RESPONSES TO REVIEWERS' COMMENTS

Dear ACP Editorial Board,

We are submitting our revised paper entitled "Contrasting ambient fine particles hygroscopicity derived by HTDMA and HR-AMS measurements between summer and winter in urban Beijing. We are grateful to the two reviewers for their insightful and constructive comments and have revised our paper accordingly to account for the reviewers' recommendations. Below please find our detailed point-by-point responses (in blue) to the reviewers' comments (in black) to the manuscript. We believe that we have satisfactorily addressed all criticisms from the two reviewers.

Thank you for your attention to this matter.

Sincerely, Fang Zhang on behalf of all authors

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 hygroscopisity 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 measuredκto 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 hygroscopisity (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),

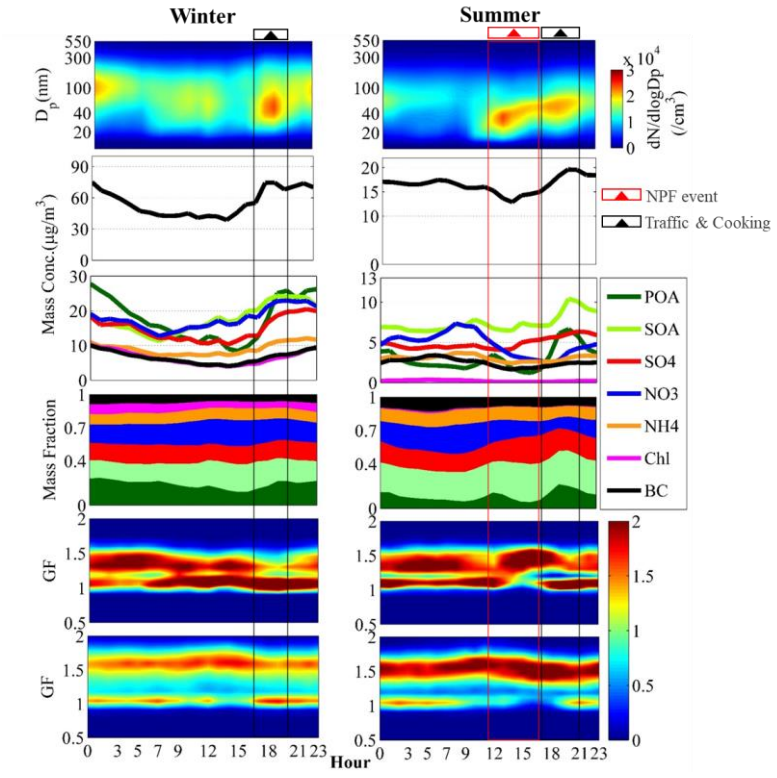


Figure R1. Campaign averaged diurnal variations in particle number size distribution;

mass concentration of PM_1, bulk mass concentration of main species in PM_1, mass fraction of chemical composition of PM_1; 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 R2 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 R2 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 ccorrelations (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).

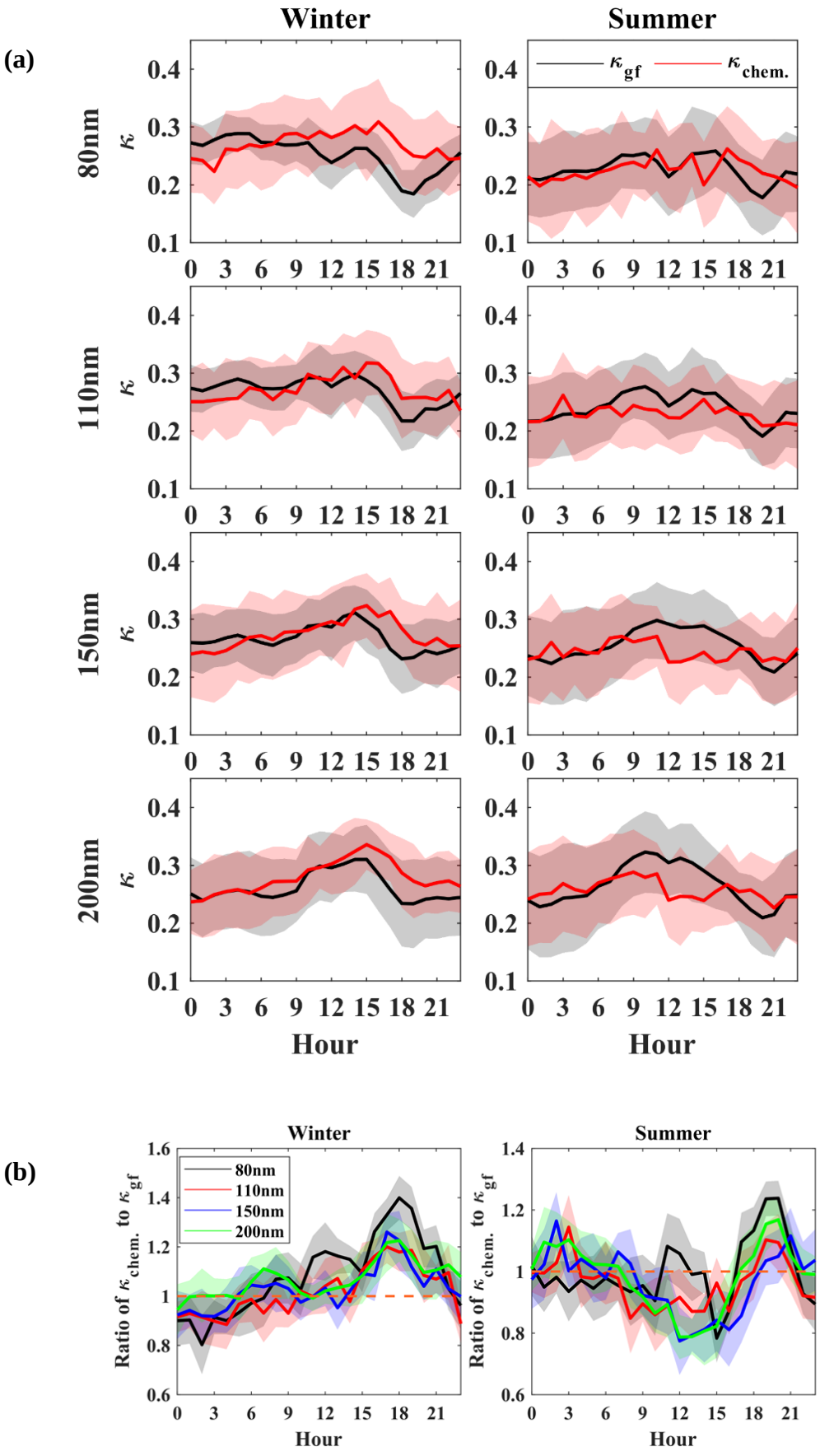


Figure R2. Diurnal variations of (a) κ_{chem} using size-resolved chemical composition

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 is 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.

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 measuredκto 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 hygroscopisity 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 measurementsand 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 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 hygroscopisity (e.g. Carrico et al., 2008; W*ex 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 constitutes 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.…"

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.

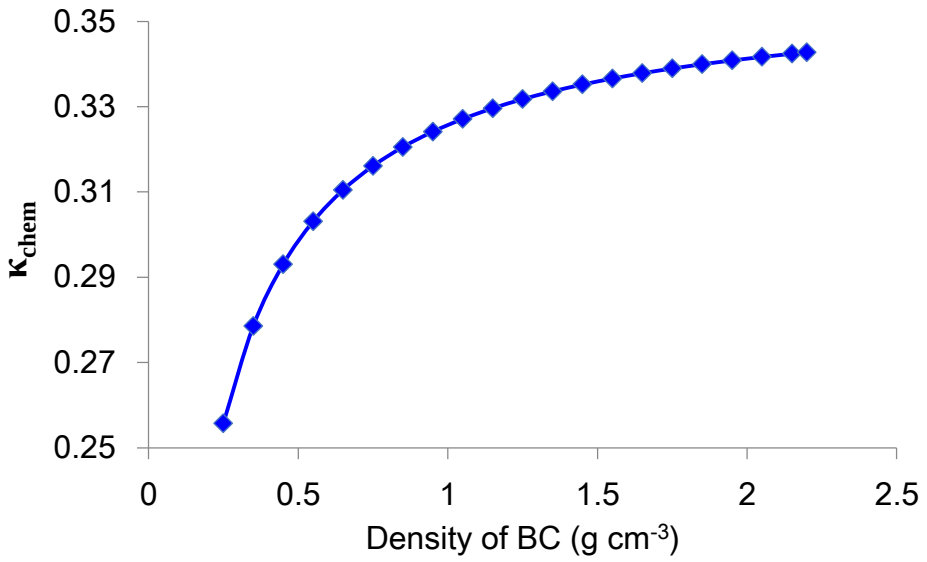
(1) A major discovery of the paper is that κ_{chem} calculated using the mixing rule cannot reflect the aerosol hygroscopicity. For example, it is found that the κ_{chem} in summer is underestimated at noon, overestimated at late peak hours, and substantially consistent with k_{gf} at midnight. Though 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 ±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 hygroscopisity. 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 hygroscopisty, future investigations need to measure the effective density and morphology of ambient BC, in particularity in those regions with complex local sources..…."

(a)



(b)

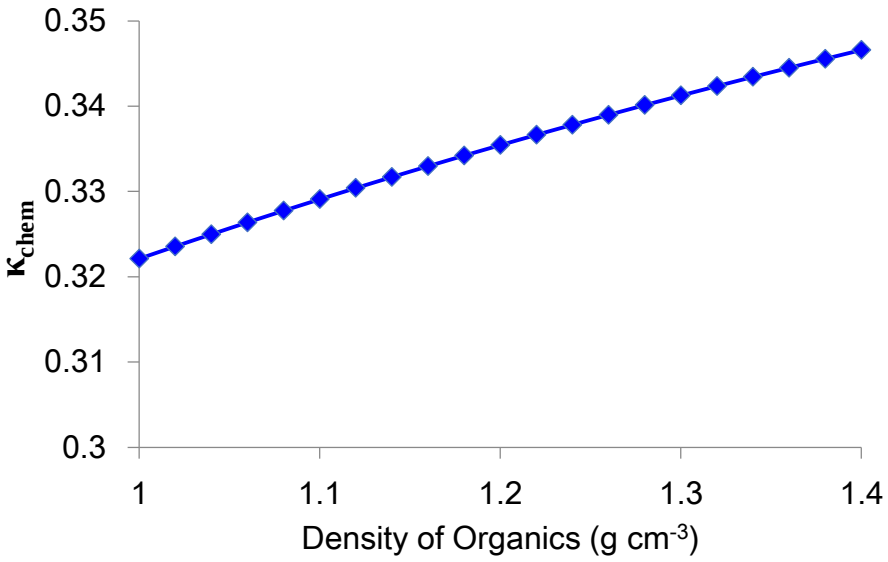


Figure R3. Sensitivity of κ_{chem} to variations of density of BC (a) and organics (b)

(b) According to the author's argument, aerosols both at noon and at midnight have core-shell structure, but why the κ_{chem}/k_{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 hygroscopisity. 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 hygroscopisity…."

(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 μg m^{-3}) and polluted (with bulk BC mass concentrations >2 μg 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 hygroscopisity 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 hygroscopisity (e.g. Carrico et al., 2008; W*ex 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 ±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 hygroscopisity. 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 hygroscopisty, 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

measuredκto 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 hygroscopisity, 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.

