We would like to thank all five reviewers for their detailed and constructive comments. They have greatly helped to improve the structure and content of our work. Our replies are given in red color below. The revised manuscript is attached in the end of this file.

Answers to Referee #1

The authors appreciate the time the reviewer has spent on our manuscript, assisting us to produce a higher quality, understandable publication. All the requested comments and suggestions are addressed and introduced to the revised version of the manuscript.

Major comments:

1. The authors should describe the exact calculation procedure possibly with mathematical equations for lines 171–174.

Reply: After obtaining GF-PDF, which was represented as $c(HGF)$, ensemble mean hygroscopic growth factor (HGF), number fraction of particles at each mode and spread of each mode was calculated according to the following equations (Gysel et al., 2009; Tan et al., 2013):

$$HGF_{mean} = \int_0^{\infty} HGF \cdot c(HGF) d(HGF). \tag{1}$$

$$\sigma = \left(\int_0^{\infty} (HGF - HGF_{mean})^2 \, c(HGF) d(HGF) \right)^{1/2}. \tag{2}$$

$$NF^{a,b} = \int_a^b c(HGF) d(HGF). \tag{3}$$

Here HGF_{mean} is the number weighted mean hygroscopic growth factor, σ is the standard deviation of GF-PDF, which is used as a measure for the degree of mixing of aerosol population. $NF^{a,b}$ represents the number fraction of particles in which $a < HGF < b$.

2. Sect. 2.1 and later. The arrival height of 150 m above the ground is unusually low; the model performs better at higher levels. This raises the question about the representatively of these air mass trajectories. The authors should discuss and explain their selection, and/or present similar trajectories for at least 2 more but larger arrival heights (e.g. one just below and one above the fee troposphere). In addition to that, the authors should describe how the major trajectory clusters and their frequency in Fig. 7 were exactly derived from the individual trajectories.

Reply: We agree with the Referee that the HYSPLIT model might not work properly when the arrival height was set as low as 150 m in this study. Hence, we performed the back trajectory analysis using the HYSPLIT model for arrival heights at 300 m, 700 m, and 1000 m above ground level. For each arrival height, cluster analysis was then used to group these entire 156 back trajectories into mean trajectories, e.g. clusters for different experimental periods of interest. The basic principle is to merge trajectories that are spatially near each other and form groups or clusters that represent these trajectories. This is computationally achieved by minimizing the differences between trajectories within a cluster and maximizing the differences

between clusters. The detailed equations and calculation procedure are available in the HYSPLIT Tutorial document (https://www.ready.noaa.gov/documents/Tutorial/html/traj_clus.html). Results of the back trajectory analysis for different arrival heights are illustrated in Fig. R1, Fig. R2 and Fig. R3 in this response respectively. There are no significant differences between the results of the three different arrival heights. However, we agree with the referee that the arrival height of 150 m is fairly low for this model. Therefore, we switched to the arrival height of 700 m, which is the mean height of the boundary layer in Guangzhou during the experimental period according to the data obtained from European Centre for Medium-Range Weather Forecasts (ERA Interim).
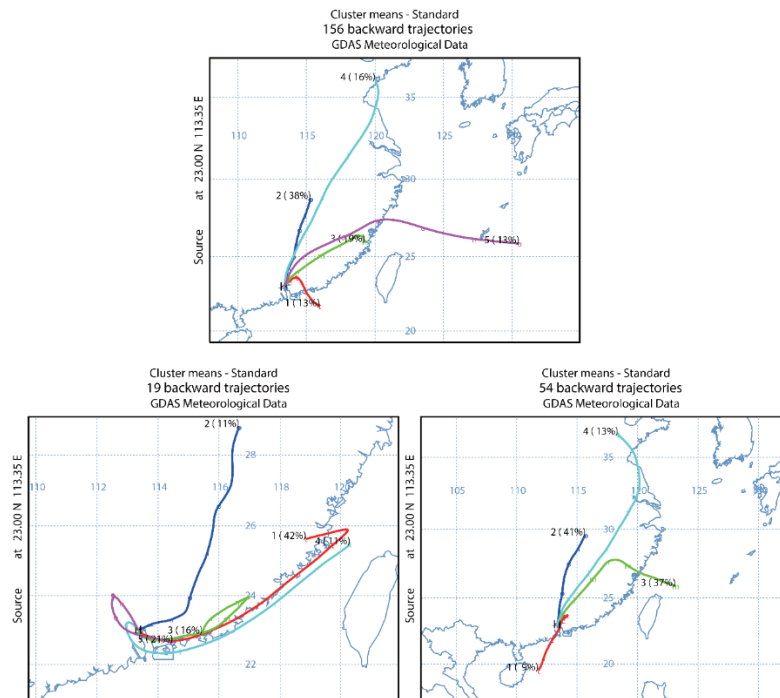

Figure R1. The major clusters for the 72-hour backward trajectory simulation for air masses arriving at the CAWNET Panyu site at a height of 300 m. The upper panel shows the results throughout the whole observational period, while the lower panel on the left side shows the one during polluted days and the one on the right-hand side is for clean days.

Figure R2. The major clusters for the 72-hour backward trajectory simulation for air masses arriving at the CAWNET Panyu site at a height of 700 m. The upper panel shows the results throughout the whole observational period, while the lower panel on the left side shows the one during polluted days and the one on the right-hand side is for clean days.
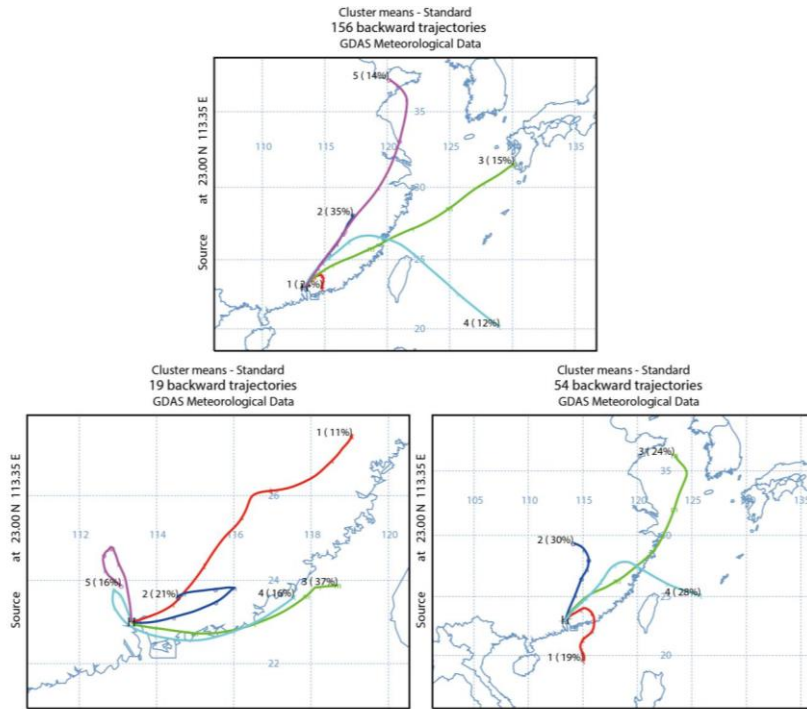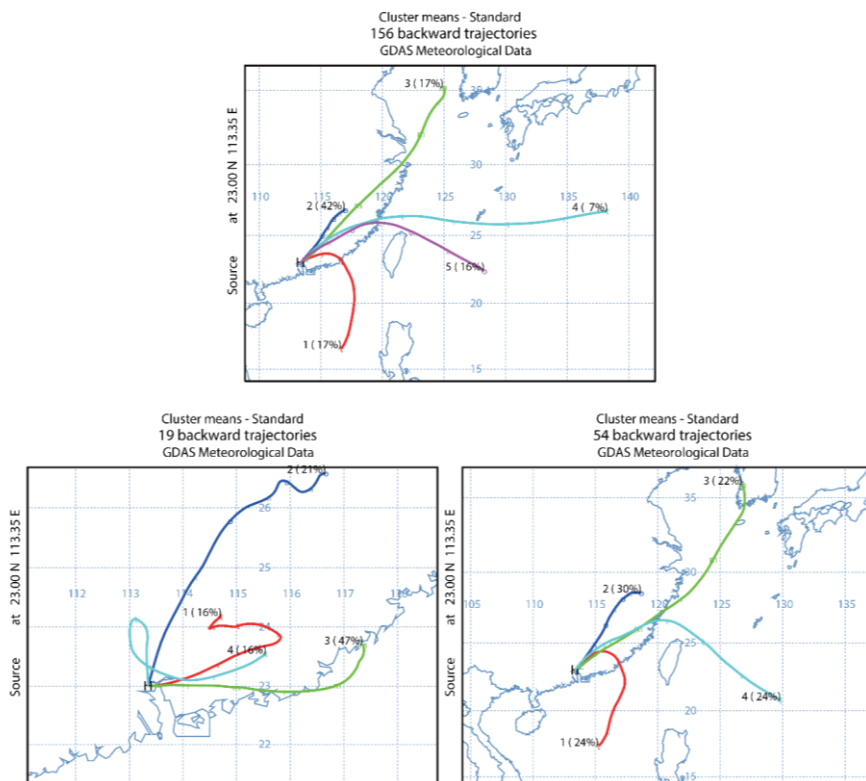

Figure R3. The major clusters for the 72-hour backward trajectory simulation for air masses arriving at the CAWNET Panyu site at a height of 1000 m. The upper panel shows the results throughout the whole observational period, while the lower panel on the left side shows the one during polluted days and the one on the right-hand side is for clean days.

3. Aerosol particles are usually grouped as: nearly hydrophobic (κ<0.10), less hygroscopic (κ≈0.10-0.20) and more hygroscopic (κ>0.20; Liu et al., Atmos. Chem. Phys., 11, 3479– 3494, 2011). The authors may want to follow this attitude, or explain and argue for their own classification.

Reply: It is a conventional way to group aerosol particles into three characterized modes regarding their hygroscopicity. However, this might not always be the case; for instance, the other studies categorized aerosol particles into two modes, namely non or less-hygroscopic mode and more-hygroscopic mode (Aklilu et al., 2006; Gysel et al., 2007; Tan et al., 2013; Yeung et al., 2014; Wu et al., 2016) according to their own data. We tried to fit the measured data into three modes; however, the fitting procedure failed for more than half of the data sets. Two-mode fitting procedure was then carried out for all of the data.

4. The authors are requested to extend the MS with explicit discussions and estimations of the uncertainty of their major conclusions to prove their significance. In addition to that, smaller changes throughout the MS, e.g. showing standard deviations of slopes for correlation lines in Fig. 10, and similar amendments could also be adopted.

Reply: Yes, we have made a comprehensive uncertainty analysis regarding our measurements and calculations. Hence, the whole section (Sect. 3.4) was revised as shown below. **In addition, we feel the previous title might not fit for the current study and we changed it to 'Mixing state and particle hygroscopicity of organic-dominated aerosols over the Pearl River Delta Region in China'.**

Minor comments:

1. It is disturbing that the terms aerosol – aerosols – aerosol particles are not used in a consistent manner in the MS (e.g. lines 64, 123 and 196). The authors should decide which option to use, and should adopt it in a coherent nomenclature.

Reply: I decided to use 'aerosol particles' in the revised manuscript to keep a coherent nomenclature.

2. Abbreviation PM stands for particulate matter (as correctly stated in line 191), but it is sometimes used for particle matter mass (e.g. line 30). The explanation of the abbreviation should be given at its first occurrence, and it is redundant to repeated it e.g. in lines 232– 233. Furthermore, simply write for instance: "The PM2.5 mass concentration varied" instead of "The range of particle mass concentration (PM2.5) varied". In addition, it is not the range that varies.

Reply: I revised the sentence to: 'The PM2.5 mass concentration varied from 20 to 180 ug/m^3, with relatively low values (roughly below 50 ug/m^3) during most of the time.'

3. Hygroscopicity usually refers only to sub-saturated conditions. Clarify line 65, or give appropriate references to back your statement.

Reply: References were added to back up my statement: 'Aerosol hygroscopicity describes the interaction between aerosol particles and ambient water molecules at both sub- and super-saturated conditions in the atmosphere (Topping et al., 2005; McFiggans et al., 2006; Swietlicki et al., 2008).'

4. Micron (e.g. lines 98, 177, Fig. 2) is not an SI unit. Micrometer should be used instead.

Reply: 'Submicron' was used as a definition for particles with sizes smaller than 1 micrometer in diameter. This term is widely used in aerosol research articles.

5. Remove the repetitions in lines 102–103 considering lines 67–69.

Reply: I modified the sentence to: 'Hygroscopicity, as an important physico-chemical property of atmospheric particles (Cheng et al., 2008; Gunthe et al., 2011; Cheng et al., 2016), has also been implemented into extensive campaigns in densely populated areas, such as North China Plain (Massling et al., 2009; Liu et al., 2011) and Yangtze River Delta (Ye et al., 2013).'

6. Revisit "self-assembly" (line 120) and "self-assembled" (line 152), or use perhaps laboratory made instead.

Reply: Yes, I used 'self-assembled' in the revised manuscript.

7. Clarify lines 185–189.

Reply: Wu et al. (2009) compared the BC concentration in PM1 and PM2.5, respectively, and found that BC aerosols mainly exist in the fine particles with roughly 80% of the BC mass in PM1. Due to the limited literature data on BC size distributions in the PRD region, we used this simplified assumption by Wu et al. (2009) to estimate the BC concentration in PM1 for this study.

8. Abscissa of Figs. 1 and 2 shows rather Date than Time, and its format of e.g. "(dd-MM)" could also be indicated. Furthermore, they could have (this) consistent format in both figures. In Fig. 2, how can be the probability in colour coding larger than 1? Explain or modify this. Put word space between measured values and their units everywhere in the figures. Extend the interpretation of your finding and discussions related to Fig. 2 within the frame of the conjunct conclusions of Cheung et al., Atmos. Chem. Phys., 16, 8431– 8446, 2016.

Reply: Figure 1 in the manuscript was modified and is shown in Fig. R4 here. The color bar in Fig. 2 in the manuscript indicates the probability density rather than probability. To integrate the probability density along the x-axis, we will obtain the probability value. This is why its value is larger than one. All figures were modified as suggested.
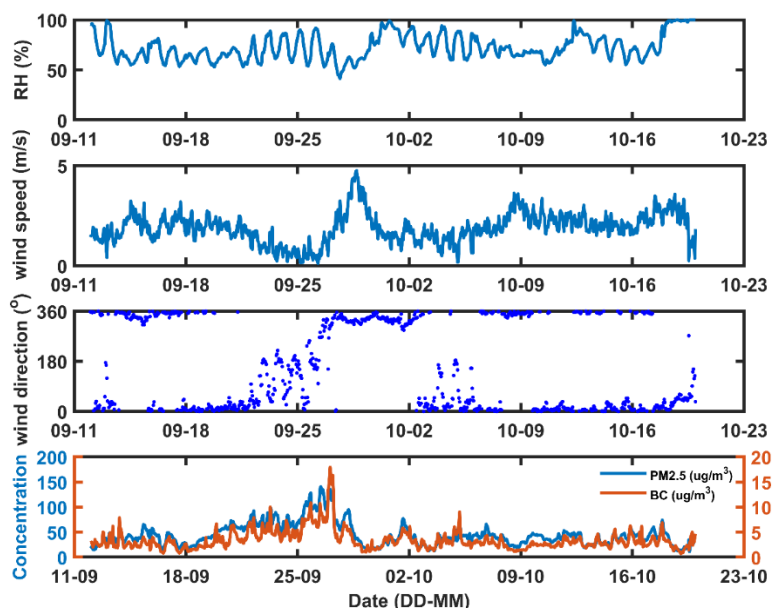
Figure R4. Time series for relative humidity (RH), wind speeds, wind directions and concentrations of PM2.5 as well as BC concentration (bottom panel).

9. Figures 3, 4 and 6 show the mean diurnal variations; the label of abscissa should be consistent in three figures; remove the tick label at 25; the time unit as "(HH)" should also be indicated; "during this study" is redundant; avoid abbreviations in the figure captions everywhere. Extend the interpretation of your finding and discussions related to the diurnal plots (Figs. 3 and 4 or Sects. 3.2 and 3.3) within the frame of the similar recent data of Enroth et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-926, 2017.

Reply: I moved Fig. 3 in the manuscript into supplement material part and modified all figures as suggested. Brief comparison was made between our results and Enroth et al. (2018).

10. All correlation scatter plots should have squared layout to facilitate better their interpretations.

Reply: Figures with x-axis and y-axis indicating the same variables was modified to have squared layout, see Fig. 8, Fig. 9 and Fig. 10 in the revised manuscript.

11. Rounding off strategy should be revised throughout the MS; e.g. of R2 in the figures or HGForg in lines 399, 405 ("1 and 1.3"), 515 or 546.

Reply: Yes, I modified all values I used in the whole manuscript to follow consistent strategy.

