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## Seasonal and spatial variations of optical properties of light absorbing carbon and its influencing factors in a typical polluted city in Yangtze River Delta, China

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Dong Chen<sup>a</sup>, Yu Zhao<sup>a,b,\*</sup>, Ritao Lyu<sup>a</sup>, Rongrong Wu<sup>a</sup>, Liang Dai<sup>a,c</sup>, Yi Zhao<sup>c</sup>, Feng Chen<sup>d</sup>, Jie Zhang<sup>b,d</sup>, Huan Yu<sup>c</sup>, Miao Guan<sup>a</sup>

<sup>a</sup> State Key Laboratory of Pollution Control & Resource Reuse and School of the Environment, Nanjing University, 163 Xianlin Ave., Nanjing, Jiangsu, 210023, China

<sup>b</sup> Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, CICAEET, Nanjing, Jiangsu, 210044, China

<sup>c</sup> School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing, Jiangsu, 210044, China

<sup>d</sup> Jiangsu Provincial Academy of Environmental Science, 176 North Jiangdong Rd., Nanjing, Jiangsu, 210036, China

## GRAPHICAL ABSTRACT



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## ABSTRACT

A major challenge in understanding radiative forcing of aerosols is accurately monitoring the light absorbing components and clarifying the main reasons of their spatial and temporal variations. In this study, the optical properties of light-absorbing carbon (LAC) in aerosols were measured over one year and the impacts from various emission sources and other influencing factors were analyzed at three sites (suburban (NJU), urban (PAES) and industrial (NUIST) in Nanjing, a typical polluted city in eastern China. With an improved method that combines online and offline techniques, we revised the multiple scattering correction factors and significantly reduced the uncertainty in measurement of absorption coefficients of black carbon (BC). The result reveals the necessity of developing the regional dependent factor for estimation of BC absorption. Relatively large mass absorption efficiency (MAE) of BC was found in summer and industrial region (NUIST), and the mixing state and coating relevant with secondary aerosol formation were the main reasons for such seasonal and site dependent variations. Distinct seasonal variations existed in the MAE of brown carbon (BrC) at NJU. In the winter, BrC from primary emissions such as diesel vehicles had a stronger absorption ability than that from secondary aerosol formation. The lowest MAE values of BrC appeared in summer, reflecting the formation of the non-absorbing biogenic secondary organic aerosol, and the effect of photobleaching. At the urban site PAES, BrC was expected to be mainly from gasoline vehicles and transport of biomass burning emissions, and had a stronger light absorbing ability than the other two sites. The results of simultaneous observations at NJU and PAES

E-mail address: yuzhao@nju.edu.cn (Y. Zhao).

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<sup>\*</sup> Corresponding author. State Key Laboratory of Pollution Control & Resource Reuse and School of the Environment, Nanjing University, 163 Xianlin Ave., Nanjing, Jiangsu, 210023, China.

indicated that the formation of fresh secondary organic aerosol enhanced the optical absorption of BC but reduced that of BrC. The impacts of various influencing factors on LAC provided effective ways to alleviate their regional radiative forcing at the city scale.

## 1. Introduction

Black carbon (BC) and brown carbon (BrC) are the two major components of light absorbing carbon (LAC). BC was conventionally considered as the light absorption species at the visible wavelengths, and BrC absorbs more light in the near-ultraviolet and blue wavelengths and its light absorption displays strong wavelength-dependence (Bond and Bergstrom, 2006). Such wavelength dependence can be described by Absorption Ångström exponent (AAE), a power exponent of wavelength. The value of AAE is traditionally assumed at 1.0 for BC while it exceeds 1.6 for BrC (Laskin et al., 2015).

The Mass Absorption Efficiency (MAE,  $m^2/g$ ) of BC is an important parameter characterizing the light absorption capacity of BC (Bond and Bergstrom, 2006), and its values vary dramatically depending on the aging of ambient aerosols (e.g., fresh, semi-aged or aged). Cui et al. (2016) found that the enhancement of MAE rises from 1.4  $\pm$  0.3 in fresh combustion emissions to 3 for aged aerosols. Besides, BC mixing state (e.g., internally or externally mixed) is a main factor influencing MAE. Bond et al. (2006) found that BC internally mixed with coating materials (such as sulfate, nitrate, ammonium and organic carbon) can absorb more solar radiation (up to 100%) than externally mixed BC. Another concern in determination of MAE is the potentially large uncertainties in the measurement methods (Cheng et al., 2011). Typically, MAE is calculated by dividing the light absorption coefficient (Abs) by the simultaneously but independently measured elemental carbon (EC, as the mass-based proxy for BC) (Cheng et al., 2011, 2017). In the most cases, Abs measurement is performed by two approaches, the filter-free method and the filter-based attenuation (Schmid et al., 2005). In the former approach, Abs and BC concentration are measured respectively with photo acoustic spectrophone (PAS) and thermal-optical (or thermal) instruments (Arnott et al., 2003), but the light absorption and BC measurements are usually conducted not for exactly the same samples (Shen et al., 2013). The principle of the filter-based attenuation is to detect the change in light transmitted through the filter substrate and aerosols (e.g., Aethalometer and Particle Soot Absorption Photometer). However, there are large uncertainties in this approach due to aerosol-filter interactions including shadowing and multiple scattering effects (Cheng et al., 2011; Ram and Sarin, 2009; Weingartner et al., 2003). Loading particles on the filter absorb a portion of the scattered light, and a reduction of optical path in the filter is caused by the shadowing effects, leading to negative effects in MAE. Multiple scattering by the filter fibers enhances the optical path length, resulting in positive bias in MAE. Weingartner et al. (2003) estimated R(ATN) with the aethalometer data, to rectify the shadowing effects. In order to reduce the deviation by multiple scattering effects, a correction factor (C) was determined by aethalometer operating with incandescent lamps (Jung et al., 2010; Weingartner et al., 2003). The values of C were reported as 2.08-2.14 for pure/external mixtures and 3.64-4.0 for internal mixtures of soot particles, and the value of 2.14 and 3.60 were directly used in ambient aerosol (Jung et al., 2010; Schmid et al., 2005; Weingartner et al., 2003). The C values used in the previous studies were summarized in Table S1 in the supplement. Compared to small variations in R(ATN) (a maximum change of 2% was reported previously, Ram and Sarin, 2009), larger variations found in the C value (an error of 40%, Shen et al., 2013) require further studies for correction of the multiple scattering effects.

