1	Organosultates in atmospheric aerosol: synthesis and quantitative analysis of
2	PM2.5 from Xi'an, Northwest China
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30	Abstract
31	The sources, formation mechanism and amount of organosulfates (OS) in atmospheric aeroso
32	are not yet well understood, partly due to the lack of authentic standards for quantification. Ir
33	this study, we report an improved robust procedure for the synthesis of organosulfates with
34	different functional groups. Nine authentic organosulfate standards were synthesized and four
35	standards (benzyl sulfate, phenyl sulfate, glycolic acid sulfate, and hydroxyacetone sulfate)

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- gry 36 were used to quantify their ambient concentrations. The authentic standards and ambient 37 aerosol samples were analyzed using an optimized ultra performance liquid chromatographyelectrospray ionization-tandem mass spectrometric method (UPLC-ESI-MS/MS). The 38 recovery ranged from 80.4% to 93.2%, the limits of detection and limits of quantification 39 obtained were 1.1-16.7 pg m⁻³ and 3.4-55.6 pg m⁻³, respectively. Measurements of ambient 40 aerosol particle samples collected in winter 2013-2014 in urban Xi'an, northwest China, show 41 that glycolic acid sulfate $(77.3 \pm 49.2 \text{ ng m}^{-3})$ is the most abundant species of the identified 42 organosulfates followed by hydroxyacetone sulfate (1.3 ± 0.5 ng m⁻³), phenyl sulfate ($0.14 \pm$ 43
- 0.09 ng m⁻³), and benzyl sulfate $(0.04 \pm 0.01 \text{ ng m}^{-3})$. Except for hydroxyacetone sulfate, which 44

45 seems to form mainly from biogenic emissions in this region, the organosulfates quantified
46 during winter in Xi'an show an increasing trend with an increase in the mass concentrations of
47 organic carbon indicating their anthropogenic origin.

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49 **1 Introduction**

Atmospheric aerosol particles represent a highly complex blend of inorganic and organic matter 50 originating from a wide variety of both natural and anthropogenic sources. The organic fraction 51 typically constitutes 20-90% of the total submicron aerosol mass and is much less constrained 52 in terms of chemical composition than the inorganic fraction (Jimenez et al., 2009; Hallquist et 53 54 al., 2009). Only ~10-30% of the particulate organic matter has been identified as specific 55 compounds despite years of effort and the use of the most sophisticated techniques available 56 (Hoffmann et al., 2011). The insufficient knowledge of the composition of organic aerosol 57 particles at the molecular level hinders a better understanding of the sources, formation and 58 atmospheric processes of organic aerosol as well as their physicochemical properties and effects on climate and human health (Noziere et al., 2015). 59

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Organosulfates are ubiquitous in atmospheric aerosol and have been detected in ambient aerosol particles from America, Europe, Asia and the Arctic during the last decade (e.g. Surratt et al., 2008; Iinuma et al., 2007; Stone et al., 2012; Hansen et al., 2014; Kourtchev et al., 2016; Surratt et al., 2007). Due to the presence of the deprotonated functional group $R-O-SO_{3}^{-}$, organosulfates are acidic and highly water soluble and therefore can enhance the aerosol hygroscopicity. These characteristics, together with the light-absorbing property of organosulfates, lead to potential impacts on climate (Lin et al., 2014).

