Response to reviewers' comments

Response to RC1:

This study provides many valuable information on the molecular-level $PM_{2.5}$ components during different levels of haze events with high-time resolution. It analyzed a wide range of individual components of $PM_{2.5}$, which allows a detailed study of various sources at the same time. The radio carbon measurements suggest a greater contribution from fossil fuels to WSOC, while the contribution of non-fossil fuels increased with increasing haze pollution, coinciding with elevated biomass burning (BB) during that time. This new finding highlight BB may be an important driver for heavy haze formation, despite great contributions of fossil fuel sources. This manuscript presents many interesting results that will deepen our understanding of haze evolution. This work is worth being published in the journal of ACP.
We appreciate the reviewer's feedback on the manuscript, and we carefully reviewed the comments and addressed each individually below, highlighting changes made in the revised manuscript.

Here are some minor comments below:

In Figure 4, I noticed that sugars and sugar alcohols have high concentrations during the last two periods, with levels relatively higher than those of anhydrosugars. Could you explain why this is the case?
The elevated levels of sugars and sugar alcohols in the last two episodes are likely due to the increased wind speeds which enhanced resuspension of biogenic detritus and soil microbes containing abundant sugars and sugar alcohols.

This study conducted ^{14}C analysis on WSOC. Why did the authors choose WSOC over other $PM_{2.5}$ components?
Actually, we did ^{14}C analysis on total carbon (TC) as well. However, this study focuses on WSOC, as the main organic components we selected are water-soluble, aligning well with WSOC. Furthermore, there are more studies on ^{14}C analysis of TC than on WSOC. WSOC also has direct and indirect impacts on global climate change by absorbing sunlight and altering the hygroscopic properties of aerosols. By conducting ^{14}C analysis on WSOC, the contribution of fossil fuels and non-fossils to haze pollution can be accurately examined. This information is helpful for climate and air pollution studies.

The sampling period is from December 31 to January 2. Why was this specific period selected? Does it overlap with the Spring Festival or any holidays?
To be honest, we did this sampling campaign based on weather forecast about air quality. Moreover, due to our curiosity about how $PM_{2.5}$ components and sources change with haze evolution, we decided to launch intensive $PM_{2.5}$ samplings at high time resolution. The whole sampling period does not overlap with the Spring Festival but with New Year's Day. However, since fireworks are banned in Nanjing, they did not affect the results of this study.

Response to RC2:

This publication aims to determine the molecular- level of $PM_{2.5}$ components and source contributions of $PM_{2.5}$ 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 $PM_{2.5}$ levels during sampling helps examine the variation trends of $PM_{2.5}$ 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 $PM_{2.5}$ 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.

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 NO_3^- 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_3^-, SO_4^{2-}, and NH_4^+. 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 $PM_{2.5}$ during winter hazy episodes in urban Nanjing were comprehensively characterized through intensive sampling. Our results revealed that OM consistently dominated the total $PM_{2.5}$, followed by NO_3^-. ^{14}C analysis showed that while fossil fuel sources primarily contributed to WSOC, non-fossil sources, notably BB, became more significant as $PM_{2.5}$ 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."

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".

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.

Response to RC5:

This manuscript reports on the molecular-level characterization of primary and secondary constituents in PM2.5 at high-time resolution in Nanjing City, China. Biomass burning (BB) was found to be the most significant contributor to organic carbon (OC). Results are supported by the presented data, and the findings are well contextualized in light of other current source tracking studies. The results are timely and will be of great interest to the readership of Atmospheric Chemistry and Physics.

We appreciate the reviewer's feedback on the manuscript and have carefully reviewed each comment, addressing them individually below while highlighting the changes made in the revised manuscript.

Here are some minor suggestions:

1. Table 1 is too large. Is it possible to move it into the supplementary materials? Maybe the authors could use 1-3 boxplot figures to replace Table 1?

