Seasonal light absorption properties of water-soluble brown carbon in atmospheric fine particles in Nanjing, China

Yanfang Chen, Xinlei Ge, Hui Chen, Xinchun Xie, Yuntao Chen, Junfeng Wang, Zhaolian Ye, Mengying Bao, Yanlin Zhang, Mindong Chen

PII: S1352-2310(18)30379-0
DOI: 10.1016/j.atmosenv.2018.06.002
Reference: AEA 16060

To appear in: Atmospheric Environment

Received Date: 12 April 2018
Revised Date: 30 May 2018
Accepted Date: 1 June 2018


This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Seasonal light absorption properties of water-soluble brown carbon in atmospheric fine particles in Nanjing, China

Yanfang Chen\textsuperscript{a}, Xinlei Ge\textsuperscript{a*}, Hui Chen\textsuperscript{a}, Xinchun Xie\textsuperscript{a}, Yuntao Chen\textsuperscript{a}, Junfeng Wang\textsuperscript{a}, Zhaolian Ye\textsuperscript{b}, Mengying Bao\textsuperscript{c}, Yanlin Zhang\textsuperscript{c}, Mindong Chen\textsuperscript{a}

\textsuperscript{a}Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CIC-AEET), School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China

\textsuperscript{b}College of Chemistry and Environmental Engineering, Jiangsu University of Technology, Changzhou 213001, China

\textsuperscript{c}Yale-NUIST Center on Atmospheric Environment, Nanjing University of Information Science and Technology, Nanjing 210044, China

\textsuperscript{*}Corresponding author, Email: caxinra@163.com

Phone: +86-25-58731394

For \textit{Atmos. Environ.}
Abstract Recently atmospheric brown carbon (BrC) is recognized as an important contributor to light absorption and positive climate forcing. In this work, daily fine particulate matter (PM$_{2.5}$) samples were collected over a full year (May 2015 – May 2016) in Nanjing, and seasonal light absorptive properties of water-soluble BrC were investigated. We found that winter samples had the strongest light absorption among four seasons. The light absorption at 365 nm (Abs$_{365}$) for all seasons linked closely with secondary organic carbon (SOC), indicating a dominant contribution from secondary sources to BrC. However primary biomass burning might also contribute to BrC as revealed by the good correlations of Abs$_{365}$ versus levoglucosan fragments and/or K$^+$, and such influence was more evident during summer. Furthermore, an Aerodyne soot-particle aerosol mass spectrometer (SP-AMS) was employed to determine the elemental ratios of BrC. We found that except in winter, the Abs$_{365}$ in general positively correlated with the average oxidation states (OS$_c$) of BrC, suggesting more BrC were produced at higher OS$_c$. The mass absorption efficiency at 365 nm (MAE$_{365}$) showed no clear dependences on OS$_c$ during spring, summer and fall, but decreased against OS$_c$ during winter, indicating chemical aging may lead to photo-bleaching of WSOM in winter. Moreover, positive responses of Abs$_{365}$ to N/C ratios were found during all seasons, indicating nitrogen-containing organics can be important BrC chromophores. Potential source areas of BrC were further discussed to improve our understanding of BrC sources in this region. **Keywords:** Brown carbon; Light absorption; Aerosol mass spectrometry; Secondary aerosol; Biomass burning
1. Introduction

Atmospheric aerosol particles play an important role in earth’s radiation budget and global climate change (e.g., Carslaw et al., 2010). Black carbon (BC) is typically treated as the most important aerosol component leading to positive radiative forcing (e.g., Bond et al., 2013; Wang et al., 2017). While recent studies indicate that a certain fraction of organic aerosols, often called “Brown carbon (BrC)” can also absorb lights at the wavelengths of near-ultraviolet (UV) and visible ranges (e.g., Bahadur et al., 2012; Cappa et al., 2012; Chen and Bond, 2010; Kirchstetter et al., 2004; Lack et al., 2012a; Laskin et al., 2015; Pokhrel et al., 2017; Saleh et al., 2013; Saleh et al., 2014). The radiative forcing of BrC has been estimated to be 19~24% of the total aerosol absorption (Feng et al., 2013; Liu et al., 2015; Zhang et al., 2017a).

Both laboratory and field studies have shown that BrC can be produced from multiple sources, including primary emissions from fossil fuel combustion (Bond et al., 2002; Yan et al., 2017) and biomass burning (Chakrabarty et al., 2010; Lack et al., 2012a; Washenfelder et al., 2015), as well as secondary formation through various reaction pathways including gas-phase and aqueous reactions (e.g., Hems and Abbatt, 2018; Laskin et al., 2015; Lin et al., 2015; Saleh et al., 2013; Zhong and Jang, 2011). The absorptivities of BrC generated from different sources are highly variable due to the different structures and concentrations of BrC chromophores (Laskin et al., 2015; Nguyen et al., 2012; Xie et al., 2017). A number of studies have been conducted to identify the BrC chromophores, but only a small fraction of organic chromophores
has been identified, including nitrophenols, aromatic carbonyls, oxygenated–conjugated compounds, nitroaromatics and sulfur-containing compounds (e.g., Desyaterik et al., 2013; Lin et al., 2015; Teich et al., 2017; Xie et al., 2017).

