Response to reviewer #2

Thank you for the positive feedback and helpful suggestions. We have addressed the comments and implemented all suggestions in the revised manuscript as detailed below.

The manuscript gives a report of aerosol hygroscopicity (HT-DMA) and composition (ACSM) measurements in the North China Plain. The authors examine data from two periods they identified based on ambient RH. They conclude that the observed difference in aerosol hygroscopicity between these two episodes was due to different chemical composition (specifically O:C ratio) of ambient aerosol particles.

The manuscript is generally written well and is fit for publication after the following issues are addressed.

1. HRH and LRH episodes and Figure 1. While the figure does give a (small and blurry) overview of the conditions during the measurement period, the actual numbers (and statistics) of the RH/T values for these periods should also be presented. Especially if these numbers are used to classify the measurement period into distinct episodes.

Response:

Thanks for this very constructive suggestion. We included more information for the two defined episodes (including both relative humidity and temperature). The following discussion was also added into the line 233 in section 4.1: "To be specific, the average RH during the HRH episode was 71% ± 22%, with an average temperature of 3 °C, while during the LRH episode the average RH was 43% ± 17%, with an average temperature of -6 °C."

2. Figure 1.

- Please make the plot larger and use higher resolution. If this is a limitation of the preprint stage of publication, then that's understandable, but for the final publication it should be more readable.

- Black line in κ plots – it's mentioned in the text what it is, but please add a label/description also to the figure itself or the caption.

Response:

Thank you for your comments. We modified Figure 1 with a better resolution, as shown below. Moreover, a description of the black line in Figure 1 of the revised manuscript was also added in its caption.

