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Comment on acp-2021-1069

Anonymous Referee #5

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-RC5, 2022

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.

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.

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?

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.

Detailed comments:

Grammatical error in the title: drive instead of drivers?

Line 21: awkward word choice in "averagely"

Line 22: awkward word choice in "positively"

Line 22: "the" is not needed before SO2

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

Line 31: "oxidation" should not be plural

Line 35: "fraction" or "percentage" would be more appropriate than "ratios"

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

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.

Line 54: best avoid language like "It seems that"

Line 75: awkward language in "referential significance"

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.

Line 84: typo in OrgSs

Line 91: typo in "describe"

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

Line 103: "FT-ICR MS results"

Line 107: membranes instead of members?

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

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?

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.

Why is sulfate lowest in the summer? Is it because there is little difference in

photochemical activity between the seasons?

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?

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

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

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

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.

Line 184: Orbitrap?

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.

Line 198: grammatical error in "make them be"

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 heterocyclic ring formation.

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

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.

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

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

Line 219-220: grammatical error in "remain large uncertainty"

Section 3.3 title is a little awkward. Consider rewording.

Line 250: replace "abundant by aromatics" with "abundant in aromatics"

Line 257: suffered may be too strong a word

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

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).

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?

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 SO2 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?

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.

Line 364: typo in “indicateing”

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)?

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

Line 424: typo in “abindance”

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