The BrC absorption can be directly measured by filter-based online instruments (Kirillova et al., 2016; Nakayama et al., 2015), such as the multi-angle absorption photometer (MAAP) and non-filter-based instruments (Laskin et al., 2015; Shamjad et al., 2015), such as photoacoustic spectroscopy (PAS) and cavity ring-down (CRD) spectroscopy (Lack et al., 2012a; Lack et al., 2006; Lack et al., 2012b; Pokhrel et al., 2017; Pokhrel et al., 2016). Moreover, water-soluble BrC has been measured semi-continuously by a particle-into-liquid sampler (PILS), coupled to a liquid waveguide capillary cell (LWCC) and an absorbance spectrometer (Liu et al., 2013; Satish et al., 2017). In addition, light absorption measurements on offline filter extracts have been conducted in both laboratory (e.g., Chen and Bond, 2010; Liu et al., 2016) and field studies (e.g., Chen et al., 2016; Zhang et al., 2017c). The advantage of this approach is that the interference by BC can be avoided. Compared to the online methods, offline technique can be easily performed in combination with other offline measurements for a better characterization of BrC.

The Yangtze River Delta (YRD) region is one of the most populated areas in China. Nanjing, as the second largest city and the provincial capital of Jiangsu Province, is also facing severe air pollution issue (Wang et al., 2016a). Some studies (e.g., Wu et al., 2017; Zhang et al., 2017b; Zhang et al., 2015) show that the organic
aerosols (OA) can account for a remarkable proportion of fine aerosol mass and are originated from multiple sources, including primary (traffic, cooking, industry, biomass burning and biogenic emissions) and secondary sources (aqueous-phase and photochemical processing). Hundreds of organic species (polycyclic aromatic hydrocarbons, carboxylic/dicarboxylic acids, hopanes, phthalates, amines and amino acids, etc.) have been identified (e.g., Wang et al., 2011; Wang et al., 2009; Wang et al., 2007). Recently, a 3-year result of light absorption of BrC in Nanjing based on continuous measurement combined with Mie-theory calculations was reported (Wang et al., 2018). The results demonstrate a significant contribution of BrC to total aerosol absorption (from 6% to 18%, and up to ~28% in biomass burning dominant season and winter). Nevertheless, studies regarding the light absorption of BrC are still scarce in this region. In this work, we investigated the light absorption properties of the water-soluble BrC via a series of offline measurements for PM$_{2.5}$ samples collected in Nanjing during 2015~2016. We focus on its seasonal behaviors, sources and dependences on bulk chemical properties.

2. Experimental Methods

2.1 Sample collection

A high-volume sampler (Laoying Ltd., Qingdao, model 2031) with a flow rate of 1.05 m$^3$ min$^{-1}$ was set on rooftop of a seven-floor building (~21 m above the ground) inside the campus of Nanjing University of Information Science and Technology in
the northern suburb of Nanjing (32.21°N, 118.72°E) (Figure S1 in the supplement).

More details can be found in our previous study (Wang et al., 2016b). A total of 272
PM$_{2.5}$ samples were collected daily (22 hours, from 12:00 p.m. to 10:00 a.m. of the
next day) from May 4, 2015 to 4 May, 2016. The samples were collected onto
pre-baked (450°C for 4 hours) quartz fiber filters (8×10 inch, Pall Life Science, USA).
Two field blanks were treated in the same manner as for the samples. The PM$_{2.5}$ mass
concentrations were determined gravimetrically using a digital balance (OHAUS
DV215CD, precision 0.01 mg) immediately after filter collection. The filters were
then wrapped in aluminum foil, sealed in polyethylene bags and stored at -18°C until
analysis.

During sampling, meteorological parameters (temperature, relative humidity,
wind speed, wind direction) were recorded at the meteorological station located near
the sampling site (~50m distance). Original hourly data were averaged into daily data.

2.2 Chemical analyses

**OC/EC:** One punched piece (diameter: 17 mm) of each filter was analyzed for
organic carbon (OC) and elemental carbon (EC) contents by the thermal-optical
OC/EC analyzer (Sunset Laboratory, USA) following the standard protocol (Birch
and Cary, 1996; Cao et al., 2017).

**Ionic species:** Two 10 mm diameter filter punches of each filter were extracted
with 15 mL ultrapure water (18.2MΩ cm, TOC< 5ppb), sonicated for 40 min at 0°C in
an ice-water bath, filtrated through 0.45 µm syringe filters (Spartan, Whatman). K+ concentrations used in this work were determined by an ion chromatograph (Aquion, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a Dionex CS12A column (20mM methanesulfonic acid as eluent). Instrument and operational details are the same as those described in Ye et al. (2017b).

**WSOC and UV-Vis absorption:** A quarter of each filter was extracted with 100 mL ultrapure water similar as for ionic species. The water-soluble OC (WSOC) concentrations were quantified by a TOC-VCPH analyzer (Shimazu, Japan) using a thermo-catalytic oxidation approach. Detailed procedures are described in Ge et al. (2014). The ultraviolet-visible (UV-Vis) light absorption spectra of the water extracts were measured using a UV-Vis spectrophotometer (UV-3600, Shimadzu, Japan) as described in Zhang et al. (2013).