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Organosulfates are tracers of secondary organic aerosol (SOA) formation and have been 69 70 demonstrated to be produced from heterogeneous and multiphase reactions (e.g. Surratt et al., 71 2008; Iinuma et al., 2007; Chan et al., 2011; Zhang et al., 2012). Chamber studies have found 72 that the oxidation of biogenic volatile organic compounds (BVOCs) including isoprene, 73 monoterpenes, and sesquiterpenes can form organosulfates on acidified sulfate particles (e.g. 74 Surratt et al., 2008; Iinuma et al., 2007; Chan et al., 2011; Zhang et al., 2012). A very recent 75 study revealed a previously unrecognized pathway for organosulfate formation through the 76 heterogeneous reaction of SO_2 with the unsaturated bond in oleic acid (Shang et al., 2016). A 77 number of biogenic organosulfates have been observed in ambient aerosol, in particular, isoprene-derived organosulfates (e.g. Kristensen et al., 2011; He et al., 2014; Liao et al., 2015; 78 79 Budisulistiorini et al., 2015). A recent study reported the formation of aromatic organosulfates by photochemical oxidation of polycyclic aromatic hydrocarbons (PAHs) in the presence of 80 sulfate seed particles (Riva et al., 2016). Aromatic organosulfates have also recently been 81 observed in urban aerosol from different locations in Asia. The presence of aromatic 82 83 organosulfates was first suggested by Stone et al. (Stone et al., 2012) based on analysis of 84 aerosol samples collected at four sites in Asia. Kundu et al. (Kundu et al., 2013) quantified 85 benzyl sulfate $(C_7H_7SO_4)$ and identified its homologous series with increasing number of methylene groups ($C_8H_9SO_4^-$ and $C_9H_{11}SO_4^-$) in Lahore, Pakistan. Furthermore, Staudt et al. 86 87 (Staudt et al., 2014) synthesized phenyl sulfate, benzyl sulfate, 3- and 4-methylphenyl sulfate and 2-, 3-, and 4-methylbenzyl sulfate and quantified them in aerosols collected in urban
samples from Lahore and Pasadena, USA as well as Nepal. Ma et al. (Ma et al., 2014) reported
the contribution up to 64% from aromatic organosulfates to the sum of identified organosulfates
in winter Shanghai, while Wang et al. (Wang et al., 2016) found aromatic organosulfates to
constitute less than 22% of the detected number of organosulfates in Shanghai, Nanjing, and
Wuhan.

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Organosulfates have been estimated to contribute 5-10% of the organic mass in fine particles 95 in the USA (Tolocka and Turpin, 2012). However, quantification of organosulfates is a 96 challenging task due to the lack of authentic standards and incomplete understanding of the 97 sources, precursors and formation processes of organosulfates. To date, many studies of 98 99 organosulfates have remained at the qualitative level, although a limited number of studies have 100 provided quantitative or semi-quantitative analysis of certain organosulfates (e.g. Kundu et al., 2013; Staudt et al., 2014; Ma et al., 2014; Olson et al., 2011; Hettivadura et al., 2017). Moreover, 101 several studies show that organosulfates are present as a wide range of species with individual 102 species such as the organosulfate derived from isoprene epoxydiols (IEPOX) contributing 0.2-103 104 1.4% of the total organic aerosol mass (Liao et al., 2015). This further complicates the 105 quantification of organosulfates. A few organosulfate standards have been synthesized for quantification purposes. For example, Olsen et al. (Olson et al., 2011) measured 0.4-3.8 ng m⁻ 106 107 ³ lactic acid sulfate and 1.9-11.3 ng m⁻³ glycolic acid sulfate in samples of PM_{2.5} (particulate matter with an aerodynamic diameter <2.5 µm) from the US, Mexico City, and Pakistan. Kundu 108 et al. (Kundu et al., 2013) measured monthly-average concentrations of benzyl sulfate ranging 109 from 0.05 to 0.5 ng m^{-3} in PM_{2.5} samples from Lahore, Pakistan. Staudt et al. (Staudt et al., 110 2014) quantified benzyl sulfate ranging from 4 to 90 pg m⁻³ in PM_{2.5} samples from Lahore 111 (Pakistan), Godavari (Nepal), and Pasadena (California), while methylbenzyl sulfates, phenyl 112 sulfate, and methylphenyl sulfates were observed intermittently in these three locations. 113 Furthermore, Hettiyadura et al. (Hettiyadura et al., 2015) developed a hydrophilic interaction 114 liquid chromatography method using an amide stationary phase providing excellent retention 115 116 of carboxy-organosulfates and isoprene-derived organosulfates, which was validated using six 117 model organosulfates including aliphatic and aromatic organosulfates.

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Previous field studies focusing on organosulfates were conducted mainly in Europe (e.g. linuma 119 120 et al., 2007; Kristensen et al., 2011; Gómez-González et al., 2008; Gómez-González et al., 2012; 121 Nguyen et al., 2014; Martinsson et al., 2017) and North America (e.g. Surratt et al., 2007; Nguyen et al., 2012; Worton et al., 2011), and only a few in China (He et al., 2014; Ma et al., 122 123 2014). The particulate air pollution has been a serious environmental problem during recent winters in China, characterized by high secondary aerosol concentrations including sulfate and 124 SOA (e.g. Huang et al., 2014; Elser et al., 2016; Wang et al., 2017). As organosulfates are 125 tracers for SOA, more studies on organosulfates will help to better understand and constrain 126 127 the SOA formation mechanisms in highly polluted regions (e.g., China) and to reconcile the 128 underestimation of particle-phase organic carbon in atmospheric models.

