Response to reviewer #2

The manuscript by Shi and Zhang et al. presents a measurement report, providing detailed description of the hygroscopicity and mixing state of the aerosols in mountain Hua in central China for few months in 2021. Despite focusing on a single location and relatively short time period, the manuscript is worth publishing due to the measurement location, and thus certain site characteristics, which have not been widely reported. The manuscript is overall well written and provides all necessary details, but I have minor concerns and suggestions for revisions that should be considered before accepting for publication.

We greatly appreciate referee#2's positive feedback and constructive suggestions which are of great value for improving the quality of our paper. Below are our point-to-point responses to the referee's comments.

1. Regarding the trajectory analysis, I wonder why the authors have selected the 24-hour long trajectories. I think reasoning for this selection is crucial and should be added to the text, especially when considering the fact that aerosols, especially the larger ones measured at the site, could originate very far. In many other studies utilizing backward trajectory analysis, longer trajectories (to my knowledge, often at least 48 hours) are usually employed (see for example, Räty et al., 2023; Khadir et al., 2023; Xu et al., 2021) to make sure long-range transport is properly captured.

Response:

We appreciate this very constructive suggestion. Following the reviewer's suggestion, we have recalculated the backward trajectories using a 72-hour duration. The resulting clusters obtained from 72-hour trajectory analysis is presented in Fig.1 below. As the results differ slightly from the previous version, we have updated the results and discussion in Sect. 3.3 accordingly. The revised content is provided below for reference: "To comprehensively evaluate the impacts of long-range transport and regional emissions on aerosol hygroscopic properties, we compared the size-resolved aerosol hygroscopicity parameter (κ) across five air mass clusters identified through trajectory analysis (Fig.5a). As Cluster 1, 2 and 4 also occurred during the latter half of the campaign, coinciding with domestic heating activities, we further divided each of these three clusters into two distinct periods. The segments during the domestic heating period of these three clusters were specifically labeled as Cluster 1 DH, Cluster 2 DH and Cluster 4 DH, where "DH" denotes the influence of domestic heating. During the first half of the campaign, which was free from significant influence of mineral dust and prior to the onset of domestic heating activities (i.e., Cluster 1, 2, and 4), aerosols exhibited clear size-dependency of κ, with κ values increasing with increasing particle size. Moreover, the κ values observed for particles of the same sizes were relatively comparable across these three clusters. Air masses associated with these clusters, particularly Cluster 1, mainly transported over relatively short distances from southeastern and southwestern regions, passing through the heavily polluted Guanzhong Plain urban agglomeration and may represent the atmospheric conditions of this regional environment. In contrast, aerosols in Cluster 3, 5 and Cluster 1 DH, 2 DH, and 4 DH displayed relatively constant κ across most particle sizes, except for sub-100nm particles, which probably had local origins rather than long-range transport, as discussed earlier.

For 200 nm particles, Cluster 1, 2, and 4 exhibited the highest κ values (~0.32), followed by Cluster 3 and 5 (~0.27), while the lowest values were observed in Cluster 1 DH, 2 DH, and 4 DH (~0.22). Given that the chemical composition of bulk aerosols is more representative of larger particles than smaller ones (Hong et al., 2018), this pattern was consistent with the average aerosol composition measured by

the online measurements. During Cluster 1, 2, and 4, aerosols were dominated by inorganic species, such as NH_4^+, SO_4^{2-}, NO_3^-, which are highly hygroscopic and accounted for over 70 % of the $PM_{2.5}$ mass fraction (see Fig.6).

For Cluster 3 and 5, the contribution of these inorganic species decreased markedly, dropping from over 70 % to less than 50 % in mass fraction, as shown in Fig.6. Concurrently, the levels of Ca^{2+}, Fe^{2+} increased substantially, from less 1 % to approximately 20 % of $PM_{2.5}$ mass. This shift may partially explain both the reduced hygroscopicity ($\kappa \approx 0.09$) and the elevated number fraction (21 %) of LH mode particles in these clusters compared to those ($\kappa \approx 0.12$, $NF_{LH} = 10$ %) in Cluster 1, 2, and 4, as these mineral dust components are generally hydrophobic or weakly hygroscopic. The influence of mineral dust was further confirmed by the strong correlation between SO_4^{2-} with Ca^{2+} ($R^2 = 0.83$) in Cluster 3 and 5, contrasting with their weak associations ($R^2 \approx 0.1$) during other clusters, where SO_4^{2-} was instead well linked to NH_4^+ ($R^2 \approx 0.9$) (see Fig.7). The co-variation of SO_4^{2-} and Ca^{2+} indicates that they possibly shared the same origins (Sullivan et al., 2009), with Ca^{2+} likely existing in the form of nearly non-hygroscopic $CaSO_4$ ($\kappa \approx 0.01$-0.05) during this episode, reinforcing the observed hygroscopicity decline relative to Cluster 1, 2, and 4. On the other hand, as particle size decreased, a slight increase in the overall aerosol hygroscopicity was observed in Cluster 3 and 5, which can be explained by the enhanced hygroscopicity of LH mode particles coupled with a small decrease in their number fraction. Given that mineral dust mainly resided in larger particles, this size-dependent trend in hygroscopicity suggests a reduced contribution of mineral dust to the hygroscopicity of smaller particles within Cluster 3 and 5.

