1	Molecular Characterization of Atmospheric Particulate
2	Organosulfates in Three Megacities at the Middle and Lower
3	Reaches of the Yangtze River
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Abstract. $PM_{2.5}$ filter samples have been collected in three megacities at the middle 16 and lower reaches of the Yangtze River: Wuhan (WH), Nanjing (NJ), and Shanghai 17 The samples were analyzed using ultra-high-performance 18 (SH). liquid chromatography (UHPLC) coupled with Orbitrap mass spectrometry (MS), which 19 allowed for detection of about 200 formulas of particulate organosulfates (OSs), 20 including dozens of formulas of nitrooxy-organosulfates, with various numbers of 21 isomers for each tentatively determined formula at each location. The number of 22 23 aliphatic OS formulas represented more than 78% of the detected OSs at the three locations, while aromatic OSs were much less numerous. OSs with two to four 24 isomers accounted for about 50% of the total OSs on average in these megacity 25 samples, and the percentage of OSs with six and more isomers in WH sample was 26 more significant than those in SH and NJ samples. Additionally, the molecular 27 formula, average molecular weight, and degrees of oxidation and unsaturation of 28 tentatively assigned OSs were compared. The results indicate that the OSs between 29 NJ and SH shared higher similarity, and the characteristics of OSs in SH varied 30 diurnally and seasonally. OSs derived from isoprene, monoterpenes, and 31 sesquiterpenes were abundant in samples from the three megacities and could be 32 produced through both daytime photochemistry and NO₃ night-time chemistry. The 33 reaction pathways leading to isoprene-derived OSs probably varied in those locations 34 because of the different NO_x levels. In addition, a number of OSs that might be 35 formed from polycyclic aromatic hydrocarbons were also detected, which underlies 36 the importance of anthropogenic sources for this class of compounds. 37

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40 **1. Introduction**

Atmospheric aerosols can scatter and absorb sunlight and provide cloud 41 condensation nuclei. Hence, they have significant impacts on air quality and climate 42 (Andreae and Crutzen, 1997; Hallquist et al., 2009). Aerosol particles contain a large 43 fraction of toxic chemical substances and are harmful to human health (Magari et al., 44 2002; Ostro et al., 2007). Organosulfates (OSs)-i.e., sulfate esters and their 45 derivatives formed from atmospheric heterogeneous and multiphase chemical 46 47 reactions (Ma et al., 2012)—are a class of organic compounds that contribute to the total abundance of atmospheric aerosol particles (Tolocka and Turpin, 2012). 48

Surratt et al. (2007) were the first to identify isoprene- and α -pinene-derived OSs in 49 ambient aerosols in the southeast US using high-performance liquid chromatography 50 coupled with electrospray mass spectrometry. Since then, tremendous progress has 51 been made in the understanding of the formation mechanisms of OSs. Experimental 52 studies show that isomeric isoprene epoxydiols (IEPOX) and methacrylic acid 53 epoxide (MAE) are formed during the oxidation of isoprene under low- and high-NO_x 54 conditions, respectively. Subsequent acid catalyzed-reactions of IEPOX and MAE in 55 the presence of sulfates can lead to the formation of OSs (Darer et al., 2011; Lin et al., 56 2012c; Lin et al., 2013; Surratt et al., 2010; Paulot et al., 2009). OSs can be formed 57 from reactions between α-pinene and OH radicals, NO₃ radicals, and O₃ in the 58 presence of sulfates, from β -pinene under high-NO_x conditions, from ozonolysis and 59 photochemical reactions of other monoterpenes (α -terpinene and γ -terpinene), and 60 from sesquiterpene (i.e., β -caryophyllene) under acidic conditions (Surratt et al., 2008; 61 Iinuma et al., 2007a; Iinuma et al., 2007b; Chan et al., 2011). Sulfate/sulfite 62 radical-induced oxidation reactions with unsaturated organic compounds including 63 isoprene, methyl vinyl ketone, methacrolein, and α -pinene in the aqueous phase 64 represent another potential formation route of OSs (Szmigielski, 2015; Rudzinski et 65 al., 2009; Noziere et al., 2010; Schindelka et al., 2013). In addition, both reactive 66 uptake of carbonyl compounds on sulfuric acid or sulfates (Liggio et al., 2005) and 67 hydrolysis reactions of organonitrates can lead to formation of OSs (Darer et al., 2011; 68 Hu et al., 2011). Very recently, OSs and sulfonates were revealed to form from 69

photo-oxidation of polycyclic aromatic hydrocarbons (PAHs) in the presence of
sulfate seed (Riva et al., 2015b).

Identification and quantification of OSs in atmospheric particulate samples have 72 been widely performed around the world (e.g., Kristensen and Glasius, 2011; Stone et 73 al., 2009; Olson et al., 2011; Zhang et al., 2012). Many studies indicate that the total 74 abundance of OSs varies from one region to another. OSs accounted for about 4% of 75 the total organic mass in ambient aerosols over the southeast Pacific Ocean (Hawkins 76 77 et al., 2010), whereas this contribution was estimated to be about 30% at the forested site of K-puszta in Hungary during summer (Surratt et al., 2008). The abundance of a 78 given OS also shows clear variation between different sampling locations. The level 79 of four aromatic OSs was estimated to be 234.4 pg m⁻³ in atmospheric PM_{2.5} in 80 Pakistan, which were much more abundant than those in California (8.9 pg m⁻³) or 81 Nepal (3.9 pg m⁻³) (Staudt et al., 2014). 82

In a given location, there are seasonal variations of OSs. For example, the 83 α -pinene-related nitrooxy-OSs were detected at high concentrations during the winter 84 85 period, followed by autumn, spring, and summer at a rural background site in Hamme, Belgium (Kahnt et al., 2013). Ma et al. (2014) also showed that the total mass 86 concentration of 17 OSs was the highest in summer and lowest in winter, while no 87 clear seasonal trend was observed in the mass concentration of benzyl sulfate (BS). 88 However, BS showed the highest concentration in winter and the lowest one in 89 summer in Lahore, Pakistan (Kundu et al., 2013), which underlies the role of both 90 regional constraints and meteorological conditions. 91

Recently, ultra-high-resolution mass spectrometry has been applied for tentative 92 determination of the molecular formulas of OSs in atmospheric aerosols samples. 93 Owing to the high mass resolution and mass accuracy of the ultra-high-resolution 94 mass spectrometer, the molecular formulas of analytes can be tentatively determined 95 without the authentic standards required with low-resolution mass spectrometers. Lin 96 et al. (2012a, 2012b) studied aerosols sampled at a rural location of the Pearl River 97 Delta Region in China and suggested that the arbitrary signal intensities of OSs 98 obtained from the humic-like fraction are often the strongest in the electrospray 99

ionization ultra-high resolution mass spectra, and that the degrees of oxidation of OSs 100 and nitrooxy-OSs are quite high. Using a similar approach, O'Brien et al. (2014) 101 showed that a significant portion of OSs was formed from biogenic precursors 102 through the epoxide pathway in Bakersfield, CA, USA. In addition, by using a 103 mixture of acetonitrile and toluene instead of a mixture of acetonitrile and water as the 104 working solvent for nano-DESI ionization, Tao et al. (2014) tentatively determined 105 many OSs with long aliphatic carbon chains and low degrees of oxidation and 106 107 unsaturation, which were presumably formed from anthropogenic precursors emitted by cars in Shanghai (SH). 108

Although it has been accepted that OSs are an important component of ambient 109 particulate matter, studies on their characteristics are rather sparse in China, especially 110 in the Yangtze River region. Ma et al. (2014) identified and quantified 17 OSs in SH. 111 As mentioned, Tao et al. (2014) compared OS characteristics such as the degrees of 112 oxidation and saturation between samples from SH and Los Angeles. While SH has 113 been a relative hotspot for OS characterization, the characteristics of OSs in the 114 115 general Yangtze River region have yet to be elucidated. Wuhan (WH), Nanjing (NJ), and SH are three megacities at the middle and lower reaches of the Yangtze River 116 with populations of over 10, 8, and 24 million, respectively (as of 2014). Tremendous 117 amounts of energy are consumed owing to the large population and rapid economic 118 development, leading to extensive emissions of anthropogenic pollutants including 119 particulate matter, volatile organic compounds (VOCs), sulfur dioxide, and nitrogen 120 oxides (Huang et al., 2011; Wang et al., 2013). At the same time, these three cities are 121 located in the subtropical zone with high emissions of biogenic VOCs (Guenther et al., 122 1995). Hence, substantial amounts of OSs are likely to exist in WH, NJ, and SH 123 aerosol particles. In this study, OSs, including nitrogen-containing OSs, were 124 specifically searched for in WH, NJ, and SH PM_{2.5} samples using an UHPLC coupled 125 to an Orbitrap-MS. Characteristics of OSs including the molecular formula, number 126 of isomers, molecular weight, and the degrees of oxidation and unsaturation were 127 analyzed and compared. The potential precursors in the megacities are also discussed. 128

