

Response to the comments of Referee #1 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 appreciate the valuable comments and suggestions from Referee #1 on our manuscript (ID: egusphere-2025-519). We have carefully revised the manuscript by taking into account of all the concerns raised by the referee. Please find our detailed point-to-point responses to these comments below. A copy of the manuscript and supplement with all the changes and other minor corrections tracked is also attached for reference.

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

In this study, Zhang et al. report an extensive molecular characterisation of organic aerosol in particulate matter (PM_{2.5}) from a forest site in the Qinling mountains, China, and investigated the influence of anthropogenic pollution on the aerosol composition. For this they sampled 33 filter samples in summer and wintertime, used liquid extraction and measured the extracts with an ultrahigh-performance liquid chromatography coupled to high-resolution Orbitrap mass spectrometry. With a non-target analysis known and unknown compounds were detected and identified. The combination of molecular fingerprints, air quality measurements, meteorological data as well as back-trajectories enables detailed interpretation of origin and transformation pathways of the sampled aerosol. Tracer species confirm the interpretation of more influence from biogenic precursors in summer and a more diverse and largely anthropogenic influenced composition in winter.

The authors have combined their comprehensive results and have produced a detailed characterization of the molecular composition of organic aerosol. The manuscript has a

good structure, meaningful illustrations and is written clear and precise. The work is worth to be published in “Atmospheric Chemistry and Physics” with some minor comments.

Response: We gratefully thank Referee #1 for the insightful and positive evaluation on our manuscript. We have seriously addressed all the concerns and revised the manuscript accordingly. Our detailed responses to these comments are as follows.

Comments

1. L84: Delete “city” in “[...] 50 km southwest of the megacity city Xi’an, as shown [...]”.

Related sentence: “This site is situated in the northern foothill of the Qinling Mountains and approximately 50 km southwest of the megacity city Xi’an, as shown in Fig. 1.”

Response: Yes, it has been deleted in the revised manuscript, as follows:

“This site is situated in the northern foothill of the Qinling Mountains and approximately 50 km southwest of the megacity Xi’an, as shown in Fig. 1.” (Lines 83–84)

2. L102: Have the authors considered that ultrasonication can influence the chemical composition due to free radical production? (Miljevic et al., 2014)

Related sentence: “A quarter of each sample in 12.56 cm² 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: Yes, we definitely agree with the referee that the ultrasonication of filter samples can degrade the chemical composition due to OH radical production under certain conditions. The chemical effects of ultrasonic irradiation mainly resulted from the high local temperature and pressures within the collapsing cavitation bubbles by the energy of ultrasonic waves (Miljevic et al., 2014). However, given that we performed the ultrasonic extraction of filter samples in a water–ice bath and the procedure lasted 10 min for each time in this study, the chemical effects should be limited under the low temperatures.

Moreover, the effects of ultrasonication on aerosol chemical composition were turned out to depend largely on the extraction solvents. As demonstrated by Hettiyadura et al. (2015), for

higher percentage of organic solvents (that is, acetonitrile and ultra-pure water in 95 : 5 by volume in their study), there were no degradation effects and only minor chemical differences 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 current study, thereby the chemical effects should be at least not significant.

Taken the above two aspects together, we believe that the chemical composition should be insignificantly affected by the ultrasonication procedure in this study. We have highlighted this point in the revised manuscript, as follows:

“The extraction system was placed in a water–ice bath to **eliminate potential evaporation or chemical reactions of aerosol components.**” (Lines 103–104).

Two references cited above are listed below:

Miljevic, B., Hedayat, F., Stevanovic, S., Fairfull-Smith, K. E., Bottle, S. E., and Ristovski, Z. D.: To sonicate or not to sonicate PM filters: Reactive oxygen species generation upon ultrasonic irradiation, *Aerosol Sci. Technol.*, 48, 1276–1284, 2014.

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.

3. L142: Calculating HYSPLIT trajectories at 34.06° N, 108.34° E, 500 m height above ground level result in a height of 1885 m above sea level, since the height of the cell grid is already 1385 m. Can the authors comment on why they used 500 m height above ground level?

Related sentence: “In addition, the backward trajectories of air masses (**500 m height above ground level** and 72 h duration) arrived at the sampling site were calculated hourly across the study periods using the Hybrid Single Particle Lagrangian Integrated Trajectory model (v5.2.1) (Stein et al., 2015).”

