

## ***Interactive comment on “A novel study of the morphology and effective density of externally mixed black carbon aerosols in ambient air using a size-resolved single-particle soot photometer (SP2)” by Yunfei Wu et al.***

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### General comments

The authors use a tandem DMA-SP2 system to measure the mass-mobility exponent, effective density, and shape factor of ambient BC particles in Beijing, China. Despite the claim to novelty made in the title similar combined DMA-SP2 measurements have already been discussed and reported in the literature, which the authors have failed to discuss. In addition, there are significant shortcomings in the manuscript itself, rang-

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ing from inadequate description of the experimental details and results to data quality issues. In my view the manuscript is at the 'early draft' stage rather than the 'under review' stage. I believe major revisions are required before the manuscript can be considered for publication in AMT. Most importantly, the authors need to better demonstrate why this study is an original contribution to the literature on the properties of ambient BC aerosols, and why their measurements should be considered artifact-free and trustworthy.

We appreciate the criticisms from the reviewer and appreciate the several useful comments which helped us improve the paper. A huge modification has performed to our manuscript by referring more useful literature, reanalyzing the experimental data and improving the English writing. We hope the reviewer will see our efforts to improve the quality of our manuscript.

I see the following major issues:

The study is not placed in appropriate context through citation of relevant literature. In the title and elsewhere (e.g. L101) the authors claim that this is a 'novel' system or measuring the morphology and effective density of black carbon particles. This is incorrect. Tandem DMA-SP2 measurements have been discussed and/or performed in a number of different studies (e.g. Gysel et al., 2011; Raatikainen et al., 2017; Zhang et al., 2016). A handful of references are cited for more general mass-mobility measurements (e.g. using an APM rather than an SP2). But the literature on this topic is more extensive than this small selection of studies would suggest, including a review on the mobility of fractal aggregates by Sorensen (2011). I suggest the authors read this review and the references therein and put more effort into placing their measurements into the context of these previous works. In particular, the authors need to demonstrate what is the original contribution of this work.

Reply: Thanks for the constructive comments. Indeed, a number of previous studies have used the tandem DMA-SP2 system to measure the physical and/or optical proper-

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ties of BC particles. A few related references have been cited in the initial manuscript (e.g., Gysel et al., 2011; Zhang et al., 2016), although a few other references were missed (e.g., Raatikainen et al., 2017). Citation of these related references has been performed in our revised manuscript. As mentioned in the introduction of the revision (Lines 129–141), the mass-mobility relationship, from which the morphology and effective density of extBC aggregates are obtained, were seldom studied in previous DMA-SP2 measurements, especially in the ambient atmosphere. The morphology and effective density of internally mixed BC (intBC) particles in the atmosphere in North China Plain were studied by using the VTDMA-SP2 measurement (Zhang et al., 2016).

We should not miss the valuable review literature (Sorensen, 2011) in our initial manuscript. We have read the literature carefully according to the reviewer's comment and found that the 'mass-mobility scaling exponent' was erroneously considered the virtual 'fractal dimension' even they have a corresponding relationship and both reflect the morphology of BC aggregates. Similar mistakes also existed in previous studies on mass-mobility relationship (e.g., Park et al., 2003). Corrections can be found in Lines 87–107, 393–396 in the revision. By carefully referring to this review article, we have improved our understanding in the subject of the morphology of BC aggregates. Then we further condense our research purpose as shown in the rewritten introduction of the revision. As presented there, although the morphology and effective density of BC aggregates have been widely studied using the TEM analysis and/or tandem techniques (e.g., DMA-APM), such studies were mainly conducted in the laboratory and/or in the source environments (e.g., in the tunnel) where the freshly emitted soot aggregates were predominant. The SP2 provides an advantage to distinguish the extBC aggregates from the thickly coated BC particles at the same time to the rBC mass determination. Thus, the DMA-SP2 can be deployed to different atmospheric environments to investigate the mass-mobility relationship of ambient extBC. Another advantage of the DMA-SP2 tandem system is that it can investigate the mass-mobility relationship of BC aggregates in a relatively larger mobility range (e.g., in the 350–750 nm mobility diameter range) due to the high sensitivity and accuracy of the SP2 in the rBC mass

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determination in this range, allowing to examine the applicability of the mass-mobility relationship obtained from previous studies and the consistence of the mass-mobility relationship determined using different tandem techniques. Previous DMA-APM measurements seldom concerned the BC aggregates in the atmosphere with mobility diameter (dmob) larger than 350 nm due to the larger measurement uncertainty in the larger particle sizes. Thus, our study should have its practical and scientific meaning, even the DMA-SP2 tandem technique is not novel. We have removed the word 'novel' in the title of our manuscript according to the reviewer's comment.

The quality of the writing is not at a suitable level for scientific publication. There are many English grammar issues - too many to list in a scientific review. Beyond this, the language is frequently too vague. To take just the first example I come across the authors state that BC can lead to 'Earth warming' on L39. I believe that authors mean 'warming of the Earth's atmosphere' or similar. There are many more examples of such lazy language throughout the manuscript.

Reply: Thanks for the professional comments. Actually, the writing of our manuscript had been polished by native English speakers before it was submitted to the journal for review. They might have made an improvement in the English grammar and writing. A number of more professional contents (e.g., the example posed by the reviewer) are still needed to improve. We checked carefully throughout our manuscript to make corrections to these similar mistakes. The revised manuscript has been further polished by a more professional agency before resubmitted for review. We hope you can see the improvement in the English writing of our revised manuscript. Besides, we also have made efforts to improve the scientific quality of this article by rewriting a large fraction of the manuscript.

