Title: Measurement report: Molecular Insights into Organic Aerosol Sources and Formation at a Regional Background Site in South China

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We appreciate the reviewers for their helpful comments on our manuscript. We have carefully considered each suggestion and question, and have revised the manuscript accordingly. In compliance with the reviewers' detailed comments, we thoroughly reviewed the text, figures and references. All corrections are clearly marked in the revised manuscript. Our responses to the reviewers' comments are provided below, with responses shown in **Blue** and revised parts highlighted in **Green**.

Response to Anonymous Referee #1

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

General Comments

RC: This manuscript presents a comprehensive investigation of organic aerosol (OA) composition, sources, and oxidative evolution in Hong Kong, utilizing a combination of high-resolution analytical techniques, including HR-AMS, TAG-TOF-MS, and HPLC-HR-MS. The authors demonstrate that during the COVID-19 lockdown period, low-oxidation OA was primarily influenced by biomass burning and gas-phase secondary organic aerosol (gas-pSOA), largely driven by air mass transport from mainland China. In contrast, high-oxidation OA was dominated by secondary inorganic aerosols (SIA), gas-pSOA, and biogenic SOA, with isoprene-derived SOA identified as the major contributor. HR-MS results indicate that CHO and CHON compounds dominated the OA composition, contributing over 60% of signal intensity and more than 40% of molecular formulas. Constrained-NMF analysis suggests that atmospheric oxidation promoted CHO accumulation, while nitrogen-related reactions increased molecular diversity. Overall, this study offers valuable insights into the molecular complexity and transformation of OA under different atmospheric conditions. I recommend publication after minor revision. However, several specific aspects require clarification or improvement prior to acceptance:

AC: We greatly appreciate the reviewer for recognizing the merits of our work and for providing valuable suggestions to improve the manuscript. We have revised the manuscript in accordance with the reviewer's comments, with all corrections clearly marked in the revised version. Please see below for our point-by-point responses to your concerns.

RC: Line 20: This is an interesting and innovative approach to source apportionment at the molecular level. The authors applied a constrained NMF model to offline HR-MS data to investigate molecular differences among various OA sources. However, the specific differences identified between these sources are not clearly presented. It is recommended that the authors elaborate on the key distinguishing features—such as dominant compound classes, oxidation levels, or representative molecular formulas—that characterize each OA source.

AC: Thank you to the reviewer for the helpful reminder. In the main text of this manuscript (Section 3.4), we have provided a detailed description of the distinguishing features of each OA source identified by the constrained NMF model. However, we previously omitted these details from the abstract. In response to the reviewer's suggestion, we have now added the corresponding results to the abstract. The revised versions are provided below.

"Using a constrained non-negative matrix factorization (NMF) approach on offline HR-MS data, we found that while CHO compounds dominated the molecules associated with each source, the degree of oxidation and unsaturation varied significantly among them. Specifically, the C-OA$_{\mathrm{NMF}}$ factor exhibited the highest O/C ratio but the lowest double bond equivalent (DBE) value, whereas the BB-OA$_{\mathrm{NMF}}$ factor was characterized by the greatest aromaticity and a high abundance of nitroaromatics. For secondary processes, sulfur additions played a more significant role in gas-pSOA than in secondary inorganic aerosols (SIA)."

RC: Lines 175-180: The authors suggest that LO-OOA1 is more influenced by anthropogenic photochemical processes involving VOCs and NOx, while MO-OOA is primarily linked to biogenic SOA formation through ozone oxidation. However, the distinction between their "primary nature" and "secondary formation pathways" remains somewhat ambiguous. Could the authors clarify how LO-OOA1 is considered to have a more primary character despite its apparent link to secondary photochemical reactions?

AC: Thanks for the reviewer's suggestion. As shown in Figure S5, we measured not only the concentrations of particle-phase organic tracers but also those of gas-phase organic compounds, including both biogenic and anthropogenic VOCs. Correlation analysis suggested that LO-OOA1 concentrations were well correlated with species associated with secondary photochemical reactions, as well as with anthropogenic VOCs (e.g., toluene and C8 aromatics). In contrast, MO-OOA concentrations showed weaker or insignificant correlations were gas-phase anthropogenic VOCs. In addition, as noted in our previous study, the low oxidation degree of LO-OOA1 suggests that it has undergone fewer oxidation processes compared to MO-OOA, indicating a more primary character for LO-OOA1. To avoid potential confusion, we have revised the description in this section. The updated version is provided below:

"……In addition, photochemical reactions involving anthropogenic emissions have been shown to play a particularly important role in the formation of LO-OOA1, whereas MO-OOA is more influenced by biogenic emissions. During the focused sampling period in this study, LO-OOA1 exhibited strong associations with gas-phase photochemical reactions involving both biogenic and anthropogenic VOCs species, as well as NOx (Figure S5). In contrast, MO-OOA was more closely linked to SOA formation processes related to the……"

RC: Lines 179: The authors state that MO-OOA shows good correlations with O_3 and biogenic SOA tracers. Could the authors provide the specific correlation coefficients (e.g., r values) and p-values to quantitatively support this statement, particularly for the relationship between MO-OOA and O3? Including these statistical details in the main text or supplementary figures would enhance the transparency and robustness of the analysis. The same places that need to be modified are in Lines 198 and 215.