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In this study, nine organosulfate standards (phenyl sulfate, 3-methylphenyl sulfate, benzyl sulfate, 2-methyl benzyl sulfate, 3-methyl benzyl sulfate, 2, 4-dimethyl benzyl sulfate, 3, 5-

- dimethyl benzyl sulfate, hydroxyacetone sulfate, and glycolic acid sulfate) were synthesized 132 using an approach modified from Staudt et al. (Staudt et al., 2014) and Hettiyadura et al. 133 (Hettiyadura et al., 2015). These authentic standards were used to optimize an ultra performance 134 liquid chromatography electrospray ionization-tandem mass spectrometric method (UPLC-135 136 ESI-MS/MS) for the quantification of organosulfates. The presence and concentration of four of these organosulfates, namely, benzyl sulfate, phenyl sulfate, glycolic acid sulfate, and 137 hydroxyacetone sulfate, were determined in ambient PM2.5 collected in urban air in Xi'an, 138 China. The rest five organosulfates were not quantified in ambient $PM_{2.5}$ because the standards 139 were synthesized at a later stage of the study. 140
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142 2 Material and methods

143 2.1 Chemicals and synthesis

The chemicals used for the synthesis of organosulfates included hydroxyacetone (99%, Sigma Aldrich), glycolic acid (99%, Sigma Aldrich), phenol (99.5%, Tic), benzyl alcohol (99.8%, Aladdin, Shanghai, China), m-cresol (99%, Sigma Aldrich), sulfur trioxide pyridine complex (98%, Sigma Aldrich), pyridine (99.9%, Sigma Aldrich), Dowex® 50WX8 (hydrogen form, 100-200 mesh, Sigma Aldrich). MilliQ water (18.2 MΩ) was used, and all other reagents were analytical grade and used without further purification.

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151 The organosulfate standards were synthesized using a general approach modified from Staudt et al. (Staudt et al., 2014) and Hettiyadura et al. (Hettiyadura et al., 2015). Fig. 1 shows the 152 reaction scheme. In general, alcohol (7.0 mmol) and sulfur trioxide pyridine complex (1.2 153 equiv.) was dissolved in dry pyridine (10 mL) in an oven-dried, three-necked flask provided 154 with magnetic stirring under nitrogen. The reaction mixture was stirred at 30 °C for 24 h, and 155 then the solvent was removed via distillation under vacuum at 50 °C. The residue was 156 redissolved in distilled water (10 mL) and titrated with 0.9 M KOH until pH was above 12. 157 158 Neat ethanol (40 mL, 65 °C) was added to the aqueous solution. The resulting solution was heated to reflux followed by a quick vacuum filtration to remove the stark white precipitate. 159 The mother liquor was then placed in a freezer (-25 °C) overnight. The potassium salts of 160 161 organosulfate formed in the mother liquor were collected by vacuum filtration, rinsed with cold ethanol three times and dried to obtain the target product. The synthesized organosulfate 162 standards were stored in refrigerator (\sim 4 °C) and no decomposition was observed after 2 years 163 as confirmed by nuclear magnetic resonance (NMR) analysis. 164

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- 166 2.2 Characterization

The synthesized products were characterized with NMR and ESI-MS. ¹H NMR and ¹³C NMR 167 spectra were recorded on a Bruker Advance-III 400 MHz spectrometer at 400 and 100 MHz, 168 respectively using trimethylsilane (TMS) as an internal standard. Chemical shifts are reported 169 in ppm downfield from the internal reference. The NMR spectra are shown in Supplementary 170 Information. The following abbreviations are used for the multiplicities: s = singlet, m =171 172 multiplet. The yield for phenyl sulfate was 45%, ¹H NMR (400 MHz, D₂O): δ/ppm 7.29-7.43 (m, 5H), ¹³C NMR (100 MHz, D₂O): δ/ppm 121.6, 126.4, 129.8, 151.2. The yield for benzyl 173 sulfate was 70%, ¹H NMR (400 MHz, DMSO-*d*6): δ/ppm 7.25-7.40 (m, 5 H), 4.76 (s, 2 H), ¹³C 174 NMR (100 MHz, DMSO-d6): δ/ppm 67.9, 127.8, 128.0, 128.6, 138.4. The yield for 175

