

1 **Organosulfates in atmospheric aerosol: synthesis and quantitative analysis of**
2 **PM_{2.5} from Xi'an, Northwest China**

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29
30 **Abstract**

31 The sources, formation mechanism and amount of organosulfates (OS) in atmospheric aerosol
32 are not yet well understood, partly due to the lack of authentic standards for quantification. In
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)
36 were used to quantify their ambient concentrations. The authentic standards and ambient
37 aerosol samples were analyzed using an optimized ultra performance liquid chromatography-
38 electrospray ionization-tandem mass spectrometric method (UPLC-ESI-MS/MS). The
39 recovery ranged from 80.4% to 93.2%, the limits of detection and limits of quantification
40 obtained were 1.1-16.7 pg m⁻³ and 3.4-55.6 pg m⁻³, respectively. Measurements of ambient
41 aerosol particle samples collected in winter 2013-2014 in urban Xi'an, northwest China, show
42 that glycolic acid sulfate (77.3 ± 49.2 ng m⁻³) is the most abundant species of the identified
43 organosulfates followed by hydroxyacetone sulfate (1.3 ± 0.5 ng m⁻³), phenyl sulfate (0.14 ±
44 0.09 ng m⁻³), and benzyl sulfate (0.04 ± 0.01 ng m⁻³). Except for hydroxyacetone sulfate, which

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.

48

49 **1 Introduction**

50 Atmospheric aerosol particles represent a highly complex blend of inorganic and organic matter
51 originating from a wide variety of both natural and anthropogenic sources. The organic fraction
52 typically constitutes 20-90% of the total submicron aerosol mass and is much less constrained
53 in terms of chemical composition than the inorganic fraction (Jimenez et al., 2009; Hallquist et
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
59 on climate and human health (Noziere et al., 2015).

60

61 Organosulfates are ubiquitous in atmospheric aerosol and have been detected in ambient aerosol
62 particles from America, Europe, Asia and the Arctic during the last decade (e.g. Surratt et al.,
63 2008; Iinuma et al., 2007; Stone et al., 2012; Hansen et al., 2014; Kourtchev et al., 2016; Surratt
64 et al., 2007). Due to the presence of the deprotonated functional group $R-O-SO_3^-$,
65 organosulfates are acidic and highly water soluble and therefore can enhance the aerosol
66 hygroscopicity. These characteristics, together with the light-absorbing property of
67 organosulfates, lead to potential impacts on climate (Lin et al., 2014).

68

69 Organosulfates are tracers of secondary organic aerosol (SOA) formation and have been
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,
78 isoprene-derived organosulfates (e.g. Kristensen et al., 2011; He et al., 2014; Liao et al., 2015;
79 Budisulistiorini et al., 2015). A recent study reported the formation of aromatic organosulfates
80 by photochemical oxidation of polycyclic aromatic hydrocarbons (PAHs) in the presence of
81 sulfate seed particles (Riva et al., 2016). Aromatic organosulfates have also recently been
82 observed in urban aerosol from different locations in Asia. The presence of aromatic
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
86 methylene groups ($C_8H_9SO_4^-$ and $C_9H_{11}SO_4^-$) in Lahore, Pakistan. Furthermore, Staudt et al.
87 (Staudt et al., 2014) synthesized phenyl sulfate, benzyl sulfate, 3- and 4-methylphenyl sulfate

88 and 2-, 3-, and 4-methylbenzyl sulfate and quantified them in aerosols collected in urban
89 samples from Lahore and Pasadena, USA as well as Nepal. Ma et al. (Ma et al., 2014) reported
90 the contribution up to 64% from aromatic organosulfates to the sum of identified organosulfates
91 in winter Shanghai, while Wang et al. (Wang et al., 2016) found aromatic organosulfates to
92 constitute less than 22% of the detected number of organosulfates in Shanghai, Nanjing, and
93 Wuhan.

