Response to Reviewers' Comments

We sincerely thank the reviewers for their valuable comments and suggestions, which help us greatly improve this paper. Below we list our point-by-point replies to the comments as well as the revisions we had made to the manuscript. The original reviewers' comments are in Italic. Our responses are marked in blue color. Revisions in the manuscript are highlighted in red color.

Review 1

General: *Extensive study of the variability in state of mixing of urban BC particles and other material with new results.*

Language: *The English formulations need substantial improvements. Several examples are pointed out in the list of detailed comments.*

Citations: *The cited literature is mostly rather recent, predominantly Chinese, and more than necessary from the own authorship, disregarding original findings and reports. Examples are given in the list of detailed comments.*

Recommendation: *Accept after addressing the list of detailed comments, thorough language editing and literature review.*

Response: We thank Reviewer 1 for all the comments and suggestions. We addressed all these comments, improved English and added reviews for more recent literatures.

Line 63: Chemical composition and "mixing state" are not the same, c.f. (Heintzenberg and Covert, 1990)

Response: We thank Reviewer 1 for pointing this out. According to Heintzenberg et al., (1990) and Winkler (1973)., we changed the original sentence "In the atmosphere, an aerosol population typically consists of aerosol particles with various sizes and chemical compositions, which is usually described as "mixing state"." to the following (line 62-71):

"Atmospheric aerosols, including BC particles, always have various sizes with distinct chemical compositions. To better understand or describe an aerosol population, "mixing state" is often used. The definition of mixing state, provided by Winkler (1973), refers to both internal and external mixtures in aerosols. In an external mixture, individual particles in a given size range consist of different chemical species. Chemical composition of particulate mass in that size range will be determined by the relative contributions of the chemically distinct particles. In an internal mixture, on the other hand, all particles in a given size range are composed of the same mixture of two or more chemical compounds (Heintzenberg et al., 1990)."

Line 66: is determined

Response: Corrected.

Line 66: composition

Response: Corrected.

Line 67: Heintzenberg & Covert 1990 precedes the cited literature by more than 20 Years.

Response: We had cited this paper in the revised manuscript (line 71-76):

"The mixing state of atmospheric BC particles is closely linked to their sources and aging processes (Weingartner et al., 1997; Gysel et al., 2003; Petzold et al., 2005; Chirico et al., 2010; Heringa et al., 2011). Aerosol hygroscopicity is determined by the chemical composition of each individual particle (Heintzenberg et al., 1990; Gysel et al., 2003; McMeeking et al., 2011; Liu et al., 2013)."

Line 74: Who is "it"? Obscure sentence

Response: We had revised the original sentence "Herich et al. (2008) combined an aerosol time of flight mass spectrometer (ATOFMS) with a hygroscopicity tandem differential mobility analyzer (HTDMA) to investigate the mixing state and hygroscopicity of BC-containing particles at an urban site in Zurich, Switzerland. It shows that most of BC-containing particles internally mixed with organics and combustion species ($^{-26}CN^-$ and $^{-42}CNO^-$) have lower hygroscopicity compared with sulfate and nitrate mixed (Herich et al., 2008).” to following (in Line 103-108 of the revised manuscript) ：

“Herich et al. (2008) combined an ATOFMS with a HTDMA to investigate the mixing state and hygroscopicity of BC-containing particles at an urban site in Zurich, Switzerland. The result shows that most of BC-containing particles internally mixed with organics and combustion species ($^{-26}\mathrm{CN}^{-}$ and $^{-42}\mathrm{CNO}^{-}$). They have lower hygroscopicity compared with sulfate and nitrate mixed (Herich et al., 2008).”

Line 82: “ambient BC particles externally and internally mixed BC particles”: Obscure formulation

Response: We had revised the original sentence “Similarly, by coupling a SP2 with a HTDMA, McMeeking et al. (2011) measured the hygroscopicity of ambient BC particles externally and internally mixed BC particles using uncoated and coated laboratory generated model BC particles. The obtained information is compared to the hygroscopicity distribution of ambient BC aerosols.” to (line 114-119):

“Similarly, by coupling a SP2 with a HTDMA, McMeeking et al. (2011) introduced a method for measuring the hygroscopicity of externally and internally mixed BC particles. They tested this technique using uncoated and coated laboratory generated model BC compounds. The obtained information is compared to the hygroscopicity distribution of ambient BC aerosols.”

Line 99: pollutant

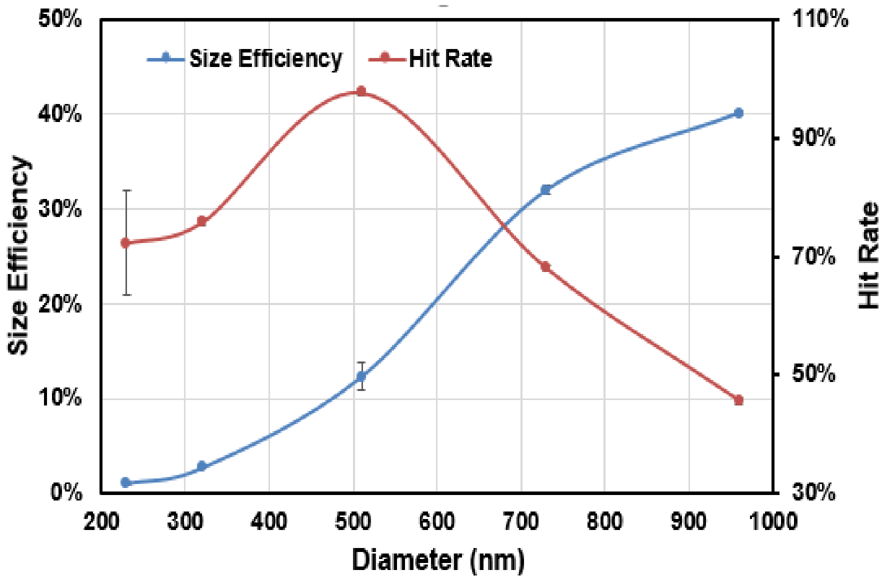
Response: Corrected.

Line 127: Sentence beginning here is missing a verb

Response: Corrected (line 195).