Previous studies found that the MAE of BrC exhibited distinct temporal and spatial variations. Hecobian et al. (2010) studied the light absorption of water-soluble organic carbon (WSOC) at 15 sites in the southeastern United States and found that MAE was higher in winter

than summer. Similar patterns were observed in Asian cities including Beijing, Xi'an and Seoul (Cheng et al., 2016; Kim et al., 2016; Shen et al., 2017). Although laboratory studies had examined optical properties of BrC from different sources and suggested MAE of BrC could be highly source dependent (Laskin et al., 2015), the main reasons for seasonal and spatial variations in MAE of ambient BrC are still insufficiently understood due to its complex sources. Biomass burning was typically considered the large primary source for BrC. Du et al. (2014) and Shen et al. (2017) found that BrC associated with biomass burning had a stronger light absorbing ability than that from other sources in Beijing and Xi'an in winter, and the MAE of BrC in Xi'an was observed to be 214% than that in Beijing. Fossil combustion was found to be another important source of BrC in Beijing during winter, and BrC from fossil fuel seemed to have a stronger optical absorbability than that from biomass burning (Yan et al., 2017). In additon to primary emissions, BrC can be generated by gas-to-particle partition processes from anthropogenic or biogenic sources (Nakayama et al., 2010; Zhong and Jang, 2011). For example, secondary organic aerosol (SOA) formation was found to be an important source for BrC in Atlanta and Los Angeles, while large differences existed in MAE values between the two cities due to various types of secondary BrC precursors (Zhang et al., 2011). Besides various types of BrC sources, chromophores in BrC may decompose and photobleach following direct photolysis, and this phenomenon could also result in remarkable seasonal fluctuation of MAE in remote regions, for example, Lulang in the Tibetan Plateau (Li et al., 2016). Although optical properties of BrC have been studied in some Chinese cities (Cheng et al., 2016, 2017; Li et al., 2016; Shen et al., 2017), very few observations were conducted simultaneously at different functional sites within one city to explore the discrepancy in MAE and its main influecing factors. It is in particular necessary for cities with complicated emission sources, as effective control of aerosol pollution requires a comprehensive understanding in formation and multiple influecing factors of the pollution.

In this study, we conducted the measurements on the optical characteristics of LAC over one year in Nanjing, a mega city in the Yangtze River Delta region (YRD) in eastern China. As one of the three developed regions in China, YRD suffered severe air pollution in the past decades (Xu et al., 2017). Nanjing is a city with intensive and complicated sources of air pollutants (Zhao et al., 2015), and the coexistence of primary aerosol emitters (e.g., coal combustion) and those of precursors for secondary aerosols (e.g., chemical and refinery industry) made it a typical case to study the multiple reasons of aerosol pollution. Based on insitu and offline measurements, we developed an improved method to calcualte the revised multiple scattering correction factor and to evaluate the BC absorption in the YRD with reduced uncertainties. Seasonal variations and spatial patterns of LAC optical properties were investigated for the first time at three different functional sites within a Chinese city, and the impacts of influencing factors were identified including primary emissions, secondary aerosol formation and atmospheric condition, etc. The effect of SOA formation on the optical properties of LAC was further quantified through simultaneous observations at different locations of the city.

## 2. Methodology

#### 2.1. Measurement sites and aerosol sample collection

Ambient aerosol samples were collected from suburban (NJU), urban (PAES) and industrial sites (NUIST) in Nanjing. The locations of the monitoring sites were shown in Fig. S1 in the Supplement. The NJU site was on the roof of the School of the Environment building (25 m above the ground level) in the Xianlin Campus of Nanjing University in the suburban area of northeastern Nanjing (32.12°N, 118.96°E), and was about 400 m away from the G25 highway. PAES was a typical urban site in the western downtown of Nanjing (32.05°N, 118.74°E), surrounded by residential, school and commercial buildings and heavy traffic (Li et al., 2015). It was on the roof of the building of Jiangsu Provincial Academy of Environmental Science, 30 m above the ground. NUIST (32.21°N, 118.71°E) was located on the meteorology building of the Nanjing University of Information Science & Technology campus, and it was a polluted industrial site due to the influence from nearby Nanjing Chemical Industry Park (NCIP), iron & steel plants, and power plants (Wang et al., 2016).

All samples were collected with  $PM_{2.5}$  samplers (TH-150C, Tianhong, China) at a flow rate of ~100 lpm. A total of 182, 45 and 44 daily (22-hr cycle starting at 9:00 a.m.)  $PM_{2.5}$  samples were obtained at NJU, NUIST and PAES respectively from November 2015 to March 2017. Particle sampling covered summer, autumn and winter at each site, as summarized in Table S2 in the supplement. The samples from November 2015 to January 2017 at NJU were used to determine the revised correction factor of multiple scattering effects on BC absorption. The other samples at NJU were used to verify the corrected values.

## 2.2. Determination of BC mass and MAE

EC measured by the thermal/optical method is generally used as BC (Cheng et al., 2011, 2016, 2017). For consistency in this study, the term BC is used in all occasions except for the measurements with the thermal/optical method, in which the term EC is used. EC and organic carbon (OC) loading on the collected filters were analyzed using an EC-OC analyzer (Sunset Laboratory, Forest Grove, OR). The analyzer worked in thermal-optical transmittance (TOT) protocol, and the temperature program used in this study was presented in our previous work (Chen et al., 2017). Optically measured elemental carbon (ECopt) was also obtained from Sunset analyzer (monitored at 678 nm), using the same analytical method as aethalometer for BC. The discrepancies between EC<sub>opt</sub> and BC were characterized by different equations and parameters that convert optical attenuation (ATN) to EC mass in Sunset analyzer and aethalometer (Liu et al., 2016a). The MAE of BC was calculated from the Abs and mass concentration of BC ( $\mu g/m^3$ ) using the following equation (Cheng et al., 2011):

$$MAE = \frac{Abs}{BC} \tag{1}$$

MAE could also be calculated using the following equation:

$$MAE(m^2/g) = \frac{b_{ATN}}{EC \cdot C \cdot R (ATN)} \times 10^3 = \frac{ATN}{ECs \cdot C \cdot R (ATN)} \times 10^3$$
(2)

where *EC* ( $\mu$ g/m<sup>3</sup>) is the mass concentration of EC in PM<sub>2.5</sub>; *ATN* is the light attenuation (a unit less parameter); *EC*<sub>s</sub> is the filter loading of EC;  $b_{ATN}$  is the attenuation coefficient of the loaded light absorption material; *C* and *R*(*ATN*) are two empirical factors for correcting the artifacts due to multiple scattering and shadowing effects, respectively (Weingartner et al., 2003). Detailed MAE and R(ATN) calculation processes and the C values used in the previous calibration studies were summarized in Supplement Section A1 and Table S1.