Response: The altitude of our sampling site is around 530 m above the sea level, as described in the manuscript, “**Atmospheric PM_{2.5} was sampled at a forest site (34.06° N, 108.34° E,**

around 530 m above sea level) in the Qinling Mountains region of central China during summer and winter seasons of 2021/2022.” This is somewhat different from the height of the cell grid (that is, 1385 m) suggested by the referee, which was possibly obtained from a different method. We used the 500 m height above ground level for calculating the back trajectories of air masses, mainly considering the requirement of HYSPLIT model and the height of planetary boundary layer in our studied area. On the one hand, it is not recommended to start the model at the height too close to the ground, because the trajectory can easily hit the ground and lose accuracy, as demonstrated by the HYSPLIT Cheat Sheet (https://www.ready.noaa.gov/documents/ppts/Cheat_Sheet_2020.pdf). On the other hand, the 500 m height is mostly situated within the planetary boundary layer and close to the height of mixed layer in our studied area, according to the results reported in previous literature (e.g., Xin et al., 2024; Wang et al., 2023). This height thus could reflect the average concentrations of air pollutants in the well-mixed boundary layer, which is suitable for investigating the transport of near-surface pollution from the surrounding urban and rural areas to the studied location. Therefore, we used the 500 m above ground level to calculate the back trajectories of air masses in our current study.

Two references cited above include:

Xin, J., Peng, K., Zhu, X., Pan, X., Wang, Q., Cao, J., Wang, Z., Cao, X., Ren, X., Yang, S., Wei, Y., Zhao, D., and Ma, Y.: AI model to improve the mountain boundary layer height of ERA5, *Atmos. Res.*, 304, 2024.

Wang, Y., Xu, T., Shi, G., Yang, F., Tang, X., Zhao, X., Wan, C., and Liu, S.: Climatology of the planetary boundary layer height over China and its characteristics during periods of extremely temperature, *Atmos. Res.*, 294, 2023.

4. L205: Can the compounds also have different transmission efficiencies in the mass spectrometer? And is therefore not just an effect of different ionization efficiencies?

Related sentence: “This result can be attributed to either the large abundance of these species in this forest atmosphere or their high ionization efficiency under ESI[−] mode, despite that quantitative analyses were not available herein due to the technical limitation.”

Response: The referee raised a good point here. We agree that organic compounds with different chemical properties (e.g., molecular size, structure, and polarity) would have varied transmission efficiencies in the mass spectrometer. Therefore, both the ionization and transmission efficiencies could affect the observed peak area intensity of organic species. We have added this information in the revised manuscript, as follows:

“This result can be attributed to either the large abundance of these species in this forest atmosphere or their high **ionization and transmission efficiencies** under ESI[−] mode, despite that quantitative analyses of the highly complex composition of organic aerosols remain challenging due to the lack of authentic standards (Evans et al., 2024; Ma et al., 2022; Noziere et al., 2015).” (Lines 204–207)

5. L206: Can the authors clarify what they mean with “technical limitations”?

The lack of authentic standards (and the fact that many compounds in ambient PM are not even precisely characterized) does not allow a quantitative approach on such a highly complex composition, independent of the analytical devices used. For example, Ma et al. (2022) and Evans et al. (2024) showed that semi-quantification is possible but with great uncertainties.

Related sentence: “This result can be attributed to either the large abundance of these species in this forest atmosphere or their high ionization efficiency under ESI[−] mode, despite that quantitative analyses were not available herein due to the **technical limitation**.”

Response: As suggested by the referee, we have clarified the meaning of “technical limitations” in the revised manuscript, as follows:

“This result can be attributed to either the large abundance of these species in this forest atmosphere or their high ionization and transmission efficiencies under ESI[−] mode, despite that quantitative analyses **of the highly complex composition of organic aerosols remain challenging due to the lack of authentic standards** (Evans et al., 2024; Ma et al., 2022; Noziere et al., 2015).” (Lines 204–207)

The following two references have been also added in the revised manuscript:

“Evans, R. L., Bryant, D. J., Voliotis, A., Hu, D., Wu, H., Syafira, S. A., Oghama, O. E.,

McFiggans, G., Hamilton, J. F., and Rickard, A. R.: A Semi-Quantitative Approach to Nontarget Compositional Analysis of Complex Samples, *Anal. Chem.*, **96**, 18349–18358, <https://doi.org/10.1021/acs.analchem.4c00819>, 2024.” (Lines 582–584)

“Ma, J., Ungeheuer, F., Zheng, F., Du, W., Wang, Y., Cai, J., Zhou, Y., Yan, C., Liu, Y., Kulmala, M., Daellenbach, K. R., and Vogel, A. L.: Nontarget Screening Exhibits a Seasonal Cycle of PM_{2.5} Organic Aerosol Composition in Beijing, *Environ. Sci. Technol.*, **56**, 7017–7028, <https://doi.org/10.1021/acs.est.1c06905>, 2022.” (Lines 693–695)

6. Figure 3: The legend is not optimally visible in panel b. Since the legends applies to all panels, maybe a central positioning above would be easier to see (compare with the legend of Fig. 4).

