Effect of Pollution Level on Size Distributions and Mixing State of Ambient Black Carbon Particles in an Urban Area during Wintertime

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ABSTRACT

We deployed a Single Particle Soot Photometer (SP2) and Single Particle Aerosol Mass Spectrometer (SPAMS) to investigate the size distribution and mixing state of ambient black carbon (BC) particles in Shanghai during the winter of 2017. The mixing state of the particles changed drastically under different meteorological conditions, and higher concentrations often occurred during haze episodes. The BC particles existed in two size modes: the condensation mode, which mainly consisted of fresh traffic-emitted particles, and the droplet mode, which encompassed heavily aged traffic-emitted particles, biomass burning particles and heavy-duty diesel engine emission particles. Whereas the heavily aged traffic-emitted particles exhibited relatively small BC cores (60–80 nm in diameter) surrounded by a thick coating (100–160 nm), the biomass burning particles displayed slightly larger cores (80–130 nm) covered by an even thicker layer (160–300 nm). However, we observed a large number of particles with large cores (150–200 nm) but a relatively thin coating (40–80 nm) on clean days. Trajectory analyses of the air masses showed that they usually originated in local areas or on the North China Plain during haze episodes but mostly migrated from the East China Sea during clean episodes. Interestingly, the BC particles in the clean air masses contained V more frequently and generated intense mass spectrum signals for Ca⁺, suggesting that these particles probably arose from heavy machinery emissions near ports. Our real-time single particle data indicates that the sources of BC aerosol can be easily identified by measuring the size distribution and mixing state of the particles.

Keywords: Black carbon, Size distributions, Mixing state, Source identification

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1 INTRODUCTION

BC aerosols, one of the strongest light-absorbing components in the atmosphere and a major contributor to positive radiative forcing, are produced by incomplete combustion of fossil fuels or biomass (Jayne *et al.*, 2000; Bond *et al.*, 2013). BC is chemically inert in the atmosphere and is mainly in the form of accumulation mode ambient aerosol particle with a diameter range between 0.01 and 1.0 μm (Bond *et al.*, 2013). BC aerosols act as a carrier for many condensable species through physical absorption and heterogeneous chemical reactions on its surface, which can finally modify its morphology, chemical composition and hygroscopicity (Zhang and Zhang, 2005). The presence of non-BC material, such as sulfate, nitrate or organic materials, is thought to increase the light absorption properties of BC particles through “lensing effect” (Wang *et al.*, 2014; Liu *et al.*, 2015; Xie *et al.*, 2019a, b). Moreover, increases in the size and hydrophilicity of BC particles can enhance their removal rate by precipitation scavenging (Liu *et al.*, 2013). These effects have important implications for understanding of radiative forcing and global climate. BC

aerosols usually have an atmospheric lifetime of approximately one week, which is sufficient to allow them to be long-range-transported to other regions (Liu *et al.*, 2011; Wang *et al.*, 2015; Targino and Krecl, 2016). Moreover, direct inhalation of BC particles causes vascular, cardiopulmonary, and respiratory diseases for human (Janssen *et al.*, 2011; Heal *et al.*, 2012). The presence of BC particle in the air also reduce visibility (Zhou *et al.*, 2012; Wang *et al.*, 2013a). Thus, BC is considered as a major air pollutant.

The mixing state of atmospheric BC aerosol is tightly linked to its sources, i.e., they can be emitted as pure BC or along with other inorganic species depending on their sources (Chirico *et al.*, 2010; Heringa *et al.*, 2011). Also, the size distribution and mixing state of ambient BC are very complex and constantly changing in the atmosphere. Atmospheric BC particles often consist of aggregates of small primary spherules 15–60 nm in diameter (Alexander *et al.*, 2008; Zhang *et al.*, 2008). They appear to be chain agglomerates after being freshly emitted from the combustion sources, and they are quickly coated by other aerosol components in the atmosphere, leading to the collapse of the chain agglomerates to more compact core-shell structures (Zhang *et al.*, 2008). Change in the morphology of BC due to a thin coating has a competition effect between light absorption enhancement and reduction, resulting in less overall variation in the absorption efficiency (Wang *et al.*, 2013c; Peng *et al.*, 2016). In contrast, a thicker coating of the scattering shell enclosing the compact BC cores enhances the light absorption of BC by the lensing effect (Schnaiter *et al.*, 2005; Khalizov *et al.*, 2009; Shiraiwa *et al.*, 2010; Peng *et al.*, 2016).