## 2.3. Determination of MSOC concentration and light absorption of BrC

To evaluate the optical absorption of BrC, light absorption by WSOC was usually reckoned to characterize the BrC spectra (Chen and Bond, 2010). However, a considerable fraction of BrC was found to be insoluble in water, and it was estimated to have a strong light absorption and to contribute 16–80% of the total absorption by methanol-extracts (Zhang et al., 2013). Therefore, the radiative forcing of BrC could be greatly underestimated significantly by using WSOC as a proxy for BrC

(Cheng et al., 2016; Lei et al., 2018; Zhang et al., 2013). Indicated by recent studies (Cheng et al., 2016, 2017; Huang et al., 2018; Lei et al., 2018), methanol soluble organic carbon (MSOC) is a better BrC surrogate compared to WSOC and is thus applied in this study.

Two punches from every filter sample were analyzed for OC and EC. One was directly measured without pretreatment, while the other was immersed in 10 ml methanol and then dried in open air for one hour before measurement. EC concentrations measured in the extracted (EC<sub>extracted</sub>) and untreated punch (EC<sub>untreated</sub>) in all samples were compared in Fig. S2 in the Supplement, and the loss of EC was estimated to account for  $2.03 \pm 2.01\%$  of the EC mass in the sample without pretreatment. We considered the loss of EC by the extraction process insignificant. In order to avoid the bias caused by the analytical artifacts, the amount of OC extracted by methanol (MSOC) was used to represent BrC mass and could be calculated following eq (3) (Cheng et al., 2016):

$$MSOC = TC_{untreated} - TC_{treated}$$
(3)

where  $TC_{untreated}$  and  $TC_{treated}$  are the total carbon (TC) concentrations of the untreated and extracted samples, respectively. In this study, the average MSOC was 8.23  $\pm$  4.84 µg/m<sup>3</sup> and accounted for 88% of the total OC mass in all samples (Fig. S3 in the Supplement). This result was similar to the fraction of 85% estimated that by Cheng et al. (2016).

Light absorption of BrC was measured at wavelengths 200 nm–800 nm with a Shimadzu UV–vis spectrophotometer (UV-2700), and BrC absorption coefficient averaged between 360 and 370 nm (Abs<sub>BrC,365</sub>) was typically selected as a simple measurement of BrC level. Detailed calculation of the absorption coefficient (Abs<sub>methanol, $\lambda$ </sub>) and MAE are provided in Section A2 of the Supplement. As described by Cheng et al. (2016), AAE can be calculated by a linear regression of log<sub>10</sub> (Abs<sub>methanol, $\lambda$ </sub>) vs. log<sub>10</sub> ( $\lambda$ ) in the wavelength range of 310–450 nm.

# 2.4. Measurements of absorption coefficient, non-methane hydrocarbons and inorganic ions concentrations

Besides offline sampling, online instrument Cavity Attenuated Phase Shift Albedo monitor (CAPS, Shoreline Science Research, Japan) was applied at NJU to improve the method of BC absorption measurement. The hourly-average aerosol extinction and scattering coefficients were measured with the instrument, and the difference between the two coefficients is the absorption coefficient. Non-filter-based absorption technique was performed at CAPS monitor to avoid the error from particle and filter interaction. The absorption coefficient measured by CAPS can thus be used to evaluate the uncertainty arising from the filter-based method, and to further improve the filter-based method. The instrument measures particle extinction and scattering coefficient at 530 nm based on cavity attenuated phase shift (CAPS) techniques (Onasch et al., 2015; Petzold et al., 2013), and the CAPS monitor operates as an integrating nephelometer to perform the light scattering measurement. CAPS monitor collects data at 1s resolution and the detection limits of light extinction and scattering were both  $< 0.5 \text{ Mm}^{-1}$ . Extinction and scattering coefficients measured by CAPS were calibrated weekly by monodisperse polystyrene particles (PSL) with diameters of 500 nm as described by Massoli et al. (2010).

Non-methane hydrocarbons (NMHCs) played an important role in SOA generation, an important source of BrC (Shao et al., 2016), therefore, measurements of NMHCs are essential to study the optical properties of BrC from secondary aerosol formation. Hourly measurements of  $C_2-C_{12}$  NMHCs were performed using a gas chromatography-flame ionization detection (GC-FID) system (Perkin-Elmer, Waltham, MA, USA) throughout 2016 at NJU and PAES. The principles of sampling and chemical analysis were addressed in a previous study (De et al., 2011). Besides OC and EC, inorganic ions were the major components of  $PM_{2.5}$  and they can be used as indicators of specific emission sources. Water soluble inorganic ions ( $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $NH_4^{+}$ ,  $K^{+}$  and

Cl<sup>-</sup>) collected on the filters were analyzed in aqueous extracts of the filters by ion chromatography (Dx-120, Dionex Ltd., USA). Cation concentrations were determined using a CS12A column (Dionex Corp.) with 20 mM MSA eluent. Anions were separated on an AS11-HC column (Dionex Corp.) with 8 mM KOH eluent. Details on the analytical procedures were provided by Li et al. (2015).

### 3. Results and discussion

# 3.1. Improved method with reduced uncertainty in the BC absorption determination

One hundred and forty-nine daily PM<sub>2.5</sub> samples from November 2015 to January 2017 at NJU were used to evaluate the uncertainty of BC absorption determination. We first applied the constant values of 2.14 (C1) and 3.60 (C2) to calculate the MAE of BC and thereby the absorption coefficient at NJU site combining Eqs (1) and (2). As summarized in Table S1, in general, the C values used in previous studies were divided into two categories, i.e., 1.8-2.2 for pure/external mixtures and 3.64-4.55 for internal mixtures of soot particles. The C values of 2.14 and 3.60 were adopted in the calculation of mass absorption efficiency of ambient aerosol samples (Cheng et al., 2011; Cui et al., 2016; Ram and Sarin, 2009; Shen et al., 2013). As shown in Fig. 1a, the relative deviations between absorption coefficients calculated by C values (Abs<sub>C 530</sub>) and those measured by CAPS monitor (Abs<sub>CAPS 530</sub>) were 19.72  $\pm$  15.21% and 34.21  $\pm$  13.34% for C<sub>1</sub> and C<sub>2</sub>, respectively, i.e., Abs<sub>C,530</sub> calculated with C1 was closer to Abs<sub>CAPS,530</sub> than that with C2. We speculated that the discrepancies in Abs<sub>C.530</sub> and Abs<sub>CAPS,530</sub> were attributed to the large uncertainty of the multiple scattering correction factor and the presence of BrC. In previous studies,  $C_1$  (2.14) was suggested for multiple scattering effect of pure or external mixture of soot (Bond and Bergstrom, 2006; Ram and Sarin, 2009; Weingartner et al., 2003). However, the actual C value in this study might be higher, because all the samples were ambient particles in which BC was commonly coated with organic components.

