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Response to the Comments on acp-2021-1069

Hongxing Jiang et al.

Author comment on "Molecular characteristics, sources, and formation pathways of organosulfur compounds in ambient aerosol in Guangzhou, South China" by Hongxing Jiang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-1069-AC1, 2022

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

Revised title: Molecular Characteristics, Sources, and Formation Pathways of Organosulfur Compounds in Ambient Aerosol in Guangzhou, South China

Manuscript ID: acp-2021-1069

Dear editor,

In compliance with the reviewers' detailed comments, we carefully revised the manuscript. We checked the text and references.

We appreciate the five reviewers for their helpful comments on our manuscript. We considered the detailed comments by the reviewers and responded to their suggestions and questions. For your and the reviewer's easiness to review the manuscript, an annotated manuscript was attached at the end of this file.

The English in this document has been checked by at least two professional editors, both native speakers of English. For a certificate, please see: http://www.textcheck.com/certificate/YTh5mL.

We sincerely appreciate your consideration. Look forward to hearing from you soon.

With Best Regards,

Dr. Jun Li

Response to Anonymous Referee #1

RC- Reviewer's Comments; AC – Authors' Response Comments

General Comments

RC: The authors presented a work that summarizes a yearlong measurement of organosulfur compounds (OrgSs) in $PM_{2.5}$ collected in Guangzhou. The authors carried out detailed characterization of the abundance and composition of OrgSs using high-resolution mass spectrometry. The authors further examined the molecular characteristics of the detected OrgSs based on the elemental compositions. The association of OrgSs with other chemical tracers and meteorological data were assessed to understand possible sources, pathways, and governing factors that explain their presence in Guangzhou based on current mechanistic knowledge gained through prior laboratory and field studies. The manuscript includes a considerably large dataset that the authors meticulously collected, examined, and compiled. My main concerns about this manuscript are related to the clarity of its presentation. Detailed comments are as follows.

AC: Thanks for providing valuable suggestions on our work. We have made revisions following the comments (corrections are marked in the revised manuscript), and the responses are shown below, with responses are in **Blue** and revised parts are in **Green**.

Specific Comments

RC1: Consistency of the main message: The abstract is highlighting epoxide chemistry, SO2 uptake and heterogeneous oxidation. However, the heterogenous reaction involving SO2 seems to get neglected in the last paragraph of the introduction. The heterogeneous oxidation was mentioned there but this point was not even given enough discussion and not backed up by convincing evidence in the manuscript (Line 411-413). The authors are urged to carefully pick their main points and make sure they are consistently articulated throughout the manuscript.

AC1: Thanks for the reviewer's reminder. We have carefully checked out the whole manuscript aimed at the problems raised by the reviewer. Now, in the revised manuscript, the last sentence of abstract was rephased into:

"The analysis of our large dataset of FT-ICR MS results suggested that relative humidity, oxidation of biogenic volatile organic compounds via ozonolysis, and NO_x-related nitrooxy organosulfate formation were the major reasons for the molecular variation of OrgSs, possibly highlighting the importance of the acid-catalyzed ring-opening of epoxides, oxidation processes, and heterogeneous reactions involving either the uptake of SO_2 or the heterogeneous oxidation of particulate organosulfates into additional unrecognized OrgSs."

To achieve the consistency with each other, the last sentence in the last paragraph of introduction were also revised, now it read as:

"We showed that in Guangzhou, where usually has high RH, oxidation levels and acidity, acid-catalysed ring-open of epoxides, heterogeneous reactions of the SO_2 uptake pathway and different oxidation processes, were potentially important formation pathways of OrgSs……"

Furthermore, in Line482, we have added a summary sentence to conclude the results obtained from the corresponding paragraph. It read as:

"These results suggested the importance of atmospheric oxidation on the molecular composition of OrgSs, but there may be distinct effects for different oxidation processes (i.e., gas-phase O_3 oxidation, liquid-phase NO_3-initiated oxidation and heterogeneous OH radical oxidation)."

RC2: Section 2.1: I think the authors should provide some necessary discussion regarding the sampling site and its connection to the emission sources. This will provide some contexts for the comparison of the samples in this study with the source samples discussed in Section 3.3. Now it gives the readers impression that the source samples are suddenly brought up from nowhere.

AC2: Thanks for the reviewer's suggestion. Now we have added a brief description about our sampling site, and the brief results source apportionment from our previous study using the same sample set in section 2.1 (detailed contributions for each source were also presented in the Supplementary text). We believe this information could be benefit to readers that why the comparisons were made between source samples and our filed samples.

"Our observation site is located at the central of Guangzhou, where coal combustion for industry and vehicle emissions significantly contributed to the particles pollution (Dai et al., 2015). Furthermore, the regional transported biomass burning organic aerosols also have impacts on the organic matters(Liu et al., 2014). Our previous source apportionment using the ^{14}C-based positive matrix factorization analysis have shown that the primary sources of fossil-fuel combustion and biomass burning averagely contributed half of organic matters at Guangzhou in total. Sources of the rest of organic matters were associated with secondary processes. It should be noted that the mixed secondary factor of isoprene-derived SOA and organic sulfates formations accounted for 44% of the secondary sources, and showed lower concentrations in winter than in summer (Supplementary text) (Jiang et al., 2021b).**"**

RC3: Line 97–98: I was confused by the criteria of excluding samples described here: "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." It seems to me that "TS to sulfate-sulfur ratios of samples greater than 2 or less than 0.5" reflects a rather loose tolerance when compared to previous studies such as Shakya and Peltier, 2015. However, "also" indicates there were other criteria. Did the authors miss something here? I was also confused by the total number of samples analyzed. It was stated here that 40 samples were reserved but later authors said a total of 55 samples were analyzed by ESI-FT-ICR MS (Line 105). How many samples are the presented data (particularly those in Table 1) representative of? Please clarify.

AC3: Thanks for the reviewer's reminder. In this study, a total **55 PM2.5 samples** were used for sulfur-containing species analysis. After data processing, finally, the sulfur-containing species concentration data for **40 samples** were reserved and used for **further discussion**. However, for FT-ICR MS analysis, the **55 PM$_{2.5}$ samples** were all processed and analyzed.

We agree with the reviewer that using a rather loose tolerance is suitable when compared to previous. However, given the low abundance of OrgSs in ambient aerosols, and the two separated analytical (IC analysis and element analysis) processes may result large uncertainties and analytical errors, thus we have to be careful and cautious in processing these data. In the end, we still decide to follow this criterion. It should be noted that we also processed our data by discarding the above criterion, though the values were changed, our obtained results such the seasonal variations and the comparisons with other studies, were all consistent with current results.

Another thing should be mentioned that we have forgot to show other criteria which used here. That is, first, we calculated the Org-S/TS, then we calculated the uncertainty of organosulfur fraction of total sulfur ($\delta_{\text{Org-S/TS}}$) according to Chen et al. (2021). As mentioned by the reference, a calculated OrgS/S greater than $\delta_{\text{OrgS/S}}$ is considered significant. By using this criterion, we exclude the unreasonable data caused by analytical uncertainties associated with measurements. Missing values were appeared in several samples because of some problems happened during the analysis procedures. Therefore, finally the sulfur-containing species concentration data for 40 samples were reserved and used for further discussion. We have made changes in section 2.1, please see the following version:

“And the TS to sulfate-sulfur ratios of samples greater than 2 or less than 0.5 were considered as a measure of gross measurement error. In this study, samples met to these conditions were excluded from further discussion. Moreover, according to Chen et al. (2021), a calculated ratio of organic sulfur to TS (Org-S/TS) greater than their uncertainty ($\delta_{OrgS/TS}$) is considered significant (detailed calculations can be found in Supplementary text). The content of organic sulfur (Org-S) was estimated as the amount of sulfate-sulfur subtracted from TS (two negative Org-S values were set as zero). By using this criterion, we exclude the unreasonable data caused by analytical uncertainties associated with measurements. Finally, the concentration data of sulfur-containing species of 40 samples were reserved and used for further discussion.”

RC4: How were PM2.5 and OM determined for calculating the fractions summarized in Table 1? Is OrgSs/OM in Table 1 same to fOS defined in Line 154?

AC4: thanks. We are sorry that we haven’t presented the concentrations of $PM_{2.5}$ and OC in this MS, which were measured and reported in our previous study. In the revised supporting information, we have added the measurement of $PM_{2.5}$ and OM, the revised is:

“A total of 55 $PM_{2.5}$ samples collected on prebaked quartz fiber filters at Guangzhou from July, 2017 to June, 2018 over a period of 24 h with a high-volume air sampler at a flow rate of 1 $m^3 \cdot min^{-1}$ (June–September: summer, October–November: fall; December–February: winter; March–May: spring). Quartz fiber filters were preheated at 450°C for 6 h before used and weighed. After sampling, each filter was wrapped with prebaked aluminum foil, sealed. Before weighing again, the $PM_{2.5}$ samples were kept at constant temperature and humidity for 24 h. The difference between two weighing is the amount of collected $PM_{2.5}$. A punch of filter (1.5 cm2) was used for carbon concentration measurement. The concentration of organic and elemental carbon were measured using an OC/EC analyzer (Sunset Laboratory,Inc.) following the NIOSH870 thermaleoptical transmittance (TOT) standard method. We converted OC to organic mass using a typical ratio of OM/OC of 1.8(Tolocka and Turpin, 2012).”

Moreover, the OrgSs/OM in Table 1 is same to f_{OS} defined in Line 185, now we have corrected the OrgSs/OM to $f_{OS.}$ Please check it.

RC5: Figure 1c: The x tick labels are roughly spaced by 3 months but the number of samples between the tick labels are not the same and didn’t match the number of samples for each season (Table 1), which seems arbitrary to me. The authors may consider spacing out the tick labels based on seasons. Please also clarify the starting and ending months for the first and last sample collected in each season in Table 1 either as a note associated with the table or in the methods section.

AC5: thanks for the reviewer’s suggestion. As mentioned above, we have added the information of seasonal division in the Supplementary text. It should be noted that the summertime was extended by a month, which is consistent with previous study (He et al., 2014). This is because Guangzhou is located at subtropical region, where still has sufficient sunshine and high temperature in September.

In Figure 1c, the x axis tick labels are spaced by each sample, though it looks like spaced by 3 months. We do this to avoid overlapping of column bar. In fact, as we mention in section 2.1, the samples with $TS/SO_4^{2-}>2$ or < 0.5 were excluded for further analysis. Therefore, only 40 samples were remained, and it caused the mismatch for number presented in Table 1 and Figure 1c.

To avoid misunderstands, we now have added notes to the captions of Table 1 and Figure 1. Please check it.