Recently, the Single Particle Soot Photometer (SP2) can measure the mass and size of the refractory BC in high time resolution (Stephens *et al.*, 2003; Schwarz *et al.*, 2006). The mixing state of BC particles can also be derived from the SP2 data (Gao *et al.*, 2007; Moteki and Kondo, 2007; Laborde *et al.*, 2012). The sizes and mixing states of BC particles have been studied only in a few regions in China using SP2 (Huang *et al.*, 2012; Wang *et al.*, 2014; Wang *et al.*, 2015; Wu *et al.*, 2016). Liu *et al.* (2019) studied the size-resolved mixing state of BC-containing particles by an SP2 and their mass spectra was measured by a Soot Particle Aerosol Mass Spectrometer (SP-AMS). They compared two online source apportionment methods using simultaneous measurements made by the SP2, and the chemical approach using the positive matrix factorization (PMF) of mass spectra from the SP-AMS for the first time (Liu *et al.*, 2019). Ding *et al.* (2019) reported comprehensive vertical profiles of BC size-related properties over the Beijing area and continental Europe. The results show that BC coatings were positively correlated with the pollution level). Some investigations on BC particles during different periods show the important role of chemical ageing to the pollution of BC particles in urban Beijing during wintertime (Wang *et al.*, 2019). At the Tibetan Plateau, the BC was overall thickly coated and the coating species were predominantly secondarily formed by photochemical reactions (Wang *et al.*, 2017). The size-resolved chemical components of the BC core and associated coatings were measured by a SP-AMS in suburban Nanjing, and the result shown that increased inorganic fraction and more oxidized organic coatings with thicker coatings, which modified the growth factor besides the determinant of particle size (Wu *et al.*, 2019). However, SP-AMS is a mass-based instrument but is short in quantifying the composition of single particle therefore mixing state.

As a highly complementary instrument to SP2, SPAMS also can detect the chemical properties of BC particles. Combining these two instruments would provide more comprehensive information about chemical and physical properties of BC particles, which can provide us an improved understanding of their sources and evolution processes. Influenced by the local pollutant emissions and long-range transport from other heavily polluted areas, the physicochemical properties of ambient BC aerosols in urban Shanghai are highly varied. In this study, the size distribution and mixing state of BC were analyzed where the observation site is near the port with increased emissions by various heavy machinery in urban Shanghai based on the measurements combining SP2 and SPAMS during a wintertime in 2017 when haze occurred frequently. The time variations in the BC core size and coating thickness were also investigated, accompanied by an analysis of its relation with its potential source contributions. In the present study, source identification of BC aerosols has been studied based on the measured BC size distribution and their mixing state. Noticeably, our previous study by Gong *et al.* (2016) investigated BC particles in a sampling site far from the port and its surrounding industrial area using SP2 and SPAMS during heavily polluted days. We compared the results from this study to Gong *et al.* (2016) and showed how fresh industrial emissions affected BC particle mixing states.

2 METHODS

In situ measurements of ambient BC aerosol were conducted from October 25 to November 3, 2017, using an SP2 (Droplet Measurement Technology, Inc., Boulder, CO, USA) (Stephens *et al.*, 2003; Baumgardner *et al.*, 2004) and a SPAMS (Hexin Analytical Instrument Co., Ltd., Guangdong, China). The sampling site was located on the sixth floor of Environmental Science building on the Jiangwan campus of Fudan University (121.5°E, 31.3°N, approximately 18 m above ground level). The site is surrounded by schools and residential areas. To the east is the ferry terminal station (approximately 500 m) while to the south is a moderately traveled four-lane road. There are no other nearby major industrial sources except the port area.

