***RC2**: ['Comment on egusphere-2025-1335'], Anonymous Referee #2, 18 Jun 2025*

Authors' Response to Referee #2 Comments

This article presents a measurement report of the concentration of main inorganic ions, of EC/ OC, and carbon isotope in fine particulate matter ($PM_{2.5}$) collected at two sites in China. The introduction section is clear and I sincerely appreciate the references up to date. Nevertheless, references are lacking in the other sections to assess the methodology and the discussion of the results. The dataset is interesting and deserves publication. Nevertheless, I have some major concerns regarding the methodology, the results and the discussion.

We thank the referee very much for his/her critical reading of the manuscript, appreciation of our work and the comments/suggestions, which helped to improve the quality of the manuscript further. The MS has been revised accordingly, and the point-by-point responses to each of the comments and suggestions are provided below.

- The two sites presented should be better described. Many research stations are available in China. Why is it interesting to compare these two in particular?

  ***Response:** For question 1,* we have added detailed description for the two sites. Changbai Mountain (temperate monsoon climate, coniferous - deciduous mixed forest) and Xishuangbanna (tropical monsoon climate, tropical rainforest) represent typical forest sites in the temperate and tropical zones of China respectively. The former is dominated by the northwest monsoon in winter, with significant aerosol transport characteristics; the latter has a highly natural environmental background value. Due to the differences in vegetation and climate between the two sites, their regulatory mechanisms for aerosol emission, deposition and composition are different. Please see Lines 60-68 in Section 2.1 in the revised MS.

  For question 2, Comparing the chemical and stable carbon isotopic compositions characteristics of $PM_{2.5}$ in these two sites is conducive to a better understanding of the influence mechanisms of different latitude forest ecosystems on atmospheric composition, and also provides a certain reference for the verification of different atmospheric models.

- Lines 74-78: please add a reference for the methodology used for EC/OC measurement

  Response: We have added two references (i.e., Wan et al. 2015; 2017) for the methodology used for EC/OC measurement in the revised MS (see Line 83).

- Lines 92-95: the description of the analytical methodology is not sufficient.

  Response: We have supplemented and improved the detailed description of the analytical methodology in the revised MS (see Line 98-110).

- Lines 98-99: repetition of the description of the filtration step.

  Response: We removed part of the description of the filtration step in the revised MS to avoid the repetition in the revised MS (see Line 113).

- Lines 101-102: the analytical methodology for the detection of NO_2^- is not clear: NO_2^- reacts with the acid to form "new nitrogen compounds", which are detected at 540 nm… which compounds?

  Response: The NO_2^- reacts with aminobenzene sulfonic acid to produce high molecular weight nitrogen compounds (azo dye). Using an UV spectrophotometer to measure the total N's absorbance at 540 nm. We have added this point in the revised MS (see Lines 115-117).

- Line 103: "aggregating" means "sum"?

  Response: Yes, we have replaced "aggregating" with "summing" for more precise expression in the revised MS (see Line 118).

- Line 117: The authors assume that carbonates are negligible since Ca^{2+} concentrations are low. But carbonates can be also as Na^+ or Mg^{2+} salts. A measurement of inorganic carbon would be more appropriate.

  Response: We agree with the reviewer's opinion that the existence of Na_2CO_3 and $MgCO_3$ is likely and the measurement of inorganic carbon would be more appropriate, if the dust contribution is highly significant. In fact, the concentrations of both Ca^{2+} and Mg^{2+} were found to be extremely low at both the sites (see Table S1 in the revised MS). Furthermore, we found significant positive correlations between Na^+ and SO_4^{2-} and Cl^- at both the sites (CB: $r = 0.43$ with SO_4^{2-}, 0.57 with Cl^-; BN: $r = 0.25$ with SO_4^{2-}, 0.62 with Cl^-). Marine-derived Na^+ primarily exists as NaCl, Na_2SO_4, and $NaNO_3$. While coal combustion and biomass burning contribute to Na^+ emissions, typically in the forms of NaCl, Na_2SO_4, and $NaNO_3$. This is particularly evident at CB in winter, where increased coal burning elevates Na^+ concentrations. Therefore, we assume that the carbonate level in these forest samples is negligible and strongly believe that this assumption would not affect the obtained results and the drawn conclusions.

- Figure 2: why one point par day instead of a continuous temporal variation?

  Response: We collected meteorological data and calculated the average values for day and night, which were consistent with the collection cycle of each of our samples. This was for the convenience of analysis.

- Paragraph 3 (results and discussion): The two sites are at low altitude, respectively CB 740 m asl and BN 872 m asl. I assume that they are in the boundary layer in summer, but CB could be in the free troposphere in winter. A discussion should be added on the environmental conditions encountered at these sites.

