A point-by-point response to reviewers

Dear Editor,

We are very pleased to submit a revised manuscript entitled with "Measurement report: Hygroscopic growth of ambient fine particles measured at five sites in China" for possible publication in journal of Atmospheric Chemistry and Physics.

I'd like to thank you for your efforts and time on handling the paper. I also would like to thank the reviewers for their valuable comments and suggestions, all of which have been considered carefully during the revision (a point-by-point response to the reviewers as follows). We believe all the comments from the reviewers have been addressed, and the paper have been greatly improved after the revision.

Yours sincerely,
Fang Zhang
On behalf of all authors

Comments from the reviewers:

Anonymous Referee #1
The manuscript (Chen et al., Measurement report: Hygroscopic growth of ambient fine particles measured at five sites of China) report the HTDMA data at major cities in China (Beijing, Shanghai, Guangzhou) as well as that from suburban areas (Xinzhou and Xingtai). The data from these places, especially that from Beijing, Shanghai, and Guangzhou, have already been well documented in literature. However, the data from various places have rarely been well complied. The manuscript should be useful for researchers who would like to know the spatial distributions of hygroscopicity of aerosol particles in China. The data quality looks acceptably good. I suggest publication of the manuscript after addressing the following comments.

Major comments
I understand that the major purpose of the manuscript is to compile the HTDMA data from five locations. It seems that the authors also have the ACSM data for all the locations. However, only the campaign average ACSM data seem to be compared with the HTDMA. It might have been possible to elucidate the controlling factors of the hygroscopicity in more detail by comparing it with the highly time-resolved ACSM data, although it might not be required for a measurement report.

Re: Thanks for the reviewer's comments. We compare the time series of mass fraction of chemical composition derived by the ACSM and the hygroscopic parameter κ derived by the HTDMA at the five sites (Fig. R1). Since the measurement of ACSM is more accurate for larger size particles (>100 nm), here only the results for 110 and 150 nm particles are presented. It shows that, at the sites, the κ generally increases with increase of the mass fraction of hydrophilic inorganic salts, and the opposite is true for organics, indicating the hygroscopicity is closely related to the chemical composition of particles. A supplement and some discussions have been added in the revised paper, in lines 359-362, or as follows:

"…This is also demonstrated by comparing whole time series of the mass fraction of chemical composition with the κ at the five sites (Fig. S4), showing that the κ generally increases with increase of the mass fraction of hydrophilic inorganic salts, and the opposite is true for organics.…"

