

Anonymous Referee #1

In this manuscript in discussion for publication in Atmospheric Chemistry and Physics (acp-2019-583), Xinxin Fan and co-authors present a field study comparing aerosol hygroscopicity in summer months relative to the those measured in winter. Measured hygroscopicity was compared to hygroscopicity based on HR-ToF-AMS measurements of composition for Beijing and northern China. The focus on this work was mixing state as a potential cause of the discrepancy between measured and estimated hygroscopicity. Interesting observations are presented and discussed in a mechanistic framework. This work is part of a larger effort to understand the air quality in China, and is important and timely. I have significant concerns, however, about the novelty of the study and the presentation of the data, which I have outlined below. The data and study de-sign are not novel, and in fact several of the same authors have written a very similar manuscript (published in ACP: <https://www.atmos-chem-phys.net/18/11739/2018/acp-18-11739-2018.pdf>) from the same field campaign.

The preparation of figures as clear and succinct visual aids to the writing is poor, and the authors invoke limited and dated studies on water uptake by mixtures of compounds. These issues could potentially be resolved with appropriate major revisions.

Regarding the novelty of the manuscript, I would urge the authors to share in the introduction the previous findings for the same dataset or the co-located instruments.

It is not clear at present the degree of overlap but it is not the policy of ACP to publish

the same data, analysis, and interpretation twice.

The difference between (for example) the CCN and HTDMA needs to be clearly stated in both the method and the interpretation and discussion of underlying physical processes. If the authors do not differentiate effectively between the scientific questions answered by similar instruments, then the study is essentially the same as the published study. This can likely be resolved but will require careful effort.

Re: We appreciate your comments. The reviewer argued that the paper published in ACP and this currently submitted one is very similar manuscript from the same field campaign. This is probably because that some vague descriptions on instruments in the Section 2.1 which may have mislead the reviewer. Indeed, the main data used in the two papers are from different campaigns, the data used in this work are from two field campaigns during November 16-December 10 of 2016 and May 25- June 18 of 2017 in urban Beijing, however, the published ACP paper just used the data from Xingtai campaign which was conducted during 1 May-15 June 2016. These have been clarified in the revised manuscript (See lines 92-98, 383-393). Furthermore, the previous paper published in ACP focused on investigating and characterizing the aerosol hygroscopicity and CCN activity at the suburban site of Xingtai, which is located about 420 km south of urban Beijing. But in the current submitted paper, we compare the size-resolved hygroscopic parameter (κ_{gf}) of ambient fine particles derived by an HTDMA (Hygroscopic Tandem Differential Mobility Analyzer) to that (denoted as κ_{chem}) of calculated by an HR-ToF-AMS (High-resolution Time-of-Flight Aerosol Mass Spectrometer) measurements using a simple rule with a uniform

internal mixing hypothesis. We mainly focus on contrasting the disparity of κ_{gf} and κ_{chem} between summer and winter in urban Beijing to reveal the impact of atmospheric processes/sources on aerosols hygroscopicity and to evaluate the uncertainty in estimating particles hygroscopicity with the hypothesis. Only in the last section (Section 3.5) of this paper, we include the observations at other sites (not only Xingtai site) just for comparison with that observed in urban Beijing. Such comparison among different sites is to identify the impact of regional emissions/sources and atmospheric processes under different environments on estimating aerosols hygroscopicity with the uniform internal mixing hypothesis. One important findings of this current paper is that, for the first time, we observe clearly that atmospheric photochemical aging of aerosols induces a coating effect from field measurement. Such effect leads to 10%-20% underestimation of the hygroscopic parameter if using the uniform internal mixing assumption. The coating effect is found more significant for these >100 nm particles observed in remote or clean regions. Our results suggest that it is critical to parameterize such an impact in model simulations to improve the evaluation of the aerosols indirect effect. In addition, in the revised version, we have made a sensitivity test to examine the effect of temporal variations in actual density of BC and organics caused by the particles aging and local sources on calculating κ_{chem} (see lines 319-346).

The figures have been revised carefully according to the comments (see the revised Fig. 1-Fig. 9).