94
95 Organosulfates have been estimated to contribute 5-10% of the organic mass in fine particles
96 in the USA (Tolocka and Turpin, 2012). However, quantification of organosulfates is a
97 challenging task due to the lack of authentic standards and incomplete understanding of the
98 sources, precursors and formation processes of organosulfates. To date, many studies of
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.,
101 2013; Staudt et al., 2014; Ma et al., 2014; Olson et al., 2011; Hettiyadura et al., 2017). Moreover,
102 several studies show that organosulfates are present as a wide range of species with individual
103 species such as the organosulfate derived from isoprene epoxydiols (IEPOX) contributing 0.2-
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
106 quantification purposes. For example, Olsen et al. (Olson et al., 2011) measured 0.4-3.8 ng m⁻³
107 lactic acid sulfate and 1.9-11.3 ng m⁻³ glycolic acid sulfate in samples of PM_{2.5} (particulate
108 matter with an aerodynamic diameter <2.5 μm) from the US, Mexico City, and Pakistan. Kundu
109 et al. (Kundu et al., 2013) measured monthly-average concentrations of benzyl sulfate ranging
110 from 0.05 to 0.5 ng m⁻³ in PM_{2.5} samples from Lahore, Pakistan. Staudt et al. (Staudt et al.,
111 2014) quantified benzyl sulfate ranging from 4 to 90 pg m⁻³ in PM_{2.5} samples from Lahore
112 (Pakistan), Godavari (Nepal), and Pasadena (California), while methylbenzyl sulfates, phenyl
113 sulfate, and methylphenyl sulfates were observed intermittently in these three locations.
114 Furthermore, Hettiyadura et al. (Hettiyadura et al., 2015) developed a hydrophilic interaction
115 liquid chromatography method using an amide stationary phase providing excellent retention
116 of carboxy-organosulfates and isoprene-derived organosulfates, which was validated using six
117 model organosulfates including aliphatic and aromatic organosulfates.

118
119 Previous field studies focusing on organosulfates were conducted mainly in Europe (e.g. Iinuma
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;
122 Nguyen et al., 2012; Worton et al., 2011), and only a few in China (He et al., 2014; Ma et al.,
123 2014). The particulate air pollution has been a serious environmental problem during recent
124 winters in China, characterized by high secondary aerosol concentrations including sulfate and
125 SOA (e.g. Huang et al., 2014; Elser et al., 2016; Wang et al., 2017). As organosulfates are
126 tracers for SOA, more studies on organosulfates will help to better understand and constrain
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.

129
130 In this study, nine organosulfate standards (phenyl sulfate, 3-methylphenyl sulfate, benzyl
131 sulfate, 2-methyl benzyl sulfate, 3-methyl benzyl sulfate, 2, 4-dimethyl benzyl sulfate, 3, 5-

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

141

142 **2 Material and methods**

143 2.1 Chemicals and synthesis

144 The chemicals used for the synthesis of organosulfates included hydroxyacetone (99%, Sigma
145 Aldrich), glycolic acid (99%, Sigma Aldrich), phenol (99.5%, Tic), benzyl alcohol (99.8%,
146 Aladdin, Shanghai, China), m-cresol (99%, Sigma Aldrich), sulfur trioxide pyridine complex
147 (98%, Sigma Aldrich), pyridine (99.9%, Sigma Aldrich), Dowex® 50WX8 (hydrogen form,
148 100-200 mesh, Sigma Aldrich). MilliQ water (18.2 MΩ) was used, and all other reagents were
149 analytical grade and used without further purification.

150

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

165

166 2.2 Characterization

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

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

188

189 2.3 PM_{2.5} samples

190 The 24-h integrated PM_{2.5} samples were collected on pre-baked (780 °C, 3 h) quartz-fiber filters
191 (8×10 inch, Whatman, QM-A, USA) using a high-volume sampler (Tisch, Cleveland, OH, USA)
192 at a flow rate of 1.05 m³ min⁻¹ from 18 December 2013 to 17 February 2014. After collection,
193 the filter samples were immediately wrapped in pre-baked aluminum foil and stored in a freezer
194 (below -20 °C) until analysis. The sampling site was located on the rooftop of the Institute of
195 Earth and Environment (~10 m above the ground), Chinese Academy of Sciences (IEECAS,
196 34.23°N, 108.88°E), which is surrounded by residential, commercial and trafficked areas.