The study design and experimental and analytical details are inadequately described, which makes it difficult to judge their suitability. For example from what I can gather, the results presented in Figs. 2 to 6 are only for rBC-containing particles that displayed a delay time of less than 2 $\mu$ s (defined as 'extBC'). This needs to be clarified and stated

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more explicitly (another example of lazy language). The suitability of using delay time to distinguish between externally and internally mixed BC particles then requires further discussion. It is not as simplistic as the authors make it out to be. The authors allude to the fact that thinly-coated BC will exhibit low SP2 delay times on L280. This is also true for moderately-coated BC (e.g. with BC volume fractions as low as 30%), which would certainly not be classified as 'externally mixed' (ExtBC). A better approach for classifying BC mixing state with the SP2 is the quantitative LEO-fit approach (Gao et al., 2007; Laborde et al., 2012). The authors need to at least discuss this more sophisticated method, the reasons why they chose to use the more simplistic delay time approach, and the consequences of this decision.

Reply: The manuscript is written to discuss the physical properties (mainly the mass-mobility relationship) of externally mixed BC (extBC) particles, although the experiment was designed for a range of research aims. For example, the experiment was originally designed to also study the mixing states (e.g., the fraction of thickly-coated BC particles and the coating thickness) and optical absorption properties (e.g., mass absorption efficiency) of size-selected BC particles, and the number/mass size distribution of BC particles in the atmosphere, similar to the experimental setup presented in Raatikainen et al. (2017). Two micro-aethalometers used to determine the aerosol absorption coefficients were also connected to the DMA and measured parallel with the SP2 (as shown in Fig.1 in the manuscript). The data analysis is still in progress. Several difficult but crucial issues should be dealt with in data processing, e.g., the effects of multi-charged particles. At the current stage, we present our first study on the mass-mobility relationship of the extBC particles, although the effects of multicharged particles are also needed to take into consideration. A number of the technical details associated with this experiment are described in current manuscript. Further studies mentioned above are also in preparation. Similar statements are also presented in the revised Section 2 (Lines 201–206).

In this study, the extBC particles are discriminated according to the delay time be-

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tween peaks of the incandescence signal and the scattering signal measured by the SP2. Only the BC-containing particles with the delay times less than the criterion are recognized as the extBC particles. The remaining BC-containing particles were considered thickly coated by non-refractory components. The criterion is determined from the frequency distribution of delay time of individual particles. As shown in Fig. S1, the frequency distribution of delay time exhibits a significantly bimodal pattern. The delay time corresponding to the minimum of the frequency distribution between the bimodal peaks is chosen as the criterion. In this study, the criterion of the time delay is selected as 2.0  $\mu\text{s}$ . Indeed, a fraction of thinly coated BC particles might be also recognized as the extBC based on the time-delay approach. A few moderately coated BC particles (e.g. with BC volume fractions as low as 30%) might also have delay times less than the criterion as mentioned by the review (Laborde et al., 2012), which might be mistakenly recognized as the extBC. To examine the stability and reliability of our results derived by using the time delay approach, we strengthen the discrimination of mixing state by decreasing the criteria of delay time from 2  $\mu\text{s}$  to 1.2  $\mu\text{s}$  and 0.4  $\mu\text{s}$ . Reducing the delay times to less than 0.4  $\mu\text{s}$  means that the incandescence signal has the same peak location to the scattering signal because the minimum unit for the signal record is 0.4  $\mu\text{s}$ . The effects of thinly and even moderately coated BC particles are expected to decrease when the delay time threshold decreased from 2.0  $\mu\text{s}$  to 1.2  $\mu\text{s}$ , and then to 0.4  $\mu\text{s}$ . However, as shown in Fig. S5 (the frequency distributions of mass-equivalent diameter of rBC core ( $d_{\text{me}}$ ) of the extBC particles, which is calculated from the measured rBC mass by assuming the rBC core is a void-free sphere with 1.8 g cm<sup>-3</sup> density, at the prescribed mobility size ranges) and Fig. S6 (the normalized number size distribution of rBC core of the extBC particles) in the revised supplemental file, the decrease in the delay time threshold has insignificant impacts on the peak location of frequency or number size distribution, i.e., the typical  $d_{\text{me}}$  of extBC at each prescribed mobility size, although the data volume used to calculate the distribution reduced significantly. As also shown in Table S1, the discrepancy in the fitted peak  $d_{\text{me}}$  values resulting from the different delay time thresholds don't exceed 3% in the

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current study. It means the differences in fitting peak values of rBC mass don't exceed 10%, which is considered as the uncertainty in the determined rBC mass at each mobility size due to the time-delay method employed to distinguish the extBC particles from the thickly coated BC particles. The thinly coated and even moderately coated BC particles mistakenly considered as the extBC discriminated by using the time-delay method appear to influence the shape of the size distribution. These particles mixed with multicharged extBC particles resulting in an increase in the size distribution at its right tail. At the current stage, we are unable to separate which particles presented in the right tail are thinly/moderately coated and which are multicharged. However, this issue should affect little on the results presented in our current study. Similar statements are also presented in the revised Section 3.2 (Lines 344–379 in the revision).