RC6: In Table 1: Why OrgSs/OM >>1. Is the unit %? If so, the fact that OrgSs/OM values were much greater than Org-S/OM is problematic. The authors should discuss possible reasons in the context of measurement uncertainties and assumptions made in the quantitative calculations.

AC6: thanks for the reviewer's reminder. We have missed the unit of OrgSs/OM and the unit of OrgSs/OM should be "%". Now we have corrected it. Please check it in Table 1.

As the reviewer mentioned, the OrgSs/OM values were much greater than Org-S/OM. It worthy mentioned that the OrgSs denotes the mass of organosulfur compounds, while the Org-S denotes the mass of sulfur in organosulfur compounds. According to our FT-ICR MS analysis, the average molecular weight of CHOS and CHONS compounds were 353 and 374, and the OrgSs were estimated based on the average molecular weight of organosulfur compounds obtained from FT-ICR MS analysis. If all of these organosulfur compounds only contain 1 sulfur atoms, then the OrgSs/Org-S could be roughly estimated as ~11 (353/32 to 374/32). However, as mentioned in section 3.2, although there are large numbers of S_2 compounds were detected in all samples, they all showed low intensity. Therefore, the OrgSs/Org-S can be also closed to 11. Though the OrgSs/OM values were greater than Org-S/OM, according to the seasonal average values in Table 1, the ratios of OrgSs/OM to Org-S/OM were in the same magnitude as the above estimations. So, we think the two ratios are reasonable.

RC7: Line 239-241: By definition, aliphatic compounds include both saturated and unsaturated compounds ((DBE − N) < 4). Therefore, aliphatic is not the most accurate term to refer to compounds with (DBE − N) <= 1. In addition, it is unclear to me how one can derive what was stated (most abundant classes in aliphatic CHNOS being C8-12 with O numbers > 7) from Figure S2e&f. Wrong referenced figures?

AC7: We agree with the reviewer. Now we have corrected the aliphatic to "saturated aliphatic". Additionally, we are sorry for the mistake of wrong referenced figure numbers as it should be Figure S2 b&c&d. Now we have corrected it, please check it in Line299.

RC8: Line 317-319: Why did the authors show the correlations with Cl^-, steranes and hopanes while the preceding discussion was primarily about the long chain alkanes? This seems out of context. Please elaborate.

AC8: Thanks. In this paragraph, we are trying to talk about the possibly sources or formation pathways for the subgroup of OSs with unidentified precursors. Here we showed that the photooxidation of long chain alkanes from fossil combustion sources of traffic emissions as well as the heterogeneous reactions were the two possible mechanisms according to the references. The chemical species of Cl^-, steranes and hopanes were all tracers of fossil combustion sources, especially vehicle emissions(Jiang et al., 2021c). Moreover, as discussed in Line 362-366, we have shown that RH probably is an important influencing factor that associated to heterogeneous reactions. From our results that those positive correlations were observed between the total relative intensity of this subgroup of OSs and the concentrations of Cl−, steranes and hopanes (ΣSH) and RH, we show the above two formation mechanisms may be all important to this subgroup of OSs in our observation site.

To make it clear, we have rephrased this sentence, and the revised sentence is:

"The total relative intensity of subgroupB1 was positively correlated with RH and the concentrations of chemical tracers associated with fossil fuel combustion (Cl^-, steranes and hopanes: ΣSH) (Figure S3), support the influences of heterogeneous reactions and photooxidation of traffic-emitted long-chain alkanes on subgroupB1, but more detailed source information is required to confirm this.”

RC9: Line 330-331 and Scheme 1: SO_4^{2-} should play a main role in the reactions with epoxides explaining OS formation under relevant atmospheric conditions as HSO4- is a much weaker nucleophile (Aoki et al., 2020).

AC9: thanks for the reviewer’s reminder. We agree with the reviewer, we have corrected the statement into “In view of the products’ molecular structure, the acid-catalyzed ring-opening of epoxides by the addition of inorganic sulfate ions usually leads to the formation of β-hydroxyl OSs (Figure 3, Scheme 1)”. And the Scheme 1 in Figure 3 were also updated. Please check it.

RC10: Line 335-337: The authors showed that there is a considerable number of compounds that could be possibly explained by epoxide pathway. What is the summed relative abundance of these compounds to total OrgSs? This is one of the highlights of the paper and there is so much potential for further discussion later in the manuscript. I would expect to see if they vary seasonally and how they correlate with other chemical tracers and environmental parameters such as SO_4^{2-}, pH, RH, LWC, etc.

AC10: thanks for the reviewer’s suggestions. We now have added the relative abundance of these OrgSs to the total in Table S11. We also described their seasonal variation that they showed decrease trends from summer to winter, and then increase in spring. The correlations between the relative abundance of these OrgSs and those chemical tracers or environmental parameters were also performed. The corresponding results were added in the last of this paragraph. Here is the revised version:

" The percentage of MS intensity for these OrgSs had a decreasing trend from summer to winter, and then increased in spring. It presented positive correlations with the fraction of SO_4^{2-} in secondary ion aerosols (SIA) (r=0.54, p<0.01), temperature (r=0.63, p<0.01) and biogenic SOA tracer (r=0.34, p<0.05), which was consistent with a recent study (Bryant et al., 2021) and suggested that the temperature and available particulate SO_4^{2-} are important influencing factors in the formation of OrgSs via the acid-catalyzed ring-opening of epoxides.**"**

RC11: Line 344-345: I don't think this statement was accurate according to what was shown in Table 1. Except for sulfate-sulfur, Org-S and TS mean values are both higher in Spring than in Autumn. Additional analysis is recommended to determine whether there are any statistically significant differences between the four seasonal averages.

AC11: thanks for the reviewer’s reminder. We are sorry we have made some small mistakes in calculating the spring average. Now we have corrected the values presented in Table 1. We also have checked the seasonal variation of the three sulfur-containing species and an ANOVA analysis was performed to test the statistically significant differences between the four seasons, significant differences between the four seasonal averages were supported by p<0.01 for all.

RC12: Line 348: cooler instead of warm seasons? In fact, all three other seasons?

AC12: thanks. Corrected. It should be cold seasons.

RC13: Line 404-406: The numbers (72%, 65%, and 75%) cited to support the statement don’t agree with Table S13. They should be 100%, 64%, and 74%, respectively. Are there errors in Table S13 or the text? Table S13 also appears to be incomplete. For example, the last three cells in the row of MTLs are missing percentage data.

AC13: thanks for the reviewer's reminder. There are some errors appeared in the main text. Now we have corrected it. Besides, values lost during copying in Table S13 have been replenished. Please check it.

RC14: Line 416: 25% is not consistent with Table 1 which shows an average OrgSs/OM of 13.9%.

AC14: thanks for the reviewer's reminder. We have corrected it.

Technical Corrections

RC15: The title: replacing "Drivers" with Drive makes more sense to me.

AC15: In following the reviewer's suggestion, we have replaced "Drivers" with "Drive" in the titles.

RC16: Please make sure the numbers in all chemical formulas are subscripted throughout the manuscript.

AC16: thanks. We have checked it and updated it.

RC17: Line 247: I think the authors intended to say Figure 2a instead of Figure S2a.

AC17: thanks. We have corrected the error. Please check it.

RC18: Line 303: I know PRD stands for Pearl River Delta but the abbreviation was not defined in the text. In a few other occasions, Pearl River Delta was used but not abbreviated.

AC18: Thanks for the reviewer's reminder. We have added the definition for the abbreviation of PRD in Line75. Please check it.

RC19: Line 353: Was reference to Figure S4 supposed to be here?

AC19: Thanks. We have added the reference Figure S4 here.

RC20: Figure 4: In the figure caption, Table S6 doesn't seem to be the correct reference for environmental parameters.

AC20: Thanks. We have corrected it.

RC21: The reference to Figure S1 is nowhere to be found in the text. Is Figure S1 complementary to Figure 1, which only show the subgroup CHOS?

AC21: Thanks. Figure S1 is complementary to Figure 1, and offers the molecular distribution of CHOS compounds. It can be referenced in Line251.

RC22: Tables S1-S4: The cell information could be better aligned. Consider adding cell outlines to guide the eyes.

AC22: Thanks for the reviewer's suggestion, we have updated the Tables S1-S4.

RC23: Table S2: What does SOC standard for? Sulfur containing organics? What is SOC formulas set? Please clarify and make sure they are defined and explained in the revised manuscript.

AC23: Thanks. the SOC denotes Sulfur containing organic compounds. SOC formulas set denotes the organosulfur compounds detected in all samples. In this study, a total of 15998 organosulfur formulas were detected in the yearlong sample set. Now we have added two notes in the Table S2. Please check it.

RC24: Table S6-S8: Please subscript atomic numbers in the chemical formulas

AC24: thanks for the reviewer's suggestions. We have corrected it.

Response to Anonymous Referee #2

General comments

RC: This paper presents new measurements of fine particle composition in Guangzhou, China in terms of total sulfur, sulfate and, by difference, organic sulfur (OrgS). Detailed molecular formula analysis is performed by ultra-high resolution mass spectrometry. Analysis focuses on identifying molecular characteristics (elemental ratios, double-bond equivalences) and primary or secondary sources. Qualitative source identification relies upon molecular formulas identified in previous chamber or source studies. The observed molecules indicate that OrgS in Guangzhou are different than other previously studied locations, although this aspect of the manuscript should be further developed. The manuscript makes significant findings, although clarifications are needed about the meaning of the data, especially in relation to differences in ionization efficiency among OrgS and potential matrix effects that affect the mass spectrometer signal. Suggestions to improve the presentation quality are provided.

AC: We greatly appreciate the reviewer for recognizing the merits of this work and for providing valuable suggestions. These suggestions would help us improve the manuscript.

Specific comments

RC1: The assumption that "different OSs may have similar ionization efficiency" is problematic, because ionization efficiencies can differ greatly across molecules. Additionally, when samples are directly infused and analyzed, they are subject to ionization suppression when ions compete in the source to be ionized. For these reasons, the ESI-MS intensity is not a reliable measure of organosulfates absolute or relative abundance. Consequently, the correlation analysis (NMDS) is unreliable for quantitative analysis of OrgS sources and formation pathways. I suggest that this entire section be removed.

AC1: We agree with the reviewer that ionization efficiencies can differ greatly across molecules.

However, studies have shown that the assumption of "different OSs may have similar ionization efficiency" can obtain reasonable results and gain qualitatively molecular information of organosulfur compounds composition (Ye et al., 2020; Kuang et al., 2016; Lin et al., 2012; Gao and Zhu, 2021). In ESI−MS spectra, peak intensity is the product of initial concentration and ionization efficiency of the neutral compound. The presence of a sulfate functional group on the organosulfates molecules makes them readily ionized during the ESI process. Because the ionization of organosulfates takes place on the sulfate functional group, and therefore, it is reasonable to assume the different organosulfates may have similar ionization efficiency. On the basis of this assumption and the fact that all of the spectra were acquired under the same ESI−MS conditions(in this study, all the samples were analyzed in the same condition, and similar carbon concentration of sample were used for analysis as reported in our previous study(Jiang et al., 2021b)), the peak intensities of the organosulfates ions could be compared to provide information on relative abundances among different samples by assuming that matrix effects were relatively constant in all samples(Lin et al., 2012; Kuang et al., 2016).

