of isoprene (Surratt et al., 2007a) are also observed in the ozonolysis experiments in the presence of OH radical scavenger, although the radical scavenger reduces formation of all OSs. The high concentration of diethyl ether used in this study precludes residual OH radical as an explanation for these products at observed concentrations. Lack of authentic standards

prevents definitive conclusion as to whether the products at *m/z* 153, 169 and 213 from photochemical oxidation and ozonolysis of isoprene are identical or are isobars. However, the sulfate ester at *m/z* 215, which was generated in high yield in this study, has been confirmed as a sulfate ester of an isoprene-derived 2-methyltetrol diastereomer (2-methylerythritol or 2-methylthreitol) by comparison with an authentic standard mixture, indicating that both hydroxyl radical and ozonolysis may contribute to 2-methyltetrol sulfate derivatives in ambient fine aerosol.

3.2 Formation of 2-Methyltetrols. 2-Methylterols have been identified in SOA from reactive uptake of isoprene epoxydiol (IEPOX) isomers on sulfate seed aerosols (Surratt et al., 2010; Lin et al., 2012). One study has also reported the formation of the 2-methyltetrols from isoprene ozonolysis in the presence of non-acidified sulfate aerosol (Kleindienst et al., 2007). In the current ozonolysis study, large quantities of 2-methyltetrols were identified in SOA. Consistent with previous studies (Surratt et al., 2007b), the yield of 2-methyltetrols is highly dependent on the acidity and composition of the sulfate seed aerosol (Figure 3), with acidified $MgSO_4$ giving the highest yield. Kleindienst et al. (2007) attributed the formation of tetrols during ozonolysis to reaction of isoprene with OH radicals generated during the reaction, estimating that 16% of the OH radicals formed reacted with isoprene. Initial concentration of diethyl ether (35-fold higher than isoprene) prevents any reaction of OH radicals with isoprene. Indeed, OH radical oxidation of diethyl ether is 46-fold higher than that with isoprene in experimental conditions used in this work (Mellouki et al., 1995; Atkinson et al., 2006). The absence of C_5-alkene triols, 2-methylglyceric acid and 3-methyltetrahydrofuran-3,4-diols, established SOA markers of isoprene photooxidation (Surratt et al., 2010; Lin et al., 2012), also argues against the formation of 2-methyltetrols by OH radical oxidation. These observations along with the high ratio of 2-methyltetrols to IEPOX-derived OSs (Table 1 and Figure 3), leads to the conclusion that isoprene ozonolysis in the presence of acidified

sulfate seed aerosol is a hitherto unrecognized source of 2-methyltetrols. Acid-catalyzed heterogeneous reactions with organic peroxides (Inomata et al., 2014) or H_2O_2 (Chen et al., 2008), likely to be present in acidic SOA as discussed above, is a possible route for formation of the 2-methyltetrols. Aerosol-phase acid-catalyzed oxidation of isoprene to the 2-methyltetrols has been proposed and demonstrated in the aqueous phase (Claeys et al., 2004b).

3.3 Field measurements. 13 of the 16 OSs identified in the chamber ozonolysis experiments (Tables 1 and 2) were detected in the ambient $PM_{2.5}$ samples from CTR and LRK sites during the 2013 SOAS campaign. As discussed above in the chemical characterization of parent ions, a number of organosulfates that have not been reported as photochemical oxidation products of isoprene are esters of known photochemical products. The significance of this observation with regard to whether these organosulfates are exclusively generated by ozonolysis via as yet unknown pathways or result from esterification of hydroxy substituents in the aerosol phase remains to be determined. Time profiles of OSs for CTR are shown in Figure 4 and for LRK, in Figure S5. The time profiles exclude the product at *m/z* 249, to which terpene photolysis may contribute substantially, and the OSs reported Table 1 such as 2-methyltetrol sulfates (*m/z* 215), to which photochemically generated IEPOX may contribute substantially, but include the OSs in Table 2, which have not been reported in photochemical experiments. The average concentrations of the ambient OSs, excluding OSs as stipulated above, were 18.3 ± 12.3 ng m^{-3} at CTR and 21.3 ± 20.7 ng m^{-3} at LRK. Time profiles of the sum of all isoprene-derived OSs identified at LRK and CTR are presented in Figures 5 and S6, respectively. The sum of concentrations of OSs we attribute to isoprene ozonolysis during the 2013 SOAS is highly correlated with the sum of all isoprene-derived OSs (r^2 = 0.75 for CTR and r^2 = 0.92 for LRK). On average, OSs derived from isoprene ozonolysis represent 14% of the sum of all isoprene-derived OSs quantified at both CTR and LRK. This is likely