Contrasting ambient fine particles hygroscopicity derived by HTDMA and HR-AMS measurements between summer and winter in urban Beijing

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Abstract

The effects of aerosols on visibility through scattering and absorption of light and on climate through altering cloud droplet concentration are closely associated with their hygroscopic properties. Here, based on field campaigns in winter and summer in Beijing, 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 to reveal the impact of atmospheric processes/sources on aerosols hygroscopicity and to evaluate the uncertainty in estimating particles hygroscopicity with the hypothesis. We show that, in summer, the κ_{chem} for 110, 150 and 200 nm particles was averagely ~10% - 12% lower than κ_{gf}, with the greatest difference between the values observed around noontime when aerosols experience rapid photochemical aging. In winter, no apparent disparity between κ_{chem} and κ_{gf} is observed for those >100 nm particles around noontime, but the κ_{chem} is much higher than κ_{gf} in the late afternoon when ambient aerosols are greatly influenced by local traffic and cooking

sources. By comparing with the observation from other two sites (Xingtai, Hebei and Xinzhou, Shanxi) of north China, we verify that atmospheric photochemical aging of aerosols enhances their hygroscopicity and may induce a coating effect which thereby 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. However, local primary sources, which result in ~~an externally mixture of the fine particles with~~ a large number of externally-mixed BC and POA (Primary Organic Aerosol) in urban Beijing~~, makes the particle much less hygroscopic and~~ during traffic rush hour time, cause 20-40% overestimation of the hygroscopic parameter. This is largely due to an inappropriate use of density of the BC that is closely associated with its morphology, and the results show that the calculation can be improved by applying an effective density of freshly BC within the range of 0.25-0.45 g cm^{-3} in the mixing rule assumption. ~~In addition, we also note lower κ_{chem} than κ_{gf} for 80, 110 and 150 nm particles during the nighttime of winter, particularly in polluted days, probably due to a nighttime coating effect driven by condensation of secondary hygroscopic species on pre-existing aerosols in cold season.~~ Our ~~results~~study suggest that it is critical to measure the effective density and morphology of ambient BC in particularity in those regions with complex local sources, so as to accurately parameterize the ~~impacts in model simulations to improve the evaluation of the aerosols indirect effect.~~effect of BC aging on particles hygroscopicity.

1. Introduction

The effects of aerosols on visibility through scattering and absorption of light and on climate through altering cloud droplet concentration are influenced by their hygroscopic growth. Understanding and reducing the uncertainty in prediction of the aerosol hygroscopic parameter (κ) using chemical composition would improve model predictions of aerosol effects on clouds and climate.

~~The hygroscopic parameter, κ, is dependent upon particle chemical composition (Gunthe et al., 2009). The~~ The hygroscopic properties of ~~an aerosol~~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). ~~The mixing~~For example, a recent laboratory study

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shown that the coexisting hygroscopic species have a strong influence on the phase state of ~~aerosol~~ particles ~~can be divided into external mixing and internal mixing. The chemical components in the aerosol~~ , thus affecting chemical interactions between inorganic and organic compounds as well as the overall hygroscopicity of mixed particles ~~are independent of each other. The chemical composition of the different types of aerosol~~(Peng et al., 2016). The field measurements also demonstrated that the hydrophobic black carbon particles ~~is different within a certain particle size range, and the mixed state is external mixing. As the aerosol particles undergo transport, coagulation, and aging/coating in the atmosphere, the chemical components become more uniformly mixed within each particle size range,~~ became hygroscopic with ~~the aerosol mixing state approaching an internal mixture. Depending on the physical properties of the different aerosol components, internal mixing can be divided into uniform internal~~atmospheric mixing and ~~"core shell" mixing (Jacobson, 2001). For uniform internal mixing the distribution of the chemical components is the same throughout each particle. "Core shell" mixing refers to a mixing state in which certain chemical components are coated or coagulated on the surface of other chemical components (such as black carbon) during~~ aging~~.~~ by organics (i.e. Peng et al., 2017). In ~~the~~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. ~~In heavily polluted areas, BC is usually mixed with other chemical components. Freshly emitted BC is mostly in an external mixed state. With the aging process, it gradually transforms into the internal mixing state (Chen, et al., 2016; Lee, et al., 2015; Wang,~~ The hygroscopicity of mixed particles and mutual impacts between the components are still poorly understood~~et al., 2017). Based on observations in the winter of Beijing urban area, Wang et al. (2019) found that the secondary aerosol generated from photochemical reactions is thickly coated on the surface of BC.~~

~~Studies~~Previous studies have shown that the difference between the κ obtained ~~using~~from H-TDMA ~~data, κ_{gf},~~or CCNc measurements and that calculated based on the volume mixing ratio of chemical components, κ_{chem}~~, depends on the mixing state and the extent of aging of the particles (Mikhailov, et al., 2015; Zhang et al., 2017). Results~~. Laboratory results from Cruz and Pandis (2000) ~~also~~ indicate that κ_{gf} of internally mixed ammonium sulfate and organic matter is higher than κ_{chem} calculated for assumed uniform

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internal mixing. ~~Similarly, in~~ 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~~), the concentration of CCN was underestimated by the calculation based on uniform internal mixing. Our previous study demonstrated that particle mixing state has large impacts on prediction of CCN concentration for the aerosol sampled in Beijing (Ren et al., 2018).~~ ; 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). ~~. (2017) observed an evident underestimation of around noontime particle hygroscopicity based on~~ Using size-resolved, not bulk, chemical composition measurements in ~~urban Beijing. Wang et al. (2018a) also noted a lower hygroscopic parameter estimated by the simple volume mixing ratio than that derived from direct HTDMA measurement at a site in North China Plain. These studies have revealed the uncertainty in the estimation of aerosol hygroscopicity parameters using chemical composition volume mixing ratios with the assumption that of uniform internal mixing, but there is still lack of a systematic investigation on the cause and magnitude of the effect. Furthermore, most studies that have been conducted compare the size-resolved hygroscopic~~

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~~parameter κ obtained with an HTDMA with κ calculated from bulk chemical composition measurements~~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.~~–~~

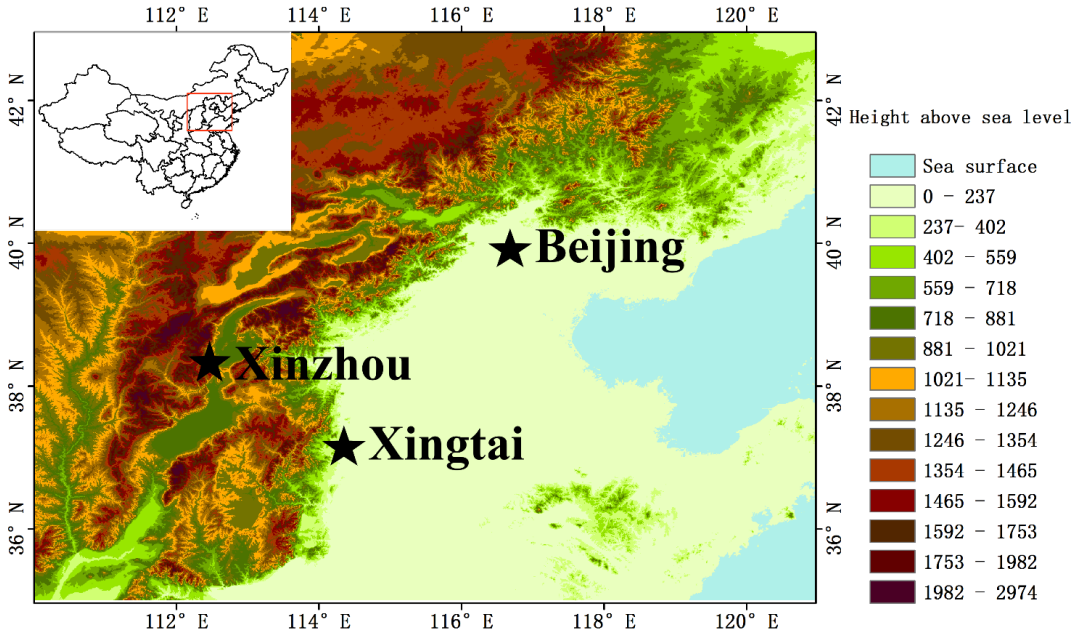
in this study. The aim of this paper is to study the hygroscopicity and mixing state characteristics of fine particles in the Beijing urban area, and to reveal the impact of atmospheric processes/sources and mixing/aging on aerosols hygroscopicity and elucidate the uncertainty in calculating the hygroscopic parameter using simple mixing rule estimates based on size-resolved chemical composition. The experiment and theory in the study are introduced in Sect. 2. The comparison between the hygroscopic parameter obtained from the HTDMA and and that calculated using size-resolved chemical composition is discussed in Sect. 3. Conclusions from the study are given in Sect. 4.

2. Experiment and Theory

2.1. Site and instruments

~~In this study, we mainly focus on analysis of the data obtained from two campaigns in urban Beijing (BJ: 39.97 °N, 116.37 °E). In addition, we also compare the results from the field campaigns with those from 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).~~ Two field campaigns are conducted during winter 2016 and summer 2017 of urban Beijing (Fig. 1, BJ: 39.97 °N, 116.37 °E) for measurements of aerosols physical and chemical properties. The BJ site is located at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences, which is between the north third and fourth ring roads in northern Beijing. Local traffic and cooking emissions can be important at the site (Sun et al., 2015). The sampling period in cold season was from 16 November to 10 December 2016, during the domestic heating period in Beijing. The sampling period in warm season was from 25 May to 18 June 2017. ~~The XT site is located in the National Meteorological Basic Station, which is about 17 km from the XT urban area. The sampling period was from 17 May to 14 June 2016. Xingtai, with a high level of industrialization and urbanization, is located in the center of the North China Plain. Due to~~

~~industrial emissions and typically weak ventilating winds, concentrations of $PM_{2.5}$, black carbon and gaseous precursors are extremely high at the Xingtai site (Fu et al., 2014). Xinzhou is located north of Taiyuan and about 360 km southwest of Beijing, in the north central part of Shanxi Province, and is surrounded by mountains on three sides. The XZ site is located in a town, surrounded by agricultural land (such as corn fields). Local emissions from motor vehicles and industrial activities have relatively little influence on the sampled aerosol (Zhang et al., 2016). Because of its location and elevation, the aerosol at the XZ site is usually aged and transported from other areas. The sampling period was from July 22 to August 26, 2014 at XZ site.~~



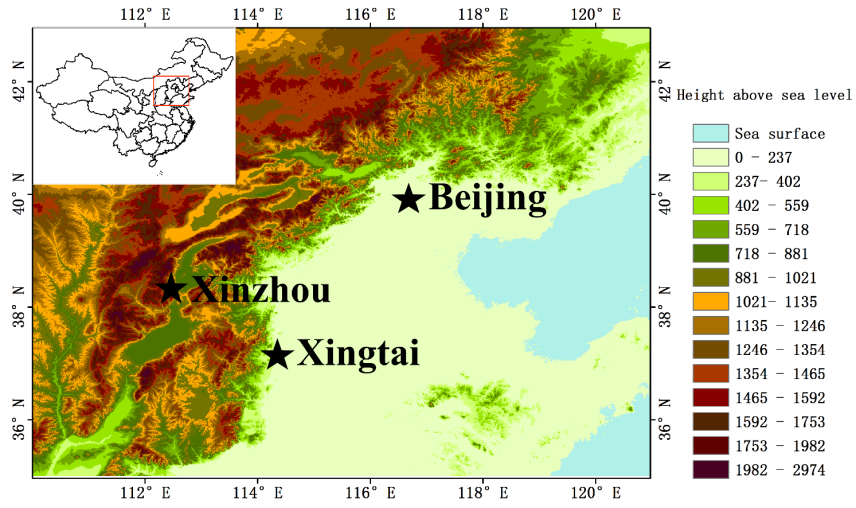


Figure 1. The map location of the sites

Particle number size distribution (PNSD) in the size range from 10 nm to 550 nm was measured with a Scanning Mobility Particle Sizer (SMPS; Wang & Flagan, 1990; Collins et al., 2002), which consists of a long differential mobility analyzer (DMA, model 3081L, TSI Inc) to classify the particle and a condensation particle counter (CPC, model 3772, TSI Inc.) to detect the size classified particles. The sampled particles were dried to relative humidity < 30% before entering the DMA. The measurement time for each size distribution was five minutes.

