

Response to reviewer#2

Thanks for the reviewer's helpful suggestions! The comments are addressed point-by-point and responses are listed below.

Comment: This paper reports a method combining a DMA with an aethalometer to obtain the BC mass size distribution (BCMSD). Two modes of the BCMSD are observed in their ambient measurement in the North China Plain with the new method. Also, they found that the BCMSD and their mixing state are equally important in estimating the aerosol direct radiative forcing, and suggested that the BCMSD should be fully considered in climate models. The method is a novel design and useful for understanding the relationship of BCMSD and their optical properties. The paper is interesting and well-organized. The conclusion is sound and may have profound impacts on the estimation of BC radiative forcing. I will recommend this manuscript for publication in ACP as long as the following comments are properly addressed.

Reply: We thank the reviewer's comments.

Comment: Specific comments: 1. Line 245 and fig. 2. It seems that the shift of particle peak diameter for BCPMSD is much more significant than PMSD. Is there any explanation? The correction procedure should be the same for both.

Reply: We thank the reviewer's helpful comments. We checked the fig. 2 (now fig. 3 in the revised manuscript) and made some revisions in fig 2.

There are three methods to calculate the PMSD. The first one is the corrected PMSD that is transformed directly from the multiple-charging corrected PNSD with multiple-charging correction. If the aerosol PNSD is $n(\log D_p) = \frac{dN}{d\log D_p}$, the corresponding PMSD after multiple-charging correction is:

$$\frac{dm}{d\log D_p} = n_V(\log D_p) \times \rho = V_p \times n(\log D_p) \times \rho = \frac{\pi}{6} \rho D_p^3 n(\log D_p) \quad (1).$$

PMSD calculated in this method corresponds to the corrected PMSD in fig. R1.

The measured PNSD without multiple-charging correction can be calculated from the multiple charging corrected PNSD as:

$$\left(\frac{dn}{d\log D_p}\right)_{raw} = \frac{\sum_{v=1}^{\infty} n(x_v)\phi(x_v,v)}{\phi(x_1,1)} \quad (2),$$

Where $x_v = \log D_{p,v}$ (noting that $x_1 = \log D_p$); $\phi(x_v, v)$ is the probability of particles that are charged with v charges at the scale parameter of x_v ; $\Omega(x, v)$ is the probability of particles that can pass through the DMA with v charges at the scale parameter x . The relationship between the x and v should meet the demand that their electrical mobility keep the same, ie

$$Z_p(D_{p,v}, v) = \frac{veC(D_{p,v})}{3\pi\mu D_{p,v}} = Z_p(D_{p,1}, 1) \quad (3),$$

where $C(D_p)$ is Cunningham slip correction:

$$C(D_{p,v}) = 1 + \frac{2\tau}{D_{p,v}} \left(1.142 + 0.558e^{-\frac{0.999D_{p,v}}{2\tau}}\right) \quad (4),$$

where τ is the gas mean free path.

The PMSD that corresponding to the measured PNSD can be calculated as

$$\begin{aligned} \left(\frac{dm}{d\log D_p}\right)_{raw} &= \left(\frac{dV}{d\log D_p}\right)_{raw} \times \rho = \rho V_p \left(\frac{dn}{d\log D_p}\right)_{raw} \\ &= \frac{\pi}{6} \rho D_p^3 \left(\frac{dn}{d\log D_p}\right)_{raw} = \frac{\pi}{6} \rho D_p^3 \frac{\sum_{v=1}^{\infty} n(x_v)\phi(x_v,v)}{\phi(x_1,1)} \end{aligned} \quad (5).$$

The PMSD calculated using this method corresponds to the calculated PMSD in the fig. R1.

The third method for PMSD measured by DMA-CPC system is calculated as:

$$\left(\frac{dm}{d\log D_p}\right)_{measure} = \frac{\sum_{v=1}^{\infty} \frac{dm}{d\log D_{p,v}} \phi(x_v,v)}{\phi(x_1,1)} = \frac{\sum_{v=1}^{\infty} \frac{\pi}{6} \rho D_{p,v}^3 n(x_v)\phi(x_v,v)}{\phi(x_1,1)} \quad (6).$$

Equation 5 can be transformed into:

$$\left(\frac{dm}{d\log D_p}\right)_{raw} = \frac{\sum_{v=1}^{\infty} \frac{\pi}{6} \rho D_p^3 n(x_v)\phi(x_v,v)}{\phi(x_1,1)} = \frac{\sum_{v=1}^{\infty} \frac{\pi}{6} \rho D_{p,1}^3 n(x_v)\phi(x_v,v)}{\phi(x_1,1)} \quad (7).$$

As $D_{p,v}$ ($v=2,3,4 \dots$) denotes the particle diameter with charged v that shares the same electrical diameter with D_p of single charged particle. Therefore, $D_{p,v}$ ($v=2,3,4 \dots$) is larger than $D_{p,1}$, and the relationship of these PMSDs using different methods is

$$\left(\frac{dm}{d\log D_p}\right)_{measure} > \left(\frac{dm}{d\log D_p}\right)_{raw} > \frac{dm}{d\log D_p} \quad (8).$$

From fig. R1, the multiple-charging corrected PMSD is significantly different from the measured PMSD. Both the magnitude and peak location are changed. As shown in

fig. R2 (fig. 3 in the manuscript), the variations of the BCMSD and PMSD show almost the same pattern before and after the multiple charging corrections.

We revised the text and figure 3 in the manuscript.

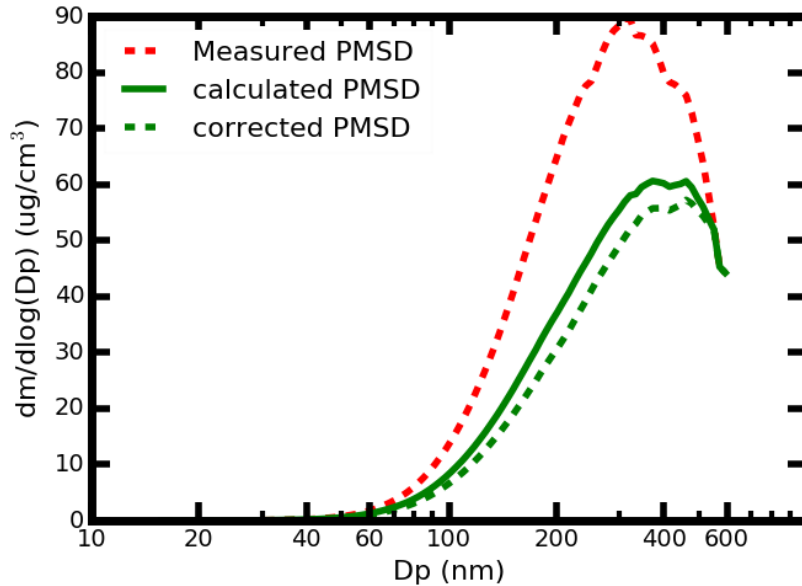


Fig. R1. Example of measured PMSD (in dotted read line), calculated PMSD from raw PNSD (in dotted green line) and corrected PMSD (in green line)

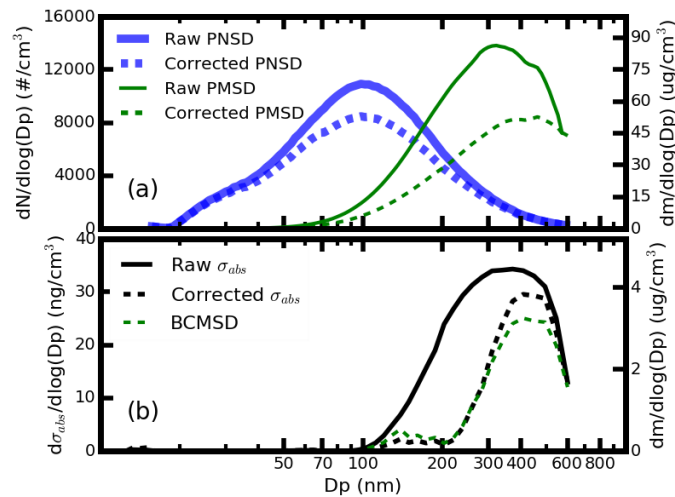


Figure R2. Case of multiple charging correction processing. (a) the multiple charging correction of the aerosol PNSD and aerosol PMSD, (b) the multiple charging correction of the size-resolved σ_{abs} . The solid line is the measured results without multiple charging corrections and the dotted line is the multiple charging corrections results.

Comment: 2. Line 306 and fig. 3. It looks strange that there is nearly no BC in the size range of 200nm-300nm. Any explanation? What does the PMSD look like? To me, it looks like the consequence of overestimation of multiple charging of BC. If the data is confirmed to be correct, proper explanation is necessary. Besides, the authors cited several SP2 measurement to support BC peak diameter range from 100nm to 200 nm. However, if I understand correctly, SP2 measures the diameter of BC core, while this study measures the size of entire particles. More references of studies with other methods may be needed.

Reply: We thank the reviewer's comments. As described in reply of comment 1 and fig.R2, the multiple-charging corrections of the BCMSD is acceptable because the consequence of multiple charging of BCMSD is almost the same as that of the PMSD.

Our measurements show that the BCMSD has two modes with the coarser mode ranging between 430 nm and 580 nm in mobility diameter. Many field measurements have revealed that most of the BC mass locates in the aerodynamic diameter range of 320 nm and 560 nm using the MOUDI (Hu et al., 2012; Huang and Yu, 2008). When the aerodynamic diameter is transformed into mobility diameter with assumption a aerosol effective density of 1.3, the measured BC aerodynamic diameter range corresponds to mobility diameter range of 280 nm and 491 nm. Therefore, the measured size range for coarser mode of BCMSD agrees well with the previous measurement.

The measured aerosol in the field site is representative of the urban aerosol. The BC particles emitted by vehicles contribute significantly to the total aerosol BC mass. These BC particles are rarely coated or thinly coated, and the BC core diameter peaks around 120 nm (Zhang et al., 2017). Therefore, the BCMSD of the smaller mode measured in our study correspond to these uncoated of thinly coated particles.

We have revised the manuscript correspondingly.

Comment: 3. Line 48, I would add another BC microphysical property hygroscopicity in this sentence, which plays an important role in BC direct and indirect radiative forcing. (Zhang et al., 2008; Peng et al., 2017)

Reply: We thank the reviewer's comment. The manuscript has been revised correspondingly.

Comment: 4. Line 275: Please add full name of GSD.

Reply: We thank the reviewer's comment. We have revised the manuscript.

Comment: 5. Line 277, "wea" should be "was"

Reply: Thanks for the comment. We have changed it.

Comment: 6. Line 279, should the BC density differ with different mixing state assumption? Externally mixed BC normally exhibits lower density. The authors can considered this as future improvement direction.

Reply: We thank the reviewer's helpful suggestions. The reviewer provided a good view of the possible direction that we should focus on.

Comment: 7. Line 329, "larger particles grew relative slower in diameter." why? I would say larger particles grew slower in diameter in a log-normal scale. If this is what the authors meant, please verify.

Reply: Thanks for the comment. For the aerosol particles smaller than 1 μm , they grow by collision and coalescence. Coalescence is much more efficient than collision (Lamb and Verlinde, 2011). For coalescence, the mass growth ratio is in proportion to the square of the diameter (R^2). However, the growth of the volume is in proportion to the cubic of diameter (R^3). Therefore, the growth ratio of aerosol particles is in proportion to the R^{-1} , which means that the larger particles grow slower than these of smaller particles in diameter do. We agree with the reviewer's idea that the larger particles appear to grow slower in a lognormal scale. We added some descriptions in the manuscript to denote it.

Comment: 8. Fig. 4 should be improved for better understanding by readership

Reply: Thanks for the comment. We merged fig. 3 and part of fig. 4 into one figure.

Comment:9. Fig. 6, is the figures made with the assumption of the same particle number concentration? If so, please verify.

Reply: Thanks for the comment. The aerosol optical properties were calculated using the measured mean aerosol PNSD and different BCMSD. It was described in section 3.3. We added some descriptions in caption of fig. 6.

Comment:10. Table 1. The mixing state here is assumed to be internally mixed, externally mixed, and core-shell mixed. But what is the mixing state assumption for the estimation with BCMSD?

Reply: We thank the reviewer's comment. When estimating the radiative effects of BCMSD, we using the same mixing states of BC as that of Ma et al. (2012) in the North China Plain (NCP). Ma et al. (2012) found that the BC mixing states in NCP is partially core-shell mixed and partially externally mixed. The number ratio of the core-shell mixed BC particle and externally mixed particle is 0.51 Ma et al. (2012). We have added some descriptions in the manuscript.

Hu, M., Peng, J., Sun, K., Yue, D., Guo, S., Wiedensohler, A., Wu, Z. (2012) Estimation of size-resolved ambient particle density based on the measurement of aerosol number, mass, and chemical size distributions in the winter in Beijing. *Environ Sci Technol* 46, 9941-9947.

Huang, X.F., Yu, J.Z. (2008) Size distributions of elemental carbon in the atmosphere of a coastal urban area in South China: characteristics, evolution processes, and implications for the mixing state. *Atmospheric Chemistry and Physics* 8, 5843-5853.

Lamb, D., Verlinde, J. (2011) *Physics and Chemistry of Clouds*. Cambridge University Press, Cambridge.

Ma, N., Zhao, C.S., Müller, T., Cheng, Y.F., Liu, P.F., Deng, Z.Z., Xu, W.Y., Ran, L.,

Nekat, B., van Pinxteren, D., Gnauk, T., Müller, K., Herrmann, H., Yan, P., Zhou, X.J., Wiedensohler, A. (2012) A new method to determine the mixing state of light absorbing carbonaceous using the measured aerosol optical properties and number size distributions. *Atmos. Chem. Phys.* 12, 2381-2397.

Zhang, Y., Su, H., Kecorius, S., Wang, Z., Hu, M., Zhu, T., He, K., Wiedensohler, A., Zhang, Q., Cheng, Y. (2017) Mixing State of Refractory Black Carbon of the North China Plain

Regional Aerosol Combining a Single Particle Soot Photometer and a Volatility Tandem Differential Mobility Analyzer. *Atmospheric Chemistry and Physics Discussions*, 1-27.

1 **Role of black carbons mass size distribution in the direct aerosol radiative forcing**

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7 **Abstract**

8 Large uncertainties exist when estimating radiative effects of ambient black carbon (BC) aerosol.
9 Previous studies about the BC aerosol radiative forcing mainly focus on the BC aerosols' mass
10 concentrations and mixing states, while the effects of BC mass size distribution (BCMSD) were not
11 well considered. In this paper, we developed a method by measuring the BCMSD by using a
12 differential mobility analyzer in tandem with an aethalometer. A comprehensive method of multiple
13 charging corrections was proposed and implemented in measuring the BCMSD. Good agreement
14 was obtained between the BC mass concentration integrated from this system and that measured in
15 bulk phase, demonstrating the reliability of our proposed method. Characteristics of the BCMSD and
16 corresponding radiative effects were studied based on field measurements conducted in the North
17 China Plain by using our own designed measurement system. Results showed that the BCMSD had
18 two modes and the mean peak diameters of the two modes were 150 nm and 503 nm respectively.
19 The BCMSD of coarser mode varied significantly under different pollution conditions with peak
20 diameter varying between 430 nm and 580 nm, which gave rise to significant variation in aerosol
21 buck optical properties. The aerosol direct aerosol radiative forcing was estimated to vary by
22 ~~22.58.45~~% for different measured BCMSDs of coarser mode, which shared the same magnitude to
23 the variation associated with assuming different aerosol mixing states (~~21.510.5~~%). Our study
24 reveals that the BCMSD matters as well as their mixing state in estimating the direct aerosol
25 radiative forcing. Knowledge of the BCMSD should be fully considered in climate models.

26 **1 Introduction**

27 Atmospheric black carbon (BC) is the second strongest absorbing components in atmosphere
28 (Bond et al., 2013) but the magnitudes of the warming effects are poorly quantified. When emitted to
29 the surrounding, BC particles transform the morphology from fractal to spherical and then grow as
30 fully compact particles with other components depositing on the BC aerosol (Peng et al., 2016). The

31 variation in the shapes of BC aerosols, together with the variation in the mixing states, can lead to
32 substantial change of aerosol optical properties (Liu et al., 2017;China et al., 2013;Wu et al.,
33 2016a;Wu et al., 2018). BC aerosols also have significant influence on the climate by interacting
34 with clouds (Koch and Del Genio, 2010;Roberts et al., 2008;Stevens and Feingold, 2009), ice and
35 snow (Bond et al., 2013). Recent study shows that the solar absorption of BC can suppress the
36 turbulence in the atmospheric boundary layer (Wilcox et al., 2016). It is found that BC emissions
37 may be responsible for the incensement of droughts and floods in China and India (Menon et al.,
38 2002). In addition, BC can pose a serve threat to human health through inhalation (Nichols et al.,
39 2013;Janssen et al., 2011).