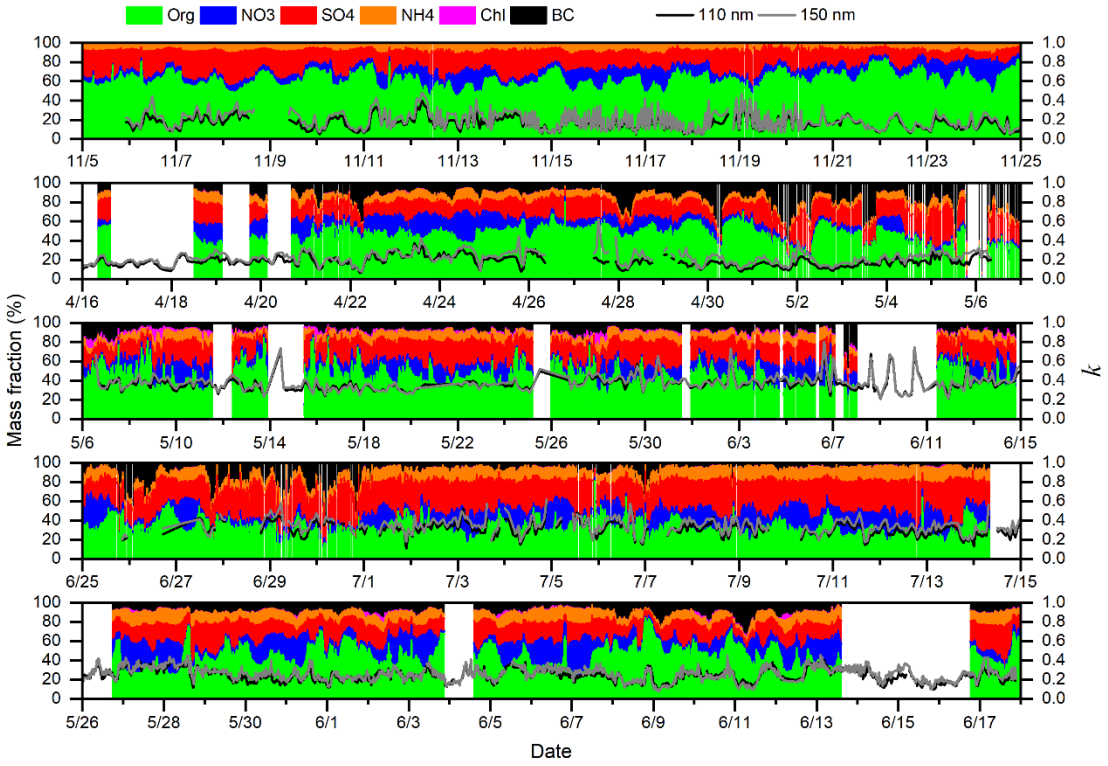

Figure R1. Time series of mass fraction of chemical composition in $PM_{2.5}$ and hygroscopic parameter κ for 110 and 150 nm particles derived by the HTDMA at the five sites (GZ, SH, BJ, XZ, and XT).

Specific comments

L154 'the non-refractory chemical compositions in PM2.5 were measured simultaneously using a quadrupole aerosol chemical speciation monitor (Q-ACSM) in real time' I wonder if the authors used a traditional aerodynamic lens or PM2.5 aerodynamic lens. It would be ideal to clarify it if chemical compositions were

measured as PM2.5.

Re: Thanks for the reviewer's comments. We used a $PM_{2.5}$ aerodynamic lens in the ACSM measurement, and the information has been added to the revised text, see lines 157-158, or as follows:

"…the non-refractory chemical compositions in $PM_{2.5}$ were measured simultaneously using a quadrupole aerosol chemical speciation monitor (Q-ACSM) with a $PM_{2.5}$ aerodynamic lens…"

L170 'This indicates different mixing states of ambient aerosol particles between urban and non-urban regions on account of their contrasting emission sources.' It would be helpful if the authors could provide more specific ideas on the potential differences in emission. I personally wonder if chemical aging of particles during atmospheric transport from urban areas to suburb regions could influence hygroscopicity.

Re: More specific information about the potential differences in emission of different sites has been added to the revised paper, in lines 173-177, or as follows:

"The urban sites are frequently influenced by local sources (e.g. traffic and cooking activities) (Sun et al., 2015; Tan et al., 2017), whereas the suburban sites are relatively clean with much less emission sources nearby and the aerosols are mainly transmitted from elsewhere and are thus more aged and well-mixed (Zhang et al., 2017; Wang et al., 2018b)."

L191 'At the non-urban sites, however, the hydrophobic modes of GF-PDFs were negligible throughout the whole measured sizes.' Figure 3 clearly demonstrates that hydrophobic modes exist even at non-urban sites, although the fraction could be smaller than the corresponding values for urban areas. I suggest modifying the statement.

Re: Thanks for the reviewer's suggestion. This statement has been revised, as follows:

"At the non-urban sites, however, the hydrophobic modes of GF-PDFs were much smaller throughout the whole measured sizes."

L205 'This could be associated with the nucleation process in the daytime, which was demonstrated that the growth of the newly formed particles is mainly contributed by hydrophilic matters' Is the hypothesis supported by the SMPS data?

Re: Yes, from the campaign-averaged diurnal variations of particle number size distribution measured by SMPS at the urban sites (GZ, SH, and BJ) (Fig. R2), an obvious new particle formation event was observed around noontime at these three sites. This figure has been added to support the statement in the supplementary information.