The 60-min-averaged BC number concentration was measured with an SP2. Ambient air was drawn into the instrument at a low flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ with a $2.5 \text{ }\mu\text{m}$ cut-point inlet cyclone. We only saved data for every hundredth particle in order to extend the sampling time without generating excessively large data sets. A SPAMS instrument was deployed simultaneously with SP2 to detect chemical composition of BC-containing particles. Descriptions of the instruments and operational principles have been described in our previous work (Gong *et al.*, 2016).

3 RESULT AND DISCUSSION

3.1 Overview of the Sampling Conditions

Temporal profiles of SO_2 , CO, K^+ , $\text{PM}_{2.5}$ and PM_{10} mass concentrations obtained at an air quality monitoring site, Shanghai Environmental Monitoring Center (Yangpu Site), which is close to our sampling site (<http://www.semc.com.cn/aqi/home/Index.aspx>), BC number concentration and BC number fraction (NF) measured by SP2 during the study are shown in Fig. 1. The CO concentration showed two major peaks, whose values reached 2.66 mg m^{-3} at 09:00 local time (LT) on

Fig. 1. Temporal profiles of gaseous pollutants (SO_2 and CO), $\text{PM}_{2.5}$ and PM_{10} mass concentrations, BC number concentration and BC number fraction (NF) with 60 min resolution. Cases 1–5 represent the five high BC concentration events during this study.

Fig. 2. BC core number size distribution and mass size distribution from SP2 measurement.

November 3, and 1.16 mg m^{-3} at 08:00 LT on October 29. SO_2 has only one significant peak on November 3. The CO concentration has the similar trend with BC number concentration on October 29 and November 3. The CO concentration does not peak on October 27 and 31, while the BC concentration peaks. The inconsistency of the temporal trends of BC and CO could be due to the 4 km distance between our sampling location and the CO monitoring site.

The $\text{PM}_{2.5}$ concentration also showed two peaks on October 29 and November 3, which maximum value reached $170 \text{ } \mu\text{g m}^{-3}$ (at 11:00 LT on October 29) and $173 \text{ } \mu\text{g m}^{-3}$ (at 09:00 LT on November 3). The PM_{10} concentration had the similar trend as $\text{PM}_{2.5}$. It varied from 21 to $218 \text{ } \mu\text{g m}^{-3}$, with an average of $51.94 \text{ } \mu\text{g m}^{-3}$.

3.2 BC Size Distribution and Number Concentration Measured by SP2

Fig. 2 shows the number and mass size distribution of BC core particles during the entire sampling period. The number size distribution ranges from 60 to 300 nm and the peak was around 60 nm. The measured number concentrations drastically dropped below 60 nm due to the low BC detection efficiency below this particle size (Gong *et al.*, 2016). The BC core mass size distribution had a peak around 180 nm, and the majority of the BC core mass was distributed between 70 and 500 nm.

As shown in Fig. 1, the BC number concentration varied from 53 particles cm^{-3} at 00:00 LT on October 25 to 1147 particles cm^{-3} at 16:00 LT on November 3, with an average of 267 particles cm^{-3} . All of the values above were based on SP2 measurement. It is found that both the BC number concentration and the $\text{PM}_{2.5}$ reached their minimum as well as their maximum at the same time. To a large extent, BC number concentration is positively correlated with $\text{PM}_{2.5}$ mass concentration. There are several exceptions. For example, $\text{PM}_{2.5}$ concentration reached $170 \text{ } \mu\text{g m}^{-3}$ at 11:00 LT on October 29, while the BC number concentration was low (298 particles cm^{-3}). On October 27, high BC number concentration was detected while $\text{PM}_{2.5}$ was low. The details are explained in the following sections.

3.3. BC Particle Classification by SPAMS

Elemental carbon (EC) peaks has been considered a distinct marker for BC aerosols. Hence, using $C_n^{+/-}$ ($n = 1, 2, 3, \dots$) as the marker, a total of 230,105 BC-containing particles were identified, accounting for about 53.91% of detected particles with mass spectra. Then, using ART-2a algorithm (Song *et al.*, 1999), BC-containing particles were classified into five groups based on their mass spectral characteristics, namely *Pure EC*, *NaKEC*, *ECOC*, *KEC*, and *Other*. Their number fractions for each group are shown in Table 1. The average mass spectral patterns of each group are shown in Fig. S1.