40 Comprehensive studies have been carried out to evaluate the climate effect of BC based on the
41 measurement of BC mass concentrations (m_{BC}) (Koch et al., 2009;Ramanathan and Carmichael,
42 2008). The m_{BC} near the ground have been well characterized (Ramachandran and Rajesh,
43 2007;Ran et al., 2016b;Reddington et al., 2013;Song et al., 2013), and the BC vertical distributions
44 are widely measured and evaluated as well (Ran et al., 2016a;Babu et al., 2011;Ferrero et al., 2011).
45 Despite these measurements, more insights into the BC microphysical properties can help to estimate
46 the influence of BC aerosols on visibility (Zhang et al., 2008), climate (Jacobson, 2001) and human
47 health (Lippmann and Albert, 1969). These microphysical properties include BC morphology (Zhang
48 et al., 2016), density (Zhang et al., 2016), complex refractive index (Bond et al., 2013),
49 hygroscopicity (Zhang et al., 2008;Peng et al., 2017),_mixing states (Moffet et al., 2016;Raatikainen
50 et al., 2017), and particularly, the mass size distribution (BCMSD) (Cheng et al., 2012;Cheng and
51 Yang, 2016;Gong et al., 2016). Knowledge of BCMSD is not only helpful to study the mixing state
52 of BC aerosols (Raatikainen et al., 2017), but also essential to model the role of BC in evaluating
53 regional and global climate accurately-. BC radiative effects is highly sensitive to the emitted BC
54 particle size distribution (Matsui et al., 2018). The health impacts of BC are significantly related to
55 BCMSD (Turner et al., 2015). Furthermore, the information of BCMSD can help to study the source,
56 the evolution and the mixing state of ambient BC aerosols (Yu et al., 2010).~~However, few studies~~
57 ~~have focused on the characteristics of the BCMSD, and the BCMSD properties under different~~
58 ~~polluted conditions are not known yet.~~

59 Many methods have been proposed to measure the BCMSD. For instance, the BCMSD was
60 measured by sampling the aerosol in the size range from about 50 nm to several micrometers onto

61 quartz fiber filter substrates using a micro-orifice uniform deposit impactor (MOUDI)
62 (Venkataraman and Friedlander, 1994;Guo, 2016). Cheng et al. (2014) developed a method to
63 measure the BCMSD by employing two aethalometers in parallel, with one to measure total m_{BC}
64 and the other to measure m_{BC} below specific particle sizes using a size cut-off inlet. The above two
65 methods measure the BCMSD corresponding to the aerodynamic diameter. The Single Particle Soot
66 Photometer (SP2) is developed and widely used because it provides single particle information, hence
67 the BCMSD and the mixing state of the atmospheric aerosols can be derived directly (Schwarz et al.,
68 2006;Gao et al., 2007;Huang et al., 2012;Singh et al., 2016). –The BCMSD corresponding to the
69 ambient aerosol mobility diameter can be measured by using a differential mobility analyzer (DMA)
70 in tandem with SP2 (Raatikainen et al., 2017). However, the laser-induced incandescence method
71 cannot provide reliable information about the particles beyond the range of 70 nm and 400 nm
72 (Moteki and Kondo, 2010), which results in the lack of the knowledge of the BCMSD characteristics
73 for these aerosols over 400 nm. The results from MOUDI find that a great amount of BC locates at
74 the aerodynamic diameter range of larger-between than 370 and 1000 nm (Hu et al., 2012;Huang and
75 Yu, 2008). However, the measurements of MOUDI cannot give detailed information of the BCMSD
76 evolution due to the low temporal and diameter resolution (Hu et al., 2012;Huang and Yu, 2008). The
77 characteristics of the BCMSD larger than 370 nm is not well studied due to the limitation of the
78 instrument.

79 Recently, Ning et al. (2013) and Stabile et al. (2012) proposed a new method to measure the
80 BCMSD by using differential mobility analyzer (DMA) in tandem with Aethalometer (AE). This
81 method has the potential of measuring the BCMSD from 20 nm to 584 nm with high time resolution.
82 We develop and validate the BCMSD measurement system based on the works of Ning et al. (2013).
83 The developed measurement system was employed in a field campaign in the North China Plain. The
84 characteristics of the measured BCMSD were studied based on the field measurement. Furthermore,
85 the effects of BCMSD variations on the aerosol optical properties and corresponding direct aerosol
86 radiative properties were evaluated. The aerosol optical properties were calculated by using the Mie
87 scattering theory. The direct aerosol radiative forcing (DARF) were estimated by using the Santa
88 Barbara DISORT (discrete ordinates radiative transfer) Atmospheric Radiative Transfer (SBDART)
89 model.

90 The structure of this paper are organized as follows. Section 2 gives the information about the

91 instrument setup and field measurement. Section 3 gives the detailed method used in this study,
92 which contains: 1, conducting multiple charging corrections when deriving the aerosol BCMSD and
93 2, evaluating the aerosol optical and radiative properties for different BCMSD. Results and
94 discussions are shown in section 4. The conclusion is drawn in the last part.

95 **2 Instrument Setup**

96 The measurement system setup was based on the works of Stabile et al. (2012) and Ning et al.
97 (2013) as schematically shown in Fig.1. The ambient sample aerosol particles were firstly dried to
98 below relative humidity of 30% through a Nafion drying tube before passing through to the DMA
99 (Model 3081, TSI, USA). The DMA scanned aerosol particles with diameter ranges from 12.3 to 697
100 nm over a period of 285 seconds and started another scanning after a pause of 15 seconds, so one
101 complete cycle took 5 minutes. The sheath and sample flow rates of the DMA were 3 lpm and 0.5
102 lpm, respectively. The quasi-monodisperse aerosols that passed through the DMA were further
103 divided into two flows: with one lead to an aethalometer (AE51, Model 51, MicroAeth, USA) with a
104 flow rate of 0.2 lpm to measure the σ_{abs} at 1 second time resolution; and
105 the other one with flow rate of 0.3 lpm flow directed to a CPC (Model 3772, TSI, USA), which
106 counted particle number concentrations at 0.1 second resolution. Clean air with a flow rate of 0.7
107 lpm was used to compensate for the CPC inlet flow, which had default flow rate of 1 lpm. Overall,
108 the combination system of DMA, CPC and AE51 could provide one PNSD and ~~BCMSD~~
109 size-resolved σ_{abs} scan every 5 minutes. If the mass absorption coefficient (MAC) at a given
110 diameter is known, the BCMSD can be derived correspondingly.

111 ~~At the same time, another~~ aethalometer (AE33, Model 33, Magee, USA) was used to measure
112 the σ_{abs} or m_{BC} with a time resolution of 1 minute. The mass concentration of particles with
113 diameter smaller than 2.5 μm (PM_{2.5}) was concurrently measured with time resolution of 1 minute
114 during the filed observations by the Tapered Element Oscillating Microbalance (TEOM)
115 Dichotomous Ambient Particulate Monitor (1405-DF), which was an indicator of the pollution
116 conditions.

117 From 21 March to 9 April in 2017, an intensive field measurement was conducted to
118 characterize of the ambient dry aerosol BCMSD corresponding to aerosol mobility diameter at the
119 AERONET BEIJING_PKU station (N39°59', E116°18'). This station was located on one roof of
120 Peking University campus in the north west of Beijing, China. There were two main streets, Chengfu

121 Road to the south and Zhongguancun Street to the west that surrounding the station. The aerosol
122 sampled at this station were mainly composed of urban roadside aerosols (Zhao et al., 2018).

123 3 Methodologies

124 3.1 Retrieving the BCMSD

125 ~~Four–Five~~ steps were involved to calculate the BCMSD using the raw data from the
126 measurement system: 1), correcting the ‘loading effect’ and ‘multiple scattering effect’ of $\sigma_{abs}m_{BC}$
127 measured by AE51; 2), matching the instrument time between the AE51 and CPC; 3), matching the
128 measured $\sigma_{abs}m_{BC}$ and diameter to get the raw BCMSDsize-resolve σ_{abs} that is not involved in
129 multiple charging corrections; 4), conducting the multiple charging corrections of the measured raw
130 BCMSDsize-resolved σ_{abs} ; 5), transforming the size-resolved σ_{abs} into BCMSD.

131 3.1.1 Obtaining the raw BCMSDsize-resolved σ_{abs}

132 The aethalometer (AE51 and AE33) is a well-developed and widely used instrument to measure
133 the $\sigma_{abs}m_{BC}$ (Drinovec et al., 2015;Hansen et al., 1984). When absorbing aerosols accumulates on
134 the sample filter of the aethalometer continuously, the $\sigma_{abs}m_{BC}$ can be determined by concurrently
135 measuring the light intensities I after the fiber filter and the light intensities I_0 transmitted through
136 reference spot which is free of aerosol loading. The light attenuation (ATN) is defined as:

$$137 \quad ATN = 100 \cdot \ln\left(\frac{I_0}{I}\right). \quad (1)$$

138 The total σ_{abs} mass of BC of the loaded particle on the filter is given by:

$$139 \quad \sigma_{abs,tot}m_{BC,tot} = \frac{A \cdot ATN}{100 \cdot \sigma_{BC}}, \quad (2)$$

140 where A is the sample spot area on the filter and σ_{BC} is the mass attenuation cross-section of BC.

141 The instantaneous σ_{abs} can be calculated through The equivalent m_{BC} can be calculated through
142 the increment of $\sigma_{abs,tot}m_{BC,tot}$:

$$143 \quad \sigma_{abs}m_{BC} = \frac{\sigma_{abs,tot}m_{BC,tot}}{\Delta t} = \frac{A \cdot \Delta ATN}{100 \cdot \sigma_{BC} \cdot F \cdot \Delta t}, \quad (3)$$

144 where F is the flow rate and ΔATN is the ATN variation during the time period of Δt . The $\sigma_{abs,tot}$
145 can be transformed to m_{BC} when the mass attenuation cross-section (MAC) of BC is known.
146 Traditionally, a constant MAC at 7.7 g/m² was used to deduce the m_{BC} (Drinovec et al., 2015).

147 Corrections of the measured σ_{abs} are necessary because the systematic bias exists due to the
148 prevailingly known ‘loading effect’ and multiple scattering effect (Drinovec et al., 2015;Virkkula et
149 al., 2015;Virkkula et al., 2007). The AE33 can directly provide the corrected $\sigma_{abs}m_{BC}$ values

150 through measuring two light intensities of two spots with different BC load efficiencies (Drinovec et
151 al., 2015). For AE51, The correcting method in Virkkula et al. (2007) was adopted:

$$\sigma_{abs, corrected} m_{BC, corrected} = (1 + k \times ATN) \sigma_{abs, uncorrected} m_{BC, uncorrected},$$

(4)

154 where k is the correction factor and a constant value of 0.004 is employed in this study to correct
155 the $\sigma_{abs} m_{BC}$ from AE51. In the first part of the supplementary material, we showed that the loading
156 effects corrections of $\sigma_{abs} m_{BC}$ from AE51 were essential and the value of $\sigma_{abs} m_{BC}$ from AE33
157 could be used as a reference for the measured BCMSD. As for the multiple scattering corrections,
158 Zhang et al. (2018) compared the measured σ_{abs} measured by AE33 and by Multi-Angle
159 Absorption Photometer (MAAP) at Tsinghua University, which is about 2 km away from our
160 measurement site. They recommended a compensation factor of 2.6 to be used and we adopted the
161 same factor in our study.

162 Time correction was needed because time gaps between voltages implied on the DMA (particle
163 size) and sample particles measured by different instruments were not the same. The time correction
164 procedures were conducted every day during the field measurement to ensure that the time deviations
165 of the CPC and the AE51 were constrained within 2 seconds.

166 Fig. S3 gave the time series diagram of scanned aerosol diameters by DMA, measured $\sigma_{abs} m_{BC}$
167 from AE51, and the aerosol number concentrations counted by CPC. The aerosol PNSD (or
168 BCMSD-size-resolved σ_{abs}) could be calculated by matching the DMA diameter and the measured
169 aerosol number concentrations (or measured $\sigma_{abs} m_{BC}$) by simply using the single particle charge
170 ratio for each electrical mobility diameter. These measured PNSD and BCMSD-size-resolved σ_{abs}
171 did not consider the effect of multiple-charging corrections and are labeled as raw aerosol PNSD and
172 raw aerosol size-resolved σ_{abs} , BCMSD-

173 **3.1.2 Multiple charging corrections of raw size-resolved σ_{abs} , BCMSD-**

174 In the work of Ning et al. (2013) study, lots of efforts were made to evaluate the performance of
175 the instrument. They considered the diffusion corrections and particle charging corrections. However,
176 the particle charging corrections were limited to single particle charge ratio as they mentioned that
177 they simplified the particle charge correction by applying the peak electrical mobility for the
178 calculation of representative particle size for each mobility bin and single particle charge ratio for

179 each primary mobility. They ignored the fact that the aerosol samples selected by the DMA were
180 quasi-monodisperse with different charges and different diameters.

181 We proposed a new algorithm for the multi-charge corrections of the BCMSDsize-resolved σ_{abs} .
182 Multi-charge corrections to the measured size distribution were prevailing when the DMA was used
183 to scan the aerosol sizes. When the DMA and CPC are used together to measure the aerosol particle
184 number size distribution (PNSD), the multi-charging corrected aerosol PNSD can be significantly
185 different from the raw measured one (Bau et al., 2014;He and Dhaniyala, 2013;He et al., 2015). As
186 shown in the results part of this study, the multi-charge corrections of the BCMSDsize-resolved
187 σ_{abs} could cause differences in both the magnitude and shape of the BCMSDsize-resolved σ_{abs} .
188 Therefore, it is necessary to perform multi-charge corrections on the size-resolved σ_{abs} BCMSD.
189 This study developed a new algorithm to correct the size-resolved σ_{abs} from measured
190 value from measured m_{BC} based on the work of Hagen and Alofs (2007) and Deng et al. (2011).

191 When the DMA is charged with a negative voltage, those aerosols with a small range of
192 electrical mobility (Z_p) can pass through the DMA:

$$193 \quad Z_p = \frac{q_{sh}}{2\pi VL} \ln\left(\frac{r_1}{r_2}\right), \quad (5)$$

194 where q_{sh} is the sheath air flow rate; V is the average voltage on the inner center rod; r_1 and r_2
195 are the outer and inner radius of annular space respectively. The Z_p is related with D_p by
196 elementary charge (e), number of elementary charges on the particle (n), and gas viscosity poise (μ)
197 with:

$$198 \quad Z_p = \frac{neC(D_p)}{3\pi\mu D_p}, \quad (6)$$

199 where $C(D_p)$ is Cunningham slip correction:

$$200 \quad C = 1 + \frac{2\tau}{D_p} \left(1.142 + 0.558e^{-\frac{0.999D_p}{2\tau}}\right), \quad (7)$$

201 where τ is the gas mean free path. From equation 7, aerosol particles can have the same Z_p despite
202 that they have different n and D_p . At the same time, there exists a relatively larger portion of
203 multiple charged particles for those particles with diameters between 100 nm and 400 nm when the
204 ambient aerosols pass through the X-ray (Tigges et al., 2015;Wiedensohler and Fissan, 1988).
205 Through the above discussion, the selected aerosols by DMA at a given electrical mobility can have
206 different charges which will correspond to different diameters.

207 When the scan diameter is set as Dp_i for the singly charged particles and the respective voltage

208 of DMA is V_i ($i=1, 2, \dots, I$), aerosol particles with electro-mobility of $Z_{p,i}$ ($i=1, 2, \dots, I$) can pass
 209 through the DMA and the observed σ_{abs} by AE51 can be expressed as:

$$210 \quad R_i = \int_0^{\infty} G(i, x)A(x)n(x)dx, \quad (8)$$

211 where x is the scale parameter, with the definition of $x = \log(Dp_i)$, $A(x)$ is the average
 212 σ_{abs} of single particles for scale parameter x , and $n(x) = dN/d\log Dp$ is aerosol
 213 PNSD that is the multiple charging corrected results from the measured aerosol PNSD. We define the
 214 kernel function $G(i, x)$, which is crucial to the algorithm, as:

$$215 \quad G(i, x) = \sum_{v=1}^{\infty} \phi(x, v)\Omega(x, v, i), \quad (9)$$

216 where $\phi(x, v)$ is the probability of particles that are charged with v charges at the scale parameter
 217 of x (Wiedensohler, 1988). $\Omega(x, v, i)$ is the probability of particles that can pass through the DMA
 218 with v charges at the scale parameter x (Knutson and Whitby, 1975). In this study, the maximum
 219 value of v is 10.

220 The multiple charging corrections can be expressed as computing the $A(x_i^*)$, in which x_i^* is the
 221 predetermined scale parameter from the DMA. To get the numerical integration results of equation 9,
 222 the diameter interval that is 1/50 of the measured diameter is used. Thus, equation 9 can be written as

$$223 \quad R_i = \int_0^{\infty} G(i, x)A(x)n(x)dx = \Delta x_i \sum_{j=1}^{50} \beta_j G(i, x_{i,j})A(x_{i,j})n(x_{i,j}), \quad (10)$$

224 where $\beta = \begin{cases} 0.5, & j = 1, J \\ 1, & \text{otherwise} \end{cases}$; $x_{i,j}$ is the j^{th} ($j=1, 2, \dots, 50$) parameter that locates at the parameter x_i and
 225 x_{i+1} and $A(x_{i,j})$ ($i=1, 2, \dots, I; j=1, 2, \dots, 50$), the BC mass ratio at scale parameter $x_{i,j}$, is expressed
 226 as the linear interpolation of the values at the measured diameters.

$$227 \quad A(x_{i,j}) = A(x_i) + P_i(x_{i,j} - x_i), \quad (11)$$

228 where P_i is the slope of the linear interpolation result of

$$229 \quad A(x_k^*) = C + P_i \cdot x_k^*. \quad (12)$$

230 x_k^* refers to these five diameters that are nearest to the predetermined scale parameter x_i . C is the
 231 intercept of the linear interpolation result.