**WSOM:** The offline SP-AMS analysis details were similar to those reported previously (e.g., Ye et al., 2017a; Ye et al., 2017c). Briefly, the water extracts were nebulized with argon using a constant output atomizer (TSI Model 3076). The generated aerosols were dehumidified by a silica gel diffusion dryer, and subsequently analyzed by the SP-AMS. Purified water was aerosolized before every sample measurement to cleanse the system, and extracts of blank filters were treated in the same way as a system blank. Note the offline AMS technique was mainly used to obtain the ion-speciated mass spectra of water-soluble organic matter (WSOM) (e.g., Chen et al., 2017; Daellenbach et al., 2016; Daellenbach et al., 2017; Ge et al., 2017;
Ye et al., 2017a). In this work, we only used the elemental ratios determined by the SP-AMS measurements. Examples of the high resolution mass spectra (HRMS) of WSOM were presented in Fig. S2. Detailed mass spectral analyses and source apportionment of WSOM will be presented in our future work.

2.3 Data analyses

2.3.1 Light absorption coefficients

The UV-Vis light absorption data were fitted into a power law function (Hecobian et al., 2010) over the range 300–600 nm according to:

$$\text{Abs}_\lambda = k \cdot \lambda^{-\AA}$$  \hspace{1cm} (1)

Where \(\text{Abs}_\lambda\) is the light absorbance at wavelength \(\lambda\), \(k\) is a scaling constant, and \(\AA\) is the absorption Ångström exponent (AAE) which describes the spectral dependence of light absorption from chromophores in solution.

The light absorption data is converted to an absorption coefficient at a wavelength \(\lambda\) (\(\text{Abs}_\lambda, \text{Mm}^{-1}\)) by equation (2) (Hecobian et al., 2010):

$$\text{Abs}_\lambda = (A_\lambda - A_{700}) \cdot \frac{V_f}{V_a \cdot L} \ln(10)$$  \hspace{1cm} (2)

Where \(A_{700}\) (mean value of 695–705 nm) is a reference to account for baseline drift, \(V_f\) is the volume of water that filter was extracted into, \(V_a\) is the volume of sampled air, and \(L\) is the optical path length (1 cm) of the quartz cuvette in the UV-vis spectrometer.

The mass absorption efficiency (MAE, \(\text{m}^2\text{g}^{-1}\)) at 365 nm was then calculated by
equation (3): \[ \text{MAE}_{365} = \frac{\text{Abs}_{365}}{C_{\text{WSOC}}} \] (3)

Where \( C_{\text{WSOC}} \) is the WSOC concentration. We used WSOC concentrations here for consistency and comparison with previous results. In fact, as we are able to calculate the WSOM concentrations (Section 2.3.2), we can determine \( \text{MAE}_{365} \) using \( \text{Abs}_{365}/C_{\text{WSOM}} \). Scatter plot of the two sets of \( \text{MAE}_{365} \) was shown in Fig. S3. They correlated very well (\( r \) of 0.96) but differed with a factor of \( \sim 2 \) as the average OM/OC ratio was \( \sim 2 \) (Section 2.3.2).

2.3.2 Elemental and OM/OC ratios of WSOM

The SP-AMS data were analyzed using the Igor-based ToF-AMS Analysis Toolkit (Squirrel v.1.57A and Pika v1.16A, available at: http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/). The \( \text{CO}^+ \) signals were from fragmentation of organic species without influences from \( \text{N}_2^+ \) signals, as we used argon as carrier gas. Due to the possible influences from carbonates on organic \( \text{CO}_2^+ \) signals (Bozzetti et al., 2017; Xu et al., 2013), we set it equal to \( \text{CO}^+ \). Signals of \( \text{H}_2\text{O}^+ \), \( \text{HO}^+ \) and \( \text{O}^+ \) were then scaled to \( \text{CO}_2^+ \) according to Aiken et al. (2008): \[ \text{H}_2\text{O}^+ = 0.225\times\text{CO}_2^+, \quad \text{HO}^+ = 0.05625\times\text{CO}_2^+, \quad \text{O}^+ = 0.009\times\text{CO}_2^+. \]

The oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios were calculated according to Canagaratna et al. (2015), nitrogen-to-carbon (N/C) ratios were derived based on Aiken et al. (2008), all of which were used to calculate the organic matter-to-organic carbon (OM/OC) ratios. The WSOM concentrations were
then calculated by using the WSOC concentrations determined by the TOC analyzer (Section 2.2) and the OM/OC ratios (OM/OC\textsubscript{WSOM}), as shown in equation (4):

\[ \text{WSOM} = \text{WSOC} \cdot (\text{OM/OC})_{\text{WSOM}} \]  

The annual average OM/OC ratio was 2.02 ± 0.1 (average ± 1 σ)(1.79−2.24), consistent with the values for WSOM reported earlier (Xu et al., 2017; Ye et al., 2017c).

2.3.3 Primary and secondary OC estimations

The EC-tracer method (Turpin and Huntzicker, 1995) was used to infer the primary OC (POC) and secondary OC (SOC), as follows:

\[ \text{POC} = \text{EC} \cdot (\text{OC/EC})_{\text{pri}} \]  
\[ \text{SOC} = \text{OC} - \text{POC} \]  

Where (OC/EC)\textsubscript{pri} refers to the OC/EC ratio for primary OA, and the minimum measured value (1.63) among all samples was used here. It should be noted that such treatment may introduce uncertainties as the primary OA (such as biomass burning and coal combustion emissions) may have large OC/EC ratios, and the ratios also vary among different sources. However, as EC is exclusively from primary sources, the POC scaled from EC also come from primary sources; the accuracy of POC/SOC estimates is difficult to quantify, a reasonable estimate is <20% for our study based on Wu and Yu (2016), considering the measurement uncertainties of <12% for OC and EC (Ye et al., 2017c), an average SOC/OC of 0.65, and a sampling size of 272.