197

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

220 kV, source temperature was 150 °C, desolvation temperature was 350 °C, desolvation gas (N₂)
221 flow rate at 800 L h⁻¹, cone gas (N₂) flow rate was 150 L h⁻¹, and collision gas (Ar) flow rate
222 was 0.16 mL min⁻¹. All data were acquired and processed using MassLynx software (version
223 4.1). All samples and standard spectra were background subtracted.

224

225 2.5 Quality control

226 For every 10 analyses, a procedural blank and a spiked sample—namely, real ambient samples
227 spiked with known amounts of a standard solution of organosulfates to be quantified were
228 measured to check for interference and cross-contamination. The external standard method was
229 used for quantitative determination of the analytes. The limits of detection are defined as the
230 minimum detectable peaks of individual species with a signal-to-noise (S/N) ratio of 3:1. The
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
233 known amounts of a standard solution of organosulfates. The differences between these two
234 measurements were divided by the amounts of organosulfates spiked to calculate the recoveries
235 of individual organosulfates. This recovery test also provides an indication of potential matrix
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
238 samples were collected and analyzed, and the data reported here were corrected for the field
239 blanks.

240

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
244 molecular ion for each organosulfate was assigned to the deprotonated molecule (R–O–SO₃⁻).
245 Major sulfur-containing product ions included the sulfite ion radical ($\cdot\text{SO}_3^-$, m/z 80) that is
246 formed from the homolytic cleavage of the O–S bond, the sulfate ion radical ($\cdot\text{SO}_4^-$, m/z 96)
247 that is formed from the homolytic cleavage of the C–O bond, the bisulfite anion (HSO₃⁻, m/z
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
250 glycolic acid sulfate produce phenoxide (C₆H₅O⁻, m/z 93), 3-methylphenoxide (C₇H₇O⁻, m/z
251 107) and glycolate (C₂H₃O₃⁻, m/z 75) anions, respectively, formed from neutral loss of SO₃. The
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
254 sulfate and glycolic acid sulfate are similar to those reported by Hettiyadura et al. (Hettiyadura
255 et al., 2015) and the spectrum of benzyl sulfate is similar to that reported by Kundu et al. (Kundu
256 et al., 2013), confirming the identity of the compounds.

257

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

264 dipole interactions. A gradient elution procedure was applied and the aqueous portion of the
265 mobile phase increased from 7-43%, leading to the baseline separation of four organosulfates
266 within 6 min (Fig. 3a). The retention time was 0.86 min for phenyl sulfate, 0.96 min for benzyl
267 sulfate, 1.10 min for hydroxyacetone sulfate and 5.78 min for glycolic acid sulfate, respectively.
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
271 for those containing carboxyl and hydroxyl functional groups. It should be noted that the
272 chromatographic peak-broadening occurred particularly for phenyl sulfate and hydroxyacetone
273 sulfate when analyzing the ambient samples (Fig. 3b). This might be explained by matrix effects
274 due to the complex samples, which can influence the partitioning of analyte between the
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
277 because the transition pair of precursor and product ions used in the MRM mode of the mass
278 spectrometer guarantees selectivity and accuracy.

279

280 3.2 Method validation

281 Table 2 shows the analytical performance of the method under optimized UPLC and MS/MS
282 conditions. The calibration curves of each organosulfates are highly linear ($R^2 \geq 0.995$), ranging
283 from 0.1-40 ng mL⁻¹ for phenyl sulfate and benzyl sulfate, from 0.3-120 ng mL⁻¹ for
284 hydroxyacetone sulfate, and 2.0-800 ng mL⁻¹ for glycolic acid sulfate. The recoveries,
285 determined by analyzing ambient samples spiked with known amounts of organosulfate
286 standards, ranging from 80.4-93.2%. The good recoveries indicate high extraction efficiency,
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)
289 ranged from 0.03 to 0.42 ng mL⁻¹ and 0.09 to 1.4 ng mL⁻¹ of the extracts, respectively. This
290 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
291 the current set-up (see experimental section).

