Molecular Characteristics of Organosulfur Compounds in Guangzhou, South China: Heterogeneous Secondary Reactions Drivers the Molecular Distribution

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Abstract. Organosulfur compounds (OrgSs), especially organosulfates, have been widely reported at large quantities in particulate organic matter found in various atmospheric environments. Despite various kinds of organosulfates and their formation mechanisms being previously identified, a large fraction of OrgSs remain unexplained at the molecular level, impeding further knowledge on additional formation pathways and critical environmental parameters that help to explain their concentrations. In this work, the abundance and molecular composition of OrgSs in fine particulate samples collected in Guangzhou was reported. Our results revealed that organic sulfur can averagely contribute to 30% of total particulate sulfur, and showed positively correlations with the SO_2 ($r=0.37$, $p<0.05$) and oxidants ($NOx+O_3$, $r=0.40$, $p<0.01$). Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) results presented that more than 80% by number of the detected OrgSs in our samples have the elemental composition of $O/(4S+3N) \geq 1$, indicating that they were largely in the form of oxidized organosulfates and/or nitrooxy organosulfates . Many OrgSs, which are tentatively attributed to previously identified biogenic and anthropogenic origins, were also present in aerosols derived from freshly-emitted combustion sources. Results show that the formation of OrgSs through an epoxide intermediate pathway could be as much as 46%, and the oxidants levels could explain 20% variation of organic sulfur mass. The analysis from our large FT-ICR MS dataset suggests that relative humidity, oxidation of biogenic volatile organic compounds via ozonolysis, and NOx-related nitrooxy organosulfate formations were the major reasons for the molecular variation of OrgSs, possibly highlighting the importance of heterogeneous reactions involving either the uptake of SO_2 or the heterogeneous oxidations of particulate organosulfates into additional unrecognized OrgSs.

1 Introduction

Organosulfur compounds (OrgSs) have been widely identified in atmospheric media including fog, rainwater, and ambient
35   aerosols, and account for a substantial fraction of ambient OM mass, with ratios as large as 50% (Surratt et al., 2007; Altieri
et al., 2009; Mazzoleni et al., 2010; Luk´Acs et al., 2009; Tolocka and Turpin, 2012; Surratt et al., 2008), with potentially
adverse effects on the global climate system and toxicity to human health (Jimenez et al., 2009; Noziere et al., 2015; Nozière
et al., 2010; Nguyen et al., 2012; Bates et al., 2019; Daellenbach et al., 2020). OrgSs are a class of relatively stable and long-
lived organic compounds, including not only organosulfates (OSs), but also sulfoxides, sulfonates, and sulfones, with OSs
40   identified as the most abundant class (Olson et al., 2011; Chen et al., 2020; Tolocka and Turpin, 2012). A series of studies
have reported the hygroscopicity (Peng et al., 2021), light absorption properties (Nguyen et al., 2012; Fleming et al., 2019),
and potential toxicity (Lin et al., 2016) of OSs, further highlighting the importance of studying the sources and formation
mechanisms of OrgSs.

Various mechanistic studies have revealed the possible reaction pathways by which OSs form. The acid-catalyzed ring opening
45   of epoxides in the presence of sulfuric acid seeds has been widely adopted to explain the formation of OSs from isoprene and
other volatile organic compounds (VOCs) (Eddingsaas et al., 2010; Iinuma et al., 2007a; Lin et al., 2013; Bruggemann et al.,
2020; Surratt et al., 2010; Lin et al., 2012). Furthermore, heterogeneous reactions between SO_2 and unsaturated compounds or
aerosol-phase organic peroxides were also identified to generate OSs both by simulation experiments and field observations
(Shang et al., 2016; Passananti et al., 2016; Ye et al., 2018; Zhu et al., 2019). Other mechanisms such as nucleophilic
50   substitution of organic nitrates by sulfate (Surratt et al., 2007; Iinuma et al., 2007b; Surratt et al., 2008), sulfate esterification
of alcohols/epoxides (He et al., 2014), and sulfoxy radical-initiated oxidation of unsaturated compounds (Nozière et al., 2010;
Huang et al., 2019; Wach et al., 2019; Huang et al., 2020) have also been proposed in many studies. Nighttime NO3-initiated
oxidation of VOCs is considered an important formation mechanism of nitrooxy-organosulfates (NOSs) (Iinuma et al., 2007b;
Bruggemann et al., 2020). It seems that the presently proposed formation pathways presumably explain the large variety and
55   ubiquity of OSs; and the above mechanisms suggest that OSs distributions can depend on both precursors of VOCs and
inorganic gas (e.g., SO2, NOx, NH3) concentrations, as well as environmental conditions, such as relative humidity (RH),
aerosol acidity and oxidant concentrations. However, the OrgSs composition in the actual atmosphere is complex, and most of
the present studies only focused on the existing known Oss (Ye et al., 2020; Hettiyadura et al., 2019; Hettiyadura et al., 2017;
Wang et al., 2018), with a large fraction of OrgSs (67-79%) remaining unexplained at the molecular level other than the OSs
60   with known precursors (Chen et al., 2021). Additionally, recent analysis of high-resolution mass spectrometry data showed
that OrgSs detected in freshly emitted sources samples, particularly coal combustion aerosols (Song et al., 2018; Cui et al.,
2019; Tang et al., 2020), have a similar molecular composition to classical OSs, complicating the source apportionment and
discrimination of reaction mechanisms of OrgSs in the real atmosphere. The above works suggest that there is insufficient
understanding of the comprehensive sources, formation mechanisms and influencing factors of OrgSs overall for ambient
65   samples (Bruggemann et al., 2020), which makes it an urgent need to fully understand their molecular composition.

Guangzhou is a megacity in South China where featured high temperature, RH and oxidation levels throughout the year, and is heavily influenced by biogenic−anthropogenic interactions. Studies have shown that Guangzhou often suffers haze events influenced by biomass burning and fossil fuel combustion (mainly vehicle emissions), and organic aerosols can account for large fractions of the total PM2.5 in haze (Jiang et al., 2021b; Dai et al., 2015; Liu et al., 2014). Additionally, the high emissions of anthropogenic pollutants (e.g., NOx and SO2) and high concentrations of nitrate and sulfate are present in the particle phase, which makes the particles very acidic (He et al., 2014). Although several studies have reported the concentrations and possible formation mechanisms of biogenic VOCs (BVOCs) derived OSs in the Pearl River Delta region (Bryant et al., 2021; He et al., 2014), these OSs only represented a small fraction of organic aerosol mass. Therefore, a better understanding of the chemical composition, source and influencing factors of OrgSs in Guangzhou will be important to know the particulate pollution and decrease the SOA concentration. It will have referential significance for areas where show high temperature, humidity and oxidation levels which promote the occurrence of secondary processes.