Actually, the thickness of a BC-containing particle can be retrieved using a specific approach, i.e., lead-edge-only (LEO) fitting (Gao et al., 2007). The method can be used to estimate the optical size of the particle using the scattering signal detected by SP2 at its initial stage (e.g., the first 5%) by assuming certain parameters, including the refraction indices of coating material and the rBC core. By comparing with the mass-equivalent diameter of the rBC core determined by using the incandescence signal, the thickness of the coating can be estimated. However, this approach needs the scattering signal measured by the split channel (with a two-element APD) of the SP2, which is used to determine the center location of the Gaussian-distributed laser beam. Unfortunately, this channel of our SP2 was out of work during the experiment. We failed to use this method to estimate the coating thickness of the BC-containing particle in the present study. However, the 'coating thickness' is not a crucial quantity in our current study because only the extBC particles without coating or with thin coating were concerned. The 'coating thickness' can be used to verify the results currently presented. Similar statements can also be found in the revised Section 2.3 (Lines 248–267 in the revision)

We are also preparing a new experiment which is similar to the presented one by

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employing a SP2 with all detect channels well performed. Moreover, because a number of assumptions are employed in the LEO fitting and the subsequent Mie calculation, large uncertainties also exist in the retrieved coating thickness. For instance, the size of the rBC core ( $d_{me}$ ) is determined from the rBC mass (calculated according to the linear relationship between incandescence single peak and rBC mass calibrated before and after the experiment) by assuming it is a void-free sphere with  $1.8 \text{ g cm}^{-3}$  density. If the BC particle is not void-free and has a low density (Zhang et al., 2016), the size of the rBC core might be underestimated. In addition, the optical size of the particle largely depends on the refraction indices of the coating materials and the rBC core, which are usually known for a specific site. Generally, the coating thickness is not a crucial quantity in our current study of the morphology and density of uncoated extBC aggregates. It can provide a validation of our discrimination of extBC but should have little influence on our final analysis and discussions presented in current study.

The material as presented gives cause to question the quality of the measurement data, but insufficient details are provided to fully make this assessment. Specific points are highlighted below in relation to Fig. 2, which contains features that require explanation (absence of clearly defined peaks for multiply charged particles, presence of peaks with rBC mass approaching 0). In addition for reasons that are not yet satisfactorily explained, the effective density results presented in Fig. 5 are systematically lower than previous measurements (both the previous studies already cited by the authors as well as previous DMA-SP2 measurements that were also conducted in Beijing but are not yet discussed; Zhang et al., 2016). Given these issues, the authors should include further data and explanations to build confidence in their results and to confirm that the measurements are artifact-free. For example, were PSL spheres or other monodisperse particles (e.g. aquadag for the SP2 measurements) used to confirm that the DMA was operating correctly? What quality checks were performed to ensure the SP2 was operating correctly? (E.g. laser and detector block properly aligned, laser power levels, flow rate checks, comparison of calibration curves with previous calibration curves of the instrument).

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Reply: Thanks for the comments, we have increased the description in the detail of the experiment and data processing in the revision. Meanwhile, we used the number size distribution of rBC core of the extBC particles in the revision instead of the initial frequency distribution of rBC mass of the extBC particles. The normalized number size distribution is a more practical quantity in the scientific research and has lower artificial uncertainties than the frequency distribution which depends on the bin-size used to calculate the frequency. We have completely reanalyzed our dataset and present more reliable results in the revision. Discussions on the measurement uncertainty are also presented. Specific responses to the review's queries are presented point-to-point below.

1. Peaks with rBC mass approaching 0 presented in the frequency distribution of rBC mass are likely attributed to the measurement noises of the SP2. Explicit discussions are also presented in the response to the No.18 specific comment. The smaller rBC masses approaching 0 were also observed in the SP2's incandescence calibration using size-selected Aquadag particles (Fig. R1). As shown in Table R1, the number contribution of measurement noises gradually increases from 1% at 140 nm dmob to 37% at 750 nm dmob. The noises should be resulted from the SP2 measurement only and not presented in the CPC measurement. As shown in Fig. R2, if the noises are not eliminated, the counting efficiency of SP2 (calculated as the ratio of number concentration measured by the SP2 to that counted by the CPC at a given mobility) shows an increase trend with increasing dmob. While after correction to the effect of these noises, the counting efficiency of SP2 is stably close to 100% in the 125–750 nm dmob range. We have used the normalized number size distribution of rBC core of the extBC particles instead of the initial mass frequency distribution. The effect of these small rBC masses on the number size distribution is significantly reduced due to data processing.

As also shown in Fig. R1 and Table R1, the doubly charged particles shown a discernable minor peak in the frequency distribution of the incandescent peak height in the

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calibration using Aquadag particles. Since the Aquadag particles generated from the aerosol generator can be considered as the bare BC, the mobility of Aquadag particles should be only related to their masses and morphologies, resulting in the clear peak of multicharged particles. However, in the ambient atmosphere, it is more complex even for the extBC particles. As mentioned above, a fraction of thinly coated particles is also recognized as extBC based on the time-delay discrimination. These particles coexisted with the multicharged particles result in a combined effect on the size distribution of rBC core of the extBC particles at a given mobility. They mainly result in an increase in the size distribution at its right tail and have few effects on the determined typical dme of extBC. Similar statements can be found in Lines 344–379 in the revision. Anyway, based on the clear distinguishable minor peak presented in the frequency distribution of the incandescence peak height for the multicharged bare BC particles (Aquadag particles) and the adequate detection efficiency of SP2, we propose the DMA-SP2 system operated normally in this experiment.