292

293 3.3 Quantification of organosulfates in ambient aerosol

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

305

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

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

318

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

334

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

351

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355

356 **Reference**

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

| Organosulfate | Deprotonate molecule (<i>m/z</i>) | Product ion (<i>m/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 ₂ H ₃ SO ₆ ⁻ (155) | C ₂ H ₃ O ₃ ⁻ (75) HSO ₄ ⁻ (97) | 26 | 18 14 | 5.78 ± 0.03 |

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

| Organosulfate | Linear range (ng mL ⁻¹) | Linearity (R ²) | Recovery % | LOD (pg), injection volume (5 μL) | LOQ (pg), injection volume (5 μL) | LOD* (pg m ⁻³) | LOQ* (pg m ⁻³) |
|---------------------------|--|--------------------------------|---------------|--|---|-------------------------------|-------------------------------|
| 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 sulfate | 0.3-120 | 0.997 | 93.2 | 2.1 | 6.9 | 16.7 | 55.6 |
| Glycolic acid sulfate | 2-800 | 0.995 | 92.0 | 0.27 | 0.88 | 2.1 | 7.1 |

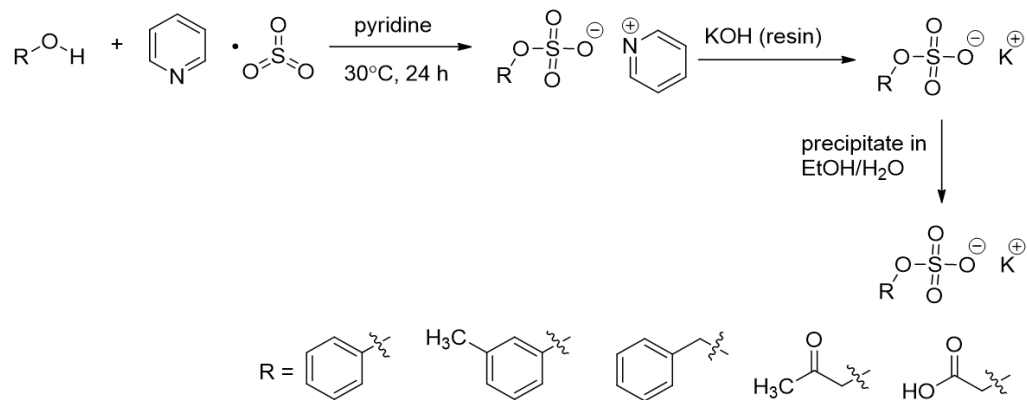
560 *For analyzing 6×0.526 cm punches of filters collected with high-volume samplers (sampling
 561 at 1.13 m³ min⁻¹ for 24 h on 8”×10” filters).

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592 Table 3. The quantification of organosulfates at Xi'an and comparison with data reported in the
 593 literature

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

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599 Figure 1. General scheme for the synthesis of organosulfate, modified from Staudt et al.
 600 (Staudt et al., 2014) and Hettiyadura et al. (Hettiyadura et al., 2015).