12. Lines 288–289: Remove "black carbon or" from "with black carbon or soot".

Reply: Yes, I removed 'black carbon or' from the text.

13. Line 319: Consider writing "compounds with different water uptake ability" instead of "compounds of different water uptake ability".

Reply: Yes, I changed it to 'compounds with different water uptake ability' in Line 319 in the revised manuscript.

Answers to Referee #2

The authors appreciate the time the reviewer has spent on our manuscript. We thank a lot for the concern raised by the reviewer here, which we agree we did not notice and consider earlier. Hence, we tried our best to include more assumptions and uncertainty analysis into the revised version of the manuscript to address the comments and suggestions given by the reviewer. We hope the new version of the manuscript could meet the requirements for publication.

Major comments:

1. The closure analysis compares ACSM-derived HGF for PM1 with HTDMA-measured HGF for 100 nm or 150 nm particles. What was the mode diameter (in terms of mass diameter distribution) of the particle population of PM1? If the mode diameter of PM1 is significantly larger than 150 nm, the estimated HGForg can be significantly underestimated, because the hygroscopicity generally increases with the diameter in the accumulation mode (at least for 50 nm - 250 nm particles as shown in Liu et al. ACP, 2011). Is it possible that the estimated low HGForg is affected by such systematic biases?

2. In line 328-331, the authors mentioned that the measured HGF values for the mixed particles are less sensitive to the relationship of HGForg vs. O:C. I agree with this statement. However, this implies that the derived parameterization of HGForg = 0.3*O:C + 0.87 can be highly uncertain, as it is not well constrained by the measurements. I noticed that including the O:C-dependent HGForg only improves R^2 from 0.5 to 0.51 (Fig.10 vs. Fig. 9 d). In this case, what is the error associated with the parameterization?

3. Related to the previous comment, the proposed relationship would predict a HGForg value smaller than 1 for O:C < 0.43. This can be misleading. What does a HGForg value smaller than 1 mean? Is it just because of measurement errors?

4. The authors reported a best-fit HGForg value of 1.1. The error bar associated with this value should also be reported. Errors of both HTDMA and ACSM, along with the uncertainties associated bulk vs size-resolved closure analysis should be considered.

5. Even if the HGForg = 1.1 value is accurate, I don't think the authors can assert that "the CCN concentrations would probably be over-predicted as the organic material in these locations appeared to be close to hydrophobic". Several studies have shown that the CCN activity can be higher than that predicted based on the HGForg at _90% RH. For example, alpha-pinene-derived SOA has a kappa value of _0.04 at 90% RH, but the CCN-derived kappa value is around 0.1 (see Pajunoja et al., 2015), which is close to the value used in climate models. The low hygroscopicity derived at subsaturation regime does not necessarily indicate a low CCN activity.

Reply: As all of the above questions are related to each other, so we combine the answers to address the comments together.

Number size distributions of particles within the diameter range 10 - 400 nm was measured by the SMPS in this study. Hence, the mode diameter in terms of mass diameter distribution of the particle population of PM1 could not be determined directly. Cai et al. (2017) showed that the mode diameter of the mass size distribution of the chemical composition of PM1 was around

300 - 400nm for aerosols sampled at the same measurement site during the same season of 2014. We agree that the estimated HGForg could be underestimated. However, size-resolved chemical composition information of ambient aerosols for current study is not available. We therefore considered the differences in the mass fraction of each component between PM1 and 145 nm particles obtained from Cai et al. (2017) and applied this assumption with certain uncertainties (20%) into the current study to make further evaluations. A newly determined parameterization of HGForg as a function of O:C ratio was given in the revised manuscript. We also performed a comprehensive uncertainty analysis for the hygroscopicity-composition closure and gave potential reasons from other sources of errors associated within this study.

With the new derived parameterization between HGForg and O:C, the values of HGForg values were all above one, which also indicates the size-resolved chemical composition taken from the above-mentioned assumption is physically reasonable. **The revised manuscript was attached in the end of this file.**

We agree with the reviewer that the sentence 'the CCN concentrations would probably be over-predicted as the organic material in these locations appeared to be close to hydrophobic' is not properly used here. Hence, we deleted it.

In conclusion, we feel the previous title might not fit for the current study and we changed it to 'Mixing state and particle hygroscopicity of organic-dominated aerosols over the Pearl River Delta Region in China'.

Technical issues:

1. The authors should describe how the HTDMA was calibrated and how the data inversion was performed. Did the measurements reproduce literature values for pure compounds (e.g., ammonium sulfate)? Was the RH sensor calibrated? Did the two DMAs have a shift in diameter? Was the DMA transfer function considered in data inversion?

Reply: The calibration of the HTDMA was mainly performed in two steps. First, the electronic mobility diameter of particles was calibrated using polystyrene latex (PSL) spheres with known sizes. If the mean particle sizes measured by both DMAs are within the nominal sizes of PSL spheres, then both DMAs are capable to select a certain sized particles with required accuracy. Otherwise, the voltage supplying to either DMA should be corrected by using a voltage reference (here, as a voltage meter) until the nominal sizes of PSL is reached. Secondly, calibration of the HTDMA was done by measuring the HGF of ammonium sulfate at a certain RH, for instance, 90%. The measured HGF values for ammonium sulfate at a certain RH should match rather well with theoretical predictions (for instance, HGF=1.71 at RH=90%) with about 2% deviation. The measured growth factor distributions were fitted into bimodal lognormal distributions using a corrected data inversion approach by TDMAfit algorithm assuming all particles follow a Gaussian distribution (Stolzenburg, 1988; Stolzenburg and McMurry, 2008) The detailed description about calibration of the instrument and the data inversion approach for this study is given in Tan et al. (2013).

2. The O:C ratio was estimated from the f44 measured by a quadrupole ACSM, presumably less accurate than that measured by the HR-ToF-AMS. What was the uncertainty of the ACSM-derived O:C?

Reply: The uncertainties of the HR-ToF-AMS to quantify O:C have been discussed previously and are approximately to be ±0.1 as determined by Aiken et al. (2007) and Aiken et al. (2008).

The uncertainties of determining O:C for ambient aerosols using other types of AMS and ACSM is not well established. However, Ng et al. (2011) demonstrated that due to the similarities with AMS, all the methods that already have been developed for the usage of AMS are capable to be used in ACSM data analysis. The largest differences between ACMS and AMS are that ACSM is not designed to measure mass size distribution and it has a lower detection limit (e.g. 0.2 ug/m3). Hence, we believe that the O:C ratio determined by ACSM should not deviate significantly than the one from AMS.

3. Figure 2. Unit of the color bar is missing.

Reply: We added the unit for the color bar in Fig. 2 in the manuscript.

Answers to Referee #3

The authors appreciate the time the reviewer has spent on our manuscript, assisting us to produce a higher quality, understandable publication. All the requested comments and suggestions are addressed and introduced to the revised version of the manuscript.

The authors present a study of low hygroscopicity of organic material in anthropogenic aerosols under pollution episode in China. The data set is rich, but the manuscript has two major deficiencies that should be addressed prior to considering further review. (1) The upper particle size ranges detected by different instruments are quite different: 145 nm for HTDMA, 1um for ACSM and 2.5 um for Aethalometer. Before drawing any conclusions, the authors should consider the uncertainties caused by different size ranges of particles being measured when integrating all dataset. (2) Most of previous studies showed that the hygroscopic growth factors of secondary organic aerosols are below 1.2. For example, the water-soluble organic carbon measured by Martin Gysel et al., has a hygroscopic growth factor of up to 1.17. In this study, the HGForg below 1.1 is actually comparable to those in other observations. Therefore, the low hygroscopicity of organic material cannot be a compelling result. Reference Gysel, M., et al., Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol. Atmos. Chem. Phys., 2004. 4(1): p. 35-50.

Reply: Yes, the Reviewer is right that the upper particle size ranges detected by different instruments are quite different. For BC measurements, Wu et al. (2009) compared the BC concentration in PM_1 and $PM_{2.5}$, respectively and found that BC aerosols mainly exist in the fine particles with roughly 80% of the BC mass in PM_1. Due to the limited literature data on BC size distributions in the PRD region, we used this simplified assumption by Wu et al. (2009) to estimate the BC concentration in PM_1 for this study. In addition, the ACSM-derived HGF is not sensitive to the change in BC mass concentration, which was also discussed in the uncertainty analysis in the revised manuscript; see the attached Section.

For the other chemical components measurements, ACSM only measured their mass concentration in PM_1, which should not be compared directly with the one measured by HTDMA with a certain size. However, size-resolved chemical composition information of ambient aerosols for current study is not available. Cai et al. (2017) measured size-resolved chemical composition of ambient aerosols obtained from the same measurement site during the same season of 2014. Their results showed that the average organic mass fraction of PM1 were about 16% lower than that of 145 nm particles. We therefore considered the differences of mass fraction of each component in between PM1 and 145 nm particles obtained from Cai et al. (2017) and applied this assumption with certain uncertainties into the current study to make further evaluations. A newly determined parameterization of HGForg as a function of O:C ratio was given in the revised manuscript. We also performed a comprehensive uncertainty analysis for the hygroscopicity-composition closure and gave potential reasons from other sources of errors associated within this study.

For the second comment: After taking into account of the size-dependent chemical composition of aerosols, HGForg value was shifted from 1.1 to 1.26, which was close to the one as 1.18 used by Yeung et al. (2014) measuring the hygroscopicity of ambient aerosols in September 2011 at the HKUST Supersite, less than 120 km away from our measurement site. I agree with the reviewer that the determined hygroscopicity of organic material is not significantly different from the ones from other

studies. However, without identifying the hygroscopicity of organic material for current environmental background, one should always use the assumed parametrization for the hygroscopicity of organic material from other environments with big cautions. In addition, this study is, to our knowledge, the first time to identify the hygroscopic properties of the organic material and their O:C dependency, which may help us understand the chemical composition, sources and aging processes of atmospheric aerosols in this region. **After considering the difference of chemical composition between size-resolved aerosols and bulk ones, we feel the previous title might not fit for the current study and we changed it to 'Mixing state and particle hygroscopicity of organic-dominated aerosols over the Pearl River Delta Region in China'.**

Answers to Referee #4

The authors appreciate the time the reviewer has spent on our manuscript, assisting us to produce a higher quality, understandable publication. The requested comments and suggestions are addressed and introduced to the revised version of the manuscript.

General Comments:

This paper is attempting to compare many components of the measured aerosol: four different aerosol sizes, two different HGF modes, clean vs polluted conditions, and diurnal trends. It's a complicated set of comparisons, and different sections of the paper address different things. The reader would benefit if the authors would more clearly state what each section is comparing, and only include the most relevant comparisons. For example, the first paragraph of section 3.2 discusses the diurnal trends of the mean HGF, but quickly states that there are no significant trends – probably because in the next section we can see that the LH and MH modes have opposite trends, and the mean HGF, which is the average of the two, sees these trends cancel out. So why include the mean HGF at all? Another example is at the end of section 3.3, where the authors demonstrate that the HGF dependence is different in clean and polluted conditions. If this is true, the authors should be careful in the rest of the paper to distinguish between clean and polluted conditions in their other analyses.

Reply: We shortened the paragraph discussing the diurnal variation of the mean HGF and moved Fig. 3 into the supplement material and restructured the whole section substantially as requested. We also made closure analysis for polluted and clean days similar as Sect. 3.4 to improve the Results and Discussion section with more detailed arguments. The new section was attached in the end of this file.

Secondly, the authors should identify the primary message of the manuscript and more clearly describe this result. Is it that the hygroscopicity's lower-than-expected dependence on O:C is attributed to a higher concentration of organics with larger molecular weights? If so, the authors should discuss this further. Are there experimental measurements available to support this? If this is the main conclusion, what should the reader learn from the extensive look into the dependence on inorganics, on the diurnal averages, which is what the majority of the results section is about?

Reply: According to the other Referees' comments, ACSM-derived HGF should not be directly compared with the one measured by HTDMA, since ACSM measured the bulk aerosols while HTDMA measured the HGF of size-resolved particles. We therefore considered the differences of mass fraction of each component between PM1 and 145 nm particles obtained from Cai et al. (2017), which measured the size-resolved chemical composition of ambient aerosols obtained from the same measurement site during the same season of 2014 and applied this assumption with certain uncertainties into current study to make further evaluations. A newly determined parameterization of HGForg and its O:C dependency was given in the revised manuscript. We also performed a comprehensive uncertainty analysis for the hygroscopicity-composition closure and gave potential reasons from other sources of errors associated within this study. After taking into account of the size-dependent chemical composition of aerosols, HGForg value was shifted from 1.10 to 1.26. We hence feel our previous discussion and arguments were improper given. Hence we deleted related arguments at several places and

modified the body text. However, even considering the size-resolved chemical composition of aerosols, we still observed the hygrosocpicity of organic compounds in current study has a relatively low O:C dependence. This finding is not completely unexpected, as Wu et al. (2016), which studied the particle hygroscopicity in the urban atmosphere of Beijing, also observed similar relation between HGForg and O:C ratio of ambient aerosols. Wu et al. (2016) discussed that the addition of both alcohol and carboxylic functions could elevate the O:C ratio of organic aerosols but form species with different hygroscopicities. This could be a possible reason to explain that the variation of O:C of organic aerosols is not necessarily responsible for the changes in hygroscopicity. This comparison and possible discussions were given in the revised manuscript.

Specific Issues:

Line 86 - 90: What is the relevant difference here between oxidation level and the oxygenation state? Insert a sentence here detailing why oxidation level is theoretically correlated with water uptake, since this is an important part of the results.

Reply: The oxygenation state is a more robust measure of the degree of oxidation for organic aerosols, while oxidation level, represented as O:C, sometimes may be affected by hydration and dehydration processes taking place in the atmosphere. We added a sentence into the text: They found that the oxidation level or the oxygenation state of the entire organics, which directly affects their corresponding solubility in water, is the major factor drives the water uptake ability of the organic fraction in aerosols.

Line 90 - 92: It is stated that the knowledge of the dependency of hygroscopicity on oxidation level is unknown in urban China. Since this is the main focus of the paper, include a line indicating why this environment is different.

Reply: However, knowledge on the hygroscopicity of organic material and its dependency on the oxidation level of organics in urban background areas under high aerosol mass loading conditions, for instance, in China, where air pollution has become one of the top environmental concerns (Chan et al., 2008), is limited.

Line 152 - 173: More details about the HTDMA should be included in this section. The second DMA is operating in SMPS mode? How fast/frequent are the scans and therefore what is the time-resolution for retrieval of the HGF? How frequently does the first DMA cycle between the 4 diameter set points? How are doubly- and triplycharged particles that are transmitted by the first DMA handled? Are the particle size distributions plotted in the bottom frame of Figure 2 from SMPS scans by the first DMA or from some other technique?

Reply: Before operating in HTDMA mode, the second DMA was bypassed. The aerosol particles, after being introduced into the first DMA, was directed into the CPC to measure the number size distribution of the ambient aerosols. This is how we obtained the SMPS scans. Hence, the bottom frame of Fig. 2 in the manuscript is directly from our HTDMA system when SMPS mode is on. The time resolution for a whole scan including the SMPS scans and HTDMA scans of particles of 4 different sizes are around one hour. Multiply charge correction was performed during data inversion procedure according to the method introduced by Gysel et al. (2009).

Line 178: What are 'Ambient-improved' ratios? Either define this term or leave it out and direct the reader to a reference.

Reply: We changed the sentence to: 'The oxygen to carbon (O:C) were then estimated by their relationship to the mass fractions of m/z44 (f44) to the total organic mass according to Canagaratna et al. (2015).'

Line 184 - 186: Briefly state what the simplified approach is. Is all the BC assumed to be in PM1? Or a weighted fraction?

Reply: Wu et al. (2009) compared the BC concentration in PM_1 and $PM_{2.5}$, respectively, and found that BC aerosols mainly exist in the fine particles with roughly 80% of the BC mass in PM1. Due to the limited literature data on BC size distributions in the PRD region, we used this simplified assumption by Wu et al. (2009) to estimate the BC concentration in PM_1 for this study.

Line 188: The line "individual size bins" is confusing. I assume the authors are referring to the 4 sizes selected by the first DMA? Replace with something similar to "the ACSM measures only accumulation mode aerosol, and therefore the Aitken mode particles may have a different chemical composition".

Reply: We changed the sentence to: 'It is necessary to note that the ACSM measures the chemical composition of bulk aerosols, which may be significantly different from those of Aitken mode particles.'

Line 191: Briefly state what instrument was measuring the PM2.5 chemical concentrations. An AMS?

Reply: The $PM_{2.5}$ mass concentration was measured by an Environmental Dust Monitor (EDM, Grimm model 180).

Line 209 - 212: What is the justification for assuming the aerosol is completely neutralized? What would the effect be on the results be if it were not completely neutralized?

