Response to RC4:

The paper explores the molecular composition and source contributions of PM2.5 samples collected at high temporal resolution during winter haze events. The results highlight the predominance of organic matter and identify biomass burning as the most significant source of organic matter/organic carbon. The data provide valuable insights for the analysis and modeling of particle growth and composition during haze episodes. However, given the paper's title, "Significant Role of Biomass Burning in Heavy Haze Formation in a Megacity," I anticipated a more detailed discussion of the mechanisms and evidence supporting biomass burning's role in particle growth during these events. This critical aspect is not adequately addressed in the manuscript's current structure and analysis. While the work is promising and merits publication, it requires major revisions to address the major comments outlined.

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:

1. Line 223: The OC/EC average ratios fell in a range of 8.7-13.3, close to those measured in regions influenced by biomass burning (BB). What were the OC/EC ratios reported in previous studies, and how do they compare to those from other sources?

The OC/EC ratios can differ significantly across various sources. Generally, higher OC/EC ratios indicate a greater contribution from biomass burning or secondary formation, while lower ratios are typically associated with fossil fuel emissions (Turpin et al., 1995; Zhang et al., 2014; Zhang et al., 2008). For additional OC/EC values from different sources, please refer to the paper by Cao et al. (2006). Relevant papers for OC/EC values are also provided.

Cao, G., Zhang, X., and Zheng, F.: Inventory of black carbon and organic carbon emissions from China, Atmospheric Environment, 40, 6516–6527, https://doi.org/10.1016/j.atmosenv.2006.05.070, 2006.

Chow, J. C., Watson, J. G., Lu, Z., Lowenthal, D. H., Frazier, C. A., Solomon, P. A., Thuillier, R. H., and Magliano, K.: Descriptive analysis of PM2.5 and PM10 at regionally representative locations during SJVAQS/AUSPEX, Atmospheric Environment, 30, 2079–2112, https://doi.org/10.1016/1352-2310(95)00402-5, 1996.

Novakov, T., Andreae, M. O., Gabriel, R., Kirchstetter, T. W., Mayol-Bracero, O. L., and Ramanathan, V.: Origin of carbonaceous aerosols over the tropical Indian Ocean: Biomass burning or fossil fuels?, Geophysical Research Letters, 27, 4061–4064, https://doi.org/10.1029/2000GL011759, 2000.

Zhang, X. Y., Wang, Y. Q., Zhang, X. C., Guo, W., and Gong, S. L.: Carbonaceous aerosol composition over various regions of China during 2006, Journal of Geophysical Research: Atmospheres, 113, https://doi.org/10.1029/2007JD009525, 2008.

Zhang, Y.-L., Li, J., Zhang, G., Zotter, P., Huang, R.-J., Tang, J.-H., Wacker, L., Prévôt, A. S. H., and Szidat, S.: Radiocarbon-Based Source Apportionment of Carbonaceous Aerosols at a Regional Background Site on Hainan Island, South China, Environ. Sci. Technol., 48, 2651–2659, https://doi.org/10.1021/es4050852, 2014.

2. Line 230: WSOC is often composed of BB-derived and aged OC. What are the possible mechanisms to form those SOC/SOA? There are several publications talking about the BB-aqSOA formation, and it is required to expand the explanation here.

Thanks for your good advice. According to your suggestion, we add some discussions about the possible mechanisms to form those SOC in lines 265 as below:

"…indicating BB was an important contributor to WSOC. Soluble organic gases derived from BB, such as phenols, can react with oxidants in the aqueous phase to form SOA in aerosol liquid water and clouds, significantly contributing to SOA formation. Moreover, this aqueous SOA formation greatly increases as relative humidity (RH) increases (Zhang et al., 2024). Given the high relative humidity during the most polluted periods, aqueous SOA production from BB-derived organic gases mostly likely play a crucial role in heavy haze formation. Aqueous SOA generation from BB emissions was also confirmed by many other studies (Gilardoni et al., 2016; Li et al., 2021, 2014; Xiao et al., 2022), highlighting the importance of BB emissions in atmospheric oxidation processes."