hydroxyacetone sulfate was 45%, ¹H NMR (400 MHz, DMSO-*d*6): δ /ppm 4.22 (s, 2 H), 2.11 176 (s, 3 H), ¹³C NMR (100 MHz, DMSO-*d*6): δ/ppm 26.9, 71.4, 207.0. The yield for glycolic acid 177 sulfate was 35%, ¹H NMR (400 MHz, DMSO-*d*6): δ/ppm 4.07 (s, 2H), ¹³C NMR (100 MHz, 178 DMSO-d6): δ /ppm 65.0, 173.1. The organosulfate standards were recrystallized in ethanol 179 180 for purification and purity of these synthesized standards is >95%, confirmed by NMR 181 analysis. Exact mass spectra were recorded on a high-resolution mass spectrometer (HR-MS, Q Exactive Plus, Thermo Scientific, USA) equipped with an ESI source in the negative ion 182 mode (ESI-). The ESI conditions were as follows: spray voltage -3.2 kV, collision energy (CE) 183 40 V for benzyl sulfate and 45 V for hydroxyacetone sulfate, 3-methylphenyl sulfate, glycolic 184 acid sulfate and phenyl sulfate, capillary temperature 350 °C, aux gas heater temperature 320 °C, 185 sheath gas flow rate 35, aux gas flow rate 10. The mass resolving power was 70,000. Data 186 187 acquisition was performed with m/z ranging from 50 to 200.

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189 2.3 PM_{2.5} samples

The 24-h integrated $PM_{2.5}$ samples were collected on pre-baked (780 °C, 3 h) quartz-fiber filters (8×10 inch, Whatman, QM-A, USA) using a high-volume sampler (Tisch, Cleveland, OH, USA) at a flow rate of 1.05 m³ min⁻¹ from 18 December 2013 to 17 February 2014. After collection, the filter samples were immediately wrapped in pre-baked aluminum foil and stored in a freezer (below -20 °C) until analysis. The sampling site was located on the rooftop of the Institute of Earth and Environment (~10 m above the ground), Chinese Academy of Sciences (IEECAS, 34.23°N, 108.88°E), which is surrounded by residential, commercial and trafficked areas.

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198 2.4 Sample analysis

199 A portion of the filter (6×0.526 cm² punch) taken from each sample was sonicated for 25 min 200 in 9 mL of acetonitrile (ACN)/water mixture (95:5, V/V). The extracts were filtered through a $0.22 \ \mu m$ polypropylene membrane syringe filter to remove insoluble material. The eluate was 201 202 concentrated almost to dryness with a gentle stream of purified nitrogen (99.999%) at 45 °C using an evaporation system (TurboVap® LV, biotage), then redissolved in 500 µL of 203 acetonitrile/water mixture (V/V, 95:5). The prepared samples were stored at 4 °C in the 204 205 refrigerator and analyzed within 24 h. The separation and quantification were realized using a ACQUITY UPLC system (equipped with a quaternary pump, autosampler, and thermostated 206 column compartment) coupled to a tandem mass spectrometer (Xevo TQ MS, Waters, USA). 207 The separation was carried out using a BEH amide column (2.1mm×100 mm, 1.7 µm particle 208 209 size, Waters, USA) equipped with a pre-column. The column was maintained at 35 °C and the flow rate of mobile phase was 0.25 mL min⁻¹. A 5 µL injection volume was used for quantitative 210 analysis of samples and standards. The optimized mobile phase A (organic) consisted of 211 ammonium acetate buffer (5 mM, pH 8.5) in ACN and ultra-pure water (95:5, V/V) and mobile 212 phase B (aqueous) consisted of ammonium acetate buffer (5 mM, pH 9) in ultra-pure water. A 213 mobile phase gradient was used: mobile phase A was maintained at 98% for 2 min, then 214 215 decreased to 60% from 2 to 5 min and then held there for 2 min; from 7 to 12 min mobile phase 216 A was returned to 98%. Organosulfates were detected by a TQ MS equipped with an ESI source 217 in the negative ion mode. The mass spectrometer was operated in multiple reaction monitoring (MRM) mode. Optimized MS conditions for the four organosulfates chosen for the field studies 218 (e.g., cone voltages and collision energies) are listed in Table 1. The capillary voltage was 2.7 219

kV, source temperature was 150 °C, desolvation temperature was 350 °C, desolvation gas (N₂)
flow rate at 800 L h⁻¹, cone gas (N₂) flow rate was 150 L h⁻¹, and collision gas (Ar) flow rate
was 0.16 mL min⁻¹. All data were acquired and processed using MassLynx software (version
4.1). All samples and standard spectra were background subtracted.