In this study, the molecular composition of atmospheric OrgSs over an urban site in Guangzhou, was characterized by negative ESI-FT-ICR MS through accurate mass measurements. The application of high-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) or Orbitrap mass spectrometry coupled with electrospray ionization (ESI) in studying atmospheric OrgSs has qualitatively provided more molecular information on OrgSs composition (Ye et al., 2020; Kuang et al., 2016; Lin et al., 2012; Gao and Zhu, 2021). Moreover, the FT-ICR MS results combined with chemical tracers and meteorological data were used to evaluate the possible formation pathways and driving factors of OrgSs. We show that liquid-phase related reactions such as heterogeneous oxidation and acid-catalyzed ring-open of epoxides, were potentially important formation pathways of OgrSs in Guangzhou, due to the high RH, oxidation levels and acidity in this region. This is consistent with a recent field observation that gas-phase oxidation and heterogeneous/multiphase reactions play important roles in SOA formation in Guangzhou (Guo et al., 2020).

2 Experimental methods

2.1 Collection of PM2.5 samples and sulfur-containing species analysis.

A total of 55 PM$_{2.5}$ samples collected at Guangzhou from July, 2017 to June, 2018 were used for organosulfur analysis. Detailed information about the samples and the measurement of organic tracers, water-soluble inorganic ions, and meteorological parameters including trace gases, temperature, and relative humidity, was describe in our recent studies (Jiang et al., 2021b; Jiang et al., 2021a). Here, the total fine particulate sulfur (TS) was measured by elemental analyser (Elemental, Germany) and directly compared to inorganic sulfate measured by ion chromatography (IC), and the TS to sulfate-sulfur ratios were calculated (Chen et al., 2021; Shakya and Peltier, 2013; Tolocka and Turpin, 2012). Detailed descriptions of the analysis procedures are presented in the Supporting information (SI). As assumed, if particulate sulfur was present only as SO$_4^{2-}$, the calculated ratio often shifts from 1 to the small range of 0.9-1.1 using an error propagation method (Shakya and Peltier, 2015, 2013). In this study, the TS to sulfate-sulfur ratios of samples greater than 2 or less than 0.5, which were considered as a measure of gross

measurement error, were also excluded from further analysis (Shakya and Peltier, 2015). Finally, 40 samples were reserved, the content of organic sulfur (Org-S) was estimated as the amount of sulfate-sulfur subtracted from TS, and two negative Org-

100   S values were set as zero.

2.2 FT-ICR MS analysis on organosulfur compounds

The feasibility of the method is based on its high mass resolution in identifying mass peaks in conjunction with the assignment of formulas using narrow mass tolerance (< 1ppm absolute mass error for FT-ICR MS result). Previous studies have indicated that the OSs are readily ionized in negative ESI mode, and most of them were observed only in negative mode (Lin et al.,

105   2012; Kuang et al., 2016). A total of 55 $PM_{2.5}$ samples were used for negative ESI-FT-ICR MS analysis and each sample was ultrasonic extracted with methanol in a cold-water bath(Jiang et al., 2021a). The methanol extracts were filtered with PTFE members, concentrated, and directly injected into a 9.4T solariX XR FT-ICR mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) in negative ESI modes at a flow rate of 180 mL h^{-1} (Jiang et al., 2021a; Jiang et al., 2020). Detailed operating conditions are presented in SI. The mass range was set as150–800 Da, and a total of 128 continuous 4M data FT-

110   ICR transients were co-added to enhance the signal-to-noise ratio and dynamic range. Field blank filters were processed and analysed following the same procedure to detect possible contamination. It should be noted that, the general molecular characteristics of the samples and their molecular linkages to light absorption properties were reported in our previous study (Jiang et al., 2021a), here, we focused on the detailed composition of OrgSs and their influencing factors and potential formation mechanisms.

115   ## 2.3 Data processing and statistical analysis

A custom software was used to calculate all mathematically possible formulas for all ions with a signal-to-noise ratio above 4 using a mass tolerance of ±1 ppm. The compounds assigned as $C_cH_hO_oN_nS_s$ with s = 1, 2 will be collectively referred to as organosulfur compounds (OSs) including CHOS (n = 0) and CHONS (n = 1,2). The identified formulas containing isotopomers (i.e., ^{13}C, ^{18}O or ^{34}S) were not discussed. The double bond equivalent (DBE) is calculated using the equation: DBE = (2c+2-

120   h+n)/2. Additionally, the modified index of aromaticity equivalent (Xc) was also calculated to estimate the degree of aromaticity, with the calculations presented in SI (Yassine et al., 2014; Ye et al., 2020).

We assume that the different OSs may have similar ionization efficiency (Bateman et al., 2012), because the sulfate functional group are readily ionized during the ESI process (Lin et al., 2012). However, the ionization efficiencies may vary among different OSs compounds for other reasons, such as surface activity on ESI droplets (Kuang et al., 2016). Although all of the

125   spectra were acquired under the same conditions, the sum-normalized peak intensities of the organosulfur compounds provide information on the relative abundances among different samples. To evaluate the associations between environmental variables and OrgSs compounds, we conducted non-metric multidimensional scaling (NMDS) analysis based on Bray−Curtis distances in R using the vegan package (Jiang et al., 2021a). Three-dimensional ordination is calculated with stress values 0.09. The selected environmental parameters (Table S12) that have relationships or influences with/on the OrgSs composition were also

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130   fitted on the bitplots to evaluate the relationships between the distributions of OrgSs and environmental conditions, with *p*-values calculated over 999 permutations. Spearman correlation between the sum-normalized intensities of individual molecules and some important environmental variables/chemical tracers was performed in R, and then VK diagrams were plotted for each variable based on the Spearman correlation coefficients (Kellerman et al., 2014). Molecules found in at least 4 samples were adopted for correlation analysis. A false discovery rate-adjusted *p*-value was applied to avoid errors arising from using a

135   large dataset.

3 Results and discussion

3.1 Abundance of sulfur-containing species

The annual average concentrations of TS, inorganic sulfate-S and Org-S were 1.94 μg/m^3, 1.31 μg/m^3, and 0.62 μg/m^3, respectively (Table 1). The concentrations of Org-S over Guangzhou were higher than those observed in Hungary (0.02−0.33

140   μg/m^3) (Surratt et al., 2008; Luk´Acs et al., 2009), and close to the upper-bound measured in the U.S. (0.50 μg/m^3), while the percentage of Org-S to fine particles (1.4%) was in the range of 0.75−2.0% estimated in U.S.A (Table S1). These results suggest that Org-S plays a larger relative role in the atmosphere and is probably essential to the high particle pollution in Guangzhou compared to other sites. Our measurement of annual Org-S to TS ratios is 0.33, which is significantly higher than that of ambient aerosols at four sites of Asia (0.01− 0.08) (Stone et al., 2012), the Arctic region (0.08), Hungary (0.06−0.20),

145   the U.S. (up to 0.22). A study conducted in Germany estimated that up to 40% of the TS mass fraction can be contributed by organic molecules, which is consistent with our work. The higher ratios at our measurement than at other sites may arise from many reasons such as the high anthropogenic emissions, high relative humidity, or aerosol acidity levels, which were beneficial to the formation of compounds (Bruggemann et al., 2020).