Another thing deserved to be mentioned is that though the different molecules are subject to different ionization suppression, or even a same molecule may subject to different ionization suppression in different samples, the relative abundance of compounds were also used for comparing in several good papers after keeping the analysis under the same conditions(Kellerman et al., 2015; Kellerman et al., 2014).

NMDS analysis based on the relative abundance of each compound were successfully applied in identified the factors that have associations with molecular distribution. And we think the NMDS analysis is reasonable and could provide useful information about the composition of organosulfur compounds.

Based above reasons, we decided to not to deleted the parts regard to NMDS analysis. For more clear understanding about the assumptions, we have added a additional sentence in the section 2.3. please check it.

"We assume that the different OSs may have similar ionization efficiency (Bateman et al., 2012), because the sulfate functional group on the OSs molecules are readily ionized during the ESI process and the ionization of OSs often takes place on the sulfate functional group (Lin et al., 2012). Based on this assumption and the fact that all the samples with similar carbon concentration were analysed in the same condition in this study (Jiang et al., 2021b)), the peak intensities of the OSs ions could be compared to provide information on relative abundances among different samples by assuming that matrix effects were relatively constant in all samples(Lin et al., 2012; Kuang et al., 2016). However, the ionization efficiencies may vary among different OSs compounds for other reasons, such as surface activity on ESI droplets (Kuang et al., 2016), but the sum-normalized peak intensities of the organosulfur compounds provide information on the relative abundances among different samples."

RC2: Significant clarification is needed in the presentation of the results and if the numerical values represent number intensities (i.e. the frequency of occurrence of a particular molecular formula) or mass spectral intensities. For example, in Figure 1, in several places it is not clear what is the meaning of "relative abundance." In Figure 2, the meaning of "abundance" is not clear. Another example, is "the most abundant chemical formula" at line 232. Do these refer to intensity by number (of formulas) or intensity of MS signal? As a remedy, this could be clarified by indicating "signal intensity" instead of "abundance" or "contribution." The same clarification is greatly needed throughout the text. Please apply this correction to the entire results and conclusion sections.

AC2: thanks for the reviewer's suggestion. We have made corrections in following the reviewer's suggestion. Now the phase of "relative abundance" all have been changed into "percentages of MS intensity" across the main text. Please check it in the corresponding parts.

RC3: Section 3.1 – In the comparison of OrgS to total S to other locations, some of the selected studies focus specifically on organosulfate / sulfur (not OrgS compounds / total S). This distinction is important because OrgS includes organosulfates and other S-containing compounds. Please consider this in the discussion and comparison.

AC3: thanks for the reviewer's reminder. In table S1, which shows the comparison between the results obtained in this study and reported in previous works, we have added notes to emphasize the difference between organosulfate and OrgS compounds. in the main text (Line193), we also have added notes to presented that data used for comparison from the past works only took organosulfates into consideration. Actually, in the main text, only those corresponding parameters were used for comparison, for example, Org-S concentrations were compared to Org-S concentrations in Table S1, but not to those data marked by OS.

RC4: Additionally, a potential contributor to OrgS in this study is methane sulfonic acid (MSA), which can account for a significant amount of PM mass in marine and near-coastal environments. A more accurate estimate of organosulfates could be gained by measuring MSA and discussing its contribution to total S. In the case new measurements cannot be made, can an upper limit be inferred from literature?

AC4: thanks. In following the reviewer's suggestion, we have calculated the ratio of MSA-sulfur to Org-S. The MSA-sulfur concentration was obtained from a previous study that measured in HongKong (lack observation data in Guangzhou), which is a megacity near Guangzhou (Huang et al., 2015). The average ratio of MSA-sulfur to Org-S were 5.8±8.0 from the upper bound estimation. In section 3.1 of the revised MS, we have added several sentences to describe the result of estimation:

"Methanesulfonic acid (MSA) may account for a significant amount of the OrgSs mass in Guangzhou because it is a coastal city in southern China. The ratio of MSA-sulfur to Org-S was calculated based on the upper limit of the MSA-sulfur concentration (0.023 μg/m^3) measured in Hong Kong (a megacity near Guangzhou) during marine air mass influenced days (Huang et al., 2015). The estimated average ratio of MSA-sulfur to Org-S was 5.8±8.0, indicating that marine aerosols are probably also a non-ignorable source leading to the high Org-S values.

RC5: The equation at like 154 appears incorrect. If Org-S refers to organic sulfur, then the equation should have the atomic mass of S in the denominator, rather than the molecular weight of sulfate.

AC5: thanks for the reviewer's reminder. We have corrected the error in the corresponding equations, and updated the data presented in Table 1. PLEASE check it.

RC6: Please number equations.

AC6: thanks. It has been corrected.

RC7: How was organic matter estimated? This is not mentioned in the methods, but should be included since OM is used for calculation of values in Table 1.

AC7: thanks. We have added the estimation of Organic mass both in Line188-189 in the main text and Supplementary text.

The revised version in the main text is:

"……organosulfate and sulfur, respectively. The organic mass was derived from 1.8 times of the OC concentration measured by the Sunset OC/EC analyzer according to Tolocka and Turpin (2012). In this study, the intensity-weighted average MW of OrgSs obtained from the FT-ICR MS analysis (see section 3.2) was used in the calculations. Our estimates of the OrgSs mass……"

The added information in the is Supplementary text is:

"The difference between two weighing is the amount of collected PM$_{2.5}$. A punch of filter (1.5 cm^2) was used for carbon concentration measurement. The concentration of organic and elemental carbon were measured using an OC/EC analyzer (Sunset Laboratory,Inc.) following the NIOSH870 thermaleoptical transmittance (TOT) standard method. We converted OC to organic mass using a typical ratio of OM/OC of 1.8(Tolocka and Turpin, 2012)."

RC8: Further discussion of how Guangzhou compares to other locations is needed. It is suggested that the sources and molecular distribution of organosulfates is different in Guangzhou than other places, but further explanation of how they are different and potential reasons why are needed.

AC8: thanks for the reviewer's suggestion. In section 3.1, we have compared the concentration of Org-S and the ratios of Org-S/TS and OrgSs/OM to the measurements in other places, and gave some possible explanations about these comparisons. Furthermore, in Section 3.2.1 and 3.2.2, the general molecular characteristics of CHOS and CHONS compounds were also compared with other studies. We expressed that the organosulfur compounds in Guangzhou might suffer complex atmospheric oxidation processes and affected by emissions from different sources. All these differences from the comparison results also suggested that the OgrSs in Guangzhou might have clear distinctive molecular composition compared to other places due to the spatiotemporal heterogeneity, which urges further discussion on the sources and molecular distribution of OrgSs.

RC9: Line 246 – Table S5 does not show "a substantial overlap" of ambient samples and source samples. This table only summarizes data from source samples. To improve the comparison to Guangzhou, please add the Guangzhou values to this table. Also, to improve the discussion, please incorporate secondary source data from the literature to show the relationship between primary/secondary sources and how they relate to ambient measurements in Guangzhou.

AC9: thanks for the reviewer's suggestion. In Table S5, we only showed the summary of the calculated molecular characteristics of organosulfur compounds groups detected in source samples by FT-ICR MS. The detailed information about the molecular characteristics of organosulfur compounds groups detected in Guangzhou has been listed in Table S2. To avoid duplication of data presentation, we did not add them to Table S5. More intuitive comparison is shown in Figure 2a, and Table S5 is only a supplementary data of Figure 2a. Additionally, there are limited works have reported the molecular characteristics of organosulfur compounds in SOA detected by FT-ICR-MS or other HR-MS, and most of the present studies only reported SOME specific organosulfates compounds appeared in the generated SOA. And thus, it is very hard to combine these compounds into Table S5, and that is why we did not present secondary source data in there.

RC10: Line 247 – Figure S2a does not show source data. Do you mean Figure 2a?

AC10: yes, it is a wrong figure reference. It should be Figure 2a. we have corrected it.

RC11: I disagree that all studies listed at lines 58-50 "only focused on the existing known Oss". More than one of the cited works include qualitative analysis and identification of new formulas.

AC11: thank. In following the reviewer's suggestion, we have revised this sentence, it now reads:

"However,…… many present studies focused on the existing known OSs because they were abundant in particles(Ye et al., 2020; Hettiyadura et al., 2019; Hettiyadura et al., 2017; Wang et al., 2018). A recent study showed that there is a large fraction of OrgSs (67-79%) remaining unexplained ……**"**

RC12: The following sentence at line 83 is contradictory – "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…" By definition a heterogeneous reaction cannot happen in the liquid phase.

AC12: thanks. In this sentence, we wanted to state that water can involve in the heterogeneous reaction of absorbing gas precursors by liquid, so we say "liquid-phase related heterogeneous oxidation". We agree this may not accurate, and we have revised this sentence:

"We showed that in Guangzhou, where usually has high RH, oxidation levels and acidity, acid-catalysed ring-open of epoxides, heterogeneous reactions of the SO_2 uptake pathway and different oxidation processes, were potentially important formation pathways of OrgSs……."

RC13: Clarification needed in the abstract: Add standard deviation to the percent of total sulfur that is attributed to organic sulfur (at line 21).

AC13: thanks. We have corrected, it now reads:

"……the ratio of the annual average mass of organic sulfur to total particulate sulfur was 33±12%……**"**

RC14: Line 284, Cui et al. (2019, Environ. Sci. Process. Impacts. 2018, 20 (11), 1524−1536) showed that alkene triols can be artifacts of analysis. I suggest avoiding reporting correlation to a potential artifact.

AC14: thanks, we agree with the reviewer that alkene triols can be artifacts of analysis. According to Cui et al. (2018), the potential artifact was resulted from the thermal degradation of methyltetrol sulfates, and therefore, we use 2-Methylthreitol and 2-Methylerythritol as the tracer of isoprene. Now the revised sentence is:

"……which was partially supported here by the positive correlation between their sum-normalized intensity and the concentration of MTLs (SOA tracers of isoprene, the sum of 2-methylthreitol and 2-methylerythritol) (r=0.73, p<0.01)(Li et al., 2013)."

RC15: Line 316, citations are needed to support that unsaturated fatty acids were the source.

AC15: thanks, we have added a reference in the corresponding part. Please check it.

RC16: Formatting of Supplemental tables should be improved to increase readability.