- 224
- 225 2.5 Quality control

For every 10 analyses, a procedural blank and a spiked sample-namely, real ambient samples 226 spiked with known amounts of a standard solution of organosulfates to be quantified were 227 measured to check for interference and cross-contamination. The external standard method was 228 used for quantitative determination of the analytes. The limits of detection are defined as the 229 minimum detectable peaks of individual species with a signal-to-noise (S/N) ratio of 3:1. The 230 231 recoveries were determined by the analysis of the spiked samples: we first measured a filter 232 punch without spike and then measured the second punch from the identical filter spiked with known amounts of a standard solution of organosulfates. The differences between these two 233 measurements were divided by the amounts of organosulfates spiked to calculate the recoveries 234 of individual organosulfates. This recovery test also provides an indication of potential matrix 235 236 effect. The reproducibility (relative standard deviation, RSD) was determined by measuring 237 five identical samples that were subjected to the same pretreatment procedure. The field blank samples were collected and analyzed, and the data reported here were corrected for the field 238 239 blanks.

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241 **3 Results and discussion**

242 3.1 Mass spectral fragmentation and UPLC separation

243 Each synthesized organosulfate was analyzed by high resolution tandem MS (MS/MS). The molecular ion for each organosulfate was assigned to the deprotonated molecule $(R-O-SO_3)$. 244 Major sulfur-containing product ions included the sulfite ion radical ($(SO_3, m/z 80)$) that is 245 246 formed from the homolytic cleavage of the O-S bond, the sulfate ion radical (\cdot SO₄, m/z 96) that is formed from the homolytic cleavage of the C–O bond, the bisulfite anion (HSO₃, m/z) 247 248 81) that is formed from hydrogen abstraction followed by the heterolytic cleavage of the O-S 249 bond, and the bisulfate anion (HSO₄, m/z 97). Phenyl sulfate, 3-methylphenyl sulfate, and glycolic acid sulfate produce phenoxide (C₆H₅O⁻, m/z 93), 3-methylphenoxide (C₇H₇O⁻, m/z250 107) and glycolate ($C_2H_3O_3^-$, m/z, 75) anions, respectively, formed from neutral loss of SO₃. The 251 252 mass spectra of these compounds are shown in Fig. 2. The mass spectrum of phenyl sulfate is 253 similar to that reported by Staudt et al., (Staudt et al., 2014), the mass spectra of hydroxy acetone sulfate and glycolic acid sulfate are similar to those reported by Hettiyadura et al. (Hettiyadura 254 255 et al., 2015) and the spectrum of benzyl sulfate is similar to that reported by Kundu et al. (Kundu et al., 2013), confirming the identity of the compounds. 256

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The ESI-MS/MS in MRM mode is applied for the quantification of individual organosulfates. This can greatly enhance the selectivity and sensitivity by monitoring a transition pair of precursor and product ions and thus eliminating potential interferences from the complex aerosol matrix. Table 1 shows the optimized ESI- conditions and the transition pairs for each organosulfate studied. The organosulfate standards were separated by UPLC using a BEH amide column that retains extremely polar compounds through ionic, hydrogen bonding and

dipole interactions. A gradient elution procedure was applied and the aqueous portion of the 264 mobile phase increased from 7-43%, leading to the baseline separation of four organosulfates 265 within 6 min (Fig. 3a). The retention time was 0.86 min for phenyl sulfate, 0.96 min for benzyl 266 sulfate, 1.10 min for hydroxyacetone sulfate and 5.78 min for glycolic acid sulfate, respectively. 267 268 The mobile phase was buffered to slightly basic pH to maintain the deprotonated state of the 269 organosulfates, which favors the separation. The amide functionalization of the BEH stationary 270 phase introduces hydrogen bonding and strengthens interaction with organosulfates particularly for those containing carboxyl and hydroxyl functional groups. It should be noted that the 271 chromatographic peak-broadening occurred particularly for phenyl sulfate and hydroxyacetone 272 sulfate when analyzing the ambient samples (Fig. 3b). This might be explained by matrix effects 273 due to the complex samples, which can influence the partitioning of analyte between the 274 275 stationary phase and mobile phase, particularly for those analytes with weak retention on the 276 column. However, the quantification of organosulfates is not affected by the peak broadening because the transition pair of precursor and product ions used in the MRM mode of the mass 277 spectrometer guarantees selectivity and accuracy. 278