Table 1: Concentration (μg·m^{-3}) of sulfur-containing species and their fractionation in the PM$_{2.5}$ aerosols from Guangzhou.

Species/ratios	Spring (n=7)	Summer (n=13)	Autumn (n=5)	Winter (n=15)	Average (n=40)
TS	2.03±0.63	1.57±0.68	1.97±0.97	2.25±0.64	1.94±0.72
Sulfate-sulfur	1.37±0.51	1.03±0.48	1.50±0.92	1.52±0.55	1.31±0.60
Org-S	0.66±0.19	0.54±0.28	0.47±0.27	0.72±0.21	0.62±0.26
Sulfate-sulfur/TS	0.66±0.09	0.67±0.14	0.74±0.11	0.66±0.10	0.67±0.12
Org-S/TS	0.34±0.09	0.33±0.14	0.26±0.11	0.34±0.10	0.33±0.12
OrgSs/OM	16.1±5.3	15.1±7.3	10.3±4.8	13.0±6.3	13.9±6.6
Org-S/OM (%)	4.3±1.5	3.9±1.9	2.8±1.8	3.5±1.8	3.7±1.8
Org-S/PM$_{2.5}$ (%)	1.3±0.4	1.8±0.7	1.1±0.4	1.4±0.5	1.4±0.6

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150   In this study, it is possible to estimate the fraction of OrgSs to the organic mass as the necessary mass-weighted average MW
        (or rather C/S ratio) of all organosulfates can be obtained from FT-ICR MS (Luk´Acs et al., 2009). According to Tolocka and
        Turpin (2012), the fractional contribution of organosulfates to the organic mass (f_{OS}) can be estimated using the following
        equation:

$$f_{OS} = MW_{OS} \cdot Org\text{-}S \, / \, (MW_{Sulfate} \cdot Organic\ Mass)$$

155   where MW_{OS} and $MW_{Sulfate}$ denote the molecular weight of organosulfate and sulfate, respectively. Our estimates of OrgSs
        mass to organic matter mass are in the range of 0-30%, which are comparable to the 30% observed in PM_{10} organic mass over
        Hungary (Surratt et al., 2008), and in the range of 5-50% estimated in several sites for fine particulates. Despite the method
        may cause large uncertainties associated with our estimate, the likely importance of these estimates clearly showed that OrgSs
        may be responsible for a sizable fraction of ambient OM and PM mass, and it is essential to perform the detailed chemical
160   characterization of OrgSs to improve the understanding of their sources, formation pathways and fates in the ambient
        environment.

3.2 FT-ICR MS analysis on organosulfur compounds

        In this study, a total of 15998 organosulfur formulas were detected in the organic extracts of yearlong sample set from the FT-
        ICR MS analysis, and the organosulfur formulas detected in each sample accounted for 33±4% of the total number of assigned
165   molecules on average and 24−62% of the total abundance (mean: 44±8%). These compounds are distributed over a wide mass
        range. Based on the numbers of S and N atoms that appeared in each formula, these OrgSs can be grouped as $CHOS_1$, $CHOS_2$,
        $CHON_1S$ and $CHON_2S$. The fractions of the four subgroups are listed in Table S2, with approximately 90% of the molecular
        number and 96% of the total abundance of OSs attributed to $CHOS_1$ and $CHON_1S$. Since a sulfate group ($-OSO_3H$) carries
        four oxygen atoms and nitrooxy ($-ONO_2$) carries three oxygen atoms, and they are all readily deprotonated in ESI, OrgSs with
170   excess oxygen atoms ($o/(4s+3n) \geq 1$) are likely organosulfates (OSs) or nitrooxy-organosulfates (NOSs). However, other OrgSs
        such as sulfonates, may also exist but have not been further detected. As many as 82−92% of detected OrgSs in samples have
        $o/(4s+3n) \geq 1$, suggesting that these compounds are potential OSs or NOSs, which is consistent with previous studies (Lin et
        al., 2012; Tao et al., 2014; Wang et al., 2019).

3.2.1 CHOS compounds

175   Table S2 summarizes the averaged characteristics (molecular weight, elemental ratios, and DBE) of assigned CHOS and
        CHONS compounds. The majority (87−95%) of CHOS formulas in 55 samples contain enough oxygen atoms to allow for the
        assignment of $-OSO_3H$ ($o/4s \geq 1$) in their formulas. The average intensity-weighted H/C, O/C, O/S and DBE values for CHOS
        compounds were 1.77±0.03, 0.52±0.07, 6.7±0.4 and 2.77±0.20, respectively. The H/C ratios are close to or higher than ambient
        aerosols (O'brien et al., 2014; Willoughby et al., 2014; Jiang et al., 2016; Jiang et al., 2020), clouds (Zhao et al., 2013; Bianco
180   et al., 2018) and rainwater (Altieri et al., 2009) collected in the different places of the world measured by negative ESI-FT-
        ICR MS, indicating that the OrgSs are enriched with saturated structures (Table S3). However, the O/C ratios of OrgSs

