RC1: 'Comment on egusphere-2025-1335', Anonymous Referee #1, 26 May 2025

Authors' Response to Referee #1 Comments

Dear reviewer,

Thank you very much for your critical reading of the manuscript, appreciation of our work and comments/suggestions, which helped to improve the quality of the manuscript. The manuscript is revised accordingly, and our point-by-point responses to all the comments are provided below. Please see the revised manuscript for details of the revisions.

1. Writing and Readability

The manuscript is generally well-structured encompassing the conventional format of scientific articles. The language is clear and concise, facilitating comprehension. However, there are occasional grammatical errors and awkward phrasings that could benefit from careful proofreading. For instance, the sentence:

"Further fossil fuel combustion contributed more significantly at CB than at BN." could be rephrased for clarity as:

"Furthermore, fossil fuel combustion contributed more significantly at CB than at BN."

Overall, the manuscript is accessible to readers with a background in atmospheric sciences or environmental chemistry.

Response: Thank you for your insightful comments and suggestions. We have revised the sentence as recommended. We have further carefully reviewed and revised the manuscript. In response, we have:

- Page 1, Line 25: Further the recent studies found that the $PM_{2.5}$ affects the productivity and aggravates socio-economic inequality.
  We have modified it to: Furthermore, recent studies have found that $PM_{2.5}$ affects the productivity and aggravates socio-economic inequality.
- Page 2, Line 37: Currently, research on the origins of $PM_{2.5}$ has been widely carried out worldwide
  We have modified it to: Recent research on the sources of $PM_{2.5}$ has been extensively conducted worldwide.
- Page 3, Line 73： The filter membrane was enclosed in aluminum foil after every sampling, and put into a sealed plastic pouch, and stored away from light.
  We have modified it to: The filter membrane was immediately wrapped in aluminum foil, sealed in a plastic pouch, and stored away from light after sampling.
- Page 4, Line 80: OC and EC were analyzed using a semi-continuous OC/EC analyzer (Sunset Laboratory, USA), which separates OC and EC by heating the sample at different temperatures and distinguishes between OC and EC by using a laser or light

source to monitor changes in the reflected or transmitted light of the sample during the heating process.

We have modified it to: The mass concentrations of OC and EC were measured using a semi-continuous thermal/optical OC/EC analyzer (Sunset Laboratory, USA). The distinction between OC and EC is achieved via real-time monitoring of light reflectance/transmittance changes during the heating process using a laser/light source, i.e. the IMPROVE protocol of the protective visual environment (Wan et al., 2017; 2015).

2. Scientific Content

2.1. Experimental Design

The study investigates the chemical and stable carbon isotopic compositions of $PM_{2.5}$ collected from two forest sites in China—Changbai Mountain (CB) in the north and Xishuangbanna (BN) in the south—during summer and winter periods. The sampling strategy includes day and night collections, providing temporal resolution. The analysis encompasses carbonaceous and nitrogenous components, water-soluble inorganic ions (WSIIs), and $\delta^{13}C$ of total carbon ($\delta^{13}C_{TC}$).

While the study design is comprehensive, there are concerns regarding certain methodological choices:

Filter Material: The use of quartz filters for collecting $PM_{2.5}$ samples intended for WSII analysis is questionable. Quartz filters are known to have high blank values for certain ions, which can interfere with accurate quantification. Although the authors mention using blanks to correct for background levels, the inherent high background of quartz filters, especially for cations like Na^+, Ca^{2+}, and Mg^{2+}, can compromise the reliability of the measurements. Alternative filter materials, such as Teflon or PCT, are more suitable for WSII analysis due to their lower blank values.

Response: Thank you for raising this important point regarding filter selection for WSII analysis. We agree that quartz filters may exhibit higher blanks for certain ions. In our study, quartz filters were selected primarily for their high collection efficiency for $PM_{2.5}$ and thermal stability, and compatibility with multi-component analysis (including fatty acids, aldehydes/ketones). To minimize random variability, field blanks were collected both at the beginning and end of sampling for each site and season, followed by blank correction. Currently, quartz filters are also widely used for ion analysis in numerous studies (Meng et al., 2014; Cao et al., 2017).