In addition, more previous studies and references on water uptake by mixtures of

compounds have been included in the introduction, and some words about the definition of mixing state have been removed in the revised version. The revised introduction is as follows,

“ ...The hygroscopic properties of both the natural and anthropogenic aerosols, in addition to being affected by its chemical composition (Gunthe et al., 2009), are also affected by the particle mixing state and aging (Schill et al., 2015; Peng et al., 2017). For example, a recent laboratory study shown that the coexisting hygroscopic species have a strong influence on the phase state of particles, thus affecting chemical interactions between inorganic and organic compounds as well as the overall hygroscopicity of mixed particles (Peng et al., 2016). The field measurements also demonstrated that the hydrophobic black carbon particles became hygroscopic with atmospheric mixing and aging by organics (i.e. Peng et al., 2017). In a heavily polluted atmosphere, the aerosol sources and sinks are varied, the physical and chemical processes experienced by the aerosols are complex, and the mixing state and its impact on aerosols hygroscopicity is more complicated. The hygroscopicity of mixed particles and mutual impacts between the components are still poorly understood.

Previous studies have shown that the difference between the κ obtained from H-TDMA or CCNc measurements and that calculated based on the volume mixing ratio of chemical components, κ_{chem} . Laboratory results from Cruz and Pandis (2000) indicate that κ_{gf} of internally mixed ammonium sulfate and organic matter is higher than κ_{chem} calculated for assumed uniform internal mixing. But Peng et al (2016) found that, for sodium chloride and organic aerosols mixed particles, the measured growth factors by H-TDMA were significantly lower than calculations from the mixing rule methods. In some field studies on aged aerosols, the κ was underestimated by the calculation based on uniform internal mixing assumption and thus lead to an underestimation of CCN concentration (Bougiatioti, et al., 2009; Chang, et al., 2007; Kuwata, et al., 2008; Wang, et al., 2010; Ren et al., 2018). However, for primary emissions dominated periods, the κ value from calculations based on bulk chemical composition was much higher than that measured by H-TDMA measurements (Zhang et al., 2017). The various results from previous studies suggest distinct effects of aerosols mixing state on their hygroscopicity. Overall, to what extent do the differences depend on the mixing state and the extent of aging of the particles, and how the different atmospheric processes and what kinds of mixing structure of the particles may result in those disparity between measured and calculated hygroscopic parameter have not been clearly clarified by the previous studies. A comprehensive and systematic investigation on the cause and magnitude of the effect has been lacking.

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....”

The difference between (for example) the CCNc and HTDMA has been stated in the revised version (see lines 179-189) or 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)...”

Comments on figures and interpretation of figures:

The figures do not always serve as appropriate and helpful guides to the writing. The number of figures in both the manuscript and the supplement could be reduced. Not all figures are discussed, and several figures seem to be entirely redundant. The data in the figures is difficult to interpret due to the overlapping error bars.

Re: As commented by the reviewer, we have considered how to organize the figures very carefully, and removed most of the figures in both the main manuscript and the supplement in the revised version. In addition, the Figures in the main text were replotted due to the overlapping error bars (see the revised Fig. 1-Fig. 9).

Figure 3: It's not clear why this figure does not take the full page width, as it already seems to exceed a 1-column width. It would be helpful to include markers for “morning traffic,” “afternoon traffic,” or other factors that influence these timeseries. The reader is without a frame of reference. Also, in the caption it would be helpful to see the location for these time series, or whether these are averaged for all sites.

Re: The figure and caption have been revised per the reviewer's comments (see below),