Table 1. Names, numbers and fractions of the five types of BC-containing particles detected by the SPAMS instrument.

Type	Number of particles	Fraction of particles
Pure EC	11,307	4.91%
KEC	118,886	51.66%
NaKEC	19,346	8.41%
ECOC	68,883	29.94%
Other	11,683	5.08%
Total BC-containing	230,105	100%

Pure EC particles only presented BC fragment ions (C_n^+ and C_n^-) in both positive and negative ion mass spectra. There was no or very small signals of secondary species, such as sulfate or nitrate, indicating that pure EC type were freshly emitted.

NaKEC particles exhibited strong signals for BC fraction in both positive and negative ion mass spectra; in addition, potassium ($^{39}K^+$) and sodium ($^{23}Na^+$) in positive ion mass spectra and nitrate ($^{-46}NO_2^-$ and $^{-62}NO_3^-$) and sulfate ($^{-97}HSO_4^-$) in the negative ion mass spectra were also exhibited. This group was similar to diesel vehicle emissions (Li *et al.*, 2013; Li *et al.*, 2017).

Mass spectra of ECOC (EC mixed with Organic Carbon) particles showed that BC internally mixed with organic carbon (OC) signals, such as $^{37}C_3H^+$, $^{43}CH_3CO^+$, $^{50}C_4H_2^+$, $^{51}C_4H_3^+$, $^{61}CH_3C(OH)^+$ = OH^+ , $^{62}(CH_3)_2NHOH^+$, and a small signal $^{23}Na^+$ in the positive ion mass spectra, along with BC fragment ions (C_n^+). There was a very high signals for sulfate ($^{-97}HSO_4^-$) and nitrate ($^{-46}NO_2^-$ and $^{-62}NO_3^-$) in the negative ion spectra, suggesting they were aged BC particles that had been aged in the atmosphere. BC particles with various intensities of OC, nitrate and sulfate signals were detected in ambient aerosols by many other ATOFMS (Aerosol Time-of-Flight Mass Spectrometer) studies (Dall'Osto and Harrison, 2006; Moffet *et al.*, 2008; Ault *et al.*, 2009), and this particle type is usually assigned to aged traffic emissions (Healy *et al.*, 2012).

KEC particles were characterized by an intense $^{39}K^+$ signal in the positive ion mass spectra and relatively strong signals for $^{-26}CN^-$ and $^{-42}CNO^-$ in the negative ion mass spectra. Significant fragments of levoglucosan, $^{-71}C_3H_3O_2^-$ and $^{-73}C_3H_5O_2^-$ were also observed. Typical BC fragments C_n^- appeared in the negative ion mass spectra. High signals at $^{-97}HSO_4^-$, $^{-46}NO_2^-$ and $^{-62}NO_3^-$ were also observed, suggesting a significant accumulation of secondary inorganic materials can coat on BC particles in a short time (Reid *et al.*, 2005; Leskinen *et al.*, 2007). This type of mass spectra was previously observed in several field studies and assigned to either biomass burning or coal combustion or both (Moffet *et al.*, 2008; Bi *et al.*, 2011; Healy *et al.*, 2012; Wang *et al.*, 2013b; Gong *et al.*, 2016).

Other particles, which were not grouped into any of the previous four types, accounted for 5.08% in number, including ash, dust, heavy metal and sea salt particles, and they were not the focus in this article. The average mass spectra of this type are displayed in Fig. S1(e).

Noticeably, the particles analyzed by SPAMS are in the size range of 200–2000 nm, and the detection efficiency decreases sharply below 400 nm and above 1200 nm (Li *et al.*, 2011). The majority of the ambient BC particles are smaller than 200 nm (Kondo *et al.*, 2006); thus, SPAMS has low detection efficiency for pure BC particles.

3.4 Mixing State and Size Distribution of Internally Mixed BC Particles

3.4.1 Temporal variations of internally mixed BC particles

A comparison of the internally mixed BC particles number concentration between SP2 and SPAMS is provided in Fig. 3. Considering the different cut-off diameters of SP2 (120 nm < particle diameter [D_p] < 600 nm) and SPAMS (200 nm < vacuum aerodynamic diameter [D_{va}] < 1200 nm), we also plotted the temporal variations of BC-containing particles with vacuum aerodynamic particle size in the size range from 200 to 600 nm.