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280 3.2 Method validation

281 Table 2 shows the analytical performance of the method under optimized UPLC and MS/MS conditions. The calibration curves of each organosulfates are highly linear ($R^2 \ge 0.995$), ranging 282 283 from 0.1-40 ng mL⁻¹ for phenyl sulfate and benzyl sulfate, from 0.3-120 ng mL⁻¹ for hydroxyacetone sulfate, and 2.0-800 ng mL⁻¹ for glycolic acid sulfate. The recoveries, 284 determined by analyzing ambient samples spiked with known amounts of organosulfate 285 standards, ranging from 80.4-93.2%. The good recoveries indicate high extraction efficiency, 286 287 low sample matrix effect and low error from sample pretreatment and the UPLC-MS 288 measurement. The limit of detection (LOD, S/N=3) and limit of quantification (LOQ, S/N=10) ranged from 0.03 to 0.42 ng mL⁻¹ and 0.09 to 1.4 ng mL⁻¹ of the extracts, respectively. This 289 corresponds to LODs of 1.1 to 16.7 pg m⁻³ and LOQs of 3.4 to 55.6 pg m⁻³, respectively, using 290 the current set-up (see experimental section). 291

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293 3.3 Quantification of organosulfates in ambient aerosol

Ambient PM_{2.5} samples were extracted and analyzed by UPLC-MS/MS following the same 294 procedure as the OS standards. The four selected organosulfates were identified according to 295 the transition pairs of precursor and product ions of individual compounds on the MS/MS as 296 297 well as the UPLC retention time. Table 3 shows the concentrations of phenyl sulfate, benzyl sulfate, hydroxyacetone sulfate, and glycolic acid sulfate in PM_{2.5} samples collected at Xi'an 298 (this work), together with concentrations reported in the literature from other locations 299 300 worldwide for comparison. In our samples from Xi'an glycolic acid sulfate (average 77.3 \pm 49.2 ng m⁻³, range 18.1-155.5 ng m⁻³) was the most abundant species of the identified 301 organosulfate followed by hydroxyacetone sulfate (average 1.3 ± 0.5 ng m⁻³, range 0.9-2.6 ng 302 m⁻³), phenyl sulfate (average 0.14 \pm 0.09 ng m⁻³, range 0.04-0.31 ng m⁻³) and benzyl sulfate 303 (average 0.04 ± 0.01 ng m⁻³, range 0.03-0.06 ng m⁻³). 304

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The concentration of glycolic acid sulfate quantified in this study is about one order of magnitude higher than those reported in the literature (see Table 3), indicating the substantial

formation of this secondary organic compound in polluted urban Xi'an. Glycolic acid sulfate 308 can form efficiently from glycolic acid relative to glyoxal in the presence of acidic sulfate 309 particles (Olson et al., 2011). While both organic precursors (glycolic acid and glyoxal) have 310 biogenic and anthropogenic origins, they form mainly from the oxidation of anthropogenic 311 312 emissions during winter in Xi'an. The concentrations of particle-phase glyoxal and glycolic 313 acid measured at Xi'an during winter have been reported to be significantly higher compared to other studied regions (e.g. Kawamura and Yasui, 2005; Miyazaki et al., 2009; Cheng et al., 314 2013), which therefore may explain the elevated glycolic acid sulfate. The concentration of the 315 other three organosulfates quantified in this study was much lower, but falling into the ranges 316 measured in other regions. 317