130 2. Material and methods

131 2.1 Collection of PM_{2.5} samples

Eight PM_{2.5} samples were collected at three locations: two in WH, two in NJ, and 132 four in SH, as shown in Figure 1 and Table 1. Samples covering 24 h were collected 133 in WH from January 26 to 27 (sample ID: WH winter, WHW) and from June 15 to 16, 134 2012 (sample ID: WH summer, WHS). The WH site was located on the rooftop of a 135 dormitory building (30°29'N, 114°24'E) that is about 20 m above ground at 136 137 ZhongNan University of Economics and Law near a commercial street. NJ samples were collected from August 29 to 30, 2012, for 12 h for each sample (samples ID: NJ 138 summer daytime, NJSD; NJ summer nighttime, NJSN). The NJ site was located in the 139 Chinese national meteorology observatory facility at the Nanjing University of 140 Information Science and Technology (32°12'N, 118°42'E), which is about 15 km 141 north of the downtown area and about 2 km west of clusters of steel mills and 142 petrochemical refinery facilities (Zheng et al., 2015). 143

SH samples were collected for 12 h from January 17 to 18, 2013 (sample ID: SH winter daytime, SHWD; SH winter nighttime, SHWN), and July 28 to 29, 2013 (sample ID: SH summer daytime, SHSD; SH summer nighttime, SHSN). The SH site was located on the rooftop of a teaching building at Fudan University (31°18′N,

121°30′E) about 20 m above ground with surrounding residential and commercial
properties and a major highway to the south of the site (Xiao et al., 2015; Ma et al.,
2014). Table S1 provides a comparison of air quality and meteorological conditions
between the sampling days and the seasonal average in SH.

PM_{2.5} was collected on 90 mm quartz-fiber filters (Whatman Company, UK) using a middle-flow impact aerosol sampler (Qingdao Hengyuan Tech Co., Ltd., HY-100) operating at 100 lpm. All filters were prebaked at 500°C for 5 h to remove residual organics before use. After sample collection, filters were wrapped in prebaked aluminum foil and stored at -20°C before further analysis.

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158 2.2 Sample analysis

159 One-fourth of each filter was put into an amber vial with 6 mL of methanol

(Optima[®] LC/MS, Fischer Scientific, UK) and shaken for 20 min on an orbital shaker 160 set to 1000 rpm. The extract was then filtered through a glass syringe on a 0.2µm 161 PTFE membrane (13 mm, Pall Corporation, USA). These two steps were performed 162 twice, and the extracts of each filter were recombined and blown almost to dryness 163 under a gentle stream of nitrogen. The extracts were then reconstituted in 1 mL of a 164 1:1 v/v mixture of water (Optima[®] LC/MS, Fischer Scientific, USA) and acetonitrile 165 (Optima[®] LC/MS, Fischer Scientific, USA). For the analysis, 100 µL of the final 166 167 reconstituted extract was diluted by adding 100 µL of water. 5µL of these diluted solutions (50 µL in the case of the NJSD sample) were analyzed by UHPLC (Dionex 168 3000, Thermo Scientific, USA) coupled to a Q-Exactive Hybrid Quadrupole-Orbitrap 169 MS (Thermo scientific, USA). The efficiency and the repeatability on three replicates 170 of the extraction protocol were checked using four standards: methyl sulfate, octyl 171 sulfate, dodecyl sulfate, and camphor sulfonic acid. The results showed that their 172 average extraction efficiencies were 71.4, 95.0, 97.7, and 94.0%, respectively (Table 173 S2). Analytical replicates were not considered because the final sample extract 174 175 volume was quite low (200 μ L), and the remaining volume after the first injection was preferentially kept in case of specific analytical doubt rather than systematically 176 injected. 177

Analytes were separated using a Waters Acquity HSS T3 column (1.8µm, 178 100×2.1 mm) with mobile phases consisting of (A) 0.1% formic acid in water 179 (Optima[®] LC/MS, Fischer Scientific, USA) and (B) 0.1% formic acid in acetonitrile 180 (Optima[®] LC/MS, Fischer Scientific, USA). The concentration of eluent B was 181 initially kept at 1% for 2 min, then increased to 100% in 11 min, kept at 100% for 2 182 min, decreased to 1% in 0.1 min, and kept at 1% for 6.9 min. The Q-Exactive Hybrid 183 Quadrupole-Orbitrap mass spectrometer was equipped with a heated electrospray 184 ionization source. It was operated in the negative ion mode with a spray voltage of 185 -3.0kV, a mass resolving power of 140 000 at m/z 200, and a scanning range of 50-186 750 m/z. The Q-Exactive mass spectrometer was externally mass calibrated daily 187 using a 2 mM sodium acetate solution that provides a series of negative adduct ions in 188 the range of 50-750 m/z. 189

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191 2.3 Data processing

The obtained chromatograms were analyzed with Progenesis QI software (V1.0, 192 Waters Corporation) by assuming that the extracted ions in the range of 50-750 m/z193 [M-H] were formed from loss of a proton from the analytes. In contrast to direct 194 separation provides meaningful help in distinguishing 195 infusion, the LC quasi-molecular ions and potential in-source formed adducts for the same 196 197 chromatographic retention time. A molecular formula calculator was then used to mathematically assign all possible formulas for an extracted quasi-molecular ion with 198 a mass tolerance of ± 2 ppm. These molecular formulas can be expressed as 199 $C_cH_hO_0N_nS_s$, where c is the number of carbon atoms in the range of 1–40, h is the 200 number of hydrogen atoms in the range of 2–80, o is the number of oxygen atoms in 201 the range of 0–40, n is the number of nitrogen atoms in the range of 0–3, and s is the 202 number of sulfur atoms in the range of 0-2. Formulas were further constrained by 203 setting H/C, O/C, N/C, S/C, and double bond equivalent to carbon number ratios 204 205 (DBE/C) in the ranges of 0.3-3.0, 0-3, 0-0.5, 0-0.2, and 0-1, respectively. This was done to ensure that the retrieved molecular formula do exist in nature (Fuller et al., 206 2012; Lin et al., 2012a; Lin et al., 2012b). 207

The number of ions with more than one reasonable formula within 2 ppm mass 208 tolerance accounted only for 1.5% of the total number of tentatively determined ions, 209 and the formulas with the best accuracy are listed in Table S3. The peak intensities of 210 isotopically substituted ions were constrained by their low abundance and were hence 211 not systematically checked. Compounds that satisfy these criteria and present a 212 213 number of oxygen atoms greater than or equal to 4s+3n ($4s+3n\leq 0$) were tentatively 214 regarded as OSs or nitrooxy-OSs. However, tandem MS experiments were not conducted on the S- and N-containing ions detected in these eight ambient samples. 215 Therefore, other S- and N-containing compounds, such as sulfonates or compounds 216 bearing nitro groups, may also be involved (e.g., Riva et al., 2015b; El Haddad et al., 217 218 2013) due to the lack of using tandem MS experiments to provide insights into the structures of these ions. 219

In this study, the abundance of an OS refers to the area of its chromatographic peak, 220 and the number of isomers for an OS is based on the number of chromatographic 221 peaks observed for given m/z values. Note that the obtained number of isomers may 222 vary significantly when the separation method is further optimized. Then, the 223 arbitrary abundances of all isomers for a given m/z value are added up. The arbitrary 224 abundance of the most abundant OS or nitrooxy-OS in each sample is defined as 225 100%, and only OSs and nitrooxy-OSs with an arbitrary abundance larger than 0.5% 226 227 of the most abundant one in the same sample are presented. The signal-to-noise ratios of the least abundant OSs in each sample are greater than 10 with a noise level of ca. 228 1×10^4 arbitrary units. Note that the arbitrary abundance of a given OS does not 229 directly reflect its concentration compared to others in the same sample because the 230 ionization efficiency is compound and solvent specific in electrospray ionization. Also, 231 similar ionization efficiency is assumed for a given OS in different samples as similar 232 retention times are observed and as UHPLC separation resolves most of the matrix 233 components. 234

Blank filters were processed and analyzed in an identical way, and blank correction was made as follows. The presence of targeted quasi-molecular ions in the blanks was systematically verified, and if a chromatographic peak was indeed detected, then it was retained (i.e., considered as real) only if the sample-to-blank ratio of the peak area was greater than 10, with the blank value being subtracted prior to further processing. The DBE value of a molecule reflects the degree of its unsaturation. The DBE value is usually calculated as:

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$$DBE = \frac{2c+2+n-h}{2}$$
 (Eq. 1)

Not taking into account the two double bonds involved in each sulfate group, the DBE values of OSs calculated by Eq. 1 represent the unsaturation degree of the side carbon chain (eventually bearing oxygen and nitrogen atoms). In addition, one can note that this equation adds one DBE unit for each nitrate group. Molecular formulas with DBE<0 and formulas that disobey the nitrogen rule were discarded. The difference between the DBE value and the number of N atoms (DBE-n) is the most conservative criterion to determine whether a compound is aliphatic: the number of OSs with
(DBE-n) < 4 can be regarded as the minimum number of aliphatic OSs (Lin et al.,
2012b).