394 an underestimate due to complete exclusion of *m/z* 249 and OSs reported Table 1, which
395 could be formed by other chemical processes, such as photooxidation of isoprene.

396 Correlation of on-line gas-phase O_3 concentration with OSs is weak and suggests that
397 formation of OSs occurred upwind of the sampling site, as demonstrated for other SOA
398 tracers (Budisulistiorini et al., 2015). Since this study supports isoprene ozonolysis as an
399 important source of 2-methylterols, correlation of 2-methyltetrols and OSs from isoprene
400 ozonolysis was calculated and is presented in Figure 5 for both sampling sites. At LRK, a
401 moderate correlation (r^2 = 0.40) suggests a contribution to 2-methyltetrols from isoprene
402 ozonolysis at this site during the 2013 SOAS campaign. Conversely, the weak correlation at
403 CTR (r^2 = 0.18) indicates a smaller role of isoprene ozonolysis in the formation of 2-
404 methyltetrols at this site.
405
406 **4. CONCLUSIONS**
407 In the present study, the impact of acidified sulfate aerosol on SOA composition
408 arising from isoprene ozonolysis was systematically examined in smog chamber studies.
409 Chemical characterization of SOA demonstrated substantial yields of OSs and 2-methylterols
410 from ozonolysis of isoprene in the presence of acidified sulfate seed aerosol. The presence of
411 an OH radical scavenger in chamber studies resulted in decreased concentrations of products
412 that could be identified, indicating a contribution to oxidation by OH radicals. Nevertheless,
413 substantial particle-phase concentrations of both OSs and 2-methyltetrols from ozonolysis in
414 the presence of an OH scavenger suggest that the SOA yields from isoprene ozonolysis may
415 be underestimated by current models. Furthermore, SOA yields from isoprene ozonolysis
416 have hitherto been determined either without seed particles (Sato et al., 2013) or in the
417 presence of non-acidified aerosols (Kleindienst et al., 2007). Further supporting the
418 conclusion that the contribution of ozonolysis to the isoprene-derived SOA budget is likely

underestimated, OSs identified in our chamber experiments but not previously reported as products of reactive uptake of photochemical isoprene oxidation were quantified in $PM_{2.5}$ samples collected from two rural sites in the southeastern U.S. SOA yields from isoprene ozonolysis have been reported to increase in the presence of acidified sulfate seed aerosol (Jang et al., 2002); however, SOA composition was not characterized and no hypotheses were offered with regard to mechanisms underlying this effect. A substantial yield of 2-methyltetrols in the presence of a large excess of OH scavenger supports isoprene oxidation by an alternative pathway, such as acid-catalyzed oxidation by organic peroxides in accord with a previous hypothesis (Claeys, 2004b). A potential source of organic peroxides in the aerosol phase is sCI oligomerization and subsequent uptake, recently reported by Inomata et al. (2014). Further investigation is required to understand how acidified sulfate seed aerosols take up organic peroxides from the gas phase and how particle-phase reactions might degrade organic peroxides into low-volatility products (e.g., OSs) in order to develop mechanisms of SOA formation from isoprene ozonolysis in the presence of acidified sulfate aerosol.

