General.

We would like to express our sincere appreciation to the editor and reviewers for their valuable feedback and constructive suggestions, which significantly improved the manuscript. We have carefully addressed all the reviewers' concerns and made the necessary revisions. Responses to specific comments raised by the reviewers are described below. All changes made in the revised manuscript are highlighted in red, and our detailed responses to the specific comments are presented below in blue.

Comments of Referee #3 and our responses to them

Comments:

This study examines the formation and pollution of aerosol nitrogen-containing organic compounds (NOCs) in $PM_{2.5}$ *across three Chinese cities during winter. The authors systematically compare the relative abundance, precursors, and formation mechanisms of various NOCs in cities with varying energy consumption patterns. The study emphasizes the significant role of anthropogenic aromatics and aqueous-phase processes in the occurrence of urban aerosol NOC pollution, particularly during haze days. The overall results provide valuable insights into the complex interactions between emissions, meteorological conditions, and aqueous-phase chemical processes in NOC formation. In general, this study advances our understanding of urban aerosol NOCs and will be of interest to Atmospheric Chemistry and Physics readers. The work is solid and well-written, and I recommend it for publication following minor revisions.*

Response: We are very grateful for your professional and thoughtful review of our manuscript. We have revised the manuscript to address the comments. Our responses to the specific comments and changes made in the manuscript are given below.

Specific comments:

1) *Line 69: "nitrogen oxide" change to "nitrogen oxides"*

Response: Thank you for pointing this out. The term "nitrogen oxide" has been corrected to "nitrogen oxides" in the revised manuscript (Lines 69-70).

2) *Line 80-82: I recommend rephrasing this sentence. Here is a suggestion: Several observational studies have found a positive correlation between aerosol NOC abundance and either aerosol liquid water (ALW) or relative humidity (RH).*

Response: Thank you for your suggestion. The revised sentence is clearer and more concise. The revision has been made in the revised manuscript (Lines 80-81).

3) *Line 87: 'large emissions of NOC precursors…'. A reference is recommended to be added here.*

Response: Thank you for your suggestion regarding Line 87. The relevant references have been added to support the statement in the revised manuscript (Lines 87-88).

4) *Line 169-172: "...which included CHO−, CHON−, CHONS−, and CHOS− in ESI− mode and CHO+, CHON+, and CHN+ in ESI+ mode". The use of "-" and "+" signs in the molecular formulas here needs clarification. It is unclear whether they refer to the detected ion forms or the molecular forms. This ambiguity should be addressed.*

Response: Thank you for your valuable comment regarding the clarification of the "−" and "+" signs. The "−" and "+" signs following the molecular formulas indicate the detection ion modes, corresponding to negative (ESI−) and positive (ESI+) electrospray ionization modes, respectively. To avoid ambiguity, we have added the following explanation in the manuscript as described below (Lines 176–179).

Lines 176–179: …Unless otherwise indicated, the molecular formulas presented in the manuscript refer to neutral molecules. The "−" and "+" symbols denote the detection ion modes, which correspond to ESI− and ESI+ modes, respectivel.

5) *Line 222: "...proposed by Ehhalt and Rohrer (Ehhalt and Rohrer, 2000), which was reported…", the citation format of the reference is incorrect. Please correct it.*

Response: The revision has been made in the revised manuscript (Line 233).

6) *Line 227-231: The authors used non-metric multidimensional scaling (NMDS) for visualizing the distribution of NOCs. Have you considered alternative data visualization methods, such as principal component analysis (PCA)? If not, could you please clarify the specific advantages of using NMDS in this context?*

Response: Thank you for your insightful comment regarding the use of non-metric multidimensional scaling (NMDS) for visualizing the distribution of NOCs.

We selected NMDS because it is well-suited for analyzing complex datasets with non-linear relationships and semi-quantitative data (Taguchi and Oono, 2004; Bialik et al., 2021). Unlike principal component analysis (PCA), which assumes linear relationships and is sensitive to data scaling (Bialik et al., 2021), NMDS does not rely on these assumptions and focuses on preserving the rank order of dissimilarities. This flexibility makes NMDS particularly suitable for our dataset, where the underlying relationships are likely non-linear. Thus, given these advantages, we decided to use NMDS for our analysis, as it better suited the nature of our data.

7) *Section 2.4: Regarding the potential pathways for NOC formation, have the authors considered bimolecular reactions, such as oligomerization reactions, as potential mechanisms in the formation of NOCs?*

Response: Thank you for your valuable comment regarding the potential pathways for NOC formation.

In this study, we primarily focused on the following reaction pathways: imination reaction, intramolecular N-heterocyclic reaction, hydrolysis reaction, dehydration reaction, oxidation reaction, and their mixed reactions. These pathways were able to explain 76% of CHON+ compounds, 61% of CHN+ compounds, and 65% of CHON− compounds, indicating that the classification of potential pathways for NOC formation in our study is representative.

While bimolecular reactions, such as oligomerization, could contribute to certain atmospheric processes, they were not included in this study. This is because the atomic variations involved in oligomerization are too complex to be effectively described using the "precursor-product pairs" approach employed here. To clarify, we have added the following statement to the revised manuscript (Lines 220-223).

Lines 220-223: …In particular, certain reaction pathways (e.g., oligomerization) were not included in this study due to the complexity of the atomic changes involved, which could not be effectively characterized using the "precursor-product pairs" approach...