The HTDMA system used in this study has been described in detail in previous publications (Tan et al., 2013; Wang et al., 2017; Zhang et al., 2017). Here, only a brief description is given. A Nafion dryer dried the sampled particles to relative humidity < 20%, after which the steady state charge distribution was reached in a bipolar neutralizer. The first differential mobility analyzer (DMA_1, model 3081L, TSI Inc.) selected the quasi-monodisperse particles through applying a fixed voltage. The dry diameters selected in this study were 40, 80, 110, 150, and 200 nm. The quasi-monodisperse particles were humidified to a controlled RH (90% in this study) using a Nafion humidifier. A second DMA (DMA_2, same model as the DMA_1) coupled with a water-based condensation particle counter (WCPC, model 3787, TSI Inc.) measured

the particle number size distributions of the humidified aerosol. RH calibration with ammonium sulfate was carried out regularly during the study.

The hygroscopic growth factor (Gf) is defined as the ratio of the mobility diameter at a given RH to the dry diameter:

$$\mathrm{Gf} = \frac{D(RH)}{D(dry)}$$

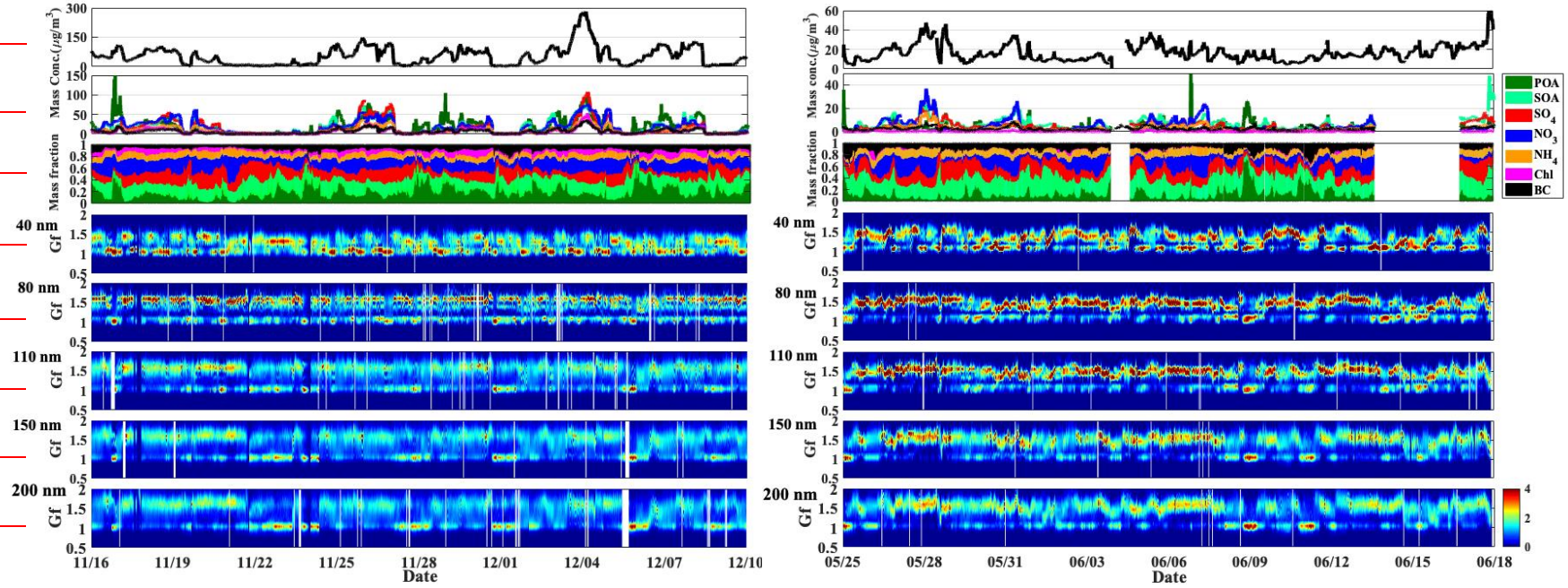
The Gf probability density function (PDF) is retrieved based on the $TDMA_{inv}$ algorithm developed by Gysel et al. (2009). Dry scans in which the RH between the two DMAs was not increased were used to define the width of the transfer function.

Size-resolved non-refractory submicron aerosol composition was measured with an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS; Xu et al., 2015). The particle mobility diameter was estimated by dividing the vacuum aerodynamic diameter from the AMS measurements by particle density. Because the uncertainty caused by the fixed density across the size range is negligible (Wang et al. 2016), here, the particle density is assumed to be 1600 kg m^{-3} (Hu et al., 2012). AMS positive matrix factorization (PMF) with the PMF2.exe (v4.2) method was performed to identify various factors of organic aerosols. Xu et al. (2015) have described the operation and calibration of the HR-ToF-AMS in detail. Black carbon (BC) mass concentration was derived from measurements of light absorption with a 7-wavelength aethalometer (AE33, Magee Scientific Corp.; Zhao et al., 2017).

2.2. Data

The time series of the submicron particle mass concentration PM_1, ~~(Fig. 2a),~~ bulk mass concentrations of the main species in PM_1 ~~(Fig. 2b),~~ mass fraction of the chemical composition of PM_1 ~~(Fig. 2c),~~ and probability density function of growth factor (Gf-PDFs) for 40~~, 80, 110,~~ and 150~~, 200~~ nm particles ~~(Fig. 2d h)~~ during the campaign are presented in Fig. ~~2. As shown in Fig. 2, quite~~2. Quite distinct temporal variability of aerosol chemical and physical properties was observed between winter and summer. The average mass concentration of PM_1 was 55.2 μg/m^3 in the winter and 16.5 μg/m^3 in the summer during our study periods. In this study, we define the conditions when the mass concentration in winter period was < 20

μg m^{-3} and >80 μg m^{-3} as clean and polluted conditions, respectively. Organic aerosol (OA), consisting of secondary organic aerosol (SOA) and primary organic aerosol (POA), was the major fraction during both the winter and summer sampling periods. POA concentration was higher than that of SOA in the winter, which reflects the influence of primary emissions such as coal combustion OA (COOA) in Beijing (Hu et al., 2016; Sun et al., 2016). In contrast, SOA usually dominated in the summer, which is ~~evidence~~evident that secondary aerosol formation played a key role in the source of PM_1~~. Figs. 2d-h show the time series of the probability density functions (PDFs) of GF for 40, 80, 110, 150, and 200 nm particles, respectively~~. Distinct hydrophobic (with Gf of ~1.0) and more hygroscopic (with Gf of ~1.5) modes were observed from Gf-PDFs of both small and large particles. Sometimes the more hygroscopic mode particles were more concentrated and at others the hydrophobic particles were. In general though, the more hygroscopic mode dominated for larger particles (i.e. 150~~ and 200~~ nm), and the less hygroscopic mode did for the smallest particles (e.g. 40 nm~~) (Fig. 2d-h and Fig. S1~~). Occasionally, only the hydrophobic mode was evident for 150~~ and 200~~ nm particles, which occurred when POA dominated the PM_1. Only the hygroscopic mode was discernable for 40 nm particles during new particle formation (NPF) events that occurred more frequently in summer than winter (Fig. ~~S2~~3).


Winter
Summer
(h)
(f)
(g)
(a)
(b)
(c)
(d)
(e)
Mass Conc.(μg/m3)
Mass fraction
Gf
40 nm
80 nm
110 nm
150 nm
200 nm
POA
SOA
SO4
NO3
NH4
Chl
BC
11/16
11/19
11/22
11/25
11/28
12/01
12/04
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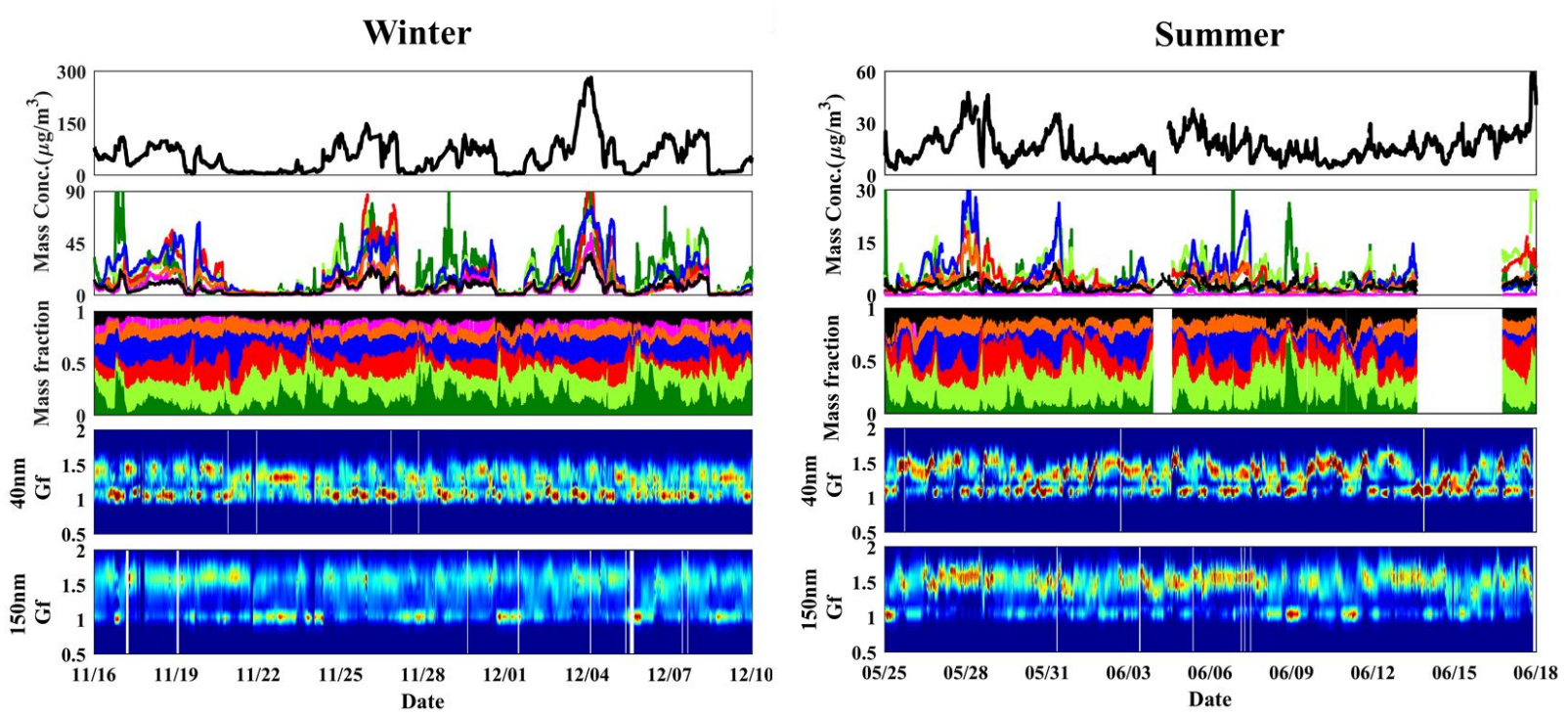

Figure 2. –Winter (left) and summer (right) time series of ~~(a)~~ mass concentration of PM_1~~; (b),~~ bulk mass concentration of the main species in PM_1~~; (c),~~ mass fraction of the chemical composition of ~~PM1; (d-h)~~$PM_1$and Gf-PDFs for 40~~, 80, 110,~~ and 150 ~~and 200~~ nm particles.