However, after analysis, it was found that the concentrations of the samples from the Mt. Changbai site were higher than Xishuangbanna. Moreover, the blank values in Mt. Changbai site were generally low (The Ca^{2+}, and Mg^{2+} in the blank were almost 0). The interference of the blank values of the quartz filters on the samples could be ignored through blank correction. For the samples from the Xishuangbanna site, the inherently high background of the quartz filters did interfere with Na^+, Ca^{2+}, and Mg^{2+} in the samples, which was also the reason for the ion imbalance at Xishuangbanna. Therefore, during the analysis, we tried our best to avoid analyzing these cations from the Xishuangbanna site. We have provided an explanation in Section 2.2.2 (Page4, Line106) and made corresponding revisions to the analysis in Section 3.3.1 (Page15, Line 268-280). Please refer to the revised manuscript for detailed modifications.

References:

Cao, F., Zhang, S.-C., Kawamura, K., and Zhang, Y.-L.: Inorganic markers, carbonaceous components and stable carbon isotope from biomass burning aerosols in Northeast China, Science of The Total Environment, 572, 1244-1251, https://doi.org/https://doi.org/10.1016/j.scitotenv.2015.09.099, 2016.

Meng, J., Wang, G., Li, J., Cheng, C., Ren, Y., Huang, Y., Cheng, Y., Cao, J., and Zhang, T.: Seasonal characteristics of oxalic acid and related SOA in the free troposphere of Mt. Hua, central China: Implications for sources and formation mechanisms, Science of The Total Environment, 493, 1088-1097, https://doi.org/10.1016/j.scitotenv.2014.04.086, 2014.

Trajectory Analysis: The study employs backward trajectory analysis at a fixed altitude of 500 meters to infer the potential sources of air masses. However, this approach may not accurately represent the transport pathways of surface-level aerosols, especially considering the diurnal variation of the planetary boundary layer (PBL). During nighttime, the PBL can be shallow, and air masses at 500 meters may reside in the residual layer, not interacting with surface emissions. Therefore, trajectory analyses should consider the dynamic nature of the PBL and possibly include multiple altitudes to capture a more representative range of transport pathways.

Response: We agree with your insights. Through literature review, we found that the daytime PBL height in the study area during summer can reach 1000-1200 m, while the nocturnal stable boundary layer may shrink to 200 – 400 m (Wu et al., 2024). Based on this, we have recalculated 72-hour backward trajectories for three characteristic heights (300 m, 500 m, and 1000 m) during typical sampling days to more comprehensively characterize aerosol sources. We corrected the descriptions in Section 3.1 (Page 7, Line 143). In addition, we also removed the air mass trajectory in Figure 1 (Page 3) and placed the new air mass trajectory in Figure 2 (Page 7) in the revised MS.

Reference:

Wu Wenlu, Chen Haisha, Guo Jianping, Xu Zhiqi and Zhang Xiaoyan: Regionalization of the Boundary-Layer Height and its Dominant Influence Factors in Summer over China [J]. Chinese Journal of Atmospheric Sciences (in Chinese), 48, 1201-1216, https://doi.org/10.3878/j.issn.1006-9895.2212.22183, 2024.

