Point-by-point response to review comments

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Title: "Significant secondary formation of nitrogenous organic aerosols in an urban atmosphere revealed by bihourly measurements of bulk organic nitrogen and comprehensive molecular markers"

Author(s): Xu Yu, Min Zhou, Shuhui Zhu, Liping Qiao, Jinjian Li, Yingge Ma, Zijing Zhang, Kezheng Liao, Hongli Wang, Jian Zhen Yu

We thank the reviewer for his/her constructive comments. Each of these comments has been addressed and detailed in our point-by-point response given below. The exact comment text from the reviewer is in black and italic style while our response text is in blue and normal format in this document. The revised texts are marked in blue in the highlighted manuscript. The line numbers mentioned below refer to those in the revised manuscript.

The manuscript by Yu et al. presented high temporal resolution aerosol ON measurements and various source markers in urban Shanghai during the fall-winter period of 2021. The authors used the PMF model to identify up to 18 sources or formation processes of aerosol ON. Despite the potential limitations of the PMF predictions, the results obtained may provide valuable insights into the origins and formation processes of ON aerosols in Shanghai and serve as valuable references for future aerosol ON research. Overall, the manuscript is well-structured and well-written. I recommend that this paper could be published in Atmospheric Chemistry and Physics once the authors address the following minor comments.

Response: We thank the reviewer for the positive comments.

Major comments:

The author used the PMF model to identify up to 18 contributors of ON, which is very impressive. However, there seem to be some contradictions in the PMF results.

For example, 1) For factor nitrate formation, ammonium also has a high load. The liquid-phase reaction of ammonium is also one of the very important pathways for the formation of ON. Why is this factor only attributed to nitrate formation here;

Response: The factors resolved in the PMF model were named based on the characteristically high loading of source indicators within each factor. Specifically, the nitrate formation factor was characterized by a high loading of nitrate. Ammonium was also abundant in this factor due to the neutralization reaction between ammonia and nitric acid.

In previous PMF analysis studies, researchers have referred to this ammonium nitrate-dominated factor using various names, such as "secondary nitrate" (Huang et al., 2021; Li et al., 2020), "secondary nitrate-rich" (Huang et al., 2018), "secondary nitrate formation processes" (Wang et al., 2019), and "nitrate-rich" (Yu et al., 2024). Despite the variations in naming, this factor consistently represents secondary formation processes characterized by significant nitrate production.

To enhance clarity and avoid ambiguity, we have revised the name of the "nitrate formation" factor to "nitrate formation processes" in the text and figures, emphasizing that this factor is primarily characterized by high nitrate loading while also containing other secondarily formed species. Similarly, we have updated "sulfate formation" to "sulfate formation processes" throughout the manuscript.

2) For Figures 2 and S3b, the average contribution of traffic emissions to ON was higher from 0:00 to 8:00 (nighttime). Shouldn't the contribution be higher during the morning and evening rush hours?

<u>Response:</u> While ON associated with vehicular emission during 0:00-8:00 was higher than other hours, we'd like to point out that the hour-to-hour variations within a 24-h cycle also indicated an elevated contribution of traffic emissions to ON during morning and evening rush hours. For example, shown in Figure 2, it is discernible that the contribution of vehicle emissions to ON peaked during 6:00-8:00 and 18:00-22:00, corresponding to morning and evening rush hours. The higher contribution of vehicle emissions at night may be attributed to the generally lower nighttime planetary boundary layer height, although the overall intensity of vehicle emissions at night might be lower compared to rush hours.