presented in this work are slightly higher than those of cloud water (Bianco et al., 2018; Zhao et al., 2013), and comparable to the values measured in east-middle Chinese cities,(Wang et al., 2016; Wang et al., 2017a) while are remarkably less-oxidized than samples of organic aerosols measured in Mainz and Chinese cities measured using high-resolution obtrip MS on pollution days (Wang et al., 2019; Wang et al., 2021b). Note that the average DBE value of $CHOS_2$ compounds is approximately 3 times that of $CHOS_1$ compounds, indicating that $CHOS_2$ probably contains numerous aromatic OSs, but $CHOS_1$ compounds are dominated by OSs with long aliphatic carbon chains and low degrees of oxidation and unsaturation.
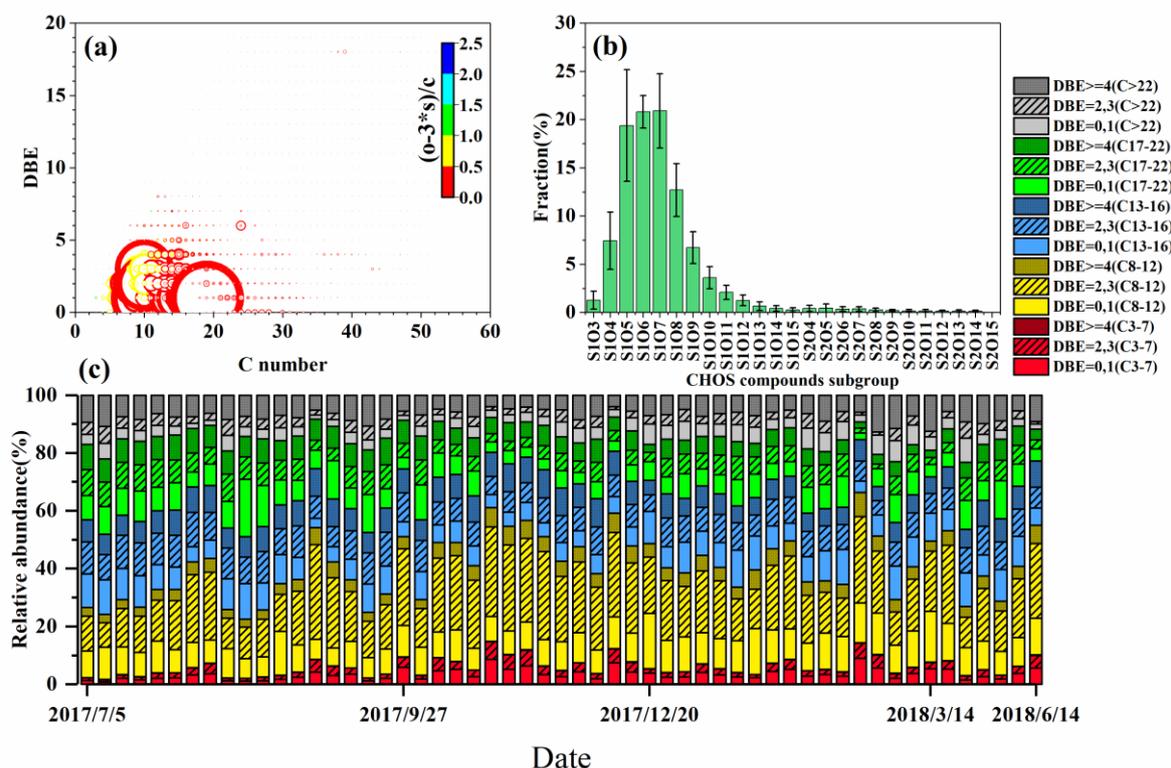
Figure 1: Molecular distribution of CHOS compounds detected by FT-ICR MS for the sample set collected in Guangzhou. (a) Double bond equivalent (DBE) vs C number for all the CHOS compounds of all samples. The colour bar and marker size denote the number of oxidation state and the average sum-normalized relative peak intensities of the compounds; (b) Classification of CHOS species into different subgroups according to the numbers of S and O atoms in their molecules; (c) Relative abundance of each subgroup which divided based on the DBE value and the length of carbon skeleton in the formulas.

Figure 1 shows the DBE, C, and O atomic distributions in the CHOS compounds. The most abundant CHOS species class identified in all our samples, had 5−7 O atoms and 1 S atom. The high number of O atoms in CHOS compounds probably suggested the existence of additional oxidized groups (e.g., hydroxyl and carbonyl). CHOS compounds with medium DBE (=2, 3) accounted for the highest average contribution (40±5%) of the total assigned CHOS compounds (Figure 1c). The

additional double bonds (or olefinic structures) make them be potential candidates for BVOCs-derived Oss (Jiang et al., 2016; Lin et al., 2012). Aliphatic (DBE ≤ 1) and aromatic CHOS compounds (DBE ≥ 4) took up 34±6% and 26±2%, respectively.

200   Note that the DBE-based criteria provide upper bound estimations of the relative abundance of aromatic OrgSs, which was about two times higher than that obtained using aromaticity equivalent (Xc). The latter was considered a better index to describe potential monocyclic and polycyclic aromatic compounds with S atoms (Ye et al., 2020; Yassine et al., 2014). The aromatic OrgSs were dominated by phenyl OrgSs with Xc values between 2.500 and 2.7143, accounting for 76±9% of the total aromatic OrgSs peak intensity, possibly indicating important influences from anthropogenic primary emissions(Figure

205   S1) (Song et al., 2018; Cui et al., 2019). It should be mentioned that the relative abundance of high-ring OSs (Xc≥ 2.7143) increased in winter and spring, suggesting the possibility of more combustion source emissions.

Meanwhile, the low and medium DBE CHOS compounds were further grouped based on the length of the carbon skeleton in the formulas and for studying the distribution of BVOC-derived CHOS compounds. The relatively low DBE (< 4) CHOS compounds with 3 to 7 carbons (C_{3-7}) are smaller compounds which could probably be the fragments produced by atmospheric

210   oxidation processes or the isoprene-derivatives. Larger compounds with $C_{>22}$ were also detected but the average contribution to the total OrgSs intensity was as small as those C_{3-7} compounds. C_{8-22} compounds were the major fraction in CHOS compounds with DBE≤3, with the C_{8-12}, C_{13-16} and C_{17-22} compounds accounting for 30±7%, 17±3% and 14±5% of the total OrgSs abundance, respectively (Figure 1c). C_{8-22} compounds were thought to likely have associations with biogenic sources related to monoterpened/sesquiterpened and their dimeric oxidation products (Kristensen et al., 2016; Daellenbach et al., 2019).

215   However, this group of OrgSs has also been reported in previous studies and proposed to be mainly derived from the photooxidation of long-chain alkanes (Tao et al., 2014; Riva et al., 2016b), and the reactions of SO_2 and unsaturated acids in ambient particle samples (Shang et al., 2016; Zhu et al., 2019). For example, compounds such as $C_6H_{11}O_6S^-$, $C_7H_{13}O_6S^-$, $C_8H_{17}O_6S^-$, and $C_{10}H_{19}O_6S^-$ were both observed in the formation processes via monoterpene ozonolysis intermediates (Ye et al., 2018) and uptake SO_2 by olefinic acid (Zhu et al., 2019). Therefore, the origins of OS with low DBE remain large

220   uncertainty and need to be confirmed by further studies.

3.2.2 CHONS compounds

As shown in Table S2, the assigned CHONS formulas in each sample accounted for 27-42% and 16-41% of the OSs compounds in formular number and abundance, respectively. These compounds have higher average MW, O/C, O/S and DBE values than CHOS compounds probably due to the presence of additional nitrate groups. Despite CHONS compounds containing two N atoms were also identified, their relatively low abundance makes them not as important as those containing

225   one N atom. In this study, 70-89% (in number) of CHONS compounds have $o/(4s+3n)≥1$, implying that these CHONS compounds are candidates for NOSs. NOSs have been demonstrated to form via photooxidation of biogenic VOCs in smog chamber experiments conducted under high NOx conditions (Surratt et al., 2008; Iinuma et al., 2007b). However, recent combustion experiments have found that fresh-emitted organic aerosols also contain a significant fraction of CHONS

230   compounds, especially in coal combustion aerosols (Song et al., 2018; Blair et al., 2017; Tang et al., 2020; Cui et al., 2019).