In addition, the concentrations of water-insoluble organic carbon (WIOC) can be
calculated by equation (7):

\[
WIOC = OC - WSOC
\]  

(7)

2.3.4 Air mass trajectories

The calculations were carried out with ZeFir, an Igor-based tool (Petit et al., 2017). The 36-h back trajectories (at 500m height) were calculated by the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, version 4.8) model (Stein et al., 2016) developed by the National Oceanic and Atmospheric Administration Air Resources Laboratory.

2.3.5 Potential source contribution analyses

The potential source contribution function (PSCF) analysis was performed to explore the air mass origins and to identify potential source areas. The methodology is described elsewhere (Polissar et al., 1999). Briefly, the PSCF is calculated as:

\[
PSCF_{ij} = \frac{m_{ij}}{n_{ij}}
\]  

(8)

Where \( n_{ij} \) is the total number of trajectory endpoints in the \( ij^{th} \) cell, and \( m_{ij} \) is the number of trajectory endpoints in the \( ij^{th} \) cell associated with values above the threshold value. The PSCF analysis was also carried out with the ZeFir toolkit with a resolution of 0.2\(^\circ\)x0.2\(^\circ\) for each grid cell. The 75\(^{th}\) percentile was chosen as the threshold value to calculate \( m_{ij} \). In order to reduce the influences of small \( n_{ij} \) on the PSCF values, a weighing function has been implemented (Petit et al., 2017):
\[
w_{ij} = \begin{cases} 
1.00 & \text{for } n_{ij} \geq 0.85 \max(\log(n_{ij} + 1)) \\
0.725 & \text{for } 0.6 \max(\log(n_{ij} + 1)) < \log(n + 1) \\
& \leq 0.85 \max(\log(n_{ij} + 1)) \\
0.475 & \text{for } 0.35 \max(\log(n_{ij} + 1)) < \log(n + 1) \\
& \leq 0.6 \max(\log(n_{ij} + 1)) \\
0.175 & \text{for } \log(n + 1) \leq 0.35 \max(\log(n_{ij} + 1)) 
\end{cases} \tag{9}
\]

3. Results and discussion

3.1 Wavelength dependence of light absorption

The samples were classified into spring (March-May, \(n=85\)), summer (June-August, \(n=45\)), fall (September-November, \(n=64\)) and winter (December-February, \(n=78\)). Figure 1a presents the average light absorption spectra of the water-soluble species during four seasons and the full year within the wavelength range of 300 - 600 nm. Overall, the average light absorption of winter samples was significantly higher than those of spring, summer and fall, and leading to a relatively high annual absorption spectrum. This is corresponding to the high concentrations of light-absorbing species in winter samples (details in Section 3.2). The absorption intensities for all samples increased sharply towards shorter wavelengths. Such shapes are consistent with previous findings of BrC (e.g., Chen et al., 2016; Hecobian et al., 2010; Liu et al., 2013), indicating that the WSOM (or a fraction of WSOM) obtained in this study was BrC.

We further calculated the AAE values through the linear regression of \(\log(\text{Abs})\) vs. \(\log(\lambda)\) (the natural logarithmic form of equation (1)) in the wavelength range of
300~600 nm. The AAE values and relevant optical properties of BC and BrC can differ substantially among different situations. Several studies report that the AAE of fresh BC particles is ~ 1 (e.g., Bond, 2001; Kirchstetter et al., 2004), while the BC particles with thicker coating can have a higher AAE (as large as 1.6) even the coating species do not absorb light (Gyawali et al., 2009). Gyawali et al. (2009) also illustrates that vehicular-related and biomass burning aerosols have different optical characteristics. Much higher AAE values ranging from ~3 to ~12 are reported for water extracts of ambient aerosols collected from urban and rural sites (Cheng et al., 2016; Du et al., 2014; Kim et al., 2016; Kirillova et al., 2014; Yan et al., 2015; Zhu et al., 2017). The laboratory chamber generated particles from various wood smoldering can also have large AAE values between ~7 and ~16 (Chen and Bond, 2010). It is also worth to mention that AAE is also pH-dependent (Mo et al., 2017; Phillips et al., 2017).