232 With $H_{i,j} = \beta_j \Delta x_i G(i, x_{i,j})n(x_{i,j})$, equation 11 can be written as

$$233 \quad R_i = \sum_{j=1}^J H_{ij} [A(x_i) + P_i(x_{i,j} - x_i)] = \sum_{j=1}^J H_{ij} A(x_i) + \sum_{j=1}^J H_{ij} P_i x_{i,j} - \sum_{j=1}^J H_{ij} P_i x_i$$

$$234 \quad = \sum_{k=1}^I (\sum_{j=1}^J H_{ij} \delta(i - k)) A(x_k^*) + \sum_{k=1}^I \left(\sum_{j=1}^J H_{ij} x_{i,j} \delta(i - k) \right) P_k - \sum_{k=1}^I \delta(i - k) P_k x_k^*$$

235
$$= \sum_{k=1}^I Q_{ik} A(x_k^*) + \sum_{k=1}^I T_{ik} P_k - \sum_{k=1}^I Q_{ik} P_k x_k^*, \quad (13)$$

236 where $\delta(x) = \begin{cases} 0, & x \neq 0 \\ 1, & x = 0 \end{cases}$,

237
$$Q_{ik} = \sum_{j=1}^J H_{ij} \delta(i - k), \quad (14)$$

238 and $T_{ik} = \sum_{j=1}^J H_{ij} x_{i,j} \delta(i - k). \quad (15)$

239 By letting the

240
$$S_i = R_i - \sum_{k=1}^I T_{ik} P_k + \sum_{k=1}^I Q_{ik} P_k x_k^*. \quad (16)$$

241 This equation is then expressed as

242
$$S_i = \sum_{k=1}^I Q_{ik} A(x_k^*), \quad (17)$$

243 or

244
$$S = QA, \quad (18)$$

245 where S and A are $I \times 1$ vectors and Q is an $I \times I$ matrix. This matrix can be solved by using the
246 non-negative least square method.

247 Finally, the A(x) can be determined and the corresponding size-resolved σ_{abs} BCMSD that is
248 multiple charging corrected can be calculated.

249 3.1.3 Transform the size-resolved σ_{abs} into BCMSD

250 MAC of different size range is necessary when transform the size-resolved σ_{abs} into BCMSD.
251 The MAC at different size should be different. When the size-resolved σ_{abs} is converted into
252 BCMSD with a constant MAC, the derived BCMSD would be biased.

253 The size-resolved MAC was calculated using the Mie scattering model (Bohren and Huffman,
254 2007). Based on the Mie scattering theory, MAC values vary for different aerosol core diameter and
255 different total diameter. Results from SP2 measurement show that the size distribution of the BC
256 core diameter peaked at around 120 nm in Beijing (Zhang et al., 2017). For each aerosol diameter,
257 the MAC value with core diameter of 120 nm was used to transform the BCASD into the BCMSD.
258 MAC values with core diameter at 120±15 nm were calculated and shown in Fig. 2. From Fig. 2, the
259 MAC varied significantly between 3.6 and 9.2 m²/g. The constant MAC values 7.7 m²/g
260 corresponded to the aerosol diameter of 269 nm. The calculated mean MAC values in Fig. 2 under
261 different diameter were used in this study.

262 3.1.3-4 Validation of the multiple charging corrections

263 An example of the multiple charging corrections of the size-resolved σ_{abs} was shown in Fig. 23.

264 The corrections of aerosol PNSD were based on the work of Hagen and Alofs (2007). As shown in
 265 Fig. 2(a), the corrected aerosol PNSD was significantly different from the original uncorrected one.
 266 There were about half of the measured particles have multiple elementary charge in the size range
 267 between 100 and 200 nm. The raw uncorrected aerosol PNSD had a peak value of 10920 cm^{-3} at 98
 268 nm while the corrected aerosol PNSD reached its peak value of 8450 cm^{-3} at 98 nm. The peak
 269 positions of the raw aerosol particle mass size distribution (PMSD, dm/dlogDp) peaked at ~~371nm~~
 270 322 nm with a peak value of ~~56-86.3~~ $\mu\text{g}/\text{m}^3$ and the corrected aerosol PMSD had a peak value of 53
 271 $\mu\text{g}/\text{m}^3$ at ~~445-461~~ nm. The peak position of the aerosol PMSD shifted a lot before and after the
 272 multiple charging corrections. The similar case for the ~~BCMSD-size-resolved σ_{abs}~~ was shown in
 273 Fig. 2(b). The shape of ~~size-resolved σ_{abs} BCMSD~~ had changed substantially due to the multiple
 274 charging corrections. The measured raw BCMSD had a peak diameter near ~~32000~~ nm and the
 275 magnitude of ~~size-resolved σ_{abs} BCMSD~~ plateau reached ~~6000 ng/m^3 at 283nm~~ 34.3 Mm^{-1} , which
 276 was in accordance with the results of Ning et al. (2013), where the multiple charging corrections
 277 were not involved. However, the corrected ~~size-resolved σ_{abs} BCMSD~~ peaks near ~~400nm~~ 410 nm,
 278 with a peak value of about ~~5500 ng/m^3 at 407nm~~ 29.5 Mm^{-1} . According to the result, a small amount
 279 of ~~$\sigma_{abs} \text{BC}$~~ remained in particles with diameter between 100nm and 200nm. The measured
 280 ~~size-resolved σ_{abs} BCMSD~~ changed a lot when multiple charging corrections were implemented,
 281 which highlighted the necessity of implementation of appropriate multiple charging corrections

282 The ~~$\sigma_{abs} \text{m}_{\text{BC}}$~~ integrated from measured ~~size-resolved σ_{abs} BCPMSD~~ changed after multiple
 283 charging corrections. Fig. S4 showed the comparison results of the ~~$\sigma_{abs} \text{m}_{\text{BC}}$~~ measured by AE33 and
 284 the ~~$\sigma_{abs} \text{m}_{\text{BC}}$~~ integrated from AE51 measurements. The ~~$\sigma_{abs} \text{m}_{\text{BC}}$~~ integrated from uncorrected and
 285 corrected ~~size-resolved σ_{abs} BCMSD~~ versus ~~$\sigma_{abs} \text{m}_{\text{BC}}$~~ measured by AE33 were shown in Fig.S4(a)
 286 and Fig.S4(b), respectively. Before multiple charging corrections, the ~~$\sigma_{abs} \text{m}_{\text{BC}}$~~ from uncorrected
 287 ~~size-resolved σ_{abs} BCPMSD~~ increased linearly with the ~~$\sigma_{abs} \text{m}_{\text{BC}}$~~ from AE33, with R^2 equaling
 288 0.87, but it was 2.37 times that of AE33 in average. As a comparison, overall magnitude of
 289 ~~$\sigma_{abs} \text{m}_{\text{BC}}$~~ integrated from corrected ~~size-resolved σ_{abs} BCPMSD~~ agreed better with that from AE33
 290 with a slope of 1.2. With the discussion above, multiple charging corrections were essential for
 291 size-resolved σ_{abs} and BCMSD measurements.

292 3.2 Fitting the BCMSD by using two log-normal models

293 Based on the measurement results, the BCMSD had two modes for most of the conditions. The

294 BCMSD are assumed to be of two log-normal distributions as:

$$295 \quad m_{fit,Dp} = \sum_{i=1,2} \frac{m_i}{\sqrt{2\pi \log(GSD_i)}} \cdot \exp\left(-\frac{[\log(D_p) - \log(D_{m,i})]^2}{2 \log^2(GSD_i)}\right), \quad (19)$$

296 Where D_p is the diameter of the aerosols; m_i is the mass of mode i ($i=1,2$); GSD_i is the geometric
297 standard deviation at mode i ($i=1,2$), and $D_{m,i}$ is the geometric mean diameter of the mode i ($i=1,2$).
298 The GSD_i and $D_{m,i}$ can be determined by using the least square method with the objective function
299 as :

$$300 \quad J = \sum_{i=1,n} (m_{Dp_i} - m_{fit,Dp_i}(D_{m1}, GSD_1, D_{m2}, GSD_2))^2, \quad (20)$$

301 Where m_{Dp_i} is the measured mass distribution at Dp_i , while m_{fit,Dp_i} is the fit mass distribution at
302 Dp_i .

303 **3.3 Estimating aerosol optical properties with different BCMSD**

304 The Mie scattering model was used to study the influence of the BCMSD variation on the
305 aerosol optical properties. When running the Mie model, aerosol PNSD and BC were necessary. ~~The~~
306 ~~aerosol PNSD and m_{BC} used here is the mean result of aerosol PNSD and m_{BC} over the whole~~
307 ~~field measurement respectively. The amount of BC particle adopted in this study is the mean value of~~
308 ~~the m_{BC} measured by AE33.~~ In this study, The BCMSD was assumed to be log-normal distributed.
309 D_m of the BCMSD was set to vary from 100 nm to 600 nm. Geometric standard deviation (GSD) of
310 the BCMSD was set to be in the range between 1.3 and 1.8. BC was treated as partially externally
311 mixed and the remaining aerosols was treated as core-shell mixed. The ratio of externally mixed
312 m_{BC} to core-shell m_{BC} was determined by the method introduced in Ma et al. (2012) and a mean
313 ratio of 0.51 was used. The density and refractive index of BC were set as 1.5 g/cm³ and 1.8+0.54i
314 (Kuang et al., 2015), respectively. The complex refractive index of non-absorbing aerosols was
315 1.53+10⁻⁷i (Wex et al., 2002) at the wavelength of 525 nm. More details of calculating the aerosol
316 optical properties by using the aerosol PNSD and BCMSD, can refer to Kuang et al. (2016).

317 The aerosol PNSD and m_{BC} used here is the mean result of aerosol PNSD and m_{BC} over the
318 whole field measurement respectively. The amount of BC particle adopted in this study is the mean
319 value of the m_{BC} measured by AE33. For each BCMSD, extinction coefficient (σ_{ext}), the scattering
320 coefficient (σ_{sca}), the single scattering albedo (SSA), and the asymmetry factor (g) could be obtained
321 from the output of Mie scattering model.

322 **3.4 Evaluating the DARF with different BCMSD**

323 In this study, the SBDART model (Ricchiuzzi et al., 1998) was employed to estimate the DARF.
324 In our study, the instantaneous DARF for cloud free conditions at the top of atmosphere was
325 calculated for irradiance wavelength range from 0.25 to 4 μm . Input of the model required the
326 profiles of aerosol σ_{ext} , SSA, g. These ~~values-profiles~~ were calculated ~~by-from the parameterized~~
327 ~~aerosol PNSD, BCMSD-profiles~~ parameterization of the aerosol vertical distributions. Details of
328 calculating the σ_{ext} , SSA and g profiles can refer to part 4 in the supplementary material. ~~The~~
329 ~~corresponding DARF for different BCMSD could be estimated.~~ In brief, the aerosol σ_{ext} , SSA
330 and g profiles were calculated based on the given aerosol PNSD and BCMSD. The DARF can be
331 estimated using the above aerosol optical profiles.

332 The aerosol optical properties and the corresponding aerosol optical profiles vary with different
333 BCMSD. Then the DARF should be different for different BCMSD. By estimating the DARF using
334 different aerosol BCMSD, the influence of BCMSD on the aerosol radiative properties can be
335 studied. More details of estimating the DARF could refer to part 4 and 5 in the supplementary
336 material. ~~The corresponding DARF for different BCMSD could be estimated. The DARF was~~
337 ~~estimated for the measured mean aerosol PNSD and m_{gc} under different BCMSD conditions to~~
338 ~~study the effects of BCMSD variations on the aerosol DARF.~~

339 **4 Results and Discussions**

340 **4.1 Measurement results of the BCMSD**

341 The time series of measured PM_{2.5}, aerosol PNSD and BCMSD were shown in Fig. 3. During
342 the observation period, the PM_{2.5} varied from 0.06 to 220 $\mu\text{g}/\text{m}^3$, with a mean value of 71.5 ± 52.56
343 $\mu\text{g}/\text{m}^3$. Three periods of heavy PM_{2.5} loading were observed: (1) PM_{2.5} increased from around 100
344 $\mu\text{g}/\text{m}^3$ to 200 $\mu\text{g}/\text{m}^3$ and decreased slowly to 1 $\mu\text{g}/\text{m}^3$ in the period 21-26, March; (2) the PM_{2.5}
345 accumulated slowly from 28 to 30, March and dissipated quickly from 30, March to 1, April; (3) the
346 rapid accumulation and dissipation of PM_{2.5} happened during 2 to 5, April. During the last five days,
347 PM_{2.5} fluctuated between 20 and 120 $\mu\text{g}/\text{m}^3$. For each pollution condition, both the aerosol total
348 number concentrations and the aerosol median diameter increased. The aerosol median diameter
349 varied between 31 nm and 169 nm with a mean value of 78 ± 31 nm.

350 ~~As for the BCMSD, a distribution with two modes could be detected. Our measurements shew~~
351 that the BCMSD had two modes with the coarser mode ranging between 430 nm and 580 nm in

352 mobility diameter. Many field measurements had revealed that most of the BC mass locates in the
353 aerodynamic diameter range of 320 nm and 560 nm using the MOUDI (Hu et al., 2012;Huang and
354 Yu, 2008). When the aerodynamic diameter was transformed into mobility diameter with assumption
355 a aerosol effective density of 1.3, the measured BC aerodynamic diameter range corresponded to
356 mobility diameter range of 280 nm and 491 nm. Therefore, the measured size range for coarser mode
357 of BCMSD agreed well with the previous measurement.

358 The measured aerosol in the field site was representative of the urban aerosol. The BC particles
359 emitted by vehicles contributed significantly to the total aerosol BC mass. These BC particles were
360 rarely coated or thinly coated, and the BC core diameter peaked around 120 nm (Zhang et al., 2017).
361 Therefore, the BCMSD of the smaller mode measured in our study corresponded to these uncoated
362 of thinly coated particles. The presence of the first mode in the size range between 100 and 200 nm
363 provided a verification of previous field measurements that the BC concentrated in the particle
364 diameter range from 100 to 200 nm. (Huang et al., 2012;Ohata et al., 2011;Wu et al., 2016b). The
365 peak diameter of second mode ranged from 300 nm to 600 nm, which agrees well with the measured
366 BCMSD by MOUDI (Klaus Willeke and Baron, 1996;Yu and Yu, 2009;Huang and Yu, 2008). The
367 main BC mass loading was in the coarser mode for the sampled particles when comparing the BC
368 mass concentrations at two modes.

369 The total m_{BC} measured by AE33 ranged from 0.1 to 14 $\mu\text{g}/\text{m}^3$ with an average of 5.04 ± 2.64
370 $\mu\text{g}/\text{m}^3$. Good consistence was achieved between m_{BC} measured by AE33 and m_{BC} calculated from
371 measured BCMSD as shown in Fig. 34(ed).

372 **4.2 Evolution of the BCMSD under different polluted conditions**

373 Log-normal distribution was used to fit each mode of the BCMSD by using the least square
374 method as introduced in section 3.2. For each mode, the geometric mean diameter (D_m) and the
375 geometric standard deviation (GSD) of the BCMSD were studied.

376 During the measurement period, both D_m and GSD of the two modes had changed significantly
377 as shown in Fig 4S7. The D_m of first and second mode varied from ~~128-139~~ to ~~162-161~~ nm and
378 from ~~430-420~~ to ~~580-597~~ nm, respectively. The corresponding mean D_m was ~~150-151~~ and ~~503-520~~
379 nm. The D_m of the two modes was found to be positive correlated in Fig. 4aS7(a). When the
380 pollution was released from the beginning to 27, March, the D_m decreased from ~~590to-597~~ to 420

381 nm and from ~~155-160~~ to ~~130-140~~ nm for the coarser mode and the smaller mode respectively. The
382 BC containing aerosols tended to be aged and grew larger when the air surrounding get polluted.

383 GSD for the coarser mode and the smaller mode showed very different properties as shown in
384 Fig. ~~4bS7(b)~~. For the second mode, GSD varied from around 1.49 to 1.68 with a mean value of 1.57.
385 The GSD get decreased with the pollution condition, which indicated that BC containing aerosols
386 tend to accumulate to a small range of diameters during the aging processing. This phenomenon was
387 consistent with the fact that larger particles grew relative slower in diameter because the growth ratio
388 of small aerosol particle is proportion to the negative power of it's diameter. For the first mode, GSD
389 ranged from ~~1.5-41~~ to around ~~1.85-86~~ with a mean value of ~~1.6263~~. However, GSD of the smaller
390 mode tend to be larger when the surrounding air get cleaner, which might be related to the complex
391 sources of the BC emission. A small amount of fresh emitted BC particles can have substantial
392 influence on the mass size distribution of the smaller mode because the BC concentrations of the
393 smaller mode were small, especially under clean conditions. In general, the GSD of coarser mode
394 was a good indicator of the BC aging process and that of the smaller mode could partially reflect the
395 complex sources of the BC fine particles.

396 The relationship between the D_m and the GSD for coarser mode was further analyzed by
397 analyzing the distribution of the D_m and GSD. The GSD and D_m had opposite trends as shown in
398 Fig 5. With the increment of the D_m from 420 to 540 nm, the mean value of GSD decreased from
399 around ~~1.6085~~ to ~~1.548-528~~ while the m_{BC} increased with the D_m . The statistical relationship
400 between D_m and GSD offered a reasonable representation of the BCMSD under different polluted
401 conditions. In the following work, mean values of the GSD at different D_m were used to for further
402 discussion. The m_{BC} and GSD is positively correlated. The m_{BC} increased from 2.4 to 8.3
403 $\mu\text{g}/\text{m}^3$ when the D_m increased from 420 to 540 nm.

404 Note that the GSD get slightly increased with the increment of D_m when D_m was larger than
405 520 nm. This might be caused by the limit diameter range of BCMSD measuring system which was
406 from 20 to 680 nm. The multiple charge corrections applied to the BCMSD could influence the
407 BCMSD when D_m of the BCMSD was near the end of the scanned diameter and may lead to
408 significant uncertainties to the BCMSD. The measurement results indicated that cases of measured
409 D_m of BCMSD larger than 520 nm were few, demonstrating that this multiple correction effect
410 influenced little on shape of measured BCMSD in most cases.