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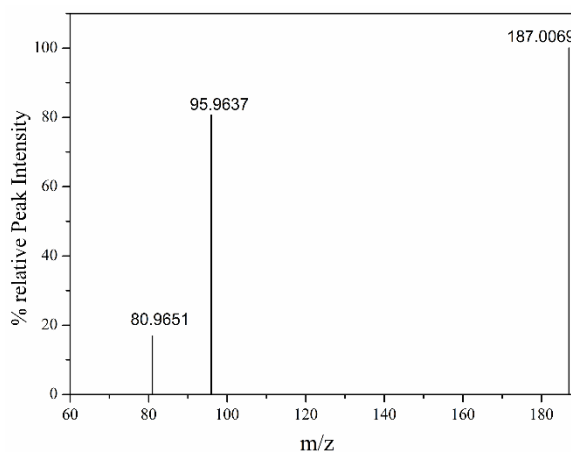
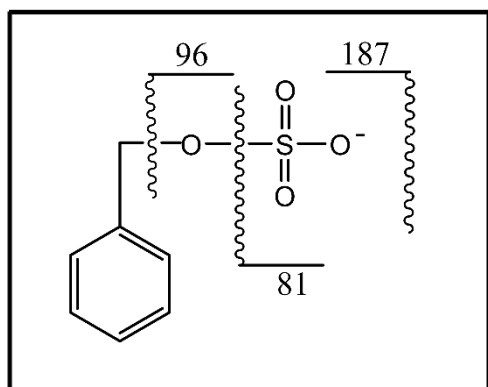
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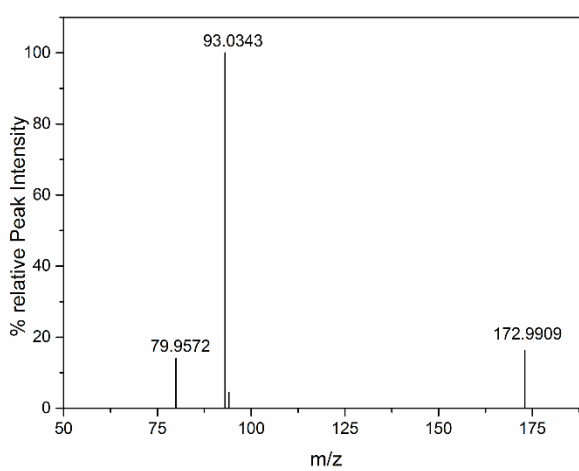
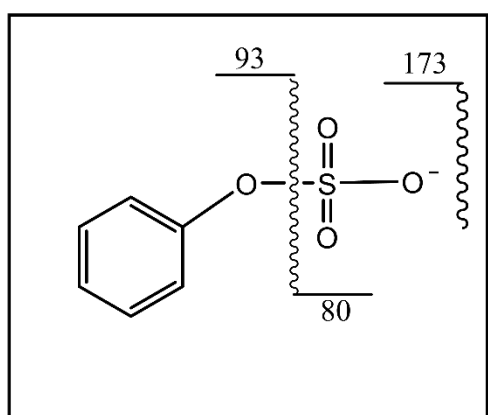
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618 (a)



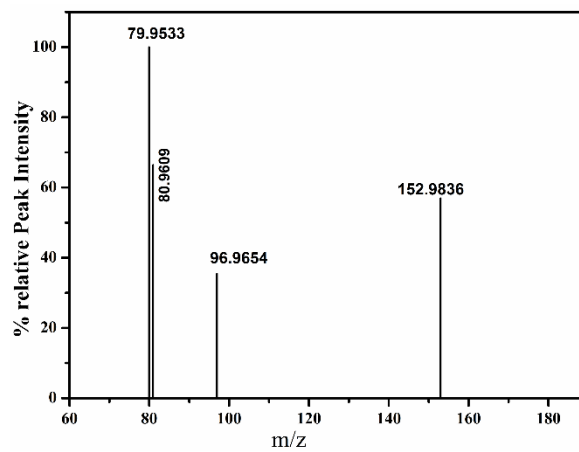
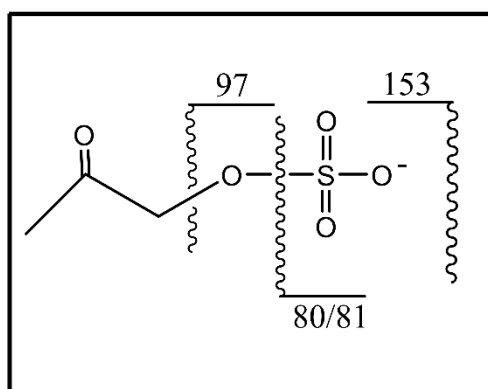
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(b)