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2.3. Theory and method

2.3.1 Derivation of the hygroscopic parameter, κ, from the growth factor (Gf)

According to κ -Köhler Theory (Petters and Kreidenweis, 2007), the hygroscopicity parameter κ can be derived using the growth factor measured by an HTDMA.

$$\kappa = (Gf^3 - 1)\left(\frac{\exp\left(\frac{A}{D_d Gf}\right)}{RH} - 1\right) \quad , \tag{1}$$

$$A = \frac{4\sigma_{s/a} M_w}{RT\rho_w} \quad , \tag{2}$$

where Gf is hygroscopic growth factor measured by HTDMA, D_d is the dry diameter of the particles, RH is the relative humidity in the HTDMA (90%, in our study), $\sigma_{s/a}$ is the surface tension of the solution/air (assumed here to be the surface tension of pure water, $\sigma_{s/a}$ = 0.0728 N m^{-2}), M_w is the molecular weight of water, R is the universal gas constant, T is the absolute temperature, and ρ_w is the density of water.

2.3.2 Derivation of the hygroscopic parameter, κ, from chemical composition data

For an assumed internal mixture, κ can also be calculated by a simple mixing rule on the basis of chemical volume fractions (Petters and Kreidenweis, 2007; Gunthe et al., 2009):

$$\kappa_{chem} = \sum_i \varepsilon_i \kappa_i \quad , \tag{3}$$

~~$\kappa_{org} = f_{POA} * \kappa_{POA} + f_{SOA} * \kappa_{SOA}$,~~ ~~(4)~~

where κ_i and ε_i are the hygroscopicity parameter and volume fraction for the ~~ith~~ individual (dry) component in the mixture, respectively~~, and f_{POA} and f_{SOA} are the volume fractions of POA and SOA in the organic component~~. The AMS provides mass concentrations of organics and of many inorganic ions. The inorganic components mainly consisted of $(NH_4)_2SO_4$ and NH_4NO_3 (Zhang et al., 2014~~; Zhang, et al., 2016; Zhang et al~~). And~~, 2017). As noted above, the organic components mainly consisted of POA and SOA.~~

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~~According to previous study,~~ the values of κ are 0.48 for $(NH_4)_2SO_4$ and 0.58 for NH_4NO_3 (Petters and Kreidenweis, 2007). To estimate κ_{org}, we used the following linear function derived by Mei et al. (2013): $\kappa_{org} = 2.10 \times f_{44} - 0.11$. We derived the volume fraction of each species by dividing mass concentration by its density. The ~~values of~~ density are ~~1720 kg m~~1.77 g cm^{-3} for $(NH_4)_2SO_4$ and ~~1770 kg m~~1.72 g cm^{-3} for NH_4NO_3. The densities of ~~all~~ organics~~, POA, and SOA~~ are assumed to be ~~1200 kg m~~1.2 g cm^{-3} (Turpin et al., 2001~~), 1000 kg m^{-3}, and 1400 kg m^{-3} respectively.~~). The κ and density ~~ofBC~~of BC are assumed to be 0 and ~~1700 kg m~~1.7 g cm^{-3}. In the following discussions, κ_{gf} and κ_{chem} denote the values derived from HTDMA measurements and calculated using the ZSR mixing rule, respectively.

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 hygroscopisity (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).

3. Results and discussion

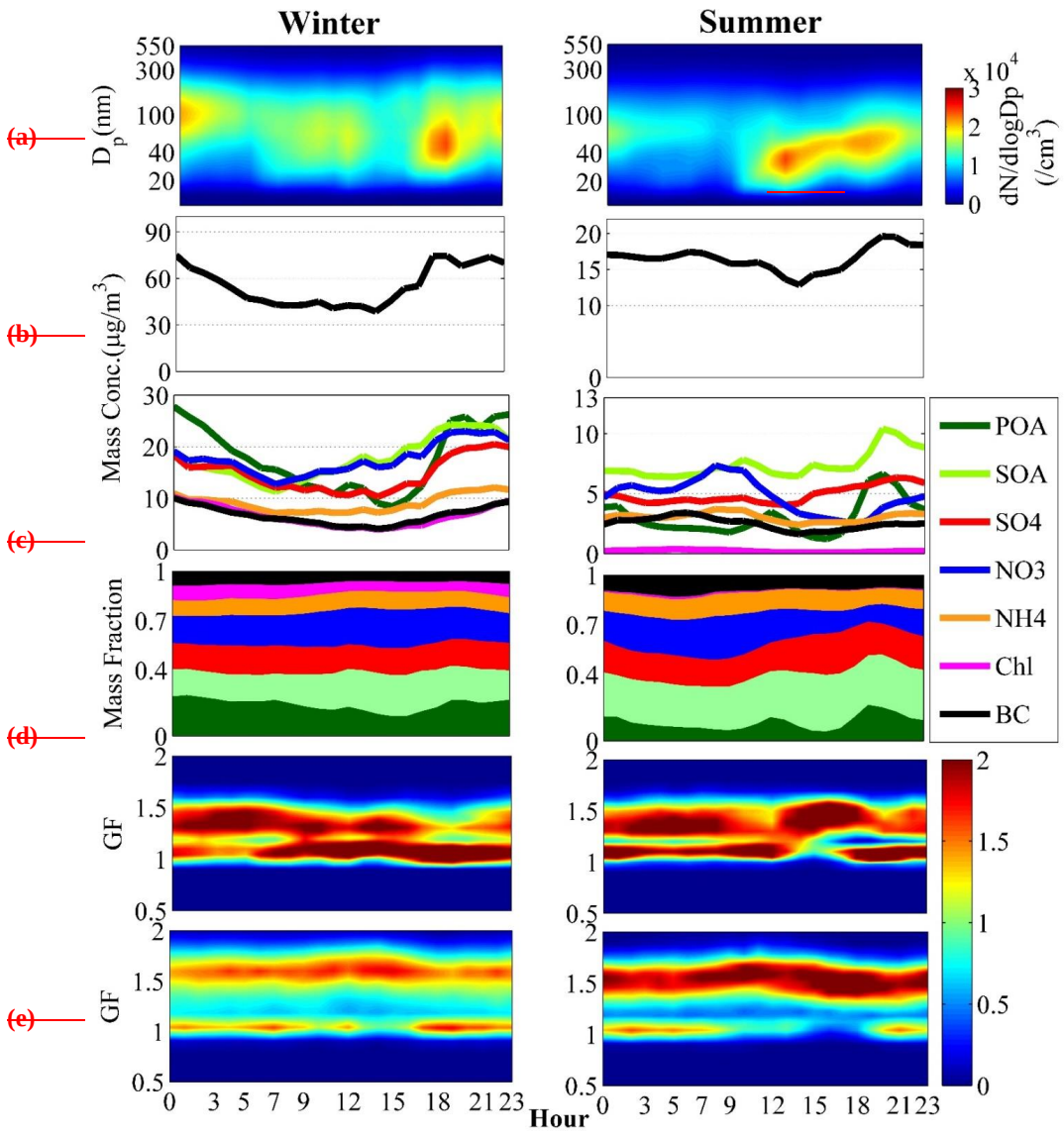
3.1. Diurnal variations of ambient fine particles physiochemical properties and hygroscopic growth factor

The diurnal variations of the PNSD, mass concentration of PM_1, mass concentration and fraction of chemical components in PM_1, and Gf-PDFs for 40 and 150 nm particles during the campaign are shown in

Fig. 3. During the summer an obvious peak value in the PNSD is observed around noontime due to NPF events that typically started around 10:00 LT (Local Time). The resulting sharp increase in number concentration of nucleation mode particles was followed by decreased concentration and a rapid growth in diameter of the particles along with increased mass concentration of SOA and sulfate in PM_1, indicating strong photochemical and secondary formation processes during daytime in the summer~~.~~ (Marked in red box in Fig. 3). In contrast, NPF was not evident during the winter period, which may in part be due to the much higher (~3x) PM_1 ~~–~~mass concentrations in the winter than in the summer.~~–~~ Note that peak values in number concentration and in mass concentrations of PM_1 and POA occurred during the early evening (17:00-21:00, LT) indicating the strong impact of local sources from traffic emissions and cooking~~.~~ (Marked in black box in Fig. 3). In addition, the diurnal cycles of aerosol physical and chemical properties are also influenced by the diurnal changes in the planetary boundary layer (PBL) that leads to accumulation of particles during nighttime when higher values of both number and mass concentration were observed.

~~Fig. 3e shows the diurnal variations of the Gf-PDFs for 40 nm and 150 nm particles.~~ Owing to the continued local and primary emissions near the study site, the Gf-PDFs for 40 nm particles generally display a bimodal shape with more and less hygroscopic modes (with Gf of ~ 1.5 and ~ 1.1 respectively) throughout the day both in winter and summer periods, indicating an external mixing state for the 40 nm particles. Note that, during nighttime and early morning in the winter, the more hygroscopic mode dominated and was shifted to higher Gf than during the daytime. This is thought to be due to heterogeneous/aqueous reactions on pre-existing primary small particles, and/or coagulation/condensation processes that are enhanced at night under lower ambient temperature and higher relative humidity, all of which result in a more hygroscopic and more internally-mixed aerosol (Liu et al., 2011; Massling et al., 2005; Ye et al., 2013; Wu et al., 2016; Wang et al., 2018a).). Interestingly, in the summer period, the concentration of the hydrophilic mode increased quickly around noontime and in the early afternoon (12:00-16:00), with a corresponding decrease in the relative concentration of the hydrophobic mode, which likely indicates a transformation of the particles from externally to internally mixing state as a result of the species condensation from the photochemical reaction (Wu et al., 2016; Wang et al., 2017), resulting in an increase in particle hygroscopicity ~~(Fig. S3).~~. 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. For 150 nm particles, the hygroscopic mode in the Gf-PDF is more dominant during daytime in particular during the summer period when the strong solar radiation promotes photochemical aging and growth, thus producing a more internally-mixed aerosol. The dominant hydrophobic mode at around 18:00 was observed both in winter and summer and reflects abundant traffic emissions and cooking sources (primarily with POA) during the early evening period ~~(Fig. 2c).~~