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For the CHONS species in this study, the CHONS compounds observed were $O_4N_1S_1−O_{15}N_1S_1$ and $O_7N_2S_1−O_{14}N_2S_1$ class species, of which the $O_7N_1S_1$ class species is the most abundant family. The most abundant chemical formula in most of the samples was $C_{10}H_{16}NO_7S^−$ with DBE =3 and m/z = 294.0653, which was usually considered to be generated from the oxidation of α-pinene in the atmosphere (Figure S2a) (Surratt et al., 2008). However, it was also identified in coal combustion-emitted

235   aerosols in a recent study, indicating that this compound probably has multiple sources (Song et al., 2018). The distribution of CHONS across DBE and carbon number are quite similar to that of CHOS (Figure S2a). Note that from the equation of DBE calculation, each nitrooxy group in the CHONS compounds also contains one double bond and therefore contributes to a DBE value of 1. Therefore, DBE values minus the number of N atoms (DBE−N) is a better criterion to determine the aromatic structure or whether this is not possible (Lin et al., 2012). CHONS compounds were dominated by olefinics ((DBE−N)=2, 3),

240   followed by aliphatic ((DBE-N)≤1) and aromatic ((DBE−N)≥4) CHONS (Figure S2c&d). Furthermore, the most abundant classes in aliphatic and olefinic CHONS were C_8-C_{12} compounds with O numbers higher than 7 (Figure S2e&f). Likewise, as described above, they were most likely formed from the reactions of anthropogenically and biogenically emitted VOCs, respectively.

3.3 Potential precursor appointment of OrgSs with previous knowledge.

245   A substantial overlap of OrgSs were observed in this work with source samples, including BBOA, coal combustion organic aerosols (CCOA) and vehicle emissions, non-road excavator and ship emissions, and tunnel aerosol samples (Table S5) (Tang et al., 2020; Cui et al., 2019). Figure S2a shows the comparison of the molecular characteristics of organosulfur compounds for our field observation and source samples. The intense OrgSs in Guangzhou were mainly composed of unsaturated aliphatic molecules, which is similar to the tunnel aerosol sample that may have undergone atmospheric aging processes. However, the

250   OrgSs in fresh vehicle emissions were abundant by aromatics, with 69% of identified OrgSs having Xc≥2.500. Despite the diesel fuel combustion-emitted aerosols also contain unsaturated aliphatic molecules with high intensity, their oxidation levels were clearly lower than those of our field samples. BBOA and CCOA were abundant with aromatic and highly unsaturated organosulfur molecules, which show distinctive molecular characteristics compared to our samples. Although 50±5% (in number) of the OrgSs identified in GZ could be attributed to aromatic OrgSs, most of them have low intensity. These results

255   probably show that although combustion sources can emit numbers of OrgSs, the low abundance of primary low-oxidative and aromatic OrgSs in ambient samples but abundant in source samples probably suggested that the OrgSs in Guangzhou suffered little or indirect influence from primary emissions (e.g., secondary formation via the combustion-emitted precursors). Additionally, we appointed the detected OrgSs into five groups based on their potential precursors, including BVOCs-derived OSs such as isoprene-derived OSs, monoterpene-derived OSs, and other BVOCs-derived OSs from the precursors of green

260   leaf volatiles. Moreover, the relative abundances of anthropogenic VOCs-derived OSs from the precursors of aromatics and anthropogenically emitted alkanes, multiple-source-derived OSs from the precursors of several carbonyl compounds, unsaturated acids and alkanes, were also summarized and calculated. Details of these OSs formulas with the determined precursors are listed in Table S6-10. It should be mentioned that the OSs that were identical to the published OSs (their

precursors have been clearly verified) were temporarily considered to have the same precursors as the published OSs in the
265 present study. This method has been widely used, as the feasibility of this method is based on the high mass resolution of HR-
MS in identifying mass peaks in conjunction with the assignment of formulas using narrow mass tolerance (Lin et al., 2012;
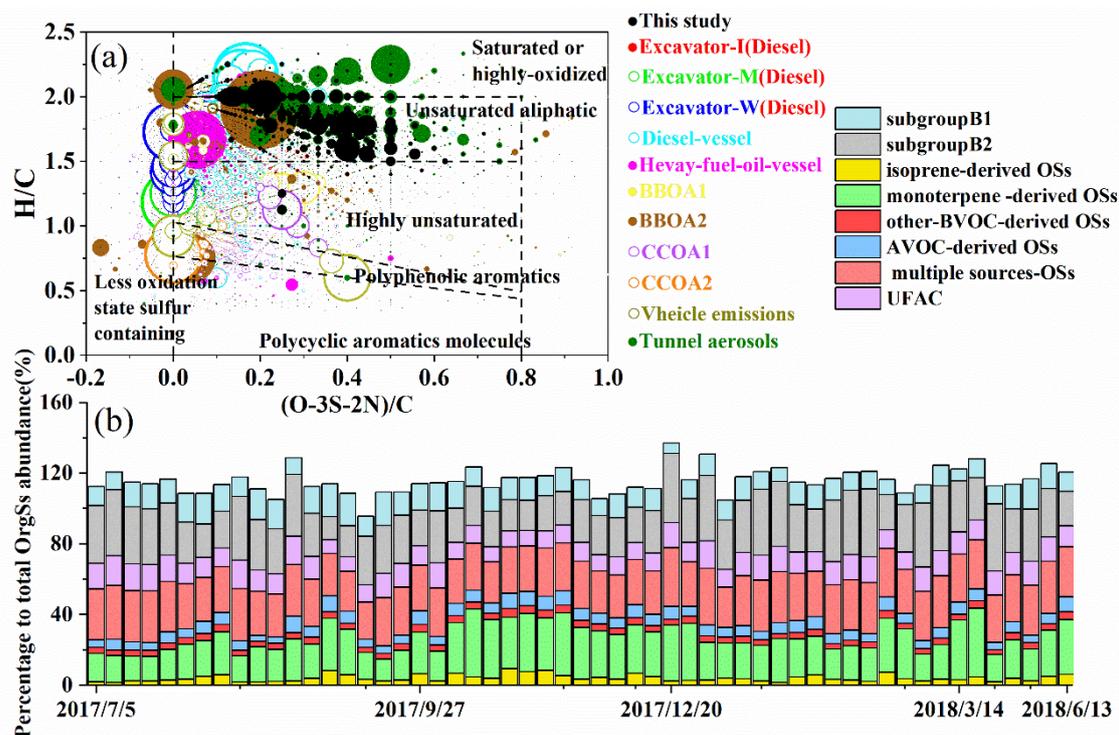Kuang et al., 2016; Ye et al., 2020).

Figure 2: (a) Van Krevelen diagrams of the filed samples collected in Guangzhou and source samples obtained from
270 **Cui et al. (2019) and Tang et al. (2020), including biomass burning organic aerosols (BBOA), coal combustion organic**
aerosols (CCOA), vehicle emissions, tunnel aerosols, and off-road engine emissions (excavator and vessel). Excavator-
I, -M and -W denotes the operation modes of idling, moving, and working, respectively. The marker size denotes the
relative abundance to the total identified organosulfur compounds. (b) Annual variations of potential precursor of
detected OSs to the total identified organosulfur compounds abundance.