Both DBE/C and the aromaticity index (AI) could be used as criteria to determine whether a compound contains aromatic rings with thresholds of DBE/C > 0.67 and AI > 0.5, respectively. However, AI is more conservative (Koch and Dittmar, 2006). The value of AI can be calculated according to:

$$AI = \frac{DBE_{AI}}{C_{AI}} = \frac{1+c-o-s-(0.5h)}{c-o-s-n}$$
 (Eq. 2)

where DBE_{AI} represents the sum of the minimum number of C=C double bonds and the number of rings in a formula containing heteroatoms, and C_{AI} represents the difference between the number of carbon and the number of potential double bonds caused by heteroatoms. If DBE_{AI} ≤ 0 or C_{AI} ≤ 0 , then AI is defined to be zero. In contrast, AI>0.5 and AI ≥ 0.67 indicate the existence of aromatic and fused aromatic ring structures in a compound, respectively (Koch and Dittmar, 2006).

In the Kendrick mass defect diagram (KMD diagram), CH₂ (14.00000) was chosen as a base unit. The Kendrick mass (KM_{CH2}) and the Kendrick mass defect (KMD_{CH2}) can be determined by Eq. 3 and Eq. 4, respectively:

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$$\text{KM}_{\text{CH}_2} = \text{Observed Mass} \times \left(\frac{14.00000}{14.01565}\right) \text{ (Eq. 3)}$$

267 $\text{KMD}_{\text{CH}_2} = \text{Nominal Mass} - \text{KM}_{\text{CH}_2} \text{ (Eq. 4)}$

where "Observed Mass" is the mass measured by the mass spectrometer, and "Nominal Mass" is the rounded integer mass of a compound.

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271 **3. Results and discussion**

272 3.1 Isomers

UHPLC separation was applied prior to MS analysis for detection of potential isomers hidden behind a given m/z value and to provide another dimension of the ambient aerosol composition complexity. As an example, Figure 2 shows the extracted ion chromatograms for $C_5H_{10}O_5S$. An OS with this molecular formula has recently been identified in laboratory-generated secondary organic aerosols either

from the ozonolysis of isoprene in the presence of sulfate aerosols or from the 278 transformations of isoprene coupled with S(IV)-autoxidation in the aqueous-phase, 279 but only one and two isomers were detected by UPLC-high-resolution MSs, 280 respectively (Riva et al., 2015a; Szmigielski, 2015). From our ambient samples, 11 281 isomers were detected in total, with varying numbers of isomers in each sample (see 282 Figure 2 and Table S3). On the other hand, only two isomers were detected in the 283 ambient PM_{2.5} samples from Diabla Gora rural site (Szmigielski, 2015). The reason 284 285 for this difference in the number of isomers among these studies might arise from the different chromatographic conditions and additional precursors, including different 286 terpenes. In addition, it is difficult to assign which isomer has been detected by Riva 287 et al. (2015a) and Szmigielski (2015) due to different chromatographic conditions and 288 detectors. 289

Additional extracted ion chromatograms are presented in the supplement for 290 C5H12O7S1, C10H17O7N1S1, and C16H32O6S1 (Figure S1). Two and four isomers were 291 detected for $C_5H_{12}O_7S_1$ and $C_{10}H_{17}O_7N_1S_1$, respectively, whereas Surratt et al. (2008) 292 293 detected one and six isomers for these OSs, also from ambient samples. A thorough analysis of UHPLC-Orbitrap MS data leads to the tentative determination of more 294 than 100 CHOS formulas and dozens of CHONS formulas, with various numbers of 295 isomers in each sample. The full list of the neutral mass, molecular formula, number 296 of isomers, retention times, and potential precursors for these assigned OSs is 297 tabulated in Table S3. Having access to the isomeric pattern of significant OSs could 298 be very helpful in the future for identifying possible OS sources. Thus, Table S3 299 provides one of the first data sets of OS isomers in ambient samples. 300

The full mass spectra in summer samples from the three megacities, including all tentatively assigned OSs, have been reconstructed to present the samples' general characteristics. In Figure 3, the X-axis corresponds to the neutral molecular weight of detected OSs, the Y-axis represents their arbitrary abundances, and the number of isomers per detected mass is color-coded. Comparison of the reconstructed mass spectra shows that the number of OSs with an identical formula and the same number of isomers that could be observed in all three megacities accounted for only 17.6% of

all the tentatively assigned OS molecular formulas. Between WHS and NJSN, the 308 proportion of OSs sharing identical formulas reached 50.3%, but only 27.9% also 309 possessed the same number of isomers. Quite similarly, between NJSN and 310 SHSD+SHSN, the proportion of OSs sharing identical formulas reached 62.8%, but 311 only 39.4% also had the same number of isomers. Between WHS and SHSD+SHSN, 312 this proportion reached 51.5%, with only 32.3% having the same number of isomers. 313 Therefore, one can consider that the samples from NJ and SH showed greater 314 similarity, especially from their isomeric patterns. This observation is in agreement 315 with the proximity of the two megacities compared to the more distant megacity of 316 WH. 317

As shown in Figure 3, OSs with two to four isomers accounted for about 50% of the total detected OSs. Those with more than six isomers accounted for the largest proportion, and OSs with one isomer were insignificant in WH. In contrast, in SH and NJ, OSs with one isomer only were preponderant, while those with more than six isomers were much less numerous. Clearly, the isomeric pattern differs significantly in WH compared to the other two megacities, probably due to the diversity in precursors and/or oxidation mechanism.

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326 3.2 Tentative assignment and potential precursors of major OSs

The gaseous precursors of many OSs in Figure 3 can be tentatively assigned, since 327 identical formulas of OSs have been observed in chamber studies. In Figure 3, OSs 328 with strong arbitrary intensities have been labeled with a letter as follows: A: 329 C5H8O3SO4; B: C5H12O3SO4; C: C6H10O3SO4; D: C7H12O3SO4; E: C9H18O2SO4; F: 330 C5H11O2NO3SO4; G: C9H16O3SO4; H: C10H17NO3SO4; I: C5H10O1(NO3)2SO4; J: 331 C16H32O2SO4; and K: C15H25NO3SO4. Among these OSs, A, C, D, and G are a series 332 of homologues, and so are E and J. A, B, F, and I could be derived from isoprene, 333 whereas D and G could be derived from limonene, C from 3-Z-hexenal, K from 334 β -caryophyllene, and H from various monoterpenes (i.e., α -pinene, β -pinene, 335 α-terpinene and terpinolene) (Chan et al., 2011; Shalamzari et al., 2014; Surratt et al., 336 2008; Gomez-Gonzalez et al., 2008). E and J were characterized by high molecular 337

weights and degrees of saturation, presumably being long-chain aliphatic OSs. In
general, many abundant OSs could be derived from isoprene, monoterpenes, and
sesquiterpenes in these three megacities.

The relative abundance of J was the highest in WH but much lower in NJSN and 341 SHSD+SHSN samples. H was the highest in the SHSD+SHSN samples, while I was 342 the most abundant in the NJSN sample. It is doubtless that I bears two nitrate groups 343 (two nitrogen atoms in its formula that fulfill the 4s+3n≤o rule) and is the most 344 345 abundant in the NJSN sample, likely due to active NO3 radical chemistry at night. F and K, which bear one nitrate group, were also guite abundant in the NJSN sample, 346 underlying the role of NO₃ chemistry at night. The isomer ratios vary from sample to 347 sample and therefore certainly carry information about their origin. These ratios and 348 possible VOC precursors for these most abundant OSs are summarized in Table S4. 349

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351 3.3 Comparison of OS characteristics

Table 1 summarizes the average characteristics (molecular weight, DBE, and 352 353 elemental ratios) of tentatively assigned CHOS and CHONS compounds. These CHOS and CHONS compounds were here tentatively regarded as organosulfates and 354 nitrooxy-organosulfates respectively, but other S- and N- containing functional groups 355 could be involved as well in small amount (Lin et al., 2012b). In addition, (o-3s)/c 356 (Tao et al., 2014) and (o-3s-2n)/c have been calculated to illustrate the number of 357 oxygen-containing functional groups per carbon atom. These two values are derived 358 from the fact that each sulfate and nitrate group respectively contains three and two 359 oxygen atoms more than do common oxygen-containing groups, such as a hydroxyl 360 or a carbonyl moiety. (0-3s)/c and (0-3s-2n)/c can therefore be regarded as measures 361 of the degree of oxidation of CHOSs and CHONS compounds, respectively. 362

The average molecular weight and DBE value of CHONS species were generally larger than those of CHOS analogues, because CHONS contains one or two more nitrate groups (the presence of one nitrate group adding one DBE unit). Measurement of the O/C ratio of OSs in Bakersfield (CA, USA) indicated that the degree of oxidation of CHONS was larger than that of CHOS throughout the day (O'Brien et al.