Reply: We are sorry that this assumption is based on previous studies (Gysel et al., 2007), which used similar ion paring scheme, and we do not fully understand the effect if the aerosols are not completely neutralized. However, we hypothesize that if our aerosols are more acid, the HGF would be higher than the predicted one as inorganic acid is more hygroscopic than its neutral form.

Line 272 - 282: See comment in General Comments. The paragraph is perhaps un necessary. What can be learned from looking at the diurnal profile of the mean HGF that isn't learned from looking at the MH and LH components separately?

Reply: We shortened this paragraph and moved Fig. 3 into supplement.

Line 296 - 299: What is the justification for the assertion that the MH mode particle experience a decrease in HGF during the day because they are uptaking less photoreactive species. Do typical reaction rates or back-of-the-envelope calculations support this assertion? Which species are involved? If this is true, how do the authors reconcile the fact the O:C ratio sharply increases during the day, and this paper indicates that there is at least a somewhat positive correlation between O:C and HGF?

Reply: I did not say they uptake less photoreactive species but rather organics from stronger photoreaction during daytime. These newly formed organics are expected to be less hygroscopic than those aged organics, which were already present in the aerosols. Here, these arguments are only related to MH mode particles, however, taking into account the mean HGF of the whole aerosol population as Fig.3 in the manuscipt, HGF values were actually higher during daytime, which is consistent with the increase in O:C during daytime.

Line 305: The authors state here that Hong 2015 and Cai 2017 report that the boundary layer height has an effect on aerosol populations, but later on line 378, they suggest it doesn't. This disagreement should be addressed more fully.

Reply: We deleted the sentence used in Line 305, but kept the one in line 378, since the logic in line 378 is more reasonable.

Line 323: The authors state that they can only compare HGFs from the HTDMA and ACSM for larger particles. But they have also demonstrated that larger and smaller particles behave differently. The authors should address any hypotheses for how HTDMA and ACSM might agree for smaller particles.

Reply: Size-dependent chemical composition should be considered into the derivation of HGF by ACSM data, thus the HTDMA_measured HGF then could be compared with the one from ACSM.

Line 325: State why HGF is expected to positively correlate with the inorganics/(organics + BC) ratio.

Reply: Inorganics are commonly quite hygroscopic, while relative to inorganics, organic and black carbon are less hygroscopic or non-hygroscopic. Hence, the more inorganics in the aerosol phase, the larger HGF and the more organics or BC in the aerosols, HGF is relatively smaller.

Line 349 and 352: The authors state the percentages 64% and 21% in reference to the back trajectories without discussing where these numbers come from. Furthermore, more information about the trajectories would be helpful, such as error bars on those percentages.

Reply: The method we used here was called cluster analysis. The details of this method could be found in http://ready.arl.noaa.gov/HYSPLIT.php. Thus only a brief introduction would be given here. The trajectories that are near each other are merged to a mean trajectory to represent those groups. When the clustering is complete, the change in the Total Spatial Variance (TSV) as the trajectories is merged into one cluster. The TSV is computed from the position vectors for the individual trajectory and its cluster mean trajectory. According to the change of TSV, we decide the number of cluster as an appropriate solution (In this work, the number is 5). The percentage of the cluster means that how many back trajectories can be represent by this cluster. According to the principle of cluster analysis and the limit of this model, the standard deviation of those percentages is not available from the model calculation directly.

Line 354: Is there an observed increase in ACSM organics on days when the trajectories indicate air masses are arriving from the inland areas? If not, why is that?

Reply: This is not clearly seen in current study, as the meteorological conditions also influence the concentration of organics in aerosols, for instance, the stagnant weather conditions during Sep 22 to 27 with low wind speed favor the accumulation of atmospheric pollutants including the mass concentration of different species. However, the air masses were mainly from coastal areas.

Line 390: Do the authors have a suggestion for why this trend (HGF depends on O:C more during clean days than polluted days) is observed? It seems like an important result, yet isn't discussed extensively in the conclusions. Additionally, why is the parameterization of the HGF-to-O:C relationship not done separately for clear vs polluted days?

Reply: As previously stated in the manuscript, during polluted days, the aerosols appeared to be from long-range transported, having longer aging history. The organic material in these aerosols were fully oxygenated, even with various O:C ratio. However, during clean days, the aerosols was mainly from local emissions or formed locally without complex histories. The changes in HGForg revealed the oxidation state of theses locally formed organic material. The closure analysis to determine the parameterization of the HGF-to-O:C relationship was done separately for clean and polluted days as above.

Line 401: Is there an operational definition for suburban aerosol? Does this just mean an aerosol population that is somewhere between typical urban and rural characteristics?

Reply: Yes, compared to urban area, it has a lower density area that separate residential and commercial areas from one another. It could be part of the urban area or exist as a separate residential community within commuting distance of a city.

Line 402 - 405: More detail about the residual fit should be added here. Is the ZSR prediction compared to all the HTDMA measured HGF? Of all sizes? Or just the polluted or clear days? Are different values derived depending on the subset of measured data to compare to?

Reply: The ZSR prediction is compared with all the HTDMA-measured HGF. Moreover, this is also done for the polluted and clean days. This is included in the revised manuscript.

Line 415: Why was the ACSM not measuring size-selected aerosol in this study, as was done in Yeung et al?

Reply: ACSM is an instrument that cannot measure the size-resovled chemical compositon of aerosols, while Yeung et al. (2014) used a High Resolution Time-of-Flight Aerosol Mass Spectrometer, which is capable to obtain the size-segregated chemical composition information. Unfortunately, during our experimental period, we did not have HR-ToF-AMS.

Line 425: More information should be included about how this parameterization was derived. What parameters were allowed to vary, and what was the parameter that was minimized? Is a R2 of 0.51 significantly better than 0.5? In the next paragraph, an improved parameterization is introduced by allowing SOA density to vary. Which parameterization is better? Why does the conclusion section only mention this first parameterization?

Reply: We gave a revised section illustrating the closure analysis, which should be much easier to understand and more reasonable. In addition, we did not include other parametrization in the conclusion, but did a comprehensive uncertainty analysis to discuss the potential errors associated within the closure analysis.

Line 430: What is the justification for stating that the hygroscopicity of organics isn't affected by the presence of inorganics?

Reply: As the results shown, HGForg was actually quite constant during the whole study, while the concentration of inorganics varied. This is an indicator that the hygroscopicity of organics in our study is not observed to be affected by the presence of inorganics.

Line 444: How are the authors accounting for error here? Presumably there is error in the measurement, which propagates through to the derivation of the parameterization.

Reply: We performed a comprehensive uncertainty analysis for the hygroscopicity-composition closure and gave potential reasons from other sources of errors associated within this study, which is shown in the revised manuscript.

Line 490: Have the authors plotted the HGF vs the concentration of certain inorganics? Say, vs ammonium sulfate or sulfuric acid to see if there is a larger trend for compounds known to be more hygroscopic?

Reply: This is actually illustrated in Fig. 4 and Fig. 7 in the revised manuscript. However, to plot the HGF vs. the concentration of ammonium sulfate may not indicate the complexity of ambient aerosols, as there was also substantial amount of organic species, which is less hygroscopic than ammonium sulfate. Even with increasing amount of ammonium sulfate concentration in aerosols, the increase of organics will cancel out the effect on HGF. This is the reason to plot HGF vs. Inorganics/(Organics+BC) is more reasonable.

Figure 2: Remove the dates from under each frame and just put them under the bottom frame. Color bar for the top four frames should be labeled. Additionally, it seems as though the MH and LH modes both have diurnal cycles between <1 and > 4. If this is simply because the total number of particles has a diurnal profile, it would be easier to see this if it was normalized to the total number of particles. In the bottom plot, because there is only one point on the y-axis, it's hard to see that it's in log space. The boundaries (i.e. 10 -1000 nm) should be indicated, with ticks to show that it is logarithmic.

Reply: I modified the figure as suggested.

Figure 3: See Comment on line 272. It's possible that this figure is not needed.

Reply: I deleted this figure and the corresponding text in the revised manuscript.

Figure 4: Is this separately out for polluted or clear days? Why not?

Reply: As the referee's request, we plotted similar figures for the polluted and clean days as shown in Fig. R1. No conclusive trend in mean HGF can be observed during the polluted and clean days similar as the mean HGF during the entire experimental period, hence, we are not going to put this figure into the revised manuscript.
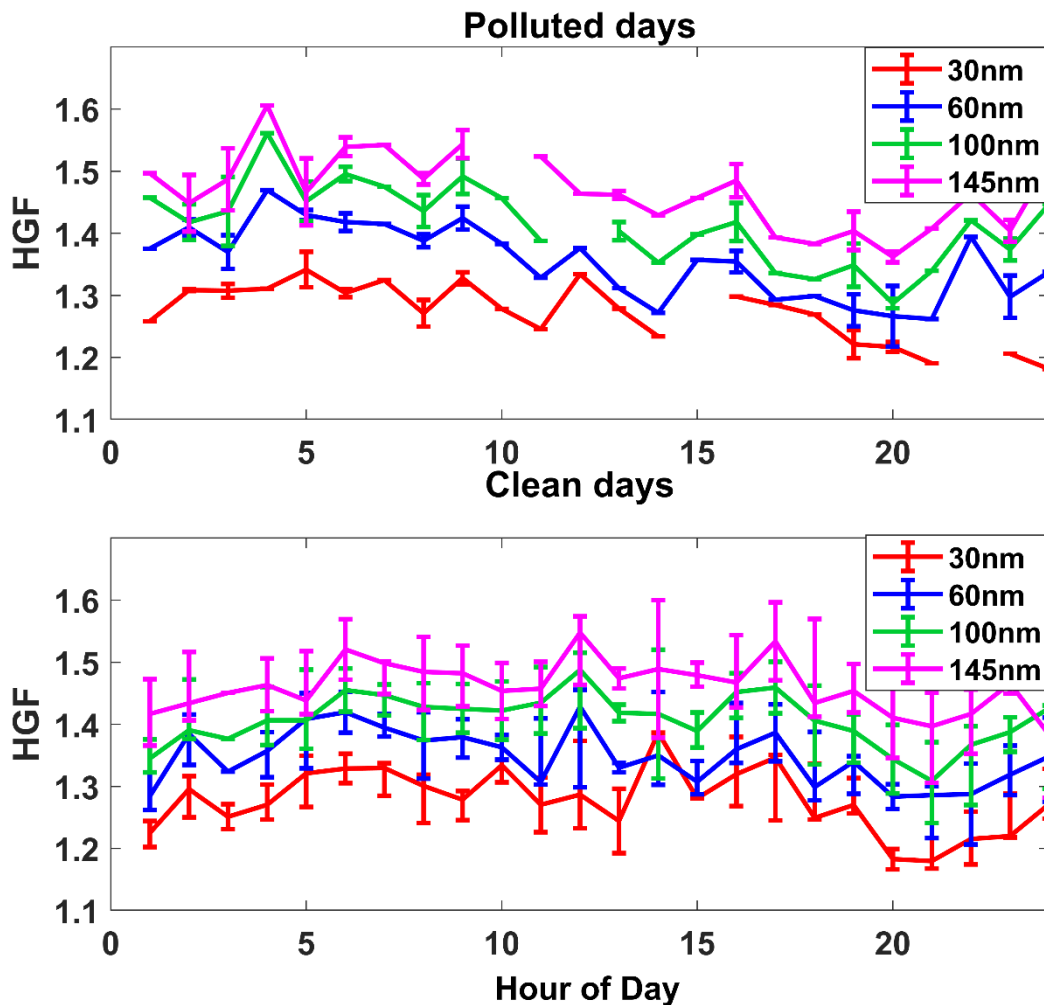
Figure R1. Diurnal variation of the mean HGF during the polluted and clean days for four different sized particles.

Figure 5: What happens if these plots are made with MH or LH HGF instead of the mean?

Reply: We understood the reason why the referee asked us to do this. However, the particle phase chemical composition data as well as the O:C ratio is the mean value of the bulk aerosols. Information of the chemical composition of each mode is not available. Poor correlation was observed when plotting the MH and LH HGF with the bulk aerosol composition.

Figure 7: The colors for these trajectories should be labeled more clearly, and described more fully in the caption and also in the manuscript. Do they represent one representative trajectory? Or a weighted average? What was the spread on those individual trajectories?

Reply: These trajectories are the clusters, which represent a group of back trajectories. The meaning of cluster has been answered in the former comments.

Grammatical/Minor:

Line 102: What does "purposes" mean here? Do you mean "properties"?

Reply: I changed to 'properties'.

Line 107: PRD, not RPD

Reply: Yes, thanks for pointing it out and we revised it as suggested.

Line 155: Tan et al. 2013b doesn't appear to be in the listed references. Neither is Tan 2013a

Reply: I added them into the reference list in the revised manuscript.

Line 159: Why denote the dry mobility diameter as D0? Why not "Dp (0% RH)"?
Reply: It is a conventional way to denote the dry mobility diameter as D0, hence, I keep it as it is.

Answers to Referee #5

The authors appreciate the time the reviewer has spent on our manuscript, assisting us to produce a higher quality, understandable publication. The requested comments and suggestions are addressed and introduced to the revised version of the manuscript.

General Comments:

This manuscript presents results of simultaneous measurements of aerosol hygroscopicity and chemical composition in suburban site in Southern China. The measurement period covers almost 1 month and both polluted and relatively clean conditions were observed. I admit that such measurement can be very costly and labor intensive, and therefore the comprehensive set of data presented in the manuscript may carry certain value for the scientific community. However, with the current state of the manuscript, authors' main conclusion is very difficult to sink in for the readers. Authors seem to persist on determining the HGForg and large part of the manuscript is dedicated for that. However, in my opinion, it is obvious from the results that the oxidation level of organics does not affect the hygroscopicity of the suburban aerosols very much, and that might pretty much be the end of the story for HGFrog. Instead, I would like to see much more in-depth discussion on diurnal variations of LH mode in smaller particles (30 and 60 nm) and how the new particle formation and subsequent growth affects the aerosol hygroscopicity. I therefore recommend that the manuscript may be acceptable for publication in ACP after major restructuring.

Reply: We thank the referee's comments regarding the results of our manuscript. The referee is correct that the new particle formation and subsequent growth affects the aerosol hygroscopicity. At the referee's request, we did a case study of particle hygroscopicity during an NPF event.

Figure R1 shows the time series of particle number concentration, GF-PDFs of 30 and 145 nm particles and the bulk aerosol chemical composition of PM1 during 04. October, 2016, during which an NPF event was observed. The NPF event started at around 10:00 am, after which we observed a substantial increase in the number fraction of MH mode particles from 0.5 to around 1, for 30 and 145 nm particles. This indicates a clear conversion of particles from externally to internally mixing. Number fraction of the MH mode for 30 and 145 nm particles decreased again to 0.5 around 17:00 pm, which might be explained by the traffic emissions during the rush hours of the day. Meanwhile, HGF of MH mode of both 30 and 145 nm particles showed a slight decrease after the NPF event started. This suggests that the candidate for the material in the MH mode particles during NPF event may be not only sulfuric acid or ammonium sulfate but also secondary organic species. The contribution from secondary organic species, which are less hygroscopic than ammonium sulfate, may dominate in the newly formed particles to be able to reduce the HGF of pre-existing particles. Similar observations was found in other studies (Levin et al., 2012; Wu et al., 2015).