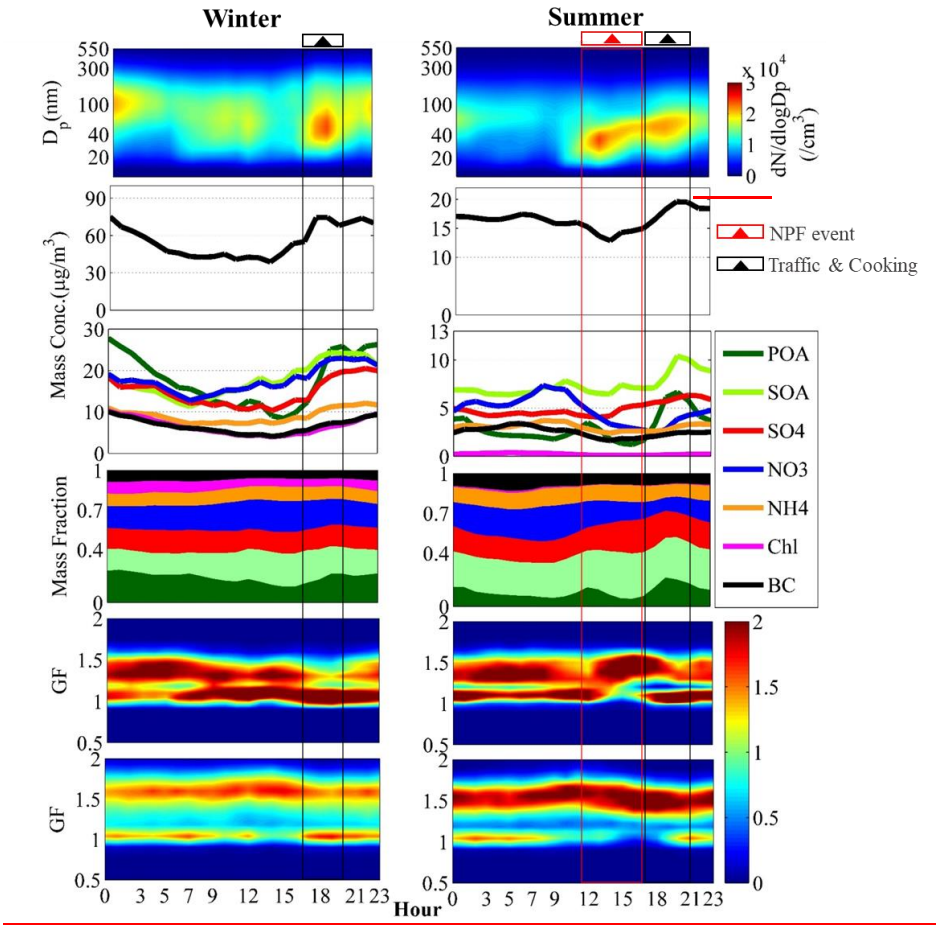
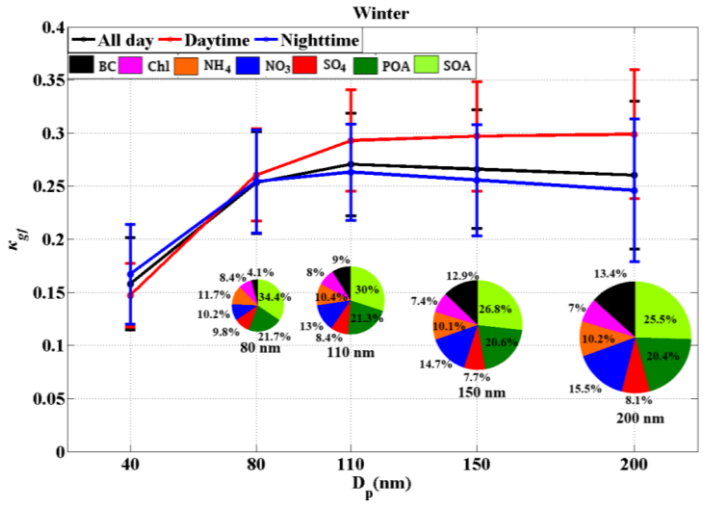


Figure 3. ~~Diurnal~~Campaign averaged diurnal variations in ~~(a)~~ particle number size distribution; ~~(b)~~ mass concentration of PM_1~~; (c),~~ bulk mass concentration of main species in PM_1~~; (d),~~ mass fraction of chemical composition of PM_1; ~~(e)~~and Gf-PDFs for 40 and 150 nm particles in winter (left panels) and summer ~~period respectively.~~(right panels) measured in urban Beijing..

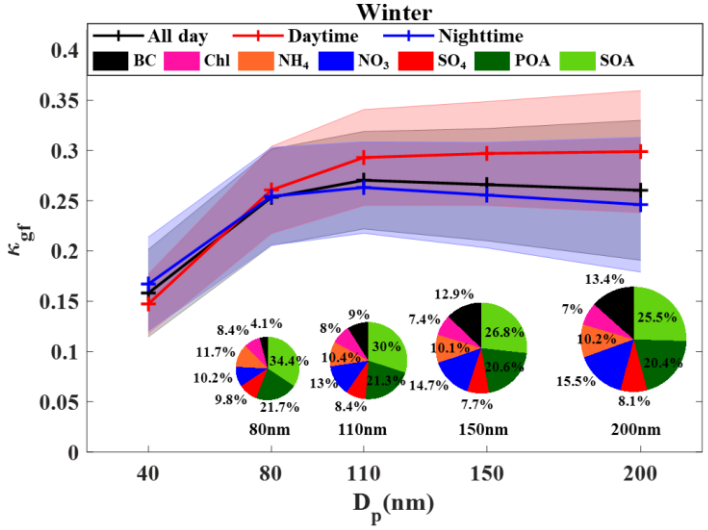
3.2 κ_{gf} dependence on D_p

The size dependence of particle hygroscopicity parameters for the winter and summer periods are presented in Fig.4. In the winter, the 40 nm particles were least hygroscopic and the hygroscopicity of larger particles (>80 nm) displayed insignificant dependence on particle size. The size independence for the larger particles is consistent with the observed similarity in mass fractions of inorganic and organic species across

(a)


Winter
All day
Daytime
Nighttime
BC
Chl
NH4
NO3
SO4
POA
SOA
κgf
Dp (nm)
80 nm
110 nm
150 nm
200 nm

(b)


Winter
All day
Daytime
Nighttime
BC
Chl
NH4
NO3
SO4
POA
SOA
κgf
Dp(nm)
80nm
110nm
150nm
200nm

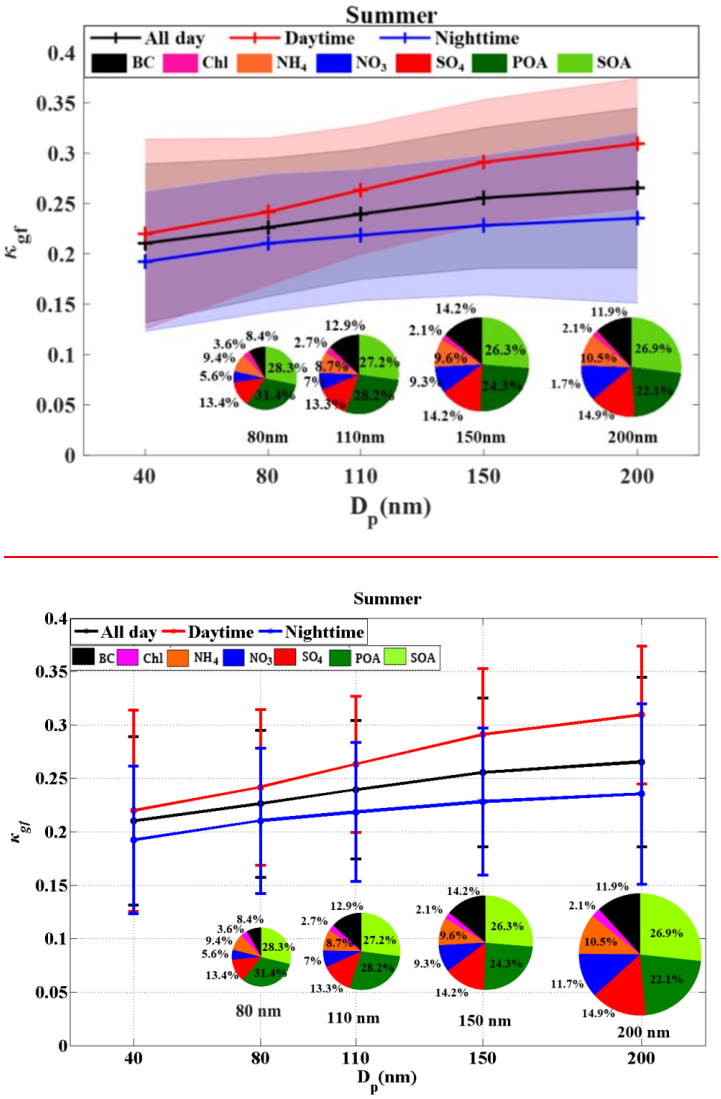


Figure 4. The dependence of κ on D_p at the urban Beijing site during ~~the study periods.~~winter (a) and summer (b). The κ values are retrieved from the size-resolved HTDMA measurements. The error bars represent $\pm 1\sigma$. The size-resolved chemical mass fractions at the corresponding D_p is also presented.

the size range as shown in the pie charts in Figure 4a. A similar dependence of particle hygroscopicity on particle size was also observed in the urban area of Beijing during the wintertime of 2014 (Wang et al., 2018b). In the summer, hygroscopicity increased with increasing particle size, which is expected based on

the size dependent patterns shown in the pie charts, with the mass fraction of POA decreasing with the particles size and the mass fraction of inorganics like sulfate and nitrate increasing with particle size.

3.3. Closure of HTDMA and chemical composition derived κ

A closure study was conducted between κ_{chem} and κ_{gf} (Fig. 5) to investigate the uncertainty of the two methods, and especially to further illustrate whether particle hygroscopicity can be well predicted by κ_{chem} calculated by assuming internal mixing. 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}.~~

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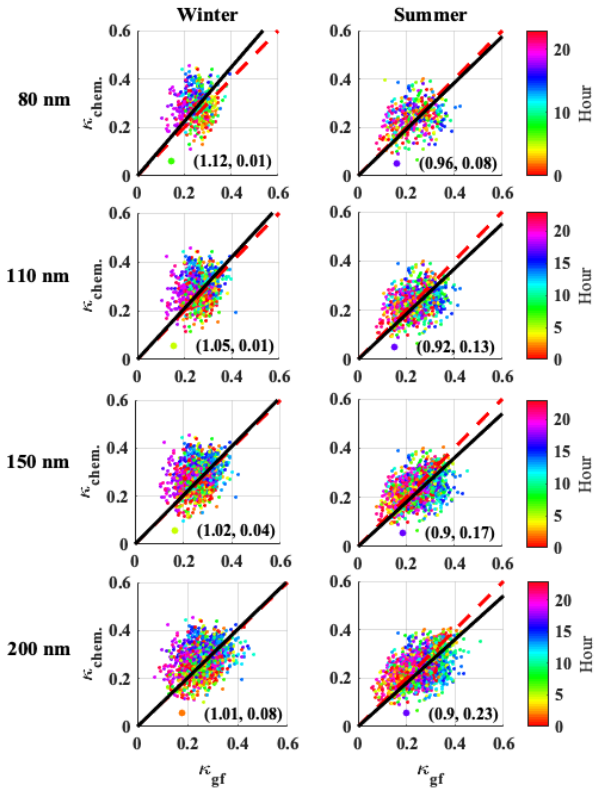

Figure 5. Closure of κ_{chem} calculated from size-resolved chemical composition data and κ_{gf} retrieved from hygroscopic growth factor by HTDMA measurements in winter (left panels) and summer (right panels) period. The dots with different color correspond to observed time of a day during the campaign as shown by

the color bar. On each plot, red dotted line is 1:1 line, black solid line is fitting line. The ~~number~~numbers in parentheses ~~is~~ are slopes of linear fits and correlation coefficients (R^2~~) and slopes of linear fits.~~).

available during the campaign, we use the bulk mass fraction of BC particles measured by the AE33 combining with size-resolved BC distribution measured by a single particle soot photometer (SP2) in Beijing (Liu et al., 2018) to estimate κ_{chem}. 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 μg m^{-3}) and polluted (with bulk BC mass concentrations >2 μg m^{-3}) conditions respectively (Liu et al., 2018).

Uncertainty in κ is due in part to measurement uncertainty of the HTDMA~~/CCNc~~ system and uncertainty resulting from non-ideality effects in the solution droplets, surface tension reduction due to surface active substances, and the presence of slightly soluble substances that dissolve at RH higher than that maintained in the HTDMA (e.g., Wex et al., 2009; Good et al., 2010; Irwin et al., 2010; Cerully et al., 2011; Wu et al., 2013). However, our previous study demonstrated that, for this region, estimates using HTDMA data are still better representing the aerosols hygroscopicity than those using the simple mixing rule based on chemical volume fractions for an assumed internal mixture (Zhang et al., 2017). Therefore, here we focus on discussing and exploring the uncertainty of κ_{chem} by taking κ_{gf} as the reference.