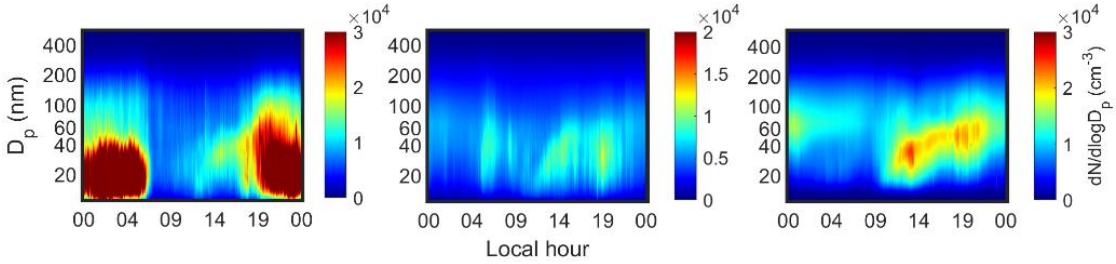

Figure R2. Campaign-averaged diurnal variations of particle number size distribution at the urban sites (GZ, SH, and BJ).

Anonymous Referee #2

This study reports hygroscopic growth measurements at five sites in China, three in urban locations and two in suburban locations. Approximately one month of measurements was conducted at each site over the years of 2016 - 2020. The studies all took place between April and July, with the exception of the study in Guangzhou which occurred in November. The observations show the smaller particles at the urban sites are usually composed of externally-mixed modes of varying hygroscopicity compared to the larger particles as well as particles of all sizes at the suburban sites. The authors also characterize the observations diurnally, as a function of PM2.5, in the presence of new particle formation and compared to chemical composition. Although numerous other HTDMA observations have been reported from China, I believe that this study is still of interest due to its greater spatial coverage and various analyses. The manuscript is well-written and the conclusions easy to follow. I recommend that the manuscript be accepted for publication provided that the authors address my scientific comments listed below, with the exception of the point about Sect 3.5 which would not be necessary for a Measurement Report but I am nevertheless interested in their explanation.

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

Scientific comments

Sect 2.2 - What was the residence time in the humidifying region? How often were calibrations conducted?

Re: The residence time in the humidifying region was 10 s (Jiang et al., 2016), and the calibrations were conducted once a month. This statement has been added to the revised text, in line 129 and lines 133-134, or as follows:

"…The humidified tube between DMA_1 and DMA_2 is controlled at RH of 90% with residence time of 10 s…"

"…The calibrations were conducted once a month…"

Can the authors comment on whether the pandemic and any ensuing lockdowns potentially affected their measurements in Shanghai and Xinzhou?

Re: The reviewer raised an interesting topic here. Indeed, the gaseous pollutants and chemical composition of aerosols might be changed during the pandemic of COVID-19, which would thereby lead to changes in particle mixing state and hygroscopicity. In North China, the study has shown that, the secondary process or atmospheric oxidation were enhanced during the pandemic of COVID-19, likely yielding more hygroscopic species like aqueous secondary organic aerosol (Zhong et al., 2021). Whereas in Yangze River Delta, the study has shown that the secondary components decreased during lockdown (Ma et al., 2021). However, the meteorological conditions, emissions, and anthropogenic sources also varies with seasons and years. It warrants further studies to clarify the impact of the pandemic in the future. We have added statements in the lines 420-430, or as follows,

"In addition, it is worth noting that measurements at the SH and XZ site were conducted during the COVID-19, when the gaseous pollutants and chemical composition of aerosols might be affected to varying degrees. This would thereby lead to changes in particle mixing state and hygroscopicity. For example, in North China, the study has shown that, the secondary process or atmospheric oxidation were enhanced during the pandemic of COVID-19, likely yielding more hygroscopic species like aqueous secondary organic aerosol (Zhong et al., 2021). Whereas in Yangze River Delta, the study has shown that the secondary components decreased during lockdown (Ma et al., 2021). However, the evaluation of such effect of the pandemic on aerosols' hygroscopicity is complex owing to that the meteorological conditions, emissions, and anthropogenic sources also vary with seasons and years. It warrants further studies to clarify such impact in the future."

Ma, J., Shen, J., Wang, P., Zhu, S., Wang, Y., Wang, P., Wang, G., Chen, J., and Zhang, H.: Modeled changes in source contributions of particulate matter during the COVID-19 pandemic in the Yangtze River Delta, China, Atmos. Chem. Phys., 21, 7343-7355, 10.5194/acp-21-7343-2021, 2021.

Zhong, H., Huang, R.-J., Chang, Y., Duan, J., Lin, C., and Chen, Y.: Enhanced formation of secondary organic aerosol from photochemical oxidation during the COVID-19 lockdown in a background site in Northwest China, Science of The Total Environment, 778, 144947, https://doi.org/10.1016/j.scitotenv.2021.144947, 2021.