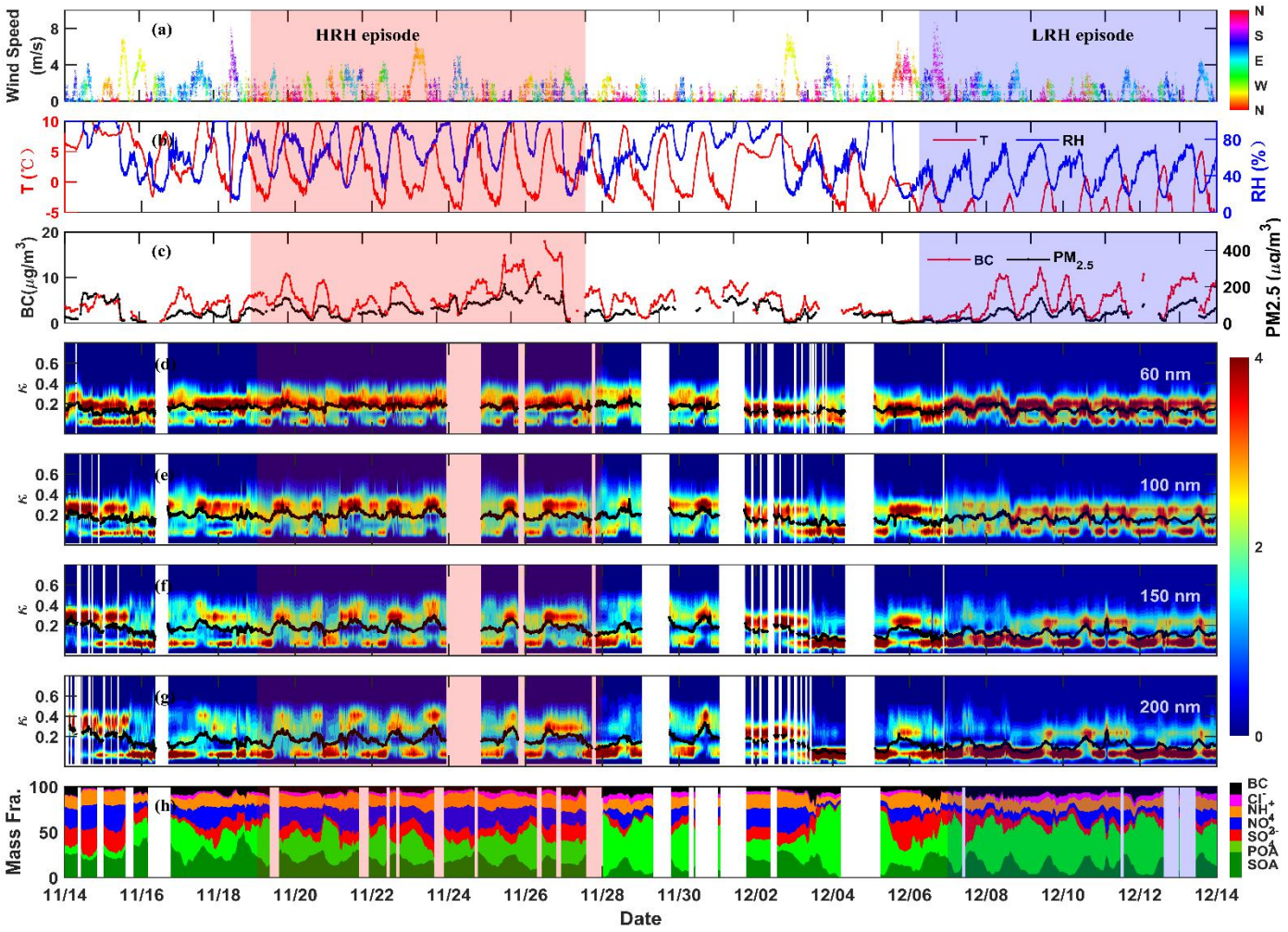

Figure 1: Time series of (a) wind speed and direction, (b) temperature and relative humidity, (c) $PM_{2.5}$ and BC mass concentrations, (d)-(g) the hygroscopicity parameter (κ) probability density function (κ-PDF) for particles at dry sizes of 60, 100, 150 and 200 nm (the black line is the averaged hygroscopicity parameter κ for particles at each size) and (h) mass fractions of the PM_1 chemical components during this field campaign.

3. Page 8, line 220: "*... mode were almost always observed for all sized particles ...*". Please quantify "almost always". Also, Fig. 1 seems to argue against that statement as the LH and MH modes are not continuous in time and have frequent gaps. As an example, LH mode for 100 nm particles during the HRH episode seems to be present (judging by the small plot) about 60% of the time.

Response:

We agree with the reviewer that current statement may not be proper and should be quantified. Therefore, we carefully analyzed the extent of external mixing during the whole campaign. By doing this, we assume that the cases that number fraction of less hygroscopic mode or more hygroscopic mode is less than 0.1 can be considered as internal mixing, where the other cases are external mixing. Based on this assumption, we found that less than 8 % of the time during the whole campaign could be

considered as internal mixing for all four sized particles. Thereby, we revised the statement in line 239 as: "Two distinct modes with $\kappa < 0.1$ as less hygroscopic (LH) mode and $\kappa > 0.1$ as more hygroscopic (MH) mode were mostly observed for all sized particles from the κ-PDF, indicating that the particles were mainly externally mixed during our measurements."

4. Figure 6: why was NFMH omitted from the plots?

Response:

Thank you for your comments. In our study, we considered our aerosols only consisting two modes: MH mode and LH mode. Therefore, NF of MH was actually 1- NF of LH mode, which is also the reason we omitted it from the plots.

5. Please include a description of and results from particle size distribution measurements mentioned in the manuscript (p. 13, after Eq. 5) and used to justify the use of 200 nm HT-DMA data.

Response:

Thank you for your comment. We plotted the averaged particle mass size distribution for the whole campaign, see the figure below, which we also added into the revised manuscript in the supplement. The discussion in line 492 at p. 14 was also modified accordingly.

