



An Improved Absorption Ångström Exponent (AAE)-Based Method for Evaluating the Contribution of Light Absorption from Brown Carbon with a High-time Resolution

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ABSTRACT

While brown carbon (BrC) might play a substantially important role in radiative forcing, an estimation of its light absorption contribution with high-time resolution is still challenging. In this study, a multi-wavelength (370–950 nm) Aethalometer was applied to obtain the wavelength dependent light absorption coefficient (σ_{abs}) of aerosols both before and after being heated to 250°C. An improved absorption Ångström exponent (AAE)-based method was developed to evaluate the contribution of BrC to light absorption at a wavelength of 370 nm ($\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$). The $\sigma_{\text{abs,BrC}}$ at 370 nm was determined from the field measured AAE values for the wavelengths from 880 to 950 nm with a one-hour resolution. The simultaneous measurements of heated aerosols help confirm the negligible influence of BrC on the σ_{abs} values across the range of 880–950 nm. Meanwhile, $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ was also estimated with previously reported methods by assuming that the AAE was equal to 1 (Method I) as well as a new approach based on the light absorption enhancement (Method II). While the estimated $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ based on our developed method and Method I is highly correlated ($r^2 = 0.78$), the difference could be as large as > 20% on average. The obtained mean $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ was negative with Method II, indicating the net production of BrC when the aerosols were heated. The difference between the values for $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ obtained by our developed method and by Method II was ~40% on average and much higher (> 50%) during the noon hour, when secondary organic aerosols and sulfate were abundant. We propose that it is more suitable to use an AAE around 0.7 for “pure” BC to evaluate the contribution of BrC to light absorption in the PRD region. The developed method thus helps improve our understanding of the light absorption and climate forcing of BrC.

Keywords: Brown carbon; Black carbon; Light absorption; Absorption Ångström exponent; Aethalometer; PRD region.

INTRODUCTION

Most climate models regard black carbon (BC) as the sole light-absorbing particulate material. However, some organic species (i.e., brown carbon/BrC) could also absorb solar radiation, and thus play an important role in radiative forcing (Liu *et al.*, 2014; Liu *et al.*, 2015; Shamjad *et al.*, 2015). Recently, high contribution of BrC to light absorption is reported worldwide from satellite and ground observations, and modeling studies (Bahadur *et al.*, 2012; Feng *et al.*, 2013;

Laskin *et al.*, 2015, and references therein). Overwhelming presence of BrC above the Yellow Sea shows the necessity for understanding more than just bulk BC and organic carbon fractions of Asian aerosols (Alexander *et al.*, 2008; Zhu *et al.*, 2013). However, the variable absorptivity of light-absorbing carbonaceous aerosols is poorly known, making it challenging to account for their roles in radiative forcing (Andreae and Gelencser, 2006; Laskin *et al.*, 2015). Therefore, an accurate estimation of BrC light absorption is essential both for constraining large uncertainties in current aerosol forcing estimates and for control policy development (Bergstrom *et al.*, 2007; Zhang *et al.*, 2013b; Saleh *et al.*, 2014).

The BrC light absorption is strongly dependent on the wavelength (Favez *et al.*, 2009; Moosmüller *et al.*, 2011),

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parameterized by absorption Ångström exponent (AAE). AAE has commonly been used to estimate the contribution of BrC to light absorption (Corr *et al.*, 2012; Kirchstetter and Thatcher, 2012). Previous studies indicate that the AAE of “pure” BC is around 1 in the climate relevant wavelength region of the solar spectrum, and the presence of BrC will increase the AAE due to its enhanced absorption at UV/near-UV wavelengths (Kirchstetter *et al.*, 2004; Yang *et al.*, 2009; Rathod *et al.*, 2017). So, the measured wavelength dependence of AAE can be used to provide a quantitative estimate of BrC (Sandradewi *et al.*, 2008; Harrison *et al.*, 2012), and also for further distinction of sources (Ajtai *et al.*, 2011; Pintér *et al.*, 2018). However, theoretical calculations and field studies have shown that the likely range of AAE for internally mixed BC varies in a range of approximate 1–1.7, depending on the size and optical properties of the particle core and non-absorbing coating and the wavelength pairs used to determine AAE (Gyawali *et al.*, 2009; Lack and Cappa, 2010; Lin *et al.*, 2016). Using a three wavelength photo-acoustic soot spectrometer (PASS-3) and aerosol mass spectrometers (AMS), Yuan *et al.* (2016) explored the relationship between the measured AAE and the relative abundance of organic aerosol to BC and derived more realistic AAE values for “pure” BC aerosol, which is significantly lower than 1. Contributions to total light absorption at 370 nm by BrC were also estimated by comparing the wavelength dependence of the absorption coefficients of aerosols before and after heating (Guo *et al.*, 2014). This is based on the assumption that the change of AAE for aerosols after heating is due to the evaporation of BrC, but the potential error of which has not been fully assessed.