As noted earlier, beginning on November 6, which encompassed the entire duration of Cluster 3, 5, 1 DH, 2 DH, and 4 DH, regional domestic heating was initiated, which may emit substantial amounts of primary aerosols, such as black carbon (BC) and primary organic aerosols (POA). These aerosols were likely transported to our observational site via advection. This interpretation aligns with the findings of Du et al. (2022), who reported a marked increase in the fraction of organic aerosols as well as BC at Mt. Hua following the initiation of domestic heating. Though no direct source apportionment of organic aerosols can be obtained by the current study, a moderate increase (approximately 7 %) in the organic mass fraction in $PM_{2.5}$ during Cluster 3 and 5, followed by a more pronounced rise in both organic (10 %) and BC fractions (5 %) during Cluster 1 DH, 2 DH, and 4 DH was observed compared to other clusters (see Fig.6), further supporting our previous hypothesis. Thus, the elevated levels of these primary aerosols, typically exhibited weak hygroscopicity (Shi et al., 2022), coupled with the high contents of weakly hygroscopic mineral dust, may synergistically drive the continued decline in aerosol hygroscopicity throughout this period.

Despite both being influenced by dust events and domestic heating activities, aerosols in Cluster 5 exhibited higher aerosol hygroscopicity (0.25) compared to Cluster 3 (0.23), mainly due to their larger number fraction of MH mode particles, accompanied by the higher hygroscopicity of LH mode particles, as shown in Fig.5. Interestingly, striking high RH levels (around 80 %) were observed in Cluster 5, which nearly doubled the values in Cluster 3 (see Fig.S5). Such high-RH conditions may facilitate some specific aerosol processes, such as multi-phase or aqueous phase reactions, potentially altering their chemical composition and may explain their elevated hygroscopicity (Tong et al., 2020). This hypothesis aligns with the results of Du et al. (2022), who observed that the contribution of aqueous-formed water soluble oxidized organic aerosols to the total water-soluble organic aerosols increased from 11.21 % under low-RH levels to over 40 % at RH > 80 %, indicating a significant transformation in the organic aerosol composition. On the other hand, we noticed that the average κ of MH mode particles in Cluster 3 and 5

was markedly greater relative to other clusters (see Fig.5). Following our preceding reasoning, we suspected that the multi-phase or aqueous phase reactions under higher-RH levels in Cluster 5, not only enhanced the hygroscopicity of LH mode particles, but also produced substantial highly hygroscopic materials, which may have persisted until the entire duration of Cluster 3 and 5. However, without detailed compositional analysis at molecular level, the exact mechanisms responsible for this exceptionally high aerosol hygroscopicity remained unclear.

In summary, during the first half of the campaign, when air masses mainly passed through the heavily polluted Guanzhong Plain urban agglomeration, aerosols were primarily composed of secondary inorganic species and exhibited the highest hygroscopicity. Starting around November 6, increased influences from both mineral dust and domestic heating activities led to a noticeable decline in aerosol hygroscopicity, particularly in larger particles. This reduction was largely attributed to the rising levels of weakly hygroscopic components, such as mineral dust tracers (e.g., Ca^{2+}, Fe^{2+}), organic components as well as BC, highlighting the combined effects of long-range transport and regional emissions on aerosol composition and properties.".

