Response to the Referee's comments on "Influence of anthropogenic pollution on the molecular composition of organic aerosols over a forest site in the Qinling Mountains region of central China"

by Xin Zhang and Yuemei Han

We greatly thank editor for the message and the valuable and insightful comments from referee on our manuscript (ID: egusphere-2025-519-R2). We have carefully revised the manuscript by considering all the concerns raised by the referee. Please find below our detailed point-to-point responses to each of these comments.

(*The blue bold, green, and black fonts represent the Referee's comments, the related text in the manuscript, and the authors' responses, respectively.*)

This study describes a detailed molecular characterization of $PM_{2.5}$ sampled from a forest site in the Qinling Mountains, China. Ambient filter samples collected during summer and winter were analyzed by ultrahigh-performance liquid chromatography and high-resolution Orbitrap mass spectrometry followed by a non-target analysis with a focus on the seasonal variability of the organic aerosol composition. Furthermore, air quality measurements, meteorological data, and back-trajectory analyses were integrated to draw detailed conclusions on aerosol origin and chemical transformation pathways. The authors conclude that chemical composition variation indicates a stronger influence from biogenic precursors in summer, contrasting with a more diverse, largely anthropogenic influenced composition in winter.

Combining non-target screening with filter samples from different seasons to investigate differences in organic aerosol composition is a widely used approach leading to already known basic results regarding anthropogenic–biogenic interactions. Orbitrap MS data provides exact mass of measured compounds from which molecular formulae can be derived using a software-based approach. To further confirm the identity of tracer compounds unfortunately only a literature review was carried out while a combination with fragmentation spectra (MS^2) and retention time comparison with well-known biogenic and anthropogenic standards would

have provided a significantly greater certainty regarding compound identification. Additionally, using electrospray ionization introduces ionization efficiency variations for compounds of different classes and chemical functionalities preventing from direct correlation of compound abundance by comparing measured signal intensities, especially if both polarity modes (ESI- and ESI+) are used.

Although the study has certain methodological weaknesses and does not provide any new fundamental scientific insights, it nevertheless provides a certain overview of the chemical composition of $PM_{2.5}$ aerosols at Qinling Mountain Station, which contributes to the general understanding of this region and encourages further studies. The manuscript is well written and structured with interesting illustrations that support the results. In general, this study is publishable and fits the thematic focus of ACP and could either be published as Research article or also maybe as Measurement report after addressing some minor comments:

Response: We greatly appreciate the referee for providing insightful and thoughtful comments on our manuscript. We have seriously addressed all the concerns and made relevant corrections in the revised manuscript according to these comments. Our detailed responses are described as follows.

Comments

1. L66: Can you define and describe this specific area (anthropogenic–biogenic intersection zones) more precisely? Why is this zone of special interest regarding aerosol chemical composition?

Related sentence: "However, the interactions of anthropogenic pollution with biogenic organic aerosols and the potential impacts are still rarely reported at the lower altitudes of this region to date, especially at the anthropogenic–biogenic intersection zones."

Response: We thank the referee for raising this question. As shown in the map of Figure 1, the sampling site in the present study was situated in the intersection area of Qinling Mountains region and Guanzhong basin, which were abundance of biogenic emissions and anthropogenic pollutants, respectively. Therefore, we defined this area to be the anthropogenic–biogenic

intersection zones. This zone is of special interest regarding aerosol chemical composition because it can reflect the anthropogenic perturbations on air quality, atmospheric chemistry, and associated climate impacts in the Qinling Mountains region. Therefore, we have added the following two statements in the revised manuscript, as follows:

"**Since anthropogenic pollutants and biogenic emissions were prevalent in this area, it is thus considered as an anthropogenic–biogenic intersection zone.**" (Lines 88–89)

"**Understand these interactions will be valuable to elucidate the anthropogenic perturbations on air quality, atmospheric chemistry, and associated climate impacts in the Qinling Mountains region.** (Lines 66–68)

2. Figure 1. (b, c): Can you include the origin of the mass concentrations in the caption. On which type of measurements is this data based?