AC: Thanks for the reviewer's reminder. In the section referenced, we used the results of correlation analysis to support our conclusion. These correlation results have been presented in the supplementary material, specifically in Figures S5 and S6. Due to the large number of species included in the correlation analysis (Line 179), it is not feasible to list the p and r values for each compound pair. However, we have now included the p and r values in the relevant sections at Lines 198 and 215. The revised version is as follows:

"The positive correlation between the results obtained from these two methods further supports the integration of the datasets (Figure S6, r=0.54, p<0.01)……"

"……Both factors showed positive correlations with temperature (r>0.50, p<0.01), consistent with previous studies indicating that elevated temperatures can enhance the emission of biogenic VOCs……"

RC: The x-axis in Figure 2a seems to be incorrect, and the symbol/icon used in Figure 3 is unclear. Please revise it to improve clarity and readability.

AC: Thank you for your careful review. We have reviewed the relevant figures and corrected the errors. The revised figures are provided below:

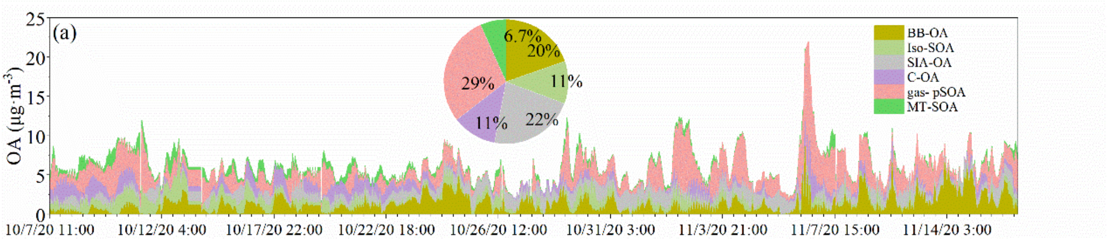

Figure 2a. (a) Temporal variations in OA concentrations attributed to each PMF factor. The accompanying pie chart shows the average contribution of each PMF factor over the sampling period.

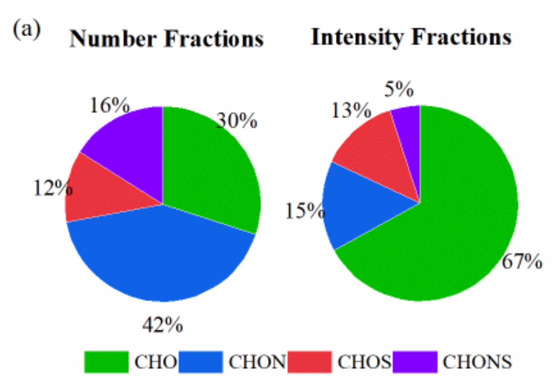

Figure 3a: (a) Average proportions of elemental compound groups, presented by both formula count and intensity.

RC: Lines 235-238: The authors state that SIA contributed the most to MO-OOA (38%), yet also suggest that highly oxidized organics in MO-OOA might not be primarily related to SIA processes. This appears somewhat contradictory. Could the authors clarify how they reconcile the high SIA contribution with the conclusion that MO-OOA is more closely linked to biogenic SOA processes?

AC: Thank you for the reviewer's comments. In Lines 235-238 of the original manuscript, we have compared the source contributions of each AMS-component. Our results showed that gas-pSOA contributed 42% to LO-OOA1, whereas its contribution to MO-OOA decreased to 21%. In contrast, SIA-OA contributed most significantly to MO-OOA (38%). Furthermore, the contribution of biogenic factors to MO-OOA increased markedly compared to LO-OOA1, rising from 15% to 33%. Given that MO-OOA exhibited a higher degree of oxidation than LO-OOA1, this elevated oxidation could be attributed to the greater contributions from SIA-OA and/or biogenic factors. However, we also observed that LO-OOA2, another AMS component with a similar oxidation degree to LO-OOA1, showed the highest SIA contribution among the four AMS components. If a high SIA-OA contribution were the primary driver of increased oxidation, LO-OOA2 would be expected to have the highest oxidation degree. Contrarily, LO-OOA2 actually exhibited a lower oxidation degree than MO-OOA. Therefore, we speculate that the formation of highly oxidized organic compounds in MO-OOA is not primarily related to SIA processes. Instead, it appeared to be more closely associated with biogenic SOA processes, particularly those involving Iso-SOA. In the revised manuscript, we have rephrased this section to improve clarity and logical flow. The updated version is as follows:

"……Therefore, the relatively higher oxidation degree of MO-OOA compared to LO-OOA1 could be attributed to greater contributions from SIA-OA and/or biogenic SOA processes. However, given that LO-OOA2 has an even higher proportion of SIA-OA (46%) than MO-OOA, along with similar contributions from gas-*p*SOA, this suggests that the formation of highly oxidized organic compounds in MO-OOA might not be primarily driven by SIA processes. Instead, it appeared to be more closely associated with biogenic SOA processes, particularly those involving Iso-SOA……"

RC: Line 370-375: The authors note that the contribution of gas-pSOA estimated by the constrained-NMF method was 1.4 times higher than that from the tracer-based PMF model, while the SIA contribution was significantly lower. Could the authors clarify how they addressed this discrepancy, and whether any compound misclassification between SIA-related and gas-pSOA-related species may have biased the NMF results?

AC: The valuable comments are greatly appreciated. In Lines 370-375 of the original manuscript, we compared the source apportionment results obtained from the tracer-based PMF model and the molecule intensity-based NMF model. Overall, the contributions of biogenic SOA, cooking, and BB to OA derived from the molecular composition-based NMF analysis aligned with those from the tracer-based PMF model. Also, the total contributions from gas-pSOA and SIA-OA were comparable between the two methods. However, a notable discrepancy was observed: the contribution of gas-pSOA to OA estimated by the NMF method was 1.4 times higher than that from the PMF model, while the contribution of SIA-OA was only 1/3 of the PMF model's estimate. These findings indicated general consistency in source apportionment results between the two approaches, with the primary difference arising from the attribution of secondary processes.

As stated in the main text (Lines 360-362), atmospheric SOA processes are highly complex, and tracer-based PMF model isolates SOA processes into SIA and gas-pSOA components. Although this separation is mathematically robust, these processes may still partially overlap in real-world conditions. For example, gas-phase oxidation (both daytime •OH oxidation and nighttime NO_3• oxidation) is a major pathway for SIA formation. This suggested that some SOA generation was associated with SIA formation via gas-phase oxidation, or that SIA might directly participate in SOA generation. Consequently, there may be partial overlap between the gas-phase oxidation formation of SIA-OA and the gas-*p*SOA identified by the tracer-based PMF model, resulting in some compounds being attributed to both gas-*p*SOA and SIA-OA. In this study, we suspected that the higher contribution of gas-pSOA determined by the NMF method may be due to an over-attribution of compounds related to SIA processes to the gas-pSOA category in the NMF analysis.

As described above, the potential misclassification of compounds between SIA-OA and gas-pSOA does not significantly affect our main results and conclusions. First, as noted in Line350-369, gas-pSOA was more closely associated with daytime gas-phase oxidation, while SIA-OA formation was primarily influenced by nocturnal oxidation. Therefore, any misclassification between SIA-related and gas-pSOA-related species may lead to an underestimation of the contribution of nocturnal oxidation to OA formation. However, this does not affect the contributions from other sources (BB, biogenic SOA, and cooking) or the overall contributions of SOA processes. Secondly, since both SIA-OA and gas-pSOA factors were mainly associated with anthropogenic emissions, we can still conclude that "both methods indicated that gas-phase oxidation of VOCs was a significant pathway for OA formation throughout the study period, particularly for anthropogenic VOCs."

In the revised manuscript, we have rephrased this section to improve its logical flow. The updated version is as follows:

"…... Although the tracer-based PMF model can mathematically separate atmospheric SOA processes into SIA and gas-pSOA, these categories may still partially overlap in real-world conditions. As discussed above, gas-phase oxidation, particularly nocturnal oxidation, is a major pathway for SIA formation. Our results suggest that, in the NMF analysis, many compounds associated with SIA processes may have been over-attributed to gas-pSOA, potentially leading to an underestimation of the contribution of nocturnal oxidation to SOA formation. However, given the relatively stable levels of SIA-OA observed during the sampling period, and considering that misclassification between SIA-related and gas-pSOA-related species did not affect the contributions from other sources (BB, biogenic SOA, and cooking) or the total SOA contributions, the results from the molecule-based NMF analysis remain reasonably robust. Importantly, both methods consistently indicated that gas-phase oxidation of VOCs was a significant pathway for OA formation throughout the study period, particularly for anthropogenic VOCs……"