

Anonymous Referee #2

In this manuscript, Fan et al. measured the hygroscopicity and chemical composition of the size-resolved aerosols at several locations in northern China, and calculated the hygroscopic parameter (κ) based on both the hygroscopic growth factor from HTDMA measurement (κ_{gf}) and the chemical composition from HR-AMS measurement (κ_{chem}). By comparing κ_{gf} and κ_{chem} , this study demonstrates clear and undisputed evidence of possible bias in estimating aerosol hygroscopicity using the chemical mixing rule. Moreover, Fan et al. provides reasonable insight on the influence of atmosphere process and aerosol mixing state on the calculation of aerosol hygroscopicity. The manuscript is well organized and written. I will recommend the publication of this manuscript in ACP, as long as the following comments are properly addressed. Note that comments 4-6 are just suggestions.

Re: We are grateful to reviewer 2 for the insightful and constructive comments and have revised our paper accordingly to account for the reviewer's recommendations.

(1) A major discovery of the paper is that κ_{chem} calculated using the mixing rule cannot reflect the aerosol hygroscopicity. For example, it is found that the κ_{chem} in summer is underestimated at noon, overestimated at late peak hours, and substantially consistent with κ_{gf} at midnight. Though I think the results should be correct, I am not fully convinced by some of the interpretation. (a) Why the external mixing of BC and POA with other components during the late peak hour will result in overestimation of κ_{chem} ?

Re: The emission of a large number of primary hydrophobic particles like BC and

POA leads to great decrease of the overall aerosol hygroscopicity. We have included discussions and statements in the revised manuscript (lines 319-346, Fig. 8) as follows (Fig. R3),

“...We suppose that the large disparity between κ_{chem} and κ_{gf} is due to temporal variations in actual density of BC and organics caused by the particles aging and local sources. The externally-mixed BC particles are with fractal structure and chain-like aggregates and have been reported with effective density of 0.25-0.45 g cm⁻³(McMurry et al., 2002), While the BC particles in the calculation is assumed as void free with effective density of 1.7 g cm⁻³. Such inappropriate assumption would lead to an underestimation of BC volume fraction and thus the overestimation in κ_{chem} during the traffic rush hour and cooking time when BC particles are mostly freshly emitted with uncompacted structure. In addition, the significant increase in volume fraction of POA during the late afternoon would result in a lower density of organics, which is expected to be smaller than the assumed one (1.2 g cm⁻³) in the calculation. A sensitivity test has been done to examine the effect of density of BC and organics on calculated κ_{chem} (Fig. 7). The result shows that the κ_{chem} value reduces by 16-33% when applying the BC effective density of 0.25-0.45 g cm⁻³. This basically explains the disparity during the traffic rush hour. However, the changes in κ_{chem} are within $\pm 4\%$ when changing the organic density from 1.0 (typical for POA) to 1.4 (typical for SOA) g cm⁻³, suggesting insensitivity of κ_{chem} to variations of organic density. The result also indicates that, to fill the gap between κ_{chem} and κ_{gf} observed at noontime, the effective density of BC should be extremely high due to the decreased sensitivity of κ_{chem} to BC density with the aging of BC. In this case, the assumed density of BC is 1.7 g cm⁻³, which reflects a very compacted and void free structure of the BC particles. The current applied value represents an upper limit for the effective density of ambient BC particles according to previous observations at a site near urban Beijing (Zhang et al., 2015), which suggested the aged BC is generally with effective density of 1.2 g cm⁻³. Using this ambient observed density would lead to further underestimation in κ_{chem} . Our results exhibit the increase of the density of BC and organics cannot explain the disparity between κ_{chem} and κ_{gf} observed around noontime in summer. This just, on the other hand, verifies the photochemical aging/coating effect on the aerosols hygroscopicity. In addition, the coexisting hygroscopic and hydrophobic species may have a strong influence on the phase state of particles, also likely affecting chemical interactions between inorganic and organic compounds as well as the overall hygroscopicity of mixed particles (Peng et al., 2016). Further investigations are needed to verify this. Our study suggest that, to accurately parameterize the effect of BC aging on particles hygroscopicity, future investigations need to measure the effective density and morphology of ambient BC, in particularity in those regions with complex local sources.....”