2014). A similar trend has been observed for $CHONS_1$ and $CHOS_1$ in SH and Los 368 Angeles aerosol samples but using the (o-3)/c ratio to measure the degree of oxidation 369 (Tao et al., 2014). In this study, however, the average degree of oxidation of CHONS 370 was only slightly larger than that of CHOS during the daytime and slightly smaller at 371 night. The use of the (0-3s)/c and (0-3s-2n)/c ratios to evaluate the degrees of 372 oxidation of the CHOS and CHONS carbon chain, respectively, allows for precise 373 comparison of the oxidation states of these two classes of compounds. The values of 374 375 the oxidation states for OSs and nitrooxy-OSs on a same sample (0.01 to 0.14 units of difference) suggest that the presence of the sulfate and/or nitrate groups is not 376 determinant. 377

The OSs with (DBE-n) < 4 accounted for 86.2, 78.5, and 78.3% of total OSs in WH, NJ, and SH, respectively, suggesting tentatively assigned OSs were mainly aliphatic OSs. Also, the number of OSs with (DBE-n) \ge 4 can be regarded as the maximum number of aromatic OSs. This value appears to be slightly higher in SH (21.7%) and NJ (21.5%) compared to WH (13.8%), possibly indicating a slightly more significant anthropogenic influence for the first two cities.

The number of OSs with DBE/C > 0.67 accounted for 2.2, 5.2, and 7.1% of total OSs, and their abundance accounted for 0.6, 1.4, and 8.0% of total abundances of OSs in WHS, NJSD+NJSN, and SHSD+SHSN, respectively. Only a few aromatic OSs with AI > 0.5 were detected, but it could be due to the fact that this value takes into account carbon-bounded S and N but not sulfate and nitrate groups (and the related oxygen atoms), underestimating the aromatic ring content. BS and its analogues were nevertheless detected in most of the samples of the three megacities.

Figure 4 shows the CH₂-Kendrick diagrams and Van Krevelen (VK) diagrams for CHOS species for the WHS, NJSD+NJSN, and SHSD+SHSN samples, respectively, and the variation in DBE is color-coded. In the CH₂-Kendrick diagram, compounds in a homologue series of compounds with identical KMD_{CH2} values form a horizontal line. The molecular formula of the homologue series 1 and 2, which have DBE values equal to zero, can be written as $C_nH_{2n+2}SO_4$ and $C_nH_{2n+2}O_1SO_4$ (n>4), respectively. Hence, the OS in the homologue series 2 contained one more hydroxyl group or ether

group than the corresponding one in the homologue series 1. Similarly, molecular 398 formula of the homologue series 3, 4, and 7 with DBE=1 can be written as 399 C_nH_{2n}O₁SO₄, C_nH_{2n}O₂SO₄, and C_nH_{2n}O₃SO₄; those for series 6, 9, 11, and 13 with 400 DBE=2 can be written as CnH2n-2O2SO4, CnH2n-2O3SO4, CnH2n-2O4SO4, and 401 $C_nH_{2n-2}O_5SO_4$; and those for series 5, 8, 10, 12, 14, and 15 with DBE=3 can be written 402 as CnH2n-4O1SO4, CnH2n-4O2SO4, CnH2n-4O3SO4, CnH2n-4O4SO4, CnH2n-4O5SO4, and 403 $C_nH_{2n-4}O_6SO_4$, respectively. For the homologue series with DBE=2 or 3, the oxygen 404 405 atoms other than those in the sulfate group probably belonged to hydroxyl, carbonyl, or carboxylic groups, because it is unlikely that a compound in this range of 406 molecular weight would contain so many ether groups. CHOS with DBE=4 or 5 407 represented 9.9, 12.2, and 9.5% of the total CHOS species in the WHS, NJSD+NJSN, 408 and SHSD+SHSN samples, respectively. 409

The region of the CH₂-Kendrick diagrams where KM_{CH2} is between 350 and 750 410 and KMD_{CH2} is larger than 0.38 appears to be of particular interest. No CHOS was 411 observed in this region in WHS, whereas up to 6.5 and 9.5% of the total CHOS were 412 413 detected there in the NJSD+NJSN and SHSD+SHSN samples, respectively. The CHOS species in this region were characterized by a high molecular weight, high 414 degrees of unsaturation and oxidation (DBE > 5 and (o-3s)/c > 0.5), and a minimum 415 amount of isomers (one isomer for 79% of CHOS in this region). Moreover, these 416 CHOS are located in the lower right region of the VK diagrams that plot H/C versus 417 (0-3s)/c ratios (Figure 4, Wu et al. 2004; Kim et al, 2003). They are thus likely to 418 contain one or more aromatic rings (DBE/C > 0.67, but AI< 0.5) and come most 419 certainly from anthropogenic precursors. 420

Fewer CHONS than CHOS species were observed (Figure 5). In the CH₂-Kendrick diagram, the KMD_{CH2} values of CHONS were generally larger than those of CHOS because of the presence of one or two additional nitrate group contributing to these KMD_{CH2} values. Similarly to CHOS species, CHONS species in a homologue series with identical KMD_{CH2} values form a horizontal line. Molecular formula of the homologue series 1 and 3 with DBE=1 can be written as $C_nH_{2n+1}NO_3SO_4$ and $C_nH_{2n+1}ONO_3SO_4$; those for homologue series 2, 4, 5, and 8 with DBE=2 can be

written C_nH_{2n-1}ONO₃SO₄, 428 as $C_nH_{2n-1}NO_3SO_4$, $C_nH_{2n-1}O_2NO_3SO_4$, and $C_nH_{2n-1}O_3NO_3SO_4$; those for series 7, 9, and 10 with DBE=3 can be written as 429 C_nH_{2n-3}O₂NO₃SO₄, C_nH_{2n-3}O₃NO₃SO₄, and C_nH_{2n-3}O₄NO₃SO₄; and those series 6 with 430 DBE=4 can be written as $C_nH_{2n-5}ONO_3SO_4$ (n>4). By comparing the molecular 431 formulas of CHOS and CHONS species, it appears that most of CHONS could 432 correspond to the addition of nitrate groups on the detected CHOS. In the VK 433 diagrams, the homologue series 1 and 3 constitute upward lines and the other ones 434 435 constitute downward lines. In the region where KM_{CH2} is between 500 and 700 and KMD_{CH2} is larger than 0.6, CHONS species with DBE values larger than 5, a high 436 molecular weight and a high degree of oxidation ((o-3s-2n)/c > 0.5) were detected in 437 NJSD+NJSN and SHSD+SHSN, but not in WHS. According to the formulas of those 438 CHONS species, their precursors were different from those for any CHOS species. On 439 the other hand, a few additional CHONS species with DBE values also larger than 5, 440 relatively low molecular weight and low degrees of saturation and oxidation 441 ((o-3s-2n)/c < 0.3) were present in the three megacities. 442

443 Figure S2 shows the numbers of CHOS and CHONS species in different mass ranges. Generally, OSs in the mass range of 250–300 Da showed the greatest variety. 444 The number of OSs in the mass range of 200-400 Da accounted for 90.5, 83.1, and 445 85.4% of determined OSs in WHS, NJSD+NJSN, and SHSD+SHSN, respectively. 446 447 OSs with molecular weights larger than 500 Da characterized by high degrees of unsaturation in the KMD diagrams existed in the NJ and SH samples, whereas the 448 molecular weight of all OSs in the WH sample was less than 500 Da. In summary, the 449 molecular characteristics of tentatively assigned OSs between NJSD+NJSN and 450 SHSD+SHSN shared better similarity, probably because NJ and SH are 451 geographically closer at the lower reach of the Yangtze River, whereas WH is at the 452 middle reach of the Yangtze River. 453