Response: Yes, the origin of the organic mass concentrations have been included into the caption of Figure 1 in the revised manuscript, as follows:

"Figure 1. (a) A map showing the sampling site at northern foothill of the Qinling Mountains region in central China. (b, c) Back trajectories of air masses arrived at 500 m above the ground level over the sampling site and their cluster analysis (represented by the thick solid lines with percentages and numbers) during the summer and winter periods. The bottom left panels **in (b, c)** present the **mean** mass concentrations of organic matter **that were measured using the carbon analyzer for aerosol samples collected on the days with** the corresponding air mass directions." (Lines 98–102)

3. L101: It is rather unusual to provide extraction solvent related information in a weight mass unit. Could you translate here mass into volume?

Related sentence: "A quarter of each sample in 12.56 cm^2 area was ultrasonically extracted using 9 g acetonitrile and water mixture in 9:1 volume for 30 min (3 g for 10 min, repeated three times)."

Response: Since the extraction solvent for each sample was weighted using an electronic

microbalance in our experimental procedures, we believe that reporting the weight mass unit would be more accurate to reflect the actual situation in this study. It is possible to transfer the mass into volume unit by assuming a density for the solvent mixture of acetonitrile and water, however, this would result in more uncertainties. Therefore, we decided to keep using the weight mass unit here eventually.

4. L102: Ultrasonication is no optimal method for filter extraction as it is known that the harsh conditions in the liquid phase due to free radical formation can lead to substantial changes in the chemical composition. Although cooling might reduce the impact, it will also reduce the extraction efficiency of the solvent mixture and therefore influence the extracted compound composition. Did you compare filter extraction by ultrasonication and orbital shaking for your specific samples?

Literature: Riesz P, Berdahl D, Christman CL. Free radical generation by ultrasound in aqueous and nonaqueous solutions. Environ Health Perspect. 1985 Dec; 64:233-52. doi: 10.1289/ehp.8564233

Miljevic, B., Hedayat, F., Stevanovic, S., Fairfull-Smith, K. E., Bottle, S. E., & Ristovski, Z. D. (2014). To Sonicate or Not to Sonicate PM Filters: Reactive Oxygen Species Generation Upon Ultrasonic Irradiation. Aerosol Science and Technology, 48(12), 1276–1284. https://doi.org/10.1080/02786826.2014.981330

Related sentence: "A quarter of each sample in 12.56 cm^2 area was ultrasonically extracted using 9 g acetonitrile and water mixture in 9:1 volume for 30 min (3 g for 10 min, repeated three times). The extraction system was placed in a water–ice bath to eliminate potential evaporation or chemical reactions of aerosol components."

Response: In the present study, we did not directly compare the filter extraction between ultrasonication and orbital shaking for specific samples. However, this topic has been investigated previously in the following literature. According to Hettiyadura et al. (2015), for higher percentage of organic solvents (that is, acetonitrile and ultra-pure water in 95 : 5 by volume in their case), there were no degradation effects and only minor chemical differences observed between the ultrasonication and rotary shaking procedures for sample treatment. In fact, the ultrasonication was determined to be a better method due to its higher precision compared

with rotary shaking (Hettiyadura et al., 2015). Similarly, we used the solvent of acetonitrile and pure water mixture in 9 : 1 volume in our present study, thereby the chemical effects should be at least not significant.

Moreover, we performed the ultrasonic extraction of filter samples in a water–ice bath to reduce the temperature, the extraction procedure lasted 10 min for each time, and the same procedure was repeated three times for each sample. Therefore, we believe that the aerosol chemical composition and extraction efficiency should be insignificantly affected by the ultrasonication procedure in this study. We will also consider to design a set of experiments to thoroughly illustrate this issue in our future study.

Reference:

Hettiyadura, A. P. S., Stone, E. A., Kundu, S., Baker, Z., Geddes, E., Richards, K., and Humphry, T.: Determination of atmospheric organosulfates using HILIC chromatography with MS detection, Atmos. Meas. Tech., 8, 2347–2358, 2015.

5. L118: Why not include phosphorus as element in the data processing? Anthropogenic compounds such as flame retardants often include phosphate groups (e.g. Tricresyl Phosphate). Chlorine may also be worth including due to its use in pesticides, provided this is relevant to the sampling region. Could you rerun the MZmine data processing including the mentioned elements and give some feedback if you can see relevant compounds, especially when the wind is coming from the city region.

Related sentence: "Briefly, the elemental composition of organic molecular species was constrained to $C_{1–40}H_{1–80}O_{0–50}N_{0–4}S_{0–2}$ in the two ionization modes, using a mass tolerance of 2 ppm."