Sect 3.4 - could the fact that the GZ study occurred in November have affected these results: more rain, changing wind patterns, etc?

Re: According to the comments, we examined the dependence of hygroscopic properties on rain and winds (wind direction and wind speed, Fig. R4). The meteorological data showed that there was no rain at GZ during the sampling period, and there is no obvious correlation between κ and wind patterns, suggesting the meteorological factors probably have not affected particle hygroscopicity. To clarify

this, we further examined the dependence of mass fraction of primary organic aerosols (POA) on the mass concentration of $PM_{2.5}$, and found that with the increase of pollution levels, the fraction of POA increased, suggesting the decrease of MH mode could be likely due to an increase of primary emission of hydrophobic POA. An explanation has been added to the revised paper of lines 266-267, or as follows:

"…the number fraction of MH mode declined slightly for 40-150 nm particles with the increase of $PM_{2.5}$ mass concentration at the GZ site, which was probably due to an increase of primary organic aerosols with the increase of pollution levels (Fig. S3)."

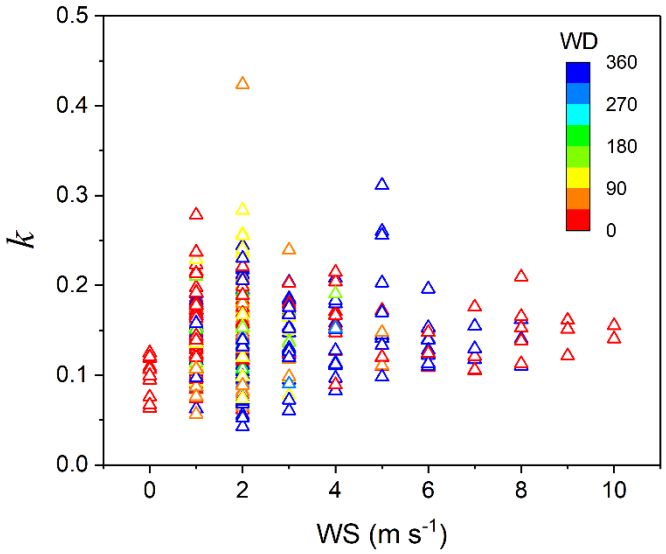

Figure R3. The dependence of κ (40 nm) on wind speed (WS) and wind direction (WD).

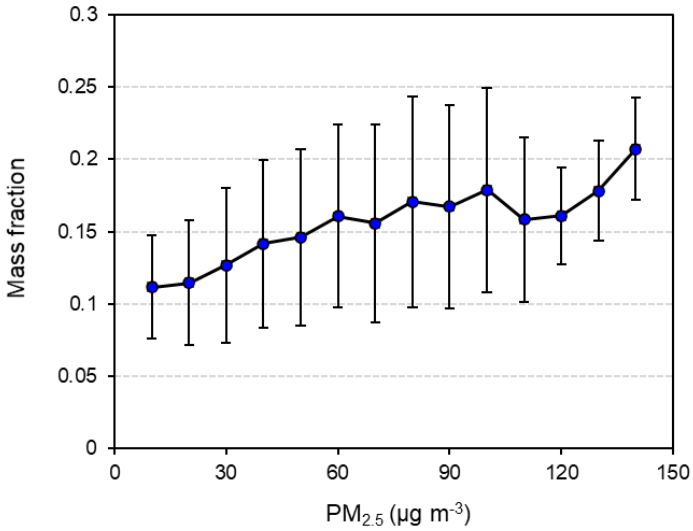

Figure R4. The dependence of mass fraction of primary organic aerosols on the mass concentration of $PM_{2.5}$.