Overall, our results support the argument that vehicle emissions contributed more significantly to ON aerosols during morning and evening rush hours. We have explicitly stated in the manuscript that "the contribution of vehicle emissions was enhanced during rush hours." (Line 247-248)

In addition, the average contribution of cooking and oxygenated cooking OA to ON were higher from 18:00 to 22:00. There should also be cooking at noon, and the photochemical reaction should be stronger, leading to more oxygenated cooking OA production;

<u>Response:</u> As shown in Figure 2, there was a small but visible peak of contributions of cooking emissions and oxygenated cooking OA to ON around noontime (12:00), indicating enhanced cooking emissions and subsequent oxidation during lunchtime. The much lower contributions of cooking emissions and oxygenated cooking OA to ON at lunchtime compared to dinnertime might be attributed to 1) Lower cooking emissions at lunchtime compared to dinnertime; 2) More favorable dispersion conditions at noontime, which effectively dilute cooking emission plumes, leading to a lower contribution of cooking emissions and oxygenated cooking OA to the observed ON. A previous field study conducted in urban Shanghai also observed a small peak of cooking emission at noontime, with substantial increase during dinnertime (Huang et al., 2021), which aligns with our findings.

Note that the average contributions over the study period shown in Figure 2 obscured the diel variation patterns of contributions on individual days. We have examined the day-by-day variations of cooking emission tracers and oxygenated cooking OA and found that they have peak concentrations during both lunchtime and dinnertime on many days. Figure R1 shows five representative days in which the concentrations of cooking emission tracers (unsaturated fatty acids) and oxygenated cooking OA (azelaic acid) and their apportioned-ON peaked during

both lunchtime and dinnertime. Therefore, the expected enhanced cooking emission and oxidation during lunchtime have been observed; however, on an average basis, more remarkable contributions of cooking emission and oxidation to ON were found during dinnertime compared to lunchtime. Figure R1 has been added as Figure S8 in the revised manuscript.

We have added more discussions in the text as following:

> Line 278-287: "It is noted that the study-wide average contributions to ON from cooking emission and their oxidation product factors were much lower at noontime compared to evening (Figure 2). This difference might be attributed to the lower cooking emissions and/or more favorable dispersion conditions during lunchtime. It is also worth noting that the study-wide average contributions shown in Figure 2 obscure the diel variation patterns on individual days. To address this, we examined the day-by-day variations of cooking emission-related tracers. On many days, both unsaturated fatty acids (indicative of primary cooking emissions) and azelaic acid (a marker of oxygenated cooking OA) exhibited bimodal peaks during lunchtime and dinnertime. Figure S8 highlights five representative days in which the concentrations of these tracers, along with their associated-ON contributions, clearly showed maxima at both mealtime periods."
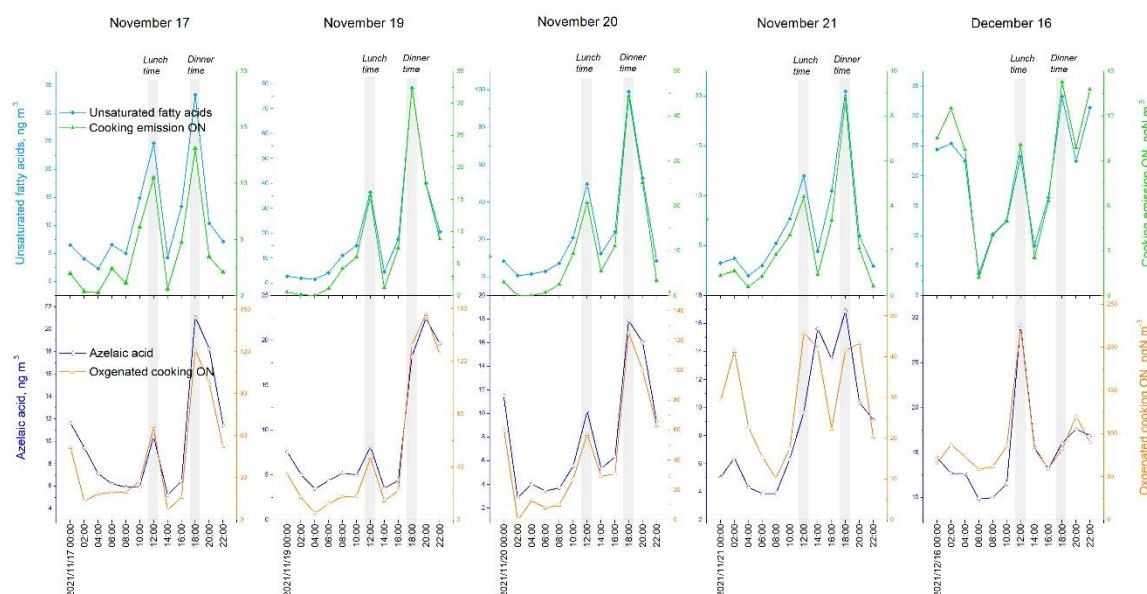

