Response to RC3:

This study explored the molecular levels of inorganic and organic components in wintertime PM2.5 using intensive sampling and a range of techniques. It also assessed the contributions of primary and secondary sources with tracer-based methods. The finding that BB may significantly influence haze formation is notable, especially compared to the fossil-dominated conditions typically observed in winter. In this regard, the biomass-burning contribution to haze can more clearly be identified compared to some recent studies conducted in India, where BB is consistently prominent, particularly during haze events. Overall, the whole manuscript is well organized. I recommend the manuscript for publication on ACP after the following comments have been well addressed.

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.

Major comments:

In lines 75-77: The authors categorized biomass burning as an anthropogenic source. While biomass burning refers to the combustion of organic materials like wood, crop residues, and other plant matter, which releases VOCs into the atmosphere. In this context, these VOCs are biogenic. Could you explain this?

In general, wildfires are classified as biogenic sources, while the burning of wood and crop residues in domestic and field settings in rural areas is considered anthropogenic. Many studies in China also categorize biomass burning as an anthropogenic source (Chen et al., 2017; Ding et al., 2017; Srivastava et al., 2022), and these references have been included in the main text.

Chen, J., Li, C., Ristovski, Z., Milic, A., Gu, Y., Islam, M. S., Wang, S., Hao, J., Zhang, H., He, C., Guo, H., Fu, H., Miljevic, B., Morawska, L., Thai, P., Lam, Y. F., Pereira, G., Ding, A., Huang, X., and Dumka, U. C.: A review of biomass burning: Emissions and impacts on air quality, health and climate in China, Science of The Total Environment, 579, 1000–1034, https://doi.org/10.1016/j.scitotenv.2016.11.025, 2017.

Ding, X., Zhang, Y.-Q., He, Q.-F., Yu, Q.-Q., Wang, J.-Q., Shen, R.-Q., Song, W., Wang, Y.-S., and Wang, X.-M.: Significant Increase of Aromatics-Derived Secondary Organic Aerosol during Fall to Winter in China, Environ. Sci. Technol., 51, 7432–7441, https://doi.org/10.1021/acs.est.6b06408, 2017.

Srivastava, D., Vu, T. V., Tong, S., Shi, Z., and Harrison, R. M.: Formation of secondary organic aerosols from anthropogenic precursors in laboratory studies, npj Clim Atmos Sci, 5, 1–30, https://doi.org/10.1038/s41612-022-00238-6, 2022.

In lines 136-145: Was the extraction procedure and measurement process for sugar compounds the same as for ions when using ion chromatography?

The extraction procedure for sugar compounds was basically the same as that for ions, except that it employed a CarboPac MA1 analytical column (4*250 mm, Dionex) and an electrochemical detector for carbohydrates analysis. Sodium hydroxide (NaOH) was used as the gradient eluent for anion determination at a flow rate of 0.4 mL/min.

In the revised manuscript, we add another reference by Liu et al. (2019) and more experimental details about the quality control. Therefore, the whole paragraph looks like below:

"Sugar compounds, … were measured using ion chromatography (Dionex ICS-5000+, ThermoFisher Scientific, USA) after being extracted with ultra-pure water (Milli-Q Reference, America). Standard curves establishment and blank correction were conducted during the analysis. Other organic compounds, including biogenic SOA tracers (isoprene, sesquiterpene, and monoterpene), diacids, and other main organic molecules appeared in the present study were determined by gas chromatography/mass spectrometry (Agilent Technologies; Santa Clara, CA). The average recoveries ranged from 70% to 110% and repeatability experiments showed that the deviation was less than 15%. All the data were corrected with field blanks. More details about measurements can be found in previous studies (Bao et al., 2023)..."

In lines 161-162: Please rewrite this sentence.
Thanks. We have changed this sentence to "Then, these $F^{14}C$ values were corrected by dividing by the reference value ($f_{nf,ref}$) to remove potential impacts of nuclear bomb tests in the 1950s and 1960s, in order to obtain the non-fossil fractions of WSOC."

In lines 228-229: High OC/EC ratios larger than about 2.0 mean high SOC formation, why? The authors should rephrase this sentence to better reflect this relationship and provide supporting evidence.
This point can be supported by an early report by Li et al. (2016) and the references therein. To better reflect the relationship and support our findings, we changed the sentence to "In addition, high OC/EC ratios observed in this study (> 2.0–2.2) indicate the presence of secondary organic aerosol (Li et al., 2016b). This may be partially attributed to BB, which is a significant source of oxidants (Chang et al., 2024) and an important contributor to SOA formation (Li et al., 2024; Lim et al., 2019; Yee et al., 2013)."
New references cited are listed below:

Li, K., Zhang, J., Bell, D. M., Wang, T., Lamkaddam, H., Cui, T., Qi, L., Surdu, M., Wang, D., Du, L., El Haddad, I., Slowik, J. G., and Prevot, A. S. H.: Uncovering the dominant contribution of intermediate volatility compounds in secondary organic aerosol formation from biomass-burning emissions, National Science Review, 11, nwae014, https://doi.org/10.1093/nsr/nwae014, 2024.