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ACKNOWLEDGMENTS

The authors wish to thank the Camille and Henry Dreyfus Postdoctoral Fellowship Program in Environmental Chemistry for their financial support. This work is also funded in part by the U.S. Environmental Protection Agency (EPA) grant R835404 and the National Science Foundation grant CHE-1404644. The contents of this publication are solely the responsibility

of the authors and do not necessarily represent the official views of the U.S. EPA. Further, the U.S. EPA does not endorse the purchase of any commercial products or services mentioned in the publication. The authors wish to thank Kasper Kristensen and Marianne Glasius (Department of Chemstry, Aarhus University, Denmark) who synthesized the 3-pinanol-2-hydrogen sulfate.

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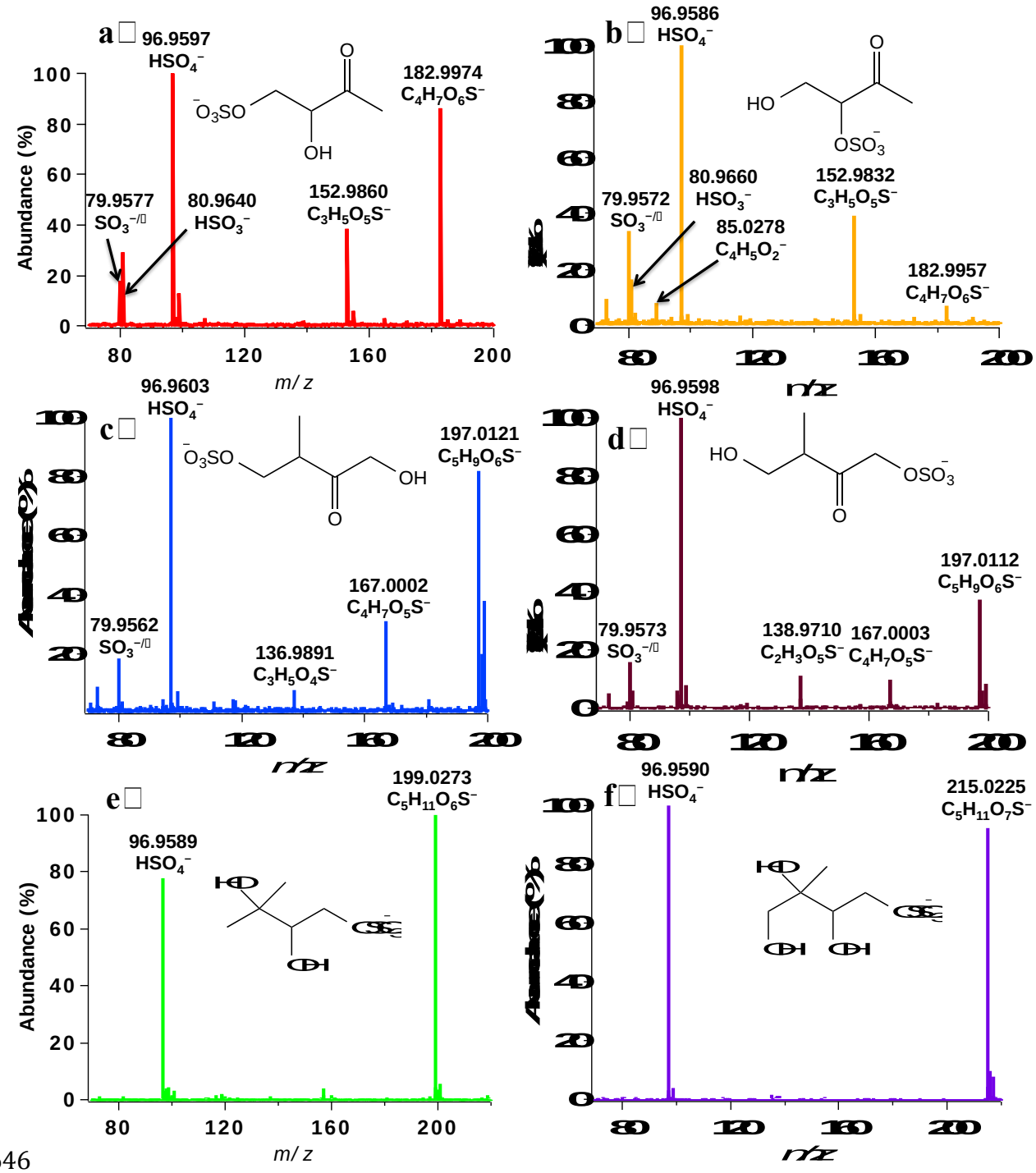