Vanadium (V) signal, a reliable marker for heavy fuel oil combustion (Ault *et al.*, 2009; Furutani *et al.*, 2011), was present in a significant portion of BC particles mass spectra. One previous study suggests that in Shanghai heavy fuel oil is mainly used by marine vessels passing by, entering or leaving the ports (Liu *et al.*, 2017). V-containing particles are typically emitted by ships or oil

Fig. 3. Temporal profiles of different particles with 60 min resolution. (a) BC number concentration measured by SP2; (b) 200–600 nm BC-containing particles measured by SPAMS; (c) total particle number measured by SPAMS; (d) the number fraction of V-containing BC particles with size in the range of 200–600 nm (f_v); (e) the number fraction of Pb-containing BC particles with size in the range of 200–600 nm (f_{pb}); (f) Pb-containing particles number chosen from BC-containing particles with size in the range of 200–600 nm.

refineries (Ault *et al.*, 2009; Healy *et al.*, 2009). The number fraction of V-containing BC particles with size in the range of 200–600 nm (f_v) was calculated (Fig. 3(d)). Elements that engine wear usually contains (e.g., Cr, Fe, Cu and Pb) are frequently found in the emissions from the tailpipes of motor vehicles (Lim *et al.*, 2007). Temporal variation of the number fraction of Pb-containing BC particles with size in the range of 200–600 nm (f_{pb}) was also plotted in Fig. 3(e).

Temporal variations of BC number concentration detected by these two instruments changed rapidly with a complex pattern, as shown in Fig. 3. For the sake of illustration, we defined the periods from 00:00 to 12:00 on October 25, 00:00 to 12:00 on October 27, 10:00 to 20:00 on October 29, 00:00 to 12:00 on October 31, 00:00 to 12:00 on November 3, as Case 1, Case 2, Case 3, Case 4, and Case 5, respectively. High-resolution temporal variations of BC number concentration shows several peaks of which formation might be due to the typical fresh plume or municipal air pollution. We will discuss this hypothesis in the following paragraphs. To better describe this phenomenon, we colored the three cases (Case 1, 2 and 4) with blue background and the other two cases (Case 3 and 5) with yellow.

For Case 1, 2 and 4, as shown in Fig. 1, both the BC number concentration and BC number fraction detected by SP2 increased sharply, while the $PM_{2.5}$ in Shanghai was maintained at lower values ($PM_{2.5} < 35 \mu g m^{-3}$). The f_v as well as f_{pb} was relatively high during this period compared with Case 3 and 5, indicating that the enhanced BC pollution level was likely from ship or heavy-duty machinery emissions near the ports. f_v displayed strong East China Sea air mass dependences (Fig. 9), consistent with the distribution of f_{pb} , as well as the number fraction of pure EC shown in Fig. 5(e). The port area is the only industrial area close to the sampling location. All of the above suggests that the ports' emissions contributed a significant fraction of BC aerosol measured at the sampling site.

Haze is defined as a weather phenomenon leading to atmospheric visibility less than 10 km due to the suspended solid or liquid particles, smoke and vapor in the atmosphere (Tan *et al.*, 2009; Lee *et al.*, 2014). Former studies indicated that high concentration of $\text{PM}_{2.5}$ is the primary factor causing haze formation (Wang *et al.*, 2012; Cheng *et al.*, 2013; Li and Zhang, 2014). In this article we define Case 3 and Case 5 as *haze period*: The $\text{PM}_{2.5}$ rapidly increased to extremely high values ($\text{PM}_{2.5} = 170 \mu\text{g m}^{-3}$ and $173 \mu\text{g m}^{-3}$, respectively), as well as the number concentration of particles with size from 200 to 2000 nm measured by SPAMS. The BC number concentration detected by SP2 peaks during Case 3 and 5. However, BC-containing particle number with size in the range of 200–600 nm measured by SPAMS was relatively low. The f_v and f_{pb} was also low during these two periods. One likely reason is that, during Case 3 and 5, the sizes of many BC particles detected by SP2 were smaller than the lower end of the SPAMS detection range.