~~Our~~The results show that, ~~in winter,~~although the slopes from linear fitting of κ_{chem} and κ_{gf} are ~~about 0.96~~ close to 1.0 ~~for particles~~, it is with ~~diameters of 80, 110, 150, and 200 nm, indicating an overall consistency of κ_{chem} and κ_{gf}. In summer, the slopes are 0.88–0.89 for 110, 150, and 200 nm particles, meaning there is about 10%–12% underestimation of κ_{chem}. However, the~~quite poor ~~correlations~~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~~. The large uncertainties~~ 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. ~~For~~

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~~example,~~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.

3.4 ~~Atmospheric~~Aerosols aging processes and sources effects indicated by diurnal cycles of κ_{chem} and κ_{gf}

The diurnal cycles of particle hygroscopicity in the summer and winter with the use of the size-resolved chemical composition observations and the ratio of κ_{chem} to κ_{gf} are shown in Fig. 6. In summer, at 09:00-15:00, the disparity between κ_{chem} and κ_{gf} is insignificant for smaller particles (80 and 110 nm), both of which show slight decrease from 09:00 or 10:00 to 12:00-13:00 due to the frequent NPF event that usually corresponds to a large fraction of organics (Fig. 3) in urban Beijing. For larger particles (150 and 200 nm), the disparity between κ_{chem} and κ_{gf} around noontime and in the early afternoon is very significant, corresponding to >20% underestimation of particle hygroscopisity by κ_{chem} (with the ratio of κ_{chem} to κ_{gf} of ~0.8). Similar patterns were also noted by Zhang et al., (2017) but which is only based on a comparison between κ_{chem} derived from bulk chemical composition and κ_{gf}. Our results ~~further clarify~~again indicate that the rapid photochemical aging of BC particles, which are generally with dominant size modes of 100-200 nm in the atmosphere, ~~leads~~may lead to the core-shell structure in which certain secondary aerosol generated from photochemical reactions is thickly coated on the surface of BC (Wang et al., 2019). The hygroscopicity of the coated BC particles may only depend on the coating layer (Ma et al., 2013), thus resulting in the noontime/early afternoon underestimation of particle hygroscopicity by κ_{chem}. While, no significant differences between κ_{chem} and κ_{gf} are observed during night time. Note that κ_{chem} is slightly higher than κ_{gf} during early evening traffic rush hour and cooking time, when emissions of primary hydrophobic particles (e.g. BC and POA) are high (Fig. ~~3b~~3), thus resulting in a large percentage of externally-mixed particles ~~(Fig. 3e, Fig. S4 and Fig. S5). Therefore, ~~). Causes of the ~~assumption of uniform internal mixing~~overestimation in κ_{chem} during the traffic rush hour and cooking time will ~~overestimate hygroscopicity according to our previous study (Zhang et al., 2017). But the~~be discussed in the following paragraph. The particles

experience rapid conversion and mixing in urban Beijing due to high precursor gases (Sun et al., 2015; Wu et al., 2016; Ren et al., 2018), and thus the coated/aged particles produced through photochemical processing in the afternoon can mix and interact with and freshly emitted primary particles emitted during rush hour (Wu et al., 2008). Therefore, during nighttime (22:00-06:00, LT), the particles are more uniform internally-mixed, which is reflective of the assumption for calculation of κ_{chem}, a much better consistency between κ_{chem} and κ_{gf} is observed. ~~And due to the relatively clean conditions overall in the summer, no large differences are observed under clean and polluted conditions (Fig. S5-S7).~~

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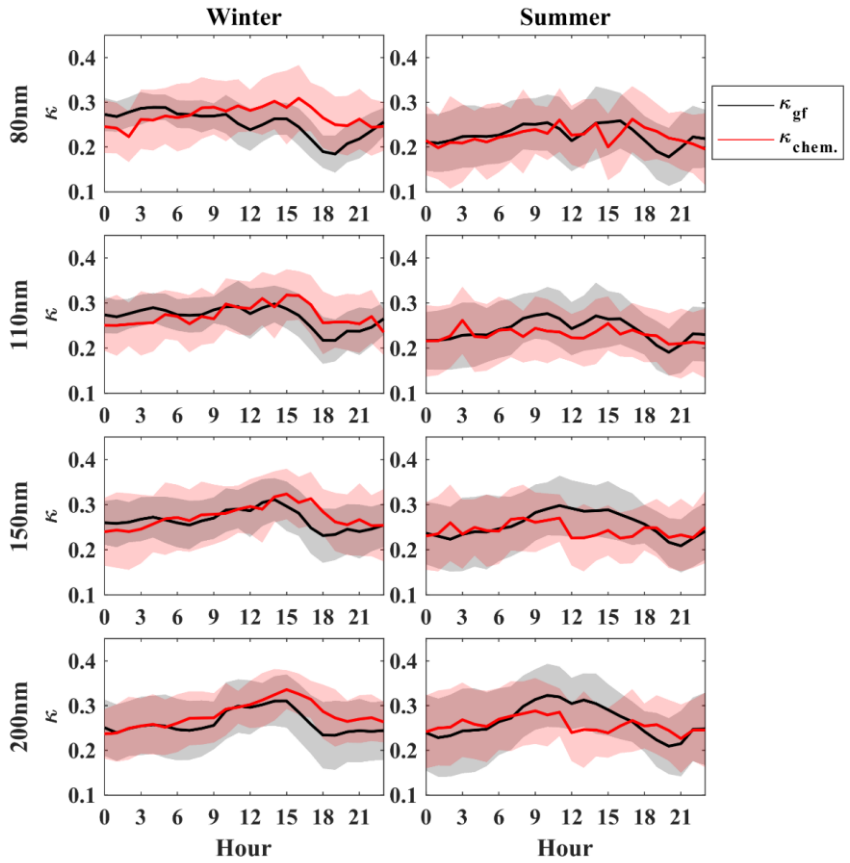
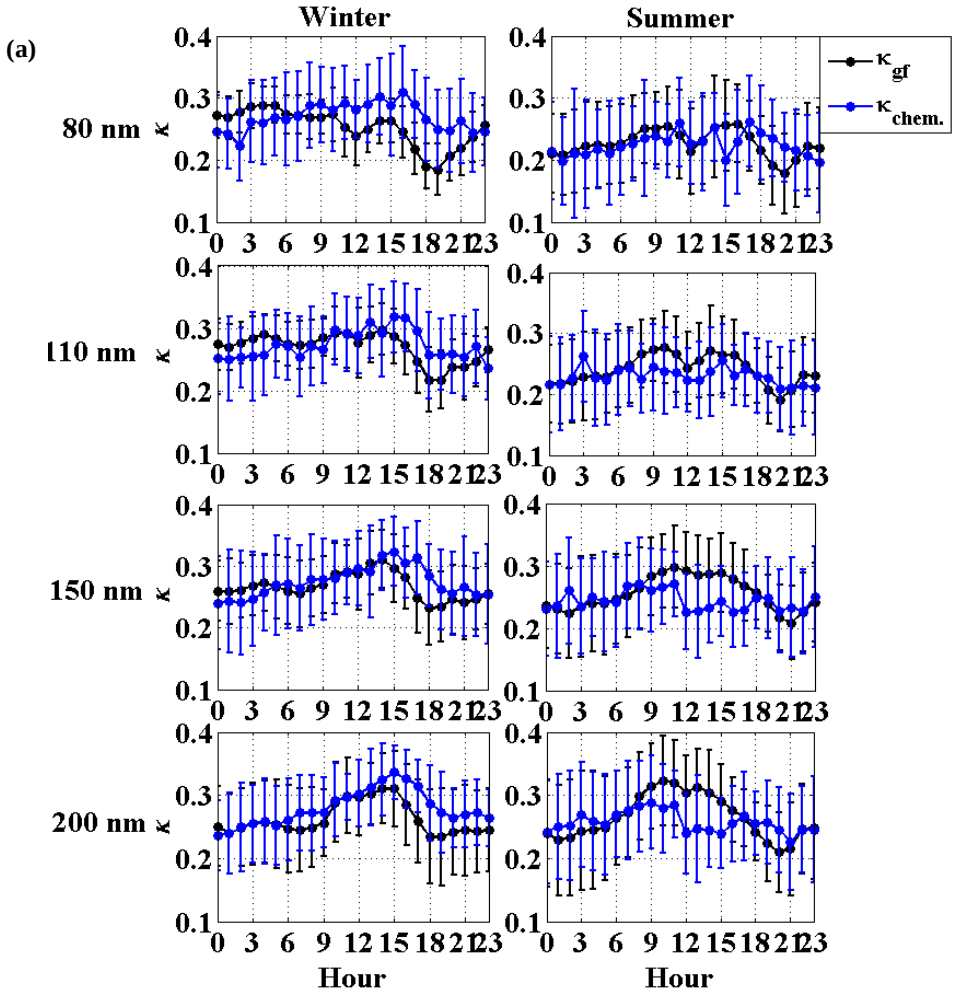
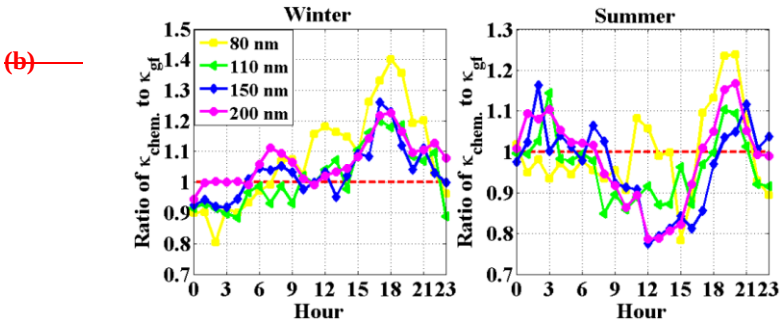

Winter
Summer
80nm
110nm
150nm
200nm
κ
0.4
0.3
0.2
0.1
0 3 6 9 12 15 18 21
Hour
κgf
κchem.

379


(a)
Winter
Summer
80 nm
110 nm
150 nm
200 nm
κ
κgf
κchem.
Hour


(b)
Winter
Summer
80 nm
110 nm
150 nm
200 nm
Ratio of κchem. to κgf
Hour

(b)

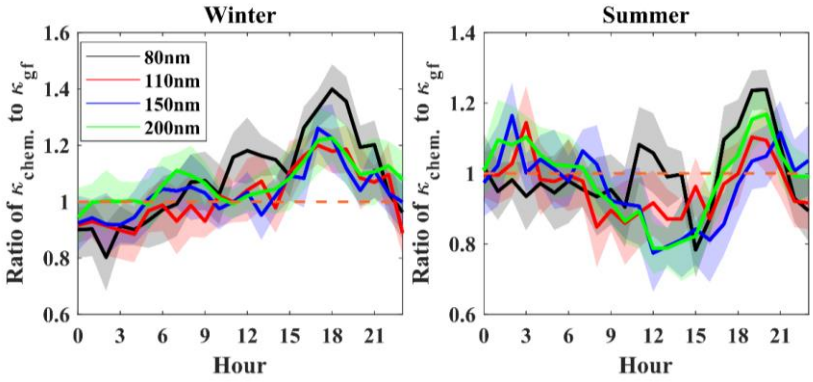


Figure 6. Diurnal variations ~~in~~of (a) κ_{chem} using size-resolved chemical composition data and κ_{gf} in winter and summer period; and (b) ratio of κ_{chem} to κ_{gf} in winter and summer period. The shade regions denote the error bars (1σ).

In winter, the disparity between κ_{chem} to κ_{gf} is insignificant at 09:00-15:00 due to the weakening effect of photochemical aging. From 15:00 to 21:00 LT, due to the strong vehicle and cooking sources around the site, the particles are dominated by the hydrophobic mode with a large concentration of externally-mixed BC and POA particles (Fig. 3~~ and Fig. S8~~), the calculated κ_{chem} is much higher than κ_{gf}, with the maximum ratio of κ_{chem} to κ_{gf} of 1.2-1.4, and the greatest disparity is observed for small particles. ~~The~~The disparity is further enhanced during clean periods when the hydrophobic mode is dominant (Fig. 7, Fig. S1).