2. The observation data have been reanalyzed. The effective densities of extBC obtained from the recalculated mass-mobility relationship at the prescribed mobility sizes are slightly lower than those obtained from the previous DMA-APM measurements. The deviations are general in the measurement uncertainty of DMA-SP2 system (~20%). The slightly lower densities of extBC aggregates are also likely due to the differences in the mass determination between APM and SP2. The APM measures the mass of whole BC aggregate, which might be composed of a fraction volatile or semivolatile materials in addition to the primary BC spherules. While the mass of rBC is determined by using the SP2. Thus, a slightly lower mass of extBC aggregates can be expected at a given mobility size. Meanwhile, the volatile and/or semivolatile materials might also result in a more compact structure of extBC aggregate due to the reconstruction effect by these materials thinly coated outside the primary BC particles. The extBC mass determined as the peak rBC mass of the size distribution of rBC core of the extBC particles might mostly correspond to the uncoated extBC which are less influenced by the volatile and/or semivolatile materials. It also results in the slightly

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lower densities obtained from the DMA-SP2 measurement than those from previous DMA-APM measurements. Anyway, the densities derived from the reanalyzed dataset are generally comparable to previous values for diesel soot particles in the laboratory and in the source environments such as in the tunnel.

The effective densities of thickly coated (internally mixed) BC (In-BC for short in the reference) particles were presented in Zhang et al. (2016). Due to the significant reconstruction by the nonrefractory components thickly coated outside the primary BC particles, these BC particles became more compact resulting in obviously higher effective densities than the uncoated BC aggregates presented in current study.

3. Before this experiment, the laser alignment was performed by the operator according to the manual provided by manufacturer step-by-step. Besides the incandescence calibration using Aquadag particles, the scattering calibration using PSL with a certain diameter (269 nm) were also carried out before and after the campaign. A slight decrease in the measured scattering peak height (low-gain) for 269 nm PSL was observed after the campaign compared to that before the campaign (from 3576 to 3555 a.d.). It indicates the laser of the SP2 was stable throughout the campaign. Since the split channel was out of work in the experiment, the absolute value of the scattering peak height for 269 nm PSL appears to be useless in this study, which is mainly used in the retrieval of particle optical size by using the LEO fitting method. In the scattering calibration of the SP2, we also delivered the 269 nm PSL to pass through the DMA before to be measured by the SP2. We examined the SP2 recorded particle number concentrations by adjusting the mobility diameters of particles through the DMA. Because the PSL particles are general spheres, their mobility diameters are equal to their geometric diameter. Thus, we found that the recorded number concentration showed a significant peak when the mobility was set to  $\sim 269$  nm for the 269 nm PSL in the calibration. It indicates the DMA was operated correctly although the number concentration was not recorded in the computer.

Generally, the DMA-SP2 system was operating correctly in the experiment.

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Fig. R1 Frequency distributions of incandescence peak height detected by SP2 for size-selected Aquadag particles at the prescribed mobility sizes. The Gaussian fitting is performed for the major peak of each distribution to obtain the typical incandescence peak height at the corresponding mobility size.

Fig. R2 Detection efficiency of the SP2 to Aquadag particles with different mobility diameter in the range of 50–750 nm selected by the DMA. The left panel shows the detect efficiency of SP2 including the effect of measurement noises and the right is noise-corrected detection efficiency.

Table R1 Number fractions of single charged particles, detection noises, and multiply charged particles at different mobility sizes in the measurement for Aquadag particles using the DMA-SP2 tandem system. As shown in Fig. R1, the high frequencies of incandescence signal peak height close to 0 are considered to be attributed to the detection noises. The major peak of the frequency distribution is attributed to single charged Aquadag particles and the minor peak at the right side of the major one is considered to be resulted from double charged Aquadag particles.

No uncertainty estimates are provided for the measurements and main results. This is important as the SP2 counting statistics and therefore measurement errors will be sizedependent. How sensitive are the reported quantities (e.g.  $D_f$ ) to these measurement uncertainties?

Reply: Discussions on the uncertainty in the determination of  $ext_{BC}$  mass have been performed in the revised manuscript. The uncertainty in the typical  $ext_{BC}$  mass at each mobility is arisen mainly from two aspects. One is the uncertainty in the  $r_{BC}$  mass measured by the SP2. It is mainly related to the uncertainty in SP2 incandescence measurement and the calibration factor that is determined from the  $r_{BC}$  mass-incandescence relationship using the standard soot particles (Aquadag particles in this study). Approximately 3% variation in the calibration factor is estimated throughout the experiment. Both considering this deviation and the uncertainty in the measured incan-

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descent signal and calibration material, we estimate the uncertainty in the measured rBC mass to be ~10%. The other uncertainty is arisen from the time-delay approach used to discriminate the extBC particles. By examining the effect of delay time threshold on the peak dme, the associated uncertainty is estimated to not exceed 10%. Thus, the total uncertainty in the typical extBC mass used in the further mass-mobility relationship analysis is ~20%. Similar discussions can also be found in Lines 277–283, 371–376 in the revision.

The counting efficiency of SP2 is calculated as the ratio of particle number concentration measured by the SP2 and that measured by the CPC at a given mobility selected by the DMA. The counting efficiency was examined using the Aquadag particles after the campaign. As shown in Fig. S4, the SP2 has adequate counting efficiencies (>90%) for Aquadag particles with mobility diameter (dmob) larger than 125 nm. The counting efficiency is stably close to 100% in the dmob range of 125–750 nm. We converted the dmob to mass-equivalent diameter (dme) of rBC according to the size-dependent effective densities of Aquadag particles (Gysel et al., 2011). The SP2 has adequate counting efficiencies (>90%) in the ~90–420 nm dme range. Thus, the mass-mobility relationship of the extBC particles in 140–750 nm dmob range presented in the current study should be reliable and has high confidence.