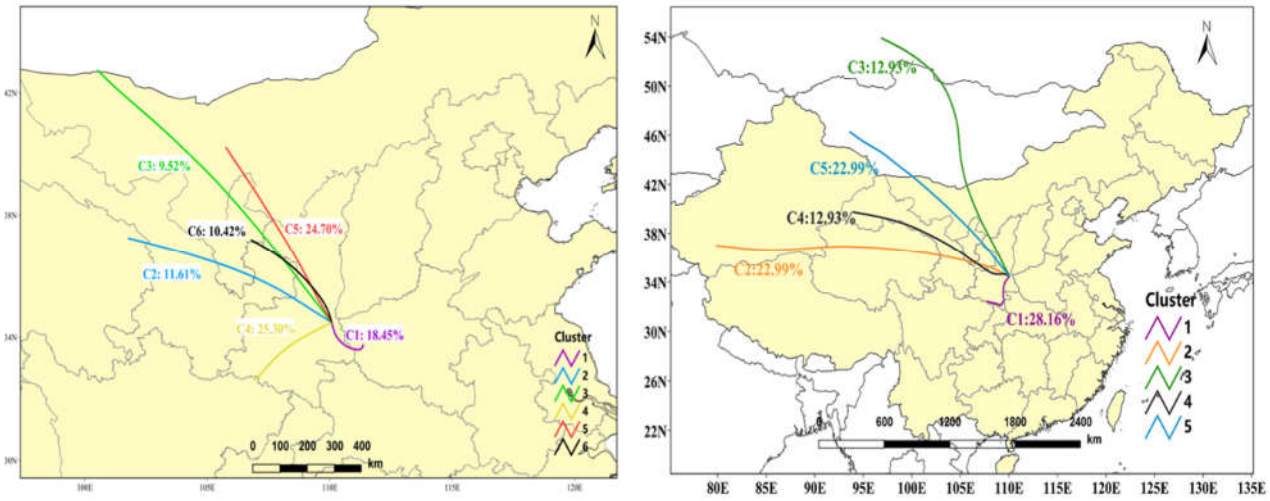

Figure 1. 24 h backward trajectories (left) and 72 h backward trajectories (right) at 2060 m above ground level during the sampling period.

2. Line 27: "improving predictions…climate impacts" Please reword as the current structuring is unclear.

Response:

Thanks for your specific comment. We have revised the sentence in Line 26 for clarity. The updated sentence now reads: "Understanding the hygroscopicity and mixing state of atmospheric aerosol particles is crucial for accurately assessing their role in cloud formation and subsequent climate impacts.".

3. Line 34: I assume the sizes of the particles are in the brackets, please make it clear by stating it explicitly (e.g., dp = 30 nm).

Response:

Thank you for this constructive suggestion. We have revised the sentence in Line 33 for clarity. The updated sentence now reads: "Results reveal a clear size-dependence of aerosol hygroscopicity, with the mean hygroscopicity parameter (κ_{mean}) increased from 0.20 for 30 nm particles to 0.30 for 200 nm particles."

4. Line 57: Do you mean dry deposition efficiency here? Please be explicit.

Response:

Thank you for your comment. In our manuscript, the term "deposition efficiency" specifically refers to the proportion of particles that deposit within the human respiratory tract. This concept focuses on aerosol behavior in the human respiratory system and distinct from atmospheric dry deposition processes.

5. Line 120: Is this division based on the Shi et al 2022? Short explanation on why and how could be also included here in addition to the reference.

Response:

In response to the reviewer's suggestion, we have revised the paragraph as follows: "Given the complex mixing states of ambient aerosols, aerosols are commonly classified into distinct hygroscopic groups based on the hygroscopicity parameter κ (Liu et al., 2011), as more-hygroscopic aerosols normally have larger κ values and less-hygroscopic particles have smaller ones. In the present work, two different hygroscopic modes were clearly identified. Accordingly, aerosol particles were categorized into two modes with respect to their hygroscopicity: a less-hygroscopic mode (LH, $\kappa <= 0.2$) and a more-hygroscopic mode (MH, $\kappa > 0.2$), consistent with the approach of Shi et al. (2022). The values of κ for each mode were calculated as the volume-equivalent mean derived from the κ-PDF within the respective κ boundaries.".

6. Figure 2 and Figure 3: Please make sure the color scale for the k-PDF is perceptually uniform as the current rainbow scale is not and should not be used.

Response:

We thank the reviewer for this important comment. As suggested, we have now replaced the rainbow color scale with a perceptually uniform color scheme (e.g., parula) for all κ-PDF figures throughout the manuscript. The updated figures are shown below.