275 Figure 2b shows the annual variations of the sum relative abundance of the above five OSs groups to the total OrgSs abundance,
with annual average proportions of 3.8±1.9%, 23±6.7%, 3.6±0.5%, 6.1±1.4% and 27±2.3% for isoprene-derived,
monoterpene-derived, other BVOCs-derived, anthropogenic VOCs-derived OSs and multiple-source-derived OSs,
respectively. The high contribution of known terpene-derived OSs to the total OrgSs intensity in GZ is consistent with previous
observations of the dominance of terpene-derived OSs in GZ (Wang et al., 2017b; He et al., 2014; Bryant et al., 2021). Several
280 highly abundant formulas of terpene-derived OSs, $C_{10}H_{16}O_7NS^-$ (m/z 294); $C_{10}H_{19}O_5S^-$ (m/z 251), $C_{10}H_{15}O_7S^-$ (m/z 279),
$C_{10}H_{17}O_7S^-$ (m/z 281) and $C_9H_{15}O_7S^-$ (m/z 267), were widely reported in previous studies as all predominantly formed by the

acid-catalyzed chemistry of BVOCs-derived oxidation products (Hettiyadura et al., 2019; Bruggemann et al., 2020). Notably, the intense specie $C_9H_{15}O_7S^-$ was also observed in the secondary products by isoprene (Meade et al., 2016), which was supported by the positive correlation between their sum-normalized intensity and the concentration of C5-alkenetriols (SOA

285   tracers of isoprene)(r=0.71, p<0.01). Considering that the isomers integrating both anthropogenic and biogenic precursors cannot be distinguished due to the application of direct infusion of FT-ICR MS analysis, compounds with specific m/z values only manifest as a single signal in the FT-ICR mass spectra, and our reported ratios may therefore have uncertainties. Furthermore, the incomplete OSs list in the SI for the different SOA precursor groups, which due to the limitation of detection techniques and trace concentrations, also leads to uncertainty in our classification.

290   Polycyclic aromatic hydrocarbons have been recognized as important precursors of aromatic OS from laboratory evidence (Riva et al., 2015). Aromatic OSs with benzyl and polycyclic aromatic carbon backbones, such as $C_6H_5SO_4^-$, $C_7H_5SO_4^-$, $C_7H_7SO_4^-$, $C_8H_7SO_4^-$, $C_9H_{11}SO_4^-$ and several OSs from photooxidation of naphthalene and 2-methylnaphthalene, were widely observed in urban and semirural fine particles worldwide (Le Breton et al., 2018; Huang et al., 2018; Wang et al., 2018; Hettiyadura et al., 2015; Bruggemann et al., 2020) and were also detected in our samples. However, there are presently too

295   few classified species of aromatic OSs with relatively low abundance. In overall, the aromatic OrgSs with Xc≥2.5 accounted for 9-20% of the total OrgSs intensity in this study, emphasizing the significant contribution of anthropogenic emissions to Guangzhou.

Among the classified OrgSs with their precursors from multiple sources, a high intensity fraction was contributed by those OrgSs from unsaturated fatty acids, with 8%−17% (average: 12%) of total OrgSs potentially assigned despite the limitations

300   imposed by the large numbers of different OrgSs variants. We observed a positive correlation between unsaturated fatty acid (USFA) -derived OSs and RH (r^2=0.19, p<0.01), probably supporting the mechanism of USFA-derived OSs formation by direct SO_2 uptake. This is consistent with a recent study showing that USFA-derived OSs accounted for a high fraction of total OSs (5%−7% sulfur of all the OrgSs) and positively correlated with RH in the PRD (Zhu et al., 2019). The authors tentatively attributed the formation of these OSs to the direct reaction of SO_2 with unsaturated acids in ambient particle samples in the

305   presence of gas-phase oxidants such as OH radical or O_3 because several laboratory studies (Shang et al., 2016; Passananti et al., 2016) have observed the dependency of USFA-derived OSs formations on RH and suggested that RH is an important influencing factor, in which increasing humidity would accelerate SO_2 uptake and thereby OS formation.

We noted that the subgroup of OSs with unidentified precursors and having C>8, DBE<3 and 3<O<7 (for CHOS)/ 6<O<10 (for CHONS), took up 27±7% abundance of the total identified OrgSs. This subgroup of OSs is characterized by a high

310   molecular weight, alkyl chains and a low degree of oxidation, and was first reported by Tao et al. (2014) who speculated that the precursors of this subgroup of OSs could be long-chain alkanes from traffic emissions. The long-chain alkanes were photooxidized by a mixture of oxidants under typical urban conditions and formed hydroxylated or carbonylated products, which were further esterified to form alkyl OSs. Riva et al. (2016a) conducted an experiment on the photooxidation of alkanes in an outdoor smog chamber and proposed that gaseous epoxide precursors with subsequent acid-catalyzed reactive uptake

315   onto sulfate aerosols and/or heterogeneous reactions of hydroperoxides can also be used to explain the formation of alkane-

derived OSs. Furthermore, the formation of OSs via heterogeneous reactions of SO_2 with unsaturated fatty acids was also important for these highly saturated OSs. The positive correlations between the total relative intensity of this subgroup of OSs and the concentrations of Cl^-, steranes and hopanes (ΣSH) and RH (Figure S3) support the above formation mechanisms, but more detailed source information remains equivocal.