Fig. 4 shows the temporal variations of size distributions of BC particles and cores as well as their coating thickness with 60 min resolution. It is found that the BC particle sizes (from SPAMS) were relatively large on October 29 (Case 3), but their BC core sizes were smaller and their coating were thicker, compared to other sampling time. Note large amount of BC particles with size from 600 to 800 nm were detected by SPAMS while only a small amount of BC particles at these sizes were detected by SP2, which was due to the decreased detection efficiency for large particle size in SP2 ($D_p > 600 \text{ nm}$) (Schwarz *et al.*, 2006; McMeeking *et al.*, 2010).

For Case 2, there were many BC particles with large core sizes (150–200 nm) and thin coating thickness (40–80 nm). Temporal variation of number concentration of such particles was plotted in Fig. 6(d). This type of BC particles was also present on October 31 (Case 4), although the $\text{PM}_{2.5}$ concentration was lower ($\text{PM}_{2.5} < 35 \mu\text{g m}^{-3}$), indicating that regional pollution caused the increase of BC number concentration. Presumably, the air masses from the East China Sea carried such BC particles to the sampling site, leading to the fast increase of this type particles.

3.4.2 Size distribution and source identification of BC particles

The average size distribution of BC particles detected by SP2 was bimodal (Fig. 5(a)). Similar to our previous study, here, we used a $D_p = 280 \text{ nm}$ to separate the condensation mode particles (left side) and the droplet mode particles (right side). The separation of condensation mode ($D_{va} = 200\text{--}550 \text{ nm}$) and droplet mode ($D_{va} = 550\text{--}1200 \text{ nm}$) was confirmed by the SPAMS data (Fig. 5(b)). Here the SPAMS size distribution was based on the number fraction of BC-containing particles in all detected particles. Similar particle size distributions were also found in other studies in China (Huang and Yu, 2008; Zhang *et al.*, 2014). Distinct chemical compositions were found between these two modes (Fig. 5(b)). EC and NaKEC particles exhibited higher number fractions in the condensation mode than in the droplet mode, while KEC and ECOC particles exhibited higher number fractions in the droplet mode. As shown in Fig. 5(c), the condensation mode mainly consisted of fresh traffic emissions with a small BC core (60–80 nm) and thin coating thickness (40–60 nm). The droplet mode mainly included biomass burning (BB) and deeply aged traffic-emitted BC particles, which were consistent to our previous study (Gong *et al.*, 2016). There are a large amount of BC particles with large core (150–200 nm) and thin coating thickness (40–80 nm) in droplet mode, which can be attributed to the distinct emission sources and meteorological conditions.

Time series of hourly averaged particle number of EC and NaKEC with size in the range of 0–400 nm and the BC particles with small core (60–80 nm) and thin coating thickness (40–60 nm) were shown in Fig. 6(a). As shown in Fig. S2(a), a good correlation ($R^2 = 0.493$) between them suggested that they might originate from the same source. EC and NaKEC are considered to be the tracers of traffic emission (Li *et al.*, 2018). The diurnal pattern of this BC type detected by SP2 further confirmed its association with traffic activities, as it showed two significant peaks during morning and evening rush hours (Fig. S2(b)). Mass spectra of EC and NaKEC (0–400 nm) was presented in Fig. 8(a); it can be found that strong signals of BC fragment ions were present in both positive and negative ion mass spectra. In addition, sodium ($^{23}\text{Na}^+$) and potassium ($^{39}\text{K}^+$) in positive ion mass spectra also exhibited. Very small signals of secondary species, such as nitrate ($^{-46}\text{NO}_2^-$ and $^{-62}\text{NO}_3^-$) and sulfate ($^{-97}\text{HSO}_4^-$) were present in the negative ion mass spectra. Therefore, BC particles with small core (60–80 nm) and CT (40–60 nm) were probably emitted by fresh traffic emission.

Fig. 4. (a) Temporal variations of entire particle size distributions for BC-containing particles (200–1200 nm) detected by SPAMS with 60 min resolution. (b), (c), (d) and (e) shows the temporal variation of BC core diameter, coating thickness and particle size (detected by SP2) and number fraction of different types detected by SPAMS with 60 min time resolution, respectively.