Sect 3.5 - I'm curious what the authors think about the source / composition of the 40 nm particles on non-NPF days

Re: On non-NPF days, the 40 nm particles are mainly from the local primary sources (e.g. cooking, traffic, etc.), which can be indicated from the measured peak particle number concentration during the rush hours, or at the lunch and dinner time (Fig. 8c). This is also illustrated by the diurnal variation of the size-resolved chemical components measured at BJ, showing that the mass fraction of cooking organic aerosols (COA) and traffic-related hydrocarbon organic aerosols (HOA) increased obviously during the rush hour, and at the lunch and dinner time on non-NPF days (Fig. R5, Sun et al., 2016; Sun et al., 2018). The XZ site is near the main road, thus is more affected by the traffic emissions including road truck emissions at night (Fig. 8c). While, the catering night market activities near the Guangzhou site, which continued until the next morning, leads to a large number of small particle emissions. Some statements have been included in the revised text of lines 315-324, or as follows:

"…On non-NPF days, the 40 nm particles are mainly from the local primary sources (e.g. cooking, traffic, etc.), which can be indicated from the measured peak particle number concentration during the rush hours, or at the lunch and dinner time (Fig. 8c). This is also illustrated by the diurnal variation of the size-resolved chemical components measured at BJ, showing that the mass fraction of cooking organic aerosols (COA) and traffic-related hydrocarbon organic aerosols (HOA) increased obviously during the rush hour, and at the lunch and dinner time on non-NPF days (Sun et al., 2016; Sun et al., 2018). The XZ site is near the main road, thus is more affected by the traffic emissions including road trucks emissions at night (Fig. 8c). While, the catering night market activities near the GZ site, which continued until the next morning, leads to a large number of small particle emissions.…"

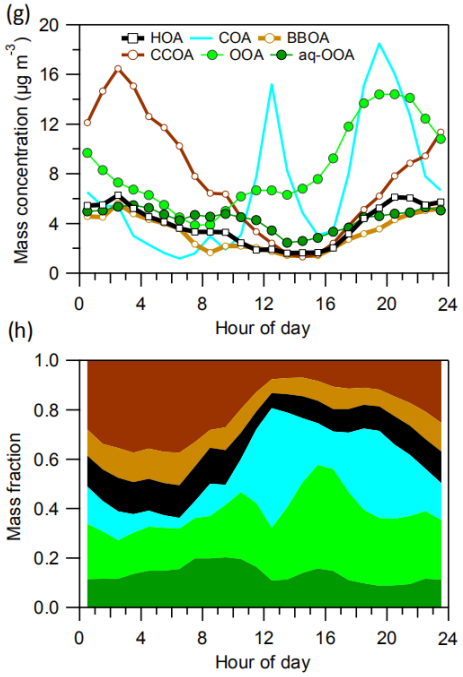

Figure R5. Average diurnal cycles of mass concentrations and mass fractions of OA factors. (from Sun et al., 2016)

Sun, Y., Du, W., Fu, P., Wang, Q., Li, J., Ge, X., Zhang, Q., Zhu, C., Ren, L., Xu, W., Zhao, J., Han, T., Worsnop, D. R., and Wang, Z.: Primary and secondary aerosols in Beijing in winter: sources, variations and processes, Atmos. Chem. Phys., 16, 8309-8329, 10.5194/acp-16-8309-2016, 2016.

Sun, Y., Xu, W., Zhang, Q., Jiang, Q., Canonaco, F., Prévôt, A. S. H., Fu, P., Li, J., Jayne, J., Worsnop, D. R., and Wang, Z.: Source apportionment of organic aerosol from 2-year highly time-resolved measurements by an aerosol chemical speciation monitor in Beijing, China, Atmos. Chem. Phys., 18, 8469-8489, 10.5194/acp-18-8469-2018, 2018.

Sect 3.6 - Are the kappa values presented in this section for each Do represent all the fractions (NH, LH, MH)? Or is it for just one of the modes? Is it possible to calculate the kappa value for each of the different modes?

Re: Yes, the kappa values presented in Fig. 10 for each D_0 represent the mean values from the GF-PDF. According to the reviewer's suggestion, we calculated the kappa value for each of the different modes, and the Figure 10 has been updated as Fig. R6, some statements have also been revised in Sect 3.6, as follows:

"…we presented campaign mean size-resolved κ for NH, LH and MH modes calculated from the H-TDMA measurements of the five sites (Fig. 10a). The measured bulk mass concentrations fraction of chemical components in $PM_{2.5}$ measured by the ACSM is also presented here (Fig. 10b). Clearly, it shows that the MH mode particles hygroscopicity was closely relevant to the chemical compositions. That is, the particles were found more hygroscopic with larger κ values at the sites such as BJ, XZ and XT where the hygroscopic inorganics account for a large mass fraction in $PM_{2.5}$…"