Figure R1 (the same as newly added Figure S8). Five representative cases in which the concentrations of cooking emission tracers (unsaturated fatty acids) and oxygenated cooking OA (azelaic acid) and their apportioned-ON peaked during both lunchtime and dinnertime.

3) For Lines 232-233. Based on my understanding, sulfates, isoprene, and α-pinene can all contribute to the formation of ON (e.g., sulfate significantly promotes the formation of organic amine salts; the sulfates and isoprene-related nitrooxy-OS formation exist…), but the authors

suggested that they do not contribute to ON. Does this conclusion require more supporting evidence?

Response: Thank you for your comment. As the reviewer mentioned, sulfate may promote the formation of ON aerosols through two potential pathways: 1) Neutralization reactions between sulfate and nitrogen-containing organic bases such as amines; 2) Sulfate-involved formation of ON species, such as nitrooxy-OS.

Regarding the neutralization reaction, we note that ammonia/ammonium is abundant in the urban Shanghai atmosphere. As shown in Figure R2, particulate sulfate and nitrate have been fully neutralized by ammonium. Additionally, the molar ratio of ammonium to sulfate was 1.8 for the PMF-resolved sulfate formation processes factor. These results suggest that sulfate and/or nitrate have limited potential to enhance the gas-to-particle (G-P) partitioning of organic bases like amines. Furthermore, the abundant presence of ammonium may inhibit the formation of ON species via acid-catalyzed reactions.

In most cases, sulfate concentrations were low (<4 μg m^{-3}) and exhibited slight variations throughout the observation period. However, ON concentrations varied significantly over the period (Figure 1). This suggests that sulfate was not a major driver of ON variations. This argument is further supported by the poor correlation (R^2 = 0.05) between sulfate and ON concentrations in this study.

The potential contribution to ON aerosol from organic nitrate formation involving the reactions between BVOCs (oxidation products) and NO_x/NO_3 radical might have been captured within the nitrate formation processes factor. In this study, we found a substantial fraction (14%) of ON was distributed in the factor of nitrate formation processes. As we proposed in the manuscript: "The ON associated with nitrate formation processes may indicate the formation of organic nitrates, which share common precursor of NO_x with nitrate." ON has stronger correlations with NO_x (R^2=0.45) and nitrate (R^2=0.39) compared to BSOA tracers (R^2=0.18), which might be the reason that organic nitrates were apportioned to the factor of nitrate formation processes rather than biogenic SOA factors. This result might be linked to the differences in the underlying formation mechanisms of organic nitrates and biogenic SOA tracers, but currently they are not well understood.

We have added further discussion in the main text:

> Line 288-294: "Sulfate formation processes exhibited negligible contributions to ON formation in this study. Note that sulfate and nitrate were fully neutralized by ammonium (Figure S9), limiting their capability to absorb organic bases such as amines and suppress acid-catalyzed ON formation pathways initiated by sulfuric acid. Furthermore, sulfate and ON displayed distinct temporal variation patterns and were poorly correlated (R^2 = 0.05), further indicating a lack of mechanistic linkage between sulfate chemistry and ON formation in the urban atmosphere of Shanghai. These findings collectively suggest that sulfate-driven processes played a minor role in ON formation under the conditions observed."