4.3 Influence of BCMSD variation on the aerosol optical properties

The aerosol optical parameters using the measured mean aerosol PNSD and mean m_{BC} corresponding to different GSD and D_m values were shown in Fig. 6. In Fig. 6(a), the aerosol g varied from 0.617-603 to 0.649-627 (variation of 5.84%). Recent work by Zhao et al, 2017 showed that the aerosol g value in the NCP may vary at a range of 10% due to the change of aerosol PNSD. Aerosol g was more sensitive to D_m when the geometric mean diameter of the BCMSD was lower than 400 nm. However, when the D_m was larger than 400 nm, the g become sensitive to both the D_m and the GSD of BCMSD. Overall, the g varied a little bit (0.617-02 to 0.624609) under the representative conditions during the measurement period. For the aerosol SSA, it was sensitive to the D_m over the whole range as shown in Fig. 6(b). SSA varied between 0.86-90 and 0.88-94 under the representative measurement conditions. The σ_{sca} had large changes from 264-325.6 Mm^{-1} to 313-364.4 Mm^{-1} . The σ_{sca} was quite sensitive to variations in BCMSD when the D_m was lower-larger than 400-450 nm as shown in Fig.6c, ~~which varied substantially from 264 Mm^{-1} to 313 Mm^{-1} .~~ In addition, variations in σ_{sca} relied more on the variations in D_m when D_m was larger-lower than 400 nm. Within the measurement conditions of BCMSD, the σ_{sca} varied from 265-328 Mm^{-1} to 280-345 Mm^{-1} . The measured GSD under different D_m went along with the gradient direction of the σ_{sca} , which mean that the evolution of BCMSD in the atmosphere influenced substantially on σ_{sca} . As for the σ_{abs} , it changed from 21.944.06 Mm^{-1} to 44.1237.27 Mm^{-1} and the corresponding mass absorption cross section (MAC) was estimated to be in the range of 4.755.44 to 9.568.08 m^2/g , suggesting that MAC of the BC aerosols should be carefully studied under different BCMSD conditions.

4.4 Influence of BCMSD on the direct aerosol radiative forcing

The estimated DARF values for different GSD and D_m conditions were estimated. When estimating the DARF, the measured mean aerosol PNSD and mean BC mass concentration were used-. The results of estimated DARF were shown in Fig. 7(a). DARF at the surface varied from -4.90-4.3 w/m^2 to -2.02-3.59 w/m^2 for different BCMSD. Within the measured BCMSD range, the DARF varied from -2.04w-3.97w/m² to -2.53.67w/m², which corresponding to 22.58.45% of variation. The heating rate within the mixed layer was a powerful indicator of the BC particles' absorbing effects, which may help evaluate the development of the boundary layer. The calculated mean heating rate within the mixed layer changed from 3.252.16 K/day to 3.892.65 K/day for different D_m and GSD, as shown in Fig. 7(b). The heating rate with the measured BCMSD range

could change from ~~3.562.24~~ to ~~3.752.50~~ with a variation of ~~5.2311.6~~%.

Mixing states of BC play significant roles in calculations of aerosol optical properties and estimations of DARF (Jacobson, 2001). As a comparison, we estimated the DARF under different conditions of BC mixing state: (1) internally mixed, (2) externally mixed and (3) core-shell mixed. Table 1 gave the estimated DARF and mean heating rate within the mixed layer under different mixing state conditions. Results showed that the DARF under different BC mixing states conditions may change by ~~21.510.50~~%, which shared the same magnitude with ~~22.58.45~~% variation of DARF caused by BCMSD variations. In addition, the heating rate was estimated to vary by ~~6.059.71~~%. These results highlighted that the BCMSD plays significant roles in variations of aerosol optical properties and estimations of DARF as well as the air heating rate caused by the existence of BC particles. It was recommended that a real time measured BCMSD be used when estimating the aerosol DARF, instead of a constant one. The BCMSD was as important as that of the BC mixing states.

5 Conclusions

Knowledge of the BC microphysical properties especially the size-dependent information can help reduce the uncertainties when estimating the aerosol radiative effects. BCMSD is an important quantity in its own right, being directly and indirectly applicable to determination the sources, aging processes and mixing states of BC aerosols. In this study, the characteristics of BCMSD were studied from the field measurement results by using our own developed measurement algorithm.

The BCMSD measurement system was developed and validated based on the works of Ning et al. (2013) by using differential mobility analyzer (DMA) in tandem with Aethalometer (AE). When deriving the BCMSD, a comprehensive multiple charging correction algorithm was proposed and implied. This algorithm was validated by closure study between the measured total m_{BC} from AE33 and the m_{BC} integrated from the measured BCPMSD using the datasets from field measurements. Results showed that the multiple charging corrections could significantly change the shapes and magnitudes of the raw measured BCPMSD. The accurate BCPMSD characteristics could be obtained by our proposed method in this paper.

The developed measurement system was employed in a field campaign in the North China Plain from 21 March to 9 April in 2017. The BCMSD was found to have two quasi-lognormal modes with peaks at around 150 nm and 500 nm, respectively. These two modes were consistent with the

471 previous measurement results by MOUDI (Wang et al., 2015;Hu et al., 2012). The amount of the BC
472 mass concentrations for the coarser mode peaks were about twice to that of the ~~fine-smaller~~ mode.

473 The characteristic of the BCMSD was studied by fitting the shape of BCMSD with a bi-normal
474 distribution. The relationships between the fitted D_m and GSD were statistically studied. During the
475 aging processing, the opposite trends for the D_m and GSD were found for coarser mode. This is the
476 first time that the coarser mode of the BCMSD were synthetically studied. The BCMSD of coarser
477 mode varied significantly under different pollution conditions with peak diameter changed between
478 430 and 580 nm. However, the relationship between the D_m and GSD for smaller mode BC aerosols
479 were more complex due to the complex sources.

480 When the BCMSD were changed with the polluted condition, the corresponding aerosol optical
481 properties changes significantly. Sensitivity studies found that the aerosol g varies from ~~0.617-603~~ to
482 ~~0.649-627~~ due to the variations in BCMSD. Aerosol g was more sensitive to D_m when the
483 geometric mean diameter of the BCMSD is in the range of 300 nm and 370 nm. The SSA can
484 changed from ~~0.9086~~ to ~~0.9394~~. The σ_{sca} experienced significant change with the variation of
485 BCMSD from ~~264-325.6~~ Mm^{-1} to ~~313-364.4~~ Mm^{-1} and the σ_{abs} changed in the range between
486 ~~21.94.064~~ Mm^{-1} and ~~44.1237.27~~ Mm^{-1} . The corresponding BC MAC was calculated to be in the
487 range between ~~4.755.44~~ and ~~9.568.08~~ m^2/g .

488 The variations in DARF were estimated due to the variations of the BCMSD by using the
489 SBDART model. Results showed that the DARF can varies by about ~~22.58.45~~% for different
490 BCMSD and the heating rate for different measured BCMSD conditions could change from ~~3.562.24~~
491 to ~~3.752.50~~, corresponding to a variation of ~~5.2311.6~~%. At the same time, the variations in DARF
492 due to the variations in the BC mixing state was estimated to be ~~21.510.5~~% and that of the heating
493 rate is ~~6.058.45~~%. Thus, the variations of the BCMSD may had significant influence on the aerosol
494 radiative budget and an accurate measurement of BCMSD was very necessary.

495
496 **Competing interests.** The authors declare that they have no conflict of interest.

497 **Data availability.** The data used in this study is available when requesting the authors.

498 **Author contributions.** GZ, CZ, JT and YK designed and conducted the experiments; CS, YY, CZ and GZ
499 discussed the results.

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502

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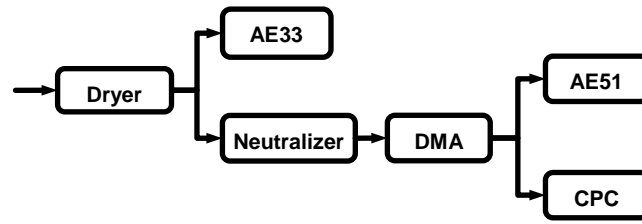
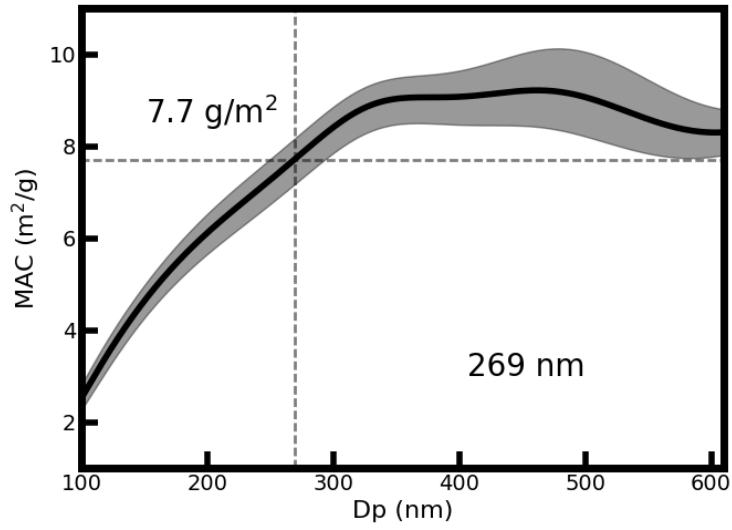


Figure 1. The schematic diagram of the instrument setup.

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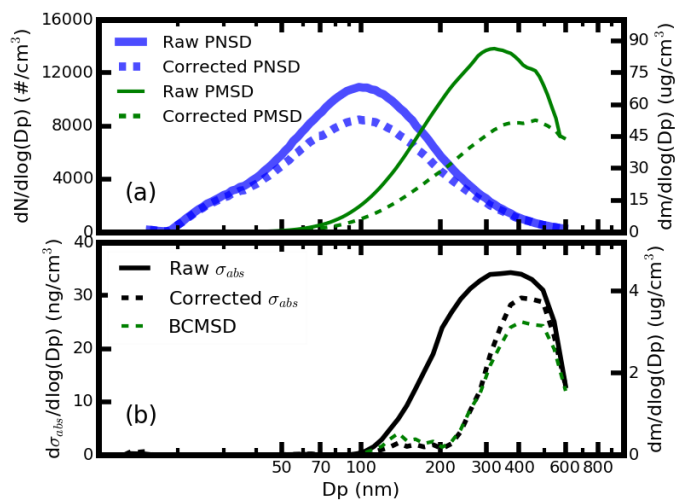


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759 **Figure 2.** Calculated mass absorption coefficient of different aerosol.

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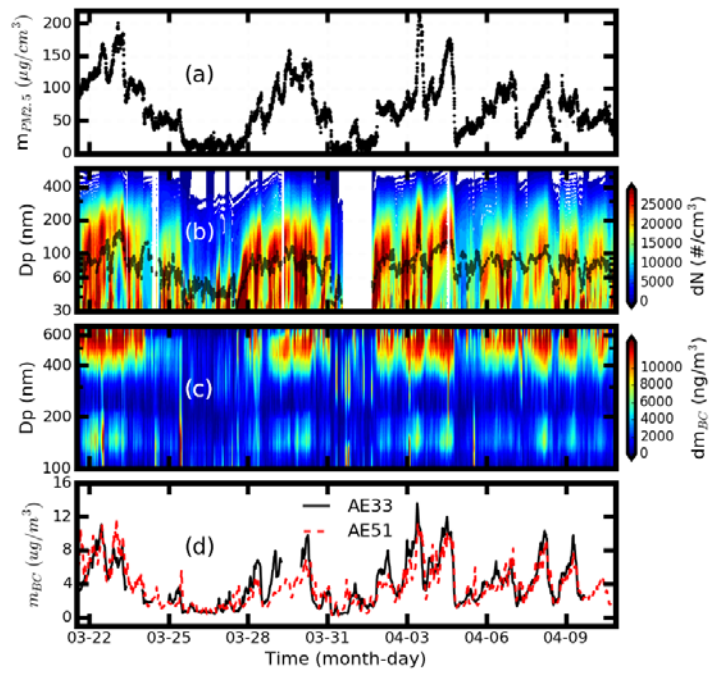


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763 **Figure 23.** Case of multiple charging correction processing. (a) the multiple charging correction of
 764 the aerosol PNSD and aerosol PMSD, (b) the multiple charging correction of the size-resolved
 765 σ_{abs} ~~the BCPMSD~~. The solid line is the measured results without multiple charging corrections and
 766 the dotted line is the multiple charging corrections results.

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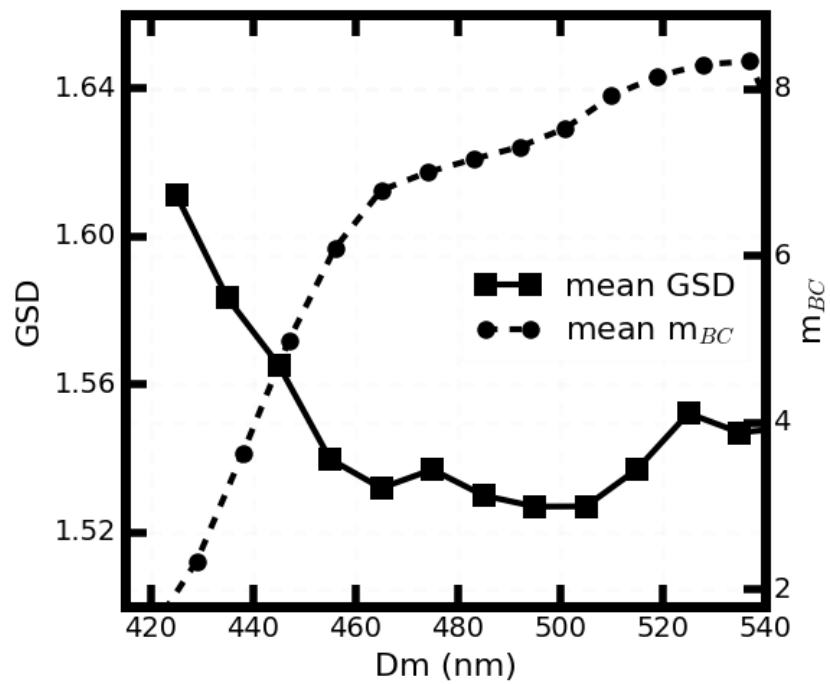
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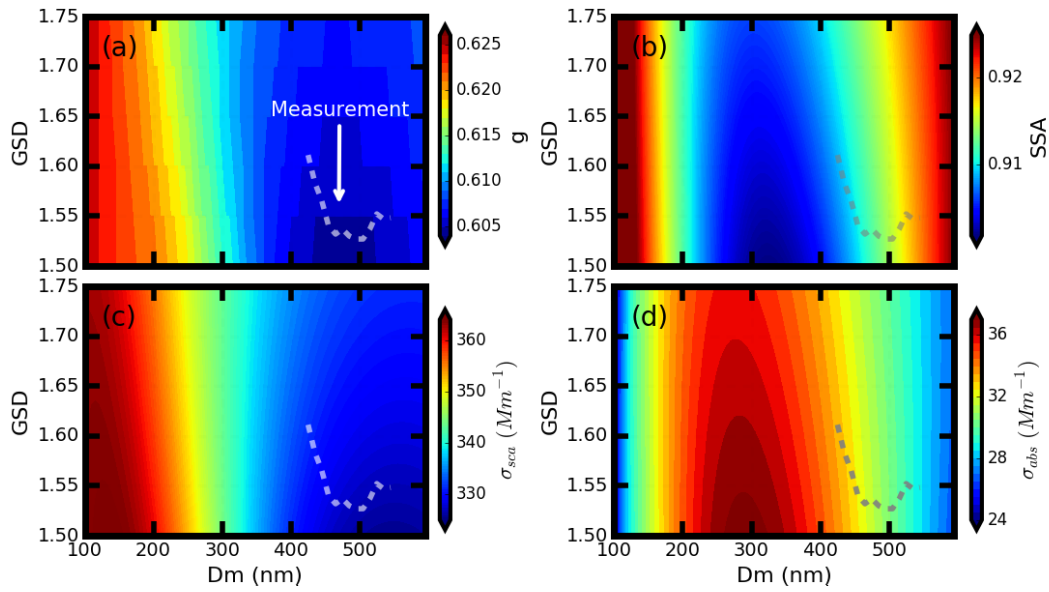
Figure 34. The measured time series of mass concentrations for (a) the PM_{2.5}; (b) the aerosol PNSD in filled color, the geometric median diameter in dotted line; ~~and~~ (c) the BCMSD and; (d) the m_{BC} by AE33 (black) and m_{BC} from integrated BCMSD from AE51 (red).



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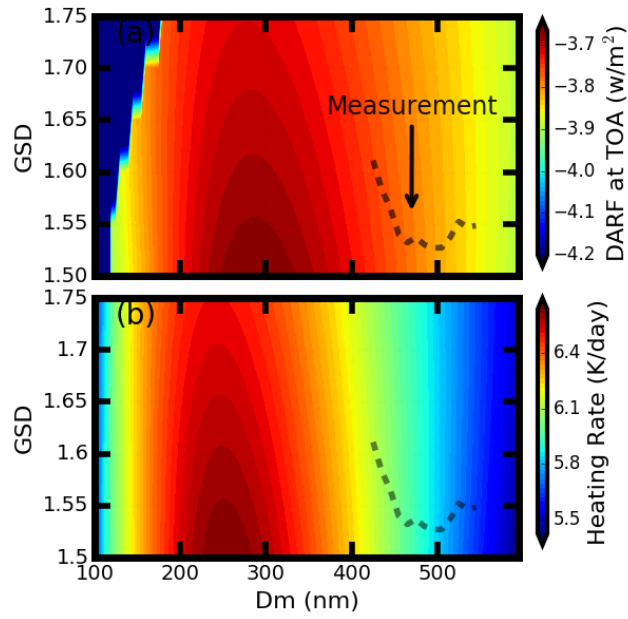
777 **Figure 5.** The relationship between the Dm and the GSD. The black dots show the real measured Dm
 778 and GSD. The black line shows the mean results of the GSD for different Dm. The black line marked
 779 with square shows the variation of mean m_{BC} with the Dm.

780



781 **Figure 6.** Variations of aerosol optics properties using the measured mean aerosol PNSD and m_{BC}
 782 under different BCMSD conditions, which are represented by different Dm and GSD values: (a)
 783 aerosol asymmetry factor, (b) single scatter albedo, (c) scattering coefficient and (d) extinction
 784 coefficient . The grey dotted line in the figure shows the evolution path of the BCMSD according to
 785 results of field measurements.