In this work, the average AAE values during four seasons were 7.15, 7.28, 6.84 and 6.74, respectively (Fig. 1b). The annual average AAE value was 6.89. Different from the absorption spectra shown in Fig. 1a, the AAE value during winter was the lowest while the mean AAE of summer samples was the largest, suggesting remarkably different chemical compositions and/or sources of BrC during four seasons. Overall, the level of AAE values observed here is comparable with some previous results determined for the water-soluble PM$_{2.5}$ species extracted by using the similar extraction protocols, such as in Tibetan Plateau (6.2 and 6.9) (Zhang et al.,
267 2017c; Zhu et al., 2017), Beijing, China (7.2 ~ 7.5) (Cheng et al., 2011), and Los
268 Angeles basin (7.6) (Zhang et al., 2013), etc. But the AAE values also appear to be
269 higher than those in high-altitude Himalayas areas (3.9~5.6) (Kirillova et al., 2016),
270 Seoul, Korea (5.84 in winter) (Kim et al., 2016), These studies demonstrate that the
271 BrC might be related to primary biomass burning emissions and/or photochemical
272 SOA formed from anthropogenic gaseous precursors, which are implicate for the BrC
273 source analyses in Nanjing as well.
274
275 3.2 Seasonal variations and sources
276 We calculated the light absorption at 365 nm (Abs$_{365}$, in M m$^{-1}$) as a proxy to
277 represent the light absorption of water-soluble BrC, as Abs$_{365}$ can avoid interferences
278 from non-organic species (such as inorganic nitrate) (Hecobian et al., 2010). The time
279 series of Abs$_{365}$, MAE$_{365}$, RH, temperature, wind direction (colored by wind speed),
280 and the concentrations of PM$_{2.5}$, WSOC, OC, EC and K$^+$, over the full year are
281 displayed in Fig. 2. Correspondingly, the seasonal and annual averaged values of the
282 aerosol species, Abs$_{365}$ and MAE$_{365}$ are further shown in Fig. 3a. The annual average
283 PM$_{2.5}$, OC, WSOC, EC, K$^+$, Abs$_{365}$ and MAE$_{365}$ values were 114.5 µg m$^{-3}$, 15.2 µg
284 m$^{-3}$, 7.2 µg m$^{-3}$, 3.2 µg m$^{-3}$, 0.7 µg m$^{-3}$, 5.7 M m$^{-1}$ and 0.76 m$^2$ g$^{-1}$ C, respectively. In
285 particular, the annual MAE$_{365}$ value is much lower than the results determined by a
286 multi-wavelength Aethalometer (Model AE-31) in Xianghe, China (2.2 at 370 nm)
287 (Yang et al., 2009) and Nanjing (11.4 in winter and 8.6 in summer) (Wang et al.,
2018), methanol-extracted BrC in Beijing (1.45) (Cheng et al., 2016), in Los Angeles basin (2.27) (Zhang et al., 2013). But the value is also comparable with some previous values determined by online PILS-LWCC-TOC system (0.71) (Zhang et al., 2013), and those in Southeastern United States (0.64 in 8 urban sites and 0.58 in 6 rural sites) (Hecobian et al., 2010) and Central Indo Gangetic Plain (1.16) (Satish et al., 2017), etc.

The annual WSOC/OC ratio was 0.46 ± 0.1, highest in summer (0.59 ± 0.12), followed by fall (0.49 ± 0.09), winter (0.47 ± 0.08) and spring (0.43 ± 0.12). These ratios are well within the range of WSOC/OC ratios reported earlier (Ye et al., 2017b; Zhang et al., 2018). The SOC/POC ratios were 2.11 ± 1.28, 1.83 ± 1.19, 2.28 ± 1.28 and 3.17 ± 1.66 in spring, summer, fall and winter, respectively. The \( \text{Abs}_{365} \) value was highest during winter (9.44 ± 4.70 \( \text{Mm}^{-1} \)) and lowest during summer (3.31 ± 2.36 \( \text{Mm}^{-1} \)), while the spring and fall samples had similar values of 4.32 ± 2.28 and 4.70 ± 2.35 \( \text{Mm}^{-1} \), respectively. The seasonal order of \( \text{Abs}_{365} \) values was in line with their corresponding \( \text{PM}_{2.5}/\text{OC/WSOC} \) concentrations, indicating the close relationships between the BrC light-absorbing ability with levels of aerosol pollutions. The seasonal variability also reflected the differences of concentrations of BrC species, sources and water solubility of the light-absorbing chromophores. A similar seasonal trend of \( \text{Abs}_{365} \) is also reported in Seoul, Korea (Kim et al., 2016), but its value (0.87~7.31 \( \text{Mm}^{-1} \)) is lower than those determined here. The \( \text{Abs}_{365} \) seasonal behavior (lowest \( \text{Abs}_{365} \) in summer and highest in winter) is also similar with those observed in
other areas of China. For example, the $\text{Abs}_{365}$ values in Beijing, China (Du et al., 2014) are 4.6 M m$^{-1}$ in spring, 3.7 M m$^{-1}$ in summer, 9.1 M m$^{-1}$ in fall and 10.1 M m$^{-1}$ in winter; in another study, the $\text{Abs}_{365}$ values over the southeastern Tibetan Plateau (Zhu et al., 2017) are 0.85 M m$^{-1}$ in spring, 0.38 M m$^{-1}$ in summer, 0.55 M m$^{-1}$ in fall and 1.04 M m$^{-1}$ in winter. Moreover, the $\text{MAE}_{365}$ of the four seasons were 0.69 m$^2$ g$^{-1}$ C, 0.51 m$^2$ g$^{-1}$ C, 0.70 m$^2$ g$^{-1}$ C and 1.04 m$^2$ g$^{-1}$ C during spring, summer, fall and winter, respectively, which was also in the same order as that of $\text{Abs}_{365}$ (Fig. 3a). This result highlights that for the same amount of BrC, those during winter appear to have a stronger light-absorbing ability.