Response: We included the C, H, O, N, and S elements in the data processing herein, because they are commonly reported components in aerosol particles. As suggested by the referee, we have rerun the MZmine data processing by adding the phosphorus (P, 0–2 atoms) and chlorine (Cl, 0–2 atoms) elements for molecular formula assignments. Indeed, the result is consistent well with our assumption that the organic species containing P and Cl elements were generally minor components, as shown in the figure below. Specifically, the summed number and peak area intensity of organic species containing P and Cl merely accounted for less than 6% and 2% of

those in total, respectively. Therefore, the main conclusions drawn from this study were not affected by the presence of those minor P- and Cl-containing species. Nevertheless, we agree that the P- and Cl-containing species would be an important topic warranting further investigation especially in some atmospheric environments such as those dominated by industrial emission sources.

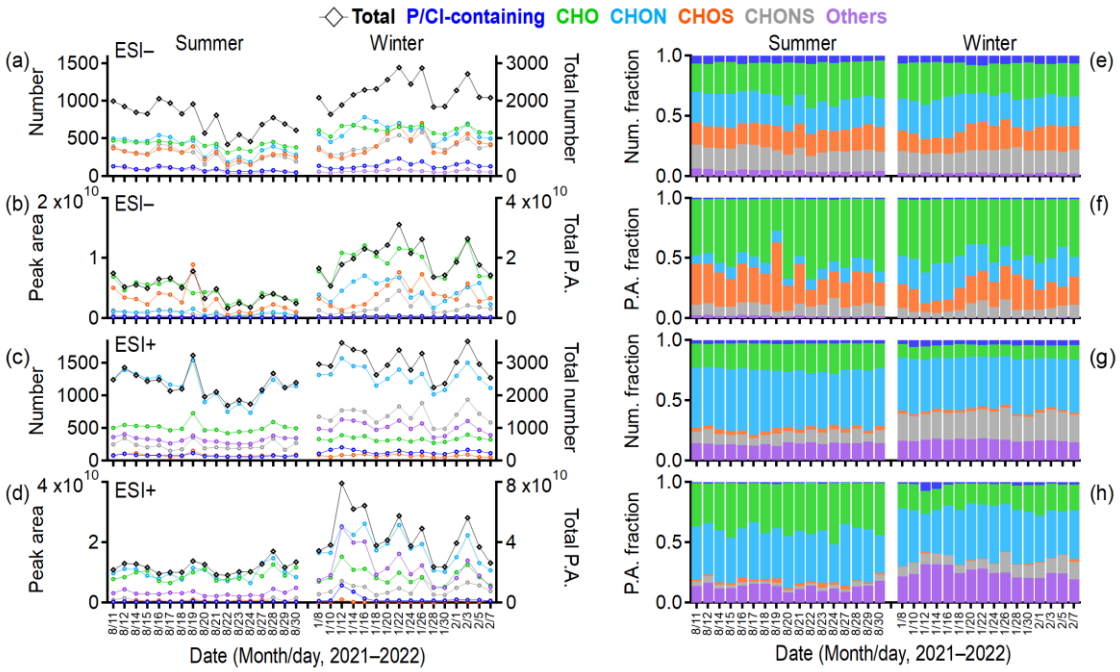

Figure. (a–d) Species number and peak area intensity of organic molecular composition, along with their corresponding number and peak area fractions (e–h), obtained from the UHPLC–HRMS analysis in negative and positive ESI modes over the study periods. Here the elements of C, H, O, N, S, P, and Cl were included for the organic molecular formula assignments.

6. L129: This method for determining the PM mass concentration is highly uncertain. If possible mass concentrations should be based on measurement data like measured particle number size distributions (PNSD).

Related sentence: "Each filter sample was weighted using an electronic microbalance before and after sampling, the difference of which dividing by the sampled air volume was used for calculating $PM_{2.5}$ mass concentration."

Response: As our present study was primarily based on the aerosol filter sampling and chemical analysis, the mass concentrations of $PM_{2.5}$ on the filter samples were therefore obtained using the electronic microbalance weighting method. This is also the traditional and widely used method for PM mass analysis for aerosol filter samples. Given that we performed the weighing procedures under the temperature and relative humidity precisely controlled conditions to avoid potential biases, the obtained PM mass concentrations should be highly reliable. The online measurement of particle number–size distributions was not available in this study, which will be a good direction for our future studies. Therefore, we have added the following statement to address this point in the revised manuscript:

"Each filter sample was weighted **before and after sampling using an electronic microbalance under well-controlled temperature (20 ± 2 °C) and relative humidity (30 ± 2%) conditions**, the difference of which dividing by the sampled air volume was used for calculating $PM_{2.5}$ mass concentration." (Lines 134–136)

7. L257: You should substantiate this statement by mentioning known biogenic emission tracers as MBTCA and pinic acid in the text if found in the data.