Line 140: What is the collection efficiency of the SPAMS, e.g., at its lower size limit of 200 nm?

Response: The collection efficiency of the SPAMS is shown in the figure below. The collection efficiency is about 1% at the lower size limit of 200 nm.



Line 173: "primary aerosol emission": obscure formulation

Response: We had changed "primary aerosol emission" to "primarily emitted combustion aerosols" (line 239).

Line 198: Fig. 2 starts at 2017-07-01 instead of 2017-07-04 as in the text and as more suitable for illustrating the TDMA-SP2" sampling intervals, which should be marked in the figure

Response: We changed Fig. 2 in the revised manuscript (also show below).

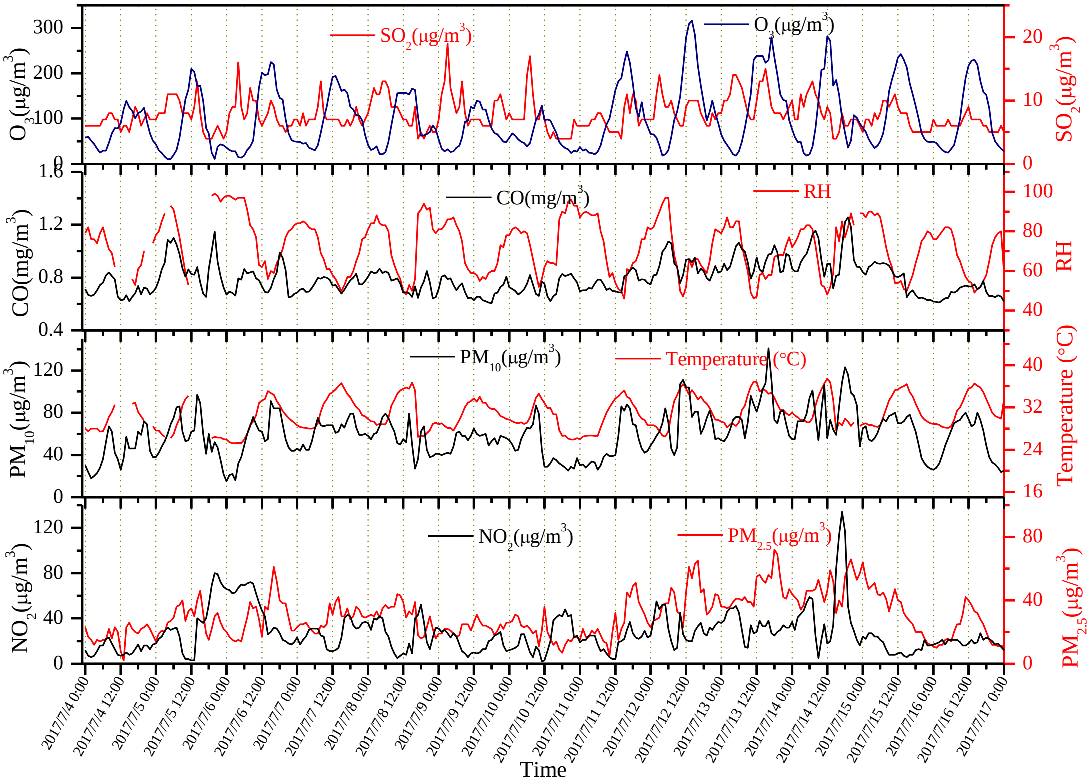


Figure 2. Temporal profiles of gaseous pollutants (O_3, SO_2, CO, and NO_2), temperature, relative humidity (RH), and $PM_{2.5}$ and PM_{10} mass concentrations.

Line 245: How do you define "total"? Total samples or truly total ambient? If the latter where does your ambient reference come from?

Response: In our study, "total" means total samples, including sampled refractory BC and non-BC particles. We had revised the original sentence to (line 307-310)：

"The number fraction of BC particles is defined as the ratio of the number concentration of sampled refractory BC particles to that of total samples, including refractory BC and non-BC particles, at a certain D_0 and GF."

Line 275: The hydrolysis of N_2O_5 has been described decades before, e.g., Mozurkewich, M., and J. G. Calvert, Reaction probabilities of N_2O_5 on aqueous aerosols, J. Geophys. Res., 93, 15,889–15,896, 1988

Response: We had cited this literature (Mozurkewich et al., (1988)) in the revised manuscript (line 344).

Line 284: "It is known that BC particles originated from traffic emissions are small". Yes but known before the cited Chinese reference

Response: We had cited the following two earlier literatures (Harris et al., 2001; Zervas et al., 2006) in the revised manuscript (line 356).

Harris, S. J., and Maricq, M. M.: Signature size distributions for diesel and gasoline engine exhaust particulate matter, J. Aerosol Sci., 32, 749–764, https://doi.org/10.1016/S0021-8502(00)00111-7, 2001.

Zervas, E., and Dorlhene, P.: Comparison of exhaust particle number measured by EEPS, CPC, and ELPI, Aerosol Sci. Technol., 40, 977–984, https://doi.org/10.1080/02786820600844093, 2006.

Line 291: Proportions

Response: We changed to "a larger proportion" (line 363).

Line 305: If you compare the volume of the coating instead of the coating thickness with varying core diameter you might come to a different conclusion

Response: If we assumed BC particles were spherical, the coating volume could be calculated based the coating thickness value. Since the total particle size (including BC core and coating materials) is fixed in this work (120, 240 or 360nm), a thicker coating thickness represents a larger coating volume. Our conclusion will still hold for the calculated coating volume.

Line 315: How low is the "low efficiency"?

Response: Please see the response to the specific comment for Line 140.

Reference

Heintzenberg, J., and Covert, D. S.: On the distribution of physical and chemical particle properties in the atmospheric aerosol, J. Atmos. Chem., 10, 383－397, https://link.springer.com/article/10.1007/BF00115781, 1990.

Mozurkewich, M., Calvert, J. G.: Reaction probability of N_2O_5 on aqueous aerosols, J. Geophys. Res. Atmos., 93, 15889 － 15896, https://doi.org/10.1029/JD093iD12p15889, 1988.