786



787

788 **Figure 7.** Variations of (a) DARF and (b) heating rate under different BCMSD conditions, which are
 789 represented by different Dm and GSD values. The black dotted line in the figure shows the evolution
 790 path of the BCMSD according to results of field measurements.

791

792 **Table 1.** Comparison of the DARF and heating rate values under different BC mixing states and
 793 different BCMSD conditions.

		Mixing State			BCMSD	
		Internal	External	Core-Shell	Minimum	Maximum
DARF	Value(w/m²)	-3.45	-3.56	-3.81	-3.97	-3.67
	Variation	10.5%			8.45%	
Heat Rate	Value(K/day)	2.51	2.32	2.53	2.24	2.50
	Variation	9.71%			11.6%	

794

1 Supplement for

2 **Role of black carbons mass size distribution in the direct aerosol radiative forcing**

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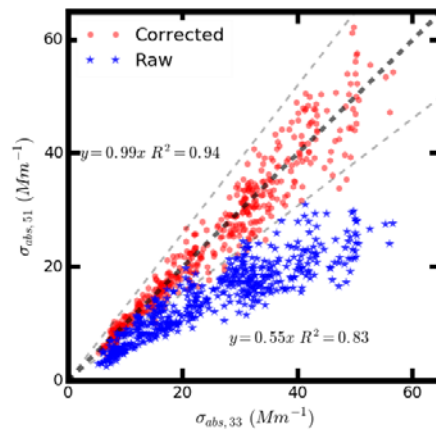
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7 **1. Correcting the AE51**

8 Fig. S1 showed the results of the loading effect corrections. At the beginning of the field
9 experiment, parallel measurement of σ_{abs} by AE51 and AE33 was conducted. Before corrections, the
10 measured σ_{abs} by AE51 and AE33 showed significant discrepancy with each other with slope and R^2
11 equaling 0.55 and 0.83. However, the σ_{abs} measured by AE33 and by AE51 with loading effects
12 corrections showed good consistency in trends and magnitudes with slope and R^2 of 0.98 and 0.94
13 respectively. These results demonstrated that the loading effects corrections of σ_{abs} from AE51 were
14 essential and the value of σ_{abs} from AE33 can be used as a reference for the measured size-resolved
15 σ_{abs} .

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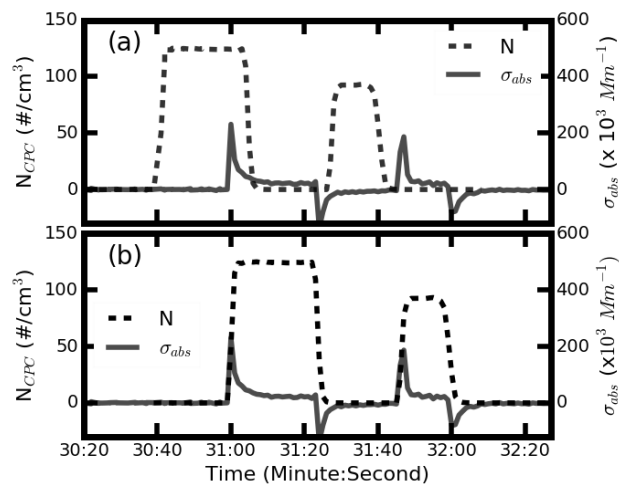
19 **Figure S1.** Comparison between the σ_{abs} measured by AE51 and AE33. The blue stars and the red
20 dots represents uncorrected and corrected σ_{abs} of AE51 respectively.

21

22 **2. Time correction**

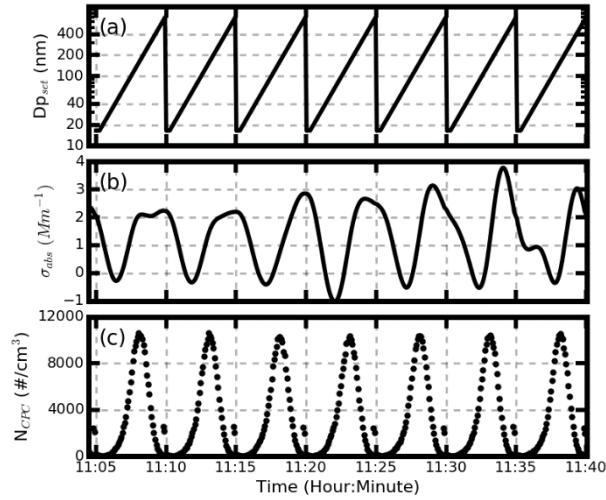
23 There were two reasons that can lead to this difference: firstly, the time of the AE51 system and
 24 the computer that controls the CPC cannot be synchronized all the time; secondly, there existed a
 25 difference in the plumbing delay time, which was the time required for particles to flow through the
 26 tubing interconnecting the DMA and CPC or AE51, and arrive at the detector. To sum up, the
 27 synchronization of the time reported by CPC and AE51 was necessary.

28 Time synchronization was conducted by measuring the time lag of the signal pulses from the
 29 DMA to CPC and AE51. The signal pulses resulted from the sudden change of the aerosol diameter
 30 scanned by DMA. Details of the method were shown below. In fig. S2, the black solid line gave the
 31 time series of the measured σ_{abs} by AE51. The dotted lines gave the time series of the aerosol number
 32 counted by CPC of (a) unsynchronized and (b) synchronized. In the beginning, the scan diameter of
 33 the DMA was set to be less than 13nm and the values measured by AE51 and CPC are nearly zero. The
 34 values get a step jump and a step drop when changing the scan diameter up to about 200nm and down
 35 back to less than 13nm. About 15s later, these procedures were conducted once again. From fig. S2(a)
 36 and fig. S2(b), the lag time of the AE51 and CPC were determined to be 20s by matching the pulse
 37 signals.



38
 39 **Figure S2.** An example of time synchronization processing, (a) for unsynchronized and (b) for
 40 synchronized. The dotted line is the aerosol number concentration time series counted by CPC. The
 41 black solid line is the σ_{abs} measured by AE51.

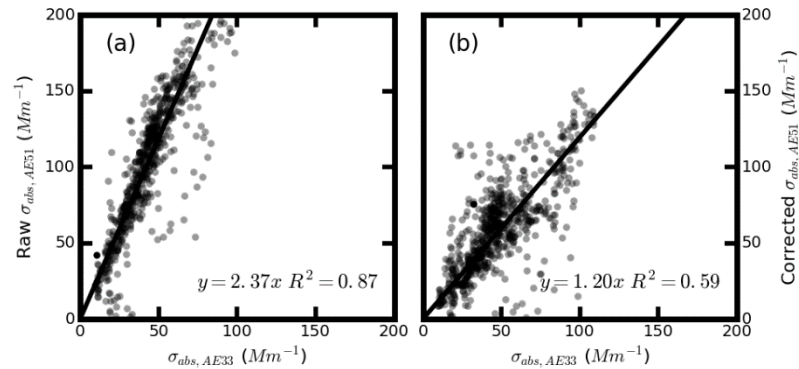
42 **3. Time series diagram of scanned aerosol diameters, measured m_{BC} and the aerosol number**



44

45 **Figure S3** (a) the diameters of the aerosols that pass through the DMA (b) The σ_{abs} values measured
46 by AE51, (c) the aerosol number concentrations measured by CPC.

47 4 Validation of the multiple charging corrections



48

49 **Figure S4.** σ_{abs} measured by AE33 versus σ_{abs} integrated from AE51 of (a) uncorrected
50 size-resolved σ_{abs} , (b) multiple-charging corrected size-resolved σ_{abs} .

51

52 5 Estimate the DARF

53 DARF is defined as the difference between radiative flux at the TOA under present aerosol
54 conditions and aerosol-free conditions:

$$55 \quad \text{DARF} = (f_a \downarrow - f_a \uparrow) - (f_m \downarrow - f_m \uparrow) , \quad (21)$$

56 Where $f_a \downarrow$ is the downward radiative irradiance and $f_a \uparrow$ is the outward radiative irradiance under
57 given aerosol distributions; $(f_a \downarrow - f_a \uparrow)$ is the downward radiative irradiance flux with given aerosol
58 distributions and $(f_m \downarrow - f_m \uparrow)$ is the radiative irradiance flux under aerosol free conditions.

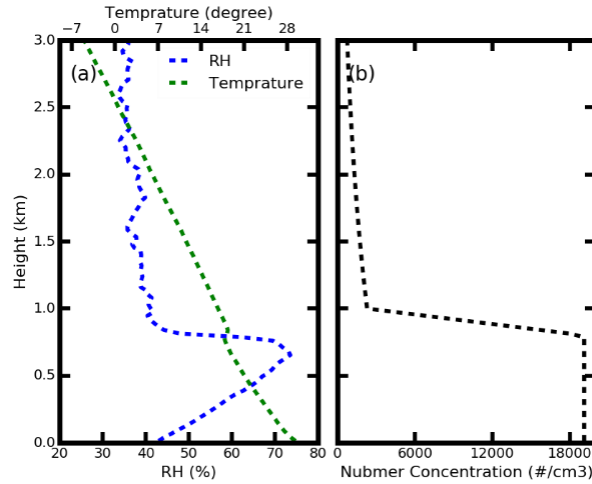
59 Input data for the SBDART are listed below. Vertical profiles of the aerosol optical properties,
60 which include the aerosol extinction coefficient (σ_{ext}), aerosol single scattering albedo (SSA) and g
61 with a height resolution of 50 m, come from the parameterization of aerosol vertical distributions (as
62 shown in fig. S4 and the next paragraph) and the results of the Mie model. Atmospheric gas and
63 meteorological parameter profiles come from the mean results of the radiosonde observations at the
64 Meteorological Bureau of Beijing (39°48' N, 116°28' E), which include profiles for water vapor,
65 pressure and temperature during the spring. Surface albedo values are obtained from the Moderate
66 Resolution Imaging Spectroradiometer (MODIS) V005 Climate Modeling Grid (CMG) Albedo
67 Product (MCD43C3) during March, 2017 of Beijing, where the field campaign is conducted. The
68 remaining input data for the SBDART are set to their default values.

69 **5.1 Parameterization of the aerosol vertical distribution**

70 Liu et al. (2009) studied vertical profiles of aerosol total number concentration (N_a) with aircraft
71 measurements, and derived a parameterized vertical distribution. In this scheme, N_a is constant in the
72 mixed layer, with a transition layer where it linearly decreases and an exponential decrease of N_a
73 above the transition layer. The same parameterized scheme proposed by Liu et al. (2009) is adopted by
74 this study as shown in fig. S4 (b). Both the study of Liu et al. (2009) and Ferrero et al. (2010) manifest
75 that the dry aerosol PNSD in the mixed layer varies little. The shape of the dry aerosol PNSD is
76 assumed constant with height, which means that aerosol PNSD at different heights divided by N_a give
77 the same normalized PNSD.

78 As for the BC vertical distribution, Ferrero et al. (2011) and Ran et al. (2016) demonstrate that BC
79 mass concentration in the mixed layer remains relatively constant and decreases sharply above the
80 mixed layer. According to this, the parameterization scheme of BC vertical distribution is assumed to
81 be the same as that of aerosol. The shape of the size-resolved BC mass concentration distribution is
82 also assumed to be the same as that at the surface.

83



84

85 **Figure S5.** The mean RH, temperature, and aerosol number concentration profiles.

86

87 **5.2 Calculate the aerosol optical profiles under the given RH profile**

88 With the vertical distribution of aerosol PNSD and BCMSD, the aerosol optical properties at a
 89 given RH profile can be calculated by using the Mie scattering model and κ -Köhler theory (Petters and
 90 Kreidenweis, 2007).

91 The aerosol hygroscopic growth is taken into consideration when calculate the aerosol optical
 92 properties under the given RH. The κ -Köhler theory (Petters and Kreidenweis, 2007) is widely used to
 93 describe the hygroscopic growth of aerosol particles by using a single aerosol hygroscopic growth
 94 parameter (κ) and the κ -Köhler equation, which is shown as

95
$$\frac{RH}{100} = \frac{gf^3 - 1}{gf^3 - (1 - \kappa)} \cdot \exp\left(\frac{4\sigma_{s/a}M_{water}}{R \cdot T \cdot D_d \cdot gf \cdot \rho_w}\right), \quad (1)$$

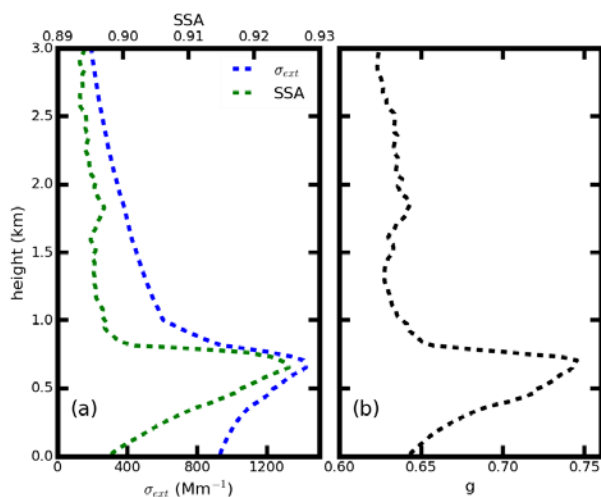
96 where D_d is the dry particle diameter; $gf(RH)$ is the aerosol growth factor, which is defined as the
 97 ratio of the aerosol diameter at a given RH and the dry aerosol diameter (D_{RH}/D_d); T is the
 98 temperature; $\sigma_{s/a}$ is the surface tension of the solution; R is the universal gas constant and ρ_w is the
 99 density of water. The aerosol hygroscopic growth parameter κ can be further used to investigate the
 100 influence of aerosol hygroscopic growth on aerosol optical properties (Tao et al., 2014; Kuang et al.,
 101 2015; Zhao et al., 2017) and aerosol liquids water contents (Bian et al., 2014).

102 The κ -Köhler theory and the Mie scattering model are combined to calculate aerosol extinction
 103 coefficient, aerosol single scattering albedo and aerosol asymmetry factor under different RH
 104 conditions. The measured mean κ , which is derived from the humidified nephelometer system (Kuang

105 et al., 2017), is used to account for aerosol hygroscopic growth. For each RH value, the gf can be
 106 calculated based on equation (1). The corresponding ambient aerosol PNSD at a given RH can be
 107 determined. The refractive index (\tilde{m}), which accounts for water content in the particle, is derived as a
 108 volume mixture between the dry aerosol and water (Wex et al., 2002):

$$109 \quad \tilde{m} = f_{V,dry} \tilde{m}_{aero,dry} + (1 - f_{V,dry}) \tilde{m}_{water} \quad (2)$$

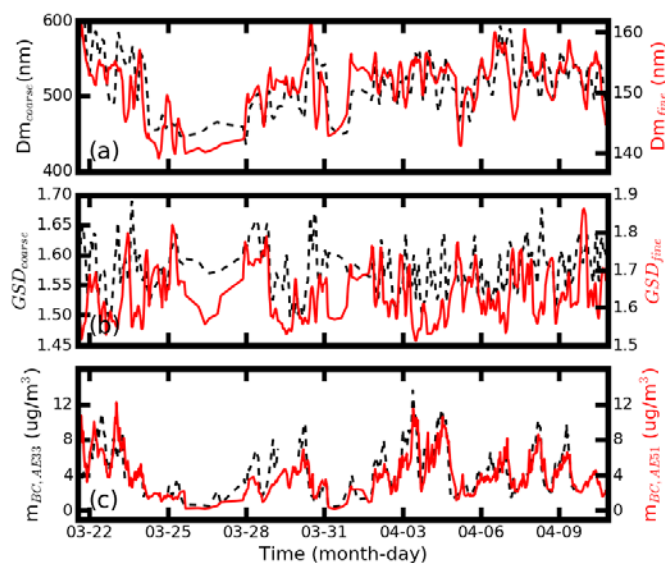
110 where $f_{v,dry}$ is the ratio of the dry aerosol volume to the total aerosol volume under a given RH
 111 condition; $\tilde{m}_{aero,dry}$ is the refractive index for dry ambient aerosols and \tilde{m}_{water} , the refractive index
 112 of water, is $1.33+10^{-7}i$. Then, the corresponding aerosol optical properties under the given RH and
 113 PNSD can also be calculated. Finally, the aerosol optical profiles can be calculated. Fig. S6 shows one
 114 of the calculated aerosol optical profiles.



115
 116 **Figure S6.** The calculated profiles of the aerosol extinction coefficient, aerosol single scattering
 117 albedo and the aerosol asymmetry factor.

118

119 **6 Relationship between the GSD, Dm and mBC**



120

121 **Figure S7.** The (a) D_m and (b) GSD of the BCMSD at coarse mode (black) and fine mode (red); (c)
 122 measured m_{BC} by AE33 (black) and measured m_{BC} from integrated m_{BC} of the BCMSD from AE51.

123

124

125

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160

1 **Role of black carbons mass size distribution in the direct aerosol radiative forcing**

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7 **Abstract**

8 Large uncertainties exist when estimating radiative effects of ambient black carbon (BC) aerosol.
9 Previous studies about the BC aerosol radiative forcing mainly focus on the BC aerosols' mass
10 concentrations and mixing states, while the effects of BC mass size distribution (BCMSD) were not
11 well considered. In this paper, we developed a method by measuring the BCMSD by using a
12 differential mobility analyzer in tandem with an aethalometer. A comprehensive method of multiple
13 charging corrections was proposed and implemented in measuring the BCMSD. Good agreement
14 was obtained between the BC mass concentration integrated from this system and that measured in
15 bulk phase, demonstrating the reliability of our proposed method. Characteristics of the BCMSD and
16 corresponding radiative effects were studied based on field measurements conducted in the North
17 China Plain by using our own designed measurement system. Results showed that the BCMSD had
18 two modes and the mean peak diameters of the two modes were 150 nm and 503 nm respectively.
19 The BCMSD of coarser mode varied significantly under different pollution conditions with peak
20 diameter varying between 430 nm and 580 nm, which gave rise to significant variation in aerosol
21 back optical properties. The aerosol direct aerosol radiative forcing was estimated to vary by 8.45%
22 for different measured BCMSDs of coarser mode, which shared the same magnitude to the variation
23 associated with assuming different aerosol mixing states (10.5%). Our study reveals that the BCMSD
24 matters as well as their mixing state in estimating the direct aerosol radiative forcing. Knowledge of
25 the BCMSD should be fully considered in climate models.