Absorption coefficient of BrC was selected at a wavelength of 530 nm (Abs<sub>BrC,530</sub>) to match Abs<sub>CAPS,530</sub>. Fig. S4 in the Supplement shows Abs<sub>CAPS,530</sub> and Abs<sub>BrC,530</sub> at NJU during the measurement period. Mean Abs<sub>BrC,530</sub> was calculated as 7.51  $\pm$  2.90 Mm<sup>-1</sup> with eq S (5), accounting for 28.21  $\pm$  11.21% of Abs<sub>CAPS,530</sub>. The result indicated that the light absorption of BrC might not be ignored even at the

visible wavelengths. In order to exclude the effects of BrC in determination of absorption coefficient of BC (Abs<sub>BC,530</sub>), Abs<sub>BC,530</sub> was derived by subtracting Abs<sub>BrC,530</sub> from Abs<sub>CAPS,530</sub>. As shown in Fig. 1a, the relative deviations between Abs<sub>BC,530</sub> and Abs<sub>C,530</sub> were estimated at 56.43  $\pm$  34.24% and 18.12  $\pm$  11.33% when C<sub>1</sub> and C<sub>2</sub> were respectively used, suggesting that considerable uncertainty remained in calculation of Abs<sub>C,530</sub> with a constant C value.

The revised multiple scattering correction factor  $(C^*)$  was further estimated based on Sunset analyzer and CAPS monitor with the following equations:

$$Abs_{BC,678} = Abs_{BC,530} \times \left(\frac{678}{530}\right)^{-AAE_{BC}}$$
(4)

$$\frac{Abs_{BC,678}}{EC} = \frac{MAE_{BC,678}}{C^* \times R(ATN)}$$
(5)

$$C^* = \frac{MAE_{BC,678} \times EC}{Abs_{BC,678} \times R(ATN)}$$
(6)

where  $AAE_{BC}$  is the AAE of BC, and the value is 1.05 and 0.90 for fresh and aged BC particles, respectively (Liu et al., 2017). In this study, we applied the enhancement of MAE ( $E_{MAE}$ ) to judge the aging of BC, and details on calculation and determination of  $E_{\text{MAE}}$  and  $\text{AAE}_{\text{BC}}$  are provided in Section A3 and Fig. S5 in the Supplement. MAE<sub>BC.678</sub> is the MAE of BC, measured by Sunset analyzer at a wavelength of 678 nm. As ECont was measured at 678 nm where BC was almost the only light absorbing component and EC measured with thermal method was independent from the mixing state of BC, the ratio of EC<sub>opt</sub> to EC could be used as an indicator of mixing state of BC. As shown in Fig. 2, MAE<sub>BC.678</sub> and  $EC_{opt}/EC$  were linearly correlated ( $R^2 = 0.78$ ) within most of the data range, and the increased MAE<sub>BC.678</sub> and EC<sub>opt</sub>/EC could probably be explained by the elevated fraction of the internally mixed BC. The linearity did not hold when  $EC_{opt}/EC$  exceeded 0.92 m<sup>2</sup>/g, indicating that soot cores reached a maximum value of absorption amplification that was independent of the coating shell size (Bond et al., 2006).

Fig. S6 in the Supplement shows the relationship between  $EC_{opt}/EC$  and C<sup>\*</sup>. Linear correlations were found between  $EC_{opt}/EC$  and C<sup>\*</sup> when  $EC_{opt}/EC$  were in the range of 0.43–0.57 (R<sup>2</sup> = 0.91) and 0.57–0.92 (R<sup>2</sup> = 0.98). When  $EC_{opt}/EC$  were below 0.43 or above 0.92, C<sup>\*</sup> and  $EC_{opt}/EC$  were not linearly correlated. The results were attributed to the fact that nearly pure soot were observed when  $EC_{opt}/EC$  ratios were less than 0.43, and that the internal mixing state reached saturation when



**Fig. 1.** Large relative deviation of absorption coefficient existed using  $C_1$  (2.14) and  $C_2$  (3.6), whereas the relative deviation significantly reduced when used C<sup>\*</sup>. (a) The relative deviation between Abs<sub>C,530</sub> calculated by multiple scattering correction factors ( $C_1$ ,  $C_2$ ) and Abs<sub>C,APS,530</sub> measured by CAPS from November 2015 to January 2017; the relative deviation between Abs<sub>C,530</sub> and Abs<sub>C,530</sub>. (b) The relative deviation between Abs<sub>C,530</sub> by using C<sup>\*</sup>,  $C_1$  and  $C_2$  in March 2017. (Abs<sub>C,530</sub> denotes the absorption coefficient calculated by multiple scattering correction factor at 530 nm; Abs<sub>C,APS,530</sub> denotes the absorption coefficient measured by CAPS at 530 nm, and it includes the light absorption effects of both BC and BrC; Abs<sub>BC,530</sub> denotes the absorption coefficient by BC at 530 nm).



Fig. 2. Dependence of mass absorption efficiency of BC (MAE<sub>BC,678</sub>) on the mixing state of BC (EC<sub>opt</sub>/EC). The hollow symbols denote the average values of MAE<sub>BC,678</sub> and EC<sub>opt</sub>/EC for each season at NJU.

the ratios were greater than 0.92.

Another 25 ambient samples collected in March 2017 at NJU were used to evaluate the applicability of C<sup>\*</sup> on BC absorption determination. As shown in Fig. 1b, mean relative deviation between  $Abs_{BC,530}$  and that calculated using C<sup>\*</sup> ( $Abs_{C^*,530}$ ) was 3.82  $\pm$  1.04%, much smaller than

the values at 46.92  $\pm$  24.33% and 18.42  $\pm$  12.21% if using C<sub>1</sub> and C<sub>2</sub>, respectively. The results indicated that development and application of the revised multiple scattering correction factor based on field measurement was essential to reduce the uncertainty in estimating the absorption coefficient when filter-based measurements were performed. Using the same method, C\* values and thereby MAE<sub>BC,678</sub> were determined at other two sites as well for further analysis. As it varies depending on the mixing state of EC (Jung et al., 2010), C\* could be predicted based on the measured mixing state of EC (EC<sub>opt</sub>/EC) and the quantitative relationship between C\* and EC<sub>opt</sub>/EC as presented in Fig. S6. This improved method can be conducted at any site where Sunset analyzer was applied for filer samples at 678 nm, because the instrument can measure thermal EC and optical EC simultaneously.

## 3.2. The optical properties of BC

Fig. 3 shows the absorption coefficient (Abs<sub>BC,678</sub>) and MAE of BC by season at NJU, PAES and NUIST. Abs<sub>BC,678</sub> in winter was generally higher than that in summer at the three sites, while  $MAE_{BC,678}$  was lower in winter than that in summer. The highest  $MAE_{BC,678}$  was found at NUIST for all the seasons. The possible reasons for such seasonal and spatial variations of  $Abs_{BC,678}$  and  $MAE_{BC,678}$  are discussed below.