We propose the uncertainties in the determined extBC mass are similar at different mobility. It means if a lower (or higher) extBC mass is expected due to the uncertainty at a given mobility, the lower (or higher) extBC mass at other mobility sizes should also be expected. Although we don't discuss the sensitivity of mass-mobility scaling exponent to the measurement uncertainty in the manuscript, its sensitivity to the fitted size range is presented in the revision (Lines 450–457). Meanwhile, the deviation in the mass-mobility relationship in a polluted episode compared to that in a clean period also investigated (Lines 471–499 in the revision).

Specific comments

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L69: 'Representativeness' instead of 'representation'

Reply: Thanks for the careful review. We have rewritten the introduction of our manuscript.

L80 - 82: The meaning of these sentences is not clear, rewording required

Reply: The initial purpose of the sentences is to express how the APM determines the mass of particles at a given mobility selected by the DMA. We have rewritten these sentences as shown in Lines 114–118 in the revision.

L92: Schwarz misspelt.

Reply: Have corrected in the revision (Line 129).

L98: Statement needs qualification. This is not true when measuring pure BC particles

Reply: We have rewritten the whole paragraph in the revision to highlight the practical significant and advantage of our study on morphology and effective density of ambient extBC in the atmosphere of urban Beijing using the DMA-SP2 tandem measurement (Lines 124–172).

L109: Please include information about the neutralizer that was used upstream of the DMA. This is especially required when considering the potential impacts of multiply charged particles as discussed in Section 3.2.

Reply: A Kr neutralizer (model 3087, TSI Inc.) was utilized upstream of the DMA to charge the particles entering into the system. A simple description of the neutralizer has been added in the revised manuscript (Lines 185–186).

L135: Please include the length of the nafion dryer and the source of the dry sheath air.

Reply: A model MD-700-12F-3 (Perma Pure LLC, Toms River, NJ, USA) nafion dryer with length of 12 inch was used. The total sample flow rate passing though the nafion

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dryer was  $\sim 0.8$  L/m. The dry sheath air was drawn by a Vacuum pump (KNF) opposite to the sample flow direction. We added these information in our revised manuscript (Lines 187–191).

L139: Some discussion is required about SP2 counting efficiency over this size range. It is not always 1, which will affect counting statistics, adding uncertainty to measurements reported at the limits of the range.

Reply: Although 33 mobility diameters was selected in each cycle, only the mobility diameters (dmob) in range of 140–750 nm are analyzed because the size distribution of rBC core of the extBC particles with a dmob smaller than 140 nm cannot exhibit a clear peak, from which the typical mass-equivalent diameter (dme) of extBC is determined.

The detection efficiency of SP2 is shown in Fig. S4 in the revised supplemental file by comparing the number concentration of generated Aquadag particles measured by the SP2 to that by the CPC at each mobility. As shown in Fig. S4, the SP2 has adequate detection efficiencies ( $>90\%$ ) for Aquadag particles with a dmob not smaller than 125 nm, equivalent to a dme larger than  $\sim 90$  nm. Thus, the detection efficiency of SP2 should not have great effects in the 140–750 nm dmob range we concerned in the current study. Since the peak dme of the size distribution of extBC at each mobility is require, the low detection efficiency of SP2 to small particles should influence little of the results derived from our analysis.

L153: The phrase 'frequency of the time lag' does not make sense. I guess the authors meant frequency distribution or histogram.

Reply: Thanks. We used the 'frequency distribution' instead of 'frequency' in the revision (Line 224).

L156: Am I correct in assuming that the 'extBC' results presented later only include particles that displayed a lag time less than 2  $\mu$ s? If so please state this explicitly.

Reply: Yes, we only analyzed the mass-mobility relationship and effective density of

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'extBC' distinguished according to the delay time between the incandescence peak and the scattering peak with lag times less than 2  $\mu$ s. Explicit statements are shown in Lines 230–247 in the revision.

Also including in the revision is the examination of the effect of delay time threshold (decrease from 2  $\mu$ s to 1.2  $\mu$ s and 0.4  $\mu$ s) on the derived mass-mobility relationship of extBC. A decrease in the lag time threshold means a stricter discriminant criteria for the extBC particles using the time-delay method. It is discussed in detail in Section 3.2 of the revision.

L162: More sensitive than what? To Fullerene soot I presume but statements like this need to be explicit, avoiding lazy language.

Reply: The incandescence signal is more sensitive to Aquadag particles than to the Fullerene or diesel exhaust soot particles which are the mainly BC particles in the atmosphere, e.g., the same mass of Aquadag particle results in a high incandescence peak than the Fullerene soot or diesel exhaust soot. Similar corrections can be found in Lines 271–274 in the revision. We have check carefully throughout our manuscript to avoid similar writing errors.

L166: Please include a Figure in the supplementary information of the two measured incandescence calibration curves. Were the incandescence calibrations performed all the way up to 750 nm or were the calibration curves extrapolated? What sort of function was fit to the calibrations curves? Were the calibrations consistent with previous calibration curves measured for this instrument (an important check to make to ensure the SP2 was operating ok)

Reply: The calibration curves before and after the campaign are showed in the revised supplemental file (Fig. S3). In the two manually calibration for the incandescence signal of the SP2, Aquadag particles with the dmob in the range of 100 nm to 450 nm (e.g., 100, 125, 150, 175, 200, 250, 300, 350, 400, 450 nm) was measured by the SP2. As shown in Fig. S3, the incandescence peak heights detected by the SP2 are

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linearly correlated with the rBC masses which are calculated according to the effective densities of Aquadag particles provided in Gysel et al. (2011). After the campaign, we also used the DMA-SP2 tandem system to measure the generated Aquadag particles automatically. The setup of the DMA-SP2 system was the same as that used to measure the ambient particles. Thus, the relationship between the incandescence peak height and rBC mass obtained from the size-selected Aquadag in the dmob range of 140–750 nm is established. As shown in Fig. S3, the linear relationship between the incandescence peak height and rBC mass is robust in the 100–750 nm dmob range for our SP2. The calibration factors (the slopes of the linear regressions) vary little during this campaign, indicating the good performance of our SP2. The good performance of our SP2 can also be validated by the high detection efficiency (>90%) of our SP2 for BC particles with dme larger than ~90 nm (Fig. S4).