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319 It is noted that the time series of glycolic acid sulfate, phenyl sulfate, and benzyl sulfate is similar to that of organic carbon (OC) and SO_4^{2-} , while the concentration of hydroxyacetone 320 sulfate did not show an increasing trend when the concentrations of OC increased (Fig. 4a). 321 Hydroxyacetone sulfate can form from photochemical oxidation of isoprene and/or isoprene 322 ozonolysis in the presence of acidic sulfate aerosols (Surratt et al., 2008; Riva et al., 2015), 323 324 although hydroxyacetone was also suggested to originate from anthropogenic emissions (e.g., 325 biomass burning and fossil fuel combustion) (Hansen et al., 2014). Also, the formation rate of biogenic hydroxyacetone sulfate and anthropogenic hydroxyacetone sulfate may different. This 326 327 may explain the lack of correlation between hydroxyacetone sulfate and OC during winter in Xi'an. The average concentrations of glycolic acid sulfate, phenyl sulfate, and benzyl sulfate 328 were 1.3-3.2 times higher during high pollution days (PM_{2.5} range of 293.7-314.5 µg m⁻³ with 329 an average of 300.6 µg m⁻³) than during low pollution days (PM_{2.5} range of 94.7-121.2 µg m⁻³ 330 with an average of 106.4 μ g m⁻³), while the average concentrations of hydroxyacetone sulfate 331 332 were rather similar between high pollution days and low pollution days (Fig. 4b). These four organosulfates together account for 0.25% of total sulfur and 0.05% of OC, respectively. 333

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335 4 Conclusions

336 Nine authentic organosulfate standards, including phenyl sulfate, 3-methylphenyl sulfate, 337 benzyl sulfate, 2-methyl benzyl sulfate, 3-methyl benzyl sulfate, 2, 4-dimethyl benzyl sulfate, 3, 5-dimethyl benzyl sulfate, hydroxyacetone sulfate, and glycolic acid sulfate, were 338 synthesized in this study using an improved robust procedure. The synthesized compounds of 339 340 benzyl sulfate, phenyl sulfate, glycolic acid sulfate, and hydroxyacetone sulfate were used as 341 standards for quantification of these molecules in ambient PM_{2.5} samples. The other five organosulfate standards were synthesized, but not used for quantification of ambient samples 342 in this study. An improved UPLC-ESI-MS/MS method was developed and optimized for the 343 quantification. The recovery ranges from 80.4-93.2%, and the limits of detection and limits of 344 quantification obtained are 1.1-16.7 pg m⁻³ and 3.4-55.6 pg m⁻³, respectively. Measurements of 345 $PM_{2.5}$ samples from Xi'an show that glycolic acid sulfate (77.3 ± 49.2 ng m⁻³) is the most 346 abundant organosulfate followed by hydroxyacetone sulfate $(1.3 \pm 0.5 \text{ ng m}^{-3})$, phenyl sulfate 347 $(0.14 \pm 0.09 \text{ ng m}^{-3})$, and benzyl sulfate $(0.04 \pm 0.01 \text{ ng m}^{-3})$. Glycolic acid sulfate, phenyl 348 349 sulfate, and benzyl sulfate show an increasing trend with the increase of OC concentrations indicating their anthropogenic origin. 350

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Organosulfate	Deprotonate molecule (m/z)	Product ion (<i>m</i> / <i>z</i>)	Cone voltage (V)	Collision energy (eV)	Retention time (min)
Phenyl sulfate	$C_{6}H_{5}SO_{4}^{-}$ (173)	SO ₃ ⁻ (80) C ₆ H ₅ O ⁻ (93)	41	20 21	0.86 ± 0.02
Benzyl sulfate	C ₇ H ₇ SO ₄ (187)	HSO ₃ ⁻ (81) SO ₄ ⁻ (96)	42	19 22	0.96 ± 0.02
Hydroxyacetone sulfate	C ₃ H ₅ SO ₅ (153)	SO ₃ ⁻ (80) HSO ₄ ⁻ (97)	32	18 20	1.10 ± 0.02
Glycolic acid sulfate	$C_2H_3SO_6^-$ (155)	C ₂ H ₃ O ₃ ⁻ (75) HSO ₄ ⁻ (97)	26	18 14	5.78 ± 0.03

528 Table 1. The optimized ESI-MS/MS parameters and UPLC retention time of measured529 organosulfates

Organosulfate	Linear range	Linearity	Recovery	LOD (pg),	LOQ	LOD*	LOQ*
	(ng mL ⁻¹)	(R^2)	%	injection	(pg),	(pg m ⁻³)	(pg m ⁻³)
				volume (5	injection		
				μL)	volume		
					(5 µL)		
Phenyl sulfate	0.1-40	0.998	80.4	0.13	0.43	1.1	3.5
Benzyl sulfate	0.1-40	0.998	89.6	0.13	0.43	1.1	3.4
Hydroxyacetone	0.2.120	0.997	93.2	2.1	6.9	16.7	55.6
sulfate	0.3-120						
Glycolic acid	2-800	0.995	92.0	0.27	0.88	2.1	7.1
sulfate							

559 Table 2. Analytical performance of the UPLC-ESI-MS/MS method for organosulfate analysis

*For analyzing 6×0.526 cm punches of filters collected with high-volume samplers (sampling at 1.13 m³ min⁻¹ for 24 h on 8"×10" filters).