We acknowledge the importance of considering a broader range of potential mechanisms, including oligomerization, for a more comprehensive understanding of NOC formation. We appreciate the reviewer's suggestion and will aim to explore this aspect in future studies.

8) *Could the authors clarify whether the higher NOC abundances observed during haze periods were mainly due to secondary processes, or could there also be a contribution from primary emissions?*

Response: Thank you for your insightful comment regarding the potential sources contributing to the higher NOC abundances observed during haze periods.

Indeed, precursor-product pairing approaches may classify NOCs from primary emissions as secondary aqueous-phase reaction products, as suggested by previous studies (Jiang et al., 2023; Su et al., 2021). Thus, our results should be interpreted as an upper limit for NOC formation associated with aqueous-phase processes. In addition, the NMDS and Spearman correlation analyses suggested that the secondary formation of NOCs was significantly enhanced during haze conditions, further supporting the importance of secondary processes in the formation of NOCs.

We also acknowledged the inherent limitations of this approach in the manuscript (Lines 215–220).

Lines 215–220: …It is important to acknowledge the potential limitations in the categorization methodology of NOC formation pathways described above. This is because the approach applied here and in previous studies (Jiang et al., 2023; Su et al., 2021) may classify NOCs as products of aqueous-phase reactions from primary emissions. Accordingly, our results can be regarded as a maximal potential (or an upper limit) for NOC generation from aqueous-phase reactions.

9) *The authors focus on the sources and formation mechanisms of NOCs. Could you briefly discuss the implications of your findings for air quality management strategies?*

Response: Thank you for your valuable comment. This study underscores that wintertime aerosol NOC pollution is strongly influenced by both the intensity of precursor emissions and the efficiency of aqueous-phase processes in transforming these precursors into NOCs. The findings emphasize the critical need for targeted emission reduction strategies to control NOC pollution and improve air quality, particularly in coal-dependent cities like Harbin. Specifically, reducing emissions of anthropogenic aromatic precursors (the dominant contributors to NOC formation in Harbin) can significantly mitigate NOC pollution levels and, consequently, improve air quality..

In addition, our results highlight the importance of transitioning to clean energy to reduce precursor emissions. For example, the decreased gradient in NOC pollution from Harbin (coal-reliant) to Beijing (partially using natural gas) to Hangzhou (without centralized heating) demonstrates the effectiveness of clean energy policies in constraining NOC pollution. Transitioning away from coal combustion and toward cleaner energy, such as natural gas or renewable energy, could be a powerful tool in reducing urban NOC pollution and improving air quality.

Furthermore, the findings demonstrate that aqueous-phase processes, especially under haze conditions, amplify the production of NOCs. This highlights the importance of controlling precursor emissions during periods of high humidity and haze to limit secondary NOC formation.

Overall, these insights can improve air quality management by prioritizing (1) reductions in aromatic precursor emissions through stricter controls on coal combustion and other anthropogenic sources, (2) the promotion of cleaner energy transitions, and (3) targeted measures to address secondary formation processes under haze conditions. Future studies should explore the long-term benefits of these strategies and refine models for predicting NOC dynamics under different environmental scenarios to support more effective policymaking.

We have included a brief discussion of these implications in the revised manuscript (Lines 649-651 and 654-656):

Lines 649-656: …It is imperative to manage precursor emissions during hazy episodes in order to restrict the increased formation of secondary NOCs in conditions of high humidity. Moreover, …

Lines 649-656: …The transition to cleaner energy sources, as evidenced by the decreased gradient of NOC pollution from HEB to BJ to HZ, represents an effective pathway for the mitigation of NOC pollution.

10) *Figure 6: It seems that the city label in the inset of Figure 6 is incorrect. The red circle and line should indicate Beijing (BJ), not HEB.*

Response: The revision has been made (Line 568).

At last, we deeply appreciate the time and effort you've spent in reviewing our manuscript.

Reference:

Bialik, O. M., Jarochowska, E., and Grossowicz, M.: Ordination analysis in sedimentology, geochemistry and palaeoenvironment—Background, current trends and recommendations, The Depositional Record, 7, 541-563, https://doi.org/10.1002/dep2.161, 2021.

Jiang, H., Cai, J., Feng, X., Chen, Y., Wang, L., Jiang, B., Liao, Y., Li, J., Zhang, G., Mu, Y., and Chen, J.: Aqueous-Phase Reactions of Anthropogenic Emissions Lead to the High Chemodiversity of Atmospheric Nitrogen-Containing Compounds during the Haze Event, Environ. Sci. Technol., 57, 16500-16511, 10.1021/acs.est.3c06648, 2023.

Su, S., Xie, Q., Lang, Y., Cao, D., Xu, Y., Chen, J., Chen, S., Hu, W., Qi, Y., Pan, X., Sun, Y., Wang, Z., Liu, C.-Q., Jiang, G., and Fu, P.: High Molecular Diversity of Organic Nitrogen in Urban Snow in North China, Environ. Sci. Technol., 55, 4344-4356, https://dx.doi.org/10.1021/acs.est.0c06851, 2021.

Taguchi, Y.-h. and Oono, Y.: Relational patterns of gene expression via non-metric multidimensional scaling analysis, Bioinformatics, 21, 730-740, 10.1093/bioinformatics/bti067, 2004.