"As the bulk chemical composition measured by ACSM may deviate significantly from that of size-resolved ones, we plotted the particle mass distribution of aerosols averaged over the entire campaign, see Fig. S1 in the supplement. From Fig. S1, we found that the mode size of the mass size distribution of aerosols during our experimental campaign was around 390 nm. Thereby, we considered that the bulk chemical composition measured by our ACSM could nearly reflect or at least be close to that of 200 nm particles."

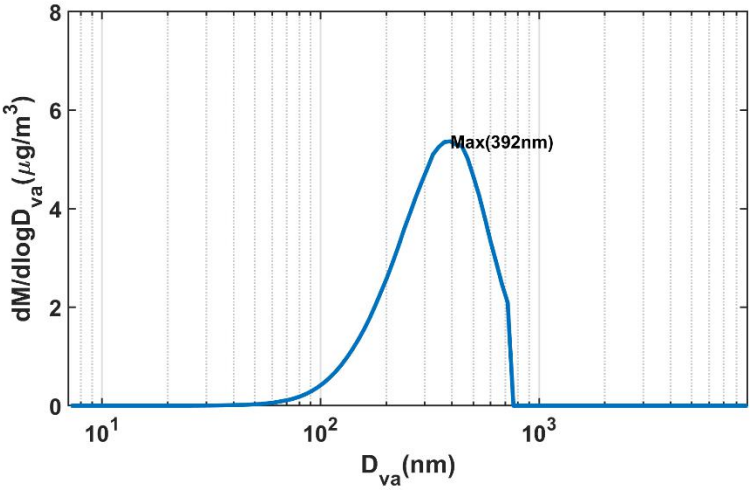

Figure 2: Particle mass size distributions.

6. Figure 8:

- What are the red points with error bars – averages over some range? Please describe.
- The figure caption says the red line is a fit to data. Should it be "black line" instead?
- How much did the ambient RH vary between individual data points on each plot? Looking at Figure 1, the RH had a fairly large diurnal variation. Also, one could almost group the individual

data points and see several trends. If the data points were, for example, colored by the ambient RH, would distinct groups emerge?

Response:

Thanks again for your detailed comments.

1) The red points (black in the revised one) in Fig.8 of the manuscript demonstrate the average κ_{SOA} data within a binned O: C with an increment of 0.1.

2) Yes, you are right. It should be the black line and we revised it accordingly.

3) We seriously considered the comment suggested by the reviewer and carefully examined how the ambient RH varied between individual data points. First, we found that during the nighttime of 6th Dec for LRH episode, ambient RH reached to as high as 100 %. These data points with such high RH level should not be considered as LRH condition based on its definition, thus we removed those data from the analysis for LRH episode. Therefore, Fig. 4-8 in the revised manuscript should be and was modified accordingly, which fortunately did not alter any conclusions that were previously obtained. Second, we replotted Fig. 8 of the manuscript by coloring the data points with ambient RH values, as shown in Fig. 3 in current file below. We speculated that the data points with similar RH ranges during both episodes might be emerged into distinct groups as suggested by the reviewer. In order to further confirm this, we divided the data points into two groups: RH < 60 % and RH > 60 % and separately analyzed the relationship between κ_{SOA} and the O:C for these two groups, as shown in Fig. 4 below. It has to be noted that the chosen of the threshold at RH of 60 % was based on the intensity of the concentrated colors, which might be arbitrary but still reasonable. We found that the results are interesting and still consistent with our aforementioned conclusion, which we added into the revised manuscript and extended the discussion. The discussion was listed below:

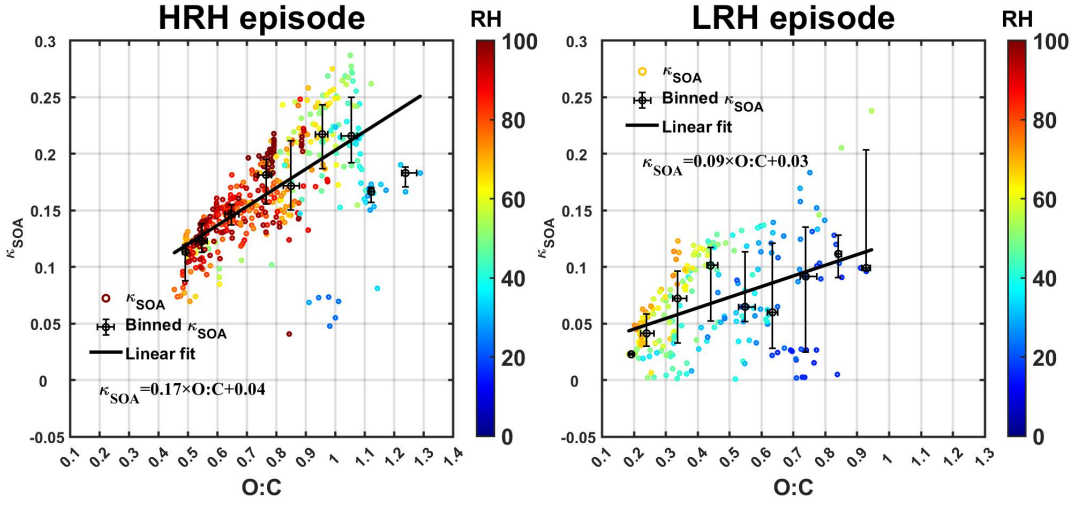

Figure 3: The plots of κ_{SOA} vs. O : C ratios during the HRH and LRH episodes. The black line is the fitting to the measured data. The black point is the data that κ_{SOA} values were binned by O: C with an increment of 0.1. The color bars indicate RH.

"As the ambient RH had a large diurnal variation during our campaign, which implies that low/high RH conditions may also be occur during any individual day of the HRH/LRH episode, we further grouped the data points of Fig. 8 into two categories according to their absolute RH values for these two episodes, as shown in Fig. 9. The threshold at RH of 60 % was set for these two categories due to the RH intensity spread in Fig. 8. At conditions of RH larger than 60 %, the hygroscopicity of SOA

under the HRH and LRH episodes both show a strong O:C-dependency, with the fitting under the LRH being more skewed. At RHs lower than 60 %, the relationship between κ_{SOA} and the O:C for these two episodes became even more closer. However, we observed that the absolute value of κ_{SOA} still varied between these two episodes, even at similar RH ranges, though their individual behavior towards the variation of O:C was similar. This implies that there still remain differences in these SOAs at different episodes but similar RH conditions, for instance, their chemical composition, indicating that the formation pathways of these SOA or the relevant reaction precursors might still be different under these two episodes. Thus, separation of these two episodes as previously defined was kept as the main conclusion was not altered and distinct groups with respect to their RH will not be merged further."