L176: Please also discuss what the prefactor k represents (e.g. Sorensen 2011).

Reply: Since the mass-mobility relationship is studied, the prefactor k here is not consistent to that in the fractal relationship of DCLA aggregates presented in Sorensen (2011). The prefactor k (actually  $\log(k)$ ) is the intercept of the linear regression of extBC mass against its mobility diameter in the logarithm scale. The k value obtained in current study is in the same order of magnitude to the previous values for soot aggregates (Park et al., 2003). Explicit discussion can also be found in the response to the No.19 specific comment. Specific discussion on k will not be presented in the current manuscript.

L191: Please provide a reference for why this value of material density was chosen.

Reply: A reference, Taylor et al. (2015), is added in our revised manuscript (Line 411).

L199: The more common phrasing for this section would be 'Data processing'. And it seems to me that Section 2.4 would be a better fit in this section rather than the measurement methodology section above.

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Reply: Thanks for the constructive comment. We have modified title of Section 3 (Lines 286–287, Line 325) and moved the section 2.4 to 3.3 according to the suggestion.

L220: It seems that this method was not used in this study. Why is it mentioned? Was it used to check the results processed with the first method?

Reply: At the beginning of the experimental setup, we intended to use the correlation method. However, during the data analysis, we found that size distributions of SP2-detected particles were inadequate for the further calculation of the correlation coefficients since the detection efficiency of the SP2 decreases dramatically in the small particle range. Therefore, the local peak method is developed in current study to identify the time difference between the size selection and the SP2 measurement. The correlation method will be used to examine the time difference between the size selection and the AE51/CPC measurements in our future study of the number and mass size distribution of BC. Similar statements are presented in the revision (Lines 317–323).

L232: 'Minimizing the multicharged particles' is too vague. Suggest 'Correcting for the presence of multiply-charged particles' or something similar.

Reply: Thanks. We adopt the suggestion of the reviewer by changing the title of Section 3.2 as 'Determination of the typical masses of extBC at prescribed mobility sizes'. We have also rewritten the whole content of this section to express explicitly how we determine the typical masses of extBC at prescribed mobility sizes. The effect of the delay time threshold chosen for the discrimination of extBC on the determined extBC masses is also discussed in the revision (Lines 326–379).

L240: Please be more specific. Exactly what parameter of the fitted curve was used to represent the mass of singly charged extBC particles?

Reply: In the initial manuscript, the mean value or expectation ( $\mu$ ) of the Gaussian distribution  $f(x) = A \exp(-\frac{1}{2} \frac{(x-\mu)^2}{\sigma^2})$  was used to represent the mass of singly charged extBC.

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We use the number size distribution instead of the rough frequency distribution of rBC core mass of the extBC particles in the revision. The peak  $d_{me}$  determined as the mode value of the lognormal function fitted to the major peak of the number size distribution of extBC is considered the typical  $d_{me}$  of extBC (singly charged) at a given mobility. We have rewritten the whole content of Section 3.2 in the revision.

Fig. 2: These curves contain features that require discussion to build confidence in the measurements. For example: related to the comment above about L156, do these frequency distributions only contain particles that display time lag less than  $2\mu s$ ? If so, why are there sharp increases in the number of particles with rBC mass approaching 0 at diameters greater than 160nm? (With no filtering of the data applied I would assume these are heavily coated particles, which is a reason why I think the filtering process is not strict enough to be able to label these particles as 'extBC'). Why do the multiplycharged particles show up as a very fat tail that does not descend to a frequency of 0 until some point beyond the upper limit of the x-axis? What do these tails in the distribution represent? (E.g. they are in contrast to what is typically seen in SP2 calibrations, when doubly and triply charged particles are observed as clear, separate gaussian peaks). I suggest adding vertical lines along the x-axis corresponding to the mass of particles selected by DMA (e.g. under the assumption of spherical particles with the material density of BC) to provide reference points to compare the measured mass distributions to.

Reply: The normalized number size distribution ( $dN/d\log D_c$ , where  $D_c$  is the mass-equivalent diameter of rBC core by assuming it is a void-free sphere with  $1.8 \text{ g cm}^{-3}$  density,  $N$  is the number concentration in a given  $D_c$  range) instead of the initially rough frequency distribution of extBC mass at each prescribed mobility in the range of 140-750 nm is presented in Fig. S6 in the revised supplemental file. Five normalized number size distributions at 140, 225, 350, 500, 750 nm  $d_{mob}$  are selected and also shown in Fig. 2 in the revision. The major peaks are more significantly through such data processing at prescribed mobility sizes. The size distributions of rBC core at

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different mobility sizes are generally used in the studies on size-resolved BC particles. For instant, Zhang et al. (2016) measured the morphology and density of internally mixed BC (In-BC for short in the reference) with SP2 and VTDMA. They used the peak diameter of the normalized volume size distribution of the In-BC core to represent the typical diameter of In-BC core at the prescribed mobility diameters selected by the DMA.