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Table 3. The quantification of organosulfates at Xi'an and comparison with data reported in theliterature

Location	Date	PM _{2.5}	OC	Organosulfate ng m ⁻³			Ref.	
		μg	μg	phenyl benzyl hydroxyacetone		glycolic		
		m ⁻³	m ⁻³	sulfate	sulfate	sulfate	acid	
							sulfate	
Riverside,	27/07/05	16.5	7.6	-	-	-	3.3	Olson et
CA								al., 2011
Mexico	26/03/06	40	8.5	-	-	-	4.1	
City (T0)								
Mexico	26/03/06	33	5.2	-	-	-	7.0	
City (T1)								
Cleveland,	15/07/07	12.7	3.9	-	-	-	1.9	
ОН								
Bakersfield,	16-18/06/10	11.1-	4.0-	-	-	-	4.5-5.4	
CA		12.0	4.8					
Lahore,	02/11/07	327.5	174.7	-	-	-	11.3	
Pakistan								
Lahore,	12/01/2007-	-	-	-	0.05-	-	-	Kundu et
Pakistan	13/01/2008				0.50			al., 2013
Lahore,	March/07	177.1	44.6	0.004	0.09	-	-	Staudt et
Pakistan								al., 2014
Godavari,	Feb/07	42.0	4.7	ND	0.004	-	-	
Nepal								
Pasadena,	5-6/06/10	41.8-	7.3-	ND	0.006-	-	-	
CA		44.1	7.6		0.007			
Centreville,	10-11/07/13	-	-	ND	ND	2.7-5.8	9-14	Hettiyadura
AL								et al., 2015
Shanghai	5-7/04/12	-	-	-	0.3-	-	-	Ma et al.,
	12-14/07/12				0.8			2014
	27-29/10/12							
	14-16/01/13							
Xi'an	18/12/13-	94.7-	14.9-	0.04-	0.03-	0.9-2.6	18.1-	This study
(n=10)	17/02/14	314.5	68.5	0.31	0.06		155.5	

$$R^{-O_{-}H} + \bigvee_{N} \stackrel{\circ}{\longrightarrow} \stackrel{\circ}{\underset{O^{-}S \sim O}{\overset{\circ}{\longrightarrow}}} \xrightarrow{\text{pyridine}}_{30^{\circ}C, 24 \text{ h}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{O}{\overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{N}{\overset{\circ}{\longrightarrow}}} \xrightarrow{\text{KOH (resin)}}_{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{O}{\overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}}} \stackrel{\circ}{\underset{R' \overset{\circ}{\longrightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\rightarrow}} \stackrel{\circ}{\underset{R' \overset{\circ}{\overset}}} \stackrel{\circ}{$$



Figure 1. General scheme for the synthesis of organosulfate, modified from Staudt et al.

- 605 (Staudt et al., 2014) and Hettiyadura et al. (Hettiyadura et al., 2015).

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623 (a)



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636 (d)



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638 Figure 2. The fragmentation (left) and mass spectra (right) of phenyl sulfate (a), benzyl sulfate

- 639 (b), hydroxyacetone sulfate (c), and glycolic acid sulfate (d).
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Figure 3. Typical chromatograms of organosulfates from the mixture of authentic standard solution and ambient $PM_{2.5}$ samples, measured with the UPLC-ESI-MS/MS method. Note: the intensity of benzyl sulfate and phenyl sulfate refers to the left Y axis and the intensity of hydroxyacetone sulfate and glycolic acid sulfate refers to right Y axis.





Figure 4. Time series of organosulfates (ng m⁻³), OC (µg m⁻³), SO₄²⁻ (µg m⁻³), and the fraction 649

of individual organosulfates in total sulfur and OC (a). The average concentrations of individual 650 organosulfates and the fractional contribution in total sulfur and OC during high and low 651 pollution days are also shown (b). 652