3.2.1. The effects of seasonal changes of emissions and meteorology on  $\operatorname{Abs}_{BC,678}$ 

As shown in Fig. 3 and Fig. S7 in the Supplement, relatively large  $Abs_{BC,678}$  were found in winter (22.6  $\pm$  8.1  $Mm^{-1}$  for 2016–2017 and 25.4  $\pm$  8.7  $Mm^{-1}$  for 2015–2016 at NJU, 18.4  $\pm$  6.1  $Mm^{-1}$  at NUIST, and 20.1  $\pm$  8.71  $Mm^{-1}$  at PAES for 2016–2017) and small  $Abs_{BC,678}$  in summer (12.1  $\pm$  5.9  $Mm^{-1}$  at NJU, 9.6  $\pm$  4.5  $Mm^{-1}$  and



Fig. 3. Box plots of optical properties of BC and BrC (including Abs<sub>BC,678</sub>, MAE<sub>BC,678</sub>, Abs<sub>BrC,365</sub> and MAE<sub>365</sub>) during spring, summer, autumn and winter for NJU, PAES and NUIST, respectively. The box plots indicate the mean concentration (square symbols) and the maximum, 99th, 75th, 50th, 25th, 1st percentiles, and minimum.

11.5  $\pm$  4.8 Mm<sup>-1</sup>at PAES and NUIST for 2016). Large Abs<sub>BC.678</sub> in winter resulted from the high BC abundances. As indicated in the Multiresolution Emission Inventory for China (MEIC, http://www. meicmodel.org/), BC emissions from Nanjing's residential sources in the winter were 2.6 times greater than those in other seasons in 2012, whereas there was no significant seasonal variations in emissions from industry, power and transportation sources all the year around (Fig. S8, Li et al., 2017). Li et al. (2015) also suggested that the residential stoves for heating in Nanjing could enhance the consumption of coal and other fossil fuels and thereby increase air pollutant emissions in winter, although there is no central heating in the city and the seasonal usage of fossil fuels has not been officially recorded vet. Thus, the elevated BC emissions from residential source in winter should be an important reason for the increased BC concentrations and high Abs<sub>BC,678</sub>. In addition, relatively stable atmospheric conditions and low precipitation amount may also contribute to the high BC loading in the winter. Jia et al. (2014) found that the length time of low mixing height in winter was consistent with the high concentrations of airborne particles and BC in Nanjing. Much lower precipitation was found in winter of 2015-2016 (35.4 mm) and 2016-2017 (54.0 mm) compared to summer (247.4 mm) and autumn (205.7 mm) of 2016 (data source: http:// www.nj.gov.cn/xxgk/sydw/qxj/ www.nj.gov.cn/xxgk/sydw/qxj/). Less precipitation in winter was expected to reduce particle scavenging and to result in higher BC concentrations in the atmosphere.

## 3.2.2. Influence of coating materials and mixing state on MAE of BC

Compared to Abs<sub>BC.678</sub>, a different seasonal pattern was found for MAE<sub>BC.678</sub>, and the variations at NJU was taken as an example and discussed below. As shown in Fig. 3 and Fig. S7, MAE<sub>BC,678</sub> at NJU was higher in summer than that in winter, and it could be explained by the enhanced radiative absorption from coatings on BC, and the increased absorption capacity of BC through the internal mixing with organic and/or inorganic aerosols. The sum of the ratios of  $SO_4^{2-}/BC$ ,  $NO_3^{-}/$ BC and (OC-BrC)/BC represented the total non-absorbing particulate matter (NA-PM) coatings, and the increased radiative absorption can be inferred from the ratio of NA-PM to BC. As shown in Fig. S9 in the Supplement, a good correlation was observed between the  $MAE_{BC,678}$ and the NA-PM to BC ratio ( $R^2 = 0.65$ ). Seasonal average of the ratio was 48.1 in summer, much greater than 29.6 in winter. The result indicated the increase in MAE<sub>BC.678</sub> was attributed to coating materials in ambient aerosols. Furthermore, the average  $EC_{opt}/EC$  was greater in summer (0.82) than that in winter (0.59) at NJU, indicating an elevated fraction of internally mixed BC in summer (Fig. 2). It resulted largely from the increased aging of BC in summer. The extent of BC aging could primarily be indicated by the changes in E<sub>MAE</sub> values. As shown in Fig. S5, the E<sub>MAE</sub> values were higher in summer (June and July, 2016) than those in other seasons. Combined with the relation between  $E_{MAE}$  and EC<sub>opt</sub>/EC presented in Fig. 2, the measurement implied that aging process could promote the increase of internally mixed BC in summer.

Based on the observation of aerosol physicochemical characteristics, similarly, Cheng et al. (2006) suggested that there was a considerably rapid aging process transforming externally mixed BC to internally mixed BC in southern China.

Table 1 lists the monthly averages of mass concentrations and optical properties of LAC in PM2.5 by site. The samples were simultaneously taken at the three sites in Aug 2016, Nov 2016, and Jan 2017. In each month, the largest MAE<sub>BC.678</sub> were found at NUIST, followed by NJU and PAES. Substantial spatial variability in MAE<sub>BC,678</sub> was typically associated with varied sources of aerosols at different locations. The ratio of OC to EC is an important indicator for the source type and intensity (Blando and Turpin, 2000). As shown in Fig. S10, poor correlation between OC and EC in the three months ( $R^2 = 0.40$ ), as well as the largest OC/EC ratio was found at NUIST among the three sites, suggesting different sources of OC and EC at the industrial site. We applied an EC-tracer method in which primary EC from combustion was commonly taken as a tracer of primary OC (Turpin and Huntzicker, 1991; Lim and Turpin, 2002), to roughly investigate the levels of secondary organic carbon (SOC) at the observation sites. The largest mean SOC concentration (7.6  $\mu$ g/m<sup>3</sup>) and SOC/OC ratio (0.57) were found at NUIST among the three sites within the same sampling period (the analogue values were 4.6  $\mu g/m^3$  and 0.52 for NJU, and 2.0  $\mu g/m^3$  and 0.17 for PAES, as shown in Fig. S10). As shown in Fig. S11 in the Supplement, larger annual mean concentration of NMHCs was observed at NUIST (34.4 ppbv) compared to NJU (22.0 ppbv) and PAES (27.1 ppbv) (Shao et al., 2016). In particular, the concentrations of benzene and n-heptane at NUIST were 1.8 and 12.6 times larger than those at PAES, respectively. Since these two components were mainly associated with crude oil refining, paint and solvent utilization (Wang et al., 2014), the results indicated that NUIST was heavily affected by VOCs emissions from industrial production. In addition, Liu et al. (2016b) found that ozone  $(O_3)$  concentration was the highest in the region of NUIST among all the monitoring sites in Nanjing, indicating the strongest atmospheric oxidation and thereby SOC formation at NUIST. As shown in Fig. S12 in the Supplement,  $MAE_{BC,678}$  exhibited a strong correlation with SOC/OC ( $R^2 = 0.66$ ), suggesting that elevated MAE<sub>BC.678</sub> at NUIST was mainly attributed to the abundance of SOA coatings on BC. The results implied that the formation of secondary aerosol, especially SOA, was an important reason for the enhancement of MAE<sub>BC.678</sub>. Abatement of VOCs emissions could help reduce the light absorption capability of BC.