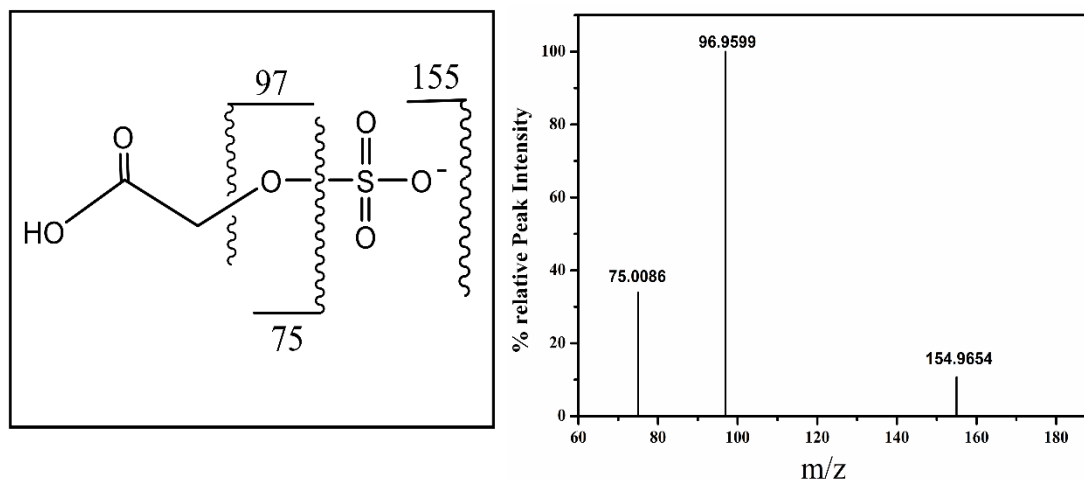
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(c)



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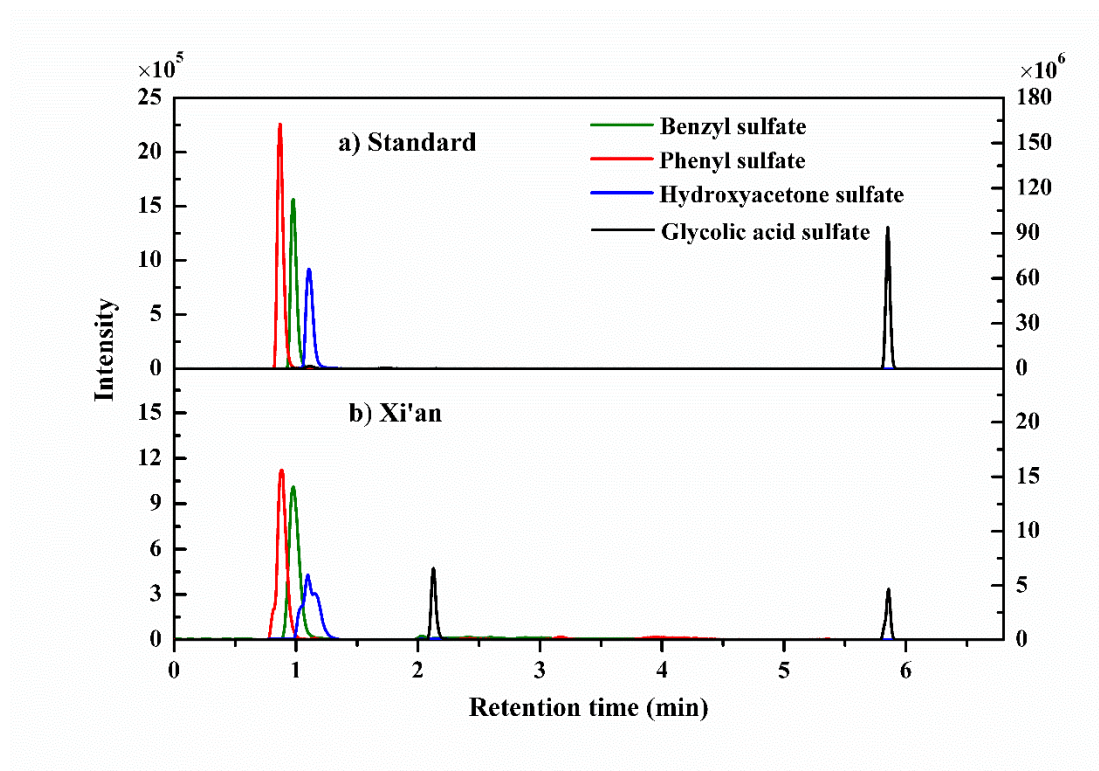
631 (d)