In the present work, the optical, physical, and chemical properties of atmospheric aerosols were measured before and after heating in the Pearl River Delta (PRD) region, China. In this region, organics are the second largest contributor for light extinction (Zhang *et al.*, 2013a; Chen *et al.*, 2016), and the average light absorption contributions of BrC at 405 nm were quantified to be ~10%. This work presents spectral measurements of light absorption coefficient (σ_{abs}) in a broad spectral range (370–950 nm) by an Aethalometer, highlighting some characteristics of light-absorbing aerosols. An improved method was developed, based on wavelength segregated AAE, in order to estimate the contribution of BrC to light absorption at 370 nm ($\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$). Meanwhile, the BrC contribution was also compared to those estimated based on the previously reported methods.

METHODS

Ambient Observation

Ambient measurements were performed at Guangdong Atmospheric Supersite (22.73N, 112.93E), a suburban site (Zhang *et al.*, 2014) in the PRD region from July 8 to August 2, 2014. Over the sampling period, ambient temperature and relative humidity generally varied between 24–37°C and 40–93%, with an average of 29°C and 73%, respectively. The concentration of PM_{2.5} varied in a wide range of 0.78–166 $\mu\text{g m}^{-3}$, with mean value of 29.7 $\mu\text{g m}^{-3}$.

Wind speed ranged between 0.3–5.1 m s^{-1} and the prevailing direction was from the southwest. Wind speed was lower (~1 m s^{-1}) during the early morning hours and was relatively higher (~2 m s^{-1}) in the afternoon.

To compare the properties of aerosols before and after heating, an automatic-controlled actuated ball valve that switches between “bypass” and “heating” on a 5-min cycle was used. The thermodenuder (TD, Dekati Ltd.) consists of a 95-cm long stainless steel tube, where the particles can be heated with controlled temperature, i.e., 250°C. The residence time of particles in the TD section is estimated to be 1.2 s, which should be enough for the effective vaporization of semi-volatile species (Villani *et al.*, 2007). Volatile or semi-volatile species, such as most organic compounds and ammonium nitrate, are supposed to evaporate during the heating (Bi *et al.*, 2015). Subsequently, these species were adsorbed in active charcoal in the adsorber section. The bypass consists of a silica tube of similar length for heating condition. In order to eliminate the influence of resident aerosols in the tubes, only the measurements during the latter 3-min of the 5-min cycle were included in the following data analysis. Particle loss could be typically represented as a function of flow rate and particle size (Stevanovic *et al.*, 2015). The test made by the manufacturer shows that particles with a physical diameter $d_p \leq 70$ nm have a size dependent particle loss, increasing from ~20% to ~40% when d_p decreases from 70 nm to 10 nm; particle loss at $d_p > 70$ nm is estimated to be approximately 20% at the total flow rate of 10 L min^{-1} , mainly attributed to the diffusion of particles. Regarding that the d_p of refractory BC was reported to be around 200 nm in the PRD region (Huang *et al.*, 2011), the particle loss might lead to a 20% negative bias for σ_{abs} measured through the heated line. The BC around 200 nm was most probably attributed to be from traffic emission, with their diurnal variation similar to that of NO_x (Qin *et al.*, 2017), as shown in Fig. S1.

The σ_{abs} was determined in 1-min resolution by an Aethalometer (AE-33, Magee Scientific) with seven wavelengths (at 370, 470, 520, 590, 660, 880 and 950 nm, respectively). A single particle aerosol mass spectrometer (SPAMS, Hexin Analytical Instrument Co., Ltd.) was deployed to measure the size and mass spectra of individual particles (Li *et al.*, 2011). Aethalometer and SPAMS shared an aerosol inlet (dried total suspended aerosols) and were placed downstream of the TD. Additionally, the concentrations of water soluble ions associated with PM_{2.5} were obtained from a Monitor for Aerosols and Gases in ambient air (MARGA) (Rumsey *et al.*, 2014). Hourly variations of organic carbon (OC)/elemental carbon (EC) in PM_{2.5} were provided by a Sunset Semi-Continuous Aerosol Analyzer. Concentration of O₃ was measured using an ozone analyzer (Model 49i, Thermo-Fisher Scientific). For comparison, all the measured parameters are presented as hourly averages in this paper. A detailed description of the instruments and the data analysis can be found in Supporting Information (SI).