## 3.3. The optical properties of BrC

As illustrated in Fig. 3, the MAE of BrC (MAE<sub>365</sub>) at PAES was the largest for all the seasons except in the winter of 2016–2017 at NJU. The strongest seasonal variation of MAE<sub>365</sub> was found at NJU: MAE<sub>365</sub> in the winter of 2016–2017 was the largest, followed by autumn, winter (2015–2016), spring, and summer. The influencing factors of seasonal

Table 1

The OC, BC and MSOC mass concentrations, and the optical absorption parameters of BC and BrC at the three sites in August, November 2016 and Ja	anuary 2017.
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Sampling time (Numbers)	Location	OC (μg/m <sup>3</sup> )	EC (μg/m <sup>3</sup> )	OC/EC	MSOC (µg/m <sup>3</sup> )	BC		BrC	
						Abs <sub>BC,678</sub>	MAE <sub>BC,678</sub>	Abs <sub>BrC,365</sub>	MAE <sub>365</sub>
						(Mm <sup>-1</sup> )	(m <sup>2</sup> /g)	(Mm <sup>-1</sup> )	(m <sup>2</sup> /g)
August 2016 (9)	NJU	$7.03 \pm 3.14$	$1.32 \pm 0.73$	$5.33 \pm 0.83$	$6.18 \pm 2.63$	$12.32 \pm 5.26$	$9.20 \pm 0.25$	$5.13 \pm 1.56$	$0.83 \pm 0.33$
	PAES	$9.08 \pm 2.65$	$1.13 \pm 0.44$	$8.03 \pm 0.65$	$6.01 \pm 1.68$	$9.89 \pm 4.56$	$8.81 \pm 0.77$	$11.10 \pm 0.68$	$1.83 \pm 0.30$
	NUIST	$11.98 \pm 3.04$	$1.26 \pm 0.56$	$9.51 \pm 0.63$	$8.61 \pm 2.12$	$14.02 \pm 5.67$	$11.10 \pm 0.68$	$12.74 \pm 2.01$	$1.48 \pm 0.59$
November 2016 (10)	NJU	$9.05 \pm 3.89$	$1.83 \pm 1.08$	$4.94 \pm 0.83$	$6.73 \pm 3.53$	$15.38 \pm 6.81$	$8.47 \pm 0.57$	$10.90 \pm 1.58$	$1.62 \pm 0.61$
	PAES	$9.77 \pm 2.57$	$1.83 \pm 0.87$	$5.34 \pm 1.08$	$7.11 \pm 3.11$	$15.51 \pm 6.77$	$8.42 \pm 0.76$	$12.37 \pm 1.07$	$1.74 \pm 0.46$
	NUIST	$13.47 \pm 3.11$	$2.08 \pm 0.67$	$6.47 \pm 0.99$	$9.38 \pm 3.22$	$21.31 \pm 7.66$	$10.20 \pm 0.77$	$13.70 \pm 2.24$	$1.46 \pm 0.69$
January 2017 (9)	NJU	$11.89 \pm 4.31$	$2.81 \pm 1.12$	$4.23 \pm 0.65$	$8.89 \pm 3.32$	$24.50 \pm 8.11$	$8.70 \pm 0.48$	$16.10 \pm 2.62$	$1.81 \pm 0.50$
	PAES	$8.61 \pm 3.46$	$2.42 \pm 1.11$	$3.56 \pm 0.40$	$6.88 \pm 2.58$	$20.20 \pm 8.01$	$8.31 \pm 0.53$	$11.83 \pm 1.13$	$1.72 \pm 0.34$
	NUIST	$15.78 \pm 4.88$	$2.10 \pm 1.27$	$7.51~\pm~0.88$	$10.27 \pm 3.84$	$22.11 \pm 7.32$	$10.50~\pm~0.98$	$14.17 \pm 2.44$	$1.38~\pm~0.41$

and spatial variations of  $MAE_{365}$  are discussed below, including the sources of BrC, the photobleaching effect, SOA precursors and the formation pathways of BrC.

## 3.3.1. The effects of primary and secondary sources on MAE of BrC

MAE<sub>365</sub> at the three sites were compared to understand the differences in the absorption of BrC from various sources. The highest MAE<sub>365</sub> were observed at PAES among the three sites except in winter (Fig. 3 and Table 1), attributed probably to primary BrC emissions. The correlations between the  $\ensuremath{\mathsf{Abs}_{\text{BrC},365}}$  and the concentration of varied chemical components in PM2.5 were presented in Fig. S13 in the Supplement. As shown in Fig. S13a, there is a poor correlation between SOC and  $Abs_{BrC,365}$  (R<sup>2</sup> = 0.13), suggesting that primary emissions were the important source of BrC at PAES. Typically, biomass burning was expected to enhance the MAE of BrC and Abs<sub>BrC,365</sub> (Cheng et al., 2016). As illustrated in Fig. S13b, the correlation coefficients between Abs<sub>BrC.365</sub> and K<sup>+</sup> concentrations (a widely accepted indicator of biomass burning) in particles at PAES were calculated at 0.91, 0.31 and 0.48 for summer, autumn and winter, respectively. The good correlation in summer indicated biomass burning as an important source of BrC. As shown in Fig. S14 in the Supplement, however, there were limited fire counts found in the urban area at PAES on a typical biomass burning day, 24 July, according to the Moderate Resolution Imaging Spectroradiometer (MODIS, https://earthdata.nasa.gov/data/near-realtime-data/firms). The backward trajectory analysis with HYSPLIT model (http://www.arl.noaa.gov/ready.html) identified that three air masses that arrived at PAES had passed through the biomass combustion region with intensive fire counts. Therefore the high MAE<sub>365</sub> at PAES in summer resulted probably from the transport of biomass burning emissions from northern Jiangsu and Anhui Provinces. In autumn and winter, the average EC/CO<sub>2</sub> ratio was 0.12  $\pm$  0.04 µg m<sup>-3</sup>/ ppmv, within the range of gasoline vehicle emissions at  $0.02-0.18 \,\mu g \,m^{-3}$ /ppmv according to Kondo et al. (2009). The results indicated that primary emission sources of BrC such as biomass burning and gasoline vehicles were the main reasons for the high light absorption capacity of BrC at the urban site in different seasons.