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633 Figure 2. The fragmentation (left) and mass spectra (right) of benzyl sulfate (a), phenyl sulfate
634 (b), hydroxyacetone sulfate (c), and glycolic acid sulfate (d).

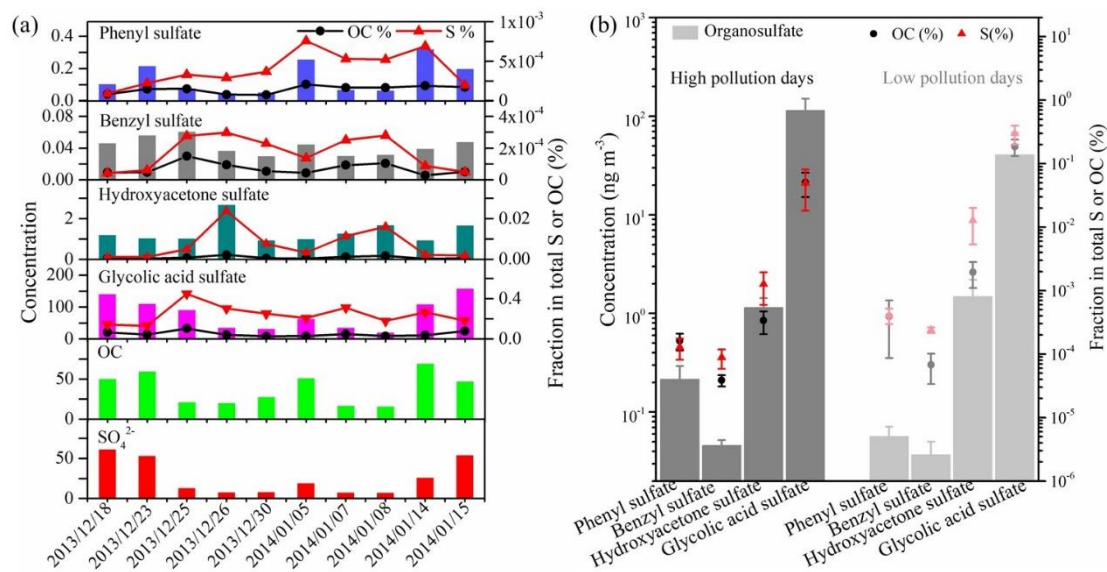
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637 Figure 3. Typical chromatograms of organosulfates from the mixture of authentic standard
638 solution and ambient PM_{2.5} samples, measured with the UPLC-ESI-MS/MS method. Note: the
639 intensity of benzyl sulfate and phenyl sulfate refers to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

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644 Figure 4. Time series of organosulfates (ng m⁻³), OC (μg m⁻³), SO₄²⁻ (μg m⁻³), and the fraction
 645 of individual organosulfates in total sulfur and OC (a). The average concentrations of individual
 646 organosulfates and the fractional contribution in total sulfur and OC during high and low
 647 pollution days are also shown (b).