Light Absorption Measurements

Generally, filter-based optical measurement instruments

(e.g., Aethalometer) must take into account the “filter loading effect” to accurately determine the σ_{abs} (Arnott *et al.*, 2005; Ajtai *et al.*, 2011). The new version Aethalometer (AE-33) used in the present study has been improved with the filter loading correction part, based on a two parallel spot measurement of optical absorption, through providing a real-time output of the “loading compensation” parameter to compensate for the “loading effect,” in detail described in the SI. The details of operation principle, data deduction, error budget of AE-33, inherent uncertainties in its technique and the corrections are extensively available in the literature (Drinovec *et al.*, 2015). The BC mass concentration is calculated from the change in optical attenuation at 880 nm in the selected time interval using the mass absorption cross section (MAC) of $7.77 \text{ m}^2 \text{ g}^{-1}$, which is close to that reported in the PRD region (Cheng *et al.*, 2011). The noise level of AE-33 at the time-base of 1 minute is $< 0.016 \text{ Mm}^{-1}$ for the σ_{abs} (<http://www.magscientific.com/>). The contribution of dust to σ_{abs} can be considered to be negligible in the PRD region (Yuan *et al.*, 2016), due to limited mass fraction (Cheng *et al.*, 2008; Zhang *et al.*, 2013a), and lower mass absorption efficiency values (Favez *et al.*, 2009).

RESULTS AND DISCUSSION

Previous Methods to Estimate the Light Absorption from BrC

Method I: Assuming $AAE = 1$ for “Pure” BC

The wavelength (λ) dependence of σ_{abs} is usually approximated by a power-law expression (e.g., Bergstrom

et al., 2007), defined as:

$$\sigma_{\text{abs}} = K \times \lambda^{-AAE} \quad (\text{R1})$$

where K is a constant. In practice for multi-wavelength measurements, AAE can be retrieved by fitting the σ_{abs} to the λ (370–950 nm), or to the different wavelength ranges (Bergstrom *et al.*, 2007). Thus, a wavelength segregated AAE value can be obtained through the logarithmic fit of R1, or $AAE = \ln(\sigma_{\text{abs}1}/\sigma_{\text{abs}2})/\ln(\lambda_1/\lambda_2)$ for two wavelengths.

The AAE has often been used as a simplified method for attributing short visible wavelength absorption to BrC (Lack and Cappa, 2010). Light absorption at longer wavelength (950 nm) is assumed to be due only to BC, and is extrapolated to the shorter wavelength using an assumed AAE, most commonly 1, which is illustrated in Fig. 1. It estimates the $\sigma_{\text{abs,BrC}}$ at 370 nm by subtracting the measured σ_{abs} to the extrapolated $\sigma_{\text{abs,BC}}$ at 370 nm (“Method I”):

$$\sigma_{\text{abs,BrC}} = \sigma_{\text{abs,370nm}} - \sigma_{\text{abs,950nm}} \times (370/950)^{-AAE} \quad (\text{R2})$$

Method II: Based on Light Absorption Enhancement

The $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ was also estimated based on the enhancements of σ_{abs} (E_{abs}), defined as the ratio of σ_{abs} for ambient and heated aerosols ($E_{\text{abs}} = \sigma_{\text{abs,ambient}}/\sigma_{\text{abs,TD}}$), at both 370 and 950 nm in previous studies (Cappa *et al.*, 2012; Guo *et al.*, 2014).

$$\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}} = (E_{\text{abs,370nm}} - E_{\text{abs,950nm}})/E_{\text{abs,370nm}} \quad (\text{R3})$$

