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Comment on acp-2021-1069

Anonymous Referee #2

Referee 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-RC2, 2022

General comments

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.

Specific comments

- 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.
- 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.

- 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.
- 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?
- 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.
- Please number equations.
- 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.
- 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.
- 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.
- Line 247 – Figure S2a does not show source data. Do you mean Figure 2a?
- 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.
- 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.
- Clarification needed in the abstract: Add standard deviation to the percent of total sulfur that is attributed to organic sulfur (at line 21).
- 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.
- Line 316, citations are needed to support that unsaturated fatty acids were the source
- Formatting of Supplemental tables should be improved to increase readability.
- 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?
- In Figure 2, why would 3S and 2N be used? sulfate has 4O and nitrate 3O.
- 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).
- 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.

- 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.

Technical corrections

22. 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.