We originally considered the sharp increases in the number of particles with very small rBC mass resulted from the detection noises of SP2 for the smaller BC particles. As claimed by the manufacture, the lower BC detection limit is  $\sim 0.3 \text{ fg}$  per particle. Thus, data filter was performed by eliminating the particles with incandescence signal peak values lower than 100. This criterion is determined from the calibration curve by using Aquadag particles (Fig. S3 in the revised supplemental file). However, the distribution concentrated at the smaller masses still existed after the data filter. Initially, we suspected the smaller masses belonged to the thickly-coated BC particles which were not separated from the extBC particles using the time delay method. However, we found that the smaller masses also existed for the bare BC particles (i.e., Aquadag). As shown in Fig. R1 and Table R1, the particles with these smaller masses accounted for only 1~9% of the total particles (after data filter by eliminating the signal with incandescence peak value lower than 100) in the range of 140–200 nm in mobility diameter. This proportion gradually increased to  $\sim 37\%$  at 700 nm. Thus, these smaller masses should not be resulted only from the 'remnant' BC particles with thick coating. We still attribute these smaller masses to measurement noises.

The Gaussian fitting for the major peak can distinctly distinguish the singly charged particles from those with double or more charges for Aquadag particles (considered as bare BC particles). However, in the case of measurement for ambient particles, it is more complex. First, the time delay approach used in this study can only distinguish the thickly-coated BC particles from those with thinly or without coating. A fraction of thinly- and/or even moderately-coated BC particles cannot be absolutely separated

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from the bare BC particles. Thus, a fraction of extBC particles claimed in this study might be thinly-coated ones. We considered the right tail of the distribution was also associated with these thinly-coated BC particles. These thinly-coated BC particles have a relatively more compact structure than the bare BC particles, resulting in larger masses in a given mobility diameter.

L252: Please provide further details for how the fit was performed. Were both the prefactor  $k$  and mass-mobility exponent  $Df$  allowed to vary freely? The  $k$  value seems to be very low in comparison to previous measurements (Sorensen 2011 and references therein), which requires explanation. How is the standard deviation of 0.04 in  $Df$  determined? How sensitive is the fitted  $Df$  to the size-dependent measurement uncertainties in rBC mass?

Reply: Actually, a linear regression of  $\log(\text{mass})$  (e.g.,  $y$ ) against  $\log(\text{dmob})$  (e.g.,  $x$ ) by minimizing the chi-square error statistic between the fitted  $\log(\text{mass})$  (e.g.,  $y_{\text{fit}}$ ) and measured ones. The chi-square error is calculated as  $\sum (y - y_{\text{fit}})^2$ . According to the mass-mobility exponential equation shown in Section 3.3 of the revision, the intercept of the linear regression should be  $\log(k)$ , and the slope is  $Df$ . We have corrected the  $Df$  mobility scaling exponent. We also illustrate the difference in  $Df$  and  $Df_m$  in the introduction section (106) according to the review literature (Sorensen, 2011). Thus, the prefactor  $k$  derived from the mobility relationship cannot be compared to that presented in Sorensen (2011). It seems to be comparable to APM measurements for the soot aggregates. For instance, the prefactor value is  $\sim 6 \times 10^{-6}$  (Park et al., 2003), close to the value presented in our study. The prefactor of mass-mobility relationship is with few concern in previous studies.

The standard deviation in  $Df_m$  is derived as the 1-sigma uncertainty estimates for the slope of linear regression of extBC mass against  $\text{dmob}$  at the logarithmic scale. The uncertainty in the determination of extBC was estimated to be  $\sim 20\%$  at each  $\text{dmob}$ , including the uncertainty in the rBC mass determined by the SP2 and that raised from the time delay method used to discriminate extBC. Similar discussion can be found in our

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revised manuscript, e.g., Lines 358–365, 463–469.

Fig. 3: Error bars are required in this figure to indicate the measurement uncertainties.

Reply: The typical mass of extBC was determined from the lognormal fitting. We also show the uncertainties in the revised Fig. 3 and Fig. 4, and discuss the uncertainties explicitly in the main content (e.g., Lines 481–499).

L263: This is a speculative statement that is not examined as thoroughly as it should be. If the sensitivity of  $Df$  to measurement uncertainty is taken into consideration is it still possible to conclude that the  $Df$  calculated here is 'relatively lower' than the previous measurements? If this result stands, can the authors provide any evidence to support their claim that fuel quality is higher in Beijing than for the studies they have cited?

Reply: The extBC mass determined at a given  $\text{dmob}$  is expected to have  $\sim 20\%$  uncertainty as presented in the revision. The uncertainties should be similar at different mobility size. Thus, the  $Df_m$ , calculated as the scaling exponent of the mass-mobility relationship should be influenced relatively low by the uncertainty in extBC mass. I mean the synchronous variations in extBC masses due to uncertainty at different  $\text{dmob}$  should have few effects on the  $Df_m$ . In the revision, we also examine the sensitivity of  $Df_m$  to the  $\text{dmob}$  range in which the power law function is used to fit the mass-mobility relationship. The  $Df_m$  fitted in 140–350 nm  $\text{dmob}$  range (2.51) is significantly larger than that fitted in 350–750 nm (2.07). It indicates the smaller extBC particles are more likely influenced by the reconstruction effect than the larger extBC (Lines 433–440).