where $\sigma_{\text{abs,BrC}}$ refers to the effective absorption coefficient

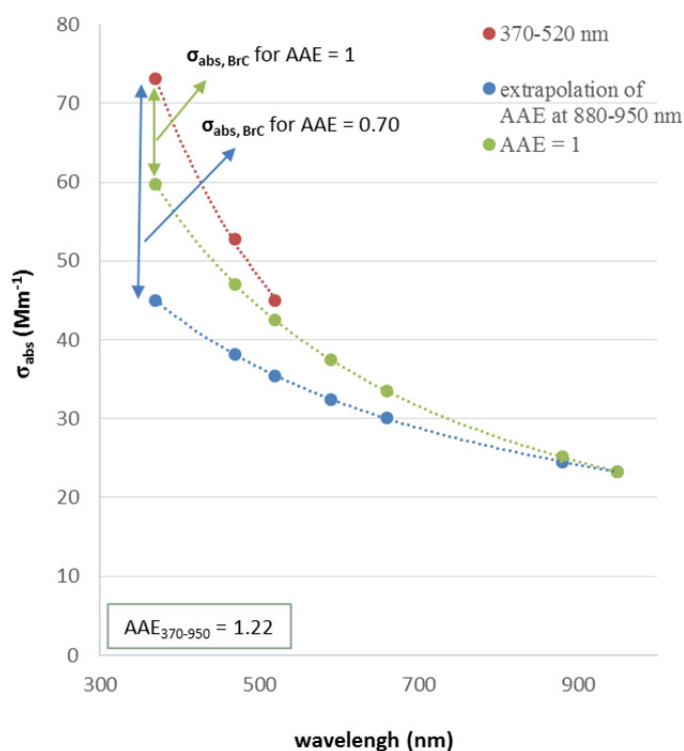


Fig. 1. An illustration of the methods to estimate the contribution of light absorption from BrC, based on the assumption of $AAE = 1$ for Method I, and $AAE = AAE_{880-950}$ for our developed method.

at 370 nm for the BrC evaporating under the TD temperature (i.e., 250°C), which is slightly different from the definition in R2. When there is no evaporative BrC, $E_{\text{abs},950\text{nm}}$ should equal $E_{\text{abs},370\text{nm}}$, since evaporation of BrC would result in larger $E_{\text{abs},370\text{nm}}$ than $E_{\text{abs},950\text{nm}}$ (Cappa *et al.*, 2012). It is worthy to note that this estimation (R3) actually represents the net result of evaporation and production of BrC in measured aerosol fraction.

An improved AAE-Based Method Developed by this Study

As far as the wavelength segregated AAE is concerned (Sandradewi *et al.*, 2008; Mogo *et al.*, 2012; Utry *et al.*, 2014), the AAE determined over the wavelength of 370–520 nm and 880–950 nm and their diurnal variations were compared in Fig. 2. $\text{AAE}_{370-520}$ were 1.36 ± 0.25 and 1.41 ± 0.22 , and $\text{AAE}_{880-950}$ were 0.70 ± 0.07 and 0.68 ± 0.08 for ambient and heated particles, respectively. $\text{AAE}_{880-950}$ were quite similar, indicating there was a thin coating and negligible lensing effect, which could be supported by the chemical composition of the ambient and heated BC-containing particles detected by the SPAMS (Fig. S2). It can be seen that $\text{AAE}_{880-950}$ varied in a narrow range (0.63–0.78, 10th–90th of the observed data), and significant difference ($p < 0.001$) was found between $\text{AAE}_{370-520}$ and $\text{AAE}_{880-950}$ for both ambient and heated particles, respectively. It reflects

that σ_{abs} becomes more sensitive to spectral variations at lower wavelengths than at higher wavelengths, which is attributed to the presence of BrC (Mogo *et al.*, 2012). While AAE is sensitive to these microphysical properties (Moosmüller *et al.*, 2009; Lack and Cappa, 2010), the influence of particle size on the AAE for heated aerosols should be limited in the present study, since the difference of hourly average $\text{AAE}_{880-950}$ for aerosols before and after heating was in a small range ($2\% \pm 2\%$). Furthermore, there is no significant correlation ($p > 0.05$) between $\text{AAE}_{880-950}$ and the mass fraction ratio of available coating materials (PM_{2.5}-BC) to BC, which further indicates limited influence of coating materials on the $\text{AAE}_{880-950}$. In contrast, the difference between $\text{AAE}_{370-520}$ for aerosols before and after heating was relatively higher ($-5\% \pm 11\%$), which is more evidently shown in their diurnal variation (Fig. 2(b)). Correlation coefficients (r^2) between $\text{AAE}_{370-520}$ and $\text{AAE}_{590-950}$, $\text{AAE}_{660-950}$, and $\text{AAE}_{880-950}$ are 0.56, 0.48 and 0.17, respectively, implying limited influence of BrC on the $\text{AAE}_{880-950}$. Overall, these results supported that $\text{AAE}_{880-950}$ may well represent the AAE of BC dominant aerosols in the present study. “Pure” BC AAE (i.e., $\text{AAE}_{880-950}$) of 0.70 ± 0.07 inferred in this study is significantly lower than the widely adopted value ($\text{AAE} = 1$) (Bond and Bergstrom, 2006). While it might not be typical to have AAE of the “pure” BC lower than 1, the