AC16: thanks for the reviewer's suggestion, parts of the Supplemental tables were reformatted to make it read easily, for example Table S1-S4.

RC17: The reaction scheme in Figure 3 should…

Be expanded to include a chemical structure (or two) of organosulfates that can form as products of scheme 2.

A reaction scheme that shows the formation of nitrooxy OS?

AC17: thanks for the reviewer's suggestion. We have updated the reaction scheme in Figure 3, and we also have added a possible reaction scheme that related to the formation of nitrooxy OS. Here is revised Figure 3:

Figure 3: The two potentially important OSs formation mechanisms in Guangzhou (Duporte et al., 2020; Ye et al., 2018; Bruggemann et al., 2020; Aoki et al., 2020; Lind et al., 1987). (a) Proposed OSs formation mechanism of acid-catalyzed ring-opening of epoxides; (b) Proposed OSs formation mechanism for heterogeneous reactions of SO2 and the secondary products from ozonolysis unsaturated hydrocarbon at high relative humidity; (c) one of possible NOSs formation pathway.

RC17: In Figure 2, why would 3S and 2N be used? sulfate has 4O and nitrate 3O.

AC18: In Figure 2, the (O-3S-2N)/C were used to replace O/C to present the oxidation state of C atom. Though sulfate has 4O and nitrate has 3O, each them only have 1 O atom connected to the carbon atom (C-O bond). Therefore, 3S and 2N be used in the calculations.

RC19: Line 361, I am surprised to see the authors state that OrgS correlates positively with pH. Usually a positive correlation is seen with H+ (not the negative logarithm of H+ concentration).

AC19: thanks. We have examined the correlations between molecules and the concentration of H^+, and similar results were obtained. Only a small number of molecules were significantly correlated with H^+.

This sentence has been revised to avoid above mis understand:

"……In this study, the pH of all samples was below 5 and we did not observe a significant correlation between pH values (or H^+) and the Org-S concentration, but a molecular-level assessment showed that a small number of individual organosulfur species were significantly correlated with the H^+ concentration, probably indicating that……"

RC20: Line 365, regarding the lack of significant correlation of OrgS with levoglucosan. It seems reasonable to conclude that biomass burning was not a significant source, however, it does not seem reasonable to extend this to all primary sources.

AC20: thanks for the reviewer's reminder. We have rephrased this sentence to make it more rigorous. Here is the revised version:

"……indicating that primary biomass burning and fossil fuel combustion probably had little or no direct impact on the variation of Org-S, which was consistent with the……"

RC21: I think that "Heterogeneous Secondary Reactions Drivers the Molecular Distribution" can be omitted from the title. The results show there are multiple drivers and the numerical results are not reliable to infer if one source or mechanism is the main driver.

AC21: thanks for the reviewer's suggestion. We have corrected it.

Technical corrections

RC22: Needs to be spell-checked and edited for grammar. Figures should be spell-checked, too. In Figure 2, for example, vehicle is spelled wrong in the legend. In Figure 3, add space after Scheme.

AC22: thanks for the reviewer's suggestion. The grammar and spelling across the main text have been checked. The errors appeared in Figure 2 and Figure 3 have been revised.

Response to Anonymous Referee #3

RC: In this work, the authors identified the key factors (e.g. relative humidity, oxidation of biogenic volatile organic compounds via ozonolysis, and NOx-related nitrooxy organosulfateformations) and processes (e.g. heterogeneous secondary reactions) for the molecular variation of OrgSs in Guangzhou. The paper is well written. The results are clearly presented and discussed. The data analysis is solid and sound. I have a few minor comments/suggestions for authors' consideration.

AC: Thanks for your recognition of our work and for providing valuable suggestions. We have made changes following the reviewer's comments and suggestions.

RC1: line 105, "A total of 55 PM2.5 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)." What would be the extraction efficiency of OSs with methanol in a cold water bath? Would there be any potential artifacts when the samples were extracted with methanol?

AC1: thanks. Though we did not calculate the extraction efficiency of OSs with methanol in a cold-water bath, many previous studies have suggested that methanol could extracted more than 90% of OC both for filed samples or fresh biomass burning samples(Chen and Bond, 2010; Cheng et al., 2017; Huang et al., 2018). Considering OSs are polar compounds, and most of OSs can be dissolved in methanol(Ye et al., 2020). The potential artifacts resulted from extraction with methanol were not tested in this study. However, in a previous study, methanol was used as eluent to collected the humic-like substance for OSs characterization. Direct using methanol as extraction solvent to extract OSs was reported by Ye et al. (2020). All these studies have successfully characterized the OSs and made comparisons between ambient samples collected at different location. Therefore, we think that there might be small or no potential artifacts resulted from extraction with methanol. The above statements have been added into Supplementary text and main text to dispel the possible doubts of the audience.

RC2: line 122, "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).." Can the authors elaborate what would be the uncertainties in determining the concentrations if we assume different OSs have the same or similar ionization efficiency?

AC2: thanks. In ESI−MS spectra, peak intensity is the product of initial concentration and ionization efficiency of the neutral compound. the different ionization efficiencies for different OSs compounds may lead to inconsistency between the ratios of peak intensities and the ratios of concentrations for different OSs compounds. And therefore, this inconsistency would hamper the use of signal intensity to compare the abundance of different OSs compounds in samples. However, it is hard to determine the uncertainties, but studies have shown that the presence of a sulfate functional group on the organosulfates molecules makes them readily ionized during the ESI process. Because the ionization of organosulfates takes place on the sulfate functional group, and therefore, it is reasonable to assume the different organosulfates may have similar ionization efficiency. (Ye et al., 2020; Kuang et al., 2016; Lin et al., 2012; Gao and Zhu, 2021). And in this study, all the samples were analyzed in the same condition, and similar carbon concentration of sample were used for analysis as reported in our previous study(Jiang et al., 2021b)). All these treatments help to reduce matrix effects during ESI- and matrix effects were relatively constant in all samples, and it make sure that the peak intensities of the organosulfates ions could be compared to provide information on relative abundances among different samples(Lin et al., 2012; Kuang et al., 2016).

In the corresponding paragraph, we have revised parts of the sentence to make it more clear. The revised version is:

“We assume that the different OSs may have similar ionization efficiency (Bateman et al., 2012), because the sulfate functional group on the OSs molecules are readily ionized during the ESI process and the ionization of OSs often takes place on the sulfate functional group (Lin et al., 2012). Based on this assumption and the fact that all the samples with similar carbon concentration were analysed in the same condition in this study (Jiang et al., 2021b)), the peak intensities of the OSs ions could be compared to provide information on relative abundances among different samples by assuming that matrix effects were relatively constant in all samples(Lin et al., 2012; Kuang et al., 2016). However, the ionization efficiencies may vary among different OSs compounds and lead to inconsistency between the ratios of peak intensities and the ratios of concentrations for other reasons, such as surface activity on ESI droplets (Kuang et al., 2016), but the sum-normalized peak intensities of the organosulfur compounds provide information on the relative abundances among different samples.”

RC3: line 155, "Our estimates of OrgSs mass to organic matter mass are in the range of 0-30%, which are comparable to the 30% observed in PM10 organic mass over Hungary (Surratt et al., 2008), and in the range of 5-50% estimated in several sites for fine particulates." Can the author elaborate how they obtain these numbers?

AC3: thanks. According the first reviewer’s suggestion, these sentences have been revised to make better comparisons with other studies. In the revised version, we show the detailed calculation about how the ratios of OrgSs mass to organic matter mass were obtained. The revised version is:

“According to Tolocka and Turpin (2012), the fractional contribution of OSs to the organic mass (f_{OS}) can be estimated using the following equation:

$$f_{OS} = MW_{OS} \cdot \text{Org-S} / (MW_{Sulfur} \cdot \text{Organic Mass}) \qquad (1)$$

where MW_{OS} and MW_{Sulfur} denote the molecular weight of organosulfur compounds and S atom, respectively. The organic mass was derived from 1.8 times of the OC concentration measured by the Sunset OC/EC analyzer according to Tolocka and Turpin (2012). In this study, the intensity-weighted average MW of OrgSs obtained from the FT-ICR MS analysis (see section 3.2) was used in the calculations. Our estimates of the OrgSs mass to organic mass ratio (41.7±19.7%) were comparable to observations of the organic mass in PM_{10} over Hungary (Surratt et al., 2008; Luk´Acs et al., 2009), and the estimation at several sites for fine particulates (Frossard et al., 2011; Tolocka and Turpin, 2012), in which only OSs were considered (Table S1). Although there can be large uncertainties associated with this method, the estimates clearly showed that OrgSs may be responsible for a sizable fraction of the ambient OM and PM mass, and it is essential to perform a detailed chemical characterization of OrgSs to improve our understanding of their sources, formation pathways, and fates in the ambient environment.

.”

RC4: line 254, "These results 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)." Can the authors eloborate why the primary aromatic OrgSs are low oxidative? What the atmospheric stabilities of other OSs?

AC4: The formation processes of aromatic OrgSs in primary combustion sources are still unknown presently. But a recent study speculated that these compounds may be produced from thermal reactions of benzenes with SO_2 during the combustion(Song et al., 2018). They have not been oxidized in the fresh aerosols, and may show lower carbon oxidation state compared to those aromatic OrgSs formed via secondary oxidation processes(Riva et al., 2015). The most abundant subgroups of OSs in fresh combustion aerosols were OS_4 and OS_5(Cui et al., 2019; Song et al., 2018), while the most abundant subgroups of OSs in this study were $O_5S_,$ O_6S and O_7S. This means that the OSs bearing more oxygen-containing function groups were more abundant in ambient aerosols.

The secondary aromatic OSs were reported formed from the gas-phase oxidation of Polycyclic Aromatic Hydrocarbons in the presence of sulfate aerosol(Riva et al., 2015). Recent studies have indicated that OSs accumulated at or near the particle surface can continuously react with gas-phase oxidants, such as hydroxyl radicals (OH), ozone (O_3), and nitrate radicals (NO_3) at the gas/aerosol interface, and tend to fragment into smaller reaction products and produce $SO_4\bullet^-$ through the cleavage of the C–O–S bond upon oxidation(Bruggemann et al., 2020). Also, OSs can undergo hydrolysis to form polyols and H_2SO_4 with rates depending on the molecular structure of the particular OSs and particle acidity(Hu et al., 2011), and hydrolysis could be a potentially important atmospheric removal process for certain OSs. The atmospheric stabilities of aromatic and other OSs were still not understood at now.

Therefore, we speculated that the OSs bearing less oxygen-containing function groups were probably derived from the direct emissions of combustion sources, or the secondary formation of PAHs from the primary emissions. And we stated that our observation **probably suggested** that the OrgSs in Guangzhou suffered little or indirect influence from primary emissions.