Lim, C. Y., Hagan, D. H., Coggon, M. M., Koss, A. R., Sekimoto, K., de Gouw, J., Warneke, C., Cappa, C. D., and Kroll, J. H.: Secondary organic aerosol formation from the laboratory oxidation of biomass burning emissions, Atmospheric Chemistry and Physics, 19, 12797–12809, https://doi.org/10.5194/acp-19-12797-2019, 2019.

Yee, L. D., Kautzman, K. E., Loza, C. L., Schilling, K. A., Coggon, M. M., Chhabra, P. S., Chan, M. N., Chan, A. W. H., Hersey, S. P., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols, Atmospheric Chemistry and Physics, 13, 8019–8043, https://doi.org/10.5194/acp-13-8019-2013, 2013.

In lines 243-245: Is the high average WISOC/OC ratio observed during the last two periods related to changes in weather conditions, such as wind speed?

The high average WISOC/OC ratio observed during the last two periods is likely related to generally increased wind speeds, because high wind speeds can resuspend more primary organic compounds from the surface into the air, such as lipid compounds.

In lines 250-252: This study used radiocarbon measurements to quantify the contributions of fossil and non-fossil sources to WSOC. I am curious why only WSOC was chosen for this analysis instead of other PM2.5 components?
In this study, we focus on WSOC because the main organic compounds we selected are water-soluble, which aligns well with WSOC. Additionally, more radiocarbon researches have been conducted on TC than on WSOC. As a key fraction of $PM_{2.5}$ and a valuable indicator for atmospheric processes such as the formation of SOA, WSOC also influences global climate change through its effects on sunlight absorption and the hygroscopic properties of aerosols. Understanding the contributions of different sources to WSOC is crucial for assessing its impact on climate. Radiocarbon measurement of WSOC allows for precise differentiation between these sources, offering valuable insights into the contributions of fossil fuels versus non-fossil sources across different haze episodes. This information is particularly useful for studying air pollution and climate change.

In lines 259-261: A high contribution from fossil fuel sources is also likely associated with low temperatures during cold times. Rising coal combustion for cooking and heating may be a result of cold weather. Hence, I suggest that the authors refine this discussion to address the potential link between cold weather and elevated fossil fuel contributions.
Thanks. We have changed it to “The high proportion of fossil fuels observed in this study can be attributable to extensive coal combustion for residential cooking and heating on cold days, and industrial activities and traffic emissions in the vicinity of the sampling sites could also contribute”.

In lines 275-279: This sentence is too long. Please rewrite it to make it more readable.
The sentence has been revised as follow: “Higher anhydrosugar concentrations in the first episode suggest greater BB impacts during heavy haze events. In contrast, the elevated levels of sugars and sugar alcohols in the last two episodes are likely due to increased wind speeds, which enhanced the resuspension of biogenic detritus and soil microbes rich in these substances.”

In lines 303-305: Change it to “…surface soil and fertilizers containing abundant potassium…”.
Changed.

In lines 326: Syringic acid should be the most abundant among lignin and resin acids during heavy haze. Modify this sentence.
Thanks. Changed to “Syringic acid was found to be the most abundant species among lignin and resin acids during heavy haze events”.
In lines 346-347: Remove “beneficial meteorological parameters” as it is improper to use “beneficial” in this context.
Removed.

In lines 353: Enhanced biogenic emissions might be also attributable to increased wind speeds.
Yes. We have changed the sentence to "…indicating enhanced primary biogenic sources during that time probably due to the rising temperature and wind speeds."

In lines 408-409: Anthropogenic emissions may be more appropriate here.
Changed.

In lines 417-419: How does biomass burning promote the formation of biogenic SOA tracers? Is it through increasing radical concentration?
Yes. Biomass burning can promote the formation of biogenic SOA tracers by increasing radical concentration, as evidenced by a recent study (Chang et al., 2024). They reported that BB-chlorine emissions leaded to elevated levels of O3 and OH radicals, thus BB plays a large role in atmospheric chemistry and oxidation process. We add this sentence "This is because BB is not only a significant source of air pollutants but also of oxidants (Chang et al., 2024), which enhances oxidation capacity and further promotes photochemistry and SOA formation" to provide a better explanation.
The reference cited is below:
Chang, D., Li, Q., Wang, Z., Dai, J., Fu, X., Guo, J., Zhu, L., Pu, D., Cuevas, C. A., Fernandez, R. P., Wang, W., Ge, M., Fung, J. C. H., Lau, A. K. H., Granier, C., Brasseur, G., Pozzer, A., Saiz-Lopez, A., Song, Y., and Wang, T.: Significant chlorine emissions from biomass burning affect the long-term atmospheric chemistry in Asia, National Science Review, nwae285, https://doi.org/10.1093/nsr/nwae285, 2024.