Hence, we believe the effect of NPF on hygroscopicity might be worth a study of its own. However, without size-resolved chemical composition of particles, we cannot make further conclusion based on current results. The findings above seem to be a little bit too weak to have a single section in the manuscript. To include these into this paper would make the manuscript unnecessarily long, which would even weaken the key points of this paper. At the other four

referees' requests, chemical composition of PM1 should not be compared with the one from size-segregated aerosols and uncertainty analysis should be implemented into the manuscript. Hence, we adopted some assumptions and performed a comprehensive uncertainty analysis regarding the hygroscopicity-composition closure. In addition, similar analysis was done for the polluted and clean days. Finally, we revised our conclusion substantially. The revised sections are attached after the answers of all comments.
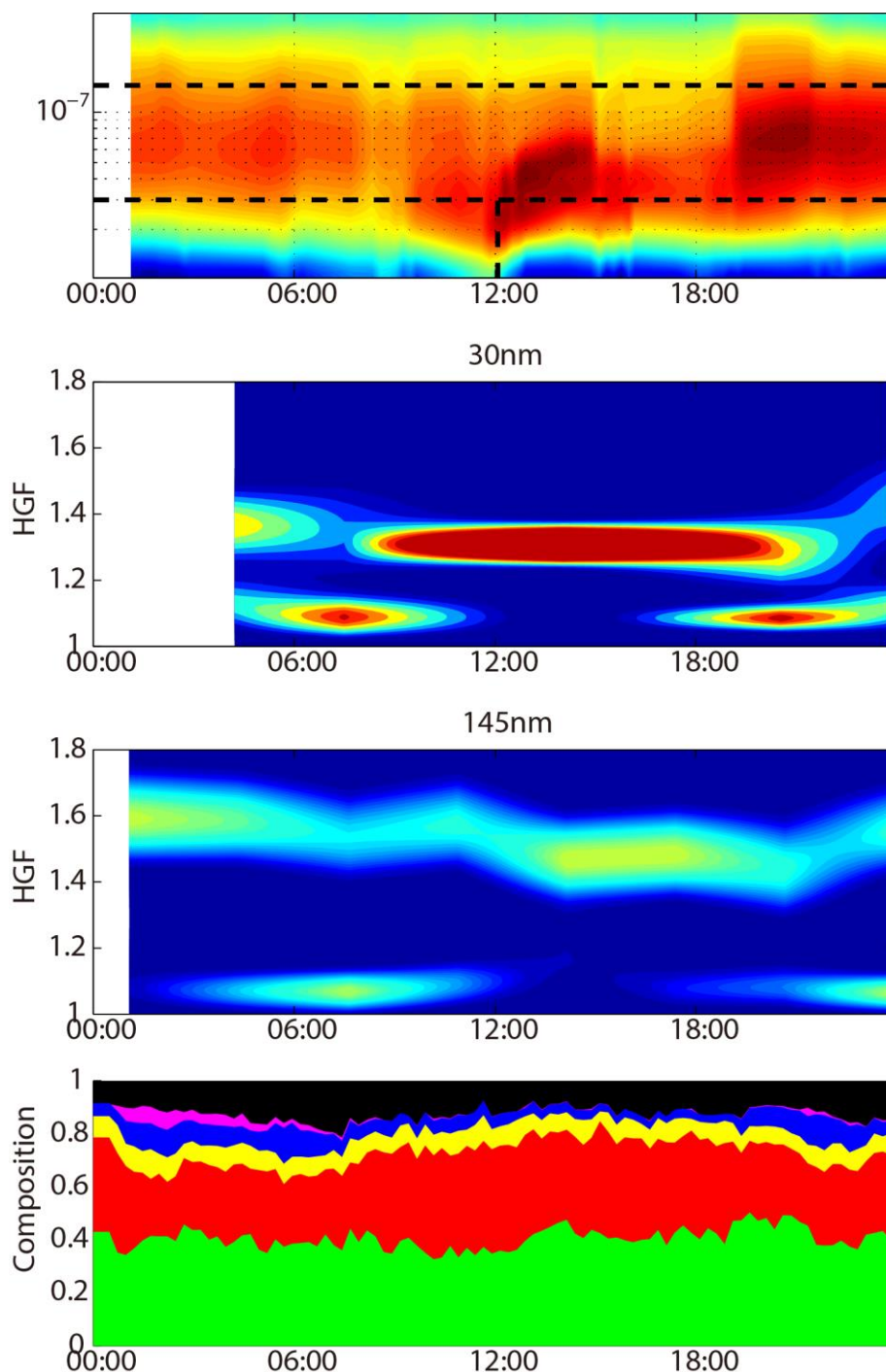

Figure R1: Time series of particle number size distribution, GF-PDFs of 30 and 145 nm particles and chemical composition of PM1 during 04, October 2016.

Specific comments

152: It is not clear from the manuscript how the HTDMA was operated to obtain the particle number size distribution (10-1000 nm) simultaneously while the instrument was measuring HGF in 4 size classes.

Reply: Before operating in HTDMA mode, the second DMA was bypassed. The aerosol particles, after being introduced into the first DMA, was directed into the CPC to measure the number size distribution of the ambient aerosols. This is how we obtained the SMPS scans. Hence, the bottom frame of Fig. 2 in the manuscript is directly from our HTDMA system when SMPS mode is on. We made a mistake before in the manuscript; actually particle number size distribution within 10-400 nm was measured, but not 10-1000nm particles. We corrected it in the revised manuscript.

175-178: It is critical to indicate the calibration procedure of ACSM and what calibration parameters were used (e.g. relative ionization efficiency of SO4). Such calibration parameters can critically affect the inorganic and organic mass fractions (and therefore the ensemble HGForg of 1.1).

Reply: Ammonium nitrate (AN) particles, generated by an atomizer, was selected by a DMA with a certain size at 300 nm. The size-selected particles were then introduced into a CPC and the ACSM. After obtaining the number concentration of AN particles, we calculated their mass concentration by multiplying the density of AN. The mass concentration obtained from the CPC was then compared with the one from ACSM. Then the corresponding RIE value for NH4 was calculated. Similar procedure was performed for ammonium sulfate particles. The RIE values for NH4 and SO4 were obtained as 5.63 and 0.78, respectively. The detailed calibration procedure was described in Ng et al. (2011).

300-303: The logical basis to support the following conclusion is not clear. "In case of smaller particles (30 nm, 60 nm), HGFs of MH group particles appeared to decrease during the afternoon until about 8:00 pm, suggesting that these particles were not long-range transported, but rather secondary formed either locally or from nearby emissions."

Reply: We changed the sentence to: 'In case of smaller particles (30 nm, 60 nm), HGFs of MH group particles appeared to decrease during the afternoon until about 8:00 pm. This is probably attributed to the intensive traffic emissions at the time of rush hour.'

462-519: Extra caution must be taken when comparing k based on supersaturation conditions and HGF based on sub-saturated conditions. The k derived from sub- and supersaturated conditions can be quite different in some cases. In such case, the discussion on potential bias on CCN concentration may not be relevant.

Reply: The last figure in the manuscript is only an illustration for the relation between the hygroscopicity of organic material and its O:C ratio. Kappa values are not directly compared with the ones of HGF. We agree with the referee that kappa derived from sub- and supersaturated conditions can be quite different in some cases. Hence, we deleted the discussion on the calculation of CCN concentration. New discussions were included in the revised manuscript.

Technical corrections

120: "self-assembly" should appear "self-assembled"

Reply: We rephrased it to 'self-assembled'.

188: what does it mean by "individual size bins"?

Reply: We changed it to: 'It is necessary to note that the chemical composition of PM1 can be different from those of size-selected aerosol particles'.

330: rephrase "uncertainties of in growth factor"

Reply: We changed it to 'uncertainties in growth factor'.

423: "as followed" should appear "as follows"

Reply: We changed it to 'as follows'.

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Mixing state and particle hygroscopicity of organic-dominated aerosols over the Pearl River Delta Region in China

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Abstract

Simultaneous measurements of aerosol hygroscopicity and particle phase chemical composition were performed at a suburban site over the Pearl River Delta Region in the late summer of 2016 using a self-assembled Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) and an Aerodyne Quadruple Aerosol Chemical Speciation Monitor (ACSM), respectively. Hygroscopic growth factor (HGF) of Aitken (30 nm, 60 nm) and accumulation mode (100 nm, 145 nm) particles was obtained under 90% relative humidity (RH). An external mixture was observed for all-sized particles during this study, with a dominant mode of more hygroscopic (MH) particles as aged aerosols dominated due to the anthropogenic influence. The HGF of less hygroscopic (LH) mode particles increased, while their number fractions decreased, during the daytime due to a reduced degree of external mixing probably from the condensation of gaseous species. These LH mode particles in the early morning or late afternoon could be possibly

dominated by carbonaceous material emitted from local automobile exhaust during the rush hours. During polluted days with air masses mainly from the coastal areas, the chemical composition of aerosols had a clear diurnal variation and a strong correlation with the mean HGF. Closure analysis was carried out between the HTDMA-measured HGF and the ACSM-derived hygroscopicity using various approximations for hygroscopic growth factor of organic compounds (HGF_{org}). Considering the assumptions regarding the differences in the mass fraction of each component between PM_1 and 145 nm particles, the hygroscopicity-composition closure was achieved using HGF_{org} of 1.26 for the organic material in the 145 nm particles and a simple linear relationship between HGF_{org} and the oxidation level inferred from the O:C ratio of the organic material was suggested. Compared with the results from other environments, HGF_{org} obtained from our measurements appeared to be less sensitive to the variation of its oxidation level, which is however similar to the observations in the urban atmosphere of other megacities in China. This finding suggests that the anthropogenic precursors or the photo-oxidation mechanisms might differ significantly between the suburban/urban atmosphere in China and those in other background environments. This may lead to a different characteristics of the oxidation products in secondary organic aerosols (SOA) and therefore to a different relationship between HGForg and O:C.

1. Introduction

Aerosol hygroscopicity describes the interaction between aerosol particles and ambient water molecules at both sub and supersaturated conditions in the atmosphere (Topping et al., 2005; McFiggans et al., 2006; Swietlicki et al., 2008). It is a key property to affect the size distribution of ambient aerosols and can indirectly give information on particle compositions (Swietlicki et al., 2008; Zhang et al., 2011). It also plays an important role in visibility degradation and multiphase chemistry due to an enlarged cross-section area of aerosol particles after taking up water in humid environment (Tang et al., 1996; Malm et al., 2003; Cheng et al., 2008; Liu et al., 2013; Li et al., 2014; Zheng et al., 2015; Cheng et al., 2016). Moreover, it determines the number concentration of cloud condensation nuclei and the lifetime of the clouds, which in turn affect the regional and global climate indirectly (Zhang et al., 2008; Reutter et al., 2009; Su et al., 2010; IPCC, 2013; Rosenfeld et al., 2014; Schmale et al., 2014; Seinfeld et al., 2016; Zieger et al., 2017).

Hygroscopicity measurements have been conducted in numerous laboratory and field conditions around the world. Different observational findings related to hygroscopic properties of particles and their chemical composition were obtained for aerosols from various environmental background conditions. (Bougiatioti et al., 2009; Park et al., 2009; Swietlicki et al., 2008; Asmi et al., 2010; Tritscher et al., 2011; Whitehead et al., 2014; Hong et al., 2015; Chen et al., 2017). Recent studies have specially focused on the hygroscopicity of organic material, as atmospheric aerosols normally contain a large number of organic species, which exhibit highly various water uptake abilities. Previous works have extensively examined and reported the hygroscopicity of the organic fraction in aerosols worldwide, including boreal forest, rural and urban background areas (Chang et al., 2010; Wu et al., 2013; Mei et al., 2013; Hong et al., 2015; Wu et al., 2016). They found that the oxidation level or the oxygenation state of the entire organics, which directly affects their corresponding solubility in water, is the major

factor drives the water uptake ability of the organic fraction in aerosols. However, knowledge on the hygroscopicity of organic material and its dependency on the oxidation level of organics in urban background areas under high aerosol mass loading conditions, for instance, in China, where air pollution has become one of the top environmental concerns in recent decays (Chan et al., 2008), is limited.

Due to the fast development of industrialization and urbanization, China has experienced increasingly severe air pollution during the few past decades (Zheng et al., 2015; Wang et al., 2017). High loadings of atmospheric aerosols can reduce visibility and lead to adverse acute and chronic health effects due to penetration and deposition of submicron particles in the human respiratory system (Dockery et al., 1993; Cabada et al., 2004; Tie et al., 2009). In order to better understand the chemical composition, sources and aging processes of atmospheric aerosols and in turn target the atmospheric pollution problems in China, measurements of atmospheric particles with various properties have increased during the recent years. Hygroscopicity, as an important physico-chemical property of atmospheric particles (Cheng et al., 2008; Gunthe et al., 2011; Cheng et al., 2016), has also been implemented into extensive campaigns in densely populated areas, such as North China Plain (Massling et al., 2009; Liu et al., 2011) and the Yangtze River Delta (Ye et al., 2013). In the Pearl River Delta (PRD) region, a metropolis in southeastern China with high aerosol loadings and low visibility probably due to anthropogenic emissions, hygroscopicity measurements have also been initiated during the past few years (Tan et al., 2013; Jiang et al., 2016; Cai et al., 2017). These previous studies have mainly focused on the statistical analysis of the hygroscopic properties of PRD aerosols and tried to give possible explanations for their temporal variations. However, the relationship between the hygroscopic properties of aerosols in PRD region and the particle phase chemical composition have not yet been systematically constrained, especially the relation of hygroscopic properties of the organic fraction in the particles to its oxidation level. Particularly, a close look at the hygroscopicity and chemical composition of particles during high aerosol loadings is also scarce.

In this study, we measured the size-dependent hygroscopic properties and non-size-resolved chemical composition by a self-assembled Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) and an Aerodyne Quadruple Aerosol Chemical Speciation Monitor (ACSM) respectively in a suburban site in PRD region. We aim to find the link between the hygroscopicity of aerosols and their chemical composition, with a focus on identifying the hygroscopic properties of the organic material and their O:C dependency for these suburban aerosols. Hygroscopic properties and chemical composition of aerosol particles under high and low aerosol loadings were particularly analyzed separately.

2. Materials and methodology

2.1 Sampling site and air mass origins

The measurements were conducted from 12 September to 19 October 2016 at the CAWNET (Chinese Meteorological Administration Atmospheric Watch Network) station in Panyu, Southern China. The site is located at the top of Dazhengang Mountain, which is in the suburban area of the megacity, Guangzhou. A figure on the geographical location is available in Tan et

al. (2013) and Jiang et al. (2016). A detailed description of the CAWNET station and the sampling inlet can be found in Tan et al. (2013) and Cai et al. (2017).

To investigate the relationship between atmospheric aerosol hygroscopicity and the transport paths or source regions of air masses, 72-hour back trajectories of air parcels arriving at CAWNET were calculated at 6-hour intervals using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model for this study. The arrival height of the trajectories was chosen to be at 700 m above ground level, which is the mean height of the boundary layer in Guangzhou during the entire experimental period according to the data obtained from European Center for Medium-Range Weather Forecasts (ERA Interim). Trajectories with similar spatial distributions or patterns were grouped together to generate clusters, representing their mean trajectories and the predominant air mass origins during the campaign.

2.2 Measurements and data analysis

A self-assembled HTDMA was deployed to measure the hygroscopic growth factor (HGF), mixing state as well as the particle number size distribution (10-1000 nm) of ambient aerosols during this study. A detailed characterization of the HTDMA system and its operating principles are available in Tan et al. (2013b). Briefly, ambient aerosols after passing through a PM_1 impactor inlet were first brought through a Nafion dryer (Model PD-70T- 24ss, Perma Pure Inc.) to be dried to RH lower than 10% and were subsequently charged by a neutralizer (Kr^{85}, TSI Inc.). These dry particles of four specific mobility diameters (D_0; 30, 60, 100 and 145 nm) were selected by the first Differential Mobility Analyzer (DMA1, Model 3081L, TSI Inc.) in the HTDMA system and then were introduced into a membrane permeation humidifier (Model PD-70T-24ss, Perma Pure Inc.) to reach 90% RH. With a second DMA (DMA2, Model 3081L, TSI Inc.) and a condensation particle counter (CPC, Model 3772, TSI Inc.), the growth factor distributions (GFDs) or the mobility diameter (D_P) of these conditioned particles at 90% RH and room temperature were measured. The hygroscopic growth factor (HGF, RH=90%) is then defined as:

$$HGF(90\%) = \frac{D_p(RH=90\%)}{D_0}. \tag{1}$$

In practice, growth factor probability density function (GF-PDF) was fitted from the measured GFDs with bimodal lognormal distributions using TDMAfit algorithm (Stolzenburg, 1988; Stolzenburg and McMurry, 2008). After obtaining GF-PDF, the ensemble average hygroscopic growth factor (HGF), number fractions of particles at each mode and the spread of each mode were calculated.

An Aerodyne Quadruple Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc.) was employed to determine the non-refractory PM_1 chemical composition and O:C of submicron aerosol particles with a 50% collection efficiency during the experimental period (Ng et al., 2011). The ratios of oxygen to carbon (O:C) were then estimated by their relationship to the mass fractions of m/z44 (f44) to the total organic mass (Canagaratna et al., 2015). The mass concentration of black carbon was measured by an Aethalometer using a $PM_{2.5}$ inlet (Hansen et al., 1982). Wu et al. (2009) compared the BC concentration in PM_1 and $PM_{2.5}$, respectively, and found that BC aerosols mainly exist in the fine particles with roughly 80% of

the BC mass in PM_1. Due to the limited literature data on BC size distributions in the PRD region, we used this simplified assumption by Wu et al. (2009) to estimate the BC concentration in PM_1 for this study. It is necessary to note that the chemical composition of PM_1 can be different from those of size-segregated aerosols and the ACSM measures the chemical composition of PM_1, which may be significantly different from those of Aitken mode particles. In addition, complimentary measurements for ambient meteorological conditions (e.g. relative humidity, wind direction and wind speed), as well as the particulate matter ($PM_{2.5}$) mass concentration measurements by an Environmental Dust Monitor (EDM, Grimm Model 180) were conducted concurrently during the experimental period.