3.4 Possible formation pathways of OrgSs and the influencing factors

As shown in the previous section, the current result suggests that OrgSs in the atmosphere on GZ were significantly influenced by different sources, including both primary emissions and secondary formations. However, although a variety of reaction pathways have been proposed for the secondary formation of OSs, the formation mechanisms of OSs in the atmosphere are not fully understood. Recently, Bruggemann et al. (2020) reviewed and summarized the OS formation pathways that have been identified thus far and outlined their potential atmospheric relevance. Overall, OS product distributions are expected to depend on precursor concentrations (including organic compounds and anthropogenic pollutants of NOx, SO_2, …), acidity, RH and oxidant concentrations. Acid-catalyzed reactions of epoxides oxidized from VOCs were shown to be kinetically feasible to produce OSs and are widely adopted to explain the formation of OSs. A recent study conducted in South China also showed high levels of isoprene-derived OSs derived from the acid ring opening reactions of isoprene-derived epoxydiols (He et al., 2018). In view of the products' molecular structure, acid-catalyzed ring-opening of epoxides by addition of HSO_4^- usually leads to the formation of β-hydroxyl OS (Figure 3, Scheme 1) (Lin et al., 2012). Thus, the OS and nitrooxy-OS generated from the epoxide pathway usually have O>4 for CHOS compounds and O>7 for CHONS compounds, respectively. Lin et al. (2012) removed $-SO3$ from the OrgSs to obtain corresponding alcohols and examined their presence by comparing them with the non-S-containing formulas in the samples collected at the Pearl River Delta. They found that 65-75% of CHOS compounds could be formed from the epoxide intermediate pathway. In our samples, an upper bound estimation for the fraction of OrgSs formed via epoxide intermediate pathway could reach half number of detected OrgSs because of 46±12% of OrgSs satisfied the aboved criterion (Table S11). Other formation pathways are also important and could contributed large fraction of OrgSs.
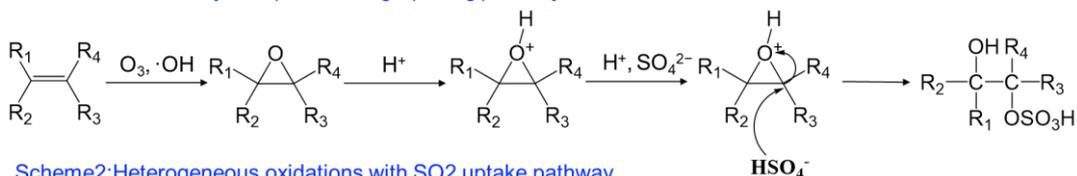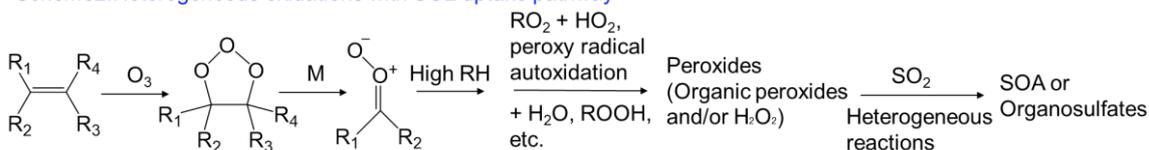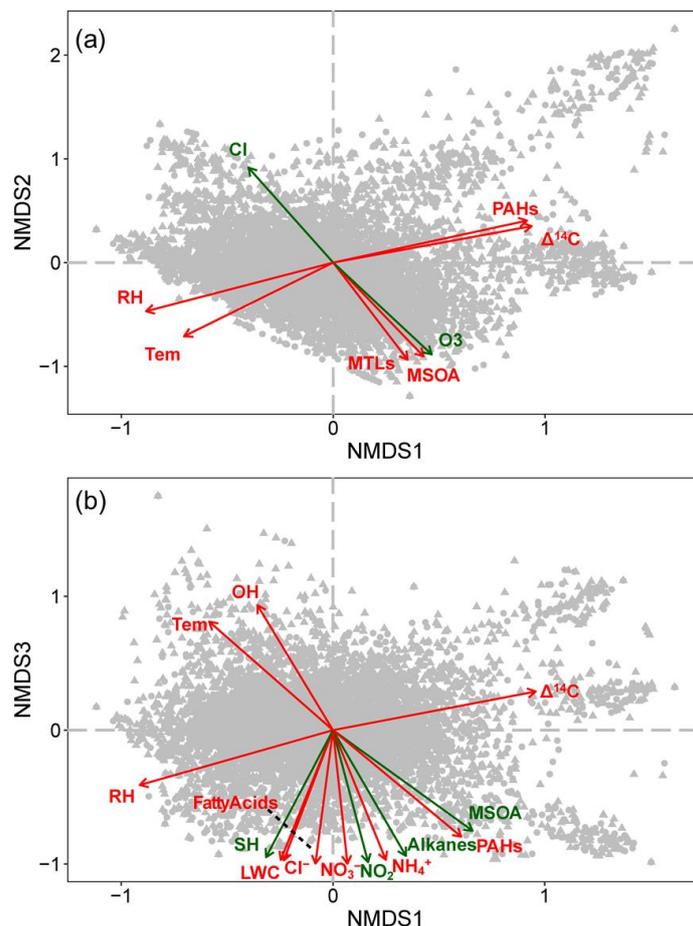
340 **Figure 3: The two potentially important OSs formation mechanisms in Guangzhou (Duporte et al., 2020; Ye et al., 2018; Bruggemann et al., 2020). (a) Proposed OSs formation mechanism of acid-catalyzed ring-opening of epoxides; (b) Proposed OSs formation mechanism for heterogeneous reactions of SO_2 and the secondary products from ozonolysis unsaturated hydrocarbon at high relative humidity.**

From the Org-S mass data, as shown in Table 1, the Org-S species along with TS and sulfate-sulfur levels exhibited clear
345 seasonal variation, with all showing higher values in autumn and winter than in spring and summer. The higher sulfur-containing species values may be due to the higher anthropogenic emissions in cold seasons. However, both the Org-S to particulate mass ratio and the OrgSs to organic mass ratio exhibit different seasonal variations compared to its concentration, with higher ratios observed in summer than warm seasons. This different seasonal characteristic may have been influenced by several factors, including precursor emissions of biogenic VOCs and high RH levels which might increase the SO_2 uptake and
350 formation of OrgSs during warm seasons (Bruggemann et al., 2020; Zhu et al., 2019). Additionally, gas-phase oxidation initiated by O_3 or OH radicals, which promote the generation of oxidation products, hydroxyl and carbonyl (Riva et al., 2016b). These were supported by the finding that the concentration of Org-S was positively correlated with oxidant levels (indicated by NOx+O_3, r=0.40, p<0.01) and SO_2 (r=0.37, p<0.05). Furthermore, we observed that the concentration of Org-S was positively correlated with the fraction of NO_3^- in secondary ion aerosols (SIA) (r=0.41, p<0.01), but negatively correlated with
355 the SO_4^{2-}/SIA ratios (r= −0.40, p<0.01), suggesting the presence of competition between SO_4^{2-} and OrgS in their formation (Figure S4). This is inconsistent with a previous observation that the OSs increased with SO_4^{2-}/SIA, which showed linear regression with particulate acid (Guo et al., 2016; Wang et al., 2018). Several studies also reported that some isoprene-derived OSs, which were produced through the reactive uptake of isoprene-epoxydiol (IEPOX) onto acidic particles, exhibited no correlation with aerosol acidity (He et al., 2014; Lin et al., 2013; Worton et al., 2013). In this study, the pH of all samples was
360 below 5 and we did not observe a significant correlation between pH values and Org-S concentration, but molecular-level assessment showed that hundreds of individual organosulfur species were positively correlated with pH, probably indicating that the variations in particulate acid have minor associations with the OrgSs formation in overall. Additionally, it is worth mentioning that we found that the concentration of Org-S has insignificant correlation with the concentration of levoglucosan and ΣSH, indicateing that primary combustion sources probably have little or no direct impact on the variation of organosulfur,
365 which is consistent with the comparison analysis in the section 3.3.

Also, our findings may support the heterogeneous reactions of the SO_2 uptake pathway which is expected because, as discussed above, the Org-S concentration was positively correlated with O_3, NO_2 and SO_2, and RH was negatively correlated with SO_2 (Ye et al., 2018; Bruggemann et al., 2020). Both laboratory studies and field observations suggested that SO_2 uptake by unsaturated compounds and naphthalene and the formation of OSs were shown to increase with higher RH levels (Zhu et al.,
370 2019; Shang et al., 2016; Riva et al., 2015) Blair et al. (2017) also reported an increase in their concentrations with increasing RH for some specific aromatic OSs in biodiesel and diesel fuel SOA. Ye et al. (2018) found that SO_2 uptake and OSs formation were shown to increase with higher RH levels for the monoterpene ozonolysis intermediate, likely owing to reactions between

SO$_2$ and organic peroxides. Given the high RH levels during the sampling campaign (average=71%) and the above results, it is reasonable to speculate that SO$_2$ was preferentially partitioned into the aqueous phase and formed HSO3$^-$, with the formation

375   of OSs through the reactions between HSO3$^-$ and the organic precursor ozonolysis intermediate, organic (hydro-)peroxides (Figure 3, Scheme 2) (Ye et al., 2018; Bruggemann et al., 2020).