RC5: line 385, "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," In addition to aerosol composition and environmental and meteorological factors, would the physical state of the aerosols (e.g. solid, liquid, semi-solid, liquid-liquid phase separation) affect the formation and transformation of OSs?

AC5: thanks. We think that the physical state of the aerosols could affect the formation and transformation of OSs. As far as we know, most of proposed OSs formation pathways in the ambient environment occurred in the aqueous phase or need the participant of water, for example, the formation of OSs mediated by sulfoxy radical anions (i.e., $SO_3\bullet^-$ and $SO_4\ \bullet^-$) in aqueous solution, the Heterogeneous Reactions of SO_2 under high RH. However, OS formation through nucleophilic substitution (SN), and aqueous-phase reactions of epoxides can be happened in the presence of sulfate and nitrate ions. The nitrate in organonitrates can be substituted by water or sulfate under common particle acidities. Furthermore, the present water/H^+/Sulfuric Acid will improve the formation of OSs through Epoxide Pathways. It should be noted that this pathway can also happen in the particle phase, e.g., IEPOX-derived OSs are considered to be formed through particle-phase reactions of bisulfate anions with isoprene-derived epoxides. A recent study reported larger abundances of monoterpene-derived highly oxidized OSs at elevated relative humidity, indicating aqueous-phase chemistry and particle phase state to be of importance. Therefore, physical state of the aerosols can affect specific reaction types of OS formations.

OSs, once formed, are primarily present in the particle phase because of their low volatilities. OSs can undergo hydrolysis to form polyols and H_2SO_4 with rates depending on the molecular structure of the particular OSs and particle acidity, and hydrolysis could be a potentially important atmospheric removal process for certain OSs. These reactions could happen in the aqueous phase. However, physical state of the aerosols can also affect the heterogeneous OH oxidation of OSs. OSs are surface-active and likely accumulate at or near the particle surface, and the OSs in the particle surface might continuously react with gas-phase oxidants, such as hydroxyl radicals (OH), ozone (O_3), and nitrate radicals (NO_3) at the gas/aerosol interface.

Thus, the physical state of the aerosols could affect the formation and transformation of OSs.

Response to Anonymous Referee #4

RC: The manuscript by Jiang et al. presents new and interesting research on organosulfur compounds in atmospheric aerosols in Guangzhou, China. The results are generally well presented, but there are also several, major issues which must be corrected in order to improve the quality of the manuscript to the level expected for publication in ACP. As there are already three reviews posted I will focus on the major comments here.

AC: thanks for reviewer's comments. The responses to the concerns of the reviewers are showing below. Please see our detailed responses.

RC1: Language and grammar need significant improvement by a person with good knowledge of English and science in the field. There are numerous language errors beyond what can be expected of reviewers to fix. The manuscript will need additional review after this editing.

AC1: thanks for reviewer's suggestions. The language and grammar now have been revised. The English in this document has been checked by at least two experts in this filed.

RC2: The title does not adequately reflect the conclusions of the work. First of all "aerosols" should be mentioned in the title. Secondly (as already pointed out by another reviewer) the results show that there are a range of sources and processes. The results and discussion in section 3.4 is not convincing enough to warrant stating that "Heterogenous secondary reactions drivers the molecular distribution". Section 3.4 also mentions the word "speculation" several times. This uncertainty should be reflected in the title.

AC2: In following the five reviewers' suggestions, we have carefully considered the accuracy of the title. Now the title has been changed into "Molecular Characteristics, Sources, and Formation Pathways of Organosulfur Compounds in Ambient Aerosol in Guangzhou, South China".

RC3: Please use correct chemical nomenclature throughout the manuscript for e.g. compounds (SO2 with lowercase 2 and so on).

AC3: thanks for reviewer's reminder. All the number in chemical nomenclature throughout the manuscript have been corrected. Please check it.

RC4: The abstract needs considerable editing of language and grammar. Please avoid using the non-specific word "various" and be more precise.

AC4: thanks for reviewer's suggestions. We have corrected parts of the abstract, and the non-specific word "various" was replaced by "hundreds of ……". The revised sentence is:

"Despite hundreds of organosulfates and their formation mechanisms being previously identified, a large fraction of OrgSs remain unexplained at the molecular level, and a better understanding of their formation pathways and critical environmental parameters is required to explain the variations in their concentrations."

RC5: L27: In my opinion this sentence is not adequately supported by the results of the study.

AC5: thanks for reviewer's suggestions. The corresponding sentence have revised. Here is the revised version:

"The results indicated that the formation of OrgSs through an epoxide intermediate pathway could account for up to 46% number of OrgSs from an upper bound estimation, and the oxidant levels could explain 20% of the variation in the mass of organic sulfur."

RC6: Line 38-39: A reference is needed for stability and lifetime of OrgSs.

AC6: thanks for reviewer's reminder. Two references were added here for supporting the relatively stable and long-lived for OrgSs.

RC7: Line 62. What are classical OSs?

AC7: classical OSs here denote those OSs have been previous widely identified and abundant in ambient aerosols, and formed via the secondary processes of biogenic volatile organic compounds (e.g., α-pinene, β-pinene) or aromatics (e.g., Benzene and naphthalene).

RC8: Line 83-84: This is not clearly shown in the study and the sentence should be rephrased.

AC8: thanks for reviewer's suggestions. We have revised this sentence. And now it reads:

"We showed that acid-catalysed ring-open of epoxides, heterogeneous reactions of the SO_2 uptake pathway and different oxidation processes, were potentially important formation pathways of OrgSs in Guangzhou where usually has high RH, oxidation levels and acidity."

RC9: Section 2.1: Please add more information about the sampling including type of area (urban background?), sampling (type of sampler, filters, frequency and length of sampling time). Furthermore it would be nice to have just a short description in the main manuscript about the extraction method. It would also be nice to have some meteorological parameters for the area for the sampling periods (T, RH), maybe in SI.

AC9: thanks for reviewer's suggestions. In short of the length of the main text, we have made little changes in the first sentence of Section2.1. The added information includes the type of sampling area and length of sampling time.

"A total of 55 atmospheric $PM_{2.5}$ samples (24h) collected at an urban site in 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., 2021a; Jiang et al., 2021b) and in the Supplementary text."

Other information includes the type of sampler, frequency, a short description about the extraction method for SO_4^{2-} analysis, a description about the analysis of organic tracers and meteorological parameters, were added into the Supporting information. Here are the added paragraphs:

"A total of 55 $PM_{2.5}$ samples collected on prebaked quartz fiber filters once a week at Guangzhou from July, 2017 to June, 2018 (June–September: summer, October–November: fall; December–February: winter; March–May: spring) over a period of 24 h with a high-volume air sampler at a flow rate of 1 $m^3 \cdot min^{-1}$. Quartz fiber filters were preheated at 450°C for 6 h before used and weighed. After sampling, each filter was wrapped with prebaked aluminum foil, sealed. Before weighing again, the $PM_{2.5}$ samples were kept at constant temperature and humidity for 24 h. The difference between two weighing is the amount of collected $PM_{2.5}$. A punch of filter (1.5 cm^2) was used for carbon concentration measurement. The concentration of organic and elemental carbon were measured using an OC/EC analyzer (Sunset Laboratory,Inc.) following the NIOSH870 thermaleoptical transmittance (TOT) standard method. We converted OC to organic mass using a typical ratio of OM/OC of 1.8(Tolocka and Turpin, 2012). Detailed information about the analysis procedures of chemical tracers, and meteorological parameters have been described in previous studies(Jiang et al., 2021c; Jiang et al., 2021b) and are included in the Table S12. The organic tracers' analysis performed included levoglucosan, polycyclic aromatic hydrocarbons [PAHs], steranes, and hopenes, biogenic SOA tracers (isoprene-derived SOA, MTLs; monoterpene-derived SOA, MSOA), fatty acids, long-chain alkanes. Online data regarding temperature, RH, and NO_x were obtained from a local monitoring station. A gas filter correlation analyzer (Thermo Scientific, Model 48i) was used to observed the CO. SO_2 and O_3 was measured with the pulsed fluorescence analyzer (Thermo Scientific, Model 43iTLE) and the UV photometric analyzer (Thermo Scientific, Model 49i), respectively. NO and NO_2 were determined with a chemiluminescence instrument (Thermo Scientific, Model 42iTL). Meteorological parameters of temperature (T) and relative humidity (RH) were measured with a portable weather station (WXT520, Vaisala, Finland). The concentration of gas-phase OH radical was approximated from a nonlinear Pad• function, and the NO_x effects were considered."

"……A piece of filter (d=24 mm) was punched for each of collected field filter and dissolved into 12 mL distilled deionized water (≥18.2 Ω). Each sample was sonicated for 30 minutes allowing the solution reaching equilibrium. Then the filtrate was filtered through 0.22 μm PTFE membrane (Jinteng, China) and stored in a prewashed clean bottle at 4 ☐ until sample analysis……**"**

RC10: Line 97: This sentence is unclear.

AC10: thanks for reviewer's suggestions. We have revised it. Now it read as:

"And the TS to sulfate-sulfur ratios of samples greater than 2 or less than 0.5 were considered as a measure of gross measurement error (Shakya and Peltier, 2015). In this study, samples met to these conditions were excluded from further analysis."

RC11: Line 138: Please provide standard deviations for all averages in the text.

AC11: thanks for reviewer's suggestions. We have corrected the problem across the text. Please check it.

RC12: line 157: please give a reference to the last part of the sentence.

AC12: thanks for reviewer's reminder. We have added two references here. Please check it.

RC13: Line 171: it is quite surprising that sulfonates were not detected.

AC13: thanks. We are sorry that this sentence was accurately stated. We have revised this sentence, and the revised version is:

"However, other OrgSs (e.g., sulfonates), may also exist, but were not further considered.**"**

RC14: Figure 1: It is not clear what the circles in 1.a represents.

AC14: thanks. In the caption of Figure 1, we have noted that the **"**Each circle denotes a molecule, and the colour bar and marker size denote the number of oxidation state and the average sum-normalized relative peak intensities of the compounds, respectively.**"**

RC15: The x-axis in 1.c must be improved as there are only a few samples per month. It should be clear which sample is shown.

AC15: thanks. The label has been corrected. Please check it.

RC16: L208-210: How can C7 compounds be derived from isoprene?