646

647 **Figure 1.** MS^2 spectra obtained for selected isoprene-derived OSs: (a) early- and (b) late-
648 eluting *m/z* 183 ($C_4H_7O_6S^-$), (c) early- and (d) late-eluting *m/z* 197 ($C_5H_9O_6S^-$), (e) *m/z* 199
649 ($C_5H_{11}O_6S^-$) and (f) *m/z* 215 ($C_5H_{11}O_7S^-$). Proposed structures for the different parent ions are
650 shown as insets on each spectrum.

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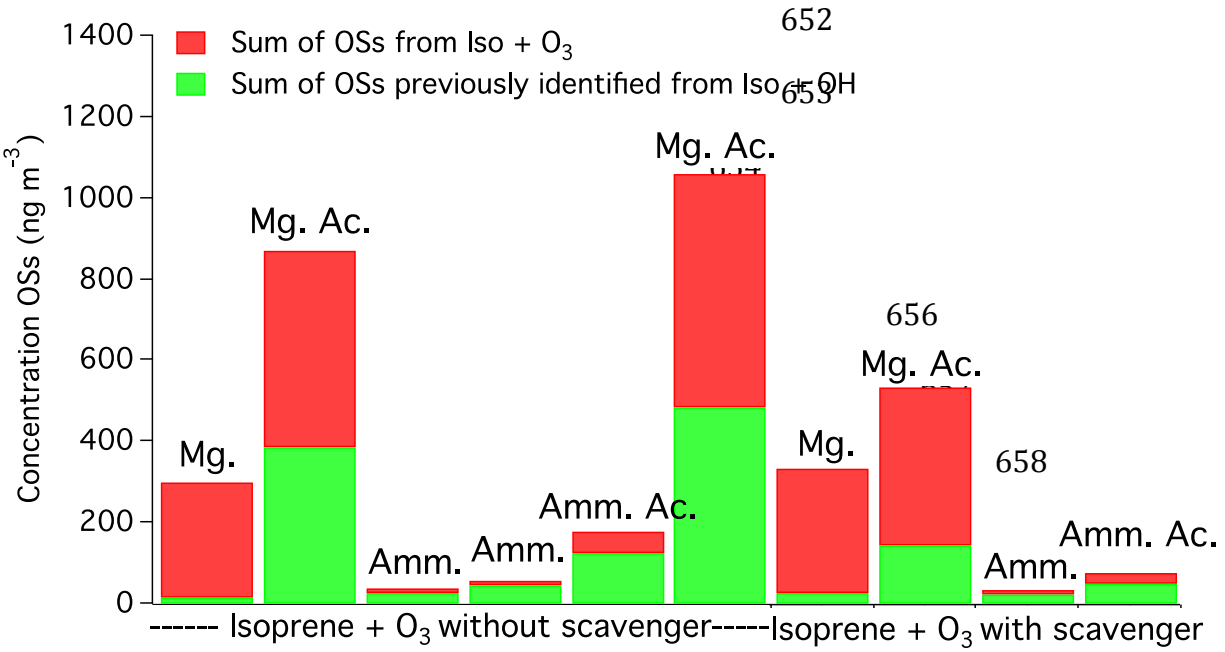


Figure 2. Quantification of the all identified OSs produced from the chamber isoprene ozonolysis (experimental conditions are reported in Tables 1 and 2). Presence of OSs in green bars have been previously reported during the photooxidation of isoprene (i.e., OSs reported in Table 1), while OSs in red bars corresponds to compounds identified only during the isoprene ozonolysis experiments (i.e., OSs in Table 2). *Mg.* and *Amm.* correspond to magnesium and ammonium sulfate seed aerosol, respectively. *Ac.* corresponds to acidified sulfate seed aerosol.