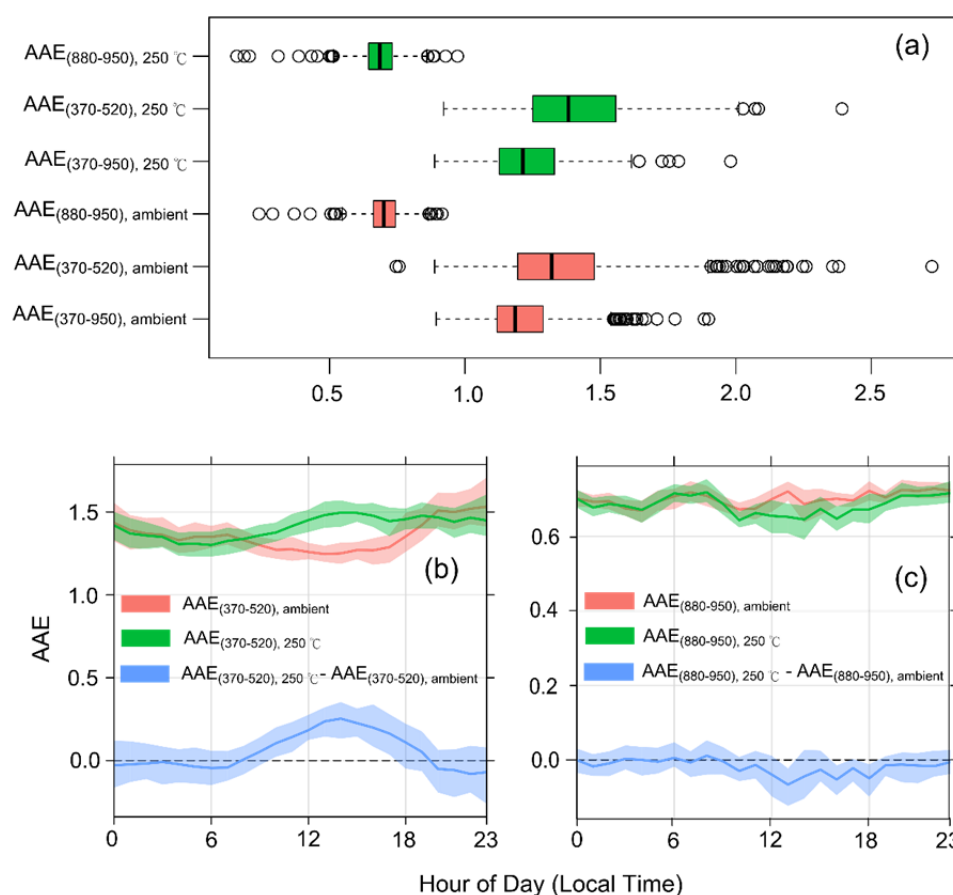


Fig. 2. (a) Comparison of AAE at the wavelength of 370–520, 880–950, and 370–950 nm, and diurnal variations of AAE at the wavelength of (b) 370–520 nm and, (c) 880–950 nm, for aerosols before and after heated, respectively.

retrieved value in this study is quite similar to that (AAE between the wavelength at 532 and 781 nm) estimated for the “pure” BC dominated from traffic emission in the same region (Yuan *et al.*, 2016). Additionally, lower AAE values (< 1) have also been reported for the “pure” BC in traffic and biomass burning emissions (Kirchstetter *et al.*, 2004), and at urban site in Beijing (Wu *et al.*, 2015). Theoretical calculation shows that AAE decreases with the increasing of “pure” BC sizes (Wu *et al.*, 2015). Regarding the reported volume equivalent diameter peak of “pure” BC to be around 200 nm in this region (Huang *et al.*, 2011), the corresponding theoretical AAE would most probably vary between 0.4 and 1 (Wu *et al.*, 2015). In addition, the fractal like structure of combustion generated BC could also be one possible explanation of the smaller value of AAE measured in this study (Moosmüller *et al.*, 2009; Lack and Cappa, 2010). Therefore, based on the assumption that BC is the dominant absorbing species over the near-IR wavelength (Shrestha *et al.*, 2014), it is proposed to apply $AAE = AAE_{880-950}$, instead of $AAE = 1$, in R2 to estimate $\sigma_{abs,BrC}$. Additionally, the input of hourly variation of $AAE_{880-950}$ further accounts for the factors (e.g., sources and atmospheric processing) that have influence on $AAE_{880-950}$ of BC dominant aerosols.

The uncertainty associated with this method was estimated through a sensitivity test. The upper and lower

bound of hourly average σ_{abs} ($\sigma_{abs} \pm \text{std}(\sigma_{abs})$, $\text{std}(\sigma_{abs})$ refers to the standard deviation of σ_{abs}) were inputted in R1 and R2 to obtain an estimate of the upper and lower bound of $\sigma_{abs,BrC}$. $\text{Std}(\sigma_{abs})$ at 1-min time base is assumed to be three times the noise level (0.016 Mm^{-1}) of AE33, and thus hourly based $\text{std}(\sigma_{abs})$, averaged over 18-min measurements of ambient aerosols could be calculated as: $3 \times \sqrt{18} \times 0.016 \text{ Mm}^{-1} = 0.2 \text{ Mm}^{-1}$. The upper and lower bounds of $\sigma_{abs,BrC}$ was calculated to be 28.8 and 27.1 Mm^{-1} on average, respectively, which is within 3% difference compared to the mean value of $\sigma_{abs,BrC}$ (28.0 Mm^{-1}).