AC16: thanks. Methacrolein (MACR, 2-methyl-2-propenal), methyl vinyl ketone (MVK, 3-butene-2-one), formaldehyde, and 3methylfuran have been shown to be the main reaction products of both the OH and O_3-initiated oxidation of isoprene(Iannone et al., 2003). Studies have shown that C7-organosulfates can be detected in MVK/MACR derived SOA(Nozière et al., 2010). Riva et al. (2016b) shown that reactions between oxidation products of isoprene hydroxyhydroperoxides and acidified particles (SO_4^{2-}) under low RH can form high abundance of C7-organosulfates ($C_7H_{13}O_8S^-$). They also showed that $C_7H_7^+$ was abundant in the oxidation products of isoprene hydroxyhydroperoxides. Rudzi´Nski et al. (2009) presented that the reactions of isoprene and sulphoxy radical-anions can produce C7 compounds, and these C7 compounds can further be oxidized into organosulphites and organosulphates. Results from Kourtchev et al. (2016) have observed an increasing fraction of smaller molecules (C3–C7) in the total observed signal from isoprene and terpene SOA at higher temperatures. Daellenbach et al. (2019) showed that the higher ISO/MT ratio in BVOC emissions in Zurich could contribute to the higher C3–C7 CHO compound contribution. All these results can support that C7 compounds be derived from isoprene. However, we are unfamiliar with the potential mechanisms of C7 compounds produced from isoprene, as we are not experts in this area.

RC17: L213-215: Even though dimeric oxidation products are very interesting, they are also found at very low levels in the atmosphere, so their contribution to organic sulfur compounds is expected to be small.

AC17: we agree with the reviewer. In Figure 1c, the C17–C22 compounds accounted for small relative abundance. However, as highlighted by Kourtchev et al. (2016), the higher contributions of dimeric and trimeric BVOC oxidation products in filed samples could be related to higher precursor and SOA mass, which is in agreement with laboratory experiments presented in the same study. They found that higher temperature affects not only the emissions from the biosphere but also the ratio between particle- and gas-phase concentration of compounds, which lead to an enhancement of less volatile dimeric compared to more volatile monomeric BVOC oxidation products. In this study, the average Temperature during the sampling period is 24 □. According to Kourtchev et al. (2016), the average maximum Temperature of 24 □ could have an oligomer fraction of 0.3 to the total intensity of all peaks in the mass spectrum. This higher relative abundance suggested the importance of dimeric oxidation products to the aerosols. However, due to our limited data, we are unable to determine the source of dimeric compounds and their contributions. The revised version is:

"As highlighted by Kourtchev et al. (2016), the higher percentages of MS intensity for dimeric and trimeric BVOC oxidation products in both filed samples and laboratory-generated SOA could be related to the higher precursor and SOA mass. They suggested that a higher temperature could lead to an enhancement of oligomers because it affects not only the biogenic emissions but also the partitioning of dimeric and monomeric compounds in the gas and particle phases. In this study, the average temperature during the sampling period was 24 □. According to Kourtchev et al. (2016), the average maximum temperature of 24±6 □ could have an oligomer fraction of 0.3 among the total intensity of all peaks in the mass spectrum. This higher percentage of MS intensity suggested the importance of dimeric oxidation products to the aerosols. However, it should be noted that C_{8-22} CHOS compounds have also been reported in previous studies and are proposed to be mainly derived from the photooxidation of long-chain alkanes from vehicle emissions (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 observed in both the formation processes via monoterpene ozonolysis intermediates (Ye et al., 2018) and uptake of SO_2 by olefinic acid (the possible olefinic acid precursors were all detected in the FT-ICR MS analysis) (Zhu et al., 2019). Therefore, due to our limited data, the origins of CHOS with a low DBE remains large uncertainties and needs to be confirmed by further studies."

RC18: L241-243: This sentence does not add valuable information and I suggest to delete.

AC18: In following the reviewer's suggestion, we have deleted this sentence.

RC19: L247: Figure S2a – you probably mean Figure 2a.

AC19: thanks. We have corrected it.

RC20: L254-257. this sentence is not clear.

AC20: thanks, it now has been corrected as:

"……Although combustion sources can emit large numbers of OrgSs, the primary low-oxidative and aromatic OrgSs abundant in source samples had a low MS intensity in our ambient samples. This probably suggested that the OrgSs in Guangzhou were less or indirectly affected by primary emissions (e.g., secondary formation via combustion-emitted precursors).……**"**

RC21: Figure 2: Figure 2a is very busy and difficult to read. I suggest to make it more clear and: not use yellow, correct typos (hevay -> heavy, vheicle -> vehicle. Figure text: filed -> field.

AC21: thanks. We have corrected the errors in Figure 2a. here is the updated version:

RC22: L290: PAHs are precursors of aromatic OSs, but they are found at low levels, so"important" could be removed here.

AC22: thanks. We have corrected it.

RC23: L301: R2 of 0.19 represents a small correlation despite the p-value.

AC23: thanks. As we noted in this paragraph, the sources and the formation of this group OSs were not understood, one of the known possible formation pathways is the direct SO_2 uptake by unsaturated fatty acids in the particle phase. Although the R^2 of the correlations is relatively small, it may partly support above mention formation mechanism in our sampling site, and it probably also suggested that there are other important formation pathways to the generation of this group of OSs.

In order to make the expression more accurate, we have modified some sentences. The revised sentences are:

"Among the classified OrgSs with their precursors from multiple sources, a high intensity fraction that was likely derived from unsaturated fatty acids (USFA) was identified, and contributed 8%−17% (average: 12%) of the total OrgSs potentially assigned, despite the limitations imposed by the large numbers of different OrgSs variants. We observed a positive correlation between USFA-derived OSs and RH (r^2=0.19, p<0.01), which partly supported the mechanism of USFA-derived OSs formation by direct SO_2 uptake……"

RC24: L325: Suggest to rephrase to: "Acid-catalyzed reactions of epoxides formed by oxidation of VOCs…" Please add a reference as well to the original work on this.

AC24: thanks. The sentence has been revised, and we also have added several references.

"It has been shown to be kinetically feasible for acid-catalyzed reactions of the epoxides formed by the oxidation of VOCs to produce Oss, and this mechanism has been widely adopted to explain OSs formation (Surratt et al., 2007; Iinuma et al., 2007; Surratt et al., 2008; Surratt et al., 2010; Lin et al., 2013).**"**

RC25: The methodology and interpretation of Figure 4 needs further explanation. Figure 4 shows that organosulfur compounds are distributed in all directions in the plot pointing to complex sources and processes.

AC25: thanks. To make the audience better understand Figure 4, we have added some background information and notes about the NMDS into section 2.3. here are the added parts:

"…...From the NMDS analysis, the OrgSs compounds were dimensionally reduced to three components (NMDS1, NMDS2 and NMDS3) with stress values 0.09. The selected environmental parameters (Table S12) that have relationships or influences with/on the OrgSs composition were also fitted on the bitplots to evaluate the relationships between the distributions of OrgSs and environmental conditions, with p-values calculated over 999 permutations. The significant correlated factors were reserved and could be considered as the possible drivers that associated with molecular distribution. Score and loading plots were constructed according to NMDS variables from each OrgSs compound (gray dots and triangles). The potential drivers that associated with molecular distribution of OrgSs were indicated by arrows. Direction and included angle of arrow show the relationship between the driver and each dimension.**"**

RC26: L432: Do you mean oxidation of VOCs in the presence of NO2?

AC26: yes, thanks for the reviewer's reminder. We have corrected it.

Response to Anonymous Referee #5

RC: In this work, the authors reported measurements of multifunctional organic compounds in ambient aerosol, focusing on the molecular formulas that contain sulfur atoms. Organosulfur (OrgS) compounds are abundant in ambient aerosol, and many are indicative of sources and/or transformation reactions in the atmosphere. There have been similar measurements in other geographical areas, but this study is the first one that is conducted in Guangzhou in southeastern China. The authors compared the relative abundances and diversity of these OrgS compounds to what is known about their formation mechanisms (from laboratory studies) and postulate that these OrgS compounds are driven by heterogeneous uptake processes.

The measurements reported in this study are difficult to make and the detailed molecular composition provides insights into formation processes for this unique group of compounds. The authors could provide more details about their quality control procedures and limitations of FT-ICR technique in quantifying OrgS compounds. The data interpretation is mostly convincing, with a few caveats. The manuscript is mostly understandable, with a lot of grammatical issues that can hopefully be rectified. Based on the scientific content, I recommend publication of this manuscript in Atmospheric Chemistry and Physics after considering the following minor comments.

AC: Thanks for recognizing our works and providing valuable suggestions. We have made changes in following the reviewer's suggestion. Please see details in the below.

RC1: In general, many of the arguments are made based on the elemental formula alone. It should be noted that FT-ICR does not provide any structural information, and the ratios (DBE, Xc) are very crude measurements of what the carbon backbone looks like. It would be great if these measurements can be compared to others that provide more structural information, such as VOCs (e.g. by GC/MS or GC/FID). Another potential direction is to look at back trajectories and air mass history.

AC1: thanks for the reviewers' suggestions. We agree with the reviewer that FT-ICR cannot provide detailed structural information.

However, from many previous studies(Lin et al., 2012; Jiang et al., 2016), the experiential analysis on the structures of elemental formula can still provider some usefully information although this analysis may lead to uncertainties. What is unfortunate is that we did not collect and analyze those gas-phase compounds (such as VOCs) during the sampling period of this study, but only measured the concentration of some organic tracers in particulate matters, which are reflected in sections 3.3 and 3.4. In section3.2, we mainly focused on the molecular composition of organosulfur compounds. From the structural analysis, we founded some information related to their sources and formation pathways. While in section 3.3 and 3.4, we further combined the molecular characteristics with organic tracers and environmental factors, to provide further evidence about the sources and formation pathways of organosulfur compounds.

Furthermore, as stated in the Supplementary text (Results from our previous work), we presented the results of back trajectory analysis and source apportionment, which have been reported in our previous study. Results showed that relative clean marine-origin air masses from the Western Pacific and South East Asia regions were dominant during summer monsoon period. During this time, DOM formed from secondary processes of isoprene and organic sulfates formations had higher contributions than that in winter. These may be the reason that higher fraction of organosulfur compounds mass to total organic mass in summer than that in winter.

RC2: Related to the previous point, there appears to be some interesting time trends in the data (e.g. in Figure 1). For example, I can see some periodicity with C8-C12 DBE0,1 and 2,3. Could these be related to where the air mass is coming from?

AC2: thanks for the reviewer's suggestion. Though back trajectory analysis can provide some source information, there are many factors that influencing the molecular composition of organosulfur compounds which cannot be total reflected by back trajectory analysis. We have tried to compare the molecular distribution of CHOS compounds with the results from back trajectory analysis (SEA and WP are marine-origin air masses, CA and MG are continental-origin air masses). It was shown that the periodicity of C8-C12 CHOS compounds with DBE= 2,3 probably have associations with the origin of air mass, but not for C8-C12 CHOS compounds with DBE= 0,1. Lower relative abundance were observed during summer when marine air masses were dominated, but higher relative abundance were observed during autumn and winter when continental air masses were dominated. It should be noted that this association was not explained, it also can be resulted from other reasons.