Line 295-304: "SOA formation from isoprene and α-pinene oxidation contributed insignificantly to the observed ON. While it is known that reactions between biogenic volatile organic compounds such as isoprene and α-pinene with NO_x or NO_3 radicals can yield organic nitrates, such contributions may have been captured within the nitrate formation factor, rather than the biogenic SOA factors, in the PMF analysis. This interpretation is supported by correlation analysis, where ON showed stronger associations with NO_x ($R^2 = 0.45$) and nitrate ($R^2 = 0.39$) than with isoprene- and α-pinene-derived SOA tracers ($R^2 = 0.18–0.19$). The apparent allocation of biogenically derived organic nitrates to the nitrate formation factor may reflect differences in the formation mechanisms of organic nitrates versus those of traditional biogenic SOA tracers. However, the specific chemical pathways governing these processes remain insufficiently understood and warrant further investigation."
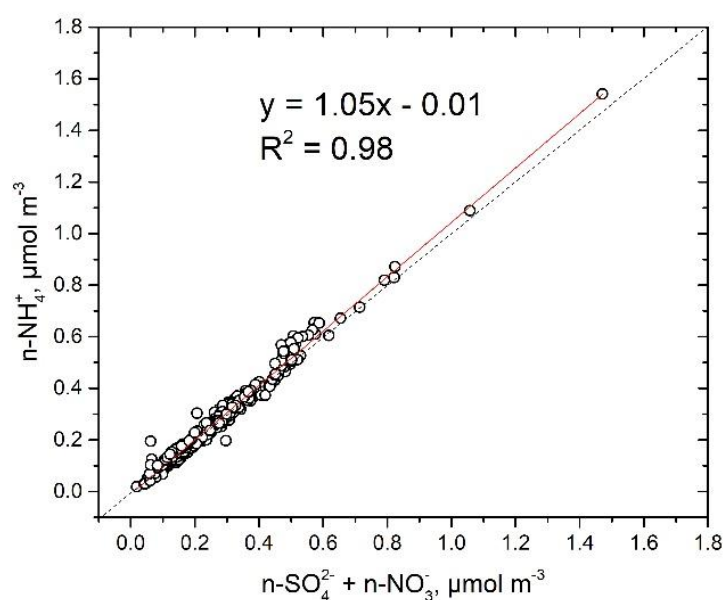

Figure R2. Charge balance between ammonium, sulfate and nitrate during the observation. This figure has been added as Figure S9 in the revised supporting information file.

4) For Lines 234-236. Generally, winter pollution should be heavier, as indicated by many previous studies in Shanghai, especially the impact of coal combustion. However, the authors mentioned that the winter case was consistent with the summer case. This doesn't seem to be in line with the actual situation.

Response: Sorry for causing the confusion. Here, we aim to argue that vehicle emissions and coal combustion were major primary sources of ON in both summer and fall-winter time. The absolute contributions in fall-winter were indeed higher than in summer. Specifically, the mass contributions of vehicle emissions and coal combustion to ON were 1.7 and 1.5 times higher than those in summer, respectively.

In the revised manuscript, we have rephrased the sentence:

> Line 245-246: "This finding was consistent with the summertime measurements at the same site that vehicle emissions and coal combustion dominated the primary emission sources of ON (Yu et al., 2023)."

5) For Lines 237-240: Why is there no consistency between the contribution of coal combustion to ON and the contribution of industrial production to ON. This is somewhat confusing.

Response: Industrial production mainly refers to manufacturing such as motor industry and electronics product manufacturing, while coal combustion is primarily associated with power plants to generate electricity. Industrial emissions and coal combustion represent different emission sources. The former is characterized by high loading of manganese (Mn), iron (Fe), and zinc (Zn), while the latter has characteristic emissions of selenium (Se) and lead (Pb). Note that the contribution of industrial emissions to ON was higher during daytime, which might be due to the more intense manufacturing activities in daytime. While the source strength for coal combustion is expected to exhibit smaller diel variation as the power plant requires continuous operation., we found an elevated contribution of coal combustion to ON at nighttime. This might be due to the lower planet boundary layer height during the nighttime that leads to an elevation of coal combustion pollutants. To summarize, the contribution of industrial emissions to ON is not expected to be consistent with that of coal combustion.