Figure 3b shows the correlation coefficients ($r$) of $\text{Abs}_{365}$ versus PM$_{2.5}$, OC, WSOC, EC and K$^+$ for different seasons and the whole year. Generally, the correlations with WSOC were strong across four seasons ($r$ of 0.80~0.93), and on a yearly basis, the correlation coefficient was 0.85 (Fig. 4a). Together, these results suggest that a significant fraction of WSOC is BrC chromophores and the similar sources for WSOC and water-soluble BrC throughout the year. The correlations between $\text{Abs}_{365}$ and OC were also tight ($r$ of 0.82~0.93) as the temporal variations of OC varied closely with WSOC in this study ($r$ of 0.91, Fig. 4b). The correlation of $\text{Abs}_{365}$ versus EC was weak, ranging from 0.33 to 0.51 for the four seasons ($r$ of 0.36 for all samples). Similarly, the correlation coefficient between $\text{Abs}_{365}$ and POC was also 0.36 (Fig. 4c) as the POC concentrations were directly scaled from EC using equation (5) in this study. On the contrary, the correlation between $\text{Abs}_{365}$ with SOC
was apparently much tighter ($r$ of 0.86, Fig. 4e). These results demonstrate that the water-soluble BrC is abundant of secondarily formed species rather than the primary species. Correspondingly, it is expected that the SOC was strongly associated with WSOC ($r$ of 0.89, Fig. 4f), while the POC was more likely composed of WIOC ($r$ of 0.61, Fig. 4d). The weak correlation of water-soluble BrC Abs$_{365}$ with POC was likely due to the low-water solubility of primary organic species, while the water-soluble BrC Abs$_{365}$ correlated moderately with WIOC ($r$ of 0.78, Fig. S4), likely indicating similar sources for WSOC and WIOC. Nevertheless, the light absorption properties of water-insoluble aerosol species remain to be elucidated.

In addition, K$^+$ ion is often used as a primary biomass burning emission tracer (Chow et al., 2007). Concentrations of this ion correlated much better with Abs$_{365}$ during summer ($r$ of 0.87, Fig. 3b) than those during spring ($r$ of 0.56), fall ($r$ of 0.46) and winter ($r$ of 0.51). This finding suggests that besides secondary sources, biomass burning can also contribute to the BrC evidently in summer. This is consistent with a recent study (Wang et al., 2018), which also suggests that biomass burning was an important source of BrC during summer in Nanjing. Cheng et al. (2013) also shows that K$^+$ as a biomass burning tracer is reliable during summer.

As is well known, levoglucosan ($C_6H_{10}O_5$) is another common biomass burning tracer compound (Simoneit, 2002; Simoneit et al., 1999). Correspondingly, $C_2H_4O_2^+$ and $C_3H_5O_2^+$ ions are electron impact ionization fragments of levoglucosan and they are often used as biomass burning OA marker ions in the AMS spectral analyses.
Therefore, we investigated the correlations between BrC Abs$_{365}$ with these two AMS ions. Their concentrations were calculated based on their corresponding mass fractional contributions in the WSOM AMS spectra and the WSOM mass concentrations derived from equation (4). As shown in Fig. 5, the BrC Abs$_{365}$ overall showed good correlations with both C$_2$H$_4$O$_2^+$ (r of 0.83−0.97) and C$_3$H$_5$O$_2^+$ (r of 0.73−0.95). Somewhat different from the correlations with K$^+$, this result indicates the possible influences of biomass burning on the BrC light absorption throughout the year. But still, summer samples correlated the best with C$_2$H$_4$O$_2^+$ (r of 0.97) and C$_3$H$_5$O$_2^+$ (r of 0.95) among four seasons, again suggesting a more obvious influence during summer than during other seasons from biomass burning. Note the good correlations with biomass burning tracer species indicate that biomass burning can contribute to the BrC, but does not mean it is the dominant contributor.

3.3 Influences of bulk chemical properties

To further unravel the features of water-soluble BrC in Nanjing, we examined the dependence of seasonal behaviors of Abs$_{365}$ on the bulk properties of WSOM. We first plotted the Abs$_{365}$ as a function of the average oxidation states (OS$_c$, defined as $2\times$O/C−H/C) (Kroll et al., 2011) of WSOM for different seasons in Figs. 6a-d. Although there are large uncertainties, statistically the Abs$_{365}$ values presented an increasing trend with OS$_c$ for spring, summer and fall samples, while there was no
clear positive correlation between Abs$_{365}$ and OS$_c$ for winter samples. Similar features were observed for Abs$_{365}$ versus O/C ratios too in Fig. S5. Consistently, the light absorption (Abs$_{365}$) tended to decrease with the increase of H/C during spring, summer and fall, but the trend was less clear-cut during winter as well (Fig. S6). These plots suggest that more BrC were produced at higher OS$_c$. It should be noted that, previous studies report that the optical properties of atmospheric BrC species can be altered significantly during atmospheric ageing, but the ageing processes may lead to photo-enhancement (Bones et al., 2010; Updyke et al., 2012) or photo-bleaching (Lee et al., 2014; Liu et al., 2016; Sumlin et al., 2017; Zhao et al., 2015), dependent upon the types of precursors and reaction conditions. As OS$_c$ is a metric of the ageing extent, the unique behavior of winter samples likely reflects that the dominant ageing processes or the precursors to form BrC in winter are different from those in other seasons in Nanjing. Of course, OS$_c$ merely represents the average properties of BrC, future molecular characterization of BrC would be essential to under the ageing processes and their impacts on BrC light absorption in details. In addition, the Abs$_{365}$ correlated very well with SOC (Fig. 4e) while the correlation with OSc was not so tight. This is because OS$_c$ was for WSOA while SOC was for bulk OC, and SOC itself may not perfectly with OSc as well, due to that SOC is an assemble of species from multiple oxidation processes and precursors.

To further investigate the BrC absorption efficiencies, we plotted MAE$_{365}$ against OSc in Figs. 6e-h. Generally, we observed no positive dependences of MAE$_{365}$ on OS$_c$
during spring, summer and fall, indicating that the “absorption efficiency” of WSOM did not change obviously with chemical aging during the three seasons. On the other hand, the MAE$_{365}$ of winter WSOM presented a decreasing trend with OS$_c$, showing that aging may lead to photo-bleaching of WSOM in winter.