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

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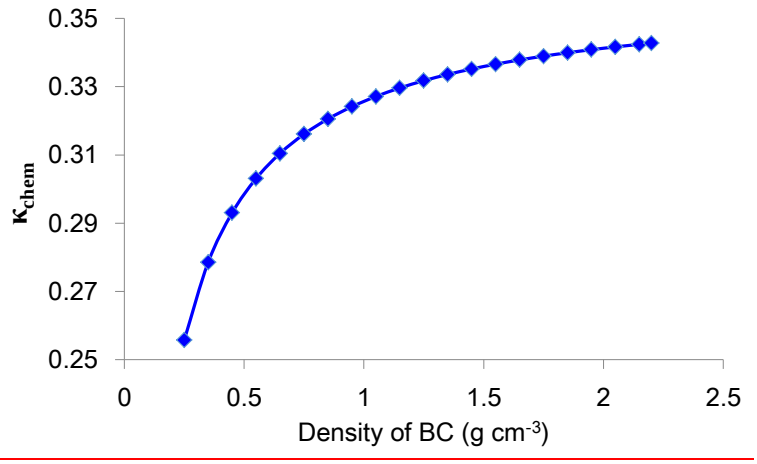
reduces by 16-33% when applying the BC effective density of 0.25-0.45 g cm^{-3}. This basically explains the disparity during the traffic rush hour. However, the changes in κ_{chem} are within ±4% when changing the organic density from 1.0 (typical for POA) to 1.4 (typical for SOA) g cm^{-3}, suggesting 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 hygroscopisity. 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 hygroscopisty, future investigations need to measure the effective density and morphology of ambient BC, in particularity in those regions with complex local sources.

(a)



(b)

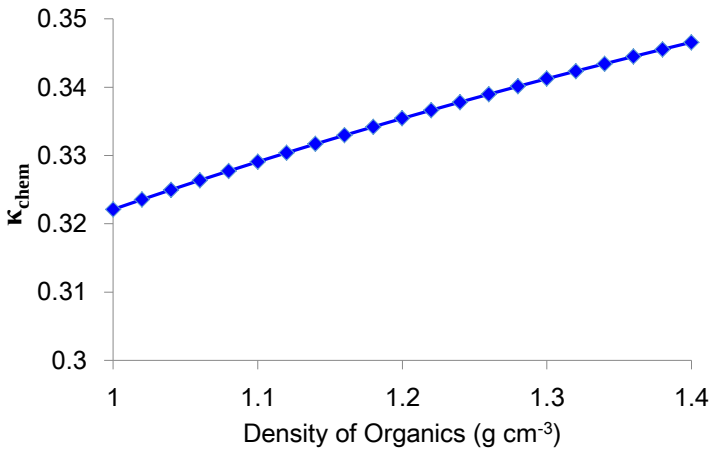


Figure 8. Sensitivity of κ_{chem} to variations of density of BC (a) and organics (b)

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 constitutes 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. Furthermore, in this study, it is calculated from a simple parametrized equation based on the AMS-measured f_{44} value reported by Mei et al. (2013). The value for f_{44} tends to be overestimated according to Fröhlich et al. (2015), which should yeild a larger κ_{chem}. Previous studies have shown that freshly emitted POA and BC particles may be rapidly coated by more hygroscopic components in polluted urban areas, resulting in enhanced hygroscopicity of the mixed particles (Zhang et al., 2004; Johnson et al., 2005; Zhao et al., 2017). Our results are consistent with those observations and clarify the photochemical aging and coating effect will largely underestimate the particles hygroscopicity using simple mixing rule based on chemical composition.

Note that during the nighttime, κ_{chem} is slight lower than κ_{gf}, with the minimum ratio of κ_{chem} to κ_{gf} of ~0.8 for 80 nm particles and ~0.9 for 110 and 150 nm particles at 02:00-04:00 LT (Fig. 6b), indicating an underestimation of particle hygroscopicity using composition data. The disparity at nighttime is further increased during heavily polluted events (Fig. S1), when the particles are more internally-mixed with only

one hygroscopic mode (Fig. 8). 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 hygroscopisity.

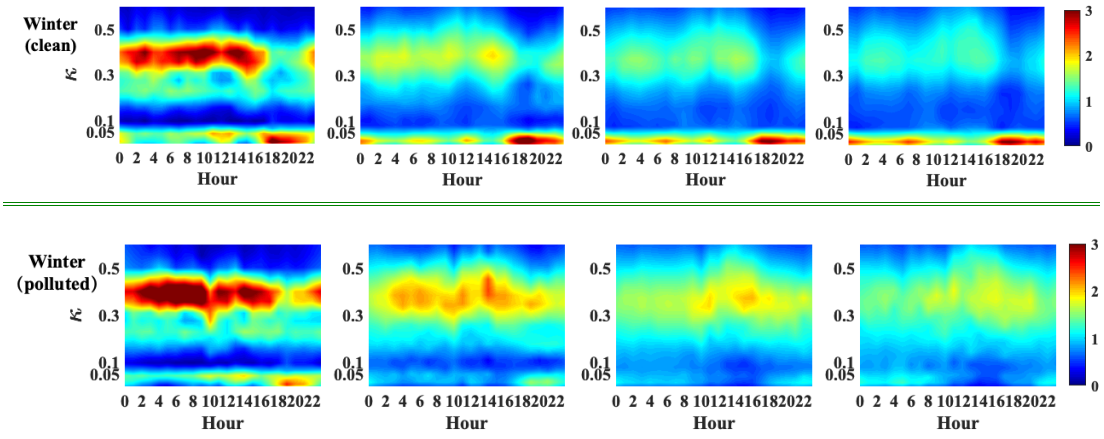
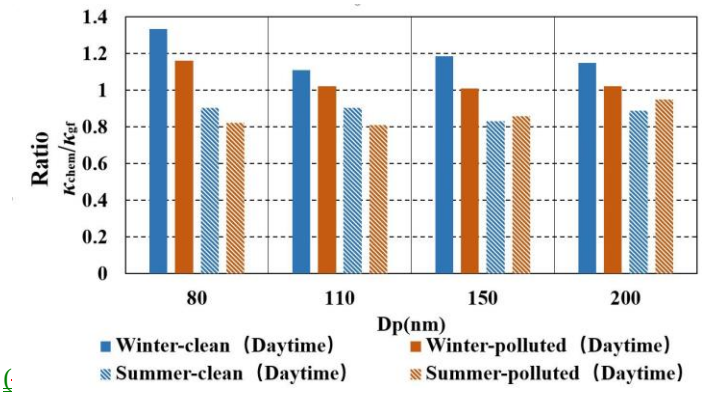


Figure 8. Diurnal cycles of κ_{gf} -PDF for 80, 110, 150 and 200 nm particles in clean and polluted events in winter.

3.5. Observation from other stations

The aging process in the summer period is related to photochemical processing in strong solar radiation conditions. The photochemical reactions produce sulfate and secondary organic aerosol, condensing on the surface of slightly- or non-hygroscopic primary aerosols (such as BC) (Zhang et al., 2008). As discussed in 3.4, the core-shell structure that accompanies aging of the particles results in calculated κ_{chem} that underestimates their hygroscopicity. To confirm such a coating effect on particle hygroscopicity, we further

examine the diurnal variations of κ_{chem} and κ_{gf} or κ_{CCNc}



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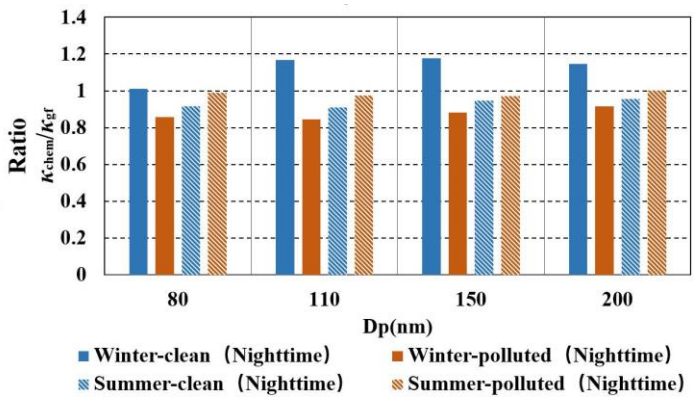
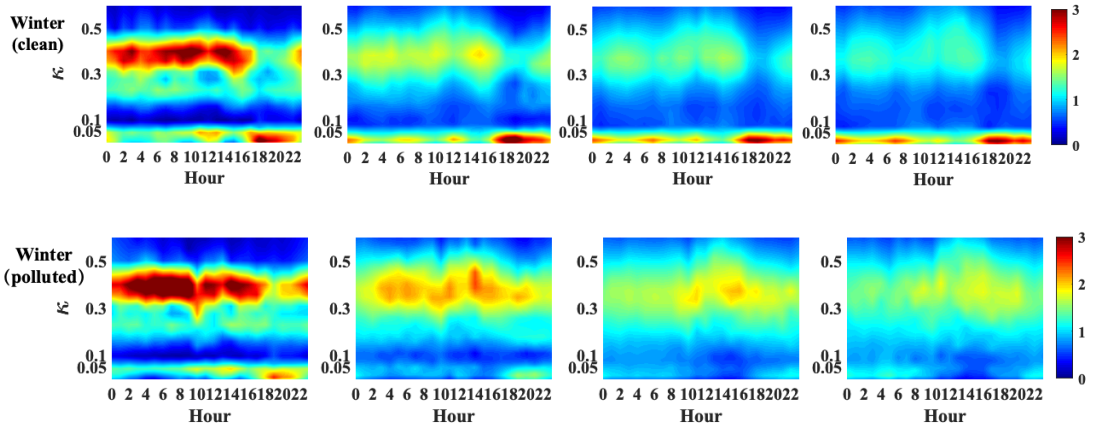


~~Figure 7. Ratio of mean κ_{chem} to κ_{gf} during daytime (top panel) and nighttime (bottom panel) under clean /polluted conditions between winter and summer period.~~

~~disparity is further enhanced during clean periods (Fig. S7, Fig. S9 and Fig. 7) when the hydrophobic mode is dominant (Fig. 8). But note that during the nighttime, κ_{chem} is slight lower than κ_{gf}, with the minimum ratio of κ_{chem} to κ_{gf} of ~0.8 for 80 nm particles and ~0.9 for 110 and 150 nm particles at 02:00-04:00 LT (Fig. 6b), indicating an underestimation of particle hygroscopicity using composition data. The disparity at nighttime is further increased during heavily polluted events (Fig. 7 and Fig. S9), when the particles are more internally mixed with only one hygroscopic mode (Fig. 8 and Fig. S8). We believe 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).~~