Figure 4: Nonmetric multidimensional scaling analysis of the influences from environmental parameters on organosulfur compounds. The three-dimensional ordination Ordinations are based on Bray−Curtis (stress = 0.09, non-

380   **liner r^2=0.99), which utilizes sum-normalized relative compound intensity. Environmental parameters listed in Table S6 were fit to the ordination. Gray-shaded circles are organosulfur compounds. Variables with significance levels of <0.05 (green) and <0.01 (red) are shown, and nonsignificant correlations are not shown.**

To better support our speculation and discern the possible environmental drivers of the molecular distribution of OrgSs, NMDS analysis of OrgSs was used (Fig. 4 and Table S12). We noted that RH is an important driver associated with the seasonal

385   distribution of OrgSs composition, as RH and temperature are clustered at the negative end of the first dimension, while Δ^{14}C was positively correlated with the first dimension. Notably, the "older" ^{14}C age of organic carbon is generally accompanied by

high RH, and the results from recent compound-specific dual-carbon isotopic (δ^{13}C and Δ^{14}C) analysis of dicarboxylic acid (SOA tracers) indicated that large fractions of organic mass were substantially contributed by the aqueous-phase transformation of fossil-fuel precursors (Xu et al., 2021a). These results may suggest the importance of aqueous-phase

390 formation of OrgSs via fossil-fuel precursors other than direct emissions from combustion sources (Wang et al., 2021a). Additionally, we found that the BVOCs-derived SOA tracers and O_3 were distributed at the negative end of the second dimension, while the anthropogenic species (e.g., NO_3^-, NH_4^+, NO_2, fatty acids, ΣSH…) and aerosol liquid water content (LWC) were negatively correlated with the third dimension, which was inversely for temperature and OH radical (Figure 4). This probably suggested the different oxidation processes in formation of OrgSs between warm and cold seasons, as cold

395 seasons often featured high anthropogenic emission and high biogenic emissions are often happen in warm seasons. The cluster of BVOCs-derived SOA tracers and O_3 probably suggested that SOA products produced by the reactions of BVOCs with O_3 are important precursors of the OrgSs in this study, which supported by recent studies showing that the daytime/nighttime O_3-related oxidation in the presence of SO_2 also potentially contribute to the organosulfates (Xu et al., 2021b; Chen et al., 2020). However, the cluster of anthropogenic organic compounds with reactive nitrogen species and LWC probably also suggested

400 the influences of aqueous-phase reactions of fatty acids and other fossil precursors on OrgSs formation, particularly the inorganic nitrogen species related formation of NOSs (Bryant et al., 2021). This is expected because aerosol LWC provide media for aqueous phase reactions (Guo et al., 2016; Liu et al., 2017; Wang et al., 2018), and positive correlations were observed between LWC and secondary inorganic aerosols (r=0.69, p<0.01), particularly the inorganic nitrogen species. Moreover, directly assessing relationships between individual compounds and LWC, NO_3^-, NH_4^+ suggested that the increase

405 of their concentrations would promote the formation of CHONS species, as 72%, 65% and 75% of the OrgSs that have positive correlations (p adjust with "fdr") with the LWC, NO_3^-, NH_4^+, are CHONS species (Table S13), respectively, further supports the OrgSs formation via aqueous-phase chemistry in Guangzhou influenced by LWC, such as NO_3-initiated oxidation, acid-catalyzed epoxide pathways (Wang et al., 2020; Xu et al., 2021b). Recently, Bryant et al. (2021) reported that oxidants and temperature are important factors that affect OSs formation in Guangzhou, and high-NOx pathways became more important

410 in the winter when usually suffering high anthropogenic emissions, while low-NO formation pathways were dominant in the summer. The observed opposite influence of OH radicals and inorganic species on OrgSs distributions also suggested the existence of OrgSs formation from heterogeneous OH radical oxidation when there was less anthropogenic emission (Chen et al., 2020; Lam et al., 2019).

4 Conclusions

415 This study reports the abundance and molecular characteristics of the atmospheric organic sulfur fraction in Guangzhou, South China, with yearly $PM_{2.5}$ samples were analyzed. Our estimation showed that organosulfur can contribute to 25% of the total organic mass on average, which is important to fine particulate pollution. Molecular composition analysis performed by negative ESI-FT-ICR MS suggested the complex chemical composition and their multiple sources. The substantial overlap of

organosulfur species observed in this study with previous chamber and field studies suggests that these alternative mechanisms

420 of organosulfur formation could be important in the atmosphere in Guangzhou. Furthermore, we also compared the organosulfur species composition with several source samples and clear differences were found among different source samples. It should be noted that many organosulfur species in our data previously classified as biogenic, anthropogenic, or unidentified sources were also found among the collected source samples. Despite most of time they show relatively low abidance than aromatic organosulfur compounds, the large human activities, and anthropogenic emissions (e.g., vehicle

425 emissions, coal combustion and biomass burning) possibly imply their important contributions oto these commonly detected species and they require additional scrutiny.

As the formation pathways and influencing factors were hardly recognized, we employed NMDS analysis based on huge data from FT-ICR MS analysis and chemical tracers. Both mass concentration and chemical composition data provide the potential OS formation of acid-catalyzed aqueous-phase reactions, and RH and oxidants (NO_x+O_3) are important environmental drivers

430 that influence the OrgSs distributions and heterogeneous reactions of SO_2 uptake in OrgSs formations. This is consistent with most previous observations of higher yields of organosulfur species at elevated RH during laboratory experiments. The oxidation of BVOCs with O_3, and anthropogenic VOCs with NO_2 were two potentially important pathways for OrgSs formation or the precursors of OrgSs. From our results, we stress that although RH is an immutable parameter, reducing the SO_2 emissions is not enough to decrease the fraction of OrgSs in the particulates but also needs to reduce NO_2 and other

435 anthropogenic emissions.

Data availability

Data are available upon request, by the corresponding authors.

Author contributions

HJ and JL designed the experiment. HJ, JT, BJ and YL carried out the measurements. HJ, JT and YM analysed the data. HJ,

440 JL and GZ organized and supported the samplings. JL and GZ supervised the study and worked for funding acquisition. MC and JT provide the original data about the source samples. HJ wrote the paper. JL, GZ, MC, YM, SZ, XZ, and GZ reviewed and commented on the paper.

Competing interests

The authors declare that they have no conflict of interest.

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