(a)

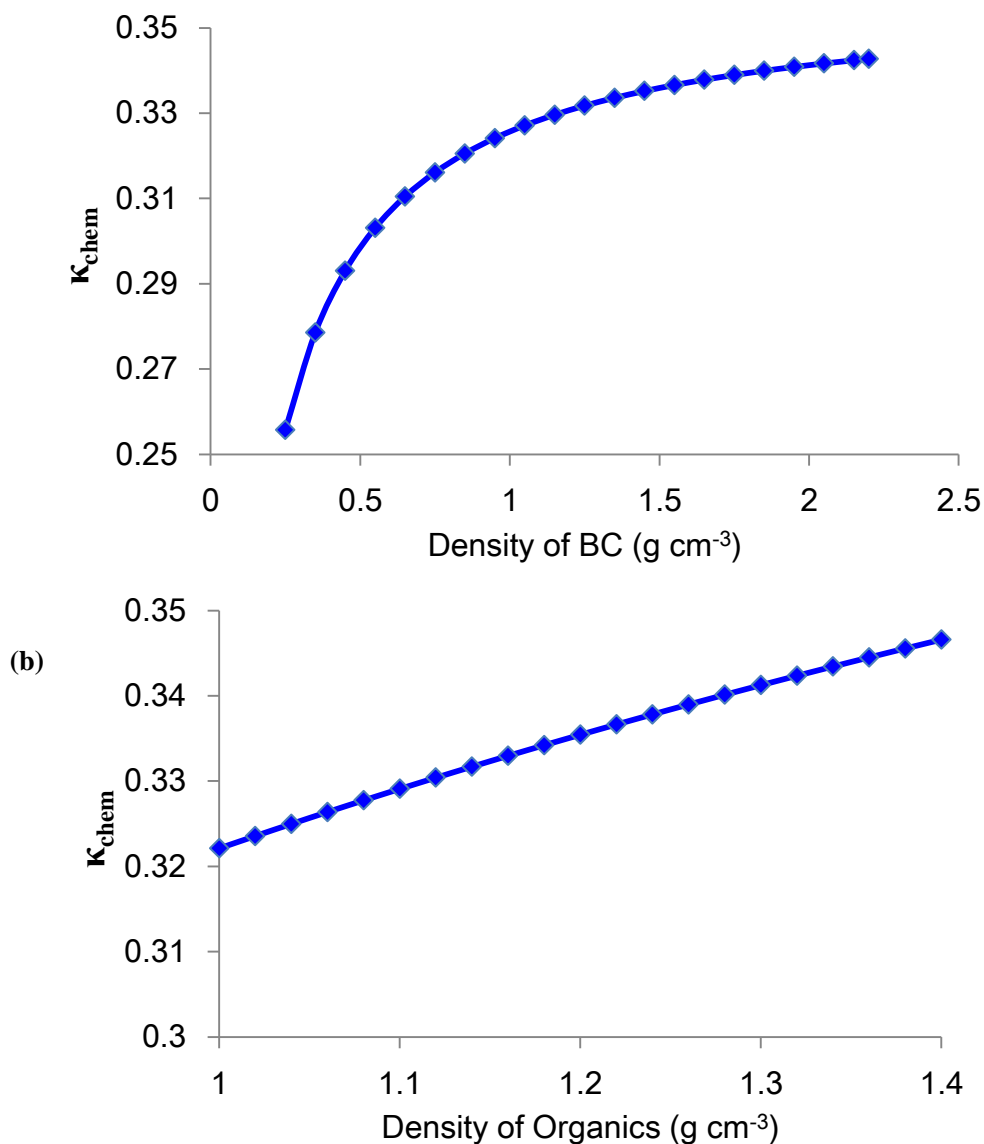


Figure R3. Sensitivity of κ_{chem} to variations of density of BC (a) and organics (b)

(b) According to the author's argument, aerosols both at noon and at midnight have core-shell structure, but why the $\kappa_{\text{chem}}/k_{\text{gf}}$ is quite distinct? More detailed interpretation and discussion are necessary.