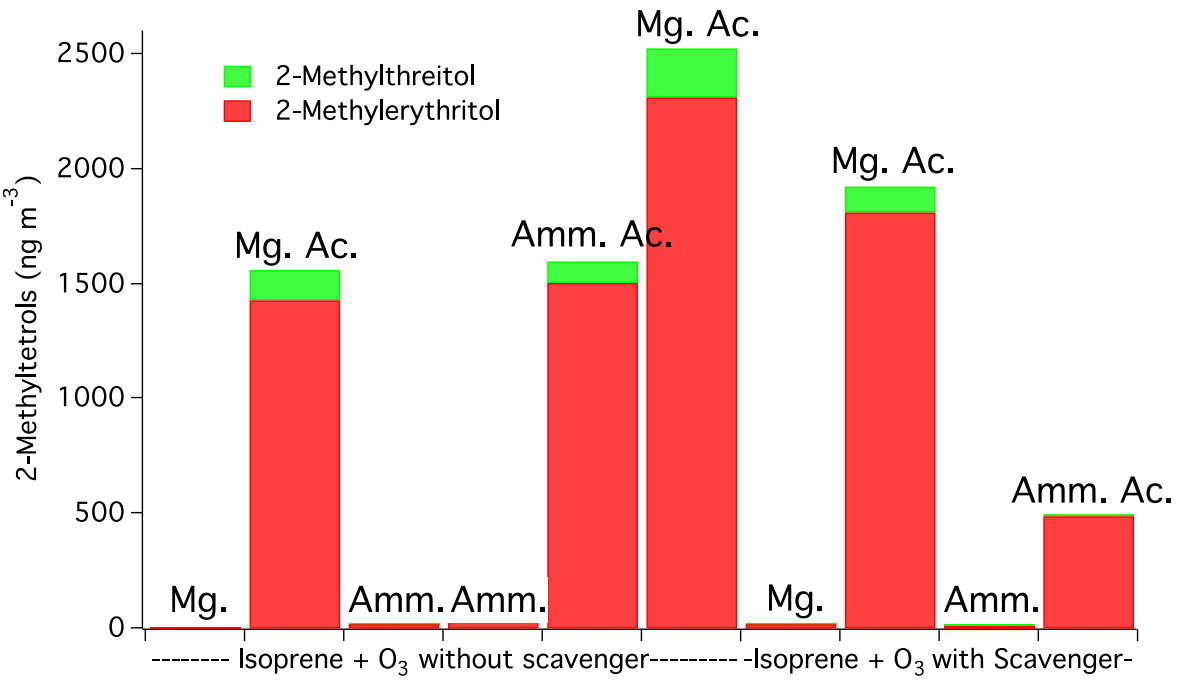
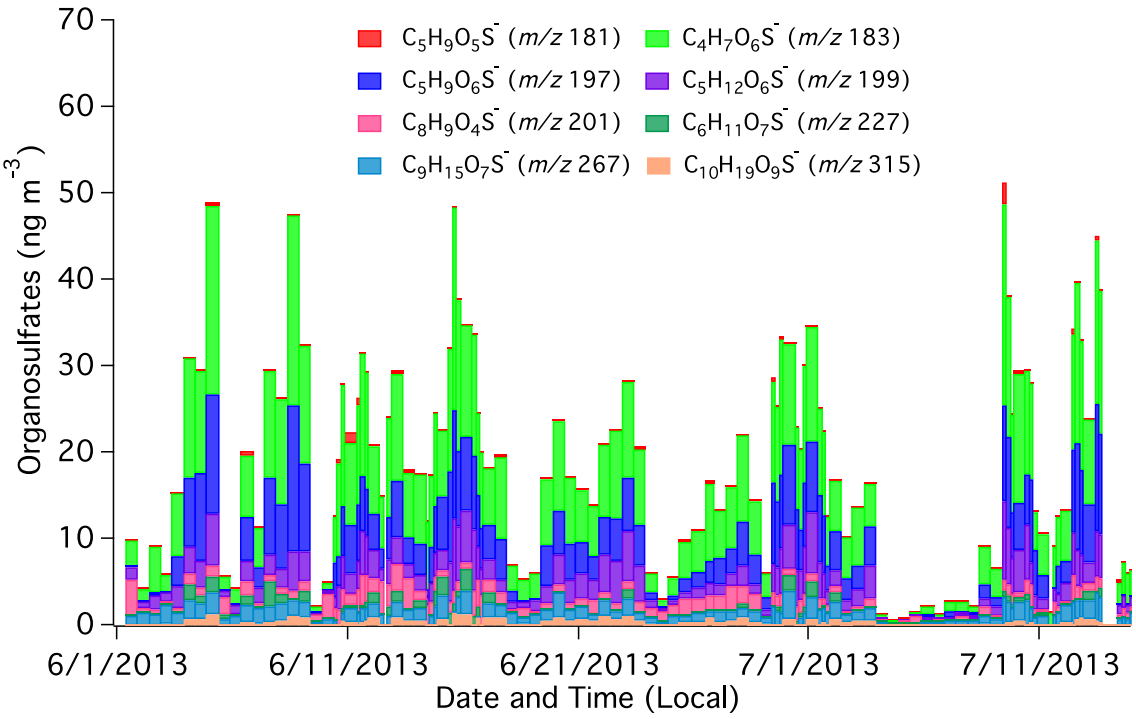


