Effects of Volatile Components on Mixing State and Size Distribution of Individual Black Carbon Aerosols

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ABSTRACT

In this study, the effects of different volatile components on the mixing state and size distribution of ambient individual black carbon (BC) aerosols were measured using thermodenudation with single-particle soot photometry and single-particle aerosol mass spectrometry from September 9 to September 27, 2018, in Shanghai, China. The volatility, chemical composition, size distribution, and core-shell structure of BC aerosol were also analysed. To understand the influence of heating temperature on the BC core-shell structure, the mixing state of ageing particles at room temperature (25°C) and the mixing state of residual material heated to 150°C and 300°C were analysed. BC was internally mixed with secondary components, such as ammonium nitrate, ammonium sulphate, a small amount of sodium nitrate, potassium nitrate, sodium sulphate and potassium sulphate, and other nonvolatile components. At 300°C, the secondary components with low volatility escaped, resulting in a thinner BC coating. However, several low-volatile non-BC substances remained, namely organic species, potassium chloride, potassium nitrate, and other nonvolatile substances. The extremely strong photochemical reaction may have produced large amounts of secondary organic carbon on the BC surface in the afternoon, with the high temperature volatilising the whole particle. However, fresh BC particles emitted from traffic during morning rush hour had ultralow volatility, with relatively fewer low-volatile components on the surface.

Keywords: Black carbon, Mixing state, Size distributions, Volatility

1 INTRODUCTION

The rapid industrialisation and urbanisation in the past few decades have led to severe air pollution across China that has adversely affected people's lives and health (Zhang *et al.*, 2015a; Lelieveld *et al.*, 2020). Although research has demonstrated that air quality in China has improved considerably in recent years (Wang *et al.*, 2018), adverse meteorological conditions, regional transport, heterogeneous reactions, and other factors have led to occasional extreme haze weather events, especially in spring and winter (Zhang *et al.*, 2015b).

Black carbon (BC) aerosol, one of the major contributors to positive radiative forcing and a key atmospheric light absorber, is produced from the incomplete combustion of wood and biomasses, such as crop residue and fossil fuels (Jayne *et al.*, 2000; Bond *et al.*, 2013). BC aerosol can be a carrier of coagulable species, and its morphology, size, chemical composition, and mixing state are influenced by physical adsorption and multiphase chemical reactions occurring on its surface (Zhang and Zhang, 2005). Several secondary components, such as nitrate and sulphate, can enhance

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the light absorption of BC particles through the lens effect (Wang *et al.*, 2014a; Liu *et al.*, 2015; Xie *et al.*, 2019). In addition, the mixing state of BC particles influences BC's hygroscopicity, affecting its rate of wet deposition removal (Liu *et al.*, 2013). An in-depth study of the mixing state of BC is essential to understanding BC's influence on radiative forcing and global climate change (Liu *et al.*, 2011; Wang *et al.*, 2015; Cre and Krecl, 2016). In addition to BC particles in the air reducing visibility (Zhou *et al.*, 2012; Wang *et al.*, 2013a), direct inhalation of BC particles can lead to diseases of the blood vessels, heart, and respiratory system (Janssen *et al.*, 2011; Healy *et al.*, 2012), implicating BC as a major air pollutant.

The mixing state of ambient BC (i.e., BC either emitted as pure BC or mixed with other inorganic components) is closely linked to its initial source (Chirico *et al.*, 2010; Heringa *et al.*, 2011). The particle size, chemical composition, and mixing state of BC in the atmosphere are complex and dynamic, and BC aerosol particles can condense on surfaces through water vapour and form a surface coating composed of secondary components, such as sulphate, nitrate, and organic carbon after ageing in the atmosphere (Pratt *et al.*, 2011). These coating components lead to changes in particle size, chemical composition, mixing state, hygroscopicity, and optical properties at the single-particle level, which hinders the traceability of such aerosols (Lelieveld *et al.*, 2002; Kanakidou *et al.*, 2005; Adler *et al.*, 2011).