2.3 Closure study

Ambient aerosol particles are mixtures of a vast number and variety of species. In order to estimate the averaged hygroscopicity of ambient particles, the Zdanovskii–Stokes–Robinson (ZSR) mixing rule (Zdanovskii, 1948; Stokes and Robinson, 1966) was assumed and the hygroscopic growth factor (HGF_m) of a mixed particle was calculated by summarizing the volume-weighted HGF of the major chemical components of aerosol particles:

$$HGF_m = (\sum_i \varepsilon_i \cdot HGF_i^3)^{1/3}, \tag{2}$$

where ε_i is the volume fraction of each species and HGF_i is the growth factor of each species present in the mixed particle. The volume fraction of each species was calculated from their individual dry densities and mass fractions from ACSM data (Gysel et al., 2007; Meyer et al., 2009) by neglecting the interactions between different species. Since ACSM measures the concentration of ions, the molecular composition can be reconstructed from the ion pairing based on the principles of aerosol neutralization and molecular thermodynamics (McMurry et al., 1983; Kortelainen et al., 2017). Several neutral molecules such as $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3, H_2SO_4 and other possible species were therefore obtained. The related properties of each species necessary for the calculation in Eq. 2 are listed in Table 1. Ensemble values of HGF_{org} were suggested, as the best-fit values of the closure analysis was achieved, which is detailed in Sect. 3.4. As suggested in early studies, the hygroscopicity of organics in the aerosol particles is dependent on their degree of oxygenation inferred from the O:C ratio (Massoli et al., 2010; Duplissy et al., 2011; Hong et al., 2015), hence, we further estimated HGF_{org} according to the degree of oxygenation presented by the O:C ratio. A similar approach to approximate the hygroscopicity of organics in particle phase based on their O:C ratio is also proposed by Hong et al. (2015). A density value of 1250 kg/m^3 was used for the organics to calculate their volume fraction, which was suggested by Yeung et al. (2014) in their closure analysis for aerosols from a similar environment.

3. Results and Discussions

3.1 Overview of measurements

Figure 1 shows the temporal variations of meteorological conditions (e.g., relative humidity, wind direction, average wind speed) and $PM_{2.5}$ as well as BC mass concentration in PM_1. In general, RH showed a clear diurnal cycle and a northern wind was frequently experienced

during this study. The PM$_{2.5}$ mass concentration varied from 20 to 180 μg/m^3, with relatively low values (roughly below 50 μg/m^3) during most of the time. Previous PM$_{2.5}$ mass concentration measurements at this site have yielded quite similar results (Jiang et al., 2016) at this season. During the period of September 22 to 27, the PRD region experienced stagnant weather conditions, with low wind speeds and fluctuating wind directions near the surface. The stagnant weather leads to the observed increase in the mass concentrations of PM$_{2.5}$ and BC, with up to about two times higher values compared with the rest of this study.

Figure 2 shows an overview GF-PDF for particles of four different diameters colored with probability density and the mass fractions of the ACSM chemical components as well as the particle number size distribution (10-400 nm) over the entire measurement period. The white gap in the mass fraction data in the fifth panel is due to an instrument failure. Particles of all sizes showed apparent bimodal growth factor distributions with a mode of more hygroscopic particles and a mode of less hygroscopic particles, indicating the particle population was mainly externally mixed. A similar feature was also observed in the PRD region previously (Eichler et al., 2008; Tan et al., 2013b; Jiang et al., 2016; Cai et al., 2017), as well as in other urban environment around the world (Massling et al., 2005; Fors et al., 2011; Liu et al., 2011; Ye et al., 2013).

In our study, the bimodal distributions had a dominant more hygroscopic (MH) mode for larger particles (100 nm, 145 nm), whereas for smaller particles (30 nm, 60 nm) these number fraction of two modes were approximately of similar magnitude. From the fifth panel in Fig.1, we can see that the total inorganics and organic material had roughly equivalent contributions to the mass fractions in PM$_1$ at the PRD region. This is not a surprise due to the stronger anthropogenic influence in our measurement site. Particle number size distributions below 10 nm were not measured by our setup, so, new particle formation events could not be systematically classified for this study. However, a subsequent particle growth from 10 nm to the accumulation mode was periodically observed. In this study, two distinguished types of days (e.g., one as 'relative clean days' during September 12 to 19 and October 9 to 15 and one as 'polluted days' during September 22, 18:00 to September 27, 9:00) were characterized by their corresponding differences in meteorological conditions, the mass concentration of PM$_{2.5}$ or BC as well as the occurrence of clear particle growth above 10 nm. Distinct analysis of aerosol hygroscopicity, chemical composition as well as air mass origins for these two periods will be further discussed in Sect. 3.3.

3.2 Hygroscopicity and mixing state

The diurnal variations of the average HGF of particles of four different sizes are illustrated in Fig. S1. In general, larger particles were more hygroscopic than smaller particles. No strong diurnal pattern of the mean HGF can be concluded from the current results, after taking into account the uncertainties associated with the mean values. This suggests complex sources and aging processes of aerosols at this suburban site.

In the upper panels of Fig. 3, we compared the diurnal variation of the HGFs of particles in the LH and MH mode. HGFs of LH mode of particles of all sizes started to increase after 10:00 am and decrease at about 3:00 pm until reaching their lowest levels at about 8:00 pm. A possible candidate for these LH mode particles could be carbonaceous material emitted from local automobile exhaust during the rush hours, with soot and water-insoluble organics as the major components. These freshly less hygroscopic particles started to age in the atmosphere by condensation of different vapors or multiphase reactions in the daytime, leading to an obvious increase in HGFs of LH mode particles without reaching that of MH mode particles. HGFs of MH mode particles of larger sizes (100 nm, 145 nm) started a slight decrease after about 10 am and then increased again between about the noon and late evening. Particles of this mode are supposed to be more aged than particles in the LH mode, having a substantial fraction of inorganic components such as sulfate and nitrate. However, during daytime when the photochemical activity is stronger, the MH mode particles are expected to experience condensation of different species, especially organics, which are less hygroscopic. Hence, a slightly lower HGF of these particles was observed in the afternoon than in the morning. In case of smaller particles (30 nm, 60 nm), HGFs of MH group particles appeared to decrease during the afternoon until about 8:00 pm, suggesting that these particles were not long-range transported, but rather secondary formed either locally or from nearby emissions.

The number fractions of different-size particles in each mode are illustrated in the lower panels of Fig. 3. For larger particles (100 nm, 145 nm), MH mode particles dominated over the LH mode particles. For smaller particles (30 nm, 60 nm), the number fraction of LH mode particles decreased dramatically after 12:00 am and increased back to the same level after 6:00 pm. A similar, yet less obvious, pattern was also observed for larger particles. This feature directly suggests that small particles have a lower degree of external mixing during the afternoon compared with the rest of the day, providing further evidence that local traffic emissions may be the major sources of those LH mode particles, especially the ones of smaller sizes.

The hygroscopicity of aerosol particles is ultimately driven by the relative abundances of compounds with different water uptake ability in the particle phase. Hence, we also looked at HGFs of aerosol particles in terms of their direct composition information. Our ACSM measured the non-size resolved chemical composition of particles, which may deviate considerably from that of Aitken mode particles, but be close to that of accumulation mode particles. This requires us to choose HGF of larger particles (100 nm, 145 nm) for the analysis. In Fig. 4, the HGFs of accumulation mode particles correlate quite well with the mass fraction ratio between inorganics and organics + BC. However, the oxidation level of the organic fraction appears to exert only a slight influence on the hygroscopicity of the suburban aerosols, with R^2 values of around 0.23. A detailed comparison between the HTDMA-measured HGFs and the predicted HGFs using size-dependent chemical composition will be given below in Sect. 3.4. Gysel et al. (2007) suggested that, compared with HGFs of pure organic particles affected strongly by their oxidation level (Duplissy et al., 2011), HGFs of mixed particles are less sensitive to the properties of uncertainties of growth factor of less hygroscopic compounds in the aerosol phase. This feature might explain why the HGFs of our suburban aerosol were influenced to a lesser extent by the oxidation level of organic compounds than aerosol particles

typically studied in smog chamber measurements or measured in a boreal forest environment (Massoli et al., 2010; Tritscher et al., 2011; Hong et al., 2015).

3.3 Comparison between polluted and clean days

In order to understand the influence of primary sources and secondary formation to the aerosol loading during different synoptic conditions (e.g., relative clean days and polluted days), we studied the chemical characteristics and physical-chemical properties of aerosols, as well as individual air mass origins, during the two distinguished periods, respectively. Figure 5 shows the diurnal variation of the major species in particle phase during the polluted and relative clean days. Concentrations of all of the displayed species were higher during the polluted period compared with the clean days. This was particularly obvious for NO_3^-, whose concentration was almost ten times higher during the polluted days. Wind speeds shown in Fig. 1 were the lowest during the polluted period, enabling local emitted air pollutants such as from traffic and cooking to accumulate. Moreover, a substantial fraction (53%) of the air mass trajectories, shown in Fig. 6, were passing along the coastal areas in the southeast of China, which is heavily populated. These coastal air masses, together with a considerable fraction (16%) of air masses circulating within the PRD region may potentially transport significant amounts of pollutants, presumably from anthropogenic emissions, to the site. Contrary to this, air masses in the clean days were mainly from the inland areas in the north. These regions are, covered with vegetation and are less influenced by anthropogenic emissions, so air masses coming from there may promote the dilution and clearance of the local pollutants at the observational site.

During the polluted days, SO_4^{2-}, NO_3^- and organics had clear diurnal patterns. Concentrations of SO_4^{2-} and organics peaked during the late afternoon, probably due to gas phase condensation or multiphase reactions associated with high levels of SO_2 or gaseous organics after long-range transport, as discussed above. Nitrate had higher concentrations in the early morning than in the afternoon. Pathak et al. (2009) suggested that high concentration of particulate nitrate could be explained by the heterogeneous hydrolysis of N_2O_5 under high relative humidity conditions. Morino et al. (2006) concluded, using both observation and thermodynamic modeling, that lower temperatures and higher RH cause an enhanced condensation of HNO_3 to the particle phase. Fig. S1 shows that RH values were higher in the early morning than other times of the day under polluted conditions. We also looked at gaseous HNO_3 concentration, obtained from MARGA measurements and found them to be less than two times higher in polluted conditions compared with clean days. The partition of HNO_3 to the particle phase due to condensation might not be able to fully explain the one-order-of-magnitude higher nitrate concentrations in particle phase in polluted days than clean days. Hence, we speculate that the heterogeneous hydrolysis of N_2O_5 could be the alternative reason for the production of the observed high concentrations of nitrate in the early morning under polluted condition. During clean days, both inorganic and organic species have lower concentration, with no strong diurnal pattern, which indirectly indicates that the influence of the elevated boundary height on the daily variation of chemical composition was minor. The concentration of BC peaked at around rush hours, suggesting traffic emissions could be one of the major sources of BC.

Considering all examined species together, the difference in the inorganics/organic+BC ratio between early morning and late afternoon was more obvious for the polluted conditions than during the clean days (lower panels of Fig. 5). The averaged O:C ratio during the polluted days was a little bit lower than during the clean days, suggesting that the organic fraction was less oxidized during pollution episode.

The HGFs correlate much better with the contribution of different species to the mass fractions during the polluted days than during the clean days (Fig. 7). However, the oxidation level had a relatively stronger influence on the HGFs during the clean days compared with the polluted days. Taken together, these observations suggest that despite the variability in its oxidation level, the hygroscopicity of the organic aerosol fraction did not vary much during the polluted days.

3.4 Hygroscopicity-composition closure

3.4.1   Approximations of the HGF_{org}

Hygroscopic growth factors of organic compounds in the ambient aerosols, HGF_{org}, cannot be determined from direct observations. However, by conducting closure analysis using different approximation approaches, HGF_{org} was estimated to range widely from about 1.0 to 1.3 for various ambient aerosols in other studies (Gysel et al., 2004; Carrico et al., 2005; Aklilu et al., 2006; Good et al., 2010; Hong et al., 2015; Chen et al., 2017). In this section, we performed a closure study between the measured and predicted HGF using a PM_1 bulk chemical composition from the ACSM. An ensemble-mean HGF_{org} (value of 1.1) was determined when the sum of all residuals (RMSE, root mean square error) between the measured growth factors and corresponding ZSR predictions reached a minimum by varying HGF_{org} between 1.0 and 1.3.

By applying this constant HGF_{org}, Fig. 8 compares the ACSM-derived HGF with the HTDMA-measured ones for four different-size particles, with the color code indicating the O:C ratio. It is obvious that the degree of agreement increased with increasing particle size. However, the bulk aerosols mainly represent the chemical composition of aerosol particles near the mass median diameter of the mass size distribution of ambient aerosol particles (Wu et al., 2013). The question then arises as to which extent the size-resolved chemical composition of aerosols (for instance, 100 nm and 145 nm particles) is comparable with the one of the bulk aerosol. Previous studies (Cai et al., 2017; Cai et al., 2018) reported that the average organic mass fraction of PM1 were about 25% and 16% lower than those of 100 nm and 145 nm particles respectively measured by High-Resolution AMS (HR-AMS) during the same season of 2014 at the same measurement site. Correspondingly, the average inorganic mass fraction of PM_1 were about 25% and 16% higher than those of 100 nm and 145 nm particles obtained in their results. Due to insufficient information of the size-resolved chemical composition of ambient aerosols, we hence made an arbitrary assumption by applying the results from Cai et al. (2017). In this section, we considered the mass fraction of organic being 25% and 16% higher and a corresponding lower inorganic mass fractions (ammonium sulfate mass fraction is decreased) at smaller sizes (100 nm and 145 nm) compared to the bulk aerosol. In addition, we assumed a 20% uncertainty in theses suggested values, thus resulting in 25%±3% and 16±3% of elevation

in organic mass fractions in the 100 nm and 145 nm particles for current study. This would lead to larger values of HGF_{org} as 1.23±0.02 (100 nm particles) and 1.26±0.03 (145 nm particles) when assuming different chemical compositions of size-resolved particles compared to the bulk aerosols, see Fig. 9. In contrast to the results from bulk chemical composition, the closure for 100 nm particles considerably improved, as the RMSE value between the HTDMA_HGF and ACSM_HGF decreased from 1.61 to 0.87 with more than 90% of the data were within 10% closure. The closure for 145 nm particles did not show any significant improvement, with no reduction in the RMSE value. However, the newly-determined HGForg is expected to be more accurate than the one reported in the previous section, as assumptions of size-dependent chemical composition was considered even though with some uncertainties. In addition, the newly-obtained HGF_{org} was close to the one (1.18) by Yeung et al. (2014), who studied the hygroscopicity of ambient aerosols in September 2011 at the HKUST Supersite, less than 120 km away from our measurement site.

Previous studies suggest that a single ensemble HGF_{org} approximation might not be capable of evaluating the hygroscopicity of ambient aerosols from different sources with various characteristics. Hence, the HGF_{org} approximation according to the O:C ratio was tested using the chemical composition of both bulk aerosols and size-resolved particles based on previous assumptions, respectively. To facilitate our comparison, the closure analysis was only conducted for the 145 nm particles. The relation between HGF_{org} and the O:C ratio based on the chemical composition of bulk aerosols was obtained as follows:

$$HGF_{org} = 0.31 \cdot O{:}C + 0.88. \tag{3}$$

This closure was no better than the one shown in Fig. 8 using a constant HGF_{org}, both being based on the chemical composition of bulk aerosols, and there was little change in the RMSE value (from 0.63 to 0.62). By taking into account of the variation of the O:C ratio, HGF_{org} ranged from 0.9 to 1.2 when using Eq. 3 with around 80% of the data having values larger than 1. This finding implies that the approximation in Eq. 3 may introduce huge errors, as 20% of the values of HGF_{org} were not physically correct. The closure considering size-dependent chemical composition of aerosols from previous assumptions is shown in Fig. 10, with a new relation between HGF_{org} and the O:C ratio as:

$$HGF_{org} = (0.32 \pm 0.01) \cdot O{:}C + (1.10 \pm 0.04). \tag{4}$$

The closure was somewhat better than in Fig. 8 according to the slightly lower RMSE value (0.58 vs. 0.63). In addition, HGF_{org} ranged from 1.1 to 1.4 with the varying O:C ratio, and there were no HGF_{org} values smaller than unity, indicating that the new relation in Eq. 4 seems more widely applicable than the one in Eq. 3. In general, by looking at the fitted slopes being much less than unity with consideration of all the discussion above, we are concerned that other potential uncertainties may remain in the closure analysis between the measurements and predictions. This motivates us to make a comprehensive uncertainty analysis of the

hygroscopic-composition closure. It is important to note that the uncertainty analysis below is taking into account the aforementioned assumption regarding the size-dependent chemical composition of aerosols.

3.4.2   Uncertainties of hygroscopicity-composition closure

Swietlicki et al., (2008) discussed the sources of error associated with HTDMA measurements and concluded that the stability and accuracy of DMA2 RH should be controlled well to maintain the nominal RH (for instance 90%). The accuracy of DMA2 RH in our system was controlled to be 90±1%. This will result in a variability in the measured HGF of ±0.04 around the reported HGF. The bias uncertainty (2.3%) associated with RH accuracy are generally smaller than the estimated uncertainty (10%) reported in HTDMA measurements (Yeung et al., 2014). For hygroscopicity-composition closure, this biased HGF will lead to a change of 2.1% in HGForg with respect to the previously-determined value of 1.26.