26 **1 Introduction**

27 Atmospheric black carbon (BC) is the second strongest absorbing components in atmosphere
28 (Bond et al., 2013) but the magnitudes of the warming effects are poorly quantified. When emitted to
29 the surrounding, BC particles transform the morphology from fractal to spherical and then grow as
30 fully compact particles with other components depositing on the BC aerosol (Peng et al., 2016). The

31 variation in the shapes of BC aerosols, together with the variation in the mixing states, can lead to
32 substantial change of aerosol optical properties (Liu et al., 2017;China et al., 2013;Wu et al.,
33 2016a;Wu et al., 2018). BC aerosols also have significant influence on the climate by interacting
34 with clouds (Koch and Del Genio, 2010;Roberts et al., 2008;Stevens and Feingold, 2009), ice and
35 snow (Bond et al., 2013). Recent study shows that the solar absorption of BC can suppress the
36 turbulence in the atmospheric boundary layer (Wilcox et al., 2016). It is found that BC emissions
37 may be responsible for the incensement of droughts and floods in China and India (Menon et al.,
38 2002). In addition, BC can pose a serve threat to human health through inhalation (Nichols et al.,
39 2013;Janssen et al., 2011).

40 Comprehensive studies have been carried out to evaluate the climate effect of BC based on the
41 measurement of BC mass concentrations (m_{BC}) (Koch et al., 2009;Ramanathan and Carmichael,
42 2008). The m_{BC} near the ground have been well characterized (Ramachandran and Rajesh,
43 2007;Ran et al., 2016b;Reddington et al., 2013;Song et al., 2013), and the BC vertical distributions
44 are widely measured and evaluated as well (Ran et al., 2016a;Babu et al., 2011;Ferrero et al., 2011).
45 Despite these measurements, more insights into the BC microphysical properties can help to estimate
46 the influence of BC aerosols on visibility (Zhang et al., 2008), climate (Jacobson, 2001) and human
47 health (Lippmann and Albert, 1969). These microphysical properties include BC morphology (Zhang
48 et al., 2016), density (Zhang et al., 2016), complex refractive index (Bond et al., 2013),
49 hygroscopicity (Zhang et al., 2008;Peng et al., 2017), mixing states (Moffet et al., 2016;Raatikainen
50 et al., 2017), and particularly, the mass size distribution (BCMSD) (Cheng et al., 2012;Cheng and
51 Yang, 2016;Gong et al., 2016). Knowledge of BCMSD is not only helpful to study the mixing state
52 of BC aerosols (Raatikainen et al., 2017), but also essential to model the role of BC in evaluating
53 regional and global climate accurately. BC radiative effects is highly sensitive to the emitted BC
54 particle size distribution (Matsui et al., 2018). The health impacts of BC are significantly related to
55 BCMSD (Turner et al., 2015). Furthermore, the information of BCMSD can help to study the source,
56 the evolution and the mixing state of ambient BC aerosols (Yu et al., 2010).

57 Many methods have been proposed to measure the BCMSD. For instance, the BCMSD was
58 measured by sampling the aerosol in the size range from about 50 nm to several micrometers onto
59 quartz fiber filter substrates using a micro-orifice uniform deposit impactor (MOUDI)
60 (Venkataraman and Friedlander, 1994;Guo, 2016). Cheng et al. (2014) developed a method to

61 measure the BCMSD by employing two aethalometers in parallel, with one to measure total m_{BC}
62 and the other to measure m_{BC} below specific particle sizes using a size cut-off inlet. The above two
63 methods measure the BCMSD corresponding to the aerodynamic diameter. The Single Particle Soot
64 Photometer (SP2) is developed and widely used because it provides single particle information, hence
65 the BCMSD and the mixing state of the atmospheric aerosols can be derived directly (Schwarz et al.,
66 2006;Gao et al., 2007;Huang et al., 2012;Singh et al., 2016). The BCMSD corresponding to the
67 ambient aerosol mobility diameter can be measured by using a differential mobility analyzer (DMA)
68 in tandem with SP2 (Raatikainen et al., 2017). However, the laser-induced incandescence method
69 cannot provide reliable information about the particles beyond the range of 70 nm and 400 nm
70 (Moteki and Kondo, 2010), which results in the lack of the knowledge of the BCMSD characteristics
71 for these aerosols over 400 nm. The results from MOUDI find that a great amount of BC locates at
72 the aerodynamic diameter range of between 370 and 1000 nm (Hu et al., 2012;Huang and Yu, 2008).
73 However, the measurements of MOUDI cannot give detailed information of the BCMSD evolution
74 due to the low temporal and diameter resolution (Hu et al., 2012;Huang and Yu, 2008). The
75 characteristics of the BCMSD larger than 370 nm is not well studied due to the limitation of the
76 instrument.

77 Recently, Ning et al. (2013) and Stabile et al. (2012) proposed a new method to measure the
78 BCMSD by using differential mobility analyzer (DMA) in tandem with Aethalometer (AE). This
79 method has the potential of measuring the BCMSD from 20 nm to 584 nm with high time resolution.
80 We develop and validate the BCMSD measurement system based on the works of Ning et al. (2013).
81 The developed measurement system was employed in a field campaign in the North China Plain. The
82 characteristics of the measured BCMSD were studied based on the field measurement. Furthermore,
83 the effects of BCMSD variations on the aerosol optical properties and corresponding direct aerosol
84 radiative properties were evaluated. The aerosol optical properties were calculated by using the Mie
85 scattering theory. The direct aerosol radiative forcing (DARF) were estimated by using the Santa
86 Barbara DISORT (discrete ordinates radiative transfer) Atmospheric Radiative Transfer (SBDART)
87 model.

88 The structure of this paper are organized as follows. Section 2 gives the information about the
89 instrument setup and field measurement. Section 3 gives the detailed method used in this study,
90 which contains: 1, conducting multiple charging corrections when deriving the aerosol BCMSD and

91 2, evaluating the aerosol optical and radiative properties for different BCMSD. Results and
92 discussions are shown in section 4. The conclusion is drawn in the last part.

93 **2 Instrument Setup**

94 The measurement system setup was based on the works of Stabile et al. (2012) and Ning et al.
95 (2013) as schematically shown in Fig.1. The ambient sample aerosol particles were firstly dried to
96 below relative humidity of 30% through a Nafion drying tube before passing through to the DMA
97 (Model 3081, TSI, USA). The DMA scanned aerosol particles with diameter ranges from 12.3 to 697
98 nm over a period of 285 seconds and started another scanning after a pause of 15 seconds, so one
99 complete cycle took 5 minutes. The sheath and sample flow rates of the DMA were 3 lpm and 0.5
100 lpm, respectively. The quasi-monodisperse aerosols that passed through the DMA were further
101 divided into two flows: with one lead to an aethalometer (AE51, Model 51, MicroAeth, USA) with a
102 flow rate of 0.2 lpm to measure the absorption coefficient (σ_{abs}) at 1 second time resolution; and the
103 other one with flow rate of 0.3 lpm flow directed to a CPC (Model 3772, TSI, USA), which counted
104 particle number concentrations at 0.1 second resolution. Clean air with a flow rate of 0.7 lpm was
105 used to compensate for the CPC inlet flow, which had default flow rate of 1 lpm. Overall, the
106 combination system of DMA, CPC and AE51 could provide one PNSD and size-resolved σ_{abs} scan
107 every 5 minutes. If the mass absorption coefficient (MAC) at a given diameter is known, the
108 BCMSD can be derived correspondingly.

109 An aethalometer (AE33, Model 33, Magee, USA) was used to measure the σ_{abs} or m_{BC} with a
110 time resolution of 1 minute. The mass concentration of particles with diameter smaller than 2.5 μm
111 (PM_{2.5}) was concurrently measured with time resolution of 1 minute during the filed observations
112 by the Tapered Element Oscillating Microbalance (TEOM) Dichotomous Ambient Particulate
113 Monitor (1405-DF), which was an indicator of the pollution conditions.

114 From 21 March to 9 April in 2017, an intensive field measurement was conducted to
115 characterize of the ambient dry aerosol BCMSD corresponding to aerosol mobility diameter at the
116 AERONET BEIJING_PKU station (N39°59', E116°18'). This station was located on one roof of
117 Peking University campus in the north west of Beijing, China. There were two main streets, Chengfu
118 Road to the south and Zhongguancun Street to the west that surrounding the station. The aerosol
119 sampled at this station were mainly composed of urban roadside aerosols (Zhao et al., 2018).

120 **3 Methodologies**

121 3.1 Retrieving the BCMSD

122 Five steps were involved to calculate the BCMSD using the raw data from the measurement
123 system: 1), correcting the ‘loading effect’ and ‘multiple scattering effect’ of σ_{abs} measured by AE51;
124 2), matching the instrument time between the AE51 and CPC; 3), matching the measured σ_{abs} and
125 diameter to get the raw size-resolve σ_{abs} that is not involved in multiple charging corrections; 4),
126 conducting the multiple charging corrections of the measured raw size-resolved σ_{abs} ; 5),
127 transforming the size-resolved σ_{abs} into BCMSD.

128 3.1.1 Obtaining the raw size-resolved σ_{abs}

129 The aethalometer (AE51 and AE33) is a well-developed and widely used instrument to measure
130 the σ_{abs} (Drinovec et al., 2015; Hansen et al., 1984). When absorbing aerosols accumulates on the
131 sample filter of the aethalometer continuously, the σ_{abs} can be determined by concurrently
132 measuring the light intensities I after the fiber filter and the light intensities I_0 transmitted through
133 reference spot which is free of aerosol loading. The light attenuation (ATN) is defined as:

$$134 \quad ATN = 100 \cdot \ln\left(\frac{I_0}{I}\right). \quad (1)$$

135 The total σ_{abs} of the loaded particle on the filter is given by:

$$136 \quad \sigma_{abs,tot} = \frac{A \cdot ATN}{100}, \quad (2)$$

137 where A is the sample spot area on the filter. The instantaneous σ_{abs} can be calculated through the
138 increment of $\sigma_{abs,tot}$:

$$139 \quad \sigma_{abs} = \frac{\sigma_{abs,tot}}{\Delta t} = \frac{A \cdot \Delta ATN}{100 \cdot F \cdot \Delta t}, \quad (3)$$

140 where F is the flow rate and ΔATN is the ATN variation during the time period of Δt . The $\sigma_{abs,tot}$
141 can be transformed to m_{BC} when the mass attenuation cross-section (MAC) of BC is known.
142 Traditionally, a constant MAC at 7.7 g/m² was used to deduce the m_{BC} (Drinovec et al., 2015).

143 Corrections of the measured σ_{abs} are necessary because the systematic bias exists due to the
144 prevalingly known ‘loading effect’ and multiple scattering effect (Drinovec et al., 2015; Virkkula et
145 al., 2015; Virkkula et al., 2007). The AE33 can directly provide the corrected σ_{abs} values through
146 measuring two light intensities of two spots with different BC load efficiencies (Drinovec et al.,
147 2015). For AE51, The correcting method in Virkkula et al. (2007) was adopted:

$$148 \quad \sigma_{abs, corrected} = (1 + k \times ATN) \sigma_{abs, uncorrected}, \quad (4)$$

149 where k is the correction factor and a constant value of 0.004 is employed in this study to correct
150 the σ_{abs} from AE51. In the first part of the supplementary material, we showed that the loading
151 effects corrections of σ_{abs} from AE51 were essential and the value of σ_{abs} from AE33 could be used
152 as a reference for the measured BCMSD. As for the multiple scattering corrections, Zhang et al.
153 (2018) compared the measured σ_{abs} measured by AE33 and by Multi-Angle Absorption Photometer
154 (MAAP) at Tsinghua University, which is about 2 km away from our measurement site. They
155 recommended a compensation factor of 2.6 to be used and we adopted the same factor in our study.

156 Time correction was needed because time gaps between voltages implied on the DMA (particle
157 size) and sample particles measured by different instruments were not the same. The time correction
158 procedures were conducted every day during the field measurement to ensure that the time deviations
159 of the CPC and the AE51 were constrained within 2 seconds.

160 Fig. S3 gave the time series diagram of scanned aerosol diameters by DMA, measured σ_{abs}
161 from AE51, and the aerosol number concentrations counted by CPC. The aerosol PNSD (or
162 size-resolved σ_{abs}) could be calculated by matching the DMA diameter and the measured aerosol
163 number concentrations (or measured σ_{abs} by simply using the single particle charge ratio for each
164 electrical mobility diameter. These measured PNSD and size-resolved σ_{abs} did not consider the
165 effect of multiple-charging corrections and are labeled as raw aerosol PNSD and raw aerosol
166 size-resolved σ_{abs} .

167 **3.1.2 Multiple charging corrections of raw size-resolved σ_{abs}**

168 In the work of Ning et al. (2013) study, lots of efforts were made to evaluate the performance of
169 the instrument. They considered the diffusion corrections and particle charging corrections. However,
170 the particle charging corrections were limited to single particle charge ratio as they mentioned that
171 they simplified the particle charge correction by applying the peak electrical mobility for the
172 calculation of representative particle size for each mobility bin and single particle charge ratio for
173 each primary mobility. They ignored the fact that the aerosol samples selected by the DMA were
174 quasi-monodisperse with different charges and different diameters.

175 We proposed a new algorithm for the multi-charge corrections of the size-resolved σ_{abs} .
176 Multi-charge corrections to the measured size distribution were prevailing when the DMA was used
177 to scan the aerosol sizes. When the DMA and CPC are used together to measure the aerosol particle
178 number size distribution (PNSD), the multi-charging corrected aerosol PNSD can be significantly

179 different from the raw measured one (Bau et al., 2014;He and Dhaniyala, 2013;He et al., 2015). As
 180 shown in the results part of this study, the multi-charge corrections of the size-resolved σ_{abs} could
 181 cause differences in both the magnitude and shape of the size-resolved σ_{abs} . Therefore, it is
 182 necessary to perform multi-charge corrections on the size-resolved σ_{abs} . This study developed a new
 183 algorithm to correct the size-resolved σ_{abs} from measured value based on the work of Hagen and
 184 Alofs (2007) and Deng et al. (2011).

185 When the DMA is charged with a negative voltage, those aerosols with a small range of
 186 electrical mobility (Z_p) can pass through the DMA:

$$187 \quad Z_p = \frac{q_{sh}}{2\pi VL} \ln\left(\frac{r_1}{r_2}\right), \quad (5)$$

188 where q_{sh} is the sheath air flow rate; V is the average voltage on the inner center rod; r_1 and r_2
 189 are the outer and inner radius of annular space respectively. The Z_p is related with D_p by
 190 elementary charge (e), number of elementary charges on the particle (n), and gas viscosity poise (μ)
 191 with:

$$192 \quad Z_p = \frac{neC(D_p)}{3\pi\mu D_p}, \quad (6)$$

193 where $C(D_p)$ is Cunningham slip correction:

$$194 \quad C = 1 + \frac{2\tau}{D_p} (1.142 + 0.558e^{-\frac{0.999D_p}{2\tau}}), \quad (7)$$

195 where τ is the gas mean free path. From equation 7, aerosol particles can have the same Z_p despite
 196 that they have different n and D_p . At the same time, there exists a relatively larger portion of
 197 multiple charged particles for those particles with diameters between 100 nm and 400 nm when the
 198 ambient aerosols pass through the X-ray (Tigges et al., 2015;Wiedensohler and Fissan, 1988).
 199 Through the above discussion, the selected aerosols by DMA at a given electrical mobility can have
 200 different charges which will correspond to different diameters.

201 When the scan diameter is set as D_{p_i} for the singly charged particles and the respective voltage
 202 of DMA is V_i ($i=1, 2, \dots, I$), aerosol particles with electro-mobility of $Z_{p,i}$ ($i=1, 2, \dots, I$) can pass
 203 through the DMA and the observed σ_{abs} by AE51 can be expressed as:

$$204 \quad R_i = \int_0^\infty G(i, x)A(x)n(x)dx, \quad (8)$$

205 where x is the scale parameter, with the definition of $x = \log(D_{p_i})$, $A(x)$ is the average σ_{abs} of
 206 single particle for scale parameter x , and $n(x) = dN/d\log D_p$ is aerosol PNSD that is the multiple

207 charging corrected results from the measured aerosol PNSD. We define the kernel function $G(i, x)$,
 208 which is crucial to the algorithm, as:

$$209 \quad G(i, x) = \sum_{v=1}^{\infty} \emptyset(x, v) \Omega(x, v, i), \quad (9)$$

210 where $\emptyset(x, v)$ is the probability of particles that are charged with v charges at the scale parameter
 211 of x (Wiedensohler, 1988). $\Omega(x, v, i)$ is the probability of particles that can pass through the DMA
 212 with v charges at the scale parameter x (Knutson and Whitby, 1975). In this study, the maximum
 213 value of v is 10.