Re: At noontime, the rapid photochemical aging of BC particles leads to the core-shell structure in which certain secondary aerosol generated from photochemical reactions is thickly coated on the surface of BC. However, the condensation effect during

nighttime is less significant (indicated by the smaller disparity between κ_{chem} and κ_{gf}) than the coating effect caused by aerosols photochemical aging at noontime, due to thinner coating layer formed on the pre-exist particles during nighttime or other factors influencing the particles hygroscopicity. We have included a statement in the revised manuscript (see lines 367-373) as follows,

“...We propose the increased underestimation during polluted conditions is likely due to enhanced condensation of secondary hygroscopic compounds (e.g. nitrate, sulfate) on pre-existing aerosols at lower temperature and higher relative humidity at nighttime (Wu et al., 2008; Wang et al., 2016; An et al., 2019). However, such condensation effect during nighttime is less significant (indicated by the smaller disparity between κ_{chem} and κ_{gf}) than the coating effect caused by aerosols photochemical aging at noontime, likely due to thinner coating layer formed on the pre-exist particles during nighttime or other factors influencing the particles hygroscopicity....”

(2) L259, “Since a size-resolved BC mass concentration measurement was not available during the campaign, we use the bulk mass fraction of BC particles measured by the AE33 combining with size-resolved BC distribution in Beijing reported by Liu et al. (2018) to estimate κ_{chem} .” As far as I know, the instrument to measure the size distribution of BC in Liu et al. (2018) is a SP2, which gives the BC core diameter. It is necessary to explain how to convert this size distribution of BC core to the size distribution of ambient aerosols.

Re: We have provided a statement in the revised version as following (also see lines 260 -263),

“...During the calculation, the BC core diameter measured by SP2 has been converted to the diameter of coated BC particles by multiplying factors of 1.4 and 2.6 under clean (with bulk BC mass concentrations $<2 \mu\text{g m}^{-3}$) and polluted (with bulk BC mass concentrations $>2 \mu\text{g m}^{-3}$) conditions respectively (Liu et al., 2018). ...”

(3) L227 and fig. 3. “the concentration of the hydrophilic mode increased quickly around noontime and in the early afternoon (12:00-16:00)”, which is explained by a transformation of the particles from externally to internally mixing state. However, I

have different opinion. From Fig. 3a, it is evident that 40 nm particles after 12:00 were dominated by new particle formation (NPF). Therefore, the decrease of hydrophobic mode could be attribute to the extremely large amount of hydrophilic particles from NPF overwhelmed all other particles.

Re: Thanks a lot for the comments. We have revised and included an explanation of “In addition, it is evident that 40 nm particles after 12:00 were dominated by NPF (Fig. 3). Therefore, the increase of hydrophobic mode particles suggests that a large amount of hydrophilic particles are generated from NPF.” in the revised manuscript (see lines 220-222).

(4) It will be better if the authors can discuss more on the similarities and differences of the hygroscopicity calculation at different sites.

Re: We have provided more details on clarify how we derive and calculate the particles hygroscopicity at different sites (lines 179-189) as follows,

“...In addition, we also compare the results from the field campaigns with those from other two sites, Xingtai (XT: 37.18 °N, 114.37 °E), and Xinzhou (XZ: 38.24 °N, 112.43 °E), in North China Plain (Fig. 1). At XZ site, we use the hygroscopic parameter (defined as κ_{CCNc}) from size-resolved CCN measurements (Zhang et al., 2014, 2016) for comparison. More detailed descriptions of the method to retrieve κ_{CCNc} can be found in (Petters and Kreidenweis (2007)). Both of the κ_{gf} and κ_{CCNc} are derived based on κ -Köhler Theory (Petters and Kreidenweis, 2007). But, different from the κ_{gf} measured by the HTDMA system which is operated at RH of 90%, the κ_{CCNc} is derived by measuring aerosols CCN activity under the condition of supersaturations with relative humidity of >100%. Previous studies from filed measurements and laboratory experiments showed that the κ_{CCNc} is generally slight larger or smaller than κ_{gf} , but they are basically comparable and can well represent an overall aerosols hygroscopicity (e.g. Carrico et al., 2008; Wex et al., 2009; Good et al., 2010; Irwin et al., 2010; Cerully et al., 2011; Wu et al., 2013; Zhang et al., 2017).”

(5) There have been several studies revealing the uncertainty of calculating hygroscopicity using the mixing rule, but few can provide proper solution. Is it possible for the authors to propose parameterized modification on the κ_{chem} to reduce

the uncertainty? If so, this paper will be enormously improved and will be far distinct from other studies. For example, should we use lower BC density value during the rush hours?