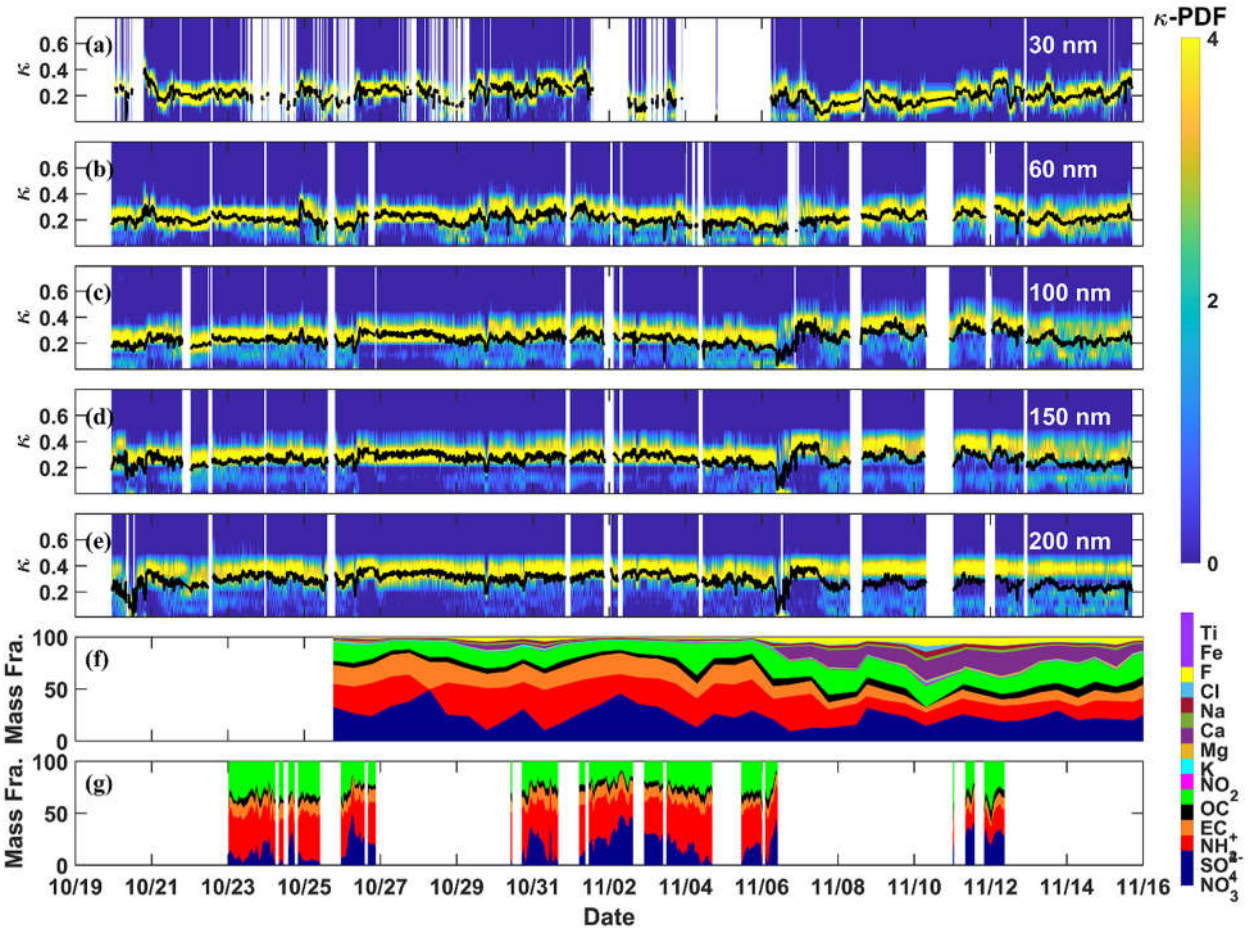

Figure 2. (a-e) Time series of κ-PDF for different particle sizes (with the black line indicating the mean κ value) and (f-g) Time series of chemical composition of $PM_{2.5}$ obtained using offline and continuous online measurements, respectively, during the sampling period.

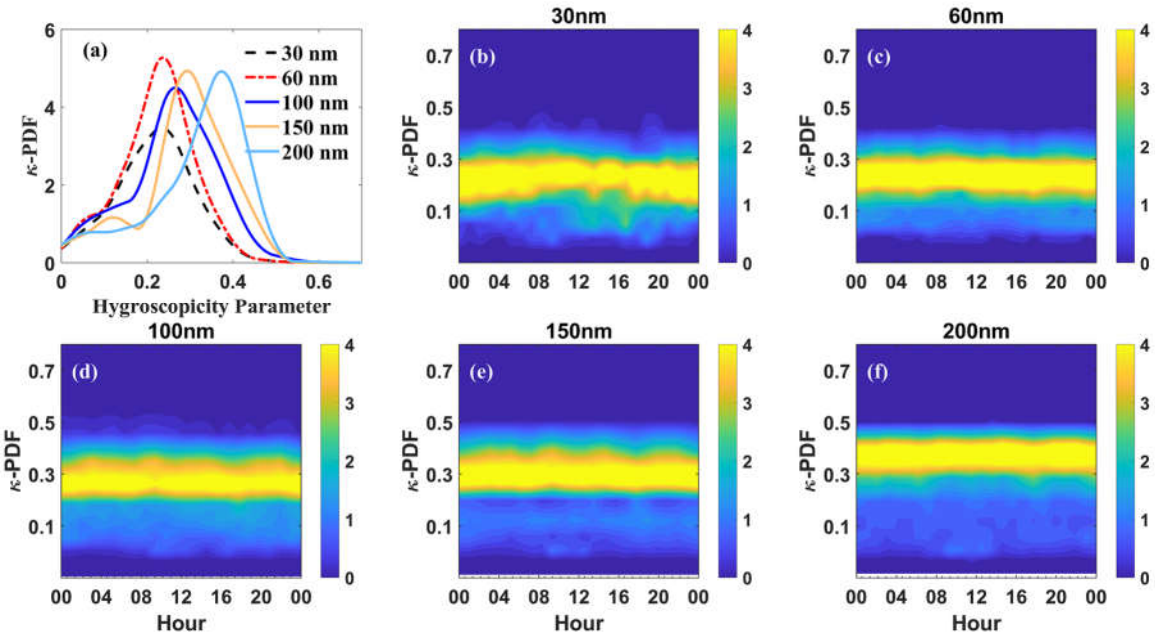

Figure 3. (a) Average *κ*-PDF for particles at different sizes; (b-f) diurnal variations of the *κ*-PDF for particles of different sizes measured during the campaign.