Response: Thank you for your suggestion. We found that the daytime PBL height in CB and BN 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). 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.

- Page 7, Table 1: Maybe illustrate the table with Figure(s) and report the table in the supplementary material file.

Response: Following the reviewer’s suggestion, we have moved Table 1 to the Supplementary Material (Table S1). The key data from Table 1 have been presented with Figure(s) in the revised MS.

- Lines 149-150: Could you please give a reference of the equations used? Equivalent concentration is obtained by dividing the molar concentration by the charge and not by the ion mass. I have never seen this formula and I assume that the following discussion needs to be revised.

Response: We have added the reference: Tian et al., 2018, in the revised MS (see Line 161).

“Equivalent Concentration ($\mu eq\ m^{-3}$) = $\frac{\text{Ion mass concentration } (\mu g\ m-3)}{\text{Molar mass } (g\ mol-1)*\text{Charge number } (z)}$”

These formulas are used to calculate the equivalent concentrations of cations and anions in aerosols, with the aim of evaluating the acid-base balance of the aerosol system. The method for calculating equivalent concentration involves dividing the molar concentration of each ion by its charge number (i.e., valence), thereby unifying ions with different charges onto a per-unit-charge basis for comparison. We have given the reference and revised the discussion. See Lines 160-140 in the revised MS.

Reference:

Tian, S., Pan, Y., and Wang, Y.: Ion balance and acidity of size-segregated particles during haze episodes in urban Beijing, Atmospheric Research, 201, 159-167, 2018.

- Lines 163: It would be interesting to treat separately anions and cations.

  Response: Following the reviewer's suggestion, we have described the abundances of anions and cations separately in the revised MS (see Lines 173-177).

- Line 166: the authors compare with urban sites… What about the comparison with rural sites?

  Response: We added a comparison with rural sites in the revised MS (see Lines 181-183).

- Line 172-179: The authors explain in deep that DMS emitted from phytoplankton can explain the high SO_4^{2-} concentration. If there such a huge marine influence, why Cl^- is so low? Please, reconsider the explanation.

  Response: We agree with the reviewer that the contribution from oceanic emissions was insignificant. In fact, such a low concentration of Cl^- is similar to that reported previously by Li et al. (2010) at CB (avg. 0.02 μg m^{-3}). Therefore, we modified the interpretation inferring that SO_4^{2-} mainly come from anthropogenic sources in the revised MS (see Lines 194-197).

  Reference:

  Li, L., Wang, W., Feng, J., Zhang, D., Li, H., Gu, Z., Wang, B., Sheng, G., and Fu, J.: Composition, source, mass closure of $PM_{2.5}$ aerosols for four forests in eastern China, Journal of environmental sciences (China), 22, 405-412, https://doi.org/10.1016/S1001-0742(09)60122-4, 2010.

- Lines 172-179: There is a long discussion on SO_4^{2-}, but nothing on NO_3^-, which is 73 times higher in winter than in summer at CB. This need an explanation.

  Response: We have added explanation in the revised MS (seen Lines 200-207). This could be linked to the increased utilization of coal for domestic heating in winter, which leads to enhanced emissions of gaseous precursors.

- Lines 184-185 and following: I wonder if the two observatories are equipped with NO_x, SO_2 and O_3 analysers. In that case, the discussion would be better supported by experimental measurements of these compounds during aerosol sampling.

  Response: Unfortunately both the observatories are not equipped with NO_x, SO_2 and O_3 analyzers, and hence there is no such possibility to provide substantial evidence of gaseous species loading to support the drawn conclusions.

- Figure 4: A concentration of NO3- equal to zero during all the summer for both sites is surprising. I wonder if something went wrong with the analysis. Have you compared this result to those obtained for sites with similar environmental conditions? Pathak et al. (10.5194/acp-9-1711-2009) found, for example, that nitrate is underestimates when the particles collected are deliquescent.

Response: The high temperatures in summer might have accelerated the photolytic decomposition of gaseous NO_2, reducing its conversion to NO_3^-. The CB and BN experience high relative humidity conditions (Fig.2). In particular, BN experiences year-round hot and humid weather, which facilitates efficient removal of NO_3^- aerosols through wet deposition processes. The lower levels of NO_3^- are consistent with those reported by Tanner et al. (2004) for rural (avg. 0.04 μg m^{-3}) and background sites (avg. 0.01 μg m^{-3}) in the Tennessee Valley, USA, particularly during summer. We included this comparison in the revised MS (see Lines 192-194).