Based on the improved AAE-based method, the temporal profiles of the estimated $\sigma_{abs,BrC}$ in Guangdong Atmospheric Supersite as well as the concentration of potassium, the correlation between $\sigma_{abs,BrC}$ and BC concentration, and the frequency histogram of the $\sigma_{abs,BrC}/\sigma_{abs,370nm}$ are shown in Fig. 3. The estimated $\sigma_{abs,BrC}/\sigma_{abs,370nm}$ distributed within a range of 30%–50%, with an average value at $37.4\% \pm 7.1\%$. Significant correlation ($r^2 = 0.72$) between the estimated $\sigma_{abs,BrC}$ and BC demonstrates their similar sources (Andreae and Gelencser, 2006; Moosmüller *et al.*, 2009; Saleh *et al.*, 2013; Guo *et al.*, 2014). The correlation between the estimated $\sigma_{abs,BrC}$ and the concentration of potassium, which is commonly used as a marker for biomass burning activities, was also observed to be significant ($r^2 = 0.38$, $p < 0.001$), indicative of potential contribution of biomass

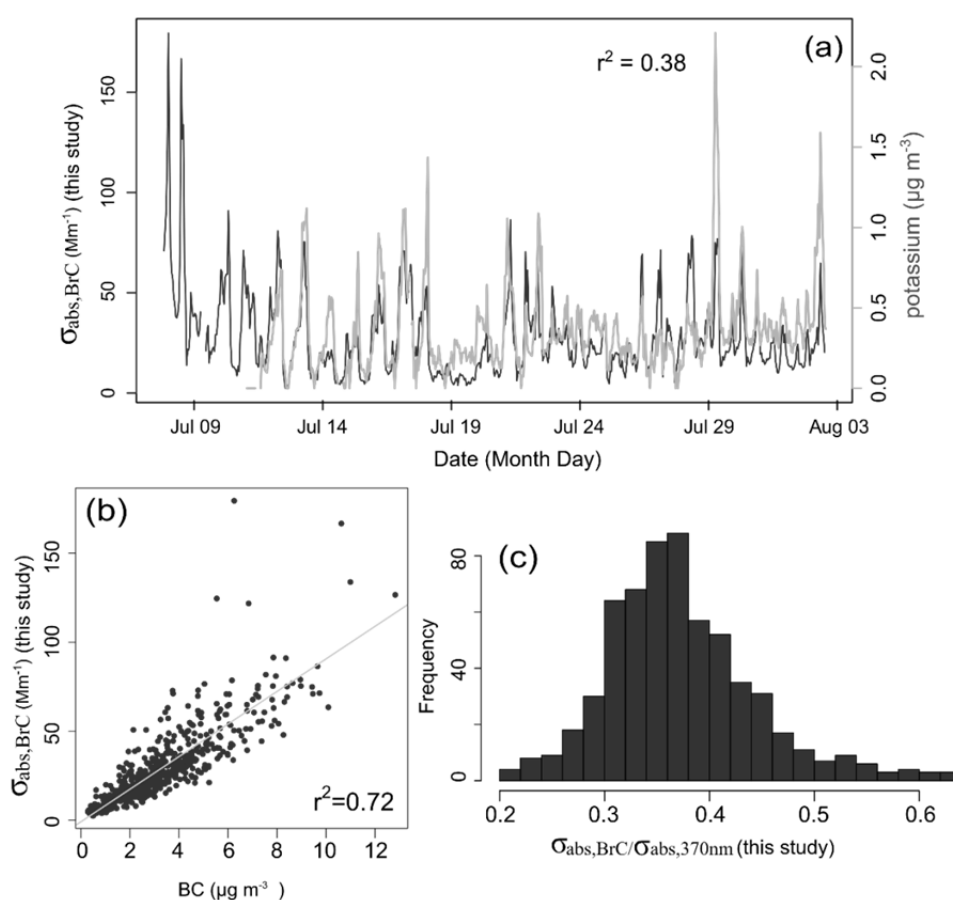


Fig. 3. (a) Temporal profile of $\sigma_{abs,BrC}$ and the concentration of potassium, (b) correlation analysis of $\sigma_{abs,BrC}$ and the concentration of BC, and (c) the histogram summarizing of the $\sigma_{abs,BrC}/\sigma_{abs,370nm}$ over this study.

burning to the observed BrC (Lack *et al.*, 2013; Saleh *et al.*, 2014; Hsiao *et al.*, 2016; Rathod *et al.*, 2017) in the PRD region. Potassium originated from sea salt and dust (Pio *et al.*, 2007) was estimated to be < 5% of the observed potassium in our study. Moderate correlation could be partly explained by that emission of BrC from biomass burning is linked to both burning condition and the emitted organic tracers (Lack *et al.*, 2013; Saleh *et al.*, 2014), and also other sources.

