## Response to RC2:

This publication aims to determine the molecular- level of PM<sub>2.5</sub> components and source contributions of PM<sub>2.5</sub> during hazy days in winter at Nanjing University of Information Science and Technology. The study has significance for assessing the air quality during the research period. Moreover, before to accepting this publication in the ACP Journal, we need to tackle significant editing concerns. Pay attention to the accompanying comments for more information.

We appreciate the reviewer's feedback on the manuscript, and we carefully reviewed the comments and addressed each individually below, highlighting changes made to the revised manuscript.

- 1. Line 128: Before the samples, the authors baked the quartz filter. What is the temperature for 5 hours of baking? Is there a standard procedure for this temperature and baking duration? Yes. The quartz fiber filters follow the standard procedure: they were pre-combusted at 450°C for 6 hours prior to sampling to eliminate potential contamination.
- 2. Following from the previous question, do you have any standard for controlling the weight of the filter?

Yes. Quartz fiber filters are weighed before sampling PM2.5 and then weighed again after sampling to monitor changes in weight. We perform this weighing in a temperature- and humidity-controlled laboratory. Additionally, we compare our weighing data with those from the National Environmental Monitoring Stations to ensure accuracy and maintain quality control.

- 3. Line 130 131: The authors mentioned collected the filed blank. Are you able to provide the chemical data in the blank field? If yes, you used the results of the field blank to calculate. Field blank filters were treated as the real samples for quality assurance, undergoing the same analysis method as real samples. Target compounds reported here were not detected in the blanks, revealing no contamination.
- 4. Line 132 133: Please explain the reason for divided into three episodes.

Dividing the data into three episodes based on PM<sub>2.5</sub> levels during sampling helps examine the variation trends of PM<sub>2.5</sub> components and their source contributions, which is useful for understanding the evolution of haze events and identifying the key driver of haze development. Additionally, previous studies often compare clean and hazy periods, there is relatively less focus on differences among various haze events.

5. Following from the previous question, do you have any standard for controlling the weight of the filter?

Yes. Quartz fiber filters are weighed before sampling PM<sub>2.5</sub> and then weighed again after sampling to monitor changes in weight. We perform this weighing in a temperature- and humidity-controlled laboratory. Additionally, we compare our weighing data with those from the National Environmental Monitoring Stations to ensure accuracy and maintain quality control.

6. Line 178 - 182: In Table 1, the authors discovered a high concentration of  $NO_3^-$ . However, you reported that  $NO_3^-$  was the second dominant species. What is the primary species from your studies? What is the source of  $NO_3^-$  from ambient air? Please add more references.

Sorry for the misunderstanding. Based on Table 1, the concentration of  $NO_3^-$  is indeed high. In the main text, we said that  $NO_3^-$  was the second most dominant species compared to OM, as illustrated in Figure 1. To clarify, we have added "Figure 1" in the sentence.

The major source of NO₃⁻ includes vehicles, coal combustion, natural gas burning and biomass burning (Zhang et al, 2014; Fan et al., 2023; Lin et al., 2024). We have added this sentence in lines 201-202.

The references cited are below:

- Zhang, H., Hu, J., Kleeman, M., and Ying, Q.: Source apportionment of sulfate and nitrate particulate matter in the Eastern United States and effectiveness of emission control programs, Science of The Total Environment, 490, 171–181, https://doi.org/10.1016/j.scitotenv.2014.04.064, 2014.
- Fan, M.-Y., Zhang, W., Zhang, Y.-L., Li, J., Fang, H., Cao, F., Yan, M., Hong, Y., Guo, H., and Michalski, G.: Formation Mechanisms and Source Apportionments of Nitrate Aerosols in a Megacity of Eastern China Based On Multiple Isotope Observations, Journal of Geophysical Research: Atmospheres, 128, e2022JD038129, https://doi.org/10.1029/2022JD038129, 2023.
- Lin, Y.-C., Fan, M.-Y., Hong, Y., Yu, M., Cao, F., and Zhang, Y.-L.: Important contributions of natural gas combustion to atmospheric nitrate aerosols in China: Insights from stable nitrogen isotopes, Science Bulletin, https://doi.org/10.1016/j.scib.2024.06.038, 2024.
- 7. Line 199: Please explain the nss- $SO_4^{2-}$  and add the references in this point "suggesting the may share similar formation pathways".

The abundance of non-sea-salt  $SO_4^{2-}$  (nss- $SO_4^{2-}$ ) was calculated by subtracting sea-salt sulfate (ss- $SO_4^{2-}$ ) from the total sulfate using the typical sulfate-to-sodium mass ratio of 0.252 in seawater (Yang et al., 2015).

Yang, G.-P., Zhang, S.-H., Zhang, H.-H., Yang, J., and Liu, C.-Y.: Distribution of biogenic sulfur in the Bohai Sea and northern Yellow Sea and its contribution to atmospheric sulfate aerosol in the late fall, Marine Chemistry, 169, 23–32, https://doi.org/10.1016/j.marchem.2014.12.008, 2015.

We revised "suggesting they may share similar formation pathways" to "suggesting they may share similar sources or formation pathways (Zhang et al. 2014)." In addition, the sentences in lines 216-220 elucidate the relationship between sulfate and nitrate formation.

The reference cited is listed below:

Zhang, H., Hu, J., Kleeman, M., and Ying, Q.: Source apportionment of sulfate and nitrate particulate matter in the Eastern United States and effectiveness of emission control programs, Science of The Total Environment, 490, 171–181, https://doi.org/10.1016/j.scitotenv.2014.04.064, 2014.

8. Line 205: What are the three SIA components.

The three SIA components refer to NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>. We have added these details to the sentence for clarity.

9. Line 298 – 299: Please explain the reason for this phenomenon in this section.

The reason has already been provided in the main text:

"This is probably because in urban areas airborne potassium can also be emitted from other important sources, such as meat cooking, refuse incineration, and resuspension of surface soil and fertilizers (Simoneit, 2002; Urban et al., 2012)."

- 10. All figures are not clear, please redraw and change the alphabet as the same in the texts. We updated the figure with high resolution (300 dpi) which should present clearly now. Let us know if you still see the blurry issue. Regarding the alphabet, we double-check the figure and text and confirm they are consistent now.
- 11. I recommend that the conclusions be evaluated and revised instead of duplicating the content from the results and statements section.

Thanks. The revised conclusion is below:

"Molecular distributions and high temporal variations of primary and secondary components in PM<sub>2.5</sub> during winter hazy episodes in urban Nanjing were comprehensively characterized through intensive sampling. Our results revealed that OM consistently dominated the total PM<sub>2.5</sub>, followed by NO<sub>3</sub><sup>-</sup>. <sup>14</sup>C analysis showed that while fossil fuel sources primarily contributed to WSOC, non-fossil sources, notably BB, became more significant as PM<sub>2.5</sub> pollution intensified. BB made a dominant contribution to OC, particularly during severe haze events, likely due to aqueous SOA formation from BB-derived organic gases. Other non-fossil sources like fungal spores were also elevated by BB, whereas plant debris contributions were higher on lighter hazy days with higher wind speeds and temperatures. Overall, these findings highlight the significant role of BB in winter haze over Nanjing and underscore the need for further research into the molecular-level identification of gaseous species from BB emissions and their role in secondary aerosol formation. Additionally, while meteorological parameters have an important influence on heavy haze formation, accurately quantifying their contribution remains a challenge for future research."