In winter, Abs\_{BrC,365} were estimated at 15.0  $\pm$  4.2, 16.1  $\pm$  5.0 and 20.0  $\pm$  5.3 Mm<sup>-1</sup> respectively for NJU, PAES and NUIST, much less than those in Beijing (26.2  $\pm$  18.8 Mm<sup>-1</sup>) and Xi'an (36.2 Mm<sup>-1</sup>) (Cheng et al., 2016; Shen et al., 2017). The mass concentrations of K<sup>+</sup> were measured at  $1.18 \,\mu\text{g/m}^3$  in the winter of 2015–2017 at NJU, 0.92 and  $1.34\,\mu\text{g/m}^3$  in the winter of 2016–2017 at PAES and NUIST, respectively. All the results were significantly smaller than the average of Beijing  $(3.12 \pm 2.52 \,\mu\text{g/m}^3)$  and Xi'an  $(8.5 \,\mu\text{g/m}^3)$  in winter (Yan et al., 2015; Shen et al., 2017). As shown in Fig. S13c, the correlation coefficients between  $K^+$  and  $Abs_{BrC,365}$  in winter were calculated at 0.52, 0.48 and 0.47 at NJU, PAES, and NUIST, respectively, smaller than that of 0.87 in the winter of Xi'an (Shen et al., 2017). Monthly fire counts in YRD 2016 derived from MODIS were presented in Fig. S15 in the Supplement. The number of fire counts in the winter was only 12% of the year, indicating that biomass burning was not a significant source of BrC in Nanjing in winter.

At NJU, as shown in Fig. 3 and Fig. S7, the largest  $MAE_{365}$  was estimated at  $1.8 \text{ m}^2/\text{g}$  in the winter of 2016–2017, much higher than that in the winter of 2015–2016  $(1.2 \text{ m}^2/\text{g})$  or summer  $(0.7 \text{ m}^2/\text{g})$ . The difference was probably attributed to the various sources of BrC. ECtracer method was employed to estimate the SOC level and the influence of SOA on BrC light absorption (Chen et al., 2017). As shown in Fig. 4, the poorest correlation between the absorption coefficient of BrC (Abs<sub>BrC,365</sub>) and SOC was found at NJU in the winter of 2016–2017 (R<sup>2</sup> = 0.18), indicating that BrC was heavily influenced by primary emissions in the period. Diesel vehicles were expected to be an important source of carbonaceous aerosols at NJU (Chen et al., 2017). The average EC/CO ratios was measured at 0.16 µg m<sup>-3</sup>/ppbv at NJU in the winter of 2016–2017, within the range of diesel vehicle emissions at 0.007–0.237 µg m<sup>-3</sup>/ppbv (Kondo et al., 2009). To test the impacts of diesel vehicles on the variations of MAE<sub>365</sub> in winter, the fraction of diesel vehicles on the G25 highway was recorded with real-time cameras from December 2016 to January 2017. As shown in Fig. 5, the variability of  $Abs_{BrC,365}$  was similar to that of diesel vehicle (including heavy-duty trucks, light-duty trucks and passenger buses) fractions ( $R^2 = 0.80$ ), confirming the contribution of diesel vehicle emissions to BrC at NJU in this season. Compared to the winter of 2016–2017, the contribution of SOA to atmospheric BrC was elevated in summer and the winter of 2015–2016, indicated by the large correlation coefficients ( $R^2 = 0.91$  and 0.70, respectively) in Fig. 4. These results suggested that BrC from diesel vehicles may have a stronger absorption ability than that from SOA formation.

It is worth noting that MAE<sub>365</sub> was larger at NJU than that at PAES in the winter of 2016–2017 (Table 1). Primary emissions were the main source of BrC at the two sites in winter as described before, and the difference in MAE<sub>365</sub> may be attributed to the varied emission sources. The OC/EC ratio was smaller at NJU than at PAES, indicating that diesel vehicle emissions had greater impacts on carbonaceous aerosols at NJU. In contrast, BrC was largely from gasoline vehicle emissions at PAES, as it was located in downtown with intensive traffic. The results implied that BrC associated with diesel vehicle emissions could be more light-absorbing than that from gasoline vehicles, and more studies on emissions are recommended to further confirm this judgment.

## 3.3.2. Reduced MAE of BrC from biogenic sources and photobleaching

As can be seen in Fig. 3 and Fig. S7, the mean MAE<sub>365</sub> at NJU was  $0.7 \text{ m}^2/\text{g}$  in summer, 71% and 86% lower than that in spring and the winter of 2015–2016, respectively, and it was the smallest for all the sites and seasons. The discrepancy was expected to be relevant with biogenic SOA precursors and the photobleaching of BrC. The highest temperatures and solar radiation (Fig. S16 in the Supplement) resulted in the enhanced emissions of isoprene and  $\alpha$ -pinene, two important precursors of biogenic SOA. As illustrated in Fig. S17 in the Supplement, the average mass fraction of isoprene in hourly NMHCs concentrations were much higher in summer (10%) than those in other seasons. Therefore, the formation of biogenic SOA, normally regarded as a non-absorbing aerosol (Kim, 2012), was likely to be more abundant in summer, leading to relatively low MAE<sub>365</sub>.

In addition, photobleaching could be another reason for decreased absorption of primary BrC (Li et al., 2016). As chemical reactions resulted in the destruction of the chromophores, the absorption of BrC was inversely proportional to the concentration of hydroxyl radical



Fig. 4. The correlation between  $Abs_{BrC,365}$  and SOC mass concentration at NJU by season.



**Fig. 5.** The absorption coefficient of BrC ( $Abs_{BrC,365}$ ) and the fractions of different types of vehicles (light-duty gasoline vehicles, light-duty trucks, heavyduty trucks and passenger buses) in G25 highway fleet from December 2016 to January 2017.

(OH) (Wang et al., 2018). Using the method by Kontkanen et al. (2016), the OH concentration at NJU was calculated based on solar radiation data, as illustrated in Fig. S18 in the Supplement. In general, the OH concentration remained at high levels in summer, followed by autumn and winter, and the result implied the elevated effects of photochemical whitening on BrC absorption in summer. The effect of photobleaching was further studied through backward trajectory analysis, as illustrated in Fig. S14. The 48-hr cluster analysis of backward trajectory indicated that all the three air masses were transported from PAES to NJU. Before arriving at NJU, the air masses passed through Purple Mountain where abundant biogenic VOCs were emitted from vegetation and the potential photobleaching of BrC during the transport could reduce MAE<sub>365</sub>.