214 The multiple charging corrections can be expressed as computing the $A(x_i^*)$, in which x_i^* is the
 215 predetermined scale parameter from the DMA. To get the numerical integration results of equation 9,
 216 the diameter interval that is 1/50 of the measured diameter is used. Thus, equation 9 can be written as

$$217 \quad R_i = \int_0^{\infty} G(i, x) A(x) n(x) dx = \Delta x_i \sum_{j=1}^{50} \beta_j G(i, x_{i,j}) A(x_{i,j}) n(x_{i,j}), \quad (10)$$

218 where $\beta = \begin{cases} 0.5, & j = 1, J \\ 1, & \text{otherwise} \end{cases}$; $x_{i,j}$ is the j^{th} ($j=1, 2, \dots, 50$) parameter that locates at the parameter x_i and
 219 x_{i+1} and $A(x_{i,j})$ ($i=1, 2, \dots, I; j=1, 2, \dots, 50$), the BC mass ratio at scale parameter $x_{i,j}$, is expressed
 220 as the linear interpolation of the values at the measured diameters.

$$221 \quad A(x_{i,j}) = A(x_i) + P_i(x_{i,j} - x_i), \quad (11)$$

222 where P_i is the slope of the linear interpolation result of

$$223 \quad A(x_k^*) = C + P_i \cdot x_k^*. \quad (12)$$

224 x_k^* refers to these five diameters that are nearest to the predetermined scale parameter x_i . C is the
 225 intercept of the linear interpolation result.

226 With $H_{i,j} = \beta_j \Delta x_i G(i, x_{i,j}) n(x_{i,j})$, equation 11 can be written as

$$\begin{aligned} 227 \quad R_i &= \sum_{j=1}^J H_{ij} [A(x_i) + P_i(x_{i,j} - x_i)] = \sum_{j=1}^J H_{ij} A(x_i) + \sum_{j=1}^J H_{ij} P_i x_{i,j} - \sum_{j=1}^J H_{ij} P_i x_i \\ 228 \quad &= \sum_{k=1}^I (\sum_{j=1}^J H_{ij} \delta(i-k)) A(x_k^*) + \sum_{k=1}^I \left(\sum_{j=1}^J H_{ij} x_{i,j} \delta(i-k) \right) P_k - \sum_{k=1}^I \delta(i-k) P_k x_k^* \\ 229 \quad &= \sum_{k=1}^I Q_{ik} A(x_k^*) + \sum_{k=1}^I T_{ik} P_k - \sum_{k=1}^I Q_{ik} P_k x_k^*, \end{aligned} \quad (13)$$

230 where $\delta(x) = \begin{cases} 0, & x \neq 0 \\ 1, & x = 0 \end{cases}$,

$$231 \quad Q_{ik} = \sum_{j=1}^J H_{ij} \delta(i-k), \quad (14)$$

$$232 \quad \text{and } T_{ik} = \sum_{j=1}^J H_{ij} x_{i,j} \delta(i-k). \quad (15)$$

233 By letting the

$$234 \quad S_i = R_i - \sum_{k=1}^I T_{ik} P_k + \sum_{k=1}^I Q_{ik} P_k x_k^* \quad (16)$$

235 This equation is then expressed as

$$236 \quad S_i = \sum_{k=1}^I Q_{ik} A(x_k^*), \quad (17)$$

237 or

$$238 \quad S = QA, \quad (18)$$

239 where S and A are $I \times 1$ vectors and Q is an $I \times I$ matrix. This matrix can be solved by using the
240 non-negative least square method.

241 Finally, the A(x) can be determined and the corresponding size-resolved σ_{abs} that is multiple
242 charging corrected can be calculated.

243 **3.1.3 Transform the size-resolved σ_{abs} into BCMSD**

244 MAC of different size range is necessary when transform the size-resolved σ_{abs} into BCMSD.
245 The MAC at different size should be different. When the size-resolved σ_{abs} is converted into
246 BCMSD with a constant MAC, the derived BCMSD would be biased.

247 The size-resolved MAC was calculated using the Mie scattering model (Bohren and Huffman,
248 2007). Based on the Mie scattering theory, MAC values vary for different aerosol core diameter and
249 different total diameter. Results from SP2 measurement show that the size distribution of the BC
250 core diameter peaked at around 120 nm in Beijing (Zhang et al., 2017). For each aerosol diameter,
251 the MAC value with core diameter of 120 nm was used to transform the BCASD into the BCMSD.
252 MAC values with core diameter at 120 ± 15 nm were calculated and shown in Fig. 2. From Fig. 2, the
253 MAC varied significantly between 3.6 and 9.2 m^2/g . The constant MAC values 7.7 m^2/g
254 corresponded to the aerosol diameter of 269 nm. The calculated mean MAC values in Fig. 2 under
255 different diameter were used in this study.

256 **3.1.4 Validation of the multiple charging corrections**

257 An example of the multiple charging corrections of the size-resolved σ_{abs} was shown in Fig. 3.
258 The corrections of aerosol PNSD were based on the work of Hagen and Alofs (2007). As shown in
259 Fig. 2(a), the corrected aerosol PNSD was significantly different from the original uncorrected one.
260 There were about half of the measured particles have multiple elementary charge in the size range
261 between 100 and 200 nm. The raw uncorrected aerosol PNSD had a peak value of 10920 cm^{-3} at 98
262 nm while the corrected aerosol PNSD reached its peak value of 8450 cm^{-3} at 98 nm. The peak

263 positions of the raw aerosol particle mass size distribution (PMSD, dm/dlogDp) peaked at 322 nm
 264 with a peak value of 86.3 $\mu\text{g}/\text{m}^3$ and the corrected aerosol PMSD had a peak value of 53 $\mu\text{g}/\text{m}^3$ at
 265 461 nm. The peak position of the aerosol PMSD shifted a lot before and after the multiple charging
 266 corrections. The similar case for the size-resolved σ_{abs} was shown in Fig. 2(b). The shape of
 267 size-resolved σ_{abs} had changed substantially due to the multiple charging corrections. The
 268 measured raw BCMSD had a peak diameter near 320 nm and the magnitude of size-resolved σ_{abs}
 269 plateau reached 34.3 Mm^{-1} , which was in accordance with the results of Ning et al. (2013), where the
 270 multiple charging corrections were not involved. However, the corrected size-resolved σ_{abs} peaks
 271 near 410 nm, with a peak value of about 29.5 Mm^{-1} . According to the result, a small amount of σ_{abs}
 272 remained in particles with diameter between 100nm and 200nm. The measured size-resolved σ_{abs}
 273 changed a lot when multiple charging corrections were implemented, which highlighted the necessity
 274 of implementation of appropriate multiple charging corrections

275 The σ_{abs} integrated from measured size-resolved σ_{abs} changed after multiple charging
 276 corrections. Fig. S4 showed the comparison results of the σ_{abs} measured by AE33 and the
 277 σ_{abs} integrated from AE51 measurements. The σ_{abs} integrated from uncorrected and corrected
 278 size-resolved σ_{abs} versus σ_{abs} measured by AE33 were shown in Fig.S4(a) and Fig.S4(b),
 279 respectively. Before multiple charging corrections, the σ_{abs} from uncorrected size-resolved σ_{abs}
 280 increased linearly with the σ_{abs} from AE33, with R^2 equaling 0.87, but it was 2.37 times that of
 281 AE33 in average. As a comparison, overall magnitude of σ_{abs} integrated from corrected
 282 size-resolved σ_{abs} agreed better with that from AE33 with a slope of 1.2. With the discussion above,
 283 multiple charging corrections were essential for size-resolved σ_{abs} and BCMSD measurements.

284 3.2 Fitting the BCMSD by using two log-normal models

285 Based on the measurement results, the BCMSD had two modes for most of the conditions. The
 286 BCMSD are assumed to be of two log-normal distributions as:

$$287 \quad m_{fit,Dp} = \sum_{i=1,2} \frac{m_i}{\sqrt{2\pi\log(GSD_i)}} \cdot \exp\left(-\frac{[\log(D_p)-\log(D_{m,i})]^2}{2\log^2(GSD_i)}\right), \quad (19)$$

288 Where D_p is the diameter of the aerosols; m_i is the mass of mode i (i=1,2); GSD_i is the geometric
 289 standard deviation at mode i (i=1,2), and $D_{m,i}$ is the geometric mean diameter of the mode i (i=1,2).
 290 The GSD_i and $D_{m,i}$ can be determined by using the least square method with the objective function
 291 as :

292
$$J = \sum_{i=1,n} (m_{Dp_i} - m_{fit,Dp_i}(D_{m1}, GSD_1, D_{m2}, GSD_2))^2, \quad (20)$$

293 Where m_{Dp_i} is the measured mass distribution at Dp_i , while m_{fit,Dp_i} is the fit mass distribution at
294 Dp_i .

295 **3.3 Estimating aerosol optical properties with different BCMSD**

296 The Mie scattering model was used to study the influence of the BCMSD variation on the
297 aerosol optical properties. When running the Mie model, aerosol PNSD and BC were necessary. In
298 this study, The BCMSD was assumed to be log-normal distributed. D_m of the BCMSD was set to
299 vary from 100 nm to 600 nm. Geometric standard deviation (GSD) of the BCMSD was set to be in
300 the range between 1.3 and 1.8. BC was treated as partially externally mixed and the remaining
301 aerosols was treated as core-shell mixed. The ratio of externally mixed m_{BC} to core-shell m_{BC} was
302 determined by the method introduced in Ma et al. (2012) and a mean ratio of 0.51 was used. The
303 density and refractive index of BC were set as 1.5 g/cm³ and 1.8+0.54i (Kuang et al., 2015),
304 respectively. The complex refractive index of non-absorbing aerosols was 1.53+10⁻⁷i (Wex et al.,
305 2002) at the wavelength of 525 nm. More details of calculating the aerosol optical properties by
306 using the aerosol PNSD and BCMSD, can refer to Kuang et al. (2016).

307 The aerosol PNSD and m_{BC} used here is the mean result of aerosol PNSD and m_{BC} over the
308 whole field measurement respectively. The amount of BC particle adopted in this study is the mean
309 value of the m_{BC} measured by AE33. For each BCMSD, extinction coefficient (σ_{ext}), the scattering
310 coefficient (σ_{sca}), the single scattering albedo (SSA), and the asymmetry factor (g) could be obtained
311 from the output of Mie scattering model.

312 **3.4 Evaluating the DARF with different BCMSD**

313 In this study, the SBDART model (Ricchiuzzi et al., 1998) was employed to estimate the DARF.
314 In our study, the instantaneous DARF for cloud free conditions at the top of atmosphere was
315 calculated for irradiance wavelength range from 0.25 to 4 μ m. Input of the model required the
316 profiles of aerosol σ_{ext} , SSA, g . These profiles were calculated from the parameterization of the
317 aerosol vertical distributions. Details of calculating the σ_{ext} , SSA and g profiles can refer to part 4
318 in the supplementary material. In brief, the aerosol σ_{ext} , SSA and g profiles were calculated
319 based on the given aerosol PNSD and BCMSD. The DARF can be estimated using the above aerosol
320 optical profiles.

321 The aerosol optical properties and the corresponding aerosol optical profiles vary with different
322 BCMSD. Then the DARF should be different for different BCMSD. By estimating the DARF using
323 different aerosol BCMSD, the influence of BCMSD on the aerosol radiative properties can be
324 studied.

325 **4 Results and Discussions**

326 **4.1 Measurement results of the BCMSD**

327 The time series of measured PM_{2.5}, aerosol PNSD and BCMSD were shown in Fig. 3. During
328 the observation period, the PM_{2.5} varied from 0.06 to 220 $\mu\text{g}/\text{m}^3$, with a mean value of 71.5 ± 52.56
329 $\mu\text{g}/\text{m}^3$. Three periods of heavy PM_{2.5} loading were observed: (1) PM_{2.5} increased from around 100
330 $\mu\text{g}/\text{m}^3$ to 200 $\mu\text{g}/\text{m}^3$ and decreased slowly to 1 $\mu\text{g}/\text{m}^3$ in the period 21-26, March; (2) the PM_{2.5}
331 accumulated slowly from 28 to 30, March and dissipated quickly from 30, March to 1, April; (3) the
332 rapid accumulation and dissipation of PM_{2.5} happened during 2 to 5, April. During the last five days,
333 PM_{2.5} fluctuated between 20 and 120 $\mu\text{g}/\text{m}^3$. For each pollution condition, both the aerosol total
334 number concentrations and the aerosol median diameter increased. The aerosol median diameter
335 varied between 31 nm and 169 nm with a mean value of 78 ± 31 nm.

336 Our measurements shew that the BCMSD had two modes with the coarser mode ranging
337 between 430 nm and 580 nm in mobility diameter. Many field measurements had revealed that most
338 of the BC mass locates in the aerodynamic diameter range of 320 nm and 560 nm using the MOUDI
339 (Hu et al., 2012;Huang and Yu, 2008). When the aerodynamic diameter was transformed into
340 mobility diameter with assumption a aerosol effective density of 1.3, the measured BC aerodynamic
341 diameter range corresponded to mobility diameter range of 280 nm and 491 nm. Therefore, the
342 measured size range for coarser mode of BCMSD agreed well with the previous measurement.

343 The measured aerosol in the field site was representative of the urban aerosol. The BC particles
344 emitted by vehicles contributed significantly to the total aerosol BC mass. These BC particles were
345 rarely coated or thinly coated, and the BC core diameter peaked around 120 nm (Zhang et al., 2017).
346 Therefore, the BCMSD of the smaller mode measured in our study corresponded to these uncoated
347 of thinly coated particles.

348 The total m_{BC} measured by AE33 ranged from 0.1 to 14 $\mu\text{g}/\text{m}^3$ with an average of 5.04 ± 2.64
349 $\mu\text{g}/\text{m}^3$. Good consistence was achieved between m_{BC} measured by AE33 and m_{BC} calculated from

350 measured BCMSD as shown in Fig. 3(d).

351 **4.2 Evolution of the BCMSD under different polluted conditions**

352 Log-normal distribution was used to fit each mode of the BCMSD by using the least square
353 method as introduced in section 3.2. For each mode, the geometric mean diameter (D_m) and the
354 geometric standard deviation (GSD) of the BCMSD were studied.

355 During the measurement period, both D_m and GSD of the two modes had changed significantly
356 as shown in Fig S7. The D_m of first and second mode varied from 139 to 161 nm and from 420 to
357 597 nm, respectively. The corresponding mean D_m was 151 and 520 nm. The D_m of the two
358 modes was found to be positive correlated in Fig. S7(a). When the pollution was released from the
359 beginning to 27, March, the D_m decreased from 597 to 420 nm and from 160 to 140 nm for the
360 coarser mode and the smaller mode respectively. The BC containing aerosols tended to be aged and
361 grew larger when the air surrounding get polluted.

362 GSD for the coarser mode and the smaller mode showed very different properties as shown in
363 Fig. S7(b). For the second mode, GSD varied from around 1.49 to 1.68 with a mean value of 1.57.
364 The GSD get decreased with the pollution condition, which indicated that BC containing aerosols
365 tend to accumulate to a small range of diameters during the aging processing. This phenomenon was
366 consistent with the fact that larger particles grew relative slower in diameter because the growth ratio
367 of small aerosol particle is proportion to the negative power of it's diameter. For the first mode, GSD
368 ranged from 1.41 to around 1.86 with a mean value of 1.63. However, GSD of the smaller mode tend
369 to be larger when the surrounding air get cleaner, which might be related to the complex sources of
370 the BC emission. A small amount of fresh emitted BC particles can have substantial influence on the
371 mass size distribution of the smaller mode because the BC concentrations of the smaller mode were
372 small, especially under clean conditions. In general, the GSD of coarser mode was a good indicator
373 of the BC aging process and that of the smaller mode could partially reflect the complex sources of
374 the BC fine particles.

375 The relationship between the D_m and the GSD for coarser mode was further analyzed by
376 analyzing the distribution of the D_m and GSD. The GSD and D_m had opposite trends as shown in
377 Fig 5. With the increment of the D_m from 420 to 540 nm, the mean value of GSD decreased from
378 around 1.608 to 1.528 while the m_{BC} increased with the D_m . The statistical relationship between
379 D_m and GSD offered a reasonable representation of the BCMSD under different polluted conditions.

380 In the following work, mean values of the GSD at different D_m were used to for further discussion.
381 The m_{BC} and GSD is positively correlated. The m_{BC} increased from 2.4 to 8.3 $\mu\text{g}/\text{m}^3$ when the
382 D_m increased from 420 to 540 nm.

383 Note that the GSD get slightly increased with the increment of D_m when D_m was larger than
384 520 nm. This might be caused by the limit diameter range of BCMSD measuring system which was
385 from 20 to 680 nm. The multiple charge corrections applied to the BCMSD could influence the
386 BCMSD when D_m of the BCMSD was near the end of the scanned diameter and may lead to
387 significant uncertainties to the BCMSD. The measurement results indicated that cases of measured
388 D_m of BCMSD larger than 520 nm were few, demonstrating that this multiple correction effect
389 influenced little on shape of measured BCMSD in most cases.

390 **4.3 Influence of BCMSD variation on the aerosol optical properties**

391 The aerosol optical parameters using the measured mean aerosol PNSD and mean m_{BC}
392 corresponding to different GSD and D_m values were shown in Fig. 6. In Fig. 6(a), the aerosol g
393 varied from 0.603 to 0.627 (variation of 4%). Recent work by Zhao et al, 2017 showed that the
394 aerosol g value in the NCP may vary at a range of 10% due to the change of aerosol PNSD. Aerosol
395 g was more sensitive to D_m when the geometric mean diameter of the BCMSD was lower than 400
396 nm. However, when the D_m was larger than 400 nm, the g become sensitive to both the D_m and
397 the GSD of BCMSD. Overall, the g varied a little bit (0.02 to 0.609) under the representative
398 conditions during the measurement period. For the aerosol SSA, it was sensitive to the D_m over the
399 whole range as shown in Fig. 6(b). SSA varied between 0.90 and 0.94 under the representative
400 measurement conditions. The σ_{sca} had large changes from 325.6 Mm^{-1} to 364.4 Mm^{-1} . The σ_{sca} was
401 quite sensitive to variations in BCMSD when the D_m was larger than 450 nm as shown in Fig.6c. In
402 addition, variations in σ_{sca} relied more on the variations in D_m when D_m was lower than 400 nm.
403 Within the measurement conditions of BCMSD, the σ_{sca} varied from 328 Mm^{-1} to 345 Mm^{-1} . The
404 measured GSD under different D_m went along with the gradient direction of the σ_{sca} , which mean
405 that the evolution of BCMSD in the atmosphere influenced substantially on σ_{sca} . As for the σ_{abs} , it
406 changed from 24.06 Mm^{-1} to 37.27 Mm^{-1} and the corresponding mass absorption cross section (MAC)
407 was estimated to be in the range of 5.44 to 8.08 m^2/g , suggesting that MAC of the BC aerosols
408 should be carefully studied under different BCMSD conditions.

