

Response to reviewer #1

We appreciated referee#1's positive feedback and constructive suggestions which are of great value for improving the quality of our paper. Our point-to-point replies to the referee's comments are listed below.

The manuscript by Shi et al. reports measurements of aerosol hygroscopicity under high and low relative humidity scenarios in the North China Plain. The results show that the kappa values are higher which mean more hygroscopic during high humidity episodes (HRH) than during low humidity episodes (LRH). This distinct difference was attributed to the different chemical composition of the particles under the two scenarios, particularly the O:C ratio, an indicative of the oxidation level. Hygroscopicity is an important aerosol property and hence understanding the influencing factors and the controlling processes is essential to mechanistic understanding the aerosol formation and the climate effects. The paper is well-prepared and can be publishable after the following issues are fully resolved.

1. In section 4.2, the comparison of CCOA and OOA between the HRH and the LRH is qualitatively fine; however, it might be more accurate to consider the significant difference of the organic fraction between the two scenarios, for example, for CCOA, they become 59%*29% (0.17) vs 46%*6% (0.028) and for OOA, the values become closer, i.e., 59%*18% (0.11) vs 46%*41% (0.19).

Response:

Thanks for the specific comment. We added discussions about the difference in organic fractions between these two scenarios in Sect. 4.2: "We can see that the mass fraction of POA in the total organics during the HRH episode was 23 % lower than that during the LRH episode. In particular, CCOA, which is the main component of POA, accounted only for 6 % of the total organics under the HRH episode, but as much as 29 % under the LRH. Considering the distinct content of total organics between the two episodes, the difference in the mass fraction of CCOA in PM₁ would be even more significant, being 2.8 % (46 %*6 %) for the HRH and 17% (60 %*29 %) for the LRH. The high level of CCOA in aerosols could be explained that during the LRH episode, the wintertime residential heating was initiated, during which a significant amount of its pollutants, for instance, CCOA, was emitted to the atmosphere (Hua et al., 2018). Moreover, we observed that the mass fraction of OOA in PM₁ during the HRH episode was 19% (46 %*41 %), being different from that (11%, e.g., 60 %*18 %) during the LRH, though only slightly higher. Thereby, the varied level of different organics in PM₁ could be one of the plausible reasons for the different κ in 200 nm between these two episodes."

2. The description (lines 290-300 on p.11) of reaction mechanism for the two periods might need to be noted since there are no more evidences to dig out the formation mechanisms during the two periods. It seems they are just speculated in this case.

Also, the average RH values for both periods should be given and compared to Sun et al. and Yu et al.'s studies. Similar notices should be given when describing Fig. 6e for the mechanisms (lines 327-329) in section 4.3.

Response:

Following the reviewer suggestion, we revised the discussion part of this paragraph. On the other hand, Kuang et al. (2020) only compared the oxidation level of OOA formed through gas-phase or aqueous-phase reaction with the ones generated in laboratory measurements by Sun et al. (2010) and

Ye et al. (2014). However, no comparison in ambient or experimental RH was specified in their works. Hence, the average RH values cannot be compared to the studies by Sun et al. (2010) and Yu et al. (2014), but instead with Kuang et al. (2020). The revised discussion was listed below:

“Kuang et al. (2020) specifically studied the formation mechanism of secondary organic aerosols for current campaign. They found that the daytime OOA formation rates correlated quite well with nitrate formation rates and thus suggested that they probably shared similar formation pathways. They further investigated the formation pathways of nitrate and concluded that during the low RH conditions, nitrate was mainly formed by the gas-phase oxidation of NO₂, while at the high RH conditions, both the aqueous-phase processes and gas-phase oxidation dominated its formation. Furthermore, they considered that gas-phase formation of OOA would mainly add mass to the condensation mode of aerosol size distribution, while aqueous-phase formation of OOA may elevate the mass in the droplet mode. After studying the diurnal evolution of aerosol mass distribution for high RH and low RH conditions, together with the indirect evidence from nitrate formation, they concluded that gas-phase formation contributed dominantly to the OOA under the low RH conditions, while at high RH conditions, when aerosol water content was high, aqueous-phase photo-oxidation were mainly responsible for the rapid OOA formation, beside the gas-phase formation. According to their further comparison with laboratory experiments (Sun et al., 2010; Yu et al., 2014), they suggested that the OOA formed through aqueous-phase reactions were normally more-oxidized compared to that formed by gaseous processes. It needs to specify that the average RH values for the HRH and LRH episode during our campaign were 71 % and 43 %, respectively, being quite close to the ones (53 % & 38 %) for the two defined RH conditions in Kuang et al. (2020). Taking all together, this could reasonably to presume that the observed lower κ for 200 nm particles under the LHR episode, not only due to the elevated POA fraction in aerosols, but also a different hygroscopic nature of OOA, compared to that under HRH.”

For the description of Fig.6e, we revised it as: “During daytime when solar radiation is stronger, higher concentration of atmospheric oxidant was typically observed (Hong et al., 2015). Thus, the associated photochemistry and other aging processes would be more favorable, leading to a more oxidized material condensing or partition into the existing aerosols and thus an elevated aerosol hygroscopicity being expected.”