Response: Yes, we agree. The legend of Figure 3 has been placed at the top central in the revised manuscript. Now it is clearly visible for all panels, as follows:

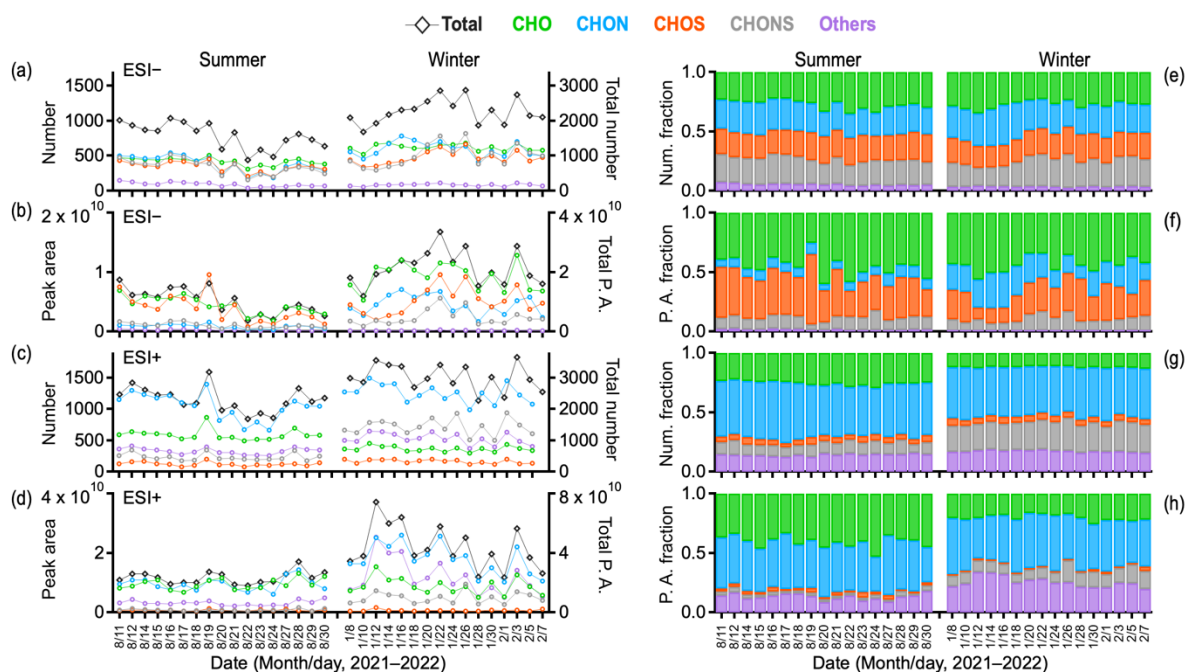


Figure 3.

7.1 Figure 5: In the caption the authors explain “[...] dashed lines inside boxes [...]”, but the lines are solid.

Related sentence: “In the box plots, the bottom and top whiskers represent the 10th and 90th percentiles, respectively, the floating boxes represent the 25th–75th percentiles, and the **dashed lines** inside boxes represent the medians.”

Response: Here we meant the “short lines” indeed. Therefore, we have made the following correction in the revised manuscript:

“In the box plots, the bottom and top whiskers represent the 10th and 90th percentiles, respectively, the floating boxes represent the 25th–75th percentiles, and the **short lines** inside boxes represent the medians.” (Lines 267–269)

7.2 Can the authors explain why they show box plots and violin plots? Since the data is not bimodal distributed, the reader can hardly get any additional information from both plots.

Response: The purpose of showing both box plots and violin plots in Figure 5 is because of the following reasons. The box plots provided the key statistic summaries of data, including the values of mean, median, maximum, minimum, and percentiles. In contrast, the violin plots presented a more intuitive depiction of the data distribution from probability density across different values. Combining these two together can provide more comprehensive illustrations of the key statistics and overall distributional profiles of the data. Therefore, we have highlighted this point in the revised manuscript, as follows:

“The **key statistics and overall distribution profiles** of these parameters were presented using the box (left) and violin plots (right), respectively.” (Lines 266–267)

8. L311: The comparison of tracer species was only made based on the sum formula? Have the authors considered fragmentation spectra to identify compounds with databases to get a higher level of confidence (e.g. aerosolomics (Thoma et al. (2022)) or the mzCloud database)?

Related sentence: “A variety of organic tracer species of anthropogenic and biogenic origins reported by previous laboratory and field studies have been found in this forest atmosphere, the details of which are summarized in Table S1–S5 of the Supplement.”

Response: Since we performed the UHPLC–HRMS analysis in the full scan mode, there were no fragmentation spectra available in this current study. Also, for most of these hundreds of organic tracer species, we could not find their fragmentation spectra in the original literature. Therefore, a parallel comparison of these species with other studies was primarily based on

the sum formula. The scan mode information of our study has been added in the revised manuscript as: “The mass range was set at m/z 50–750 in full MS scan mode, with the mass resolution of approximately 140,000 at m/z 200.” (Lines 114–115).