Gilardoni, S., Massoli, P., Paglione, M., Giulianelli, L., Carbone, C., Rinaldi, M., Decesari, S., Sandrini, S., Costabile, F., Gobbi, G. P., Pietrogrande, M. C., Visentin, M., Scotto, F., Fuzzi, S., and Facchini, M. C.: Direct observation of aqueous secondary organic aerosol from biomass-burning emissions, Proceedings of the National Academy of Sciences, 113, 10013–10018, https://doi.org/10.1073/pnas.1602212113, 2016.

Li, F., Tsona, N. T., Li, J., and Du, L.: Aqueous-phase oxidation of syringic acid emitted from biomass burning: Formation of light-absorbing compounds, Science of The Total Environment, 765, 144239, https://doi.org/10.1016/j.scitotenv.2020.144239, 2021.

Li, Y. J., Huang, D. D., Cheung, H. Y., Lee, A. K. Y., and Chan, C. K.: Aqueous-phase photochemical oxidation and direct photolysis of vanillin – a model compound of methoxy phenols from biomass burning, Atmospheric Chemistry and Physics, 14, 2871–2885, https://doi.org/10.5194/acp-14-2871-2014, 2014.

Xiao, Y., Hu, M., Li, X., Zong, T., Xu, N., Hu, S., Zeng, L., Chen, S., Song, Y., Guo, S., and Wu, Z.: Aqueous secondary organic aerosol formation attributed to phenols from biomass burning, Science of The Total Environment, 847, 157582, https://doi.org/10.1016/j.scitotenv.2022.157582, 2022.

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.

3. Line 231: WISOC normally represents primary OC. Are there any studies supporting this statement?

Yes. Zhang et al. (2014) reported that WISOC can better represent primary organic carbon (https://doi.org/10.1021/es4050852). We have cited this paper in the manuscript.

Zhang, Y.-L., Li, J., Zhang, G., Zotter, P., Huang, R.-J., Tang, J.-H., Wacker, L., Prévôt, A. S. H., and Szidat, S.: Radiocarbon-Based Source Apportionment of Carbonaceous Aerosols at a Regional Background Site on Hainan Island, South China, Environ. Sci. Technol., 48, 2651–2659, https://doi.org/10.1021/es4050852, 2014.

4. Line 245: According to the molecular level measurements, are there any molecules detected associated with BB gases, like the phenolic compounds?

Yes. We detected some phenolic compounds (i.e., lignin products), known as BB tracers, including 4-hydroxybenzoic acid, vanillic acid, and syringic acid. The discussion about them were in lines 353-371.

5.Line 252: Fig. 3 is confusing and hardly support your statement in the main text. It was described that the WSOC is likely predominantly contributed from BB, but here the authors indicated that over 60% WSOC is contributed by anthropogenic sources, like cooking, heating, and industrial activities. The authors need to explain this.

Sorry for any confusion. To clarify, while fossil fuels predominantly contribute to WSOC, the proportion of non-fossil sources instead of fossil fuels increases with rising haze pollution. This coincides with a significant intensification of biomass burning (BB) during that time, suggesting that BB could be a key driver of haze formation. This conclusion is also supported by recent research, which found that certain compounds emitted from BB, such as chlorine, can elevate oxidant levels, thereby enhancing secondary aerosol formation (Chang et al., 2024). Based on modeling work, Zhang et al. (2024) reported that the aqueous chemistry of biomass-burning phenols significantly contributes to secondary organic aerosol (SOA) formation, with this contribution increasing with relative humidity. All these findings support our conclusion that biomass burning plays a key role in WSOC formation and even the whole atmospheric chemistry.

In order to make our point clearer, we add some discussions in lines 298-304 as well: "This is further evidenced by previous reports that emphasized the contribution of aqueous-phase photochemical oxidation of BB organic gases to haze pollution (Zhang et al., 2024; Xiao et al., 2022). This aqueous-phase SOA formation could contribute more than the conventional semi-volatile SOA formation pathways, especially under polluted conditions with high relative humidity (Zhang et al., 2024). Additionally, BB-chlorine emissions could enhance oxidation capacity and further promote secondary aerosol formation (Chang et al., 2024)."