Winkler, P.: The growth of atmospheric aerosol particles as a function of the relative humidity—II. An improved concept of mixed nuclei, J. Aerosol Sci., 4, 373－387, https://doi.org/10.1016/0021-8502(73)90027-X, 1973.

Response to Review 2

Summary

The manuscript focuses on several weeks of measurements made by an HTDMA-SP2 operating in parallel with a single-particle aerosol mass spectrometer, and explores relationships between refractory black carbon (rBC) hygroscopicity, proxies for rBC "coatings" and single particle aerosol composition. Quantitative details regarding rBC aging and influences on rBC aging timescales in the literature remain rare, and the topic is important, so the subject of the manuscript is significant and well within the topic area of ACP, however the analysis is somewhat limited, and in some areas focused on observations that are less relevant to areas where current scientific understanding is low. It was unfortunate the SPAMS could not be place downstream of the HTDMA in parallel with the SP2, as that would allow for some interesting direct comparisons between particles containing rBC (or EC) at different growth factors. This weakens the overall strength and novelty of the manuscript, because many of the results presented are inferred by similar patterns or relationships in diurnal data rather than direct comparison. Despite this overall weakness, the other results are still of value and I recommend they be published once the following comments have been addressed.

Response: We thank for Reviewer 2 for the comments and suggestions. We had prepared this point-to-point response document to address Reviewer 2's comments and show the changes that we had made to improve this paper. We had done much more data analysis based on Reviewer 2's suggestions. The details of these data analysis can be found in the following point-to-point responses.

We agree that putting a SPAMS in the downstream of a HTDMA would be very informative. Indeed, we had already published a paper using this HTDMA-SPAMS experimental setup (Wang et al., 2014). However, the purpose of the current paper is to obtain high time resolution temporal variation of BC particles' properties. It is not practical to put the SPAMS in the downstream of the HTDMA for this purpose, because size selection of charged particle in DMA greatly reduces aerosol particle concentration. The particle concentration in the downstream of the HTDMA would be too low for the SPAMS to collect sufficient number of aerosol particles with an adequate time resolution during our sampling period.

We think our paper reports many new findings which could contribute significantly to the current understanding of BC particle ageing. For example, using the diurnal patterns of BC particle properties and chemical compositions, we found different atmospheric aging processes between daytime (secondary organic formation and slightly enhanced sulfate) and nighttime (nitrate formation) led to the change of BC particles' mixing states, which play a fundamental role in determining their hygroscopicity. To our knowledge, we have not seen any other paper reporting links between temporal variations of the hygroscopic growth of BC particles and atmospheric aging processes in a polluted environment. Thus, we think our results are new and can contribute significantly to the current understanding of hygroscopic growth of BC particles.

General Comments

There is very little discussion of timescales for BC aging, despite its importance and the potential opportunity for this study to provide some useful measurements to help constrain aging timescales. Including results for the fraction of BC (to total BC, not total aerosol) observed at higher GF, how it changes over time, and how it is correlated with the other chemical information would strengthen the paper.

Response: We thank Reviewer 2 for this suggestion. Ageing time scale is really an important topic. One of our previous paper has studied the ageing time scale of BC particles in a heavy pollution episode. It reports an absolute coating growth rate of ~ 20 nm/h during a pollution event in December, 2013 at our Shanghai sampling location (Gong et al., 2016). Thus, the ageing time scale for BC aerosols would be around several hours. As suggested by Reviewer 2, we had made a new figure (see the figure below) to show the fraction of BC particle at higher GF changed over time. And we had added the following section in the revised paper to discuss the BC particle ageing time scale. This section reads

"3.1.4 Diurnal variations of the distribution of BC particle growth factors

Fresh BC particles usually have low GF. Through ageing process, the GF of BC particles increase. It would be interesting to see how the GF distributions of BC particle change during a day and get a rough estimate of how fast the ageing process went. Fig. 6 shows the diurnal variations of the distribution of BC particle growth factors. Note only three GFs were measured by HTDMA-SP2 system. Here, the BC aerosol number fraction for each GF is defined as (BC aerosol number concentration for this GF)/(sum of BC aerosol number concentration for GF = 1.0, 1.2 and 1.4). It is found that the BC aerosol number fraction for GF = 1.0 reached two maxima at around 9:00 and 18:00, probably due to the rush hour traffic. Only 3 hours after 9:00 or 18:00, the BC aerosol number fractions for GF = 1.0 dropped significantly (from 0.44 to 0.26 and from 0.40 to 0.36, respectively). Meanwhile, the BC aerosol number fractions for GF = 1.4 increased (from 0.34 at 9:00 to 0.49 at 12:00 and from 0.44 at 18:00 to 0.50 at 21:00). Evidently, the GF distribution of BC particles changed rapidly even in just three hours. This change was probably due to the BC particle ageing and the ageing time scale is around several hours.

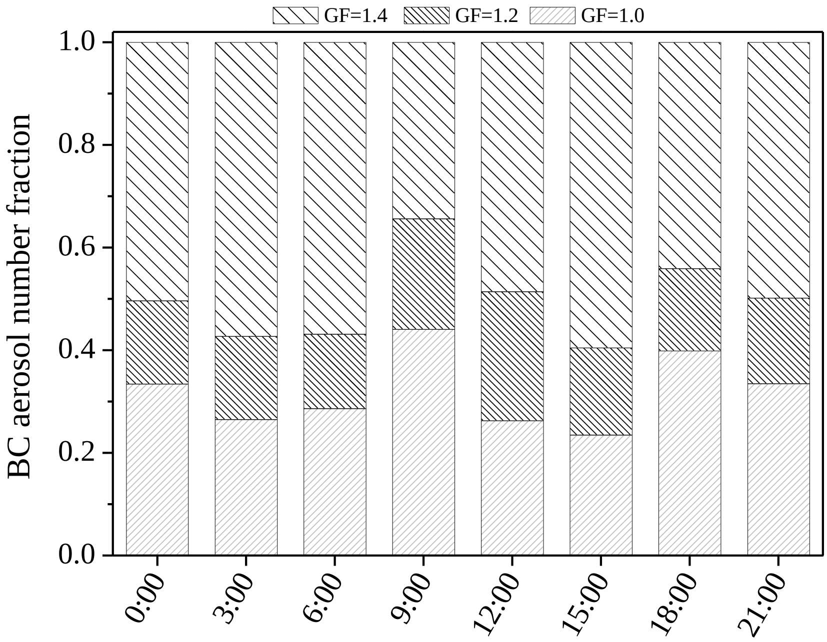


Figure 6. Diurnal variations of the GF distribution for BC particles. The BC aerosol number fraction for each GF is defined as (BC aerosol number concentration for this GF) / (sum of BC aerosol number concentration for GF = 1.0, 1.2 and 1.4)."