Nevertheless, we definitely agree with the referee that identifying compounds with the support of available fragmentation spectra from existing databases can get a higher level of confidence. To analyze organic tracer species and other specific compounds using HRMS, it would be more accurate to perform a full MS scan followed by MS/MS fragmentation scans of all ions at a wide isolation range. This should be an important topic in our future study. As a result, we have proposed this research topic in the Summary and Implications section of the revised manuscript, as follows:

“The current work focuses primarily on the non-target characterization of organic species in aerosol particles over the Qinling Mountains region based on the HRMS analysis. To further identify organic tracers and other specific substances with the aid of fragmentation spectra in existing MS databases would achieve even higher reliability. Future studies on the quantification and source apportionment of organic molecular composition will be also valuable to elucidate the complex anthropogenic–biogenic interactions and to incorporate the results into atmospheric chemistry model for improved prediction of organic aerosol burden and impacts in similar regions worldwide.” (Lines 507–512)

9. L336: Have fragmentation experiments carried out to validate the assignment of the compound classes? The functional groups of organosulfates (m/z 96.9601 (HSO_4^-) and m/z 79.9573 (SO_3^-)) as well as nitrate groups (m/z 61.9883 (NO_3^-)) are very strongly represented in the fragmentation spectra and a clear indicator for organosulfates and nitrooxy organosulfates.

Related sentence: “Among these, organosulfate and nitrooxy-organosulfate compounds (abbreviated as OSs hereafter), defined as those with sufficient oxygen atoms to assign the $-\text{OSO}_3\text{H}$ and $-\text{ONO}_2$ groups in the molecules (Brüggemann et al., 2020; Lin et al., 2012b), were important components in both seasons.”

Response: As described in the response to comment #8, the HRMS analysis was performed only in the full MS scan mode, and thereby no fragmentation spectra are available for this study. In fact, it was a commonly used method in previous literature to identify organosulfate and nitrooxy-organosulfate compounds based on the assignment of $-\text{OSO}_3\text{H}$ and $-\text{ONO}_2$ groups from HRMS analysis, although we did not carry out fragmentation experiments to validate the assignment of these classes herein. Nevertheless, we agree that this method would result in an upper limit of the predicted numbers. Therefore, we have revised/added the following statement regarding this uncertainty in the revised manuscript:

“Among these, organosulfate and nitrooxy-organosulfate compounds (abbreviated as OSs hereafter), **roughly** defined as those with sufficient oxygen atoms to assign the $-\text{OSO}_3\text{H}$ and $-\text{ONO}_2$ groups in the molecules (Brüggemann et al., 2020; Lin et al., 2012b), were important components in both seasons. **Note that the designated OSs here would correspond to those at the upper limit, since no further fragmentation spectra available.**” (Lines 336–339)

Response to the comments of Referee #2 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 Referee #2 for the helpful comments and suggestions on our manuscript (ID: egusphere-2025-519). We have seriously addressed all the issues raised by the referee and made relevant revisions on the manuscript. Please find below for the details of our responses to these comments. A copy of the manuscript and supplement with all the changes and other minor corrections tracked is also attached for reference.

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

This manuscript presents observational evidence of the seasonal variability in organic aerosol composition. However, the research approach—combining seasonal sampling with high-resolution mass spectrometry—has been widely reported in previous studies. The study does not clearly provide novel mechanistic insights or substantial advancements in the understanding of anthropogenic–biogenic interactions. As such, the conclusions drawn lack originality and scientific novelty. I regret to conclude that the manuscript, in its current form, does not meet the publication standards of the journal. My main concerns are as follows:

Response: We really appreciate the referee for providing these comments on our manuscript. We believe that it might be to some extent true that “combining seasonal sampling with high-resolution mass spectrometry has been widely reported in previous studies” in certain areas of the world. However, this is definitely not the case in the Qinling Mountains region of central China, despite its significant roles of serving as natural geographical and climatic boundary between the northern and southern China. Actually, based on our latest literature survey, the

molecular composition of organic aerosols in the Qinling Mountains region has rarely been investigated to date, especially utilizing the advanced HRMS techniques. This point has been stated in the manuscript as follows: “So far to our knowledge, this study for the first time reports the overall molecular characteristics of organic aerosols between contrasting seasons in the Qinling Mountains region based on high-resolution Orbitrap mass spectrometry.”

(Lines 76–78)

Moreover, the research approach of HRMS analysis remains to be one of the most advanced technologies in the field of atmospheric aerosol research currently. In this study, we focused primarily on the application of HRMS technique in the Qinling Mountains region for organic molecular characterization, rather than the development of this research approach itself.

Therefore, the originality and novelty of this study should not be only judged by the research approach used herein, but more importantly by the research objectives and scientific findings. We acknowledge that it is somewhat challenging to directly elucidate mechanistic insights from aerosol sampling and offline HRMS analysis under complex atmospheric conditions, compared with those using real-time measurement techniques in laboratory studies that have the capability of capturing rapid changes in specific aerosol reaction chemistry. For this sake, we have included more mechanistic insights from previous literature to strengthen our conclusions, as addressed in detail in the response to the referee’s comment #4.