A number of studies on BC have been conducted and they are mainly focused on BC mass concentration, chemical characteristics and optical properties (Wu *et al.*, 2017; Meng *et al.*, 2016). Wang *et al.* (2019) studied the BC particles in Beijing and the result revealed that the secondary components, such as nitrate, sulfate and organic components, have obvious influence on the BC properties, significant for particles with larger BC core and thicker coating. Further time-resolved investigation on BC particles indicated that the more polluted periods, the greater contribution of secondary components, and BC with thicker coating is more likely to associate with secondary components, indicating that chemical ageing plays an important role in BC pollution in Beijing (Wang *et al.*, 2019). Wang *et al.* (2021) investigated the optical properties of BC models (including bare, parted coated and embedded BC particles) constructed by Electron-Microscope-to-BC-Simulation (EMBS). The multiphase processes, condensation and coagulation of coating materials influenced the coating thickness and mixing state of BC particles in the atmosphere. And the mixing structure between BC coating and its core, coating shape and morphology of BC core directly influence the absorption enhancement of BC particles (Wang *et al.*, 2021).

Volatility, a key physical property of aerosol, is defined by how readily condensed matter vaporises (Jonsson *et al.*, 2007). Aerosol volatility is evaluated based on the evaporation of its different chemical components at characteristic temperatures. A semivolatile component can be vaporised at its boiling point, vapor pressure, and enthalpy of vaporisation, leaving a residual core with low volatility (Johnson *et al.*, 2004; Engler *et al.*, 2007). Typically, volatility is studied using thermo-denudation (TD) in conjunction with other chemical composition measurements. For example, May *et al.* (2012) measured the volatility distribution of single-component aerosol through TD in combination with TD-gas chromatography/mass spectrometry (GC/MS). TD was also coupled with aerosol time of flight mass spectrometry (ATOFMS) to determine the chemically resolved volatility of organic aerosols (Huffman *et al.*, 2009). TD was also combined with ATOFMS for the study of aerosol sizes and chemical compositions (Pratt *et al.*, 2009; Pratt and Prather, 2009). Zhai *et al.* (2015) researched the size, chemical composition, and mixing state of single particles using TD with single-particle aerosol mass spectrometry (SPAMS). However, these studies have not included BC aerosol with extremely low volatility with a refractory core.

2 METHODS

In this study, a method using SPAMS and single-particle soot photometry (SP2) downstream of TD was developed to simultaneously measure the real-time size and mixing state of ambient individual BC aerosols. The experiment was conducted in the urban area of Shanghai, a typical polluted mega-city in China. The residual components of aged BC particles at three temperatures were compared to understand the mixing state of BC and its atmospheric volatility. The effects of different volatile components on the particle size, chemical composition, and mixing state of BC

Fig. 1. Schematic of the experimental device.

were identified, which may provide insights into the effects of atmospheric processes on the mixing state of BC particles.

2.1 TD-SP2&SPAMS System

The effects of different volatile components on the mixing state and size distribution of single BC aerosols were determined using a custom-built thermo-denuder (TSI Model 3065) with a SP2&SPAMS system (Fig. 1). SP2 (DMT, Boulder, CO, USA) was used downstream of TD to measure the mass and number distribution of BC-containing particles as a function of TD temperatures, and most individual BC-containing aerosols were examined at different heating temperatures. The volatility property of BC surfaces is closely linked to mixing states. SPAMS (Hexin Analytical Instrument Co., Ltd.) was used in parallel with SP2 to determine the chemical composition of BC-containing aerosols heated using TD.

The thermo-denuder comprised a 0.04-m-long metal heating tube and a 0.07-m-long activated carbon adsorption tube (Huffman *et al.*, 2008). First, the aerosol was transmitted into the metal heating tube at a preset temperature. The volatile component encased on the surface of internally mixed particles volatilised and escaped, entering the activated carbon adsorbent in a gaseous form, which prevented its recombination with the particles after condensation. Vapourised gas phase components were absorbed by the activated carbon, and aerosols containing low-volatile components remained. The heating tube was subjected to three heating temperatures: 25°C, 150°C, and 300°C. The aerosols were in the heating tube for approximately 10 seconds.

Ambient particles were added to the thermo-denuder at a rate of $130 \text{ cm}^3 \text{ min}^{-1}$, with a $2.5 \text{ }\mu\text{m}$ cyclone impactor removing particles larger than $2.5 \text{ }\mu\text{m}$. After 1 hour, the BC concentration was measured using SP2. To prolong the experimental time without producing excessively large data sets, data were collected for every 100 particles. SPAMS was used in parallel with SP2 to determine the chemical composition of BC-containing particles. Detailed descriptions of the two detecting instruments and their operation procedures are available in the literature (Li *et al.*, 2011; Gong *et al.*, 2016). A schematic of the experimental device is displayed in Fig. 1.