Further, the bulk of the analysis is centered on diurnal plots of different parameters rather than examining relationships between those parameters. I would be interested in seeing a plot showing the relationship between these parameters over the study *(e.g., coating thickness of BC in the high GF modes versus different chemical indicators).*

Response: As suggested by Reviewer 2, we made new figures (Figure 10a, 10b, 10c) and added the following section to the revised manuscript (in Line 619-627).

"Fig. 10 (a, b, and c) compares the coating thickness of 360 nm BC particles (GF = 1.4) with other chemical indicators, such as SOC, nitrate and sulfate. It shows that there was a positive correlation between the coating thickness and the SOC concentration and a negative correlation between the coating thickness and the nitrate concentration, which is consistent with their diurnal trends. There was a positive correlation between the coating thickness and sulfate concentration. Fig. 5(b) shows the coating thickness for 360 nm BC particles whose GF = 1.4 peaked in the afternoon. Formation of sulfate was also slightly enhanced during the afternoon due to stronger solar irradiation, resulting in this correlation."

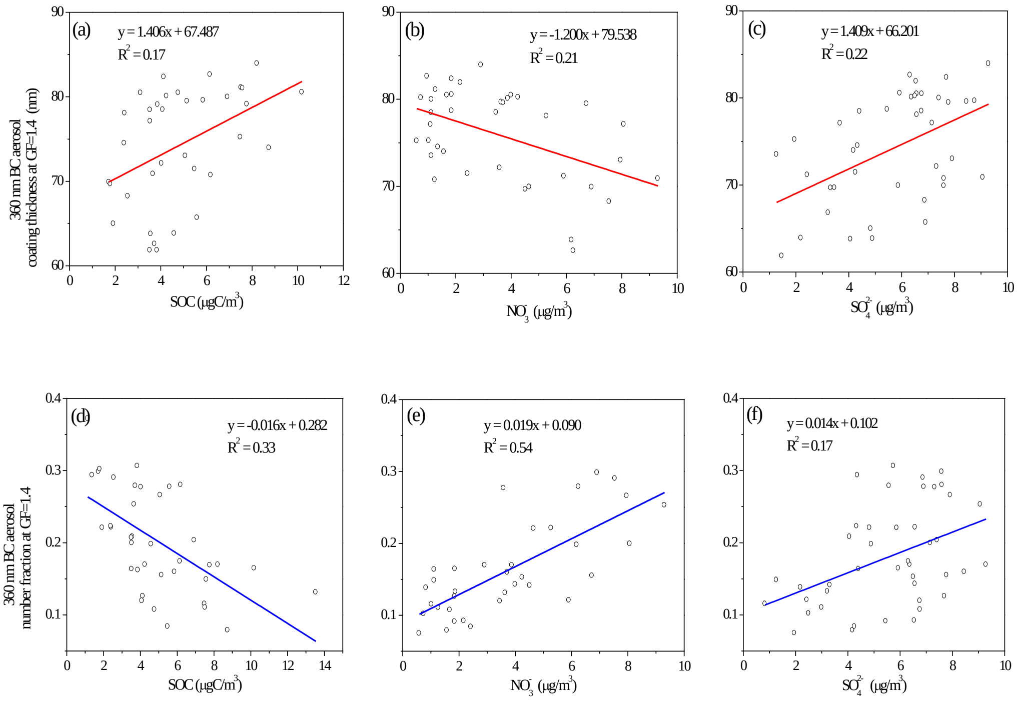


Figure 10. Relations between the coating thickness of 360 nm BC particles of which GF is 1.4 and the concentration of (a) SOC, (b) nitrate and (c) sulfate; Relations between the number fraction of BC particles in 360 nm aerosol of which GF is 1.4 and the concentration of (d) SOC, (e) nitrate and (f) sulfate."

In addition, seeing differences in the fractions present in the higher GF modes as a function of other indicators of chemical activity (nitrate production, SOC production, etc), would provide a more quantitative relationship that could potentially be extrapolated to other locations.

Response: We made new figures (Figure 10d, 10e, 10f) comparing the number fraction of BC particles in 360 nm aerosol of which GF is 1.4 and chemical indicators (SOC, nitrate and sulfate). The following discussion has been added to the revised manuscript in Line 628-636.

"Fig. 10(d, e, and f) shows the number fraction of BC particles in 360 nm aerosol of which GF is 1.4 verse the concentrations of SOC, nitrate and sulfate. It is found that the SOC had a negative correlation with the number fraction of BC particles in 360 nm aerosol of which GF is 1.4, while nitrate and sulfate had a positive correlation with the number fraction. This finding is consistent with the fact that SOC has lower GF than nitrate and sulfate salts. When more SOC is formed and more likely covers BC particles' surface, fewer BC particles' GF can reach 1.4. In contrast, when more nitrate or sulfate are formed and condense on BC particles, more BC particles' GF can reach 1.4."

Not sure this is really "first report of links between temporal variations of the hygroscopic growth of BC particles and atmospheric aging processes in a polluted environment."

Response: We have not seen any other paper which reports the links between temporal variations of the hygroscopic growth of BC particles and atmospheric aging processes in a polluted environment.

In several places the manuscript asserts that fresh BC emissions would by hygroscopic. This may be true for those arising from traffic, but is less clear for other *combustion sources, such as domestic fuel use. How prevalent is that in the Shanghai area? Some discussion of this possibility should be included.*

Response: Our paper states that fresh BC emission from traffic is hydrophobic (Lammel and Novakov, 1995; Lammel et al., 1995; Dusek et al., 2006). The SPAMS measurement shows that ~ 33% of BC particles are KEC type, which probably came from biomass burning or domestic coal combustion. Both fresh biomass burning aerosol and coal combustion aerosol contain large fraction of salts and water-soluble organics (Posfai et al., 2003; Wang et al., 2013). The growth factor of this particle type should be larger than 1.0. For example, Carrico et al measured the growth factors (GF) of fresh biomass burning aerosol directly from a burning chamber. The GFs at 85% RH vary from 1.03 to 1.6 (Carrico et al., 2010). Not all fresh BC emissions are hydrophobic. Thus, we deleted all such statements in the revised manuscript.