Figure 3. Quantification of 2-methyltetrols produced from the chamber isoprene ozonolysis (experimental conditions are reported in Table 1). *Mg.* and *Amm.* correspond to magnesium and ammonium sulfate seed aerosol, respectively. *Ac.* corresponds to acidified sulfate seed aerosol.



679

680 **Figure 4.** Temporal variations of OSs from isoprene ozonolysis-only at the CTR site during

681 the 2013 SOAS campaign.

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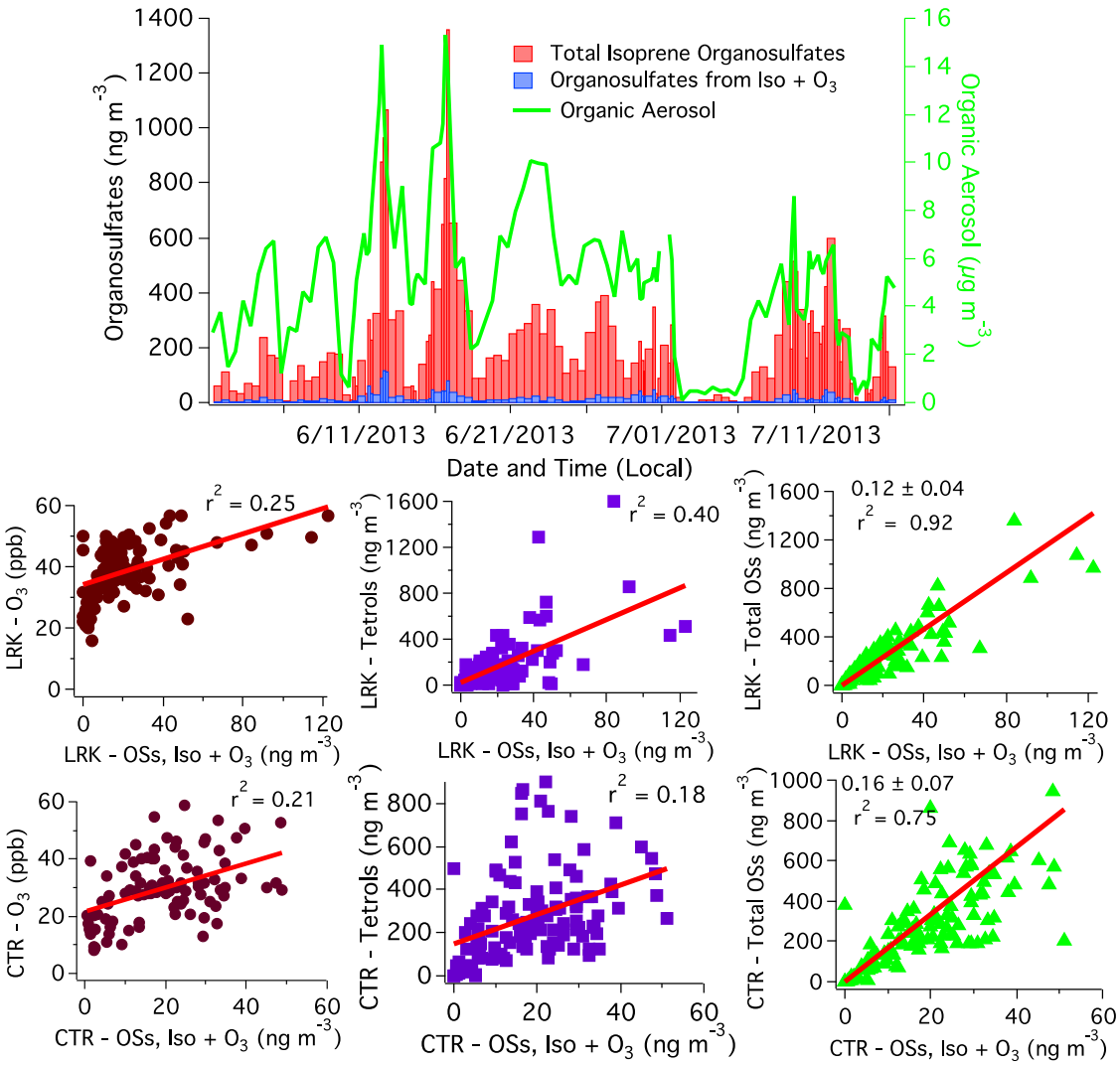

Figure 5. Temporal variations of OSs identified in the isoprene ozonolysis-only experiment and the sum of all OSs identified from isoprene oxidation (i.e., by OH and O_3) at the LRK site during the 2013 SOAS campaign (upper plot). Organic aerosol concentrations were measured by an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) (Budisulistiorini et al., 2015). and Bottom plots show correlations of the sum of OSs identified from isoprene ozonolysis-only experiments with ozone (brown markers), 2-methyltetrols (purple markers) and total isoprene OSs (green markers) from both CTR and LRK sites.

692 **Table 1.** Summary of experimental conditions and quantification of OSs from isoprene