7. Sect. 3.2 title: Please avoid using abbreviations in the title, you could use "probability density functions of k" instead. Also please define what it means.

Response:

Thank you for this constructive suggestion. A clear definition of "*κ*-PDF" has been provided upon its first appearance in the revised manuscript, as follows: "The *κ* probability density function (*κ*-PDF), indicative of a statistical distribution that describes the variation in hygroscopicity among an aerosol population, was derived from the GF probability density function (GF-PDF), which was retrieved from the measured GF distribution function (GF-MDF) using the TDMAinv algorithm (Gysel et al., 2009)." In addition, the abbreviation "*κ*-PDF" has been removed from the title of Sect. 3.2.

8. Line 235: Is the abbreviation URG defined somewhere? Even if it is, I would use the full word here too for clarity.

Response:

Thank you for your constructive suggestion. URG refers to URG Corporation. According to the reviewer's suggestion, we have replaced "URG" with "online measurement" in both the figure caption and in the revised manuscript. This change ensures a clearer description of the data source.

9. Figure 4: Are the colored lines/curves in this figure the cluster centroids? This should be stated in the caption. I believe adding a trajectory frequency map for each of the clusters would be very helpful. Please consider adding one to the supplementary material.

Response:

Thanks for your specific comment. In the revised manuscript, we have revised the manuscript accordingly. As suggested, the caption of Figure 5 now explicitly states the colored curves represent the

cluster centroids. In addition, a new figure showing the trajectory frequency for each cluster has been added to the supplementary material.

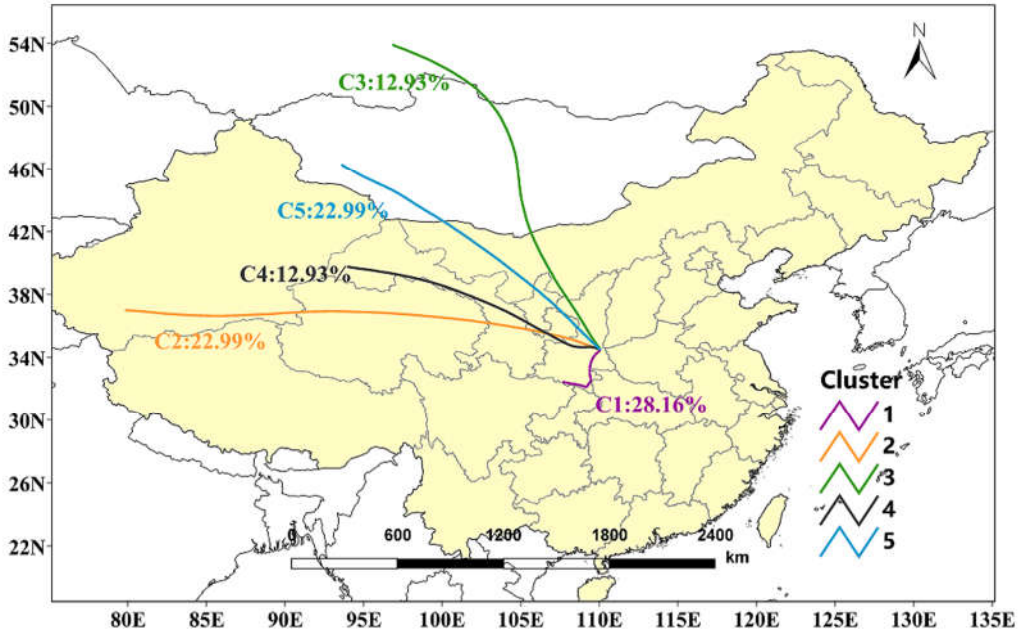

Figure 4. Cluster analysis of 72 h backward trajectories at 2060 m above ground level at the sampling site during the five trajectory-identified clusters. The line colors denote different clusters, i.e., purple for Cluster 1, yellow for Cluster 2, green for Cluster 3. black for Cluster 4, and blue for Cluster 5.