Other uncertainties pertain to the densities used for organic materials and black carbon. The density value is estimated to range between 1000 and 1500 kg/m^3 for organic materials (Kuwata et al., 2012) and 1000 and 2000 kg/m^3 for black carbon (Sloane et al., 1983; Ouimette and Flagan, 1982; Ma et al., 2011). The calculated uncertainty in the ACSM-derived HGF using the density value at each extreme for organic materials and black carbon is less than 3.2% and 2.0%, respectively, both having relatively small effect on the determination of the constant value of HGF_{org}.

Another source of uncertainty comes from the measurement of aerosol mass concentration performed by the ACSM and Aethalometer. Bahreini et al. (2009) did a comprehensive uncertainty analysis on aerosol mass concentration measurements using an Aerosol Mass Spectrometer (AMS), having similar operating principle as the ACSM, of which systematic biases are not available. Their study reported an overall uncertainty of 30% for AMS measurements and concluded that it might be better for ground-based studies. Jimenez et al. (2018) gave accuracies of 5-10% from other AMS practitioners and claimed that these estimated accuracies might be too small. Hence, we used an overall uncertainty of 20% for the mass concentration measurements in this study. The uncertainty in the BC measurements given by the manufacture of the Aethalometer is within 5% (Hansen et al., 2005; Zhang et al., 2017). The effect of the perturbation in aerosol mass concentration of each species on the ACSM-derived HGF as well as the determination of HGF_{org} are summarized in Table. 2. The change in the mass concentration of sulfate exerts the largest effect on the ACSM-derived HGF as well as the corresponding HGForg, which is not surprising since sulfate contributes the highest fraction in more hygroscopic component in aerosols.

In general, uncertainties were relatively low for each individual case discussed above. It is possible that the contribution from multiple factors could reduce the overall uncertainties. The greatest uncertainty aforesaid may still arise from the chemical composition of size-segregated aerosols, since the performance of the closure and the approximations of HGF_{org} were most sensitive to changes in the mass concentration of sulfate and organic materials in aerosols. Except for the reasons discussed previously, other factors may also cause potential effects on

the hygroscopicity closure. Pajunoja et al. (2015) showed that phase state of organic aerosols, which varies with ambient conditions, might have an effect on the determination of hygroscopicity of organic fraction in aerosols. Previous studies (Suda et al., 2014) suggested that the interaction between inorganic and organic materials within the particle phase might alter the hygroscopicity of organics in mixtures and speculated that ZSR mixing rule may not hold for inorganic dominated aerosols (Hong et al., 2015).

Nevertheless, the interpretation of the hygroscopicity-composition closure and different approximation of HGF_{org} above reveals that in order to estimate accurately the properties of ambient aerosols, we might need to have precise measurements of chemistry, including the size-dependent chemical composition of the aerosols, as well as a better prediction model for HGF.

3.4.3   Closure analysis for polluted and clean days

A similar analysis for the hygroscopicity-composition closure similar to that in Sect. 3.4.1 was performed separately for the polluted and clean days. We kept adopting the previous assumption in Sect. 3.4.1 considering the size-dependent chemical composition of aerosols in the current section. The ensemble-mean HGF_{org} value was quite close to each other between the polluted and clean days (HGF_{org}=1.30 and 1.28, respectively), and each closure is shown in Fig.S3. These values are similar to the one previously determined (HGF_{org} of 1.26) for the entire experimental period. A good closure was achieved during the polluted days with a substantially high R^2 value (0.82), whereas during the clean days, the ACSM-derived HGF did not correlate well with the one measured by HTDMA, indicating that other factors, such as the O:C ratio of organic material, might have affected the achievement of the closure.

We adopted an O:C dependent hygroscopicity of organic material in the closure analysis separately for the polluted and clean days. The resulting closure is illustrated in Fig. 11. Compared with the clean days, the hygroscopicity of organic material was found to be less dependent on the O:C ratio during the polluted days. This finding is consistent with the previous discussion on Fig.7, stating that the oxidation level had a relatively stronger influence on the HGFs during the clean days compared with the polluted days. This indicates that the organic compound, even with similar hygroscopicity may contain varying chemical species resulting from different sources or atmospheric processes during these two distinct periods. As previously stated in the manuscript, the aerosol particles appeared to have been from long-range transported during the polluted days, having a longer aging history. The organic material in these aerosol particles were fully oxygenated with a similar hygroscopicity, even for different O:C ratios. However, during the clean days, the aerosol particles were mainly from local emissions, or formed locally without complex aging histories. The changes in HGForg revealed the oxidation state of this locally-formed organic material.

3.5 Synthetic Comparisons

A number of field studies have examined the relationship between the hygroscopicity of organic compounds and their oxidation level for ambient aerosols from various representative organic aerosol sources (Chang et al., 2010; Chen et al., 2017; Duplissy et al., 2011; Hong et al., 2015a; Mei et al., 2013; Wu et al., 2013, 2016). The empirical relationship obtained from our results and these earlier studies are compared and described below in Fig. 12. It is important to note two aspects before our discussion. First, Eq. 4 considering a size-dependent chemical composition of aerosols is used here for comparison, as it has a wider application than Eq. 3. Secondly, the results from other studies shown in Fig. 12 were obtained using the hygroscopicity parameter (κ_{org}) (the left y-axis), while in this study we obtained values of HGF_{org}. Both parameters represent a quantitative measure of the hygroscopicity of organic material. Hence, we converted our obtained HGForg to hygroscopicity parameter κ by the procedure given in Petters and Kreidenweis (2007) and plotted the O:C dependent hygroscopicity parameter κ in black line in Fig. 12.

All listed studies show that the hygroscopicity of organic matters generally increases with an increasing organic oxidation level, with significant variance in the fitting slopes among all of the empirical relationships. For aerosols from near remote (Duplissy et al., 2011; Hong et al., 2015) or rural background (Chang et al., 2010) areas, covering little or no influence from anthropogenic activities, the value of O:C exhibits a stronger impact on the water uptake ability of organic materials. This indicates that the oxidation potential from photo-oxidation in the atmosphere of these backgrounds is a critical factor in determining the characteristics of organic materials. Similar to aerosols formed from biogenic precursors, the apparent O:C dependency on the hygroscopicity of organics is obvious for peat burning aerosols (Chen et al., 2017), mostly due to the complexity in the types of biomasses.

In the suburban or urban atmosphere of megacities in China (e.g. Beijing and Guangzhou), the hygroscopicity of organic material was almost constant as shown in this study and by Wu et al. (2016), being much less sensitive towards the variation in their oxidation level. It is not surprising to observe this similar O:C dependence on hygroscopcity of organic material in the rural background areas of Germany by Wu et al. (2013). This might be explained by the fact that their measurement site is located in central Germany where anthropogenic activities cannot be neglected. Wu et al. (2016) discussed that the addition of either an alcohol or a carboxylic function could both elevate the O:C ratio of the original organic aerosols. However, the corresponding hygroscopicity of these organic products may not be increased to the same extent compared with the increase in the values of O:C. This could be a possible reason to explain that the variation of O:C of organic aerosols is not necessarily responsible for the changes in hygroscopicity. In contrast, κ_{org} of aerosols at an urban site in Pasadena, California, in US exhibited a stronger increase with an increasing O:C ratio (Mei et al., 2013). They found that the relationship of their study is in line with that obtained from HTDMA measurements of SOA formed from 1,3,5-trimethylbenzene (TMB), a surrogate for anthropogenic precursors (Duplissy et al., 2011). They also deduced that the major components in SOA from TMB photooxidation are mainly mono-acids, which are quite water soluble. It is also interesting to observe that the results by Lambe et al. (2011) showed quite similar parametrization of HGForg and O:C dependence compared with the one for current study. They used a Potential Aerosol Mass (PAM) flow reactor to study the hygroscopicity of organic aerosols from the oxidation of

alkanes and terpenoids, suggesting the precursors of our organic aerosols in this study might have similar properties or same origins as these compounds in their study. The comparisons of κ_{org} or HGF_{org} as a function of O:C within these aforementioned studies suggest that anthropogenic precursors or the photo-oxidation mechanisms, might differ significantly between the suburban/urban atmosphere in China and those in the urban background of West US. This may lead to a distinguished characteristics of the oxidation products in SOA and therefore to a different relationship between κ_{org}/HGF_{org} and O:C.

4. Summary and conclusions

The hygroscopic growth factor distribution obtained in the late summer of 2016 at Panyu CAWNET station in PRD region suggests that this suburban aerosol population with a strong anthropogenic influence was almost always externally mixed. The diurnal variation of the HGF of the LH and MH mode particles of four sizes suggests that the LH mode particles were probably from local emissions, whereas the MH mode particles had a longer aging history. During daytime, an external mixing of particles decreased due to the condensation of different gaseous species onto them, which was particularly obvious for Aitken mode particles. The contribution of different species with various water affinities to the particle composition determines the variation of the mean HGF in general. However, the oxidation level of organics appeared to influence the hygroscopicity of the suburban aerosols only slightly.

The stagnant meteorological conditions favored the accumulation of pollutants originating from coastal areas in the southeast China during the polluted days. During these days, the hygroscopicity of the organic aerosol fraction was estimated to vary little despite the variability of its oxidation level. The atmosphere was cleared by the air masses from the north during clean days.

The ACSM-derived HGF correlated better with the HTDMA-measured ones for larger particles (100, 145 nm particles) compared with smaller particles (30, 60 nm particles). From the closure analysis, considering the assumption of a size-dependent chemical composition of aerosols, a new relation between the hygroscopic growth factor of organic compounds and their oxidation level was obtained for the suburban aerosols over the PRD region during the experimental periods: $HGF_{org} = (0.32\pm0.01) \times O:C + (1.10\pm0.04)$. Clearly, a moderate hygroscopicity of organic materials, with values of HGF_{org} ranging between 1.1 and 1.3, was observed and it exhibited a weak dependence on the O:C ratio for the current study. Comparison of this relation between polluted and clean days indicate that the organic material even with similar hygroscopicity during these two distinct periods may contain varying chemical species resulting from different sources or atmospheric processes.

The PRD region as one of the densely populated areas in China represents a geographical location in Asia under the subtropical marine monsoon climate system. However, these issues obtained from our results above have been discussed very little earlier, which thereby reflects a general value of our contribution. The comparison with earlier studies regarding the

relationship between HGF_{org} and O:C ratio indicates that there are substantial differences, but also some similarities, in the properties of organic compounds in aerosols among different environments, especially in urban areas. This motivates us to extend our measurement network in the future to understand better the generality of the relationship between the hygroscopicity and the oxygenation of the organic compounds.

Acknowledgements

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Table 1. Hygroscopic growth factors of all compounds and their individual density used in the ZSR calculation.

Compounds	Density (kg m^{-3})	HGF (90%)	
		Aitken Mode (30 nm, 60 nm)	Accumulation mode (100 nm, 145 nm)
$(NH_4)_2SO_4$[a]	1769	1.66	1.70
NH_4HSO_4	1780	1.74	1.78
NH_4NO_3	1720	1.74	1.80
H_2SO_4	1830	2.02	2.05
Organics	1250[b]	1.0-1.3[c]	

a: hygroscopic growth factor and density values of all inorganic was chosen from Gysel et al. (2007)

b: density of organic materials was chosen from Yeung et al. (2014)

c: hygroscopic growth factor for organic materials were varied from 1 to 1.3 according to literature values (Gysel et al., 2004; Carrico et al., 2005; Aklilu et al., 2006; Good et al., 2010; Hong et al., 2015; Chen et al., 2017)

Table 2. Sources of uncertainties associated within hygroscopicity-composition closure, given in terms of three standard deviation and their corresponding contribution to the overall uncertainty in hygroscopicity-composition closure.