Comparisons of the Method Developed in this Study with the Previous Methods

Comparison with Method I

It is necessary to note that applying AAE = 1 to anchor absorption for BC and BrC may introduce potential errors, since the AAE for ambient particles (measured between a short and long visible wavelength) has often been observed to be variable, dependent on their physical and chemical properties (Mogo *et al.*, 2012; Lack and Langridge, 2013). Fig. 1 shows the average AAE (1.36 ± 0.25 and 0.70 ± 0.07) of the ambient particles estimated from the linear fit (R1) of σ_{abs} over the wavelength of 370–520 nm and 880–950 nm, respectively.

Based on AAE = 1 assumption, $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ was calculated to be $16.8\% \pm 11\%$. While the estimated $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ based on AAE = AAE₈₈₀₋₉₅₀ (the developed method) and AAE = 1 is highly correlated ($r^2 = 0.78$, $p < 0.001$, Fig. 4), the difference can be as large as 20% on average. There were some negative values obtained when assuming AAE = 1, because the observed AAE₃₇₀₋₉₅₀ was lower than 1 during some periods. Therefore, an arbitrary attribution of AAE to be 1 may substantially underestimate the $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ in this study.

Comparison with Method II

Based on Method II, the average estimated $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ over the study was $-2.4\% \pm 11.5\%$, which indicates that production of BrC dominated over evaporation, resulted in

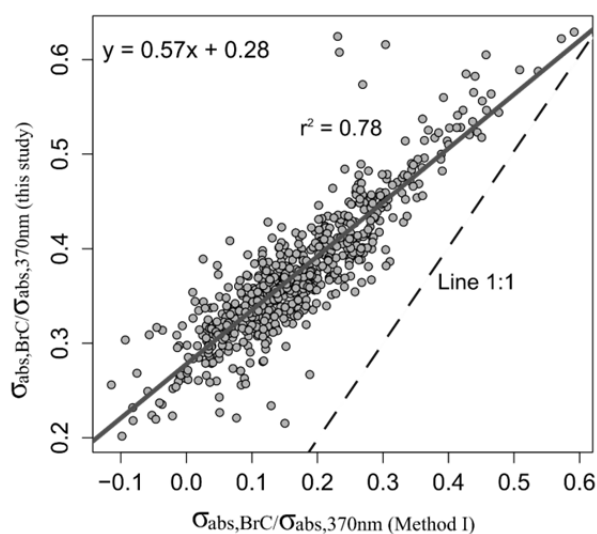


Fig. 4. Comparison of $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ estimated by our developed method and Methods I based on AAE = 1.

a net production of BrC when ambient aerosols were heated. Similar estimation in previous studies also resulted in the negative values for $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ (Guo *et al.*, 2014; McMeeking *et al.*, 2014; Nakayama *et al.*, 2014), and it was attributed to the production of BrC when ambient aerosols were heated (Nakayama *et al.*, 2014). A comparison of the $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ estimated by Method II and the developed method in Fig. 5 indicates that the production of BrC during heating periods can be substantially important, which may account for > 40% difference between the estimated $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$, and thus should be emphasized when estimating $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ with Method II. The uncertain evaporation state of BrC during heating might be partly explained by the residue chemical information (Fig. S2). The increased difference during afternoon hours (~50%) (Fig. 5) may further indicate the influence of photochemical activity on the production of BrC during the heating periods. This could be evidenced by negative correlations ($p < 0.001$) between the estimated $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ by Method II and the concentrations of secondary organic carbon (SOC, see SI) and O_3 (Fig. 6). This connection is probably explained by the conversion of SOC to BrC when aerosols were heated, and the conversion should be improved when there are high levels of SOC and O_3 . Such fraction of BrC may be attributed to low volatility oxygenated organic