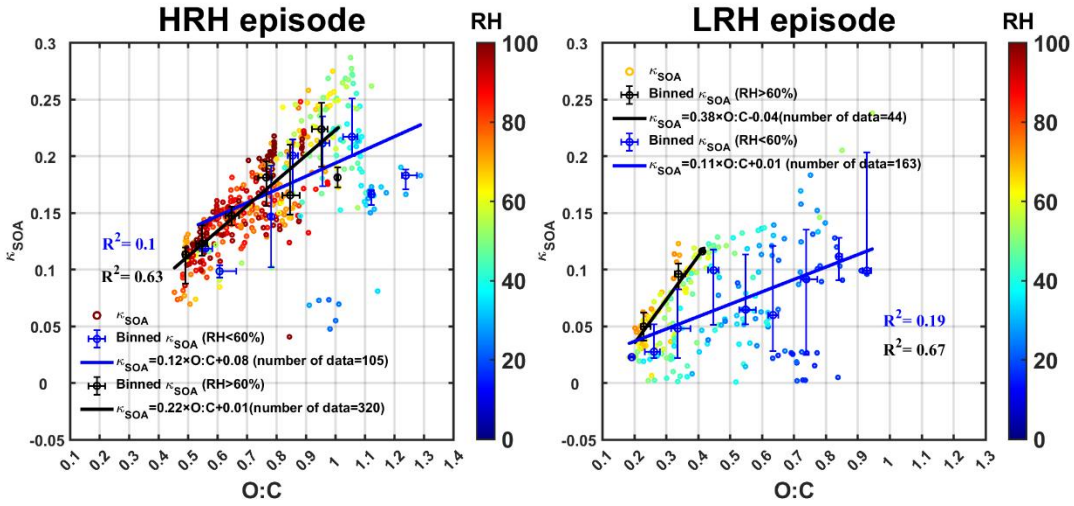

Figure 4: The plots of κ_{SOA} vs. O : C ratios during the HRH and LRH episodes. The black line and blue line are the fitting to the measured data at RH < 60 % and RH > 60 %, respectively. The blue and black point is that κ_{SOA} values were usually binned by O: C with an increment of 0.1. The color bars indicate RH.

7. Page 14, line 385: "... *RH ... was also quite high* ...". Please quantify "quite high".
Same comment for "... *low RH conditions* ..." on line 394 on the same page.

Response:

Thanks for the comment. We revised the sentences into: "The average RH during their study in Guangzhou was 72 %, being also quite high and thus suggesting potentially similar formation mechanism for secondary organic aerosols, e.g., aqueous-phase photochemistry as speculated previously." and "We found that during Wu et al. (2016)' study, ambient RH was 40 % on average. Thereby, we speculate that the similar characteristic in hygroscopicity of secondary organic aerosols in the NCP of both studies was likely due to the comparable low RH conditions, indicative of similar formation pathways."

Minor comments

8. Please check the use of underscore vs. dash throughout the manuscript. Examples include "*HT-DMA_measured*" and "*ACSM_derived*" on page 2.

Response:

Thank you for your comments. We modified the use of underscores and dashes, such as lines 44, 45, 296, 300, 484, 487, respectively.

9. Page 3, line 68: what varies – aerosol or composition?

Response:

To avoid misleading, we revised the corresponding discussion into: *"*Thus, ambient aerosols owing to their different sources and atmospheric processes, may vary greatly in their chemical compositions and thus show significant difference in their hygroscopicity.*"*

10. Page 3, line 83: "... *quite hygroscopicity* ...". Please review language.

Response:

Thanks for the comment. we revised the phrase"... quite hygroscopicity ..." to "... quite hygroscopic ...".

11. Page 6, line 162: missing "r" in "*analyzer*".

Response:

We changed "analyze" to "analyzer".

12. Page 9, line 229: sentence starting with "*Compared with* ...". Please review language and grammar. Currently it reads as if aerosols were somehow obtained and stored.

Response:

Thanks for the comment. To avoid confusion, we revised the corresponding description into: "The results in our study show that the aerosols at current station have the lowest hygroscopicity compared with aerosols in other cities or regions in China. This is more likely due to the largest contribution of organics relative to inorganic species in PM_1 at our observational site.".

13. Page 10, line 282: first sentence – please review language and grammar.

Response:

We revised the corresponding description into: "Organic fraction, which is another major component in aerosols, also varies significantly in hygroscopicity due to the exist of numerous and highly diverse organic compounds.".

14. Figure 5: suggest adding the meanings of the acronyms to the figure caption for easier reference.

Response:

Thanks for the comment. We revised the figure caption in Fig. 5 as: "A comparison of the PM_1 chemical composition during the HRH and LRH episodes. (BBOA: biomass burning organic aerosols, OOA: oxygenated organic aerosols, COA: cooking organic aerosols, HOA: hydrocarbon organic aerosols, CCOA: coal combustion organic aerosols)."