TD was used to study particle volatility. Generally, volatile temperatures below 150°C, between 150°C and 300°C, and above 300°C are classified as temperatures for highly volatile, moderately volatile, and nonvolatile components, respectively (Ishizaka and Adhikari, 2003). According to the literature, the main compounds volatilising below 150°C are ammonium chloride, ammonium nitrate, formic acid, and acetic acid. The main compounds volatilising at 150°C–300°C are secondary organic carbon, ammonium sulphate, and ammonium bisulphate. The main compounds volatilising above 300°C are potassium sulphate, potassium chloride, BC, and sea salt (Ishizaka and Adhikari, 2003). Thus, we set three temperatures in this experiment: 25°C, 150°C, and 300°C.

2.2 Sampling

The experiment was conducted from September 9 to September 27, 2018, using the TD-SP2&SPAMS system. The sampling site was on the sixth floor of the Department of Environmental Science and Engineering of the Jiangwan Campus of Fudan University ($31^{\circ}20'\text{N}$, $121^{\circ}30'\text{E}$), a

Fig. 2. Temporal profiles of $\text{PM}_{2.5}$, PM_{10} , and gaseous pollutants (CO , NO_x , and SO_2) mass concentrations with 1-hour resolution

location considerably influenced by traffic emissions and human activity due to its vicinity to commercial and residential areas.

2.3 Overview of Meteorology

Temporal profiles of $\text{PM}_{2.5}$, PM_{10} , NO_x , SO_2 , and CO concentrations during the observation period were obtained from the Shanghai Environmental Monitoring Center (Yangpu Station), which is located approximately 6 km from the sampling location. The air quality and meteorological information are displayed in Fig. 2. During the observation period, the mass concentration of $\text{PM}_{2.5}$ peaked at 8:00 on September 21 ($79 \mu\text{g m}^{-3}$), which was less than $80 \mu\text{g m}^{-3}$. The $\text{PM}_{2.5}$ mass concentrations remained below $45 \mu\text{g m}^{-3}$ at all other times. The maximum PM_{10} concentration was $103 \mu\text{g m}^{-3}$ at 20:00 on September 23, indicating that air quality was higher during that period. The measured gaseous pollutants of the study period are presented in Fig. 2. During the sampling period, the mass concentrations of CO and NO varied from 0.369 to 1.988 mg m^{-3} and from 1.00 and $131.00 \mu\text{g m}^{-3}$, respectively; the average CO and NO concentrations were 0.66 mg m^{-3} and $7.11 \mu\text{g m}^{-3}$, respectively.

3 RESULTS AND DISCUSSION

3.1 Diurnal Variation in BC Number Concentration and Proportion

A thermo-denuder was connected with SPAMS and SP2; the automatic valve was set to change the temperature every 60 minutes to enable the study of the influence of different volatile components on the ambient BC mixing state. The thermo-denuder was set at three heating temperatures to measure changes in BC particle size and core-shell structure as well as chemical composition of volatile components before and after volatilisation.

The diurnal variation in the BC number fraction (i.e., the ratio of the BC number concentration to that of total particles at a given temperature) is presented in Figs. 3(a) and 3(c). Obvious peaks occurred at 8:00 and 18:00 at room temperature and 150°C . This trend was more pronounced at

Fig. 3. Diurnal variation in BC number concentration and number fraction.