The treatment of uncertainty and variability in the results is not sufficient. More details are needed regarding variability in the diurnal data (e.g., showing as a box-and-whisker plot instead of just the averages and an interpolated fit as is currently done for these figures).

Response: We had made box-and-whisker plots for Fig. 7 in the revised manuscript.

Further, I think a little more detail regarding the uncertainties for coating thickness measurements from the SP2 or SP2-DMA composition are needed, as is more information related to the inversion and resolution of the HTDMA set up. While this might be available in previous work some brief mention of this is needed in the main text.

Response: We had added more details about SP2 and HTDMA measurement in our revised manuscript. For SP2, please see our detailed response to the specific comment for Line 123-125 below.

For HDMA set up, we had added the following sentences to line 150-155 of the revised manuscript:

"The two DMAs were operated with recirculating sheath flows and a sheath-to-sample flow ratio of 10:1. The HTDMA is encapsulated in a thermostatted box to reduce temperature fluctuations. The DMA housing temperature was controlled at 20ºC. Aerosol flow was set at 0.43 L/min (the sum of the CPC (0.4 L/min) and the SP2 (0.03 L/min) flow rates). The hygroscopicity measurement was calibrated using $(NH_4)_2SO_4$ particles."

Further, while previous work is described in the introduction, there is little comparison of the results from this study to similar measurements in other urban areas.

Response: As suggested by Reviewer 2, we had added the following discussion of comparison of the results from this study to other studies in line 415-427 and line 602-618 of the revised manuscript:

Line 415-427: "The coating thickness of BC particles from this study (20 ~ 80 nm for BC particles with electrical mobility diameter of 120 ~ 360 nm) were in the range of previous measurements from other cities. For example, Laborde et al. (2013) measured BC coating thickness in Paris during a winter time (Laborde et al., 2013). They found coating thickness was approximately 33 nm on average for rBC core size from 180 to 280 nm. Liu et al. (2013) reports an average coating thickness of ~ 40 nm for BC particles with electrical mobility diameter of 163 nm (Liu et al., 2013). A field study in London during wintertime shows that the average coating thickness for BC particles with 137 nm, 143 nm and 169 nm in diameter were ~ 15 nm, 22 nm and 33 nm, respectively (Liu et al., 2014).

The rapid change in BC particle coating thickness suggests that the ageing time scale was around several hours. This time scale is consistent with a previous modeling study (Riemer et al., 2004)."

Line 602-618: "This study shows that different atmospheric aging processes between daytime (secondary organic formation and slightly enhanced sulfate formation) and nighttime (nitrate formation) led to the change of BC particles' mixing states. This finding is consistent with our previous measurement of secondary species formation in Shanghai during the summer time. Shanghai is a typical Chinese megacity with heavy air pollution. In summer, high NO_x emission and ozone concentration led to enhanced nitrate formation via N_2O_5 pathway during nighttime (Wang et al., 2009; Pathak et al., 2009). Secondary organic aerosol and particulate sulfate are usually formed through photo-oxidation of organic vapor and SO_2 during daytime (Kroll and Seinfeld, 2008; Wang et al., 2016). The differences in aging pathways between daytime and nighttime result in different coating materials and thickness on rBC cores, which can further impact their hygroscopicity. Noticeably, Liu et al. (2013) reports that the hygroscopicity of BC particles was largely driven by the coating of ammonium nitrate (Liu et al., 2013). However, it may not be the case in Shanghai during summer time, as most of particulate ammonium in Shanghai has been found to be in the form of ammonium sulfate (Wang et al., 2009; Pathak et al., 2009). Indeed, our SPAMS spectra for BC particles do not show the presence of large ammonium peaks (Fig. S2), because most of ammonium was in the form of ammonium sulfate, which is difficult to be ionized and detected in SPAMS (Wang et al., 2009).

Recommend adoption of the term "refractory black carbon" when referring to material measured by the SP2.

Response: As suggested by Reviewer 2, we used the term "refractory black carbon" for SP2 measurement through the entire revised manuscript.

Specific Comments

64-68: There are earlier references for these findings that should be referenced.

Response: We had cited several earlier literatures (Weingartner et al., 1997; Gysel et al., 2003; Petzold et al., 2005) in the revised manuscript.

Weingartner, E., Burtscher, H., and Baltensperger, U.: Hygroscopic properties of carbon and diesel soot particles, Atmos. Environ., 31, 2311–2327, https://doi.org/10.1016/S1352-2310(97)00023-X, 1997.

Gysel, M., Nyeki, S., Weingartner, E., Baltensperger, U., Giebl, H., Hitzenberger, R., Petzold, A., and Wilson, C. W.: Properties of jet engine combustion particles during the PartEmis experiment: Hygroscopicity at subsaturated conditions, Geophys. Res. Lett., 30, 1566, https://doi:10.1029/2003GL016896, 2003.

Petzold, A., Gysel, M., Vancassel, X., Hitzenberger, R., Puxbaum, H., Vrochticky, S., Weingartner, E., Baltensperger, U., and Mirabel, P.: On the effects of organic matter and sulphur containing compounds on the CCN activation of combustion particles, Atmos. Chem. Phys., 5, 3187–3203, https://doi:10.5194/acp-5-3187-2005, 2005.

69-93: This section could be better organized by placing similar studies together and having the narrative flow more smoothly. I suggest beginning with the HTDMA-ATOFMS studies, including those by the authors, then transitioning to the HTDMA-SP2 studies and their findings. Missing from this literature review is earlier laboratory work examining BC hygroscopicity, as well as any relevant HTDMA only studies. While these are not able to discriminate between BC and non-BC containing particles, they are relevant to the manuscript's topic and some discussion would be beneficial to the reader.