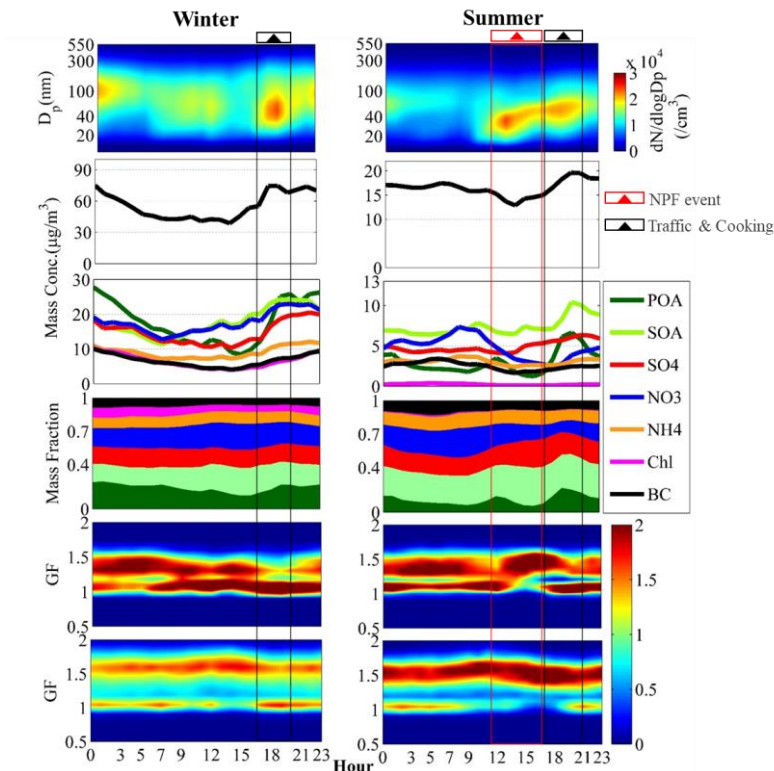


Figure R1. Campaign averaged diurnal variations in particle number size distribution; mass concentration of PM_{10} , bulk mass concentration of main species in PM_{10} , mass fraction of chemical composition of PM_{10} ; and Gf-PDFs for 40 and 150 nm particles in winter (left panels) and summer (right panels) measured in urban Beijing.

Line 218: Figure 3e is referenced before any discussion of all the other panels in Figure 3.

Re: The Fig.3 has been mentioned in the previous paragraph before line 218. However, corresponding revision of the text has been done according to the correction on Fig. 3.

Figure 5: Authors neglect to describe the two lines on each plot; are the R2 values first or second in the parentheses? Are the 1:1 lines anchored at 0? There seems to be little to no correlation between κ_{chem} and κ_{gf} .

Re: Thanks a lot for the careful check. In the revised version, we have added the description about two lines. The first number in parenthesis of each plot is the slope of

the fit line, and the second is the correlation coefficient (R^2). In figure 5, all 1:1 lines are anchored at 0. Exactly, the correlations between κ_{chem} and κ_{gf} of the 80, 110, 150, 200 nm particles both in winter and summer are poor due to the large uncertainty in one or both of the calculated parameters. The large uncertainties are likely due to the unreasonable assumption of particle mixing state, which varies with their aging and other physiochemical processes in the atmosphere. This has been stated in the text.

Line 275: These numbers don't match the figure. With R^2 values of 0.01-0.23 for the κ_{chem} and κ_{gf} correlations, I would hesitate to report the slope of the fit line. Anchoring the line and a value other than (0,0) would give a different slope with a similar R^2 value.

Re: Yes, the reviewer is right. The discussion about the slopes and R^2 has been revised (See lines 272-280) as follows,

“...The results show that, although the slopes from linear fitting of κ_{chem} and κ_{gf} are close to 1.0, it is with quite poor correlations (typically with correlation coefficients, R^2 , of < 0.3) between κ_{chem} and κ_{gf} of the 80, 110, 150, 200 nm particles both in winter and summer. The poor correlations reflect large uncertainty in one or both of the calculated parameters that are likely due to the unreasonable assumption of particle mixing state (e.g. Cruz and Pandis, 2000; Svenningsson et al., 2006; Sjogren et al., 2007; Zardini et al., 2008), which varies with their aging and other physiochemical processes in the atmosphere. Note that underestimation of κ_{chem} for the summer occurred mostly in the afternoon (Marked in blue dots in Fig. 5). This may be associated with photochemical processes at around noontime. More specific investigations of the particle mixing and aging impacts on κ_{chem} will be further addressed in the following sections....”

Line 292: In figure 6 the gap between κ_{gf} and κ_{chem} for larger particles looks similar across all plots. A closer look that κ_{chem} is higher in the late afternoon only in winter, and lower in summer. But, all the error bars appear to overlap almost completely. I strongly recommend displaying the data such that the error bars can be distinguished.

By way of example: the dotted lines in the background are unhelpful, the resolution of

the figure is not high, and the midpoint of the error bar is not entirely necessary if the error bars are symmetric above/below this point. Some authors use overlapping shaded regions. In panel B the yellow trace is hard to see. Error bars are omitted.

Re: Thanks for the comments. The figure has been revised. As the reviewer suggested, we use shaded regions to indicate the error bar (see Fig. R2).