The fuel quality is very strict in Beijing. The JING VI standard was implemented from year of 2017. We have no explicit information of the fuel quality. However, at least, we know the sulfate content is very low in the fuel with JING VI standard, which will have an important impact on the structure of BC aggregates. Besides, the local government claimed that the nitrogen oxides, particulate matters, total hydrocarbons and carbon monoxides emitted from the diesel exhausts are expected to decrease by factors of

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4.6%, 9.1%, 8.3% and 2.2% respectively if the fuel with JING VI standard is used.

L337: 'extBC' as defined with respect to delay time could also be comprised of BC mixed with small or even moderate amounts of non-BC material (e.g. L280). Additionally, the measurements reported here are lower than previous DMA-SP2 measurements of effective density in Beijing. Therefore, I find this explanation of the low effective density values measured in this study to be problematic.

Reply: We have removed the discussion in diurnal variation in Dfm due to the enlarged uncertainty of insufficient data volume in the revision. Instead, we discuss the differences in the mass-mobility relationship between a polluted episode and a clean period. Although a fraction of the thinly- and/or even moderately-coated BC might be recognized as extBC using the time delay discrimination, these particles should have few effects on the determined typical extBC mass at each dmob. Explicit discussions have been presented in our revised manuscript (Lines 331–365). Increase in the volatile and/or semi-volatile materials accompanied with the BC aggregates would increase the possibility of the BC aggregates becoming relatively more compact due to reconstruction effect. It will increase the mass, consequentially the effective density of extBC aggregates at a given dmob. Even the structure of a BC aggregate changes little, small amounts of the volatile and/or semi-volatile materials filled in the gap and/or thinly-coated outside the primary spherules of BC aggregate would have few effects on its mobility but result in a higher mass of the entire particle. The increased mass can be detected by the APM but cannot be characterized by the SP2. Similar explanation is also presented in Lines 515–518 in the revision.

The effective density of internally mixed BC (In-BC, or thickly-coated BC) was measured by the previous DMA-SP2 system (Zhang et al., 2016). These In-BC particles have been reconstructed due to the thick coating. Thus, a compact structure with much higher density was reported. The fractal-like extBC aggregates without thick coating are studied in current study, which have low effective density.

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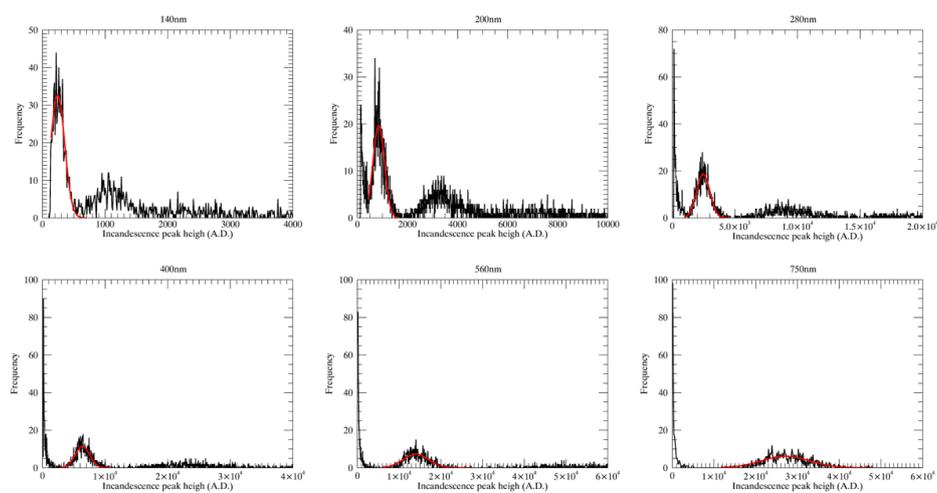
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Please also note the supplement to this comment:  
<https://www.atmos-meas-tech-discuss.net/amt-2018-408/amt-2018-408-AC2-supplement.pdf>

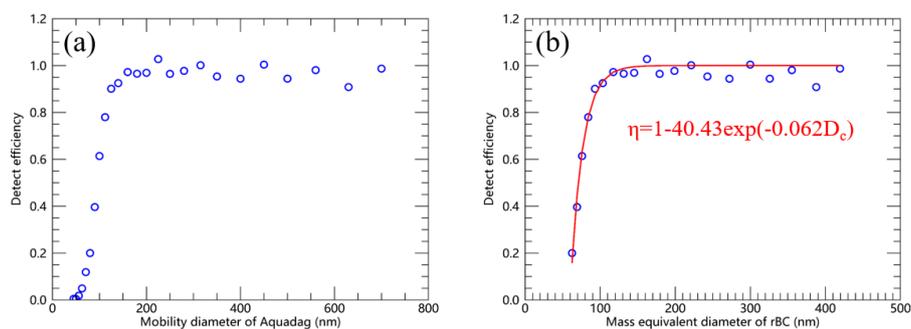
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**Fig. 1.** Frequency distributions of incandescence peak height detected by SP2 for size-selected Aquadag particles at the prescribed mobility sizes.

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**Fig. 2.** Detection efficiency of the SP2 to Aquadag particles with different mobility diameter in the range of 50–750 nm selected by the DMA. The left panel shows the detect efficiency of SP2 including the eff

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Mobility Diameter	Single charged (%)	Noise (%)	Multi-charged (%)
140	47	1	52
160	45	4	51
180	39	7	54
200	37	9	54
225	37	13	50
250	39	14	47
280	40	16	44
315	41	21	38
350	43	21	36
400	47	25	28
450	50	25	25
500	54	26	20
560	56	29	15
630	64	33	3
700	62	37	1
750	71	29	0

**Fig. 3.** Table S1 Number fractions of single charged particles, detection noises, and multiply charged particles at different mobility sizes in the measurement for Aquadag particles

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