Response: We agree with this comment, and we have reorganized this section of the revised manuscript as following (line 78-124):

"Many studies have reported the mixing state of atmospheric BC particles. For example, aerosol's mixing state can be determined using a HTDMA (Swietlicki et al., 2008), or a combined volatility-hygroscopicity TDMA (VHTDMA) (Johnson et al., 2005). Shiraiwa et al. investigated the evolution of mixing state of BC using a SP2 in the polluted air transported from Tokyo city area in summer (Shiraiwa et al., 2007). The fraction of thickly coated BC with a core diameter (D_C) of 180 nm increased at a rate of 1.9% h^{-1}. The increase rates were lower for larger D_C (Shiraiwa et al., 2007). Healy et al. used an ATOFMS to study the mixing state of BC particles in Paris (Healy et al., 2012). The smaller BC particles ($D_{va} \leq 400$ nm) were mainly externally mixed, indicating they were from local or regional sources, while bigger BC particles ($D_{va} \geq 400$ nm) were mainly internally mixed with nitrate, indicating they were from medium to long-range transport. Kuwata and Kondo (2008) conducted volatility TDMA (VTDMA) measurements and showed that the aerosol was often an external mixture of less- and more-volatile particles (Kuwata and Kondo, 2008).

According to our knowledge, there are only a few direct measurements of BC particles' hygroscopic properties in the atmosphere. One of the previously used techniques was coupling hygroscopic measurements with VTDMA system. It was found that the less volatile aerosol components were mainly composed of BC at close proximity to urban environments (Kuwata et al., 2007; Rose et al., 2011). The relationship between hygroscopicity and mixing state of BC aerosols had been studied. BC particles exposed to subsaturated sulfuric acid vapor exhibit a large change in morphology. These particles are very hygroscopic and act as efficient cloud-condensation nuclei. Coating with sulfuric acid and subsequent hygroscopic growth increase their light scattering coefficient by 10-fold and light absorption coefficient by nearly 2-fold at RH = 80% compared to uncoated BC particles (Zhang et al., 2008). Herich et al. (2008) combined an ATOFMS with a HTDMA to investigate the mixing state and hygroscopicity of BC-containing particles at an urban site in Zurich, Switzerland, and the result shows that most of BC-containing particles that internally mixed with organics species (m/z $^{-26}CN^{-}$ and $^{-42}CNO^{-}$) have lower hygroscopicity compared to those mixed with sulfate and nitrate. With a similar setup, our previous study finds that condensation of amine and secondary inorganic species would enhance the hygroscopicity of submicron particles, including BC particles (Wang et al., 2014). Laborde et al. connected a SP2 in downstream of HTDMA (RH = 90%) and shows that the majority of urban aerosol particles with high hygroscopicity (GF ≈ 1.6) do not contain a detectable refractory BC core, while hydrophobic or less hygroscopic particles ($1.1 \leq GF \leq 1.2$) have a BC core with no or little coating of soluble species (Laborde et al., 2013). Similarly, by coupling a SP2 with a HTDMA, McMeeking et al. (2011) measured the hygroscopicity of uncoated and coated laboratory generated model BC particles, which was then compared to the hygroscopicity distribution of ambient BC aerosols. Their results suggest that the dominant fraction of the BC particles does not readily act as cloud condensation nuclei (CCN) at 0.2% super saturation in an urban area. In addition, Liu et al. (2013) deployed a similar instrument setup and investigated the relation between the hygroscopic properties and mixing state of BC particles (Liu et al., 2013). It shows that the GF of BC particles was influenced by the composition of soluble materials.”

100-102: At least some of the studies mentioned here should be cited.

Response: We accepted this suggestion and compared our study with that similar measurements mentioned in the introduction. The details can be found in Part 3.3.3 of the revised manuscript.

115: As written this sounds like the cited studies used an HTDMA-SP2 system, which is not accurate. Recommend modifying slightly to: Similar to systems that couple an HTDMA with another instrument, such as those used by Herich et al. (2008), Zelenyuk et al. (2008), and Wang et al. (2014), our system used an SP2 (DMT, Boulder, CO, USA) downstream of an HTDMA to measure BC content as a function of hygroscopicity.

Response: As suggested by Reviewer 2, we had changed the original sentence "Similar to those employed by Herich et al. (2008), Zelenyuk et al. (2008) and Wang et al (2014), our HTDMA-SP2 system used a SP2 (DMT, Boulder, CO, USA) in the downstream of a HTDMA to probe BC content as a function of hygroscopicity. " to (line 141-145):

"Similar to systems that couple an HTDMA with another instrument, such as those used by Herich et al. (2008), Zelenyuk et al. (2008), and Wang et al. (2014), our system used an SP2 (DMT, Boulder, CO, USA) in the downstream of an HTDMA to measure rBC content as a function of hygroscopicity."

118: Suggest changing "monodisperse particles with a dry particle diameter" to "monodisperse dried particles"

Response: We had changed this phrase to "monodisperse dried particles" in the revised manuscript (line 146).

120: From later descriptions in the text it sounds like the wet SMPS operated in a stepped mode rather than scanning continuous mode. Please clarify.

Response: Ambient particles with three electrical mobility sizes (120 nm, 240 nm and 360 nm in dry diameter) were selected by first DMA, then humidified at a RH = 85%. For the measurement of the overall hygroscopic distribution of total ambient particles (such as Figure 3(a)), the second DMA was operated in a scanning continuous mode. For the measurement of temporal trends of the hygroscopic distribution, the second DMA was operated in a stepped mode by sending particles with fixed GFs of 1.0, 1.2 and 1.4 (representing hydrophobic, transition and hydrophilic mode, respectively) to the CPC and SP2. We clarified these operations in the revised manuscript in line 189-196.

123-125: Please provide a little more detail on the SP2 measurement for the reader, such as the SP2 response range (e.g., it will not measure BC present in particles if the BC mass is less than about 0.3-0.5 fg) and how "mixing state" is being measured (light scattering, difference between the dry DMA mobility size and effective rBC diameter, etc). Also should be careful with language here. . .mixing state is not the right term. The SP2 measures BC mass in particles and in some situations approximates "coating thickness" for assumed geometry.