25°C, which is likely due to traffic emissions in the city. As indicated in Fig. 3(a), the BC number fraction (measured using SPAMS) increased considerably with the increase of the thermo-denuder temperature. When BC was mixed with other secondary substances and the atmosphere contained numerous non-BC substances at room temperature, the BC number fraction was low. When the thermo-denuder heating temperature increased, volatile secondary substances volatilised and escaped, resulting in a decrease in the total particle number, although the BC number fraction increased. The BC number fraction was the highest at 300°C, which was attributable to most non-BC particles having been volatilised and to the low volatility of BC particles. Notably, the maximum BC number fraction was 60% at 300°C, indicating that several low-volatile non-BC substances, such as secondary organic aerosols, potassium chloride, potassium nitrate, and other hydrophilic substances, remained, which is consistent with the findings of other studies (Wang *et al.*, 2014b). Because of the collection efficiency of the instruments, the particle size was not limited in this experiment. As presented in Fig. 3(b), the number concentration of BC-containing particles was the lowest at 300°C and highest at 150°C, which is mainly due to the diameter measuring efficiency of SPAMS. At 300°C, volatile substances on the BC surface escaped, causing the overall BC size to sharply decrease and exceed the detection limit of SPAMS (200 nm). At 150°C, surface volatilisation may cause some large BC to decrease in size; thus, these particles were within the efficient diameter measurement range of SPAMS (500–700 nm). Therefore, the number concentration of BC-containing particles at the experimental temperature was significantly higher than that at room temperature. The diurnal variation in the BC number concentration at 300°C was as follows: from 15:00 to 18:00, the concentration was significantly low, whereas from 9:00 to 12:00, the concentration was high, indicating that many low-volatile components mixed on the BC surface in the afternoon. Therefore, the extremely strong photochemical reaction likely produced secondary organic carbon coatings on the BC surface, and the high temperature volatilised the entire particle. However, fresh BC particles emitted from traffic during morning rush hour have ultralow volatility, with fewer low-volatile components residing on the surface.

As presented in Figs. 3(c) and 3(d), the diurnal variation in the BC number fraction and BC mass concentrations was consistent with that identified using SPAMS. The BC number fraction increased with an increase in the heating temperature. When the thermo-denuder was heated to 300°C, the BC number fraction was high as 90%, which was significantly higher than the fractions obtained

through SPAMS. This is likely because the tube diameters of the two instruments are different; SPAMS is mainly used to measure aerodynamic particle sizes between 200 and 1200 nm, whereas SP2 is mainly used to measure optical particle sizes between 60 and 600 nm. Because BC particles in the air are mainly smaller than 200 nm (Kondo *et al.*, 2006), SPAMS underestimated the BC number concentration. Therefore, the BC number fraction measured using SP2 at 300°C was significantly higher than that measured using SPAMS.

The BC number concentration measured using SP2 exhibited obvious peaks in the morning and evening. However, no significant correlation was identified between the BC number concentration and temperature because the BC particles detected using SP2 contained refractory cores with low volatility, and heating caused only some of the coating components on the BC surface to volatilise; it did not affect BC number concentrations. That is, the BC number concentrations were identical at different temperatures, although the concentrations demonstrated clear diurnal variations, which may be caused by traffic emissions during rush hour (Dreher and Harley, 1998; Allen *et al.*, 1999; Bhugwant *et al.*, 2000). Therefore, although the BC number density was identical under different temperatures, diurnal variation occurred. Heating causes the coatings on the surface to volatilise but has no effect on the number of BC particles. According to the diurnal variation in the BC number fraction, the BC particle peak due to traffic emissions in the morning was significantly higher than the peak in the evening. From 12:00 to 15:00, the BC number fraction had a valley value, indicating that most BC particles were covered by low-volatile components or that much more non-BC particles were present in the atmosphere, which is related to the strong atmospheric chemical reactions that occur in the afternoon.

3.2 BC Aerosol Classified Using SPAMS

In this experiment, a total of 497,092 particles with positive and negative mass spectra were detected using SPAMS. Elemental carbon (EC) ion clusters detected using SPAMS are considered key markers of BC particles (Gong *et al.*, 2016). In this study, using $C_n^{+/-}$ ($n = 1, 2, 3...$) as the BC marker, 288,232 BC particles were identified, accounting for 58.0% of the detected particles. Using adaptive resonance theory (ART-2a), BC particles were classified according to their mass spectra similarities (Song *et al.*, 1999). As in other studies (Li *et al.*, 2018; Spencer *et al.*, 2007; Huang *et al.*, 2013; Gong *et al.*, 2016; Zhai *et al.*, 2017; Li *et al.*, 2018), the learning rate, vigilance factor, and iterations for the ART-2a algorithm were set to 0.05, 0.85, and 20, respectively. Finally, all BC particles were manually divided into five types based on the similarity of the main components of the particles. These types were EC, ECOC, NaKEC, KEC, and Other. The average mass spectra and number fractions for each type are presented in Fig. S1 and Table S1, respectively.