"…The mean κ values of NH and LH mode are close to 0 at the five sites, and decrease slightly with the increase of particle size…"

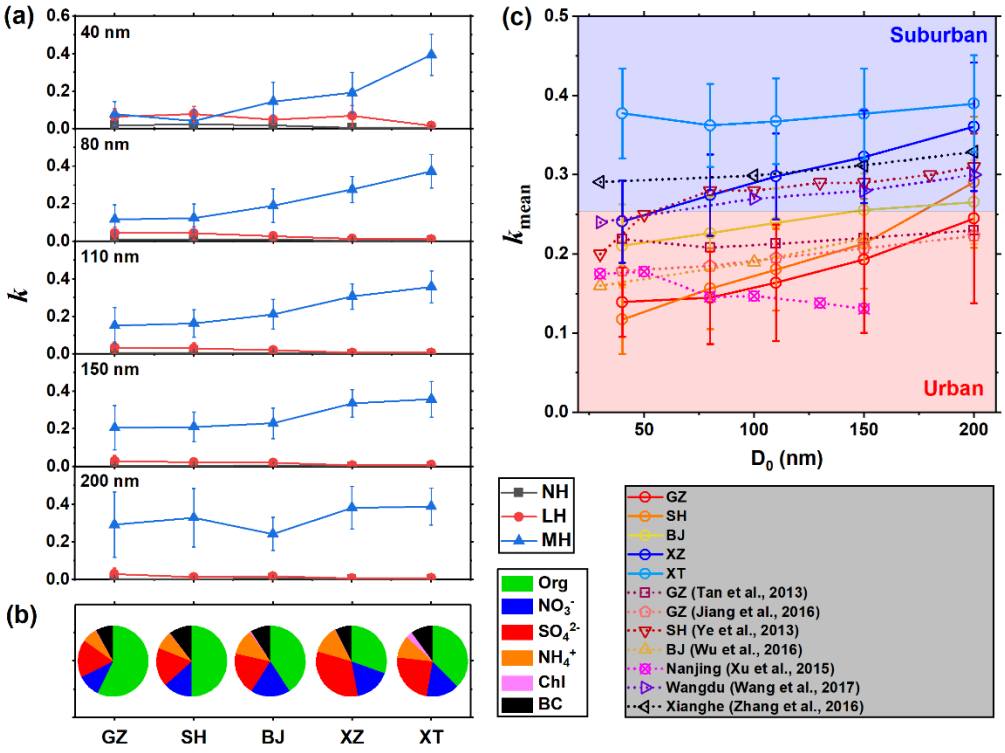

Figure R6. (a) Size-resolved mean hygroscopicity parameters (κ) nearly hydrophobic (NH), less hygroscopic (LH), and more hygroscopic (MH) for all measured particle sizes at different sites. (b) Campaign-averaged bulk mass fraction of chemical compositions of $PM_{2.5}$. The BC mass concentration of the GZ site is based on the data measured in January 2020 due to the lack of observations in November 2019. (c) size-dependent mean κ for all measured particle sizes retrieved from the H-TDMA measurements at different sites and reported by previous studies (Tan et al., 2013; Jiang et al., 2016; Ye et al., 2013; Wu et al., 2016; Xu et al., 2015; Wang et al., 2017; Zhang et al., 2016). The error bars represent $\pm 1\sigma$.

Line 365 - The authors state that the more hygroscopic mode accounts for only 20-40% of number fraction at urban sites. However, does this change significantly during NPF times?

Re: We calculated the average number fraction of each mode for 40 nm particles at each site on NPF days (Fig. R7). The number fraction of MH mode at urban sites increased slightly compared to the mean values represent the whole measurements, but the maximum number fraction of MH mode was only ~45% (at BJ), and which is still within 20-40% at the GZ and SH site, thus this conclusion does not change significantly during NPF times. A statement has been added in the revised version (lines 241-244), or as follows,

"….. on NPF days, the number fraction of MH mode at urban sites increased ~4% compared to the mean values represent the whole measurements, and the maximum number fraction of MH mode was ~45% at the BJ site (Fig. S2).