Response: We had added the following description in our revised manuscript in line 158-188:

"SP2 can measure number and mass size distribution of rBC containing particles (Baumgardner et al., 2004; Schwarz et al., 2006). Briefly, SP2 detects incandescence and scattering light signals of rBC-containing particles induced by a 1064 nm Nd: YAG intra-cavity laser. The mass of rBC is proportional to the intensity of the incandescence signal. A particle with an incandescence signal (above a threshold) is treated as an rBC particle, while a particle that only exhibits scattering signal is considered as a non-rBC particle. SP2 detection efficiency was close to unity for larger rBC particles. The minimum rBC mass that could be observed with near-unity detection efficiency was ~ 0.7 fg rBC, corresponding to 90 nm mass equivalent diameter; the detection efficiency declined rapidly at lower sizes (Gong et al., 2016). The total ambient mass concentrations of rBC were possibly underestimated because of the reduced detection efficiency for small rBC particles (Schwarz et al., 2006; McMeeking et al., 2010).

The conversion from rBC mass to the effective rBC core diameter requires to assume an effective density for rBC cores in the particles. In this study, an effective density of 1.8 g cm^{-3} was used to convert the ambient rBC mass to the mass equivalent diameter. This value was recommended by many previous studies (Bond and Bergstrom, 2006; Gong et al., 2016).

The scattering properties of externally and internally mixed rBC particles may be distorted due to particle mass loss induced by laser heating in SP2. Thus, scattered light from an rBC particle may not yield a full Gaussian waveform. The Gaussian scattering function was reconstructed from the leading edge of the scattering signal (before particle is heated by the laser), which was measured with a two-element avalanche photodiode (APD). This method can determine the scattering properties of individual rBC particles more accurately (so called LEO-fit method;(Gao et al., 2007). Optical diameter of an rBC particle (D_p) was derived from Mie theory with the LEO fitted scattering signal and rBC core size (D_c) (Moteki and Kondo, 2010; Liu et al., 2014; Laborde et al., 2013). The absolute coating thickness of an rBC particle was calculated as ($D_p - D_c$)/2, based on the assumption of a concentric core-shell morphology. However, rBC aging in the atmosphere may result in an imperfect core-shell structure (Matsui et al., 2013)."

225: I'm not sure the authors mean to attribute the reduction in particle number to size-dependent growth. . .the reduction in number is just a function of the dry size distribution. Please clarify in the text.

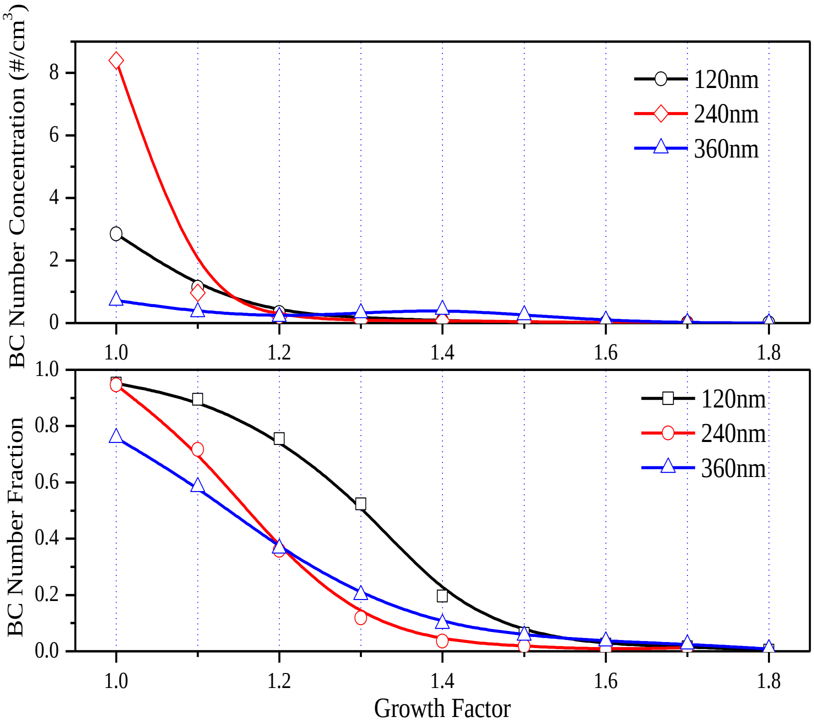
Response: To avoid possible confusion, we deleted "reducing of the particle number" and changed the original sentences "Clearly, the hygroscopic particles were typically more abundant than the hydrophobic ones. The hygroscopic growth distributions featured a size dependent hygroscopic growth, significantly reducing of the particle number and shifting to larger growth with increasing particle size, which were conventionally attributed to a size dependent chemical composition (Swietlicki et al., 2008)." to the following (line 288-292):

"Clearly, the hygroscopic particles were typically more abundant than the hydrophobic ones. These hygroscopic particles featured a size dependent hygroscopic growth, significantly shifting to larger GF with increasing particle size. This feature was conventionally attributed to a size dependent chemical composition (Swietlicki et al., 2008; Ye et al., 2013)."

228: Figure 3b shows the BC number fraction, not the number concentration, so is not a good way to support the claim of a single BC mode. What does the distribution of BC number concentration versus GF look like?

Response: As shown in the figure below, we plotted the average BC number concentration vs GF. It shows that the GF curve of BC particles peaked at GF = ~1.0. Similar to Fig. 3(b), the BC-containing number concentration decreased while the GF increased.

The scanning of hygroscopic distribution of BC particles took a long time. A certain amount of time would be needed for each GF to allow SP2 collect sufficient number of BC particles. During this time, total particle concentration could fluctuate significantly. Therefore, we would prefer using average BC number fraction rather than average BC number concentration in the revised manuscript.



Averaged hygroscopic growth distributions of BC particles.

233: I'm surprised at this decision given the focus of the paper is on BC hygroscopicity, and BC present in particles with high GF represent the most hygroscopic fraction of the ambient BC. What fraction of the BC number concentration did these particles represent? Note that the number fraction relative to other hygroscopic particles is not particularly important from a BC aging perspective, which is the focus of the paper (versus an assessment of CCN concentrations where particle type).