Thanks. Table 1 provides detailed information on various $PM_{2.5}$ components across different haze events. Given its importance, we believe it would be better placed in the main text. Figures 1-4 show the average concentrations of different species during three periods, serving the same purpose as boxplots.

2. Section 2.1: Is there a reason to choose the sampling period from 12/31/2017 to 1/2/2018. This period was the new year holiday but fireworks use was forbidden. Will that impact the conclusion of this paper?

Thank you for your question. The sampling period from 12/31/2017 to 1/2/2018 was chosen to capture data during different haze events for better understanding the haze development in winter in megacities. While fireworks usage was restricted during this period, other sources of pollution were still active. We believe the results remain reliable and valid for the study's conclusions.

3. Nanjing is a megacity in China and the major energy sources are hydropower and power plants. Where did the biomass burning come from? Is it possible to generate a figure, which includes HYSPLIT backward trajectories + FINN fire points?

Although Nanjing relies on various energy sources, biomass burning remains a significant source of pollution especially in the nearby areas. This includes agricultural residue burning, residential wood combustion, and small-scale industrial activities, as Nanjing has many rural areas where biomass fuels are important household energy in stoves for cooking and heating. Besides, long-range transport of air masses could have impacts on local atmospheric compositions as well. Thus, these practices would contribute to atmospheric pollution both in urban and rural areas. It was also reported that domestic biomass burning are highly distributed in Jiangsu (Zhou et al., 2017).

Zhou, Y., Xing, X., Lang, J., Chen, D., Cheng, S., Wei, L., Wei, X., and Liu, C.: A comprehensive biomass burning emission inventory with high spatial and temporal resolution in China, Atmospheric Chemistry and Physics, 17, 2839–2864, https://doi.org/10.5194/acp-17-2839-2017, 2017.

The HYSPLIT backward trajectories with fire points are added below:

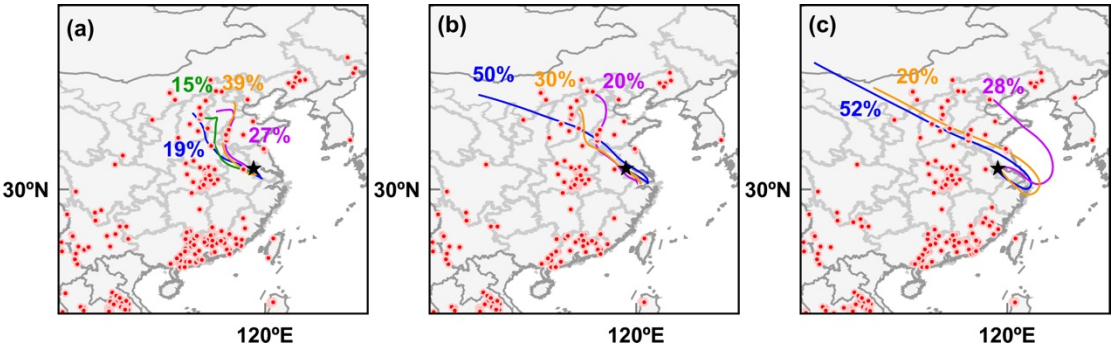

Figure S1. Three-day HYSPLIT back trajectories initiated over Nanjing with altitudes below 500 m, along with MODIS fire spots across three episodes with $PM_{2.5}$ concentrations of (a) > 200, (b) 100-200, and (c) < 100 μg m^{-3}. The black star indicates the sampling site. MODIS active fire data can be accessed here: https://firms.modaps.eosdis.nasa.gov/download/list.php.

And we also added some description in lines 182-187 in the revised manuscript as below:

"MODIS active fire/hotspot products were utilized to evaluate the impact of open biomass burning during the entire sampling period. Based on the backward trajectory analysis, the air masses throughout the sampling period were significantly influenced by biomass burning, as

illustrated in Fig. S1. By comparison, the third episode showed a greater influx of clean ocean air masses (Fig. S1c)."