3. The title of section 4.4 needs to be modified to reflect its content. This section describes the correlation between the O/C ratio and the kappa value under the two scenarios. The current title is similar to that of section 4.2. In addition, is there a better way to describe the oxidation state (level) except for the O/C ratio?

Response:

Thanks for this very constructive suggestion. According to the reviewer's suggestion, we used “Relating the SOA hygroscopicity to its oxidation level for the two episodes”.

Besides the O/C ratio, the oxidation state (OSc) is a more robust way to describe the oxidation level of organic fractions as it is not influenced by the hydration and dehydration in the atmosphere. Therefore, we calculated the OSc of organics according to Canagaratna et al. (2015) and replotted Figure 8 as shown below. Similar relationship between the SOA hygroscopicity and its oxidation state was

obtained compared to that using the O/C ratio, though the slope of the fitting line is two times larger, which is actually due to $OSc = 2 \times O : C-H : C$. As the main conclusion still holds and the O:C ratio was widely adopted in many previous studies, we kept the original figure using the O:C ratio in order to facilitate any possible future comparison.

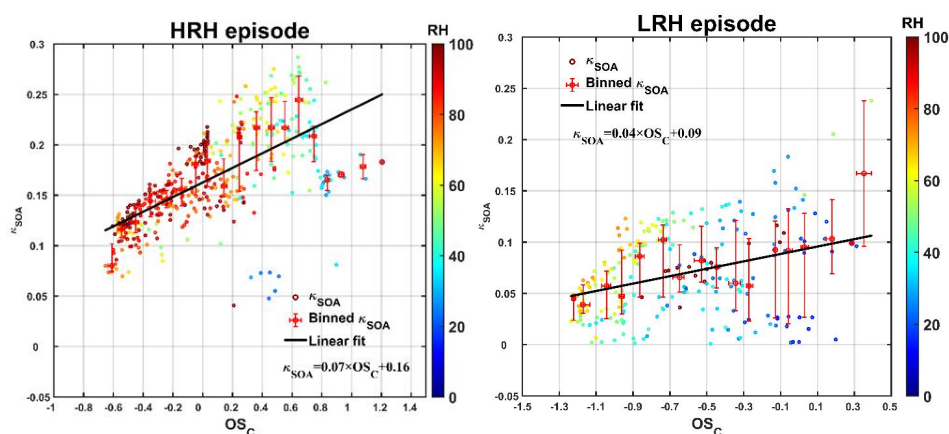


Figure 1: The plots of κ_{SOA} vs. OSc during the HRH and LRH episodes. The black line is the fitting to the measured data. The red point is that κ_{SOA} values were binned by OSc with an increment of 0.1. The color bars indicate the measured RH.

Technical Corrections

4. Line 35 on p.2, “particles” should be deleted;

Response: We deleted “particles” in the sentence in line 35.

5. Line 68, “which” here is referred to chemical composition or ambient aerosols, it seems ambiguous;

Response:

As suggested by the reviewer, we modified the sentence 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.”

6. Lines 78-79, “There also remain ... more hygroscopic”, this is an ill sentence;

Response:

Thanks for the comment. We modified the sentence into: “There are also some other studies, which focused on the secondary formed or aged aerosols, being typically characterized as more hygroscopic.”

7. Lines 89, “since decades”? You probably cannot say “since tens of years”, right?

Response:

Yes, we used “over the past decade” instead of “since decades”.

8. Line 90, “leaded to a fast...”?

Response:

Thank you for your comment, we changed “leaded to a fast...” into: “led to a fast...”.

9. Line 94, it is “showed” not “shown”;

Response:

Thank you for your comment. We revised “shown” to “showed”.

10. Line 97, “extensive efforts to investigated the...”?

Response:

Thanks for the comment. We changed “investigated” into: “investigate”.

11. Line 100, I think it is better not to use article before “different sources” here;

Response:

Thanks for the comment. We modified the sentence into: “Thus, the representative feature that how different sources, including both the primary emissions and secondary processes, impact the hygroscopicity of NCP aerosols still remains unclear.”

12. Line 224, don’t need “the experimental”;

Response:

We deleted “the experimental” in the sentence in line 245.

13. Line 237, “this phenomenon” not “this phenomena”;

Response:

Thank you for your comment, we changed “this phenomena” into: “this phenomenon”.

14. Line 269, “usually considered as mainly from...”, as here is a pronoun so it needs an object;

Response:

Thanks for the comment. We modified the sentence into: “usually considered to be mainly from ...”.

15. Line 288, “by” should be deleted;

Response:

Thanks for the comment, we deleted “by” in the sentence in line 331.

16. Line 343, “contribute” needs a “to” here;

Response:

We added “to” after “contribute” in the sentence in line 470.

17. Line 379, it is better to change “has to be” to “was” here;

Response:

We changed “has to be” to “was” in line 533.

18. Line 392, “marginally increase” should be “marginal increase” as increase is a noun here.

Response:

Thanks for the comment. We modified “marginally increase” to “marginal increase” in line 547.

References

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