RC3: Carbon number distribution: I am not sure the carbon number distribution itself can be a sign of sources. For example, gasoline engines would emit VOCs in the range of C2-C11, where a lot of the efficient SOA precursors in the C6-C9 range (the aromatics), which may overlap with monoterpene SOA carbon numbers. The authors may want to be cautious when making that argument.

AC3: thanks for the reviewer's suggestions and their reminder. We have to admit that there may exist great risks using carbon number distribution to explore the sources of organosulfur compounds. As the reviewer mentioned that gasoline engines also emit VOCs in the range of C_2-C_{11}, and so we have emphasized that "The relatively low DBE (< 4) CHOS compounds with 3–7 carbons ($C_{3–7}$) were smaller compounds, which were probably the fragments produced by atmospheric oxidation processes or isoprene-derivatives" when discussing the potential sources of C3-C7 compounds in the main text. Furthermore, we also have mentioned that the C8-C22 CHOS compounds may be mainly derived from the photooxidation of long-chain alkanes form vehicle emissions in the last of the corresponding paragraph.

Another thing we wanted to stated is that only the **low and medium DBE CHOS compounds (DBE < 4)** were further grouped based on the length of the carbon skeleton in the formulas to study their potential sources. The aromatics in atmosphere usually have **DBE values >=4,** and thus were considered not suit for using this method.

Detailed comments:

RC4: Grammatical error in the title: drive instead of drivers?

AC4: thanks, we have updated the title.

RC5: Line 21: awkward word choice in "averagely"

AC5: thanks, we have revised this sentence.

"The results revealed that the ratio of the annual average mass of organic sulfur to total particulate sulfur was 33±12%, and organic sulfur had positive correlations with SO_2 (r=0.37, p<0.05) and oxidant (NO_x+O_3, r=0.40, p<0.01)."

RC6: Line 22: awkward word choice in "positively"

AC6: thanks, we have corrected it.

RC7: Line 22: "the" is not needed before SO2

AC7: thanks, we have corrected it.

RC8: Line 25-26: awkward word choice in "attributed to … origins". Should be "of … origins" Line 28: it is unclear if the 46% and 20% values refer to the percent of variability explained (in statistical analysis) of percent of the mass

AC8: thanks. These two sentences have been revised to make them clear, here is the revised version:

“The results indicated that the formation of OrgSs through an epoxide intermediate pathway could account for up to 46% number of OrgSs from an upper bound estimation, and the oxidant levels could explain 20% of the variation in the mass of organic sulfur.**”**

RC9: Line 31: “oxidation” should not be plural

AC9: thanks, we have corrected it.

RC10: Line 35: “fraction” or “percentage” would be more appropriate than “ratios”

AC10: thanks, we have corrected it.

RC11: Line 38: I am not sure if OS are necessarily contributing to additional toxicity beyond just being PM components.

AC11: thanks. Please see my response below.

RC12: Line 42: similarly I am not sure if Lin et al (2016) necessarily shows that OS are potentially toxic. The whole IEPOX/MAE SOA mixture was evaluated, not individual components.

AC12: thanks. The referred works conducted by Lin et al (2016) suggested that IEPOX/MAE SOA mixture could lead to oxidative stress response of human lung cells. In the IEPOX/MAE SOA mixture, OSs were detected as abundant species. Thus, we speculated that OSs probably have potential toxicity. Furthermore, as PAHs are important toxicant in aerosols, the presence of aromatic organosulfur compounds in urban $PM_{2.5}$ could represent a heretofore unrecognized source of toxic products (Riva et al., 2015). More direct works are needed to verify the toxicity of OSs. Therefore, we used the words “possible potential toxicity” instead of “toxicity” in the MS.

RC13: Line 54: best avoid language like “It seems that”

AC13: thanks, we have corrected it.

RC14: Line 75: awkward language in “referential significance”

AC14: thanks, we have corrected it.

RC15: Line 80: the sentence may need some clarification. What does “more molecular information”? ESI-FT-ICR is not very quantitative and does not resolve isomers, but the resolution is very high and give better information about molecular formulas.

AC15: thanks. The “more molecular information” means that from HR-MS analysis, we could identify and found many new OSs, which help us understand the molecular composition of remaining unexplained OrgSs (67-79%).

We agree with the reviewer that ESI-FT-ICR can provide neither quantitative information nor resolve isomers. However, the high resolution and mass accuracy give better information about molecular formulas, and thus we could identify and found many new OSs.

RC16: Line 84: typo in OrgSs

AC16: thanks, corrected.

RC17: Line 91: typo in “describe”

AC17: thanks, corrected.

RC18: Line 93: what is the potential for OrgS to hydrolyze to sulfate during IC analysis?

AC18: Actually, OSs can undergo hydrolysis to form polyols and H_2SO_4 with rates depending on the molecular structure of the particular OSs and particle acidity(Bruggemann et al., 2020). However, during IC analysis, the pH of solution (~5-6) is higher than the particle acidity, which is not conducive to hydrolysis reaction. For some OSs with rapid hydrolysis rate, it still takes 2.5 hours for complete degradation under typical aerosol conditions(Bruggemann et al., 2020). Studies also shown that OSs are likely to be metastable species with respect to their corresponding alcohols (Minerath et al., 2008; Hu et al., 2011). Thus, the effects of OSs hydrolysis to IC analysis might be very small.

RC19: Line 103: "FT-ICR MS results"

AC19: thanks, it has been corrected.

RC20: Line 107: membranes instead of members?

AC20: thanks, we have corrected the error.

RC21: Line 113: "here, we focus on…" should be a separate sentence

AC21: thanks, corrected.

RC22: Section 2.3: what is the QA/QC procedure for low signal peaks? What are the criterion for inclusion and what is considered background noise?

AC22: thanks. As mentioned in Supplementary text, the possible formulas for all ions were exported using the criterion of S/N ratio > 4 and a mass tolerance of ±1ppm. Field blank filters were processed and analyzed following the same procedure to detect possible contamination, and all the contaminations in field blanks were subtracted from samples. Moreover, three duplicate representative aerosol samples were analyzed to test the reproducibility of analysis procedures. Pearson's correlation analysis of the relative intensities of all molecules between duplicates confirmed the high level of reproducibility of the selected samples (r = 0.98).

RC23: Line 123-125: were there internal standards to evaluate run-to-run changes in ionization efficiencies? Without chromatographic separation, the potential for matrix effects, such as those from ion suppression, is high. This bias can affect correlations with external variables.

AC23: thanks. The high reproducibility of replicates of FT-ICR-MS analysis under same conditions have been previously proved. In this study, three duplicate representative aerosol samples were analyzed to test the reproducibility of analysis procedures(Kellerman et al., 2014; Riedel et al., 2013). Pearson's correlation analysis of the relative intensities of all molecules between duplicates confirmed the high level of reproducibility of the selected samples (r = 0.98). Our samples were all extracted by methanol, it may contain less ions than those water-extracted fractions, and we think the ion suppression initiated by salts may be small. The large uncertainty in this study for the FT-ICR MS analysis could be resulted from the matrix effect of organics. To minimized this, we used the widely used methods(Kellerman et al., 2014; Herzsprung et al., 2020). That is, same concentration of methanol extracts (in carbon contents, relative errors of below 50% for most of samples) were used for FT-ICR-MS analysis. Furthermore, all mass spectra were calibrated externally with arginine clusters in negative ion mode using a linear calibration. The final spectrum was internally recalibrated with typical O_2 class species peaks using quadratic calibration in DataAnalysis 5.0 (Bruker Daltonics) (mentioned in SI).

RC24: Why is sulfate lowest in the summer? Is it because there is little difference in photochemical activity between the seasons?

AC24: there are several reasons may explain the lower concentration of sulfate in summer. 1. As stated in supplementary text, marine-origin air masses from the Western Pacific and South East Asia regions were dominant during summer monsoon period. 2. Lower anthropogenic emissions were found in summertime, because relative lower SO_2 concentration were observed than wintertime (Figure shown in below). 3. Despite relatively high temperatures and strong solar radiation, more wash-out processes may lead to low concentration of sulfate.

RC25: Line 155: what is the uncertainty in this estimation? I do not expect FT-ICR-MS to be quantitative without authentic standards. Is there any verification with some organosulfate standards in FT-ICR-MS?

AC25: Actually, the molecular weight of organosulfur compounds used here is the intensity-weighted average molecular weight obtained from FT-ICR MS analysis. It does not need authentic standards to quantify the concentration of each organosulfur compounds. The uncertainty in this estimation may come from the estimated organic mass and the molecular weight of organosulfur compounds. The conversion factor of 1.8 is an experiential parameters that obtained from previous measurement. Furthermore, given that the true molecular weight of organosulfur compounds cannot be measured directly or calculated, and the intensity-weighted average molecular weight obtained from FT-ICR MS analysis this study provides a relative reasonable estimation though it may be very roughly.

RC26: Line 177: is it possible to have formate clusters (thus adding O to the formulas)?

AC26: thanks. Actually, we think the possibility of having formate clusters in CHOS formulas is small. None of studies have reported this kind of sulfur-containing species in ambient aerosols as far as we known. However, we can't exclude the possibility of presence of oligomeric sulfur-containing species in aerosols which can also lead to high oxygen numbers in formulas, for example, the dimeric and trimeric OSs.

RC27: Line 179: are there characteristic H/C values? How do these compare to the H/C values measured by HR-AMS?

AC27: The average H/C ratios here is the average intensity-weighted H/C ratio of CHOS compounds. Therefore, the comparison to the H/C values measured by HR-AMS makes no sense to this study, as all these data are from the specific group CHOS compounds. Furthermore, it seems that HR-AMS analysis can't obtain the average H/C for CHOS, as we have not found the corresponding values in literatures to our knowledge.

RC28: Line 183: perhaps "central" instead of "middle"

AC28: thanks, corrected.

RC29: Line 183-184: are these formulas less oxidized than overall OA, OrgS or just the CHOS compounds? It is not clear to me whether a fair comparison is being made here.

AC29: thanks for the reviewer's reminder. In here, all the comparison are between the

CHOS in this study and in those referred works. Therefore, it should mean that the average oxidation state of CHOS compounds in this study were lower than those CHOS compounds measured in other places. Here, we have made some revision to make it clear:

"The average H/C ratios of the CHOS compounds in this study were close to or higher than those previously reported in ambient aerosols, clouds, and rainwater collected in different locations worldwide and analyzed by negative ESI-FT-ICR MS, indicating that the OrgSs in Guangzhou are enriched with saturated structures (Table S3). However, the average O/C ratios of the CHOS compounds identified in this study were slightly higher than those of cloud water, and comparable to the values measured in east-central Chinese cities, but were much lower than those of CHOS compounds in polluted organic aerosols collected in Mainz and Chinese cities measured using high-resolution Orbitrap MS."