The references used 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.

Xiao, Y., Hu, M., Li, X., Zong, T., Xu, N., Hu, S., Zeng, L., Chen, S., Song, Y., Guo, S., and Wu, Z.: Aqueous secondary organic aerosol formation attributed to phenols from biomass burning, Science of The Total Environment, 847, 157582, https://doi.org/10.1016/j.scitotenv.2022.157582, 2022.

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.

6. The authors devoted an excessive amount of text to discussing SOA tracers from other sources (sections 3.3.3 – 3.3.6), which does not directly support the article's main conclusion. It can be more concise.
Thank you. While sections 3.3.3 – 3.3.6 may appear extensive, they provide important information about SOA tracers and their sources. This detailed discussion is essential for comprehensively addressing the complex interactions and contributions of various tracers, which ultimately supports the robustness of the article's main conclusions. For example, the significant correlations between SOA and BB tracers show more evidence for the crucial role of BB in secondary aerosol formation. By including this thorough examination, we aim to offer a complete and nuanced perspective that enhances the overall validity of our findings.
In addition, we moved the lines 406-409 to the supporting material to make the text more concise.

7. The tables and figures should be cited more clearly in the manuscript to make readers understand the data and analysis. For example, line 513: due to low temperatures and high RH (Table 1 and Fig. 5-6). It is difficult for the readers to connect all figures with the text.
Thank you for your feedback regarding the clarity of citing tables and figures in the manuscript. We appreciate your suggestion to improve the connection between the text and visual data. We have ensured that the tables and figures are referenced clearly in the manuscript to align with the text. For instance, we changed the "Table 1 and Figures 5-6" to "Figs. S1-S2".

8. The introduction is over length but fails to get to the main point. For example, the 1st paragraph is not related to the topic at all. And more BB associated measurements, experimental, and modeling studies are not mentioned in the introduction.
Thanks. The first paragraph was intended to emphasize the severity of $PM_{2.5}$ pollution in the context of ozone pollution, underscoring the need to investigate $PM_{2.5}$ components and their sources for effective air quality management. To enhance its relevance to the topic, we have made revisions to better align with the focus of our study.
In line 44: "This underscores the ongoing challenge of controlling $PM_{2.5}$ pollution, especially during cold seasons in megacities. Additionally, the emergence of ozone (O_3) pollution in many urban areas complicates the situation. Rising O_3 levels, associated with increased atmospheric oxidation capacity (Kang et al., 2021), create more complex air pollution scenarios due to intricate secondary aerosol formations and the combined effects of $PM_{2.5}$ and O_3."

Moreover, we added some description about BB associated studies in lines 67-73: "BB has a substantial impact on the secondary organic aerosols (SOA) budget and climate change (Zhang et al., 2024; Chen et al., 2017). For example, substituted phenols from lignin combustion, which serve as BB tracers as well, undergo aqueous phase oxidation with photooxidants to form SOA, significantly influencing the evolution of organic aerosols (Zhang et al., 2024). However, the contribution of BB emissions to SOA formation is not yet well understood and is consequently not accurately represented in regional and global atmospheric chemistry models".

The references cited are below:

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.

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.

9. The paper is hard to read and the language needs big improvement. Try avoid using obscure, vague, and unscientific words in the manuscript. e.g.: tough, notwithstanding, aforementioned. Don't over use tentative language such as "may be".

Thanks. We have reviewed the manuscript and made targeted adjustments to enhance readability. We have replaced vague or non-scientific terms with more precise language where necessary. For example, we have substituted "tough" with "challenging," "notwithstanding" with "despite," and "aforementioned" with "previously mentioned" to improve clarity.

We acknowledge the overuse of tentative language such as "may be" and have made revisions to reduce its frequency. We believe these changes enhance the readability and precision of the text.