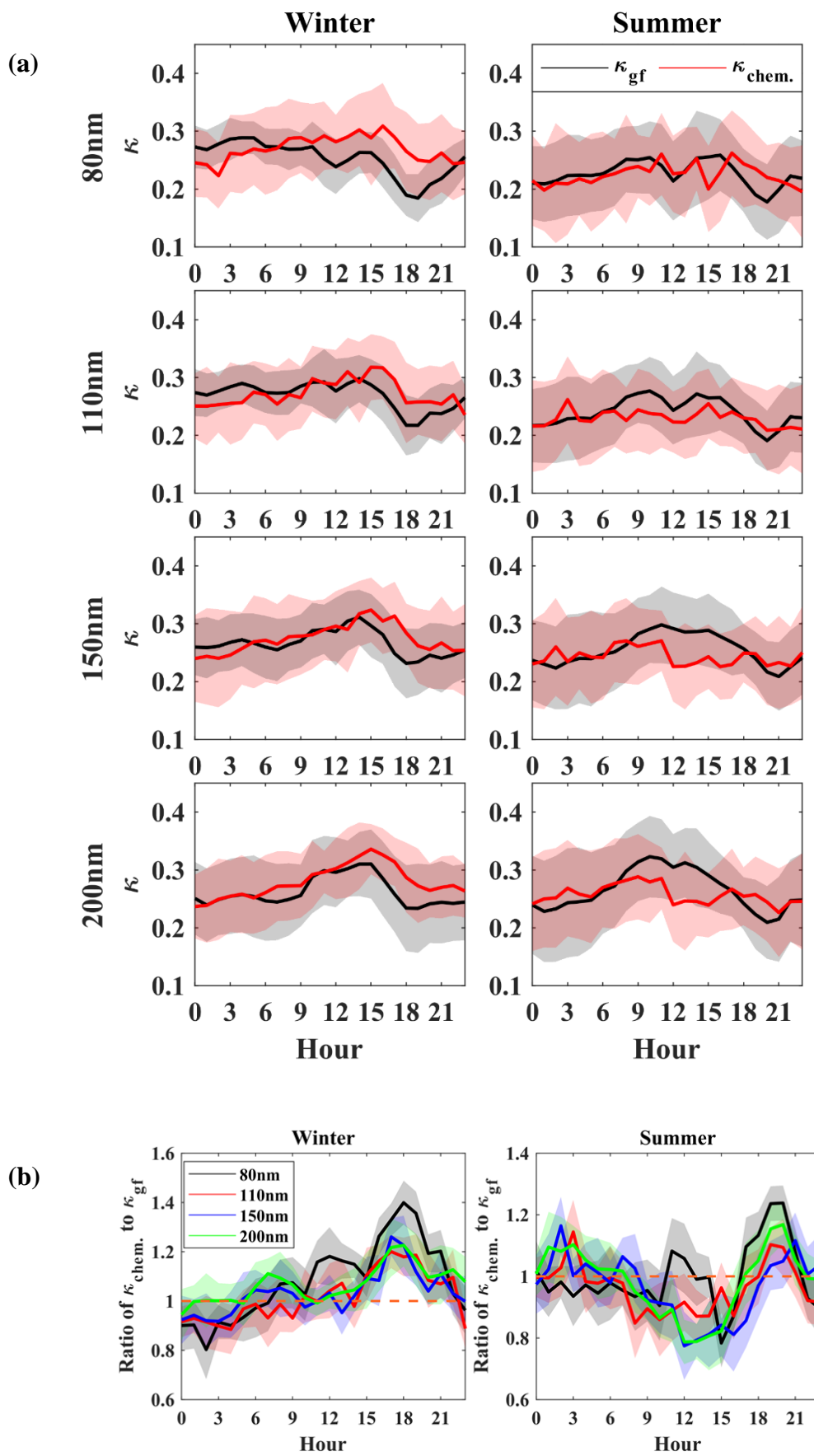


Figure R2. Diurnal variations of (a) κ_{chem} using size-resolved chemical composition

data and κ_{gf} in winter and summer period; and (b) ratio of κ_{chem} to κ_{gf} in winter and summer period. The shade regions denote the error bars (1σ).

Figure S6: How is Figure S6 different from Figure 6?

Re: To examine the impacts of pollution conditions on the diurnal variations of κ , Figure S6 (Now Fig S1 in the revised version) shows the diurnal cycles under clean and polluted cases respectively in winter; while Fig 6 just shows an overall diurnal change of κ in summer and winter.