Overall, if possible, it is recommended that the author consider the validity of the PMF results more.

Response: We appreciate the reviewer's suggestion and agree that validity of the PMF results must be carefully examined and supported. To ensure the robustness of the analysis, we have run PMF model many times and selected the solution with the most physically interpretable and consistent factor profiles. All the PMF-resolved factors have passed stability tests, confirming the reliability of the source factors. In the revised manuscript, we have also added the correlation matrix between each resolved factor (Table S2), showing their statistical independence. Importantly, as we have presented above, the identified factors are consistent with established understanding of ON sources, and the results offer new insights into the emission sources and formation processes of ON in the urban atmosphere.

More comments:

1.   Lines 35-36 and Lines 235-236: The data seems to be inconsistent, as mentioned in the abstract, the contribution of both coal combustion and vehicle emissions to ON is 21%. The value reported in the main text is 20%.

Response: Sorry for making the confusion. In the main text, we stated that "Coal combustion and vehicle emissions were the two dominant primary sources of ON, each contributing **approximately** 20% to the aerosol ON". To keep consistency, we have revised "20%" to "21%" in the main text. (Line 244)

2.   As reported by the author, the contribution of the primary sources to ON in Shanghai during winter was greater than that of the secondary processes. This seems to be a more

important conclusion. However, a significant amount of primary ON emissions are also partitioned to the particulate phase through secondary processes. For example, for organic amines from primary sources, the formation of particulate organic amine salts (they are abundant in fine particulate matter) is closely related to sulfates, nitrates, and organic acids. Therefore, I am still very confused as to why sulfate formation did not contribute to the formation of ON in this study.

Response: First, we would like to clarify that both primary emissions and secondary formation were identified as major sources of ON aerosols in urban Shanghai. The secondary formation of ON aerosols involved several pathways, as discussed in the manuscript. We agree that the gas-particle (G-P) partitioning of amines could contribute to secondary ON, particularly through reactions forming aminium salts with acidic species. As noted in Section 3.3 and supported by Figure S9, sulfate and nitrate were nearly fully neutralized by excess ammonia/ammonium in the Shanghai winter atmosphere. This neutralization likely limited their ability to drive the partitioning of amines into the particle phase via acid-base reactions.

Although organic amines have been highlighted for their roles in new particle formation and growth, previous studies have shown that nitrogen from small amines contributes less than 2% to bulk aerosol ON in most continental regions (Ho et al., 2015; Liu et al., 2017; Yu et al., 2024). In our study, a notable fraction (8%) of ON was associated with dicarboxylic acid (DCA) formation processes. As shown in Section 3.3, DCA-related ON exhibited a positive correlation with ammonium, suggesting that reactions between DCAs and NH_3/NH_4^+ may play a role in ON formation. Given the similar emission sources of NH_3 and amines, it is also plausible that reactions between DCAs and amines (i.e., organic acid + organic base) contributed to the observed ON, although this mechanism could not be directly ascertained based on our field measurements alone.

Furthermore, it is possible that some organic aminium salts were apportioned to primary emission factors in the PMF analysis. This may occur when amines are primarily emitted and subsequently undergo G–P partitioning to form aminium salts, resulting in correlations with primary source profiles. We acknowledge that PMF analysis has limitations in fully separating primary and secondary contributions, especially when secondary products retain strong source signatures.

We have added further clarification on this point in the revised section to address the reviewer's concern more explicitly.