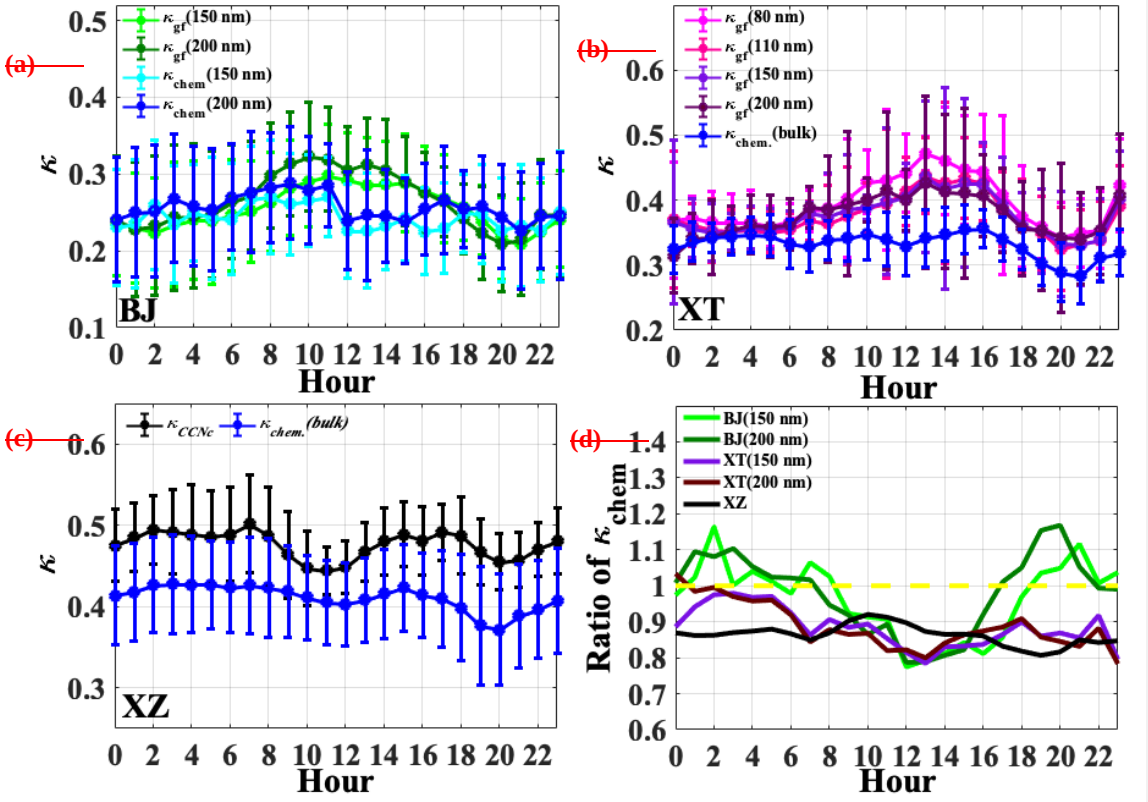


~~Figure 8. Diurnal cycles of κ_{gf} PDF for 80, 110, 150 and 200 nm particles in clean and polluted events in winter.~~

~~**3.5. Observation from other stations**~~

~~The aging process in the summer period is related to photochemical processing in strong solar radiation conditions. The photochemical reactions produce sulfate and secondary organic aerosol, condensing on the surface of slightly- or non-hygroscopic primary aerosols (such as black carbon) (Zhang et al., 2008). As discussed in 3.4, the core-shell structure that accompanies aging of the particles results in calculated κ_{chem} that underestimates their hygroscopicity. To confirm such a coating effect on particle hygroscopicity, we further examine the diurnal variations of κ_{chem} and κ_{gf} or κ_{CCNc} (derived from CCN measurements~~only at XZ site) based on observations in summer at two other sites in north China (Fig. 1). The XT site is located in the suburb of XT city, which is about 400 km south of Beijing, with high levels of industrialization and urbanization. Due to industrial emissions and typically weak ventilating winds, concentrations of $PM_{2.5}$, black carbon and gaseous precursors are usually high at the site (Fu et al., 2014). Xinzhou is located in north of Taiyuan and about 360 km southwest of Beijing, and is surrounded by mountains on three sides. Local emissions from motor vehicles and industrial activities have relatively little influence on the sampled aerosol (Zhang et al., 2016). ~~1). We~~ Because of its location and elevation, the aerosol at the XZ site is usually aged and transported from other areas. The sampling period was from July 22 to August 26, 2014 and from May 17 to June 14, 2016 at XZ and XT site respectively.

We find that the case at the ~~Xingtai (~~XT~~)~~ site is very similar to that observed in ~~Beijing (~~BJ (Fig. 9a), with a lower κ_{chem} than κ_{gf} around noon time. But, because of much less influences from the local sources at XT compared to that at BJ, such underestimation by κ_{chem} continued until night at XT (Fig. 9b). Interestingly, a noontime lower κ_{chem} was not observed in the diurnal cycles at the ~~But, because of much less influences from the local sources at XT compared to that at BJ, such underestimation by κ_{chem} continued until night at XT (Fig. 9b). Interestingly, a noontime lower κ_{chem} was not observed in the diurnal cycles at the Xinzhou (XZ)~~ site, where κ_{chem} and κ_{CCNc} had similar diurnal patterns (Fig. 9c) with a roughly constant ratio of κ_{chem} to κ_{CCNc} of ~0.8-0.9~~.~~ (Fig. 9d). This is probably because the XZ site is usually the recipient of aerosols transported from other areas that are already aged and well-mixed, with minimal impact of additional coating (Zhang et al., 2017). Also, the rate of oxidation and condensation may be slow in the relatively remote area where the gas precursors and oxidants are not as high as they are closer to sources regions. But at XT, which is located in the heavily polluted area in the north China Plain (Fu et al., 2014), aerosol emissions and processing are more similar to that in urban Beijing. These observations from other sites further confirms the the photochemical aging and coating effect that will largely underestimate the particles hygroscopicity using simple mixing rule based on chemical composition.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BJ
XT
XZ
Hour
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κgf(80 nm)
κgf(110 nm)
κgf(150 nm)
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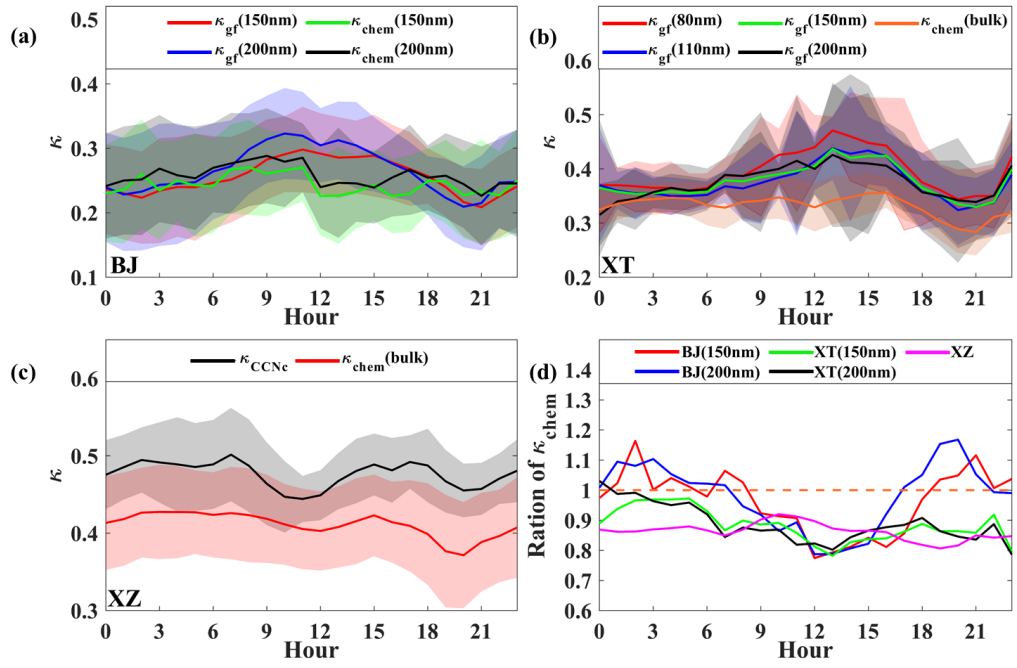
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Figure 9. Diurnal variations in (a) κ_{chem} and κ_{gf} for 150 and 200 nm particles at BJ site; (b) κ_{chem} and κ_{gf} for 40, 80, 110, 150 and 200 nm particles at XT site; (c) κ_{chem} and mean κ_{CCNc} for particles at XZ site, and (d) ratio of mean κ_{chem} to κ_{gf} at the three sites.

~~Although the underestimation in κ_{chem} may be also related to the uncertainty in the hygroscopic parameter for organics, which is calculated from a simple parametrized equation based on the AMS measured f_{44} value reported by Mei et al. (2013), Zhang et al. (2017) has shown that even the large underestimation of κ_{SOA} could not fully explain that of κ_{chem}. Furthermore, the value for f_{44} tends to be overestimated according to Fröhlich et al. (2015), which should lead to a larger κ_{chem}. Previous studies have shown that freshly emitted POA and BC particles may be rapidly coated by more hygroscopic components in polluted urban areas, resulting in enhanced hygroscopicity of the mixed particles (Zhang et al., 2004; Johnson et al., 2005; Zhao et al., 2017). Our results are consistent with those observations and clarify the photochemical aging and coating effect will largely underestimate the particles hygroscopisity using simple mixing rule based on chemical composition.~~

4. Conclusion

Using measurements of aerosol composition and hygroscopicity made in Beijing (BJ) during a winter period of 2016 and a summer period of 2017, this paper analyzes the daily variation and seasonal differences of size-resolved aerosol hygroscopicity in urban Beijing. We mainly focus on studying the disparity of κ_{gf} and κ_{chem} between summer and winter to reveal the impact of atmospheric processes and mixing state of the particles on its hygroscopicity. The uncertainty in calculating κ by using chemical composition with a uniform internal mixing hypothesis is elucidated from the diurnal variations of the difference between the calculated values: in summer, lower κ_{chem} is obtained around noontime, with a ratio of κ_{chem} to κ_{gf} of about 0.8-0.9 for large particles (i.e. 150 nm and 200 nm), showing an underestimation of particles hygroscopisity by using simple mixing rule based on chemical composition. Combining with the observation from ~~Xingtai~~XT and ~~Xinzhou~~XZ, we attribute the underestimation to the rapid noontime photochemical aging processes in summer, which induces the coating effect that will lead to a lower κ if assuming a uniform mixing of the particles. In contrast, larger κ_{chem} than κ_{gf} for >100 nm particles around noontime and in the

early afternoon is derived in winter, with the maximum ratio of κ_{chem} to κ_{gf} of 1.2-1.4 when the particles are dominated by the hydrophobic mode with a large number of externally-mixed POA particles from strong vehicle and cooking sources. ~~We suggest that, by using the simple mixing rule, the particles hygroscopisity can be underestimated up to 10% 20% for aged aerosols due to the coating effect, but will be maximally overestimated 20-40% for externally mixed particles.~~ We attribute this large disparity between κ_{chem} and κ_{gf} to changes of BC morphology that can be indicated by effective density of BC. The sensitivity test shows that it can well explain the disparity during the traffic rush hour by applying BC effective density of 0.25-0.45 g cm^{-3}. However, we suggest that,

to accurately parameterize or account for the effect of BC density on particles hygroscopisty, future investigations need to measure the effective density of ambient BC, in particularity in those regions with complex local sources.

A lower κ_{chem} than κ_{gf} for 80, 110 and 150 nm particles during the nighttime of winter is also noted, and the disparity is further enlarged in polluted days, probably due to a nighttime coating effect driven by condensation of secondary hygroscopic species on pre-existing aerosols in cold season. Our results highlight the impacts of atmospheric processes, sources on aerosol mixing state and hygroscopicity, which should be quantified and considered in models for different atmospheric conditions. ~~Long-term observations from more ground sites, as well as experiments in smog chambers, should be made to parameterize such impact in model simulations.~~

Data availability. All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Also, all data used in the study are available from the corresponding author upon request (fang.zhang@bnu.edu.cn).

Author contributions. F.Z. and ~~X.F.~~J. L conceived the conceptual development of the manuscript. X. F. directed and performed of the experiments with L.C., X.J., Y. W., and F. Z.. ~~X.~~F.Z., J.L., and X.F.~~Z~~. conducted the data analysis and wrote the draft of the manuscript, and all authors edited and commented on the various sections of the manuscript. J.L. and X.F. contribute equally to this work.

Competing interests. The authors declare no competing interests.

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