Taken these facts together, the originality and scientific novelty of this current study include the following main aspects: 1) it first provided a comprehensive insight on the chemical characteristics of organic aerosols at the molecular level in the Qinling Mountains region, which has unique and significant geographical and climatic features; 2) it first demonstrated the substantial influence of anthropogenic pollution on the organic molecular composition in this region; 3) it advanced our knowledge on the anthropogenic and biogenic interactions as well as elucidated its seasonal variabilities and underlying influencing factors. As a result, we believe that this study would initiate and promote more atmospheric aerosol researches to further understand the anthropogenic perturbations on air quality, atmospheric chemistry, and associated environmental and climate impacts in the Qinling Mountains region, and also provide important references for similar regions worldwide.

1. Line 305: this interpretation lacks strong causal linkage, as biogenic emissions—particularly monoterpene-derived secondary organic aerosols (SOA)—also predominantly fall within the C₆–C₁₁ range. Therefore, the contribution from biogenic precursors should not be overlooked when interpreting the molecular composition in this carbon number range.

Related sentence: “In contrast, the CHO and CHON species in ESI+ mode and CHONS species in both modes had increased number fractions at approximately C_{6–11} in winter, possibly resulted from the enhanced influence of anthropogenic pollution.”

Response: The referee’s viewpoint here is slightly different from what we intended to express from this statement. In fact, we did not mean to rule out the contribution from biogenic precursors at the C₆–C₁₁ range, as addressed in the context of the same paragraph: “Among them, the number and peak area fractions of organic species were particularly dominated by the C₅–C₁₁ compounds, which can be derived from both biogenic and anthropogenic sources.” (Lines 299–301). Rather, the key point here is that the increased number fractions of those species in winter were contributed by the enhanced influence of anthropogenic pollution from the surrounding areas. It is likely that the original expression was not clear enough to be understood. Therefore, we have highlighted this point for clarity in the revised manuscript, as follows:

“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.” (Lines 306–309)

2. Lines 365-370: here only discuss the seasonal variation of molecules identified under the ESI– mode using VK diagrams, while omitting the analysis of VK characteristics of compounds detected in the ESI+ mode. This incomplete treatment results in a weak logical connection between the data presented and the conclusions drawn, leading to a lack of coherence in the overall interpretation. Given that ESI+ typically captures a distinct subset

of organic compounds—often including important nitrogen- and sulfur-containing species—its exclusion leaves a significant gap in the discussion. I recommend the authors include a comparative analysis of VK diagrams under both ionization modes to ensure a more comprehensive and balanced understanding of the seasonal dynamics of organic aerosol composition.

Related sentence: “The anthropogenic and biogenic organic tracer species identified in ESI– mode were further analyzed in the van Krevelen diagram based on their elemental ratios of O/C and H/C, as shown in Fig. 8a. Except for those derived from glyoxal, isoprene, and some anthropogenic precursors with $O/C > 0.5$, other tracer species were primarily distributed in the regime with $O/C \leq 0.5$. In addition, the anthropogenic tracer species widely dispersed at the regime with H/C from approximately 0.5 to 2.5, whereas the biogenic ones were mainly situated at the $H/C \geq 1.5$ regime.”

Response: Since the VK diagrams for organic tracer species in ESI+ mode showed quite similar seasonal variation trends as those in ESI– mode, together with that organic tracer species from more precursors were identified in the ESI– mode, we therefore only discussed the results of negative mode in the original manuscript. As suggested by the referee, we have provided the results of VK diagrams for both ESI– and ESI+ modes in order to gain a more comprehensive understanding on the seasonal dynamics of organic aerosol composition. Specifically, we have revised the original Figure 8 by including the VK diagram results and seasonal variation of organic species in both ESI– and ESI+ modes (see the revised Figure 8 below). We have also modified and added the relevant discussions in the revised manuscript, as follows:

“The anthropogenic and biogenic organic tracer species identified in **the ESI– and ESI+ modes** were further analyzed in the van Krevelen diagram based on their elemental ratios of O/C and H/C, as shown in Fig. 8a. **Similar variation patterns were generally observed between the two modes. Specifically,** except for those derived from glyoxal, isoprene, and some anthropogenic precursors with $O/C > 0.5$, other tracer species were primarily distributed in the regime with $O/C \leq 0.5$.” (Lines 365–368)

“Figure 8b presents the example results on two different days (**that is, August 30 and January 26**) obtained in the **ESI– mode**.” (Lines 375–376)

“**Similar tendencies were also found for those in the two modes** across the entire study periods in summer and winter (Fig. 8c).” (Lines 380–381)