RC30: Line 184: Orbitrap?

AC30: thanks, corrected.

RC31: Line 186: Regarding the DBE being three times higher, does this account for the additional DBE that comes with an additional SO4 group? OSO3H adds 2 DBE. Perhaps the authors did account for this, but was not clear. If not, then aromaticity is not the only explanation here for additional DBE.

AC31: thanks. The double bond equivalent (DBE), more precisely is Carbon double bond equivalent. For the DBE calculation, DBE= (c+1-0.5h+0.5n), although -OSO_3H has two double bonds, but they do not contribute the carbon double bond equivalent. And therefore, in the DBE calculation in this study, the additional -OSO_3H would not increase the DBE values, and the aromaticity is the possible explanation here for the additional DBE value.

RC32: Line 198: grammatical error in "make them be"

AC32: thanks. We have corrected the error. Please check it.

RC33: Line 198: I am not sure if olefins are necessarily biogenic. Also, the additional DBE does not need to be C=C bonds. There can be ketone formation, or formation.

AC33: thanks. We want to state that VOCs emitted from biogenic sources are mainly composed by olefins, but the olefins in ambient aerosols are not necessarily from biogenic emission. We agree with the reviewer that the additional DBE may not only result from C=C bonds, but also ketone and heterocyclic ring. As we have considered these, and thus we carefully used the words "potential candidates". That means CHOS with DBE=2,3 are not necessarily BVOCs-derived OSs.

RC34: Figure 1: It seems like there are a few formulas that dominate the signal (very large circles in panel a). What are these formulas?

AC34: the several most intense CHOS species in Figure 1 are $C_{19}H_{37}O_7S^-$, $C_{10}H_{19}O_5S^-$, $C_{10}H_{15}O_7S^-$, $C_{10}H_{17}O_7S^-$, $C_9H_{15}O_7S^-$, $C_{14}H_{27}O_5S^-$, $C_{15}H_{29}O_5S^-$ (list in descending order by their average intensities). These CHOS species have low DBE values.

RC35: Line 198-199: do these DBE numbers account for potential DBE within a -OSO3H group? If not, DBE>4 might not necessarily be aromatic, and DBE < 1 would be a sulfide type compound.

AC35: we agree with the reviewer that the DBE>4 might not necessarily be aromatic, and

DBE<1 might not necessarily be aliphatic. In the DBE numbers calculations, S was not considered because they usually don’t contribute the unsaturated bonds. S atoms were generally detected in the form of -OSO_3H group or -SO_3H group in ambient aerosols as they were easily ionized in the negative ESI mode. Thus, studies tentatively attributed organosulfur compounds with DBE<1 to aliphatic-like, because they may contain saturated aliphatic structures; similarly, organosulfur compounds with DBE >4 were tentatively attributed to aromatics as they may contain saturated aromatic structures. Obviously, these attributions can lead to uncertainties, but this classification can give us a quick and intuitive compositional information.

The corresponding sentence was revised into:

“The CHOS compounds with DBE≤1 and DBE≥4, which were tentatively assigned as saturated aliphatic-like and aromatic species, took up 34±6% and 26±2% of the total CHOS intensity, respectively.”

RC36: Line 214: monoterpened / sesquiterpened? Do the authors mean monoterpenoid /sesquiterpenoid?

AC36: thanks for pointing out our errors. It has been corrected in our revised MS.

RC37: Line 219: were there observations of olefinic acids in the FT-ICR data for comparison? They should be readily ionizable in ESI(-).

AC37: yes. In the FT-ICR MS analysis, the corresponding precursors (olefinic acids) were detected. For example, the possible olefinic acids precursors of $C_{10}H_{19}O_6S^-$, $C_{17}H_{32}O_2$ and $C_{15}H_{28}O_2$, were all detected.

RC38: Line 219-220: grammatical error in “remain large uncertainty”

AC38: thanks, we have corrected the grammatical error**.**

RC39: Section 3.3 title is a little awkward. Consider rewording.

AC39: thanks. We have changed the title of 3.3 into **“**Comparison and potential precursor apportionment of OrgSs**”**

RC40: Line 250: replace “abundant by aromatics” with “abundant in aromatics”

AC40: thanks, we have replaced the phrase.

RC41: Line 257: suffered may be too strong a word

AC41: thanks, it has been corrected.

RC42: Figure 2: typos in panel a legend (vehicle and heavy)

AC42: thanks, it has been corrected. Please check it.

RC43: The comparison with CCOA is interesting. Have the authors considered that from coal burning there could be many more reduced sulfur species and heterocyclic aromatic compound with S as heteroatoms? Would this affect the interpretation and the comparison (since the x-axis in the VK diagram assumes a sulfur oxidation state of 6).

AC43: thanks. We agree with the reviewer that coal burning can emitted many reduced sulfur species and heterocyclic aromatic compound with S as heteroatoms.

However, in ambient aerosol samples, reduced sulfur species and S-heterocyclic aromatic compounds often showed low intensities, with OSs were the most abundant sulfur-containing organic species. Furthermore, in these referred works, all samples were analyzed in the negative ESI mode, which was benefit to ionized OSs but not to reduced sulfur species and S-heterocyclic aromatic compounds (Jiang et al., 2021a).

Even so, studies have shown that by using the criterion of $(o-3s-2n)<=0$, formulas can be roughly judged whether they have the possibility of containing reduced sulfur atoms(Tao et al., 2014; Blair et al., 2017). By doing this modification, it could provide another perspective for understanding the molecular composition of sulfur-containing species, especially for those reduced species.

Therefore, aerosols from coal burning are expected to contain many highly intense species with $(o-3s-2n)<=0$. This has been reflected by Figure 2a. and thus we think the reviewer's concerned problems would not have much influences on the interpretation and the comparison

RC44: Line 284-285: This comparison to isoprene tracers is very informative. It seems to be that this type of comparison can be done to support many other arguments (e.g. biogenic vs anthropogenic, relations to CCOA and BBOA etc.). Are there limitation to using these other tracers?

AC44: thanks. The limitation of using these organic tracers is not clear in this study. The stability of these organic tracers may be an important influencing factor. And for some secondary organic tracers, they only are indicators for some specific reactions, with abusing of them may lead to misleading. For examples, 2methyltetrols and C5-alkene triols, are the SOA tracers of isoprene formed through the HO_2 channel (isoprene reacts with the OH and HO_2 radicals to form hydroxy hydroperoxides, and then IEPOX in the gas phase absorbed by acidic particles can produce these species); while for 2-methylglyceric acid and 2-methylglyceric acid sulfate ester, also the SOA tracers of isoprene, which formed through the NO/NO_2-channel. In this study, we have tried using several organic tracers to link the OrgSs with some specific sources, such as biomass burning and fossil fuel combustion. However, considering the existence of atmospheric aging processes and the primary emissions may have minor effects on the composition of OrgSs, insignificant correlation was found between their tracers and Org-S concentration or total relative abundances (in the corresponding parts, we mainly studied the influences from secondary processes).

RC45: Lines 300-302: Correlation with RH alone might not be sufficient to establish that USFA is the source. SO2 uptake in general is RH dependent because in most cases SO_2 is solubility limited. Are there collocated measurements or nearby measurements? More broadly, what may be the source of USFA? I expect food cooking to be an important source so perhaps it is related to whether air mass came from a highly populated area?

AC45: thanks. We agree with the reviewer that food cooking may be an important source of USFA, especially in China, where more frying was seen in the Chinese-style cooking. As mentioned in Zhu et al. (2019), the concentration of oleic acid (molecular tracer of for cooking emissions) in the aerosols over Pearl River Delta (PRD) region can up to 5 ng m^{-3}, suggesting the importance of cooking emissions. Unfortunately, though we have measured the concentrations of several fatty acids, the oleic acid was not measured, and therefore, we cannot provide more information about the source of these USFA. As stated in the Supplementary text, we presented the results of back trajectory analysis, which have been reported in our previous study. Results showed that relative clean marine-origin air masses from the Western Pacific and South East Asia regions were dominant during summer monsoon period, while continental-origin air masses from Mongolia and Central Asia were dominant during winter monsoon period. The winter air masses could contribute to the USFA. However, in here, we only focused on the source of these tentatively assigned USFA-derived-OSs (not necessarily derived from USFA). Due to the limit data, we perform correlation analysis between them and RH to propose them a possible formation pathway. More detailed source information or formation pathways of these OSs are need further works.

RC46: Line 354: is it possible that the correlation with inorganic NO3 is simply because both are RH driven? Ammonium nitrate partitioning is strongly RH dependent.

AC46: thanks. We agree with the reviewer that NH_4NO_3 partitioning is strongly RH dependent. And our recent study also shown that RH may also be a factor that affects the concentration of atmospheric particulate NO_3 in Guangdong by altering the thermodynamic equilibrium of the reaction between gas-phase NH_3 and HNO_3 and the content of particle-phase NH_4NO_3(Su et al., 2020). That means the changing in RH would both lead to the variation of particulate NO_3^- and SO_4^{2-}/SIA ratio, which further change the aerosol acid. However, in this study, the correlations between the concentration of Org-S and RH were not observed (neg: supports; pos: oppose), therefore, we can’t exclude the possibility of indirect influences from the RH.

Org-S(á))* SO_4^{2-}/SIA ratio (â)) particle NO_3^- (á))low RH

RC47: Line 364: typo in “indicating”

AC47: thanks. it has been corrected.

RC48: Line 393: I am confused why the LWC is not very closely associated with RH. Why is that the case? Are there more important drivers of LWC (e.g. aerosol composition)?

AC48: thanks. The possible reason for this is that LWC were not only influenced by RH, but also has associated with secondary inorganic ions. The LWC from inorganic species were predicted by a thermodynamics model ISORROPIA-II via inputting the aerosol phase concentrations of inorganic water-soluble ions (Na^+, SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, Ca^{2+}, K^+ and Mg^{2+}), as well as RH and ambient temperature(Guo et al., 2015; Nguyen et al., 2016; He et al., 2018). LWC is closer to NMDS3, while RH is closer to NMDS2. The differences between the two factors probably suggested that they may have different influences on the molecular distribution of OrgSs.

RC49: Line 416: “contribute to 25% of the total…” is this “up to 25%”?

AC49: thanks, the error appeared here have been corrected.

RC50: Line 424: typo in “abundance”

AC50: thanks, it has been corrected.

RC51: Line 433: NO2? Or NO3? Or maybe just NOx.

AC51: thanks, it has been corrected.

“……oxidation of BVOCs with O_3 and oxidation of anthropogenic VOCs in the presence of NO_x were two potentially important pathways for the formation of OrgSs or their precursors**”**

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