Fig. 5. (a) D_p number size distribution histogram for the SP2-detected BC particles; (b) D_{va} number fraction distribution of SPAMS-detected BC-containing particles color coded by the particle type; (c) BC particle number distribution as a function of BC core diameter and coating thickness (the condensation and droplet modes are separated by a solid black line).

The highly aged traffic emissions had small core size (60–80 nm) and thick coating (110–160 nm in thickness). Traffic-emitted BC particles grew rapidly to the droplet mode, indicating that the ageing of traffic-emitted BC particles was fast during the heavy air pollution episode, which has been reported by our previous study (Gong *et al.*, 2016). Time series of this type BC and ECOC (0–700 nm) measured by SPAMS was shown in Fig. 6(b), and the good correlation was shown in Fig. S3 ($R^2 = 0.535$). Higher proportion of highly aged BC particles in haze days (Case 3 and Case 5) than clean days (Case 1, Case 2 and Case 4). The maximum particle number occurred in Case 5 that the $PM_{2.5}$ reached $173 \mu g m^{-3}$ (at 09:00 LT on November 3). Temporal variation of relative coating thickness (RCT; particle diameter/BC core size [D_p/D_c]) of highly aged BC particles ($D_c = 60\text{--}80$ nm and $CT = 110\text{--}160$ nm) was shown in Fig. 7. It is found that the value of the RCT was between 3 and 8, indicating that such BC particles were highly aged in the polluted atmosphere. It is worth noting that the RCT was also positively correlated with the total BC particle number detected by SPAMS in Fig. 4(a).

The previous studies show that fresh BB particles are usually coated by a thick layer of organics (Schwarz *et al.*, 2008; Sahu *et al.*, 2012; Liu *et al.*, 2014; Gong *et al.*, 2016). Here, SP2-detected particles with larger core sizes (80–130 nm) and thicker coating (160–300 nm) were selected and compared with the number concentration of KEC from SPAMS and K^+ mass concentration from monitor for aerosols and gases in air (MARGA), as shown in Fig. 6(c). Significant correlations were

Fig. 6. Temporal variation of different type particle number with 60 min resolution. (a) EC and NaKEC (0–400 nm) type particle compared with BC particle with core (60–80 nm) and CT (40–60 nm); (b) ECOC (0–700 nm) type particle compared with BC particle with core (60–80 nm) and CT (100–160 nm); (c) KEC (0–1200 nm), BC particles with core (80–130 nm) and CT (160–300 nm), and K^+ mass concentration measured by MARGA; (d) EC and NaKEC (400–800 nm) type particle number compared with BC particle number with core (150–200 nm) and CT (40–80 nm).

Fig. 7. Temporal variation of the relative coating thickness (RCT) distribution of highly aged traffic-emitted BC particles detected by SP2 with resolutions of 0.2 RCT and 60 min.

shown in Fig. S4 ($R^2 = 0.624$ and $R^2 = 0.831$, respectively), supporting the conclusion that the BC particles with larger core size and thicker coating were from biomass burning.

Temporal variation of BC particle with core size (150–200 nm) and coating thickness (40–80 nm) number concentration was shown in Fig. 6(d), which exhibits four major peaks, corresponding to BC peak events. Three BC peak events (Case 1, 2 and 4) occurred in clean days with relatively good air quality ($PM_{2.5} < 35 \mu g m^{-3}$). Obviously, higher BC concentration (Case 2 on October 27) are observed during clean days compared to haze periods (Case 3 on October 29), although lower $PM_{2.5}$ concentration is observed, which is probably indicative of the BC aerosol originating from the nearby source regions. Time series of this BC particle type, and EC and NaKEC (400–800 nm) type number concentration from SPAMS were shown in Fig. 6(d). A correlation was shown in Fig. S5 ($R^2 = 0.442$). Mass spectra extracted from Case 2 was shown in Fig. 8(b), characterized by intense $^{40}Ca^+$ and $^{56}CaO^+$ signals, as well as fragments of vanadium ($^{51}V^+$) in the positive ion mass spectra and relatively strong signals for $^{-46}NO_2^-$ and $^{-62}NO_3^-$ in the negative ion mass spectra. However, there was very small signals of sulfate, indicating that this type of BC particle had not

Fig. 8. Averaged mass spectra of different types of BC particles. Major peaks are labeled with the most probable assignments. (a) EC and NaKEC (0–400 nm); (b) EC and NaKEC (400–800 nm).