Related sentence: "Since air masses from the surrounding Qinling Mountains area in the south were more prevalent at the sampling site in summer season (Fig. 1b), biogenic emissions from forest vegetation (especially those with larger molecules such as monoterpenes and sesquiterpenes) and their oxidation products might be key factors resulting in the higher organic molecular weight."

Response: These organic tracer compounds were indeed found from the sample analysis in this study, as listed in Table S1 and S3. Therefore, we have added this point in the revised manuscript, as follows:

"Since air masses from the surrounding Qinling Mountains area in the south were more prevalent at the sampling site in summer season (Fig. 1b), biogenic emissions from forest vegetation (especially those with larger molecules such as monoterpenes and sesquiterpenes) and their oxidation products might be key factors resulting in the higher organic molecular weight, **as evidenced by the presence of a number of biogenic tracer species such as MBTCA**

($C_8H_{12}O_6$) and pinic acid ($C_9H_{14}O_4$)." (Lines 262–266)

8. Overall, to address the shortcomings of the compound identification (no measured standards and no analyzed fragmentation patterns) you should include the compound identification level system of Schymanski et. al. 2014 stating the level of identification confidence in the manuscript.

Literature: Identifying Small Molecules via High Resolution Mass Spectrometry: Communicating Confidence Emma L. Schymanski, Junho Jeon, Rebekka Gulde, Kathrin Fenner, Matthias Ruff, Heinz P. Singer, and Juliane Hollender; Environmental Science & Technology 2014 48 (4), 2097-2098; DOI:10.1021/es5002105

Response: We thank referee for this very good suggestion. The level of identification confidence for our HRMS dataset and results has been addressed in the revised manuscript, as follows:

"**Since the measurements of fragmentation patterns and reference standards were not available herein, the identification confidence of the presented results belongs to the unequivocal molecular formula level, according to Schymanski et al. (2014).**" (Lines 130–132)

"**Schymanski, E. L., Jeon, J., Gulde, R., Fenner, K., Ruff, M., Singer, H. P., and Hollender, J.: Identifying small molecules via high resolution mass spectrometry: Communicating confidence, Environ. Sci. Technol., 48, 2097–2098, https://doi.org/10.1021/es5002105, 2014.**" (Lines 754–756)

9. L308: You should discuss this more in detail as all three groups CHOS, CHON and CHONS are influenced by anthropogenic emissions. CHOS and CHON don't show any difference between summer and winter - why does the CHONS subgroup (especially in ESI-)?

Related sentence: "In contrast, prominent increases were observed for the number fractions of CHO and CHON species in ESI+ mode and CHONS species in both modes at approximately $C_{6–11}$ range during the winter period, probably resulted mainly from the enhanced influence of anthropogenic pollution from the surrounding areas, compared with those of the summer period."

Response: As suggested by the referee, we have added more discussions regarding the different variation patterns of individual subgroups in the revised manuscript, as follows:

"**Nevertheless, the degrees of influence could vary across individual subgroups, as indicated by the different variation patterns in their carbon atoms number distribution. The larger variations of CHONS species in both modes might result from the stronger influence of anthropogenic pollution compared with those of other species.**" (Lines 316–319).

10. L496: Delete during.

Related sentence: "The molecular composition of organic aerosols in atmospheric $PM_{2.5}$ was characterized using UHPLC–HRMS at a forest site in the Qinling Mountains region of central China during contrasting summer and winter seasons of 2021/2022."

Response: Since the "contrasting" here is an adjective, it would be not quite reasonable to only delete the "during" in this sentence. Therefore, we have revised the original sentence to make it clearer, as follows:

"The molecular composition of organic aerosols in atmospheric $PM_{2.5}$ was characterized using UHPLC–HRMS at a forest site in the Qinling Mountains region of central China during **the two contrasting seasons** (summer and winter) of 2021/2022." (Lines 505–506)