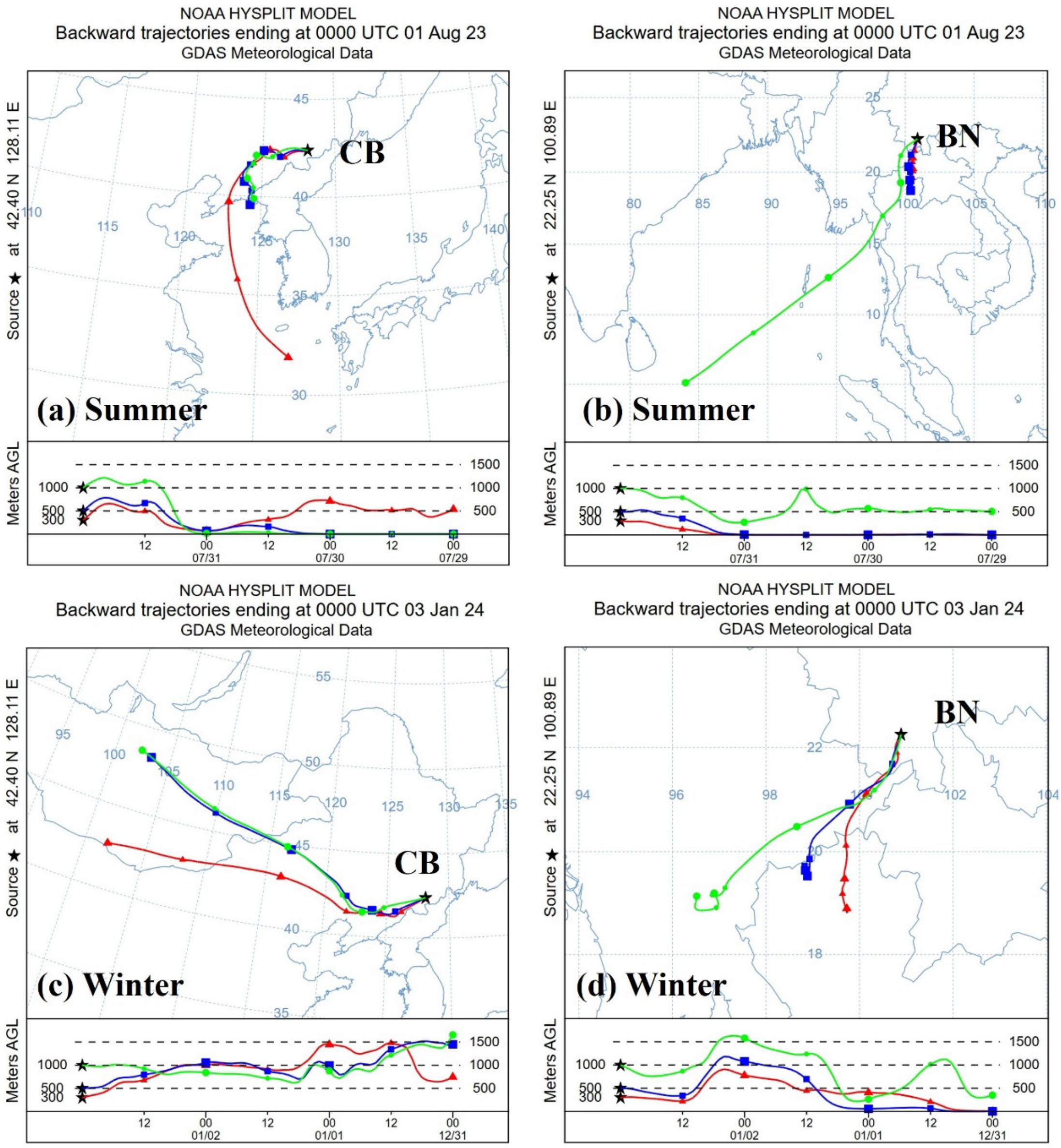

Figure 3: Clustered 72-hour backward airmass trajectories plots (above the ground level: 300m, 500m, and 1000m) at Mt. Changbai and Xishuangbanna, China during 2023-24.

2.2. Data Presentation and Interpretation

The results indicate seasonal and diurnal variations in $PM_{2.5}$ composition, with higher concentrations of carbonaceous and nitrogenous components in winter. The dominance of SO_4^{2-}, NO_3^-, and NH_4^+ at CB, and SO_4^{2-}, NH_4^+, and Na^+ at BN, is reported. The $\delta^{13}C_{TC}$ values suggest contributions from biomass burning and fossil fuel combustion.