Section 3.2:

Line 305-309: "In summary, both primary emissions and secondary formation processes were identified as major contributors to ON in the urban atmosphere of Shanghai. It is also important to note, however, that PMF analysis has inherent limitations in fully separating primary and secondary sources, particularly for compounds such as organic aminiums, which may originate from primary emissions but subsequently undergo gas-particle partitioning."

Future research should employ integrated approaches combining source apportionment, molecular characterization, and thermodynamic modeling to better constrain the sources and formation mechanisms of organic aminium aerosols. In particular, the roles of gas-particle partitioning and secondary reactions involving organic acids and ammonia/amines (NH_3/NH_4^+) warrant further investigation to elucidate their contribution to ON formation in urban environments.

References:

Ho, K. F., Ho, S. S. H., Huang, R. J., Liu, S. X., Cao, J. J., Zhang, T., Chuang, H. C., Chan, C. S., Hu, D., Tian, L. W.: Characteristics of water-soluble organic nitrogen in fine particulate matter in the continental area of China, Atmos. Environ., 106, 252-261, 2015.

Huang, D. D., Zhu, S. H., An, J. Y., Wang, Q. Q., Qiao, L. P., Zhou, M., He, X., Ma, Y. G., Sun, Y. L., Huang, C., Yu, J. Z., and Zhang, Q.: Comparative Assessment of Cooking Emission Contributions to Urban Organic Aerosol Using Online Molecular Tracers and Aerosol Mass Spectrometry Measurements, Environ. Sci. Technol., 55, 14526−14535, 2021.

Huang, X. F., Zou, B. B., He, L. Y., Hu, M., Prevot, A. S. H., and Zhang, Y. H.: Exploration of PM2.5 sources on the regional scale in the Pearl River Delta based on ME-2 modeling, Atmos. Chem. Phys., 18, 11563–11580, 2018.

Li, R., Wang, Q. Q., He, X., Zhu, S. H., Zhang, K., Duan, Y. S., Fu, Q. Y., Qiao, L. P., Wang, Y. J., Huang, L., Li, L., and Yu, J. Z.: Source apportionment of $PM_{2.5}$ in Shanghai based on hourly organic molecular markers and other source tracers, Atmos. Chem. Phys., 20, 12047–12061, 2020.

Liu, F. X., Bi, X. H., Zhang, G. H., Peng, L., Lian, X. F., Lu, H. Y., Fu, Y. Z., Wang, X. M., Peng, P. A., Sheng, G. Y.: Concentration, size distribution and dry deposition of amines in atmospheric particles of urban Guangzhou, China, Atmos. Environ., 171, 279-288, 2017.

Wang, Q. Q., Huang, X. H. H., Tam, F. C. V., Zhang, X. X., Liu, K. M., Yeung, C., Feng, Y. M., Cheng, Y. Y., Wong, Y. K., Ng, W. M., Wu, C., Zhang, Q. Y., Zhang, T., Lau, N. T., Yuan, Z. B., Lau, A. K. H., Yu, J. Z.: Source apportionment of fine particulate matter in Macao, China with and without organic tracers: A comparative study using positive matrix factorization, Atmos. Environ., 198, 183-193, 2019.

Yu, X., Li, Q. F., Liao, K. Z., Li, Y. M., Wang, X. M., Zhou, Y., Liang, Y. M., and Yu, J. Z.: New measurements reveal a large contribution of nitrogenous molecules to ambient organic aerosol, npj Clim. Atmos. Sci., 7, 72, https://doi.org/10.1038/s41612-024-00620-6, 2024.

Yu, X., Zhou, M., Li, J. J., Qiao, L. P., Lou, S. R., Han, W. Y., Zhang, Z. J., Huang, C., and Yu, J. Z.: First Online Observation of Aerosol Total Organic Nitrogen at an Urban Site: Insights Into the Emission Sources and Formation Pathways of Nitrogenous Organic Aerosols, J. Geophys. Res. Atmos., 128, e2023JD038921, 2023.