Reference:

Tanner, R. L., Parkhurst, W. J., Valente, M. L., and David Phillips, W.: Regional composition of $PM_{2.5}$ aerosols measured at urban, rural and "background" sites in the Tennessee valley, Atmospheric Environment, 38, 3143-3153, https://doi.org/https://doi.org/10.1016/j.atmosenv.2004.03.023, 2004.

- Line 251: A correlation with $R^2 = 0.51$ is not so strong

  Response: Following the Referee #1 suggestion and considering the influence of the quartz membrane on certain specific ions (Mg^{2+}, and Ca^{2+}), we removed this part of discussion in the revised MS.

- Line 258: please explain how you calculated nss-SO_4^{2-} and nss-K^+ or report a reference.

  Response: We have reported a reference in the revised MS (see Line 105).

- Lines 266-267: measurements of SO_2, NO_x and NH_3 would greatly strengthen the discussion.

  Response: We agree with the reviewer's opinion. However, unfortunately, we did not collect real-time measurements of gaseous precursors (SO_2, NO_x, NH_3) synchronously with aerosol sampling.

- Line 271: I have some concern about the concentration of NO_3^- around zero during summer at both sites, thus I'm not confident in the results and discussion about nitrate/sulphate ratios.

  Response: As detailed in response to the comment earlier, the high temperatures in summer might have accelerated the photolytic decomposition of gaseous NO_2, reducing its conversion to NO_3^-. Additionally, the higher precipitation frequency in summer could lead to the washout of NO_3^- from aerosols, further lowering its concentration. Nitrate, particularly ammonium nitrate (NH_4NO_3), exhibits strong volatility, and elevated temperatures and humidity during summer may enhance its volatilization, resulting in a decrease in particulate NO_3^- levels. Furthermore, the two forested sites are similar to background sites with minimal influence from industrial activities and traffic emissions.

This is consistent with the concentrations reported by Tanner et al. (2004) for rural (avg. 0.04 µg m^{-3}) and background sites (avg. 0.01 µg m^{-3}) in the Tennessee Valley, USA, particularly during summer.

In the discussion, we have limited the seasonality of the conclusions, and data from summer (due to extremely low NO_3^- concentrations) were not included in the key conclusions.

Reference:

Tanner, R. L., Parkhurst, W. J., Valente, M. L., and David Phillips, W.: Regional composition of $PM_{2.5}$ aerosols measured at urban, rural and "background" sites in the Tennessee valley, Atmospheric Environment, 38, 3143-3153, https://doi.org/https://doi.org/10.1016/j.atmosenv.2004.03.023, 2004.

- Line 284: The air masses arriving at CB and BN during summer show a strong marine influence. How do you explain such a low concentration of Cl^- (not discussed anywhere else in the article)?

  Response: Though the air mass trajectories are showing the transport of oceanic air parcels, the obtained data did not show any such impact at significant level. Since our interpretations mainly depend on the data rather than the air mass trajectories, we did not focus much to discuss it in depth. However, the lower concentration of particulate Cl^- in summer may be attributed to the formation of gaseous HCl, which is volatile under high-temperature and high-humidity conditions and could escape from aerosols. The result is comparable to previously reported levels at Mt. Changbai (avg. 0.02 µg m^{-3}) and Mt. Dinghu (avg. 0.02 µg m^{-3}) (Li et al., 2010). We have added this point in the revised MS (see Lines 270-273).

  Reference:

  Li, L., Wang, W., Feng, J., Zhang, D., Li, H., Gu, Z., Wang, B., Sheng, G., and Fu, J.: Composition, source, mass closure of $PM_{2.5}$ aerosols for four forests in eastern China, Journal of environmental sciences (China), 22, 405-412, https://doi.org/10.1016/S1001-0742(09)60122-4, 2010.

- Lines 308-311: references are missing about the studies cited.

  Response: We have added 3 references: Chow et al. 2007; Schauer eta l., 1999; Chen et al., 2005, in the revised MS (see Lines 320&322).

- General remark: The title promises chemical and stable carbon isotopic compositions, but it is mainly focused on physicochemical characteristic, which is not such a novelty. Only short paragraphs are devoted to stable isotopes, which could really improve the novelty of the work.

  Response: We have improved the discussion about stable isotope ratios in the revised MS (see Lines 366-374&384-389). The main objective of this study is to analyze the physicochemical characteristics of aerosols (e.g., source apportionment, seasonal variations), which serves as the foundation for understanding atmospheric aerosol behavior. Stable carbon isotope (δ^{13}C) analysis is employed as an auxiliary tool to validate the contribution of certain sources.

Thank you again for your detailed and constructive review. We have revised the MS according to all your comments, which improved the quality of the MS. We sincerely hope that these revisions are satisfactory to you for your approval for final publication.