As recent studies (e.g., Budisulistiorini et al., 2017) report that nitrogen (N)- or sulfur-containing organic compounds are possible BrC chromophores. Here, we investigated Abs$_{365}$ as well as MAE$_{365}$ against N/C ratios during four seasons in Fig. 7 (we did not calculate Abs$_{365}$ versus S/C ratios, as S/C ratios were very small and noisy in this work). Except a few outliers in summer and fall, generally speaking, both Abs$_{365}$ and MAE$_{365}$ values seemed to positively respond to the increase of N/C ratios during all time. This result manifests that N-containing organics are effective BrC light-absorbing chromophores in Nanjing. Nitroaromatic compounds were identified as important BrC compounds previously in biomass burning emissions (Cao et al., 2017; Lin et al., 2016). Note we indeed observed N-containing ion fragments with a benzene ring in the AMS spectra, suggesting the existence of nitroaromatics in our PM$_{2.5}$ samples even though in a very low level. Therefore, results in Fig. 7 likely verifies the possible contribution of biomass burning to BrC as well. Of course, a majority of the N-containing organic fragments in the AMS spectra are small $m/z$ ions without a benzene ring, which are likely from other types of organic nitrogen species, including amines, amino acids, amides etc (Ge et al., 2011a, b). Whether or not these species are effective chromophores, their sources, formations and contributions to
light absorption, are yet to be carefully investigated in the future.

3.4 Potential source areas

The potential source contributions (PSC) from different geological locations to the water-soluble BrC Abs$_{365}$ were illustrated in Fig. 8. We also conducted the back trajectory analyses and presented the results in Figs. 9 and 10 for the four seasons. Winter air masses can be classified into four clusters while three clusters were identified for other seasons. There were significantly different source area contributions among four seasons to the Abs$_{365}$.

During spring, the BrC potential source areas mainly distributed in the southwest and southeast of Nanjing, consistent with the cluster analyses of air mass back trajectories shown in Fig. 9a. The average values of Abs$_{365}$ from Cluster 1 and Cluster 2 were much higher than that of Cluster 3 (Fig. 10a). Cluster 1 (46.3% of total trajectories) had a relatively short length, intercepting the local/regional emissions in the Yangtze River Delta (YRD) region. Cluster 2 (38.1%) originated from Hunan province and travelled across Anhui province, which could also play an important role in affecting the absorbability of BrC in Nanjing in spring. Cluster 3 (15.6%) started from Liaoning province, and passed through Bohai Sea, Shandong Peninsula and Huanghai Sea, which delivered relatively clean air, and had less influences on BrC. In addition, the PSC distributions of Abs$_{365}$ were also similar to those of SOC (Fig. S7a) but not to POC (Fig. S8a) and K$^+$ (Fig. S9a), supporting that secondary source was a
dominant contributor of BrC during spring.

During summer, the BrC potential source areas mainly located in southeast of Nanjing (<100 km), confined within a relatively small region in Jiangsu and Anhui Provinces (Fig. 8b). Correspondingly, the air masses were also dominated by Cluster 1 (60%) with very short length (Fig. 9b). It should be noted that, the PSC hotspots of SOC (Fig. S7b), POC (Fig. S8b) and K$^+$ (Fig. S9b) also appeared in the southeast near Nanjing, indicating the important contributions from both primary (biomass burning) and secondary sources. Cluster 3 (17.8%) passed through the North China Plain (NCP) and the corresponding BrC seemed to be the most light-absorptive among the three clusters. Cluster 2 (22.2%) originated from Huanghai Sea and bring about less BrC compounds. In addition, maps of the fire spots in China during 2015 summer were presented in Fig. S10a-c. Obviously, lots of fire points were found in the regions overlapping with trajectories of Cluster 1 and Cluster 3, proving the biomass burning influences on BrC during summer. Such burning activities along with these clusters likely include crop burning during harvest seasons.

In fall, local Nanjing and Anhui Province were identified as the most potential source areas, as shown in Fig. 8c. Correspondingly, the BrC in Cluster 3 from such areas apparently had a higher light absorptivity than those in the other clusters (Fig. 10c), although it was not dominant (31.1%, less than 45.3% of cluster 2 from Huanghai Sea) (Fig. 9c). Also, the Abs$_{365}$ PSC distributions were highly similar to SOC (Fig. S7c) rather than POC (Fig. S8c) and K$^+$ (Fig. S9c) indicating a more
significant role of secondary source to BrC during fall.

For the case of winter, the potential source areas mainly located close to the sampling site (Fig. 8d). Correspondingly, the dominant air mass trajectory (Cluster 1, 52.56%) was also the shortest. Hotspots of SOC (Fig. S7d), POC (Fig. S8d) and K\(^+\) (Fig. S9d) were all concentrated in a narrow region, all demonstrating that overall local emissions might be major sources of these species and BrC. Such local emissions may also include enhanced residential burning (such as cookstove emissions) during winter. However, on average, the BrC with large light absorptivity was not from Cluster 1, but from Cluster 2 (10.26%) and Cluster 4 (15.38%), which passed through NCP and southern China, respectively (Fig. 10d). This was also likely associated with BrC from biomass burning, and further inspection indeed found lots of fire events in these regions during February (Fig. S10f). While during the other two months, biomass burning unlikely played important roles but more likely contributions from secondary and aged local emissions were important.