### 3.3.3. Influence of aged SOA on MAE of BrC

As shown in Fig. 3 and Fig. S7, MAE<sub>365</sub> in the winter of 2015–2016 was slightly larger than that in spring at NJU. BrC was expected to be mainly from SOA formation in both seasons, and the difference in MAE<sub>365</sub> may result from varied mechanisms of secondary BrC formation related to ammonium ion (NH<sub>4</sub><sup>+</sup>). As suggested by the previous study, the absorption capability of BrC would be enhanced when aged

BrC was formed from fresh BrC via its aqueous reaction with NH<sub>4</sub><sup>+</sup> (Updyke et al., 2012). In this study, the mean concentration of NH<sub>4</sub><sup>+</sup> was measured at 8.33  $\pm$  3.21 µg/m<sup>3</sup> in the winter of 2015–2016, almost 40% higher than that in the spring (5.34  $\pm$  3.73 µg/m<sup>3</sup>) at NJU. As shown in Fig. S13d in the Supplement, moreover, the correlation between Abs<sub>BrC,365</sub> and NH<sub>4</sub><sup>+</sup> concentrations was much stronger in the winter. The results implied that the aged secondary BrC from aqueous reactions could have a stronger optical absorption than the fresh secondary BrC. Therefore, improved control of ammonia emissions in winter is expected to reduce the optical absorption of BrC.

## 3.4. The impacts of fresh SOA formation on LAC light absorption

A typical process of SOA formation was detected through the simultaneous observations at upwind (NJU) and downwind (PAES) sites in January 2017. Dominating wind in this period came from the east, as shown in Fig. S19a in the Supplement. Three identified air masses arrived at PAES based on back trajectory analysis, and two of them (Clusters 1 and 2) passed through both sites (Fig. S19b). As shown in Fig. 6a, PM<sub>2.5</sub> concentrations at PAES were observed at 4.2, 5.0, 2.7 and 2.6 µg/m<sup>3</sup>, larger than those at NJU on Jan 1, 15, 21 and 22, respectively. Meanwhile similar increment in OC concentrations at PAES were also observed compared to NJU, while no significant difference in concentrations of other main components  $(SO_4^{2-}, NO_3^{-}, NH_4^{+})$  and EC) was detected (Fig. 6b). As illustrated in Fig. S19b, the O<sub>3</sub> concentrations were observed at 33% and 24% larger at PAES and XWL (another urban observation site located in the air mass pathway) than that at NJU on Jan 21-22, while those of NO2 were 27% and 16% smaller, respectively. The result suggested that SOA formation was probably the major reason for the increased OC. AAE could serve as a qualitative indicator of the particle size of aerosols, i.e., large and small values of AAE indicated the dominance of fine and coarse particles, respectively (Panicker et al., 2013; Zhao et al., 2017). Based on the daily AAE as summarized in Table S3 in the Supplement, the mean AAE of Jan 1, 15, 21 and 22 was calculated as 4.79 at PAES, 12% larger than 4.28 at NJU, implying an increased abundance of fine mode particles generated from photochemical processes. These data provided supporting evidence for the hypothesis that SOA was generated through photochemical processes along the air mass pathway.

Typically, the reactions between SOA and  $NH_3/NH_4^+$  may take days, and it may take significant time to produce aged SOA. As the sampling time for each filter (22 h in this study) was much shorter than



**Fig. 6.** Spatial variation of chemical species mass concentrations at NJU and PAES in January 2017. (a) The increased  $PM_{2.5}$  and OC mass concentrations at PAES compared to NJU site. (b)  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $NH_4^{+}$  and EC mass concentrations at NJU and PAES.

the time needed for the fresh SOA to be aged (72 h indicated by Updyke et al. (2012)), the aged SOA could hardly be formed with the transport of air mass. Therefore, fresh SOA was expected to play an important role in the changes of OC concentrations.

To calculate the net increase in SOC generated in the transport process from NJU to PAES, we assumed OC to EC ratio at NJU ((OC/ EC)<sub>NJU</sub>) as "the primary OC to EC emission ratio" in the EC-tracer method, as described in details in Section A4 of the Supplement. Table S3 lists the light absorption of BC and BrC at the two sites in January 2017. Compared to NJU, larger MAE<sub>BC,678</sub> were estimated at PAES on Jan 1, 15, 21 and 22 when SOC concentrations increased, indicating fresh SOA formation enhanced the light absorbing ability of BC. In contrast, lower MAE<sub>365</sub> was measured at PAES than those at NJU, and the mean MAE<sub>365</sub> values was calculated to decrease by 0.26 m<sup>2</sup>/g with an increment of 1 µg/m<sup>3</sup> in the SOC. The result indicated that fresh SOA by photochemical processes would reduce light absorbing ability of BrC.

## 4. Conclusions

Light absorption properties of BC and BrC were investigated at three sites in Nanjing, a city with complicated sources of airborne aerosols. With the multiple scattering effect, the relative deviation between calculated (Abs<sub>C.530</sub>) and measured absorption coefficients of BC (Abs<sub>BC,530</sub>) was 56.43  $\pm$  34.24% from November 2015 to January 2017 at NJU. The deviation could be reduced to less than 5% through estimation and application of the revised multiple scattering correction factor. Seasonal and spatial patterns of LAC were thoroughly analyzed to reveal the main influencing factors on optical properties of aerosols. At NJU, the largest  $\operatorname{Abs}_{BC,678}$  was observed in winter, resulting from the high BC abundances. However,  $MAE_{BC,678}$  in winter was not as high as that in summer and spring, due to the enhanced radiative absorption from abundant coating materials on BC and the change of the mixing state of BC in the latter seasons. Distinct seasonal variations existed in  $MAE_{365}$  at NJU, with the mean estimated at  $0.7\,m^2/g$  and  $1.8\,m^2/g$  in summer and winter of 2016-2017, respectively. The discrepancy resulted from the elevated photobleaching of BrC and non-absorbing biogenic SOA formation in summer and the intensive emissions from diesel vehicles in winter. The largest MAE<sub>365</sub> were found at the urban site PAES for all the seasons except for winter, implying that BrC from primary sources had a stronger light absorption ability compared to those from secondary formation. Based on the simultaneous observations at NJU and PAES in January 2017, we found that the formation of fresh SOA could enhance the light absorbing ability of BC but reduce that of BrC. To mitigate the impacts of LAC on climate and visibility, the emissions from primary sources with large amount of BC (residential) and strong light absorption ability of BrC (biomass burning and transportation) need to be effectively controlled.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2018.11.022.

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