Parameter	Uncertainty (3 standard deviation)	Uncertainty in measurements	HGForg (relative to 1.26)
RH (DMA2)	1%	2.3% in measured HGF	3.2%
Organic density	18%	2.6% in ACSM_derived HGF	3.2%
BC density	33%	1.0% in ACSM_derived HGF	2.0%
NH4, NO3 mass concentration	20%	0.6%, 0.5%	0.8, 1.6%
SO4 mass concentration	20%	1.8%	4.0%
Organics mass concentration	20%	1.4%	3.2%
BC mass concentration	5%	0.1%	0.8%
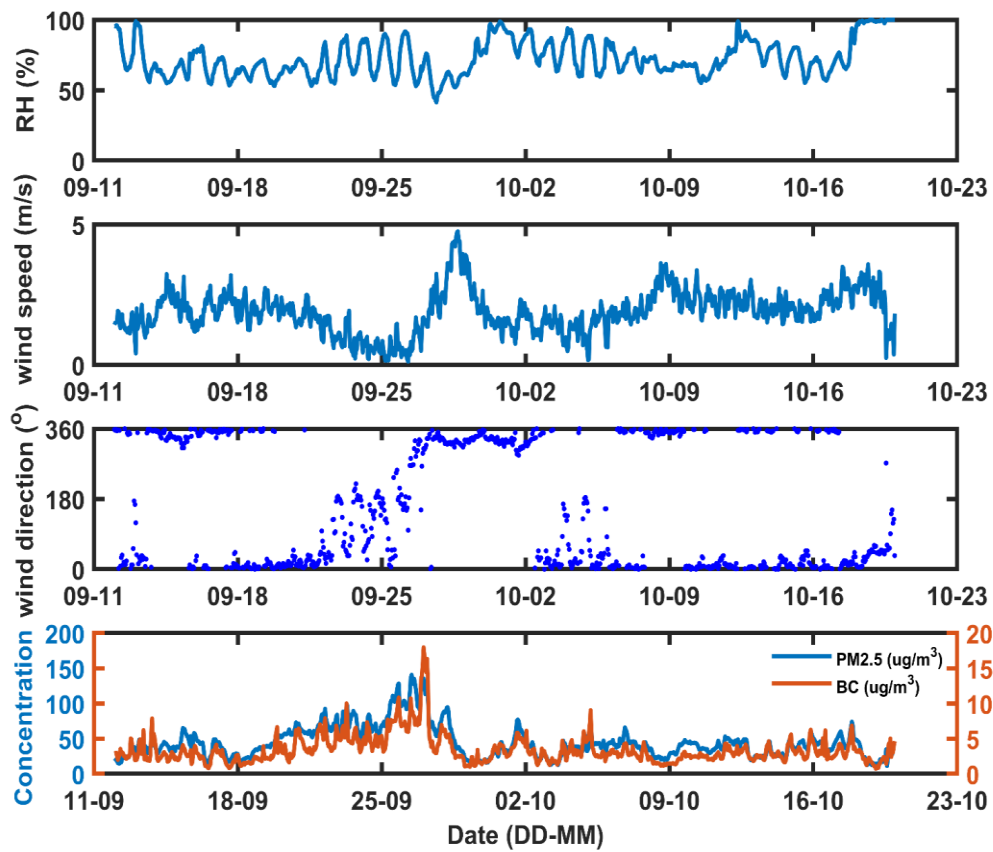
Figure 1. Time series for relative humidity, wind speeds, wind directions and concentrations of PM$_{2.5}$ as well as BC concentration (bottom panel).
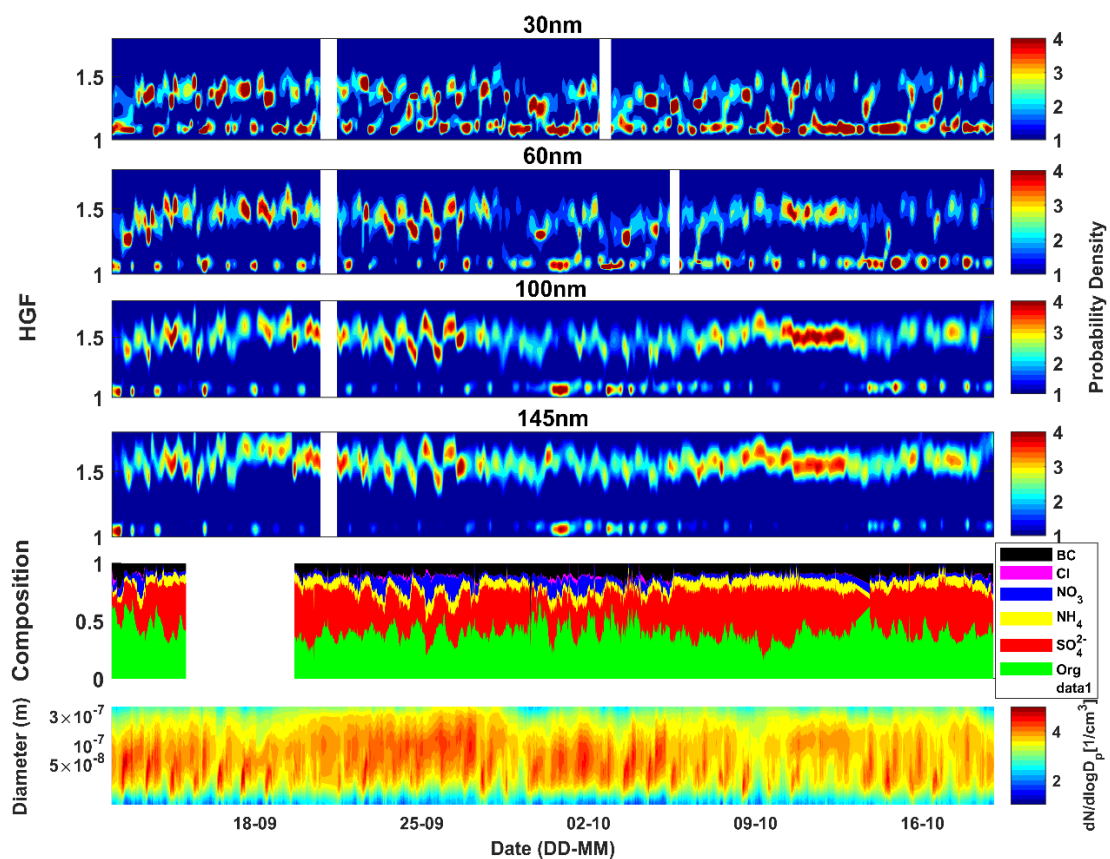
Figure 2. Time series of hygroscopic growth factor distribution for 30, 60, 100 and 145 nm particles using HTDMA in the upper four panels with the color code indicating probability density. Time series of mass fractions of chemical species in submicron particles and particle number size distribution within 10-400 nm using ACSM and DMPS, respectively in the lower two panels.
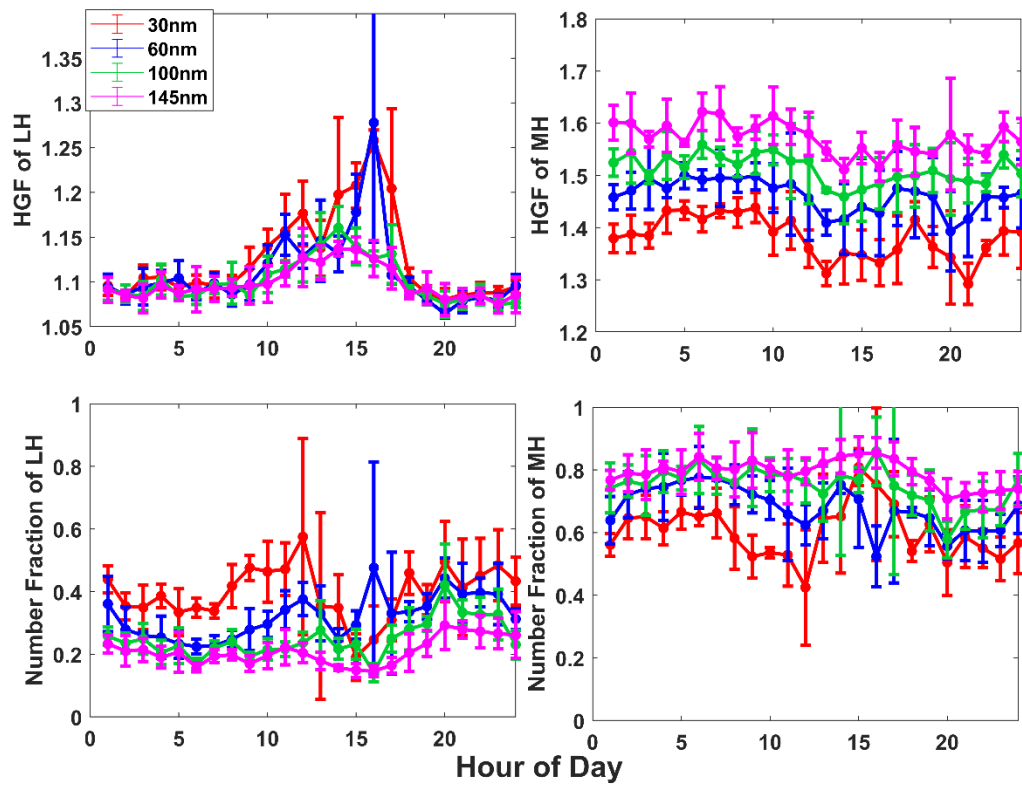
Figure 3. Diurnal variation of the HGF of less hygroscopic (LH) and more hygroscopic (MH) mode particles and their respective number fractions.
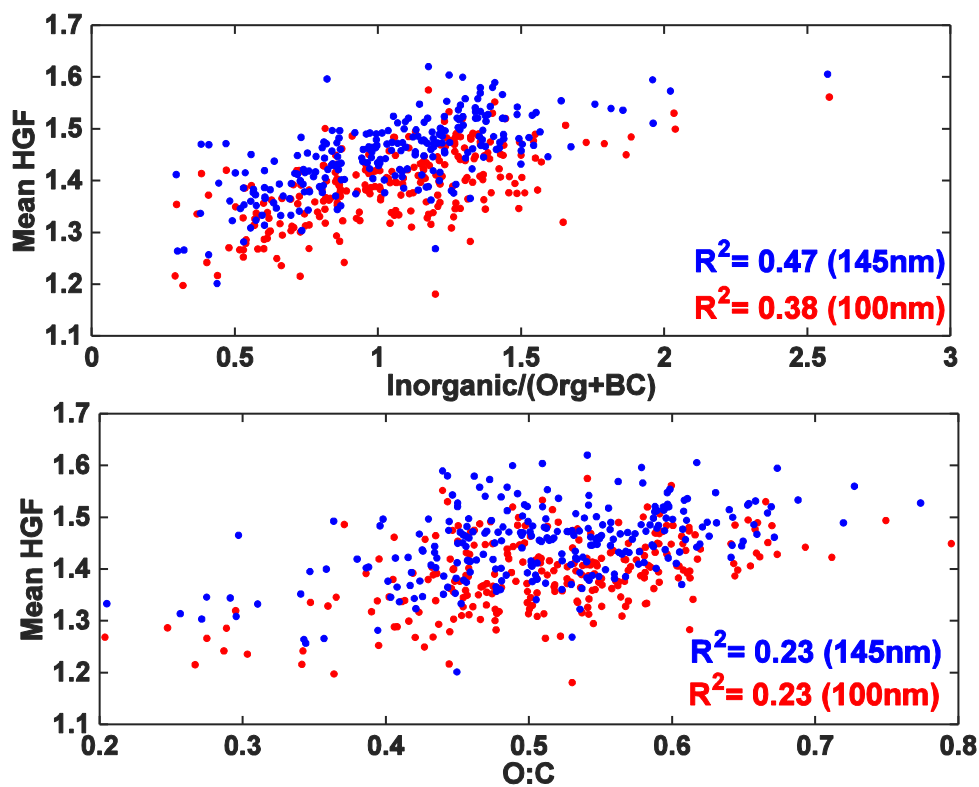
Figure 4. The correlation between the mean HGF of accumulation mode particles (100 nm, 145 nm in size) and the contribution of different species in the particle phase as well as the O:C of the organic materials.
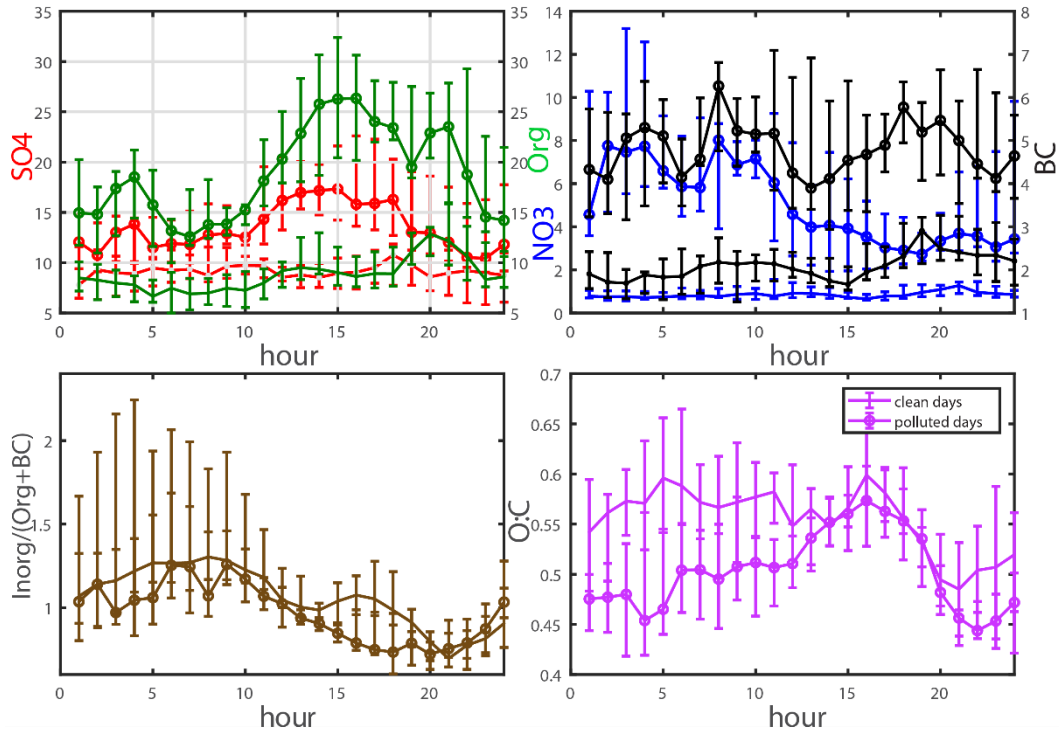
Figure 5. Diurnal variation of mass concentration of SO_4^{2-}, organics, NO_3^-, BC in particle phase, the O:C ratio of organics and their relative contribution in particle phase composition during clean days and polluted days, respectively.
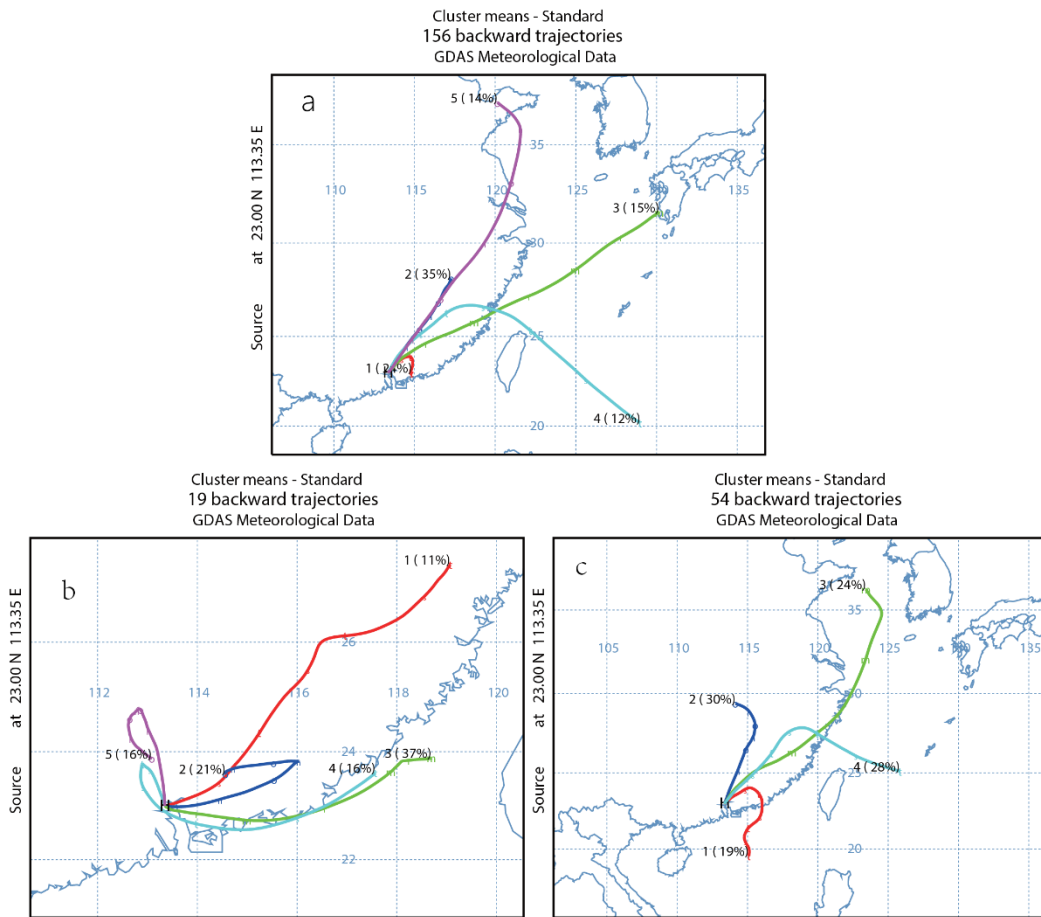
Figure 6. The major clusters for the 72-hour backward trajectory simulation for air masses arriving at the CAWNET Panyu site with an arrival height of 700 m. The upper panel shows the results throughout the whole observational period, while the lower panel on the left side shows the one during polluted days and the one on the right-hand side is for clean days. All trajectories that are near each other were merged to a mean trajectory to represent the entire groups by cluster analysis. The percentage number beside the labeled cluster indicates how many back trajectories can be represented by this cluster.
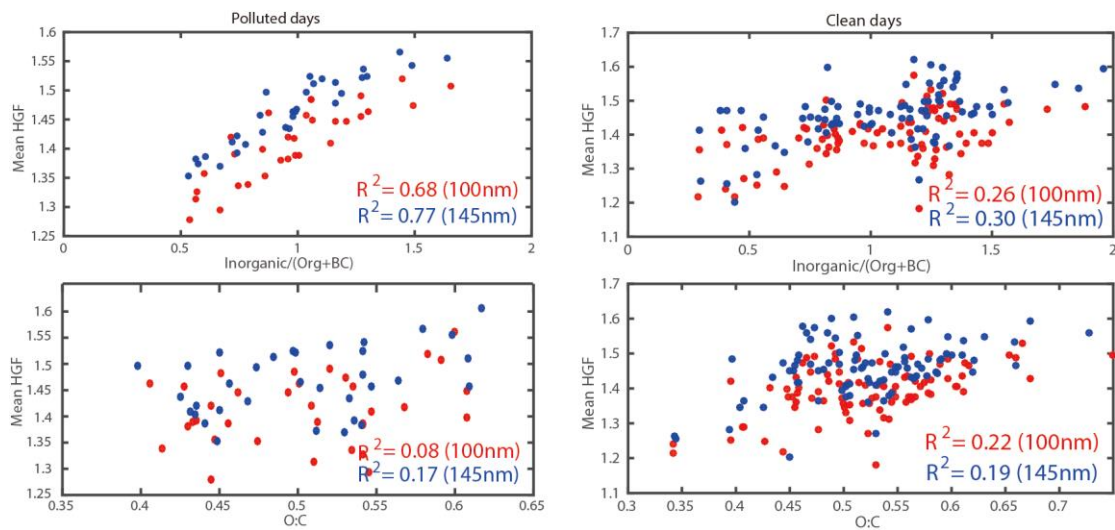
Figure 7. The correlation between the mean HGFs of accumulation mode particles (100 nm, 145 nm in size) and the contribution of different species in the particle phase as well as the O:C of the organic materials during polluted days and clean days, respectively.
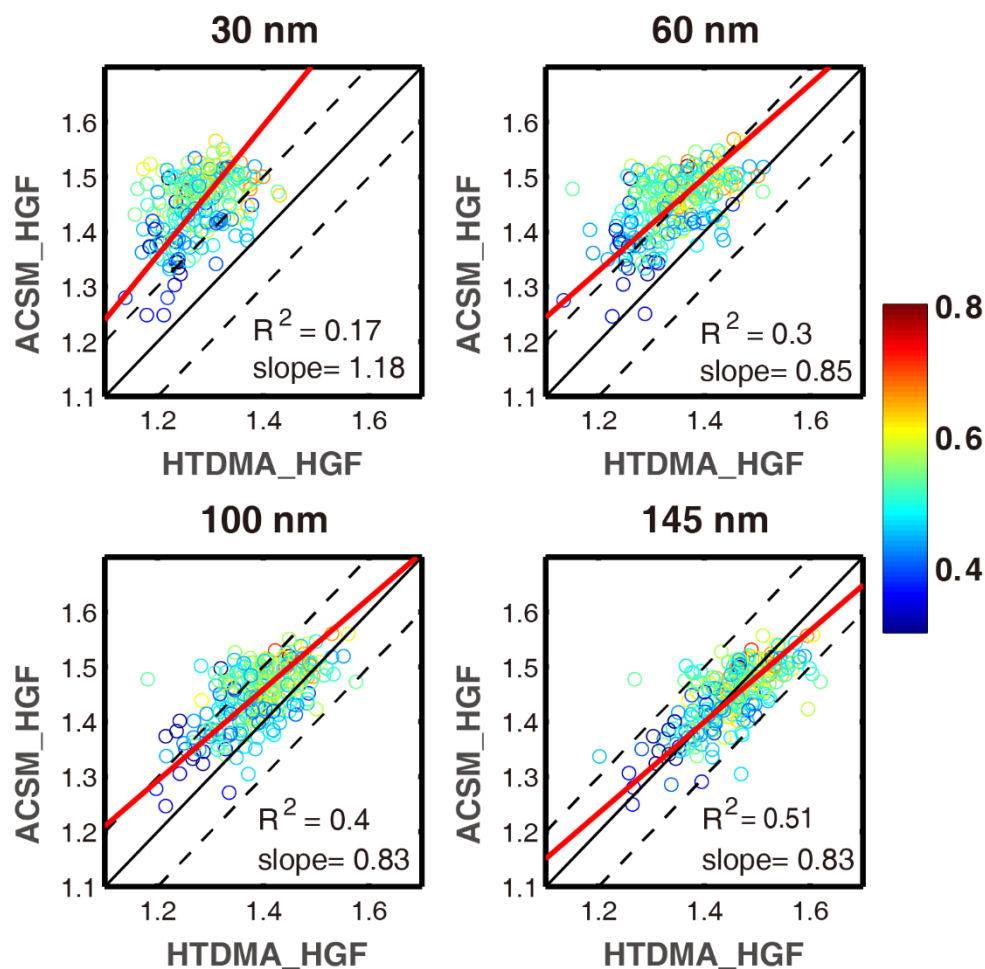
Figure 8. Closure study between the HTDMA-measured HGFs and the ACSM-derived HGFs. The dash lines indicate the 1:1 line, while the red ones are the lines fitted to the data points. The color bar indicates the O:C ratio of the organic aerosol fraction. The black solid lines indicate the 1:1 line and the black dash lines represent ±10% deviation, while the red lines are the lines fitted to the data points. The color bar indicates the O:C ratio of the organic aerosol fraction.
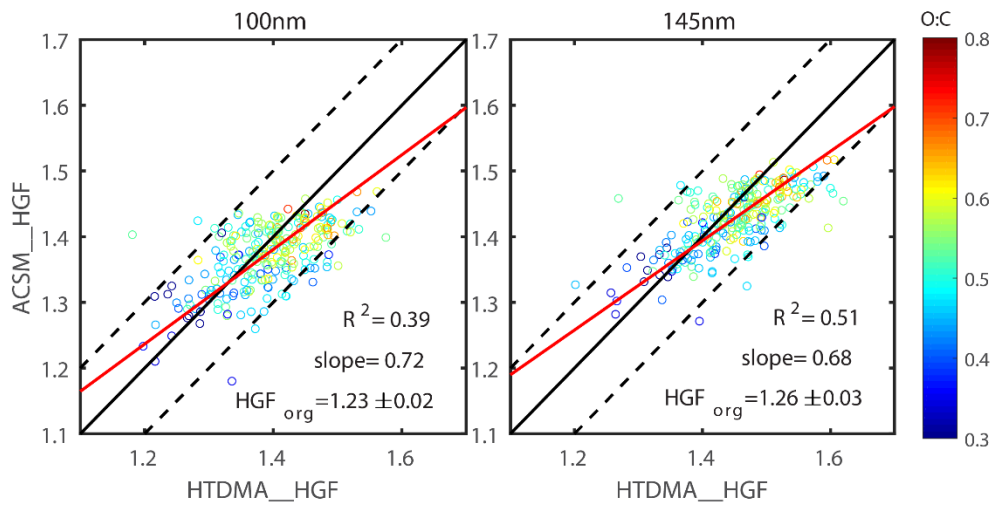
Figure 9. Closure study between the HTDMA-measured HGFs and the ACSM-derived HGFs assuming the average inorganic mass fraction of PM1 were about 25%± 3% and 16% ±3% higher and the average ammonium sulfate mass fraction of PM1 were about 25%± 3% and 16% ±3% lower than those of 100 nm and 145 nm particles. The black solid lines indicate the 1:1 line and the black dash lines represent ±10% deviation, while the red lines are the lines fitted to the data points. The color bar indicates the O:C ratio of the organic aerosol fraction.
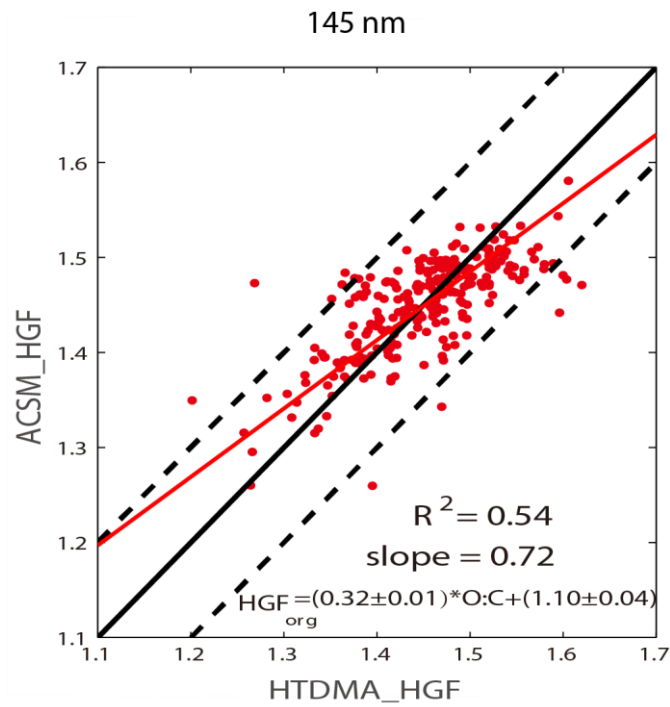
Figure 10. Closure analysis with the best fitting between the measured HGFs and the ACSM-derived ones using the O:C-dependent HGForg for 145 nm particles. The assumption of size-dependent chemical composition of aerosols was considered to determine the ACSM-derived HGFs. The equation is the achieved approximation for HGForg as a function of the O:C ratio of organic aerosol fraction.
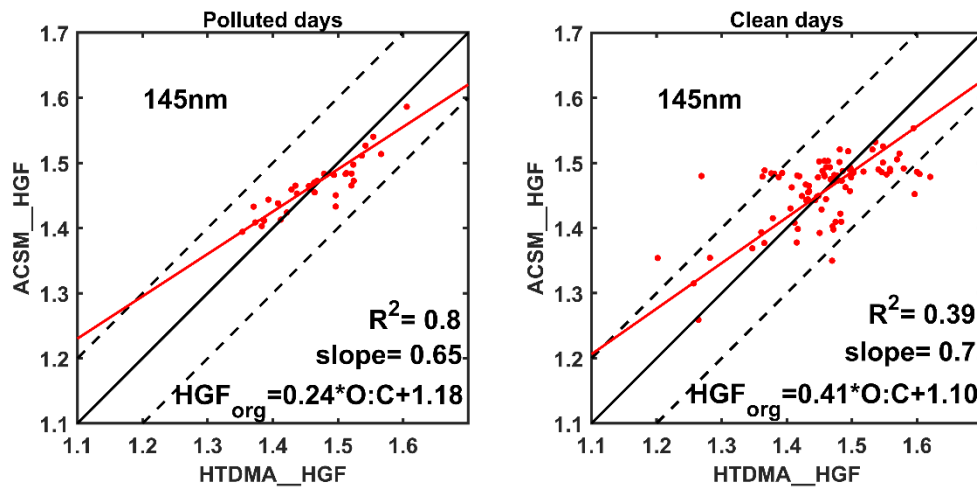
Figure 11. Closure analysis with the best fitting between the measured HGFs and the ACSM-derived ones using the O:C-dependent HGF_{org} for 145 nm particles during the polluted and clean days, respectively. The equation is the achieved approximation for HGF_{org} as a function of the O:C of organic aerosol fraction. During the polluted days, HGForg is less sensitive to the changes in the O:C ratio of organic material compared with the ones during the clean days, indicating different organic species during these two distinct periods.
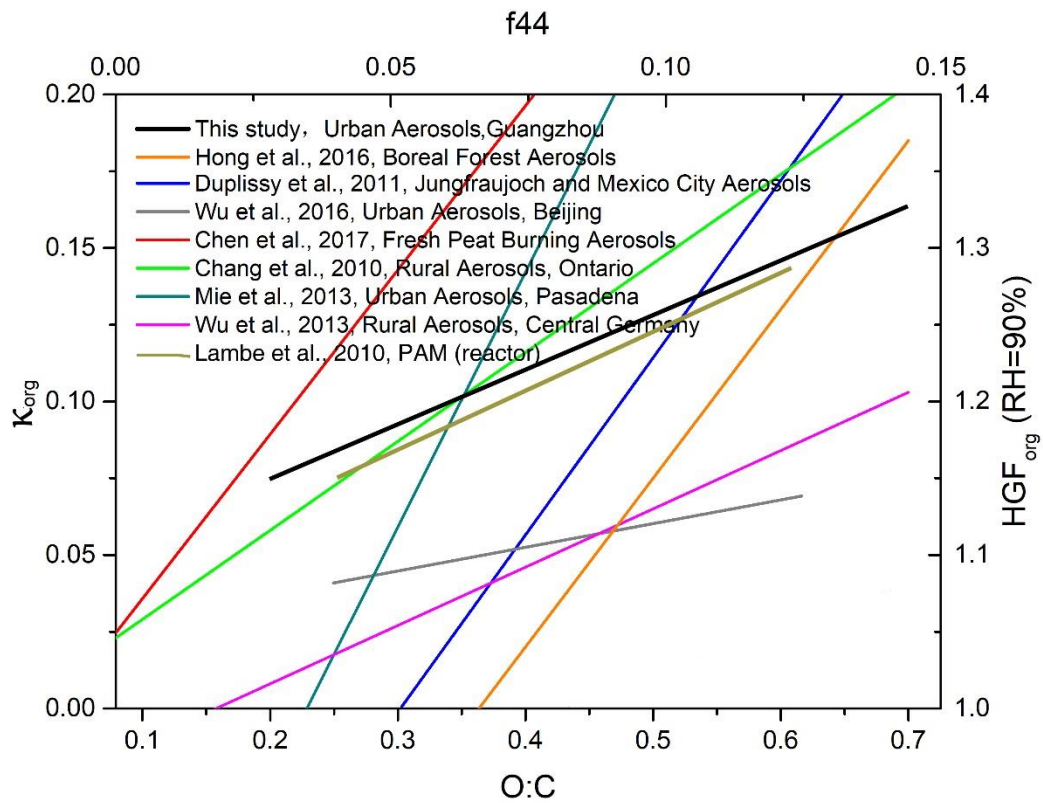
Figure 12: Comparison with earlier studies on the hygroscopicity of organic material with atomic O:C ratio (or *f44* from chemical composition data) obtained from different environmental background areas.
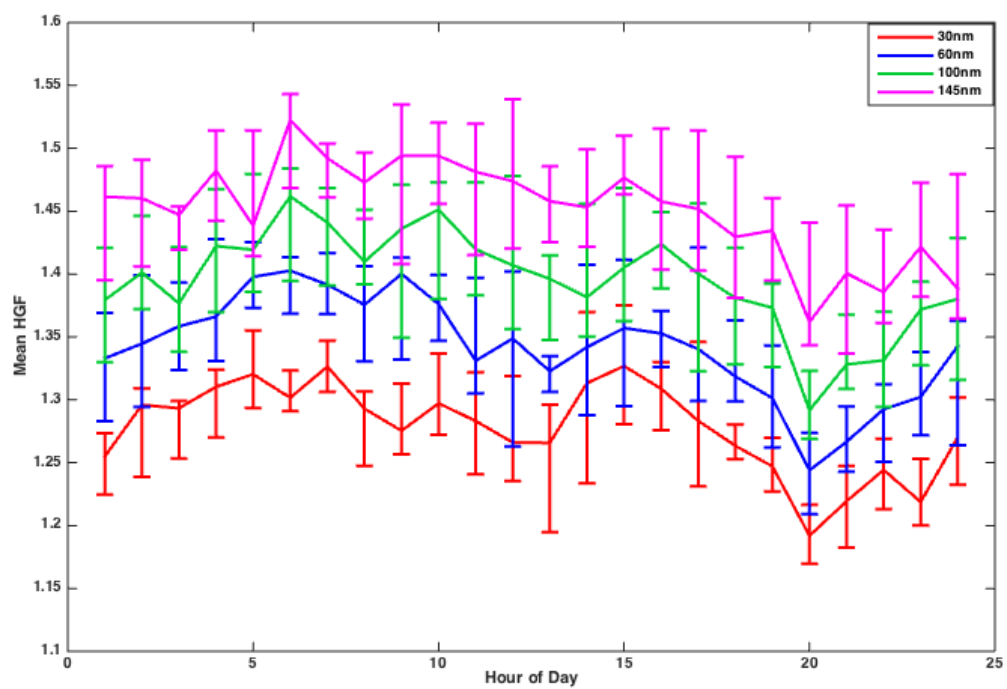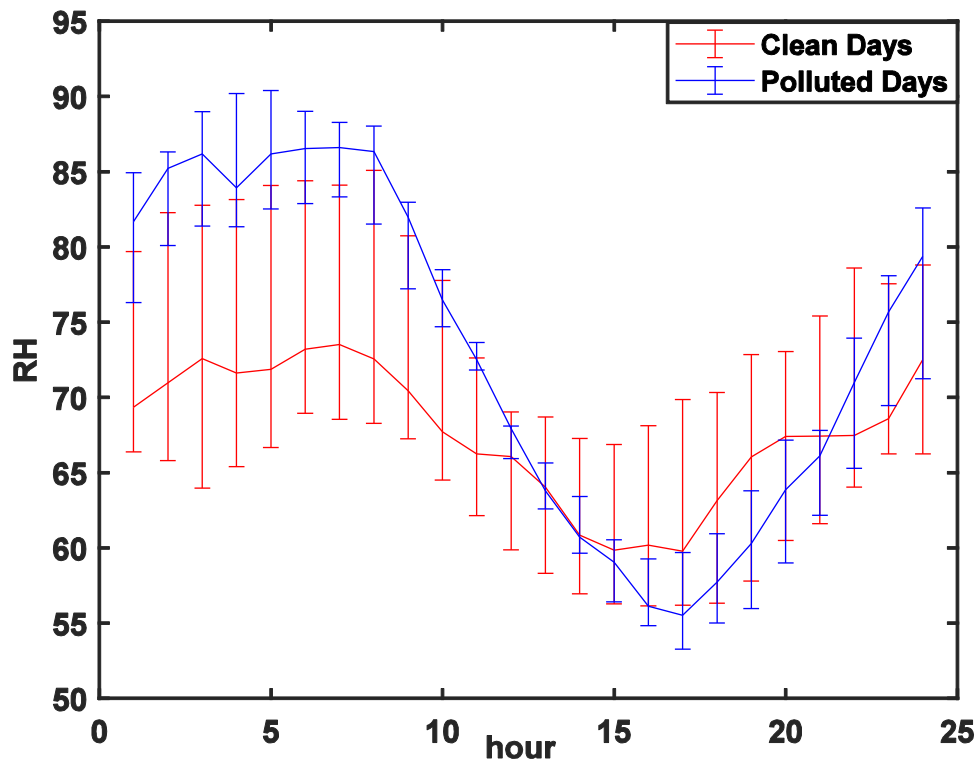
Supplement:

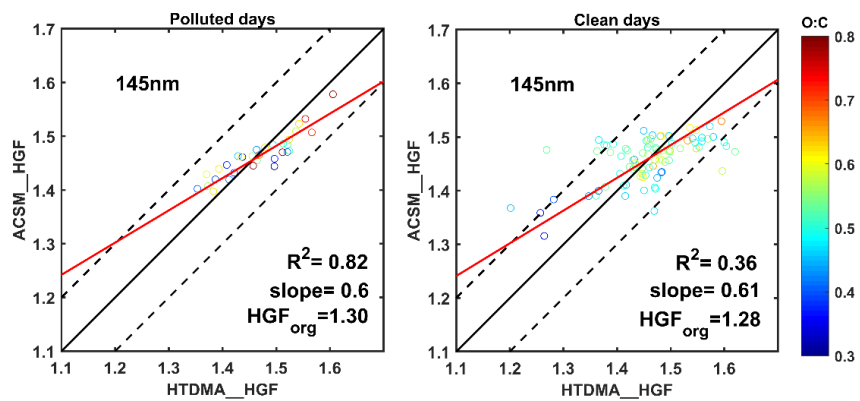Figure S2: Diurnal variation of relative humidity during the polluted and clean days.

Figure S3. Closure analysis with the best fitting between the measured HGFs and the ACSM-derived ones using constant HGF_{org} for 145 nm particles during the polluted and clean days, respectively.