693 ozonolysis that have previously been identified in isoprene photooxidation experiments
694 (Surratt et al., 2008).

		Sulfate seed aerosol									
		Mg.	Mg. Ac.	Amm.	Amm.	Amm. Ac.	Mg. Ac.	Mg.	Mg. Ac.	Amm.	Amm. Ac.
Scavenger		----------Yes----------						----------No----------			
[Isoprene] (ppb)		108	105	104	104	97	96	99	102	100	103
[O_3] (ppb)		118	123	134	134	117	133	118	130	115	126
$[M - H]^-$	**(*m/z*)**	**Mass concentration (ng m^{-3})**									
$C_3H_5O_5S^-$	(152.9861)[a]	4.1	30.4	7.5	7.5	9.8	57.5	2.8	32.3	6.7	5.0
$C_3H_5O_6S^-$	(168.9820)[a]	*N.d.*	*N.d.*	5.9	3.5	14.9	9.1	*N.d.*	*N.d*	4.8	2.1
$C_5H_9O_7S^-$	(213.0071)[a]	*N.d.*	35.1	2.3	7.4	7.1	37.9	*N.d.*	12.4	*N.d.*	*N.d.*
$C_5H_{11}O_7S^-$	(215.0225)[a]	12.8	320.7	12.7	28.8	94.5	390.5	24.1	98.9	10.7	41.0

695 [a] *Quantified using synthesized IEPOX-derived OS. Different isomers for one ion have been summed;*
696 *N.d.: not detected. Mg. and Amm. correspond to magnesium and ammonium sulfate seed aerosol,*
697 *respectively. Ac. corresponds to acidified sulfate seed aerosol.*
698

699 **Table 2** Summary of experimental conditions and quantification of OSs from isoprene
700 ozonolysis not reported as products of isoprene photolysis.