“**In ESI– mode**, the number fraction of organic species in the aromatic regime was on average $21 \pm 2\%$ on individual days in winter, which was higher than those of $17 \pm 2\%$ in summer.” (Lines 381–382)

“**Likewise, in ESI+ mode**, the number and peak area fractions of aromatic species were slightly higher in winter than in summer, while those of aliphatic species were higher in summer.” (Lines 384–386)

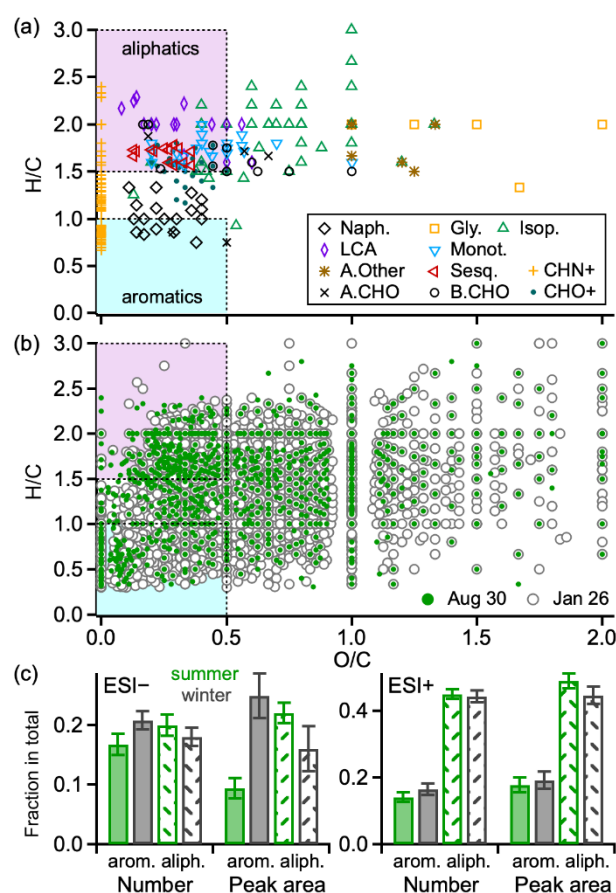


Figure 8. van Krevelen diagrams plotting of (a) organic tracer species derived from anthropogenic and biogenic precursors **in both modes (as listed in Table S1–S5)**, and (b) organic species identified on a summer day (August 30) and a winter day (January 26) in ESI– mode. (c) Averaged number and peak area fractions of organic species in aromatic and

aliphatic molecular structures for summer and winter samples **in ESI⁻ and ESI⁺ modes**. In panels (a, b), the shaded pink ($H/C \geq 1.5$, $O/C \leq 0.5$) and cyan ($H/C \leq 1.0$, $O/C \leq 0.5$) areas represent aliphatic and aromatic regimes, respectively. The O/C was replaced by $(O-3S)/C$ or $(O-3S-2N)/C$ in the case of organosulfates or nitrooxy-organosulfates. The error bars in panel (c) represent 1σ standard deviations for all the samples in each season.

3. Lines 395-410: The conclusions regarding the influence of relative humidity on the molecular characteristics of organic species are solely based on compounds identified under the ESI⁻ mode. This raises concerns about the completeness of the analysis, as ESI⁻ and ESI⁺ modes often detect different classes of organic compounds with distinct physicochemical properties. Relying only on ESI⁻ data may lead to a biased or incomplete understanding of humidity-driven processes. A more balanced interpretation should incorporate results from both ionization modes to better capture the full range of organic species affected by relative humidity.

Response: As suggested by the referee, we have performed further analysis with regard to the influence of relative humidity on the molecular characteristics of organic species in the ESI⁺ mode during the study periods. The results eventually showed that the overall variation trends of the number of organic species under different RH conditions were to some extent similar between the two ionization modes (see Figure S2 below and also in the revised Supplement), although the RH influence on organic species in the ESI⁺ mode were not as strong as those in the ESI⁻ mode. This is most likely associated with the distinct physicochemical properties of organic species in these two ionization modes, that is, basic organic substances were readily protonated and thus detected in the positive mode, while acidic substances were easily deprotonated and more sensitive in the negative mode. As a result, we have added the relevant discussions regarding the influence of RH on organic species in the ESI⁺ mode in the revised manuscript, as follows:

“In contrast, the similar but weaker dependence on RH was found for organic species in the ESI⁺ mode (Fig. S2 in the Supplement), probably associated in part with their distinct physicochemical properties compared with those in the ESI⁻ mode. This result

also indicates that the influence of RH could be stronger for acidic organic substances, since these were more readily deprotonated and sensitive to be detected in negative mode than the basic ones (Laskin et al., 2018).” (Lines 416–419)

The following literature also has been added in the References section of the revised manuscript:

Laskin, J., Laskin, A., and Nizkorodov, S. A.: Mass spectrometry analysis in atmospheric chemistry, *Anal. Chem.*, 90, 166–189,

<https://doi.org/10.1021/acs.analchem.7b04249>, 2018. (Lines 647–648)

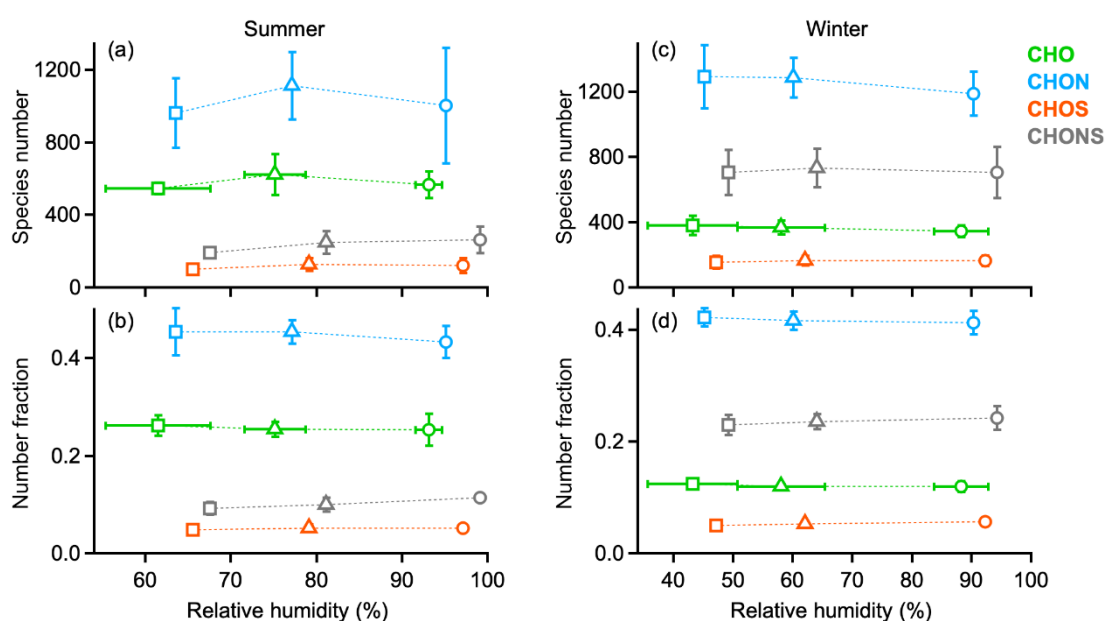


Figure S2. Species number and the relative fractions of organic molecular subgroups in positive ESI mode under varied relative humidity conditions in (a, b) summer and (c, d) winter periods. The symbols of each type shared the same RH values (that is, $62 \pm 6\%$, $75 \pm 4\%$, $93 \pm 2\%$ in summer and $43 \pm 8\%$, $58 \pm 7\%$, $88 \pm 5\%$ in winter) but were offset horizontally for a clear vision. The horizontal error bars in the CHO species represent 1σ standard deviations of RH values. The vertical error bars represent 1σ standard deviations for all the samples in each RH condition.

In addition, we have also added the following result (Figure S4) and relevant discussions regarding the influence of temperature on organic species in ESI+ mode into the Supplement, for a more comprehensive understanding on the influence of meteorological factors.

“The species numbers of all organic subgroups in ESI– mode were almost comparable at the mean temperatures of 21.5 ± 0.8 and 24.5 ± 0.8 °C in summer, while they were largely increased at the highest temperature level of 27.6 ± 1.0 °C (Fig. S3 in the Supplement).”

(Lines 430–432)

“The species number and fraction of organic subgroups in ESI+ mode varied insignificantly with temperature as well (Fig. S4 in the Supplement).” (Lines 433–434)