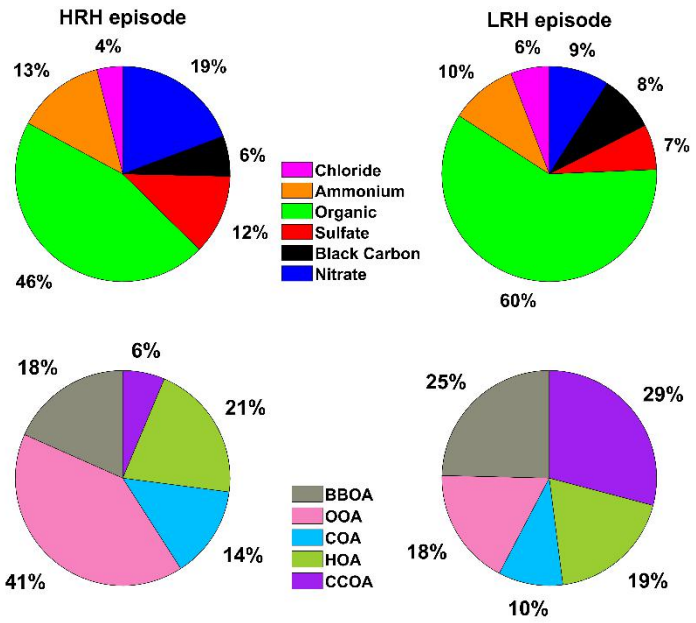

Figure 5: A comparison of the PM_1 chemical composition during the HRH and LRH episodes. (BBOA: biomass burning organic aerosols, OOA: oxygenated organic aerosols, COA: cooking organic aerosols, HOA: hydrocarbon organic aerosols, CCOA: coal combustion organic aerosols).

15. Page 11, line 291: Kuang et al. (2020) isn't on the references list.

Response:

Yes, we added it into the reference list.

16. Beginning of section 4.3: Figure 6 is discussed, but not referenced.

Response:

Thanks for the comment. We modified the sentence into: "To better understand the influence of human activities and secondary formation on the aerosol hygroscopicity of current study on a daily scale, we compared the diurnal variation of the number fractions and individual κ of LH and MH mode particles under these two episodes, as shown in Fig. 6.".

17. Eq. (5) on page 13: some of the text seems very small – were nested subscripts used by accident (from εBC onward)?

Response:

Thank you for your comments. We modified Eq. (5) on page 14 as suggested.

18. Page 14, line 383: "... *moderate**ly** hygroscopic*". Please fix.

Response:

Thanks for the comment. We modified "moderate hygroscopic" to "moderately hygroscopic" in the revised manuscript.

19. Page 14, line 392: please review language and grammar.

Response:

Thanks for the reviewer's specific comments. We rephrased the sentence as: "Similarly, Wu et al. (2016), performed in the urban area of the NCP, showed marginal increase in hygroscopicity with the O : C ratio, being approximate to the ones for our LRH aerosols.".

References

Kuang, Y., He, Y., Xu, W., Yuan, B., Zhang, G., Ma, Z., Wu, C., Wang, C., Wang, S., Zhang, S., Tao, J., Ma, N., Su, H., Cheng, Y., Shao, M., Sun, Y., 2020. Photochemical Aqueous-Phase Reactions Induce Rapid Daytime Formation of Oxygenated Organic Aerosol on the North China Plain. Environ. Sci. Technol. 54, 3849–3860. https://doi.org/10.1021/acs.est.9b06836

Wu, Z.J., Zheng, J., Shang, D.J., Du, Z.F., Wu, Y.S., Zeng, L.M., Wiedensohler, A., Hu, M., 2016. Particle hygroscopicity and its link to chemical composition in the urban atmosphere of Beijing, China, during summertime. Atmos. Chem. Phys. 16, 1123–1138. https://doi.org/10.5194/acp-16-1123-2016