Response to RC6:

The report studied molecular composition and source contributions of PM2.5 during winter hazy days. The ^{14}C measurements of WSOC and further characterization of organic matters reveal that biomass burning is an important driver for the haze formation, in contrast to the fossil-dominated "normal" situation in Nanjing in winter. The findings are interesting to the atmospheric chemistry community. The manuscript is generally well-written and presented with solid evidence. It has both values regarding molecular-level characterization and source tracking. I would like to recommend accepting this manuscript for publication in ACP after addressing the following comments.

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:

1. The title can be changed to "Significant role of biomass burning in heavy haze formation in Nanjing, a megacity in China: Molecular-level insights from intensive PM2.5 sampling on winter hazy days".
   Thanks. We have changed.

2. The main contribution of biomass burning is likely related to significant chlorine emissions, which was reported by Chang et al. 2024 (*National Science Review*, nwae285, https://doi.org/10.1093/nsr/nwae285) to affect the long-term atmospheric chemistry and air quality in Asia. The authors can compare this work with the study by Chang et al. to support these findings in the manuscript.
   Thanks very much for your suggestion. We have added additional descriptions about this reference paper to provide more evidence in the revised manuscript, specifically in lines 302-304, 451-453, 533-535 and 549-550.

Minor:

1. The pie charts in Figure 1 are a little blurry.

Thank you for pointing that out. We have improved the resolution of the pie charts in Figure 1 to ensure they are clearer in the revised manuscript.

2. Keep the font size in the figure legend consistent (e.g., Fig 4)

Thanks. We have changed the font size in the figure legends throughout the manuscript, including Figure 4.

Response to CC1:

The authors conduct a study reporting a molecular-level characterization of primary and secondary constituents in PM2.5 during haze events, using high-time resolution data obtained from intensive sampling at approximately 2-hour intervals and comprehensive analytical methods. The findings are both informative and useful, as comparative analyses of PM2.5 components across different haze events are still lacking. With the growing global attention on the role of biomass burning, such as residential wood combustion, in atmospheric chemistry, and given the rarity of high-resolution molecular-level characterization, I recommend this work for publication in ACP, provided that the following issues are properly addressed.

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

Specific comments:

In lines 26-28: The authors found the contribution of non-fossil fuels increased with increasing haze pollution. However, it was shown that fossil fuel sources made a dominant contribution to WSOC. More explanations should be given here.

The increased non-fossil contribution 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 supported 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.

In lines 136-145: More experimental details need to be here about the quality control.
In the revised manuscript, we have added more description about the quality control. 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 160-163: The $F^{14}C$ values were obtained by dividing by the reference isotopic ratio from 1950. Why is further correction needed by dividing by another reference value? This process is a bit confusing.
First, dividing by the reference isotopic ratio in 1950 (i.e., $(^{14}C/\ ^{12}C)_{1950}$) is to obtain $F^{14}C$ values. Then, correct these $F^{14}C$ values for the nuclear bomb effects of the 1950s and 1960s by dividing by the reference value ($f_{nf,ref}$) to determine the non-fossil carbon fractions (f_{nf}). Since modern carbon can originate from both BB and biogenic (bio) sources, $f_{nf,ref}$ should be divided into $f_{bb,ref}$ and $f_{bio,ref}$. In this study, $f_{bb,ref}$ (1.11) and $f_{bio,ref}$ (1.01) were used as the upper and lower limits of $f_{nf,ref}$, with their median value (1.06) representing the middle value of $f_{nf,ref}$.

In lines 418-420 and 499-500: The authors suggest that BB could enhance oxidation reactions and secondary formation of certain species. Could you provide additional evidence to support this claim?
In lines 451-452, we have added following evidence: "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."
In lines 533-535, we have included evidence such as: "Chlorine emissions from BB were found to increase oxidant levels, such as O_3 and OH radicals, largely impacting atmospheric chemistry and oxidation process (Chang et al., 2024)."
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.