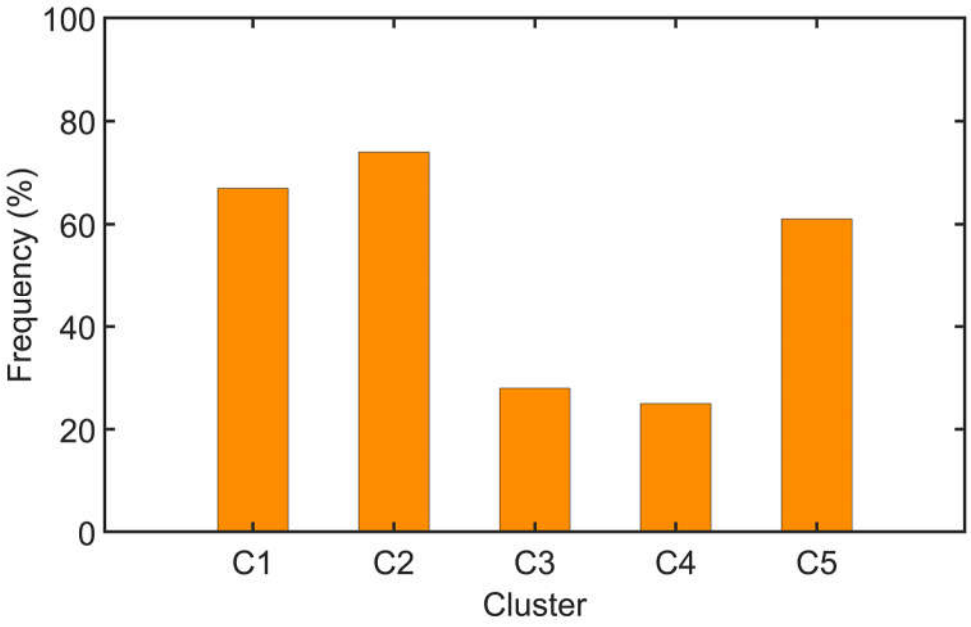

Figure 5. Frequency distribution of backward trajectories. (Fig.S8 in the SI)

10. Line 245: “was not obviously observed” – what do you mean by this? If you did not measure it, you should say “was not investigated” instead or you could also just say “was not observed” if that’s is what you mean.

Response:

As suggested by the reviewer, we modified the sentence into: “However, such an influence on aerosol chemical composition and their hygroscopicity was not observed at the current study”.

11. Sect. 3.3/trajectories: You mention trajectory clusters but provide no details on how the clusters were obtained. I am assuming a method of k-mean clustering or similar, however, this should be mentioned in the methods where you first describe your trajectory calculations. The trajectory frequency figure that I suggested to include could then be referenced in the method section already, and later noted in this 3.3 if necessary.

Response:

We thank for the reviewer for this constructive suggestion. In the revised manuscript, we have added a description of the clustering approach in Section 2.4, where trajectory calculations are introduced. In addition, as suggested, we have included a figure showing the trajectory frequency in the supplementary material (see Fig.S8 in the SI) and referenced appropriately. The added text reads as follows: “This study employed the cluster analysis method proposed by Draxler et al (Stein et al., 2015), where the clustering criterion was defined such that the spatial variance of each cluster corresponds to the sum of squared distances between individual trajectories and the mean trajectory of that cluster. The total spatial variance (TSV) was calculated as the sum of the spatial variances of all clusters. The final clustering result was obtained by minimizing the increase in TSV. The trajectory frequency distributions for the resulting clusters are provided in Fig. S8.”.

12. Figure 7: I would remove the lined between the points in this figure. You are comparing the hygroscopicity values for different sites and sizes, not necessary looking on how the hygroscopicity changes with size as you can also have particles with different origins (i.e., larger particle is not the smaller one that has grown larger). Please considering increasing both marker and text size in this figure too.

Response:

Thank you for your constructive suggestion. We have removed the lines between the points in Figure 8 (formerly Figure 7) and only showed the individual data points to better highlight the comparisons. Additionally, we have increased both the marker and text sizes in the figure to enhance readability. The updated figure is shown below.