Figure S1 and others: Kappa should not be negative and this could indicate evaporation of some fraction of particles.

Re: These figures have been revised (see an example as follows, Fig. R3). But it was removed from the revised version according to reviewer's comments.

Figure R3. Mean probability density functions of hygroscopicity parameter derived from hygroscopic growth factor for 40, 80, 110, 150, 200 nm in winter and summer period respectively.

Comments on underlying physical processes

The readership may already have an understanding of internal vs external mixtures.

The description of internal vs external mixing is not succinct and does not contain many references – I suggest reducing the length of this review and incorporating the following elements: more quantitative information, more references and conclusions drawn from previous work.

Re: More previous studies and references on water uptake by mixtures of compounds have been included in the introduction, and some words about the definition of mixing state have been removed in the revised version (Lines 50-82) as follows,

“ ...The hygroscopic properties of both the natural and anthropogenic aerosols, in addition to being affected by its chemical composition (Gunthe et al., 2009), are also affected by the particle mixing state and aging (Schill et al., 2015; Peng et al., 2017). For example, a recent laboratory study shown that the coexisting hygroscopic species have a strong influence on the phase state of particles, thus affecting chemical interactions between inorganic and organic compounds as well as the overall hygroscopicity of mixed particles (Peng et al., 2016). The field measurements also demonstrated that the hydrophobic black carbon particles became hygroscopic with atmospheric mixing and aging by organics (i.e. Peng et al., 2017). In a heavily polluted atmosphere, the aerosol sources and sinks are varied, the physical and chemical processes experienced by the aerosols are complex, and the mixing state and its impact on aerosols hygroscopicity is more complicated. The hygroscopicity of mixed particles and mutual impacts between the components are still poorly understood.

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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....”

Line 53: Are they? Water uptake by coated particles (including those coated with aliphatic compounds) is likely not inhibited.

Re: This should be “.....In the case of external mixing, the chemical components in the aerosol particles are independent of each other, and the chemical composition of the different types of aerosol particles is different within a certain particle size range.”

However, we have made a through revision of the introduction part.

Line 71-73: There have been continuing studies of the hygroscopicity of mixed aerosols

under controlled conditions, which may provide additional framework for mechanistic discussion.

<https://pubs.acs.org/doi/full/10.1021/acscentsci.5b00174>

<https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2011JD016823>

<https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2007JD009274>

<https://pubs.acs.org/doi/10.1021/acs.jpca.5b09373>

Re: We really appreciate your comments. These studies above listed are very helpful for improving our understanding of hygroscopicity of mixed aerosols. More discussions about the effect of mixed aerosols on hygroscopicity have been included in the revised manuscript by referring these studies in both the introduction, method and the interpretation and discussion of underlying physical processes.

For example,

Lines 50-55, “The hygroscopic properties of both the natural and anthropogenic aerosols, in addition to being affected by its chemical composition (Gunthe et al., 2009), are also affected by the particle mixing state (Schill et al., 2015; Peng et al., 2017). For example, a recent laboratory study shown that the coexisting hygroscopic species have a strong influence on the phase state of particles, thus affecting chemical interactions between inorganic and organic compounds as well as the overall hygroscopicity of mixed particles (Peng et al., 2016). The field measurements also demonstrated that the

Lines 61-66, “Previous studies have shown that the difference between the κ obtained from H-TDMA

or CCNc measurements and that calculated based on the volume mixing ratio of chemical components, κ_{chem} . Laboratory results from Cruz and Pandis (2000) indicate that κ_{gf} of internally mixed ammonium sulfate and organic matter is higher than κ_{chem} calculated for assumed uniform internal mixing. But Peng et al (2016) found that, for sodium chloride and organic aerosols mixed particles, the measured growth factors by H-TDMA were significantly lower than calculations from the mixing rule methods. In some field studies on aged aerosols,”

Lines 184-189, “...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 field 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).....”

Lines 351-355, “...Besides the impacts of BC aging (changes in morphology/density) and variations of the overall density of organics on particles hygroscopicity, uncertainty in κ_{chem} may be related to the uncertainty in the hygroscopic parameter for organics that could vary widely over a range of diverse constituents of SOA (Suda et al., 2012). However, Zhang et al. (2017) shown that using a smaller or larger κ_{SOA} could not fully explain the overestimation during traffic hours or the underestimation around noontime....”