While the data presentation is generally clear, there are areas where further clarification is needed:

Ion Balance: The study does not discuss the ion balance between measured cations and anions. An imbalance could indicate missing species or analytical errors. Given the use of quartz filters, which can introduce artifacts, a discussion on ion balance would strengthen the reliability of the WSII data.

Response: For the samples from the Xishuangbanna site, the inherently high background of the quartz filters did interfere with Na^+, Ca^{2+}, and Mg^{2+} in the samples, which was also the reason for the ion imbalance at Xishuangbanna. Therefore, during the analysis, we tried our best to avoid analyzing these cations from the Xishuangbanna site. We added an explanation in Section 2.2.2 in the revised MS (Page4, Line 106).

Source Apportionment: The authors rely on $\delta^{13}C_{TC}$ values and the relative abundance of chemical species to infer sources. However, more robust source apportionment techniques, such as Positive Matrix Factorization (PMF) or Chemical Mass Balance (CMB) modeling, could provide quantitative estimates of source contributions and reduce uncertainty.

Response: Thank you for your suggestions. We conducted an analysis in combination with PMF modeling. After preliminary evaluation, the current data exhibits the following issues, which may not meet the requirements for the PMF model.

We attempted to run the analysis on samples from Mt. Changbai with relatively higher concentrations than Xishuangbanna, but found that the dataset contains missing values, and some key species (such as Cl^-, EC, NO_3^-, and K^+) have concentrations below the detection limit. There are a total of 100 pieces of $\delta^{13}C_{TC}$ data, some of which were not measured due to their too low concentrations. Therefore, there is also the problem of many missing values. These results in an incomplete data matrix, which may compromise the stability of the model.

Additionally, the low-concentration data has a poor signal-to-noise ratio (SNR), and the high measurement uncertainty makes the PMF analysis susceptible to random errors.

Finally, the interpretability of the model's factors is weak. After multiple test runs, we found that the resolved factor profiles poorly match the characteristics of potential pollution sources, making it difficult to identify their origins based on environmental significance or literature comparisons (e.g., K^+ and Cl^-, conventional biomarkers for biomass burning, exhibited no significant common factor).

2.3. Novelty and Contribution

The study contributes to the limited data on $PM_{2.5}$ composition in forested regions of China, particularly regarding $\delta^{13}C_{TC}$ measurements. However, the findings largely corroborate existing knowledge about the sources and seasonal variations of $PM_{2.5}$. The use of $\delta^{13}C_{TC}$ as a tracer is valuable, but its application here does not yield novel insights into source apportionment beyond what is already known.

Specific Comments

Line 117: The authors state that the contribution of $CaCO_3$ to aerosols is negligible, yet later identify soil as a significant source of $PM_{2.5}$. This appears contradictory, as soil dust typically contains substantial amounts of calcium carbonate. Clarification is needed to reconcile these statements.

Response: We have corrected this statement in combination with the problem of ion measurement (Page15, 268-279).

Table 1: The table1 appears to have two different legends, which may cause confusion. Ensuring consistency in table legends is essential for clarity.

Response: Thank you for pointing out this important issue. Following the Referee #2 suggestion. We have moved Table 1 to the Supplementary Material (Table S1).

1. Conclusion

The manuscript provides valuable data on $PM_{2.5}$ composition in two forested regions of China, with a focus on seasonal and diurnal variations. However, methodological concerns, particularly regarding filter selection for WSII analysis and the trajectory analysis approach, need to be addressed. The study's findings align with existing literature, and while the inclusion of $\delta^{13}C_{TC}$ measurements is commendable, it does not substantially advance the understanding of $PM_{2.5}$ sources.

Recommendation: Major revisions are necessary to address the methodological issues and enhance the robustness of the source apportionment analysis. Incorporating more suitable filter materials, refining trajectory analyses, and employing quantitative source apportionment models would significantly strengthen the study.

Re： Thank you again for your detailed and constructive review. We have revised the MS as recommended. We sincerely hope that these revisions are satisfactory and get your approval for final publication.