Response: As the GF increase, BC particle number concentration and its number fraction decrease sharply (as shown in the above figure). The number of BC particles with high GFs (GF ≥ 1.5) was only 2.76% in total BC particles in this study. Therefore, our three GF selections (1.0, 1.2 and 1.4) can cover the major portion of total BC particles.

As suggested by the general comments by Reviewer 2, we had added a new figure (Fig. 6) to the manuscript to discuss the change of the relative fractions among BC particles with different GFs (see the detailed response to the general comments above). This new figure is very informative from a BC ageing perspective.

247-253: This section is essentially a description of BC diurnal patterns in an urban environment, and should refer to earlier papers first describing this behavior from observations in the 1990s.

Response: We had cited the following earlier literatures in our revised manuscript.

Allen, G. A., Lawrence, J., Koutrakis, P.: Field validation of a semi-continuous method for aerosol black carbon (aethalometer) and temporal patterns of summertime hourly black carbon measurements in southwestern PA, Atmos. Environ., 33, 817–823, https://doi.org/10.1016/S1352-2310(98)00142-3, 1999.

Bhugwant, C., Cachier, H., Bessafi, M., Leveau, J.: Impact of traffic on black carbon aerosol concentration at la Reunion Island (Southern Indian Ocean), Atmos. Environ., 34, 3463–3473, https://doi.org/10.1016/S1352-2310(99)00405-7, 2000.

Dreher, D. B., Harley, R. A.: A fuel-based inventory for heavy-duty diesel truck emissions, J. Air Waste Manage., 48, 352–358, https://doi.org/10.1080/10473289.1998.10463686, 1998.

261-263: Careful with this statement. The reduction in the fraction of BC measured for a specific GF does not necessarily follow from fresh BC being below 200 nm. The larger BC measured at GF = 1.0 is presumably "fresh" as well, and in the absence of other particles the ratio would still be expected to be 1. Factors driving the BC number fractions at GF = 1.0 may be more related to the behavior of non-BC containing particles and their size dependence.

Response: We accepted the reviewer's advice and had revised this paragraph as following (line 323-331):

"As shown in Fig. 4(b), hydrophobic BC particles accounted for the largest percentage among three GFs for all D_0s. However, the number fractions of hydrophobic BC particles decreased with the increased D_0. For D_0 = 120 nm, 240 nm, 360 nm, the maximum number fractions of the hydrophobic BC particles were ~80%, 70% and 60%, respectively. One possible reason is that the majority of fresh BC particles diameter are smaller than 200 nm (Kondo et al., 2006), corresponding to our finding that relatively lower fractions of BC particles were detected at larger sizes. In addition, factors affecting the BC number fractions at GF = 1.0 may also be related to the behavior of non-BC containing particles and their size dependence."

281-286: Take care not to treat D_0 as the BC particle diameter, as the dry size reflects the size of the mixed particle, not just the BC. The amount of BC in the particle could still be small if it were mixed with other material, bringing its total size to D_0 (and also increasing the hygroscopicity). So the increasing fraction of BC particles referred to in this section likely more reflects aging rather than a different source.

Response: We agreed with this comment and had pointed out both possibilities (ageing and different sources) in line 348-361 of the revised manuscript as following:

"Fig. 4(b) also shows the diurnal variations of number fractions of transition and hydrophilic mode BC particles. Unlike the hydrophobic mode BC particles, the transition and hydrophilic mode (GF = 1.2 and 1.4) BC particles with larger sizes tended to contribute higher number fractions of total particles. This trend was more pronounced for the hydrophilic mode (GF = 1.4): the maximum number fractions of BC particles were ~10%, 10% and 20% for D_0 = 120 nm, 240 nm, 360 nm, respectively. One possible reason is that the sizes of fresh BC particles are likely to be small. The median diameter of BC particles originated from traffic emissions are usually < 200 nm (Harris et al., 2001; Zervas et al., 2006; Xue et al., 2015). They have to grow to larger sizes (e.g. 360 nm) through ageing/coating, which also increases their hydroscopcity. Another possible reason is that these hydrophilic BC particles were from a different source. A candidate is biomass burning (BB) aerosols, which have slightly higher hygroscopicity than those from traffic emissions (Laborde et al., 2013). Detail discussion of BB aerosol will be shown in Section 3.2. ”

294: This section is too brief and ignores many subtleties in the data that are potentially interesting. I’m not sure that the derived coating thicknesses can make physical sense given the growth factors. For example, the GF = 1.0 results all show average coating thicknesses of at least 20-35 nm, suggesting a significant volume of non-BC material, which must also have a GF = 1.0. While this is certainly possible, it seems unlikely that particles with this much coating can have GF = 1.0. More likely is some type of shape effect, which would play a larger role for fresh, hydrophobic BC that are likely to be aggregates and non-spherical. In this case the mobility size to core diameter relationship is not simply that predicted for spheres and used to derive coating thickness.

Response: We thank Reviewer 2 for this suggestion. We had added the following discussion in the revised manuscript (Line 381-398).

“In this study, the main uncertainty associated with the HTDMA-measured GF of soot particles was influenced by particle morphology. For fresh BC particle with an aggregate structure, the mobility diameter (D_{mob}) measured by a DMA is normally larger than its geometric volume/mass equivalent diameter (D_{ve}) (DeCarlo et al., 2004). However, coating on soot aggregates can modify its morphology (Weingartner et al., 1997; Lewis et al., 2009; Pagels et al., 2009) by making soot aggregate more compact. Change of particle morphology affects D_{mob} measurement. It has been reported that more compact BC particles tend to exhibit smaller mobility diameter and higher effective density (Zhang et al., 2008; Pagels et al., 2009). In HTDMA measurements, if BC-containing particles’ shape are significantly fractal, the water adsorption process in HTDMA would likely make them more compact, and therefore their GFs soot particles would be underestimated. These effects are less pronounced for particles which are less fractal. Due to the limitation of HTDMA, the complex morphology or ρ_{BC} of BC-containing particles cannot be explicitly determined in this study. Thus, a conventional core-shell model for a BC-containing particle has to be assumed. The GF = 1.0 results show an average coating thicknesses of ~ 20-35 nm, suggesting the presence of non-BC materials or the effect of non-spherical shape on size measurement.”

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