The EC particles demonstrated clear EC ion clusters (C_n^+ and C_n^- , $n = 1, 2, 3...$) in both positive and negative ion mass spectrometry. The signal for the secondary components ($^{-97}\text{HSO}_4^-$, $^{-46}\text{NO}_2^-$, and $^{-62}\text{NO}_3^-$) was weak, indicating pure EC in the atmosphere that did not undergo ageing and newly emitted pure EC.

The ECOC particles mainly demonstrated EC ion clusters, and in the positive ion mass spectra, the clusters were mixed with organic carbon signals ($^{+37}\text{C}_3\text{H}^+$, $^{+39}\text{C}_3\text{H}_3^+$, and $^{+43}\text{CH}_3\text{CO}^+$). Strong sulphate ($^{-97}\text{HSO}_4^-$) and nitrate ($^{-46}\text{NO}_2^-$ and $^{-62}\text{NO}_3^-$) signals were identified in the negative ion mass spectra. The sizes of the ECOC particles were much larger than those of pure EC particles, indicating that ECOC particles are formed by EC particles after atmospheric ageing.

KEC particles mainly originate from biomass or coal burning (Moffet *et al.*, 2008; Bi *et al.*, 2011; Healy *et al.*, 2012; Wang *et al.*, 2013b; Gong *et al.*, 2016; Li *et al.*, 2018). The notable characteristic of KEC particles is that the positive ion mass spectra contain $^{+39/41}\text{K}^+$ and $^{+213/215}\text{K}_3\text{SO}_4^+$ signals (Silva *et al.*, 1999; Hudson *et al.*, 2004), whereas the negative ion mass spectra contain $^{-26}\text{CN}^-$ and $^{-42}\text{CNO}^-$ signals. Levoglucosan fragments ($^{-71}\text{C}_3\text{H}_3\text{O}_2^-$ and $^{-73}\text{C}_3\text{H}_5\text{O}_2^-$) are also observed.

The NaKEC particles demonstrated EC fragment ions in both positive and negative ion mass spectra. Moreover, $^{+23}\text{Na}^+$ and $^{+39}\text{K}^+$ and $^{-97}\text{HSO}_4^-$ and $^{-46}\text{NO}_2^-$ and $^{-62}\text{NO}_3^-$ were present in the positive and negative ion mass spectra, respectively. According to the literature, these ions were likely emitted by diesel vehicles (Li *et al.*, 2013; Li *et al.*, 2017).

The Other category, comprising particles not belonging to the four aforementioned groups, included heavy metal, dust, ash, and sea-salt particles and accounted for 7.66% of BC-containing particle number. This type of particle was not the focus of this study.

Fig. 4. Diurnal variation in BC-containing particle size.

3.3 Mixing State and Size Distribution of Individual BC Particles

3.3.1 Diurnal variation in BC size distribution

The diurnal variation in BC particle size, measured using SPAMS, is presented in Fig. 4. Notably, aerosols detected using SPAMS were mainly distributed between 400 and 1200 nm, and detection efficiency decreased when the size became smaller than 400 nm and larger than 1200 nm (Li *et al.*, 2011). As indicated in the figure, the BC aerosol size was related to the thermo-denuder heating temperature. The BC size was maximum at 150°C. One reason for this may be that heating causes low-volatility components in the air to coat the BC surface, enlarging the entire particle. Another reason is that volatilisation of the surface components causes the reduction of sizes of some large BC aerosols, and they coincidentally fall within the SPAMS detection range. The diurnal variation in BC-containing particles showed a bimodal distribution, with two peak values appearing at 3:00 and 12:00, which is attributable to the decrease in urban traffic emission in these two periods. The BC particles emitted by vehicles are smaller than those from other BC sources (Harris and Maricq, 2001; Zervas and Dorlhène, 2006; Xue *et al.*, 2015). Many vehicles emit fresh BC particles during rush hour in both the morning and evening, resulting in clear valley values in BC-containing particle sizes, which is consistent with the diurnal variation in the EC and NaKEC size distribution. Studies have indicated that EC and NaKEC mainly originate from motor vehicle emissions (Li *et al.*, 2018; Li *et al.*, 2021). The sizes of EC and NaKEC particles are significantly smaller than those of KEC and ECOC particles under the same temperatures, which is consistent with previous results (Li *et al.*, 2018). The size of ECOC particles increased with an increase in the heating temperature. This may be because high temperatures cause some ECOC surface components to volatilise, leading to a decreased particle size that falls within the efficient detection range of SPAMS. The ECOC size at night was larger than that in the day at 300°C, which differs from the diurnal change that occurred at 25°C. However, the EC and NaKEC particle sizes decreased with an increase in temperature. This is because the volatile components on the surface escaped with volatilisation due to the high temperature, resulting in smaller particle sizes.