454

455 3.4 Formation pathways of isoprene-derived OSs in three megacities

456 Isoprene has been shown to be an important precursor of OSs in the three 457 megacities. Previous studies suggest that IEPOX ($C_5H_{10}O_3$) and MAE ($C_4H_6O_3$) are

two key reactive intermediates that are formed during isoprene oxidation under low-458 and high-NO_x conditions, respectively. Subsequent acid catalyzed-reactions of IEPOX 459 and MAE in the presence of sulfates lead to the formation of C5H12O3SO4 and 460 C₄H₈O₃SO₄, respectively (Surratt et al., 2010; Worton et al., 2013), with the C₄ OS 461 being promoted under high-NO_x conditions compared to the C₅ OS. C₅ and C₄ OSs 462 could also be formed from sulfate/sulfite radical-induced oxidation reactions with 463 isoprene and its oxidation products (i.e., methyl vinyl ketone, and methacrolein) in the 464 aqueous phase, respectively (Schone et al., 2014; Noziere et al., 2010). Since the 465 liquid water content is not available for our ambient samples, these aqueous reaction 466 pathways are not considered here. 467

In this study, the S/C ratio has been limited to 0–0.2 to assure that the obtained compound exists in nature (Lin et al., 2012a; Tao et al., 2014; Wozniak et al., 2008). As a result, C4H₈O₃SO₄ has been eliminated by this criterion. Manually extracted ratios of the abundances of C4H₈O₃SO₄ to C₅H₁₂O₃SO₄ (denoted hereafter as C4/C₅ ratios) were used to elucidate the major formation pathway of isoprene-derived OSs in the three megacities.

In SH winter daytime samples, the C_4/C_5 ratio was 8.9 and decreased to 0.20 during summer. In WH, the C_4/C_5 ratio was equal to 0.22 in winter and 0.13 in summer. In both cases, these observations are consistent with the C₄ OS being promoted with higher winter NO_x levels but also suggest that even in winter, isoprene OSs are formed under low-NO_x conditions. In the NJSD sample, the C₄/C₅ ratio was about 2.5, suggesting that the high-NO_x pathway might dominate in summer in NJ (Dong et al., 2013).

481

482 3.5 Comparison of OSs in the SH samples

For a more accurate comparison, the abundance of $C_{10}H_{17}NO_3SO_4$ in the SHSN sample (the highest one from all the SH samples) was set arbitrarily to 100%, and an abundance limit corresponding to 0.5% of this value was used to include or exclude the OSs from the four SH samples in the following comparison. Figure 6 shows that the number of OSs in the SHSD and SHSN samples was much larger than those in the

SHWD and SHWN samples, respectively, consistent with a higher photochemical activity and/or higher precursor emissions in summer than in winter. The number of OSs in the SHSN and SHWN samples, especially the number of CHONS, was much larger than that in the SHSD and SHWD samples, respectively, consistent with the previous observation in Figure 3 (see section 3.2) that much more CHONS is present during nighttime.

As shown in Figure 7, the total arbitrary abundances of OSs in the SHSD and 494 495 SHSN samples were 2.1 and 3.0 times higher than in the SHWD and SHWN samples. The total arbitrary abundances of CHOS did not display significant differences 496 between SHSD and SHSN or between SHWD and SHWN. However, the arbitrary 497 abundances of CHONS in these SHSN and SHWN samples were 5.0 times and 2.2 498 times higher than in the SHSD and SHWD samples. This is consistent with an 499 expected nighttime chemistry of NO₃. Moreover, the variety (Figure 6) and the 500 abundance (Figure 7) of CHONS in both SHWN and SHSN samples were far larger 501 than those in SHWD and SHSD. 502

503 The fact that the SHSN sample showed higher abundance and variety of CHONS than the SHWD sample seems to point toward a CHONS formation driven by both 504 daytime photochemistry (and/or precursor emission) and subsequent nighttime NO3 505 chemistry. Similar trends of higher CHONS abundance during nighttime than during 506 daytime were observed in Beijing, China (van Pinxteren et al., 2009), Atlanta, GA 507 (Hatch et al., 2011), and Bakersfield, CA, USA (O'Brien et al., 2014). However, He et 508 al. (2014) observed a reverse trend at a regional background site in the Pearl River 509 Delta region (concentrations of nitrooxy-OSs were higher during daytime), 510 concluding that photochemical reactions could also lead to the formation of a 511 significant amount of nitrooxy-OSs. This photochemical pathway could contribute to 512 the formation of the nitrooxy-OSs detected during daytime, even if they showed only 513 relatively low abundances in this study. 514

Figure 7 shows the carbon number-based arbitrary abundance of CHOS and CHONS. In all four samples, more than 60% of the OSs were characterized by 5 to 10 carbon atom chains. In the SHSD and SHSN samples, C₅ and C₁₀ were the most

abundant. Isoprene and monoterpenes could be the main precursors for most of the C_5 518 and C₁₀ OSs (Riva et al., 2015a; Surratt et al., 2008). On the other hand, a recent work 519 (Riva et al., 2015b) suggests that a number of observed C_{10} OSs (e.g., $C_{10}H_{12}O_7S_1$) 520 might be derived from PAHs. In addition to C_5 and C_{10} , the relative abundances of C_8 , 521 C₉, and C₁₄₊ were also high in the SHWD and SHWN samples, hinting at additional 522 precursors. In contrast, C10 derived from monoterpenes always represented the 523 dominant category in spring, autumn, and winter in the Pearl River Delta, South 524 525 China, and in Taiwan (Lin et al., 2012b), underlying a lesser anthropogenic influence in these two regions than in the Yangtze River region. 526

The VK diagrams of CHOS and CHONS in the SH samples are presented in 527 Figure S3, which represents a combination of Figure 4 and Figure 5 (with a lesser 528 number of OSs accounted for). OSs in the four samples were characterized by similar 529 degrees of saturation. OSs with a low degree of saturation and a high molecular 530 weight existed in all four samples. Table 1 and Figure S3 show that the average 531 degree of oxidation of OSs in the SHSD and SHSN samples was higher than those in 532 533 the SHWD and SHWN samples, which is consistent with a promoted photochemical activity in summer. 534

535

536 4. Conclusions

In this study, atmospheric PM_{2.5} samples in WH, NJ, and SH were analyzed using an UHPLC-Orbitrap MS. More than 100 formulas of CHOS and dozens of formulas of CHONS with various numbers of isomers were tentatively determined in each sample. These CHOS and CHONS compounds were here tentatively regarded as organosulfates and nitrooxy-organosulfates respectively.

Aliphatic OSs represented at least 78% of the tentatively determined OSs in the three megacity summer samples, while there was much less aromatic OSs. Comparison of the molecular formula, number of isomers, average molecular weight, and degrees of saturation and oxidation suggests that OSs in aerosol samples from NJ and SH shared more similarities.

547

7 Major OSs in these ambient samples could be derived from biogenic precursors

(isoprene, monoterpenes, and sesquiterpenes), but also from PAHs. Isoprene appeared to be most likely one of the important precursors in the three megacities, and the influence of NO_x level on the nature of isoprene-derived OSs is consistent with the literature. Clearly, the identity, precursors, and formation mechanisms of many OSs have yet to be positively elucidated. The systematic use of chromatographic separation prior to MS detection appears essential given the variety of the precursors and the resulting isomers.

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566 **References:**

- Andreae, M. O. and Crutzen, P. J.: Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052-1058, doi:10.1126/science.276.5315.1052, 1997.
- Chan, M. N., Surratt, J. D., Chan, A. W. H., Schilling, K., Offenberg, J. H., Lewandowski, M., Edney, E. 569 O., Kleindienst, T. E., Jaoui, M., Edgerton, E. S., Tanner, R. L., Shaw, S. L., Zheng, M., Knipping, E. 570 571 M., and Seinfeld, J. H.: Influence of aerosol acidity on the chemical composition of secondary 572 organic aerosol from beta-caryophyllene, Atmos. Chem. Phys., 11, 1735-1751, 573 doi:10.5194/acp-11-1735-2011, 2011.
- 574 Darer, A. I., Cole-Filipiak, N. C., O'Connor, A. E., and Elrod, M. J.: Formation and stability of
 575 atmospherically relevant isoprene-derived organosulfates and organonitrates, Environ. Sci. Technol.,
 576 45, 1895-1902, doi:10.1021/es103797z, 2011.
- Dong, X. Y., Gao, Y., Fu, J. S., Li, J., Huang, K., Zhuang, G. S., and Zhou, Y.: Probe into gaseous
 pollution and assessment of air quality benefit under sector dependent emission control strategies
 over megacities in Yangtze River Delta, China, Atmos. Environ., 79, 841-852,
 doi:10.1016/j.atmosenv.2013.07.041, 2013.
- El Haddad, I., Marchand, N., D'Anna, B., Jaffrezo, J.-L., and Wortham, H.: Functional group composition of organic aerosol from combustion emissions and secondary processes at two contrasted urban environments, Atmos. Environ., 75, 308-320, doi:10.1016/j.atmosenv.2013.04.019, 2013.
- Fuller, S. J., Zhao, Y. J., Cliff, S. S., Wexler, A. S., and Kalberer, M.: Direct surface analysis of
 time-resolved aerosol impactor samples with ultrahigh-resolution mass spectrometry, Anal. Chem.,
 84, 9858-9864, doi:10.1021/ac3020615, 2012.