409 **4.4 Influence of BCMSD on the direct aerosol radiative forcing**

410 The estimated DARF values for different GSD and D_m conditions were estimated. When
411 estimating the DARF, the measured mean aerosol PNSD and mean BC mass concentration were used.
412 The results of estimated DARF were shown in Fig. 7(a). DARF at the surface varied from -4.3 w/m^2
413 to -3.59 w/m^2 for different BCMSD. Within the measured BCMSD range, the DARF varied from
414 -3.97 w/m^2 to -3.67 w/m^2 , which corresponding to 8.45% of variation. The heating rate within the
415 mixed layer was a powerful indicator of the BC particles' absorbing effects, which may help evaluate
416 the development of the boundary layer. The calculated mean heating rate within the mixed layer
417 changed from 2.16 K/day to 2.65 K/day for different D_m and GSD, as shown in Fig. 7(b). The
418 heating rate with the measured BCMSD range could change from 2.24 to 2.50 with a variation of
419 11.6%.

420 Mixing states of BC play significant roles in calculations of aerosol optical properties and
421 estimations of DARF (Jacobson, 2001). As a comparison, we estimated the DARF under different
422 conditions of BC mixing state: (1) internally mixed, (2) externally mixed and (3) core-shell mixed.
423 Table 1 gave the estimated DARF and mean heating rate within the mixed layer under different
424 mixing state conditions. Results showed that the DARF under different BC mixing states conditions
425 may change by 10.50%, which shared the same magnitude with 8.45% variation of DARF caused by
426 BCMSD variations. In addition, the heating rate was estimated to vary by 9.71%. These results
427 highlighted that the BCMSD plays significant roles in variations of aerosol optical properties and
428 estimations of DARF as well as the air heating rate caused by the existence of BC particles. It was
429 recommended that a real time measured BCMSD be used when estimating the aerosol DARF, instead
430 of a constant one. The BCMSD was as important as that of the BC mixing states.

431 **5 Conclusions**

432 Knowledge of the BC microphysical properties especially the size-dependent information can
433 help reduce the uncertainties when estimating the aerosol radiative effects. BCMSD is an important
434 quantity in its own right, being directly and indirectly applicable to determination the sources, aging
435 processes and mixing states of BC aerosols. In this study, the characteristics of BCMSD were studied
436 from the field measurement results by using our own developed measurement algorithm.

437 The BCMSD measurement system was developed and validated based on the works of Ning et
438 al. (2013) by using differential mobility analyzer (DMA) in tandem with Aethalometer (AE). When
439 deriving the BCMSD, a comprehensive multiple charging correction algorithm was proposed and

440 implied. This algorithm was validated by closure study between the measured total m_{BC} from AE33
441 and the m_{BC} integrated from the measured BCMSD using the datasets from field measurements.
442 Results showed that the multiple charging corrections could significantly change the shapes and
443 magnitudes of the raw measured BCMSD. The accurate BCMSD characteristics could be obtained
444 by our proposed method in this paper.

445 The developed measurement system was employed in a field campaign in the North China Plain
446 from 21 March to 9 April in 2017. The BCMSD was found to have two quasi-lognormal modes with
447 peaks at around 150 nm and 500 nm, respectively. These two modes were consistent with the
448 previous measurement results by MOUDI (Wang et al., 2015; Hu et al., 2012). The amount of the BC
449 mass concentrations for the coarser mode peaks were about twice to that of the smaller mode.

450 The characteristic of the BCMSD was studied by fitting the shape of BCMSD with a bi-normal
451 distribution. The relationships between the fitted D_m and GSD were statistically studied. During the
452 aging processing, the opposite trends for the D_m and GSD were found for coarser mode. This is the
453 first time that the coarser mode of the BCMSD were synthetically studied. The BCMSD of coarser
454 mode varied significantly under different pollution conditions with peak diameter changed between
455 430 and 580 nm. However, the relationship between the D_m and GSD for smaller mode BC aerosols
456 were more complex due to the complex sources.

457 When the BCMSD were changed with the polluted condition, the corresponding aerosol optical
458 properties changes significantly. Sensitivity studies found that the aerosol g varies from 0.603 to
459 0.627 due to the variations in BCMSD. Aerosol g was more sensitive to D_m when the geometric
460 mean diameter of the BCMSD is in the range of 300 nm and 370 nm. The SSA can changed from
461 0.90 to 0.94. The σ_{sca} experienced significant change with the variation of BCMSD from 325.6 Mm^{-1}
462 to 364.4 Mm^{-1} and the σ_{abs} changed in the range between 24.064 Mm^{-1} and 37.27 Mm^{-1} . The
463 corresponding BC MAC was calculated to be in the range between 5.44 and $8.08 \text{ m}^2/\text{g}$.

464 The variations in DARF were estimated due to the variations of the BCMSD by using the
465 SBDART model. Results showed that the DARF can varies by about 8.45% for different BCMSD
466 and the heating rate for different measured BCMSD conditions could change from 2.24 to 2.50,
467 corresponding to a variation of 11.6%. At the same time, the variations in DARF due to the
468 variations in the BC mixing state was estimated to be 10.5% and that of the heating rate is 8.45%.
469 Thus, the variations of the BCMSD may had significant influence on the aerosol radiative budget and

470 an accurate measurement of BCMSD was very necessary.

471

472 **Competing interests.** The authors declare that they have no conflict of interest.

473 **Data availability.** The data used in this study is available when requesting the authors.

474 **Author contributions.** GZ, CZ, JT and YK designed and conducted the experiments; CS, YY, CZ and GZ
475 discussed the results.

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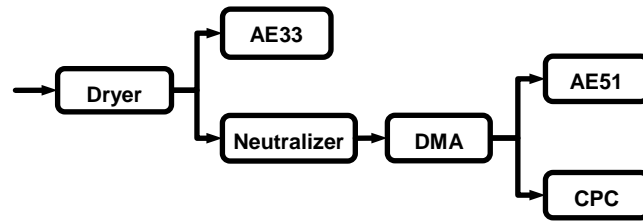
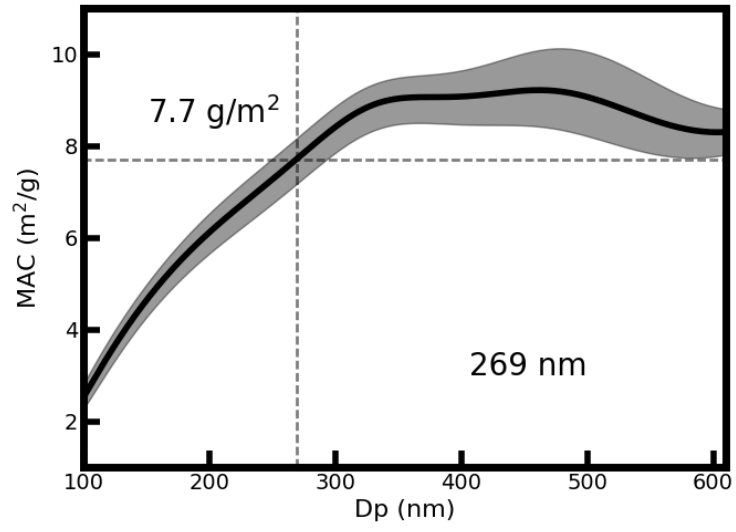


Figure 1. The schematic diagram of the instrument setup.

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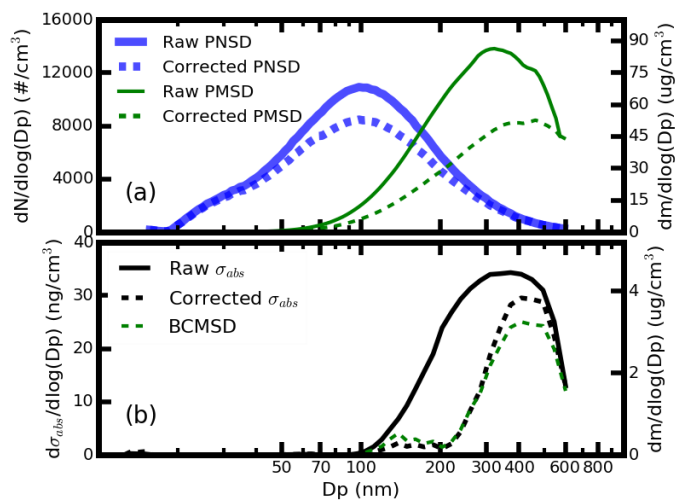


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735 **Figure 2.** Calculated mass absorption coefficient of different aerosol.

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739 **Figure 3.** Case of multiple charging correction processing. (a) the multiple charging correction of the

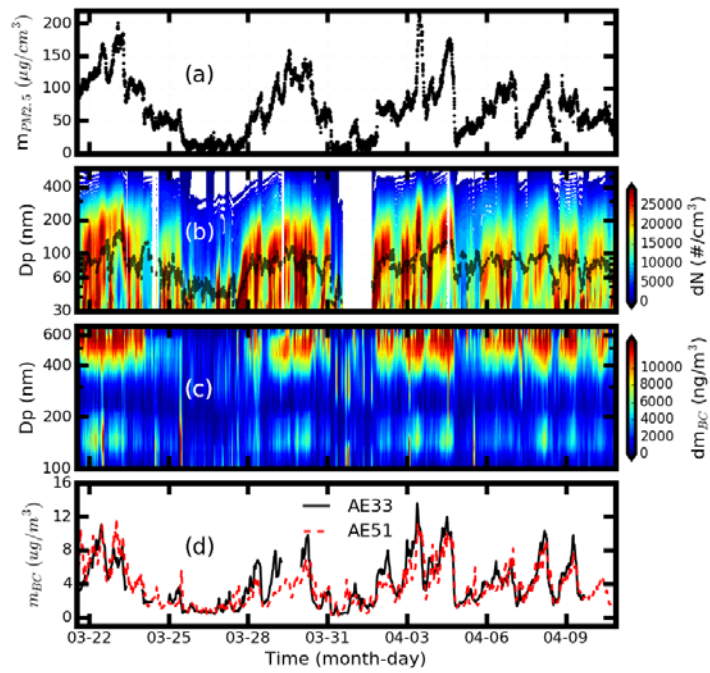
740 aerosol PNSD and aerosol PMSD, (b) the multiple charging correction of the size-resolved σ_{abs} .

741 The solid line is the measured results without multiple charging corrections and the dotted line is the

742 multiple charging corrections results.

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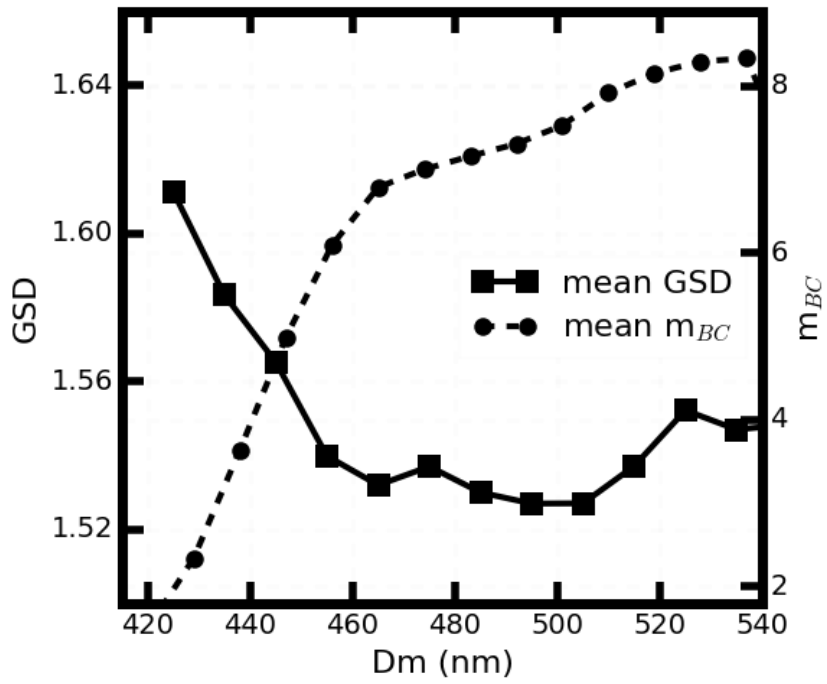
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Figure 4. The measured time series of mass concentrations for (a) the PM_{2.5}; (b) the aerosol PNSD in filled color, the geometric median diameter in dotted line; (c) the BCMSD and (d) the m_{BC} by AE33 (black) and m_{BC} from integrated BCMSD from AE51 (red).

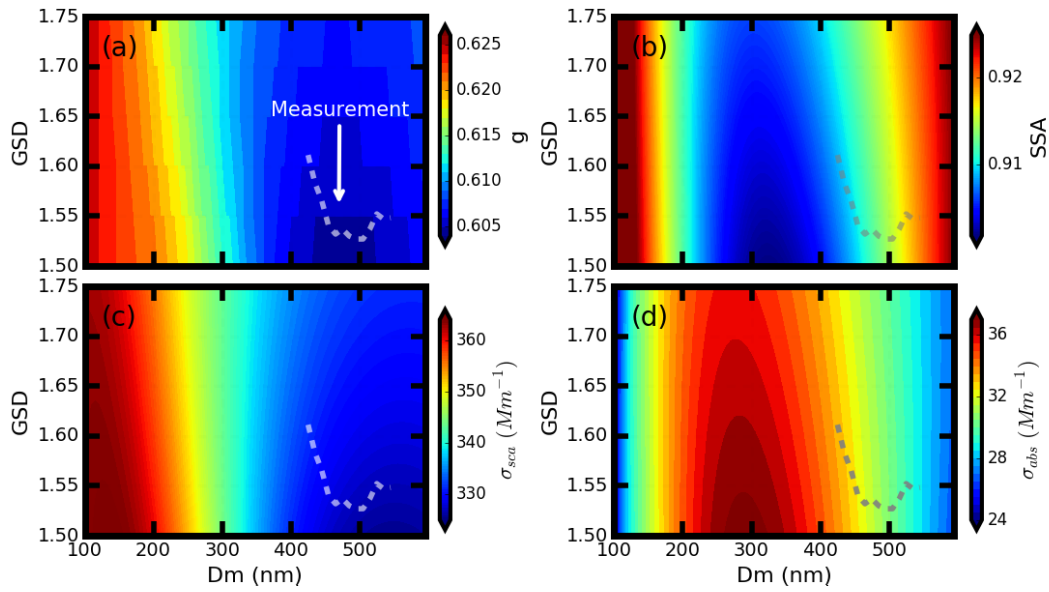
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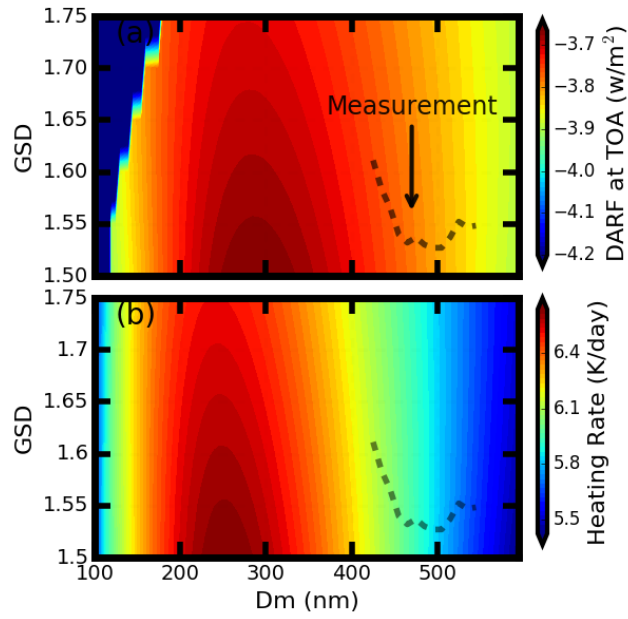
753 **Figure 5.** The relationship between the Dm and the GSD. The black dots show the real measured Dm
754 and GSD. The black line shows the mean results of the GSD for different Dm. The black line marked
755 with square shows the variation of mean m_{BC} with the Dm.

756



757 **Figure 6.** Variations of aerosol optics properties using the measured mean aerosol PNSD and m_{BC}
 758 under different BCMSD conditions, which are represented by different D_m and GSD values: (a)
 759 aerosol asymmetry factor, (b) single scatter albedo, (c) scattering coefficient and (d) extinction
 760 coefficient . The grey dotted line in the figure shows the evolution path of the BCMSD according to
 761 results of field measurements.

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763

764 **Figure 7.** Variations of (a) DARF and (b) heating rate under different BCMSD conditions, which are
 765 represented by different Dm and GSD values. The black dotted line in the figure shows the evolution
 766 path of the BCMSD according to results of field measurements.

767

768 **Table 1.** Comparison of the DARF and heating rate values under different BC mixing states and
 769 different BCMSD conditions.

		Mixing State			BCMSD	
		Internal	External	Core-Shell	Minimum	Maximum
DARF	Value(w/m²)	-3.45	-3.56	-3.81	-3.97	-3.67
	Variation	10.5%			8.45%	
Heat Rate	Value(K/day)	2.51	2.32	2.53	2.24	2.50
	Variation	9.71%			11.6%	

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