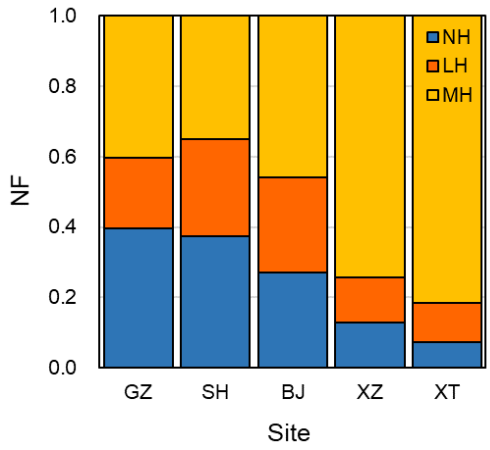

Figure R7. Campaign-averaged number fraction (NF) of nearly hydrophobic (NH, blue), less hygroscopic (LH, orange), and more hygroscopic (MH, yellow) group for 40 nm particles at each site on NPF days.

Minor and Technical comments:

Title - consider changing to "measured at five sites in China"

Re: Revised.

Line 103 - should be "field campaign"

Re: Revised.

Eq (3) - consider inserting a multiplication symbol between GF and c

Re: Revised.

Line 215 - consider changing to "the aged particles"

Re: Revised.

Figure 5 - I understand that the current emphasis is on comparing the composition of each size particles over the five sites. However, have you considered making each site a panel with the sizes on the x-axis? This would make it easier to see how the hygroscopicity changes with size.

Re: Revised.

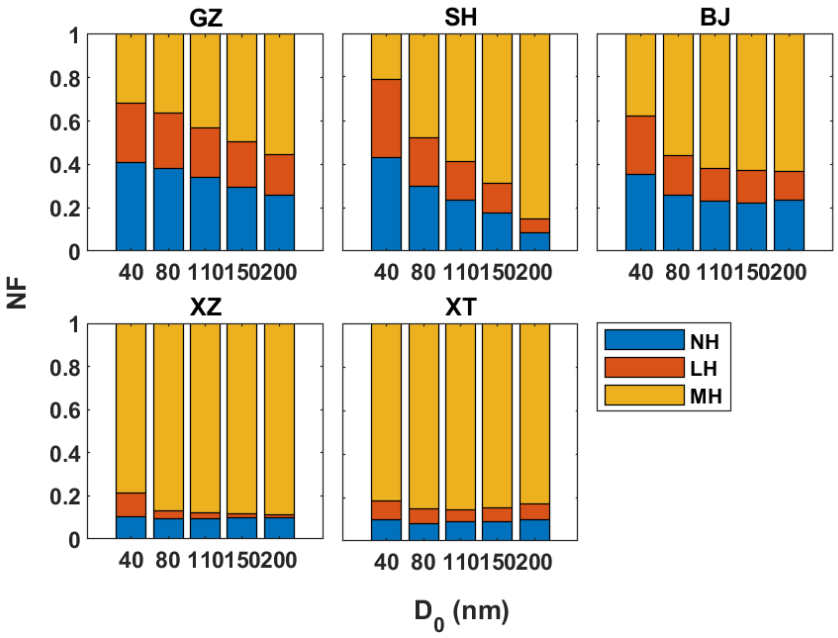

Figure R8. Campaign-averaged number fraction (NF) of nearly hydrophobic (NH, blue), less hygroscopic (LH, orange), and more hygroscopic (MH, yellow) group for 40-200 nm particles at each site.

Line 293 - Consider spelling out NCP since you only use it 3 times

Re: Revised.

Figure 8 - What do the dots in panels b and d represent? It is not explained in the caption.

Re: Revised. The dots in panels b and d represent the mean GF values.

Line 345 - edit to "owing to the fact that"

Re: Revised.

Line 368 - edit to "aggregated PM2.5"

Re: Revised.

Lines 370-372 - I'm having trouble understanding this sentence. Are you trying to explain the spatial variability? Or attributing the observed differences to the spatial variability? Please clarify

Re: This sentence has been revised, as follows:

"The distinct dependence of aerosol hygroscopicity on $PM_{2.5}$ concentrations among the sites is attributed to the spatial variability of particle formation mechanisms with the evolution of pollution events in different regions of China."

Line 489 - the reference for Liu et al., 2011 is repeated

Re: Revised.

General - Replace "accumulated particles" with "accumulation mode particles"

Re: Revised.