- Gomez-Gonzalez, Y., Surratt, J. D., Cuyckens, F., Szmigielski, R., Vermeylen, R., Jaoui, M.,
 Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Blockhuys, F., Van Alsenoy, C.,
 Maenhaut, W., and Claeys, M.: Characterization of organosulfates from the photooxidation of
 isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-) electrospray
 ionization mass spectrometry, J. Mass Spectrom., 43, 371-382, doi:10.1002/jms.1329, 2008.
- 593 Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L.,
 594 Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and
 595 Zimmerman, P.: A global-model of natural volatile organic-compound emissions, J. Geophys. Res.

596 Atmos., 100, 8873-8892, doi:10.1029/94jd02950, 1995.

- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J.,
 Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma,
 Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G.,
 Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt,
 J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues,
 Atmos. Chem. Phys., 9, 5155-5236, doi:10.5194/acp-9-5155-2009, 2009.
- Hatch, L. E., Creamean, J. M., Ault, A. P., Surratt, J. D., Chan, M. N., Seinfeld, J. H., Edgerton, E. S.,
- Su, Y. X., and Prather, K. A.: Measurements of isoprene-derived organosulfates in ambient aerosols
 by aerosol time-of-flight mass spectrometry-Part 2: Temporal variability and formation mechanisms,
 Environ. Sci. Technol., 45, 8648-8655, doi:10.1021/es2011836, 2011.
- Hawkins, L. N., Russell, L. M., Covert, D. S., Quinn, P. K., and Bates, T. S.: Carboxylic acids, sulfates,
 and organosulfates in processed continental organic aerosol over the southeast Pacific Ocean during
 VOCALS-REx 2008, J. Geophys. Res. Atmos., 115, D13201, doi:10.1029/2009jd013276, 2010.
- He, Q. F., Ding, X., Wang, X. M., Yu, J. Z., Fu, X. X., Liu, T. Y., Zhang, Z., Xue, J., Chen, D. H.,
 Zhong, L. J., and Donahue, N. M.: Organosulfates from pinene and isoprene over the Pearl River
 Delta, south China: Seasonal variation and implication in formation mechanisms, Environ. Sci.
 Technol., 48, 9236-9245, doi:10.1021/es501299v, 2014.
- Hu, K. S., Darer, A. I., and Elrod, M. J.: Thermodynamics and kinetics of the hydrolysis of
 atmospherically relevant organonitrates and organosulfates, Atmos. Chem. Phys., 11, 8307-8320,
 doi:10.5194/acp-11-8307-2011, 2011.
- Huang, C., Chen, C. H., Li, L., Cheng, Z., Wang, H. L., Huang, H. Y., Streets, D. G., Wang, Y. J.,
 Zhang, G. F., and Chen, Y. R.: Emission inventory of anthropogenic air pollutants and VOC species
 in the Yangtze River Delta region, China, Atmos. Chem. Phys., 11, 4105-4120,
 doi:10.5194/acp-11-4105-2011, 2011.
- 621 Iinuma, Y., Muller, C., Berndt, T., Boge, O., Claeys, M., and Herrmann, H.: Evidence for the existence
 622 of organosulfates from beta-pinene ozonolysis in ambient secondary organic aerosol, Environ. Sci.
- 623 Technol., 41, 6678-6683, doi:10.1021/es070938t, 2007a.
- 624 Iinuma, Y., Muller, C., Boge, O., Gnauk, T., and Herrmann, H.: The formation of organic sulfate esters
 625 in the limonene ozonolysis secondary organic aerosol (SOA) under acidic conditions, Atmos.
 626 Environ., 41, 5571-5583, doi:10.1016/j.atmosenv.2007.03.007, 2007b.
- Kahnt, A., Behrouzi, S., Vermeylen, R., Shalamzari, M. S., Vercauteren, J., Roekens, E., Claeys, M.,
 and Maenhaut, W.: One-year study of nitro-organic compounds and their relation to wood burning in
 PM₁₀ aerosol from a rural site in Belgium, Atmos. Environ., 81, 561-568,
 doi:10.1016/j.atmosenv.2013.09.041, 2013.
- 631 Kim, S., Kramer, R. W., and Hatcher, P. G.: Graphical method for analysis of ultrahigh-resolution

- broadband mass spectra of natural organic matter, the van Krevelen diagram, Anal. Chem., 75,
 5336-5344, doi:10.1021/ac034415p, 2003.
- Koch, B. P. and Dittmar, T.: From mass to structure: An aromaticity index for high-resolution mass data
 of natural organic matter, Rapid Commun. Mass Sp., 20, 926-932, doi:10.1002/rcm.2386, 2006.
- Kristensen, K. and Glasius, M.: Organosulfates and oxidation products from biogenic hydrocarbons in
 fine aerosols from a forest in North West Europe during spring, Atmos. Environ., 45, 4546-4556,
 doi:10.1016/j.atmosenv.2011.05.063, 2011.
- Kundu, S., Quraishi, T. A., Yu, G., Suarez, C., Keutsch, F. N., and Stone, E. A.: Evidence and
 quantitation of aromatic organosulfates in ambient aerosols in Lahore, Pakistan, Atmos. Chem. Phys.,
 13, 4865-4875, doi:10.5194/acp-13-4865-2013, 2013.
- Liggio, J., Li, S. M., and McLaren, R.: Heterogeneous reactions of glyoxal on particulate matter:
 Identification of acetals and sulfate esters, Environ. Sci. Technol., 39, 1532-1541,
 doi:10.1021/es048375y, 2005.
- Lin, P., Rincon, A. G., Kalberer, M., and Yu, J. Z.: Elemental composition of HULIS in the Pearl River
 Delta region, China: Results inferred from positive and negative electrospray high resolution mass
 spectrometric data, Environ. Sci. Technol., 46, 7454-7462, doi:10.1021/es300285d, 2012a.
- Lin, P., Yu, J. Z., Engling, G., and Kalberer, M.: Organosulfates in humic-like substance fraction
 isolated from aerosols at seven locations in East Asia: A study by ultra-high-resolution mass
 spectrometry, Environ. Sci. Technol., 46, 13118-13127, doi:10.1021/es303570v, 2012b.
- Lin, Y. H., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S. L.,
 Knipping, E. M., Edgerton, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.: Isoprene epoxydiols
 as precursors to secondary organic aerosol formation: acid-catalyzed reactive uptake studies with
 authentic compounds, Environ. Sci. Technol., 46, 250-258, doi:10.1021/es202554c, 2012c.
- Lin, Y. H., Zhang, H. F., Pye, H. O. T., Zhang, Z. F., Marth, W. J., Park, S., Arashiro, M., Cui, T. Q.,
 Budisulistiorini, H., Sexton, K. G., Vizuete, W., Xie, Y., Luecken, D. J., Piletic, I. R., Edney, E. O.,
 Bartolotti, L. J., Gold, A., and Surratt, J. D.: Epoxide as a precursor to secondary organic aerosol
- 658 formation from isoprene photooxidation in the presence of nitrogen oxides, P. Natl. Acad. Sci. USA,
 659 110, 6718-6723, doi:10.1073/pnas.1221150110, 2013.
- Ma, Y., Chen, J. M., and Wang, L.: Characteristics and formation mechanisms of atmospheric
 organosulfates, Prog. Chem., 24, 2277-2286, 2012.
- Ma, Y., Xu, X. K., Song, W. H., Geng, F. H., and Wang, L.: Seasonal and diurnal variations of
 particulate organosulfates in urban Shanghai, China, Atmos. Environ., 85, 152-160,
 doi:10.1016/j.atmosenv.2013.12.017, 2014.
- Magari, S. R., Schwartz, J., Williams, P. L., Hauser, R., Smith, T. J., and Christiani, D. C.: The
 association of particulate air metal concentrations with heart rate variability, Environ. Health
- 667 Perspect., 110, 875-880, 2002.
- Noziere, B., Ekstrom, S., Alsberg, T., and Holmstrom, S.: Radical-initiated formation of organosulfates
 and surfactants in atmospheric aerosols, Geophys. Res. Lett., 37, doi:10.1029/2009gl041683, 2010.
- O'Brien, R. E., Laskin, A., Laskin, J., Rubitschun, C. L., Surratt, J. D., and Goldstein, A. H.: Molecular
 characterization of S- and N-containing organic constituents in ambient aerosols by negative ion
 mode high-resolution nanospray desorption electrospray ionization mass spectrometry: CalNex 2010
 field study, J. Geophys. Res. Atmos., 119, 12706-12720, doi:10.1002/2014jd021955, 2014.
- 1075 field study, J. Geophys. Res. Almos., 119, 12700-12720, doi:10.1002/2014jd021955, 2014.
- Olson, C. N., Galloway, M. M., Yu, G., Hedman, C. J., Lockett, M. R., Yoon, T., Stone, E. A., Smith, L.
- 675 M., and Keutsch, F. N.: Hydroxycarboxylic acid-derived organosulfates: synthesis, stability, and