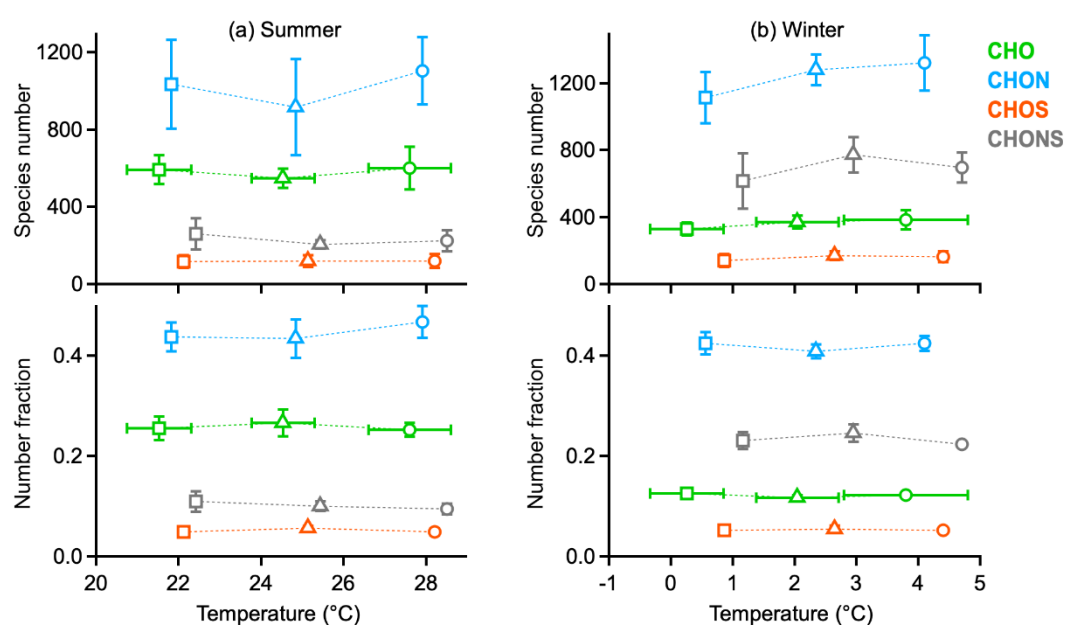


Figure S4. Species number and the relative fractions of organic molecular subgroups in positive ESI mode under varied temperature conditions in (a) summer and (b) winter periods. The symbols of each type shared the same temperature values (that is, 21.5 ± 0.8 , 24.5 ± 0.8 , 27.6 ± 1.0 °C in summer and 0.3 ± 0.6 , 2.0 ± 0.7 , 3.8 ± 1.0 °C in winter) but were offset horizontally for a clear vision. The horizontal error bars in the CHO species represent 1σ standard deviations of temperature values. The vertical error bars represent 1σ standard deviations for all the samples under each temperature condition.

4. Lines 450-475: The authors primarily rely on positive and negative correlations with gaseous and particulate pollutants, as well as SOR, NOR, and Ox, to infer their influence on the chemical composition of organic aerosols. However, the correlation-based analysis lacks mechanistic support, making the conclusions less convincing. Furthermore, the discussion remains rather superficial and does not adequately elucidate the underlying interactions between pollutants and organic aerosol formation. It is recommended that the authors incorporate mechanistic insights from previous literature to strengthen the scientific basis and credibility of their conclusions.

Response: We hope the referee could understand that the dataset of this study was mainly derived from HRMS measurement of aerosol filter samples, thereby the correlation-based analysis of organic species with air pollutants was one of the efficient methods to explore the underlying interactions. We acknowledge that although the offline HRMS analysis had advantages in determining organic molecular composition and identifying reaction products, it remains challenging to directly elucidate specific reaction mechanisms, especially under atmospheric conditions with complex influences of multiple environmental factors. Actually, the conclusions drawn from the correlation-based analysis in our current study are highly consistent with some previous laboratory studies. Therefore, as recommended by the referee, we have incorporated the following mechanistic insights to strengthen the scientific basis and credibility of our conclusions in the revised manuscript:

“This phenomenon **could partly** result from the chemical transformation of these species into **other chemically diverse substances (e.g., CHON and CHONS) through acid-catalyzed heterogeneous reactions and/or aqueous phase chemistry in the presence of anthropogenic air pollutants (Darer et al., 2011; Fan et al., 2022; Kwong et al., 2018; Lam et al., 2019).**” (Lines 466–469)

“**Another proposed explanation is that the productions of CHO and CHOS species were to some extent governed by the consumption of anthropogenic pollutants at the low concentration levels in summer (Fig. 2c), as those reported in some other ambient atmospheres (Lin et al., 2022; Riva et al., 2019; Wang et al., 2020).**” (Lines 469–472)

“**Possible reaction pathways include such as biogenic isoprene and monoterpene**

precursors being oxidized by nitrate radicals to form condensable organic nitrates and nitrooxy-organosulfates (Hamilton et al., 2021; Ng et al., 2017).” (Lines 473–475)

“These species might be partly associated with primary emissions (Song et al., 2018; Zhong et al., 2023), such as those of biomass burning and fossil fuel combustion from the surrounding rural and urban areas.” (Lines 479–480)

“This is consistent with previous studies that oxidant levels were one of the most important governing factors for the production of organosulfur species by limiting the oxidation of organic precursors (Bryant et al., 2021; Wang et al., 2021f).” (Lines 487–489)

The following literatures have been added in the References section to support our conclusions in the revised manuscript:

“Darer, A. I., Cole-Filipiak, N. C., O’Connor, A. E., and Elrod, M. J.: Formation and stability of atmospherically relevant Isoprene-derived organosulfates and organonitrates, *Environ. Sci. Technol.*, **45**, 1895–1902, <https://doi.org/10.1021/es103797z>, 2011.” (Lines 564–566)

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(Lines 736–743)

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