Re: This is a good point. We have made a sensitivity test to examine the effect of density of BC on calculated κ_{chem} , and included statements and discussions about this in the revised version (lines 319-346, Fig. 8) as follows (Fig. R4),

“...We suppose that the large disparity between κ_{chem} and κ_{gf} is due to temporal variations in actual density of BC and organics caused by the particles aging and local sources. The externally-mixed BC particles are with fractal structure and chain-like aggregates and have been reported with effective density of 0.25-0.45 g cm⁻³ (McMurry et al., 2002). While the BC particles in the calculation is assumed as void free with effective density of 1.7 g cm⁻³. Such inappropriate assumption would lead to an underestimation of BC volume fraction and thus the overestimation in κ_{chem} during the traffic rush hour and cooking time when BC particles are mostly freshly emitted with uncompacted structure. In addition, the significant increase in volume fraction of POA during the late afternoon would result in a lower density of organics, which is expected to be smaller than the assumed one (1.2 g cm⁻³) in the calculation. A sensitivity test has been done to examine the effect of density of BC and organics on calculated κ_{chem} (Fig. 7). The result shows that the κ_{chem} value reduces by 16-33% when applying the BC effective density of 0.25-0.45 g cm⁻³. This basically explains the disparity during the traffic rush hour. However, the changes in κ_{chem} are within $\pm 4\%$ when changing the organic density from 1.0 (typical for POA) to 1.4 (typical for SOA) g cm⁻³, suggesting insensitivity of κ_{chem} to variations of organic density. The result also indicates that, to fill the gap between κ_{chem} and κ_{gf} observed at noontime, the effective density of BC should be extremely high due to the decreased sensitivity of κ_{chem} to BC density with the aging of BC. In this case, the assumed density of BC is 1.7 g cm⁻³, which reflects a very compacted and void free structure of the BC particles. The current applied value represents an upper limit for the effective density of ambient BC particles according to previous observations at a site near urban Beijing (Zhang et al., 2015), which suggested the aged BC is generally with effective density of 1.2 g cm⁻³. Using this ambient observed density would lead to further underestimation in κ_{chem} . Our results exhibit the increase of the density of BC and organics cannot explain the disparity between κ_{chem} and κ_{gf} observed around noontime in summer. This just, on the other hand, verifies the photochemical aging/coating effect on the aerosols hygroscopicity. In addition, the coexisting hygroscopic and hydrophobic species may have a strong influence on the phase state of particles, also likely affecting chemical interactions between inorganic and organic compounds as well as the overall hygroscopicity of mixed particles (Peng et al., 2016). Further investigations are needed to verify this. Our study suggest that, to accurately parameterize the effect of BC aging on particles hygroscopicity, future investigations need to measure the effective density and morphology of ambient BC, in particularity in those regions with complex local sources.....”

(6) For several times, the current manuscript cited Zhang et al. (2017), which is one

of the previous studies done by the same group on the same topic. Therefore, it is appropriate to make a clear statement of the unresolved issues in the previous paper or what improvement has been made to this study so that the reader can easily understand the novelty of this paper.

Re: We have included the following statement in the revised version (also see lines 77-82),

“...In the atmosphere, the κ , which is related to the particle mixing state diversity, varies largely across the size range of ambient fine particles (Rose et al., 2010). Previous study only compared the measured κ to that calculated based on bulk chemical composition (Zhang et al., 2017). Using size-resolved, not bulk, chemical composition measurements in different seasons is expected to provide more comprehensive understanding and insights of how the aerosols mixing state influence on their hygroscopicity, motivating our analysis that employs size-resolved chemical composition measured by an HR-ToF-AMS in this study.”

Other minor comments:

(1) fig. 2 is not reader-friendly. Please work out some way to make the information more clear.

Re: Revised.

(2) fig.3. There are totally 12 sub-figures here. Please consider naming each sub-figures rather than the current way (which is not clearly demonstrated).

Re: Revised.

(3) L150 and L160, the full term and the abbreviations of probability density functions (PDF) should be provided the first time in the text.

Re: Revised.

(4) Fig. 5, L266, should be “slopes of linear fits and correlation coefficients”.

Re: Revised.