		Sulfate seed aerosol									
		Mg.	Mg. Ac.	Amm.	Amm.	Amm. Ac.	Mg. Ac.	Mg.	Mg. Ac.	Amm.	Amm. Ac.
Scavenger		----------Yes----------						----------No----------			
[Isoprene] (ppb)		108	105	104	104	97	96	99	102	100	103
[O_3] (ppb)		118	123	134	134	117	133	118	130	115	126
$[M - H]^-$	**(*m/z*)**	**Mass concentration (ng m^{-3})**									
$C_4H_7O_6S^-$	(182.9957)[b,*]	7.1	67.4	3.4	4.6	21.6	101.7	*N.d.*	53.4	7.4	16.3
$C_5H_{11}O_6S^-$	(199.0273)[a,*]	*N.d.*	12.4	*N.d.*	*N.d.*	1.1	22.1	*N.d.*	14.5	*N.d.*	0.4
$C_5H_7O_5S^-$	(179.0010)[a]	*N.d.*	5.7	*N.d.*	*N.d.*	1.8	3.7	*N.d.*	*N.d.*	*N.d.*	*N.d.*
$C_5H_9O_5S^-$	(181.0168)[a]	*N.d.*	4.1	*N.d.*	*N.d.*	*N.d.*	9.1	*N.d.*	7.8	*N.d.*	*N.d.*
$C_5H_9O_6S^-$	(197.0121)[b]	*N.d.*	82.5	2.2	*N.d.*	12.5	115.9	*N.d.*	28.5	0.6	4.0
$C_8H_9O_4S^-$	(201.0209)[b]	273.8	294.9	7.3	6.3	5.5	276.6	307.9	278.2	4.5	5.5
$C_6H_{11}O_7S^-$	(227.0215)[a]	*N.d.*	2.5	7.3	*N.d.*	0.7	4.2	*N.d.*	0.7	*N.d.*	*N.d.*
$C_9H_{13}O_6S^-$	(249.0434)[c]	0.3	1.6	*N.d.*	*N.d.*	0.6	2.8	*N.d.*	1.8	0.3	0.4
$C_9H_{15}O_7S^-$	(267.0531)[c]	*N.d.*	3.1	*N.d.*	*N.d.*	*N.d*	6.5	*N.d.*	0.9	*N.d.*	*N.d.*
$C_{10}H_{19}O_9S^-$	(315.0739)[c]	*N.d.*	6.7	*N.d.*	*N.d.*	3.2	9.1	*N.d.*	1.4	*N.d.*	*0.6*
$C_{13}H_{11}O_{10}S^-$	(359.0072)[c]	*N.d.*	4.0	*N.d.*	*N.d.*	*N.d.*	8.4	*N.d.*	0.9	*N.d.*	*N.d.*
$C_{15}H_{15}O_{12}S^-$	(419.0329)[c]	*N.d.*	0.9	*N.d.*	*N.d.*	*N.d.*	1.9	*N.d.*	0.4	*N.d.*	*N.d.*

701 *[a] Quantified using propylsulfate; [b] quantified using authentic IEPOX-OS; [c] quantified using authentic OS*
702 *(monoterpenes, OS-249). Different isomers for one ion have been summed; N.d.: not detected. Mg. and Amm.*
703 *correspond to magnesium and ammonium sulfate seed aerosol, respectively. Ac. corresponds to acidified sulfate*
704 *seed aerosol. * Published (Safi Shalamzari et al., 2013).*