In lines 419-423: The whole sentence is too long. Besides, low levels of pinic acid during the first episode may be due to high relative humidity as well.
Thanks. We changed it as below:
"However, pinic acid did not exhibit the highest concentration during the heavy haze period with the greatest BB contribution. This may be due to pinic acid undergoing further reactions at high relative humidity, forming highly oxidized polar compounds through the addition of a molecule of water and the opening of the dimethylcyclobutane ring (Claeys et al., 2007)."

In lines 460-463: This is a bit confusing. The authors need to provide more evidences or references for support this conclusion. The pronounced correlations might indicate that they share similar sources, formation mechanisms, or atmospheric processing pathways.
We agree. The sentence has been changed to "There were also pronounced correlations between glyceric acid and aromatic acids such as iPh and benzoic acid ($r = 0.63–0.71$, $p < 0.01$), implying that they may undergo similar atmospheric processing pathways".

In lines 497-498: Changing "primary vehicle exhaust emissions" to "primary emissions" may be more reasonable. The result also suggests that they are probably mainly produced in the atmosphere by the photochemical oxidation of various organic precursors.

Yes, we agree. We changed the sentence to “Such findings mean secondary formation is an important pathway of dicarboxylic acids on hazy days in urban Nanjing, apart from primary emissions.”

In line 500: The authors can cite some references here. For example, the papers by Kawamura et al., 2016, Atmospheric Research. DOI: 10.1016/j.atmosres.2015.11.018

Thanks. We cited this paper in the manuscript.

In lines 503-504: Change “secondary sources (e.g., PAHs and biogenic VOCs including …)” to “secondary sources (e.g., oxidation reactions of PAHs and biogenic VOCs …”.

Changed.

In lines 510-513: The authors can find more references to support BB’s significant impact on fine particle formation. Some reports found that species released by BB can enhance radical concentration and atmospheric oxidation capacity.

Thanks for your suggestion. We have changed the sentence as below:

“This could be attributed to the increased domestic wood/crop combustion for heating and cooking in the surrounding area, driven by low temperatures and high relative humidity during this period (Figs. S1-S2). BB-chlorine emissions have been shown to elevate O_3 and OH radical levels, significantly impacting oxidation processes (Chang et al., 2024). In addition, soluble organic gases from BB can dissolve in aerosol/cloud liquid water and subsequently react with aqueous phase oxidants to form SOA, with these reactions increasing with increasing RH (Zhang et al., 2024).”

The references cited are listed below:

Chang, D., Li, Q., Wang, Z., Dai, J., Fu, X., Guo, J., Zhu, L., Pu, D., Cuevas, C. A., Fernandez, R. P., Wang, W., Ge, M., Fung, J. C. H., Lau, A. K. H., Granier, C., Brasseur, G., Pozzer, A., Saiz-Lopez, A., Song, Y., and Wang, T.: Significant chlorine emissions from biomass burning affect the long-term atmospheric chemistry in Asia, National Science Review, nwae285, https://doi.org/10.1093/nsr/nwae285, 2024.

Zhang, J., Shrivastava, M., Ma, L., Jiang, W., Anastasio, C., Zhang, Q., and Zelenyuk, A.: Modeling Novel Aqueous Particle and Cloud Chemistry Processes of Biomass Burning Phenols and Their Potential to Form Secondary Organic Aerosols, Environ. Sci. Technol., 58, 3776–3786, https://doi.org/10.1021/acs.est.3c07762, 2024.

In line 525: Replace “produced by …” with “from”.

Replaced.

In lines 542-543: This may also indicate fossil fuel sources make a dominate contribution to SOC formation during urban haze events in winter.

Yes. We changed this to “…indicating anthropogenic VOCs make a dominate contribution to SOC in these urban aerosols”.

In lines 544-546: A large amount of fossil fuel combustion during cold periods could also contribute.

We agree. The description has been changed to "…probably resulting from significantly reduced biogenic VOCs and largely increased fossil fuel combustion during cold winter periods".

In lines 553-555: Rewrite.
Changed to "Molecular distributions and high temporal variations of primary and secondary components in $PM_{2.5}$ during winter hazy episodes in urban Nanjing were comprehensively characterized through intensive sampling".