General.

We would like to appreciate the editor for providing the valuable comments and a better perspective on our work to improve the manuscript. We have revised our manuscript by fully taking all comments into account. All the changes made and appeared in the revised text are shown in red. All detailed answers to comments are displayed in blue.

Comments of editor and our responses to them

I would like to thank the authors for their thorough responses to all the points raised by the reviewers. The document was well organized and easy to follow, and the explanations and additions to the text have significantly improved the manuscript.

Nevertheless, I still have a few minor points for which I would appreciate further clarification. Addressing these would, in my view, make the manuscript suitable for acceptance.

Response: We deeply appreciate 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.

1. Main point is concerning Reviewer 1 (R1), specifically questions 11 and 12 (Q11-Q12) regarding the methodology used to estimate secondary NAC (%). The elevated secondary NAC % observed at the northern and southern Chinese stations (~90%), is totally dependent on the NAC/[Tracer] ratio value, using CO as tracer (Eq. 1). As stated in the manuscript and also in the replies to the reviewer, the authors followed Salvador et al., 2021; Liu et al., 2023; Chen et al., 2023. The measurements presented by those authors were performed in much faster time resolution, capturing more realistic oscillation on the NAC/tracer ratio, allowing for example to measure during rush hour and/or to capture specific biomass *burning events. Since in this manuscript the sampling was performed in a 2-3 day frequency cycle, representing more regional average levels (L153-154), what would be the implications of such approach in the results? Could that implicate in an overestimation of the secondary NAC fraction? In addition, did the authors conducted any sensitivity tests around the 15% suggested by Chen et al., 2023 and adopted in this manuscript? On the other hand, based on further presented results it is reasonable that secondary NAC fraction be larger in the southern than in the northern Chinese stations (i.e. O3, nitrate, ALC, …), however, the larger estimations compared to previous studies (also conducted during the wintertime in China and considering the huge heterogeneity in such a large country!) raises some concern about the elevated obtained amounts. For this reason, I'd like to ask the authors to comment and to add some text discussing the methodology limitations and possibly uncertainties. For example, if appliable, the authors could conduce some sensitivity tests and generate some uncertainty around the obtained%. Unfortunately, the previous studies did not present any discussion on that.*

Response: We greatly appreciate your valuable and constructive comments on our manuscript. We fully understand your concerns regarding the uncertainties associated with the calculation of secondary NACs. While no systematic discussion on the uncertainties of this calculation method has been documented in previous studies, we fully agree with your critical and insightful comments. Accordingly, we have added a detailed discussion on the potential uncertainties of this calculation approach in the revised manuscript.

The 15% threshold was selected primarily to facilitate direct and consistent comparison with the results reported in previous studies (Liu et al., 2023; Cai et al., 2022). Theoretically, the adoption of high-frequency measurement data in the above calculation can better capture the realistic fluctuations in the [NACs]/[Tracer] ratio. In both previous relevant studies (Liu et al., 2023; Cai et al., 2022) and the present work, 12–24 h integrated observation data are commonly used for this calculation, and the resulting values largely reflect the regional average levels of secondary NACs. More importantly, given that the atmospheric lifetime of NACs is significantly shorter than that of tracer (i.e., CO), calculating the [NACs]/[Tracer] ratio using non-high-frequency data may lead to an underestimation of the actual [NACs]/[Tracer] ratio, which in turn causes an overestimation of the calculated secondary NAC fraction. Thus, the secondary NAC values calculated in this study only represented the maximum average fractions of secondary NACs over the study period. These values were exclusively used for internal data comparison within this study, as well as for cross-comparison with results reported in previous studies that employed an analogous calculation method based on non-high-frequency observation data (Liu et al., 2023; Cai et al., 2022).

Lines 411−426: …The 15% threshold was selected primarily to facilitate direct and consistent comparison with the results reported in previous studies (Liu et al., 2023; Cai et al., 2022). Theoretically, the adoption of high-frequency measurement data in the above calculation can better capture the realistic fluctuations in the [NACs]/[Tracer] ratio. In both previous relevant studies (Liu et al., 2023; Cai et al., 2022) and the present work, 12–24 h integrated observation data are commonly used for this calculation, and the resulting values largely reflect the regional average levels of secondary NACs. More importantly, given that the atmospheric lifetime of NACs is significantly shorter than that of tracer (i.e., CO), calculating the [NACs]/[Tracer] ratio using non-high-frequency data may lead to an underestimation of the actual [NACs]/[Tracer] ratio, which in turn causes an overestimation of the calculated secondary NAC fraction. Thus, the secondary NAC values calculated in this study only represented the maximum average fractions of secondary NACs over the study period. These values were exclusively used for internal data comparison within this study, as well as for cross-comparison with results reported in previous studies that employed an analogous calculation method based on non-high-frequency observation data (Liu et al., 2023; Cai et al., 2022)…

2. Please clarify in the legend of the Fig. S1 the reason for different colors (red and blue) for the stations.

Response: In the figure, the blue text labels represent northern cities, and the red text labels represent southern cities.

Supporting information

Figure S1. …In the figure, the blue text labels represent northern cities, and the red text labels represent southern cities.

Figure S5. …In the figure, the blue text labels represent northern cities, and the pink text labels represent southern cities.

3. Please verify the color legend used to represent north and south in Figure S6.

Response: We greatly appreciate your careful and thorough review of our manuscript. The revision has been made in the revised manuscript (Figure S6).

Figure S6. Temporal variations in the contribution of secondarily formed NACs to the total measured NACs mass in $PM_{2.5}$ in (a) southern and (b) northern cities.

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

References

Cai, D., Wang, X., George, C., Cheng, T., Herrmann, H., Li, X., and Chen, J.: Formation of Secondary Nitroaromatic Compounds in Polluted Urban Environments, J. Geophys. Res.: Atmos., 127, e2021JD036167, https://doi.org/10.1029/2021JD036167, 2022.

Liu, X., Wang, H., Wang, F., Lv, S., Wu, C., Zhao, Y., Zhang, S., Liu, S., Xu, X., Lei, Y., and Wang, G.: Secondary Formation of Atmospheric Brown Carbon in China Haze: Implication for an Enhancing Role of Ammonia, Environ. Sci. Technol., 57, 11163-11172, 10.1021/acs.est.3c03948, 2023.