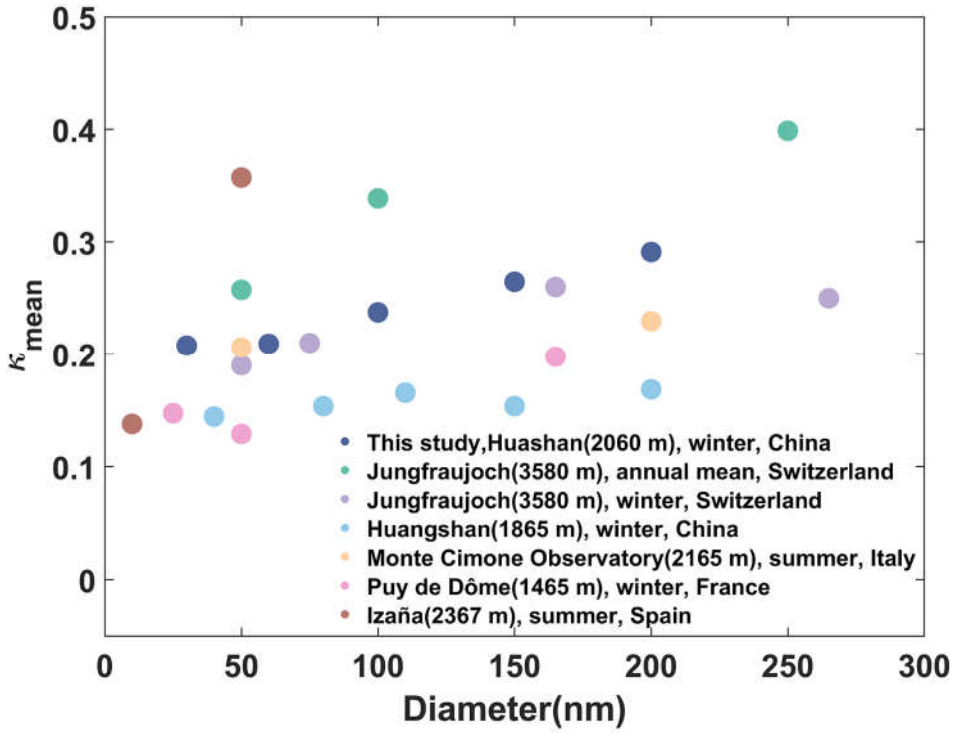

Figure 6. Comparison of aerosol hygroscopicity measured at different high-altitude sites around the world. (Figure 8 in manuscript)

13. Supplementary figures & Figure 3a, Figure 5, Figure 7: Please avoid using red and green in the same figure to accommodate color blind readers.

Response:

Thanks for your specific comment. In the revised manuscript, we have adjusted the color scheme of Supplementary Figures, Figure 3a, Figure 5, and Figure 7 to avoid using red and green in the same figure, thereby improving accessibility for color-blind readers.

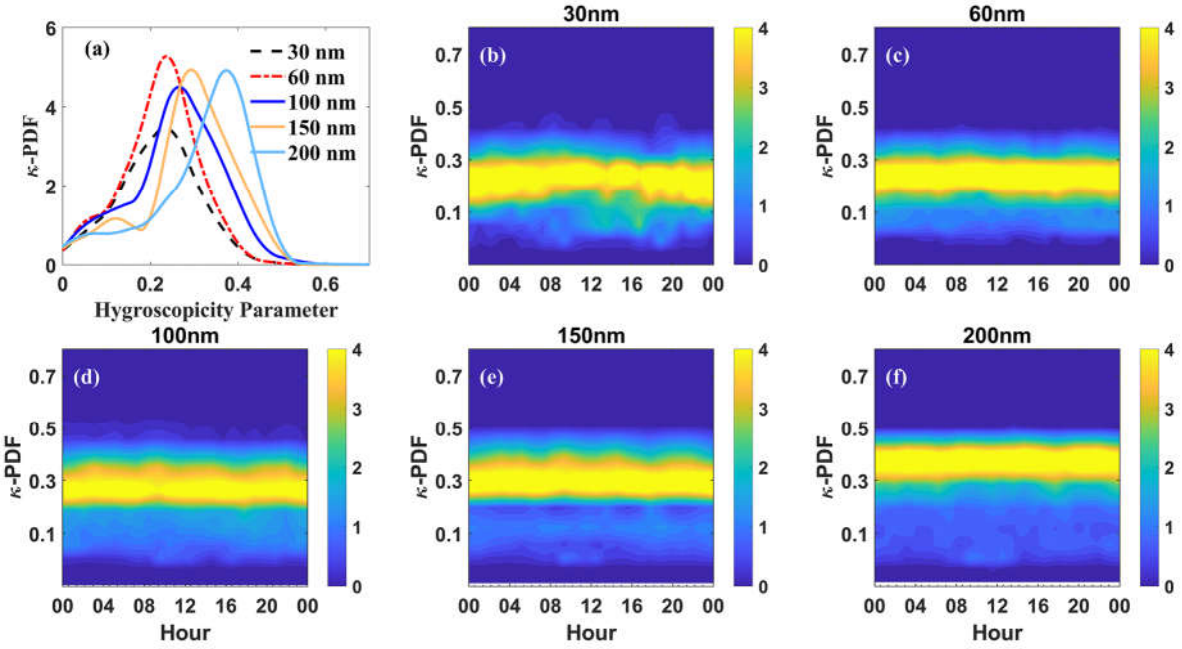

Figure 7. (a) Average *κ*-PDF for particles at different sizes; (b-f) diurnal variations of the *κ*-PDF for particles of different sizes measured during the campaign. (Figure 3 in manuscript)