- quantification in ambient aerosol, Environ. Sci. Technol., 45, 6468-6474, doi:10.1021/es201039p,
 2011.
- Ostro, B., Feng, W. Y., Broadwin, R., Green, S., and Lipsett, M.: The effects of components of fine
 particulate air pollution on mortality in California: Results from CALFINE, Environ. Health
 Perspect., 115, 13-19, doi:10.1289/ehp.9281, 2007.
- Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg,
 P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene, Science, 325,
 730-733, doi:10.1126/science.1172910, 2009.
- Riva, M., Budisulistiorini, S. H., Zhang, Z., Gold, A., and Surratt, J. D.: Chemical characterization of
 secondary organic aerosol constituents from isoprene ozonolysis in the presence of acidic aerosol,
 Atmos. Environ., doi:10.1016/j.atmosenv.2015.06.027, 2015a.
- Riva, M., Tomaz, S., Cui, T., Lin, Y.-H., Perraudin, E., Gold, A., Stone, E. A., Villenave, E., and Surratt,
 J. D.: Evidence for an unrecognized secondary anthropogenic source of organosulfates and
 sulfonates: Gas-phase oxidation of polycyclic aromatic hydrocarbons in the presence of sulfate
 aerosol, Environ. Sci. Technol., 49, 6654-6664, doi:10.1021/acs.est.5b00836, 2015b.
- Rudzinski, K. J., Gmachowski, L., and Kuznietsova, I.: Reactions of isoprene and sulphoxy
 radical-anions a possible source of atmospheric organosulphites and organosulphates, Atmos.
- 693 Chem. Phys., 9, 2129-2140, 2009.
- Schindelka, J., Iinuma, Y., Hoffmann, D., and Herrmann, H.: Sulfate radical-initiated formation of
 isoprene-derived organosulfates in atmospheric aerosols, Faraday Discussions, 165, 237-259,
 doi:10.1039/c3fd00042g, 2013.
- Schone, L., Schindelka, J., Szeremeta, E., Schaefer, T., Hoffmann, D., Rudzinski, K. J., Szmigielski, R.,
 and Herrmann, H.: Atmospheric aqueous phase radical chemistry of the isoprene oxidation products
 methacrolein, methyl vinyl ketone, methacrylic acid and acrylic acid--kinetics and product studies,
 Phys. Chem. Chem. Phys., 16, 6257-6272, doi:10.1039/c3cp54859g, 2014.
- Shalamzari, M. S., Kahnt, A., Vermeylen, R., Kleindienst, T. E., Lewandowski, M., Cuyckens, F.,
 Maenhaut, W., and Claeys, M.: Characterization of polar organosulfates in secondary organic
 aerosol from the green leaf volatile 3-Z-hexenal, Environ. Sci. Technol., 48, 12671-12678,
 doi:10.1021/es503226b, 2014.
- Staudt, S., Kundu, S., Lehmler, H. J., He, X. R., Cui, T. Q., Lin, Y. H., Kristensen, K., Glasius, M.,
 Zhang, X. L., Weber, R. J., Surratt, J. D., and Stone, E. A.: Aromatic organosulfates in atmospheric
 aerosols: Synthesis, characterization, and abundance, Atmos. Environ., 94, 366-373,
 doi:10.1016/j.atmosenv.2014.05.049, 2014.
- Stone, E. A., Hedman, C. J., Sheesley, R. J., Shafer, M. M., and Schauer, J. J.: Investigating the chemical nature of humic-like substances (HULIS) in North American atmospheric aerosols by
 liquid chromatography tandem mass spectrometry, Atmos. Environ., 43, 4205-4213, doi:10.1016/j.atmosenv.2009.05.030, 2009.
- Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L.,
 Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for
 organosulfates in secondary organic aerosol, Environ. Sci. Technol., 41, 517-527,
 doi:10.1021/es062081q, 2007.
- 717 Surratt, J. D., Gomez-Gonzalez, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E.,
- Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R.
- 719 C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, J. Phys.

- 720 Chem. A, 112, 8345-8378, doi:10.1021/jp802310p, 2008.
- 721 Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P.,
- Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary
 organic aerosol formation from isoprene, P. Natl. Acad. Sci. USA, 107, 6640-6645,
 doi:10.1073/pnas.0911114107, 2010.
- Szmigielski, R.: Evidence for C₅ organosulfur secondary organic aerosol components from in-cloud
 processing of isoprene: Role of reactive SO₄ and SO₃ radicals, Atmos. Environ.,
 doi:10.1016/j.atmosenv.2015.10.072, 2015.
- 728 Tao, S., Lu, X., Levac, N., Bateman, A. P., Nguyen, T. B., Bones, D. L., Nizkorodov, S. A., Laskin, J.,
- Laskin, A., and Yang, X.: Molecular characterization of organosulfates in organic aerosols from
 Shanghai and Los Angeles urban areas by nanospray-desorption electrospray ionization
 high-resolution mass spectrometry, Environ. Sci. Technol., 48, 10993-11001, doi:10.1021/es5024674,
 2014.
- Tolocka, M. P. and Turpin, B.: Contribution of organosulfur compounds to organic aerosol mass,
 Environ. Sci. Technol., 46, 7978-7983, doi:10.1021/es300651v, 2012.
- van Pinxteren, D., Bruggemann, E., Gnauk, T., Iinuma, Y., Muller, K., Nowak, A., Achtert, P.,
 Wiedensohler, A., and Herrmann, H.: Size- and time-resolved chemical particle characterization
- during CAREBeijing-2006: Different pollution regimes and diurnal profiles, J. Geophys. Res.
 Atmos., 114, D00g09, doi:10.1029/2008jd010890, 2009.
- Wang, L., Du, H. H., Chen, J. M., Zhang, M., Huang, X. Y., Tan, H. B., Kong, L. D., and Geng, F. H.:
 Consecutive transport of anthropogenic air masses and dust storm plume: Two case events at
 Shanghai, China, Atmos. Res., 127, 22-33, doi:10.1016/j.atmosres.2013.02.011, 2013.
- Worton, D. R., Surratt, J. D., LaFranchi, B. W., Chan, A. W. H., Zhao, Y. L., Weber, R. J., Park, J. H.,
 Gilman, J. B., de Gouw, J., Park, C., Schade, G., Beaver, M., St Clair, J. M., Crounse, J., Wennberg,
 P., Wolfe, G. M., Harrold, S., Thornton, J. A., Farmer, D. K., Docherty, K. S., Cubison, M. J.,
 Jimenez, J. L., Frossard, A. A., Russell, L. M., Kristensen, K., Glasius, M., Mao, J. Q., Ren, X. R.,
 Brune, W., Browne, E. C., Pusede, S. E., Cohen, R. C., Seinfeld, J. H., and Goldstein, A. H.:
 Observational insights into aerosol formation from isoprene, Environ. Sci. Technol., 47,
- 748 11403-11413, doi:10.1021/es4011064, 2013.
- Wozniak, A. S., Bauer, J. E., Sleighter, R. L., Dickhut, R. M., and Hatcher, P. G.: Technical Note:
 Molecular characterization of aerosol-derived water soluble organic carbon using ultrahigh
 resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry,
 Atmos. Chem. Phys., 8, 5099-5111, doi:10.5194/acp-8-5099-2008, 2008.
- Wu, Z. G., Rodgers, R. P., and Marshall, A. G.: Two- and three-dimensional van Krevelen diagrams: A
 graphical analysis complementary to the Kendrick mass plot for sorting elemental compositions of
 complex organic mixtures based on ultrahigh-resolution broadband Fourier transform ion cyclotron
 resonance mass measurements, Anal. Chem., 76, 2511-2516, doi:10.1021/ac0355449, 2004.
- Xiao, S., Wang, M. Y., Yao, L., Kulmala, M., Zhou, B., Yang, X., Chen, J. M., Wang, D. F., Fu, Q. Y.,
 Worsnop, D. R., and Wang, L.: Strong atmospheric new particle formation in winter in urban
 Shanghai, China, Atmos. Chem. Phys., 15, 1769-1781, doi:10.5194/acp-15-1769-2015, 2015.
- 760 Zhang, H. F., Worton, D. R., Lewandowski, M., Ortega, J., Rubitschun, C. L., Park, J. H., Kristensen,
- 761 K., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Jaoui, M., Offenberg, J. H., Kleindienst, T. E.,
- Gilman, J., Kuster, W. C., de Gouw, J., Park, C., Schade, G. W., Frossard, A. A., Russell, L., Kaser,
- 763 L., Jud, W., Hansel, A., Cappellin, L., Karl, T., Glasius, M., Guenther, A., Goldstein, A. H., Seinfeld,