4. Conclusions

This work investigated the light absorption properties and sources of water-soluble BrC in atmospheric fine particles collected from 4 May 2015 to 4 May 2016 in Nanjing. We also conducted chemical analyses of OC, EC, WSOC, K\(^+\), and SP-AMS analyses on the water-soluble organics. The light absorption and mass absorption efficiency at 365 nm were found to be both stronger during winter than
during other seasons. The AAE values were in a range of 6.74~7.28 with an annual
average of 6.89. The BrC light absorption at 365 nm (Abs$_{365}$) correlated very well
with SOC during all seasons, indicating a significant contribution from secondary
sources. We also investigated the correlation between Abs$_{365}$ and the biomass burning
marker K$^+$ and levoglucosan (using its AMS fragments), and found that biomass
burning could contribute to BrC as well, but more evidently in summer.

The Abs$_{365}$ generally positively responded to the increase of OS$_c$ during spring,
summer and fall, indicating more BrC at higher OS$_c$. While the dependences of
MAE365 against OS$_c$ were less clear-cut during these three seasons, MAE365 during
winter displayed an decreasing trend against OS$_c$, implying chemical aging may lead
to photo-bleaching of BrC in winter. Furthermore, overall positive correlations of
Abs$_{365}$ and MAE$_{365}$ with N/C ratios were found throughout the year, suggesting that
nitrogen-containing organics are important BrC chromophores in Nanjing. PSCF
analyses further showed the different source regions to BrC during different seasons,
and in particular, pointed out that biomass burning in North China Plain or sometimes
southern China could have more impacts on BrC during summer and winter
(especially February in this work). Overall, our study provides valuable insights into
BrC in densely populated regions. Future investigations are strongly needed,
including investigation of light absorption properties of water-insoluble species,
quantification of the contributions from primary and secondary sources to BrC, and
the molecular characterization of possible BrC chromophores, etc.
Acknowledgements

This work was financially supported by the Natural Science Foundation of China (91544220, 21577065 and 21777073) and the Jiangsu Natural Science Foundation for distinguished young scholars (BK20150042).

Appendix A. Supplementary data

Supplementary data related to this article can be found at: xxx....

References


Bones, D.L., Henricksen, D.K., Mang, S.A., Gonsior, M., Bateman, A.P., Nguyen, T.B.,


Saleh, R., Robinson, E.S., Tkacik, D.S., Ahern, A.T., Liu, S., Aiken, A.C., Sullivan,


atmospheric measurements during EAST-AIRE. Atmos. Chem. Phys. 9, 2035-2050.
Figures

**Figure 1.** Seasonal and annual averaged light absorption spectra of water-soluble aerosols: (a) linear scale and (b) log scale. The fitted Absorption Ångstrom Exponents (AAE) are shown in (b).

**Figure 2.** Time series of (a) temperature (T) and relative humidity (RH), (b) wind direction (WD) colored by wind speed (WS), (c) PM$_{2.5}$, WSOC, OC, K$^+$ concentrations, Abs$_{365}$ and MAE$_{365}$ during the study period (BJT, Beijing Time).
Figure 3. (a) Seasonal and annual averaged PM$_{2.5}$, WSOC, OC, K$^+$ concentrations, Abs$^{365}$ and MAE$^{365}$; (b) Correlation coefficients of Abs$^{365}$ versus EC, K$^+$, WSOC, OC and PM$_{2.5}$ during four seasons and the full year.
**Figure 4.** Scatter plots of (a) BrC \( \text{Abs}_{365} \) versus water soluble organic carbon (WSOC), (b) water-soluble organic carbon (WSOC) versus organic carbon (OC); (c) BrC \( \text{Abs}_{365} \) versus primary organic carbon (POC), (d) water-insoluble organic carbon (WIOC) versus primary organic carbon (POC), (e) BrC \( \text{Abs}_{365} \) versus secondary organic carbon (SOC), and (f) water-soluble organic carbon (WSOC) versus secondary organic carbon (SOC) (data are classified into four seasons).
Figure 5. Correlation coefficients of $\text{Abs}_{365}$ versus $\text{C}_2\text{H}_4\text{O}_2^+$ and $\text{C}_3\text{H}_5\text{O}_2^+$ for the four seasons and full year.
Figure 6. $\text{Abs}_{365}$ and $\text{MAE}_{365}$ as a function of $\text{OS}_c$ during spring, summer, fall and winter (Data are grouped into a few bins. The whiskers above and below indicate the 90th and 10th percentiles, the upper and lower bounds of boxes represent the 75th and 25th percentiles, and the lines and crosses inside the boxes are median and mean values).
Figure 7. \( \text{Abs}_{365} \) and \( \text{MAE}_{365} \) as a function of N/C ratios during spring, summer, fall and winter (Data are grouped into a few bins. Meanings of the boxes are the same as those described in Fig. 6).
Figure 8. The potential source contributions to BrC Abs$_{365}$ during (a) spring (b) summer (c) fall and (d) winter (colored by the PSCF values).
Figure 9. Clusters of the 36-h back trajectories during (a) spring (b) summer (c) fall and (d) winter.

Figure 10. The average $\text{Abs}_{365}$ values of the different clusters during (a) spring (b) summer (c) fall and (d) winter.
Light absorption properties of one-year aerosol samples in Nanjing were characterized.

BrC light absorption is stronger during winter in Nanjing

BrC is closely associated with secondary organic species

BrC is influenced by biomass burning, especially in summer.

Nitrogen-containing organic compounds are likely BrC chromophores in Nanjing