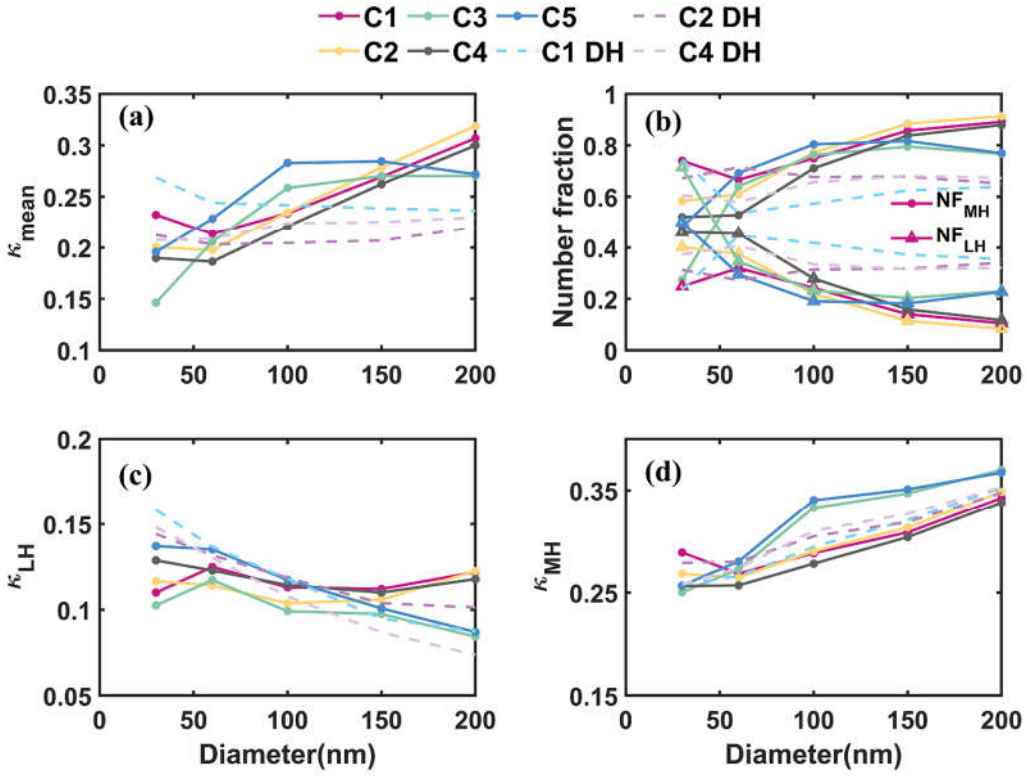

Figure 8. Cluster analysis corresponding to (a) mean aerosol hygroscopicity parameters *κ*, (b) the number fraction of LH and MH mode particles, (c) and (d) the mean *κ* values of LH and MH mode particles at different sizes. (Figure 5 in manuscript)

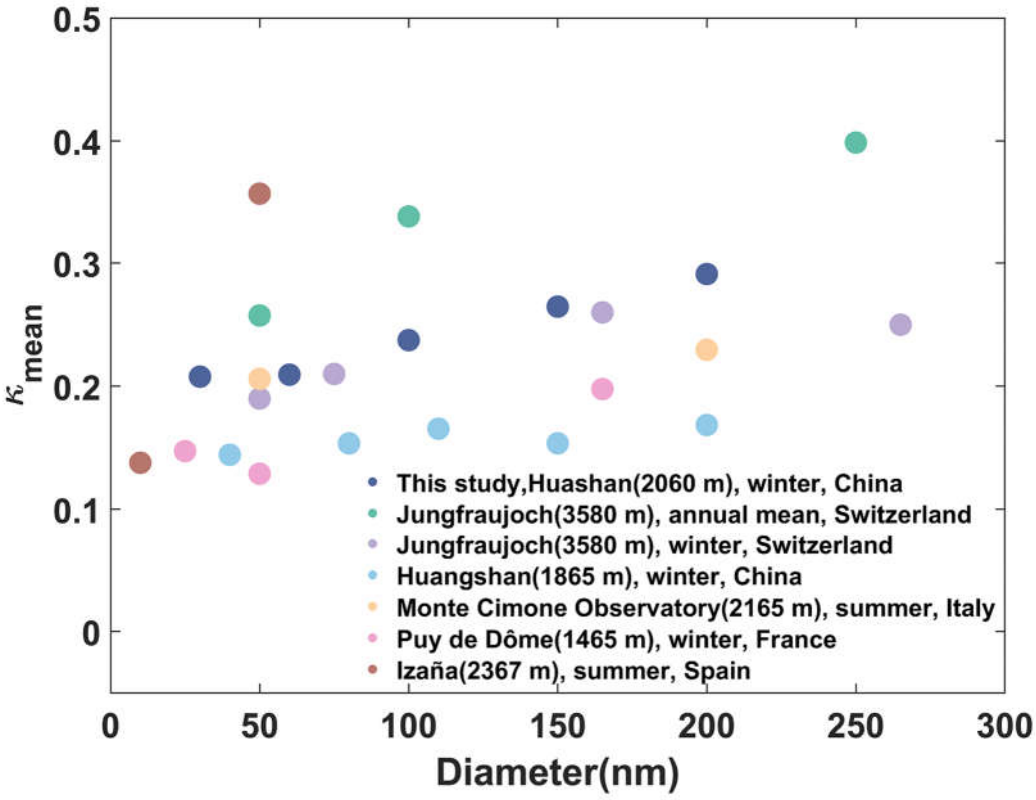

Figure 9. Comparison of aerosol hygroscopicity measured at different high-altitude sites around the world. (Figure 8 in manuscript)

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