- 764 J. H., Gold, A., Kamens, R. M., and Surratt, J. D.: Organosulfates as tracers for secondary organic
- 765 aerosol (SOA) formation from 2-Methyl-3-Buten-2-ol (MBO) in the atmosphere, Environ. Sci. Technol., 46, 9437-9446, doi:10.1021/es301648z, 2012. 766
- 767
- Zheng, J., Ma, Y., Chen, M. D., Zhang, Q., Wang, L., Khalizov, A. F., Yao, L., Wang, Z., Wang, X., and Chen, L. X.: Measurement of atmospheric amines and ammonia using the high resolution 768
- 769 time-of-flight chemical ionization mass spectrometry, Atmos. Environ., 102, 249-259,
- 770 doi:10.1016/j.atmosenv.2014.12.002, 2015.

Location	Sample ID	Sampling time	Number of formulas	CHOS ^a			CHONS ^b				
			(CHOS/CHONS)	MW	DBE	(o-3s)/c ^c	H/C ^d	MW	DBE	(o-3s-2n)/c ^e	H/C
Wuhan	WHW	9:00 a.m., Jan. 26 - 9:00 a.m., Jan 27, 2012	149/43	266.6±57.2	2.56±2.60	0.37±0.25	1.68±0.44	311.0±60.5	3.61±2.57	0.35±0.13	1.58±0.46
	WHS	8:30 a.m., Jun. 15 - 8:30 a.m., Jun. 16, 2012	213/55	287.9±60.8	2.16±1.64	0.39±0.23	1.75±0.36	318.1±53.8	2.98±1.52	0.40±0.17	1.69±0.34
Nanjing	NJSD	7:30 a.m 7:30 p.m., Aug. 29, 2012	139/54	288.9±67.9	1.82±1.32	0.39±0.25	1.83±0.27	313.6±48.2	2.56±1.08	0.44±0.21	1.79±0.23
	NJSN	7:30 p.m., Aug. 29 - 7:30 a.m., Aug. 30, 2012	160/72	294.0±97.3	3.21±3.84	0.46 ± 0.34	1.65 ± 0.45	335.2±74.3	3.46±2.30	0.43±0.20	1.66 ± 0.37
	NJSD+NJSN	Combination ^f	205/83	304.8±93.5	3.00±3.47	0.43 ± 0.32	1.68±0.41	332.5±70.7	3.28±2.21	0.44±0.21	1.69±0.35
	SHWD	7:30 a.m 7:30 p.m., Jan. 17, 2013	125/32	274.3±81.1	2.38±2.56	0.39±0.31	1.72±0.46	328.7±132.2	4.22±3.95	0.44±0.33	1.53±0.57
Shanghai	SHWN	7:30 p.m., Jan. 17 - 7:30 a.m., Jan. 18, 2013	159/54	270.0±71.1	2.54±2.39	0.40 ± 0.29	1.69±0.44	303.9±51.9	2.98 ± 2.50	0.38±0.17	1.71 ± 0.46
	SHWD+SHWN	Combination ^f	168/59	277.2±71.2	2.63±2.59	$0.40{\pm}0.29$	1.68 ± 0.46	325.8±92.0	3.59±3.50	0.42 ± 0.27	1.64 ± 0.52
	SHSD	8:00 a.m 8:00 p.m., Jul. 28, 2013	165/40	296.4±84.7	2.76±2.66	0.47 ± 0.32	1.68 ± 0.42	348.2±115.4	4.03±3.48	0.61 ± 0.43	1.55 ± 0.52
	SHSN	8:00 p.m., Jul. 28 - 8:00 a.m., Jul. 29, 2013.	122/51	278.1±73.9	2.36±2.48	0.48 ± 0.29	1.74 ± 0.40	319.2±73.0	3.26±2.93	0.45±0.22	1.69±0.44
	SHSD+SHSN	Combination ^f	168/58	296.3±84.7	2.77±2.65	0.47±0.31	1.68±0.42	337.6±102.2	3.52±3.04	0.53±0.38	1.64±0.47

Table 1. Summary of sampling location, sampling time, Molecular Weight (MW), Double Bond Equivalents (DBE), and Elemental Ratios (arithmetic mean ± standard deviation) of tentatively assigned CHOS and CHONS.

^a Molecules with (o-4s)/c<0 were not included.

^b Molecules with (o-4s-3n)/c<0 were not included.

^c (o-3s)/c infers to the extent of oxidation for a CHOS molecule.

^d H/C refers to the ratio between hydrogen atom and carbon atom in a molecule.

^e (o-3s-2n)/c refers to the extent of oxidation for a CHONS molecule.

^f Combination of two samples for a comparison purpose.

Figure Captions

Figure 1. Locations of Wuhan (WH), Nanjing (NJ), and Shanghai (SH) in China.

Figure 2. LC chromatograms of tentatively determined $C_5H_{10}O_5S_1$ (potentially from isoprene). A chromatogram for the NJSD sample is not included because a large amount of sample injection led to corruption of peaks and hence inaccurate retention times and worse peak resolution.

Figure 3. Mass spectra of detected CHOS and CHONS reconstructed from extracted ion chromatograms (UHPLC-Orbitrap MS analysis, negative ionization mode). X-axis corresponds to the molecular weight (Da) of identified species. The number of isomers for a given formula is marked by colors. A, neutral mass = 211.9993 Da, $C_5H_8O_7S_1$; B, neutral mass=216.0306 Da, $C_5H_{12}O_7S_1$; C, neutral mass=226.0150 Da, $C_6H_{10}O_7S_1$; D, neutral mass=240.0307 Da, $C_7H_{12}O_7S_1$; E, neutral mass=254.0827 Da, $C_9H_{18}O_6S_1$; F, neutral mass=261.0157 Da, $C_5H_{11}O_9N_1S_1$; G, neutral mass=268.0620 Da, $C_9H_{16}O_7S_1$; H, neutral mass=295.0729 Da, $C_{10}H_{17}O_7N_1S_1$; I, neutral mass=363.1356 Da, $C_{15}H_{25}O_7N_1S_1$.

Figure 4. (a–c) CH₂-Kendrick diagrams and (d–e) Van Krevelen diagrams for CHOS. The color-coding indicates the DBE values calculated from Eq. 1. The molecular formula of the homologue series 1 to 15 can be written as $C_nH_{2n+2}SO_4$, $C_nH_{2n+2}O_1SO_4$, $C_nH_{2n}O_1SO_4$, $C_nH_{2n}O_2SO_4$, $C_nH_{2n-4}O_1SO_4$, $C_nH_{2n-2}O_2SO_4$, $C_nH_{2n-4}O_2SO_4$, $C_nH_{2n-4}O_2SO_4$, $C_nH_{2n-2}O_2SO_4$, $C_nH_{$

Figure 5. (a–c) CH₂-Kendrick diagrams and (d–e) Van Krevelen diagrams for CHONS. The color-coding indicates the DBE values calculated from Eq 1. The molecular formula of the homologue series 1 to 10 can be written as $C_nH_{2n+1}NO_3SO_4$, $C_nH_{2n-1}NO_3SO_4$, $C_nH_{2n-1}ONO_3SO_4$, $C_nH_{2n-1}ONO_3SO_4$, $C_nH_{2n-1}ONO_3SO_4$, $C_nH_{2n-1}ONO_3SO_4$, $C_nH_{2n-1}ONO_3SO_4$, $C_nH_{2n-3}O_2NO_3SO_4$, $C_nH_{2n-3}O_3NO_3SO_4$, $C_nH_{2n-3}O_3NO_3SO_4$, and $C_nH_{2n-3}O_4NO_3SO_4$, respectively (n>4).

Figure 6. Number of C atoms of CHOS and CHONS as a function of molecular weight in the Shanghai samples. Note that only compounds with a relative abundance greater than or equal to 0.5% of that of C₁₀H₁₇O₇N₁S₁ in the SHSN sample are shown in this figure.

Figure 7. Relative abundance distributions of CHOS and CHONS in the Shanghai samples. Note that only compounds with a relative abundance greater than or equal to 0.5% of that of C₁₀H₁₇O₇N₁S₁ in the SHSN sample are shown in this figure.



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7