Fig. 9. Representative HYSPLIT backward trajectories with the air masses from local areas, North China Plain (NCP), and East China Sea. The five figures represent Case 1, Case 2, Case 3, Case 4 and Case 5 in turn.

undergone much ageing in the atmosphere, thus corresponding to thinner coating thickness, suggesting that the BC particles with larger core size (150–200 nm) and thinner coating thickness (40–80 nm) were likely to originate from nearby source regions without undergoing long-range transport and ageing. All of the above mass spectra characteristics meet the criteria for the identification of heavy machinery because calcium containing soot is a well-established tracer for heavy-duty diesel vehicle (Li *et al.*, 2013).

Source regions responsible for BC particle peak events can be deduced by performing an air mass backward trajectory analysis, with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Godłowska *et al.*, 2015). The BC number concentration in the sampling site was influenced by these air masses and the representative trajectories are shown in Fig. 9. Most trajectories are classified into three different types with pollution originating from (1) local areas (2) long-range transport from the North China Plain (NCP) and (3) transport from East China Sea.

As shown in Figs. 9(a), 9(b) and 9(d), all of the three cases (Case 1, Case 2 and Case 4) were influenced by air mass from the East China Sea. From the Fig. 2, it is found that the number fractions of V-containing and Pb-containing BC particles with aerodynamic particle size in the range from 200 to 600 nm were slightly higher than other two cases (Case 3 and Case 5). And temporal variation of number concentration of BC particle with core size (150–200 nm) and coating thickness (40–80 nm) have peaks in these three cases (Case 1, Case 2 and Case 4). This kind of BC is carried by the air masses from the East China Sea, carrying small amounts of V-containing particles, which indicates that this type of BC emitted by ship or the heavy-duty machinery nearby the port.

As shown in Fig. 9(c), Case 3 is impacted by long-range transports from NCP, and BC particles

number concentration measured by SPAMS were extremely high while BC number concentration detected by SP2 was low (Fig. 3). Most of BC particles during Case 3 were large ($D_{va} > 600$ nm) while the number fraction of pure EC was relatively low (Fig. 4(e)), indicating the ageing process during the long-range transport grew BC particles to larger sizes. In contrast, the BC particle peak during Case 5 was caused by local pollution. BC particles with large core size and thin coating thickness were likely to be from the ports near our sampling site.

4 CONCLUSIONS

In this study, we characterized the ambient BC particles during both clean and polluted periods in wintertime Shanghai by analyzing their size distribution and mixing state with an SP2 and a SPAMS, which can detect the physical and chemical properties of BC aerosol at the resolution of a single particle. The SP2-measured number concentration averaged $268 \text{ particles cm}^{-3}$ and peaked at $1147 \text{ particles cm}^{-3}$ on November 3, 2017, at 16:00 LT. The number and mass size distributions of the BC cores fell approximately in the ranges of 60–300 nm and 60–500 nm with peaks around 60 nm and 180 nm, respectively.

The internally mixed BC particles displayed a bimodal size distribution: The condensation mode, which was distinguished by a small core (60–80 nm) and a thin coating (40–60 nm), primarily consisted of fresh traffic emissions, whereas the droplet mode comprised biomass burning emissions, heavily aged traffic emissions and heavy-duty diesel emissions (from engines or ships). The droplet mode particles originating from traffic and biomass burning exhibited a small core (60–80 nm) with a thick coating (100–160 nm) and a medium-sized core (80–130 nm) with an extremely thick coating (160–300 nm), respectively. Interestingly, BC particles arriving in air masses from the East China Sea contained a large core (150–200 nm) surrounded by a thin layer (40–80 nm), most likely identifying heavy machinery near ports as the source.

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SUPPLEMENTARY MATERIAL

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