3.3.2 Diurnal variation in BC chemical composition

The diurnal variation in BC number concentrations identified using SPAMS is presented in Fig. 5. Generally, the maximum number concentrations for each category were attained at 150°C, mainly due to the volatilisation of the surface components of large particles. This resulted in the particle

Fig. 5. Diurnal variation in BC particle number.

size decreasing and falling within the measurement range of SPAMS. At 300°C, all of the volatile components on the BC surface volatilised, leading to a sharp decrease in BC size, which decreased to below the minimum detection range of SPAMS (200 nm). Therefore, at 300°C, the BC number concentration was the lowest. At 25°C, elevated EC and NaKEC number concentrations occurred at 7:00, which can be explained by the increase in traffic emissions during rush hour (Dreher and Harley, 1998; Allen *et al.*, 1999; Bhugwant *et al.*, 2000). Lower boundary layer heights in the early morning also enhanced this trend. Similar trends occurred at 150°C and 300°C. The number of all types of BC was the lowest at 300°C, which can be explained by the majority of BC sizes being much smaller than the SPAMS detection limit. At 25°C, elevated KEC concentrations occurred at 18:00, which may be caused by the use of straw for cooking in rural areas around Shanghai in the evening. Favourable diffusion conditions, a higher daytime boundary layer, and a lower boundary layer at night are key factors that caused the KEC concentration to be higher at night than that during the day.

3.3.3 Diurnal variation in BC core-shell structures

The diurnal variation in average BC cores and coating thicknesses at different temperatures are displayed in Fig. 6. The smallest core size and the thickest coating occurred in the TD at the lowest temperature. As the temperature increased, the coating decreased and the BC core size increased. The BC coating volatilised and escaped during the heating process, causing the coating to become thinner. In this experiment, particles of different sizes flowing into SP2 were not limited to enable the detection of BC particles from different sources. Because SP2 has an efficient size range of 70 to 600 nm, most ambient BC particles below 200 nm can be collected using SP2. As indicated in Fig. 6, the BC core size was inversely correlated with its coating thickness. This experiment used the average results of numerous BC particles, which were affected by the detection efficiency of the instruments. At 300°C, the BC coating was thicker in the day than at night because of the different chemical compositions of the coating. The coating components were mainly secondary organic carbon generated by photo-oxidation in the daytime and secondary inorganic salts at night. The low volatility of secondary organic carbon prevents them from easily escaping. However, secondary inorganic salts are highly volatile and escaped completely from the BC surface when it was heated to 300°C. This resulted in a thicker BC coating being observed during the day than at night at 300°C.

Fig. 6. Diurnal variation in BC core size and coating thickness.

4 CONCLUSIONS

In this study, a TD-SP2&SPAMS system was applied to explore the effects of different volatile components on the mixing state and size distribution of ambient individual BC aerosols in Shanghai. Three temperatures (25°C, 150°C, and 300°C) were selected for observation of the diurnal variations in the BC mixing state. The average mass spectra of five BC types at three heating temperatures were compared. At room temperature, strong signals of nitrate and sulphate were observed in ECOC and KEC particles, suggesting that they were highly aged. After secondary components coated on BC surfaces volatilise, the residue on the BC core with a simplified mixing state can enable the identification of the primary source of BC when heated using TD.

The results demonstrated that, at room temperature, BC mixes with other secondary substances, and the BC number fraction becomes low. At 300°C, the secondary components volatilise, resulting in a thinner BC coating. Due to the decrease in the particle number and BC with low volatility at 300°C, the BC number fraction increases to approximately 60%, indicating the presence of some low-volatility non-BC substances, which may be secondary organic aerosols, potassium chloride, potassium nitrate, and other extremely low-volatility substances. This study demonstrated that atmospheric ageing considerably influences the BC mixing state. Information on diurnal variation in the BC mixing state and core-shell structure is essential to the evaluation of the ageing process, wet removal, and the climate effects of BC aerosol.

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SUPPLEMENTARY MATERIAL

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