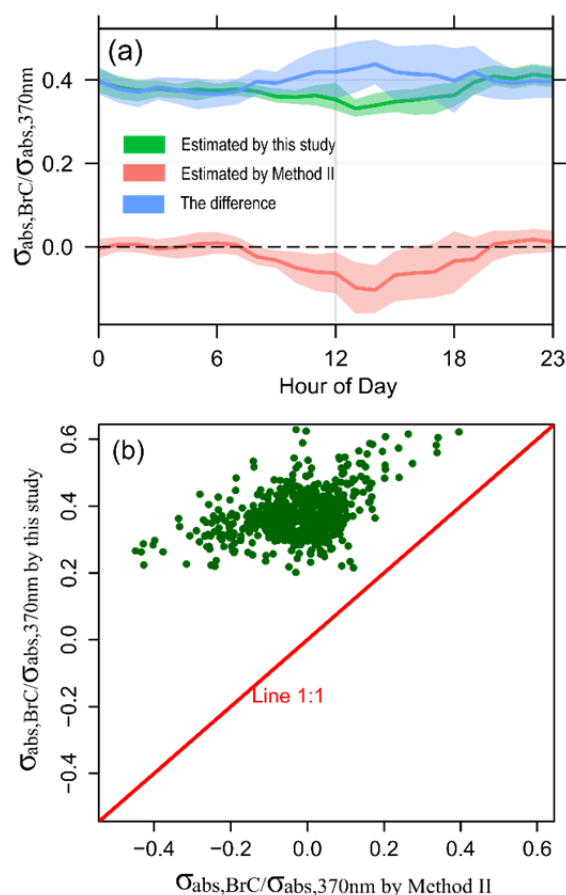


Fig. 5. Comparisons of (a) diurnal variations and (b) hourly averaged $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ estimated by Methods II and our developed method.

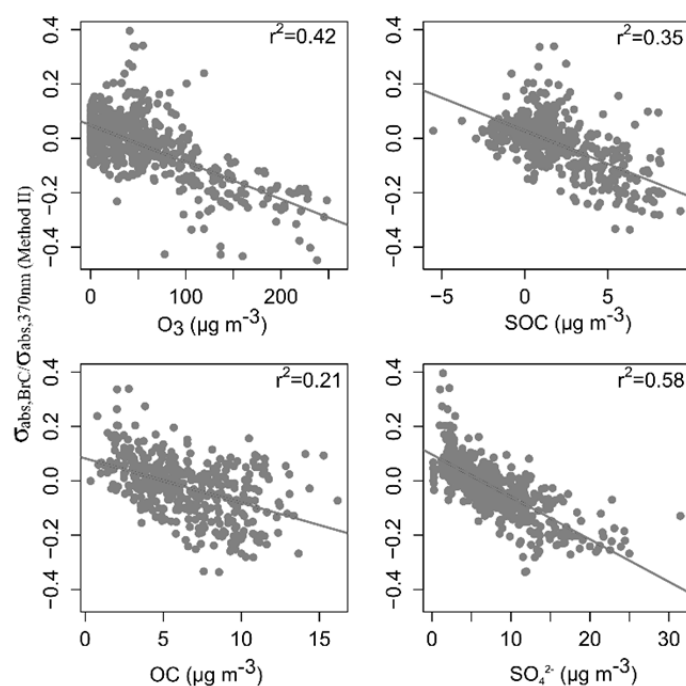


Fig. 6. Correlation plots between the $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ estimated by Method II and the concentrations of O_3 , SOC, OC and sulfate.

compounds, which has also been detected in heated (300°C) particles (Poulain *et al.*, 2014). Therefore, the estimated $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ based on Method II should suffer substantial error when there is high abundance of SOC.

From the co-located SPAMS, it was observed that detected number for internally mixed OC and sulfate (OC-sulfate) particles, which is frequently observed in the atmosphere of PRD region (Zhang *et al.*, 2015), substantially increased during noon hours when aerosols were heated (Fig. S3). More efficient detection of these particles in this case is probably linked to increased absorption of ablation laser by heated OC-sulfate particles (Hatch *et al.*, 2014). Without strong absorbing EC cores, the increased absorption is therefore more likely attributed to the formation of absorptive species (i.e., BrC) in heated OC-sulfate particles. Together with significant correlation between the estimated $\sigma_{\text{abs,BrC}}/\sigma_{\text{abs,370nm}}$ and SOC and sulfate (Fig. 6), it is suspected that the formed BrC during heating measurements might be linked to organosulfate, which was ionized to fragments representative of OC and sulfate in the internally mixed OC and sulfate particles (Hatch *et al.*, 2011). Light absorption at shorter wavelength had been observed for organosulfate (Song *et al.*, 2013). Although secondary organic aerosol (SOA) produced by photo-chemical ageing may contribute to BrC (Lambe *et al.*, 2013; Saleh *et al.*, 2013), our results indicate primary emission plays a dominant role. As discussed above, significant correlations between the estimated $\sigma_{\text{abs,BrC}}$ and BC, and potassium were observed. Furthermore, there is no correlation ($r^2 < 0.01$) between the estimated $\sigma_{\text{abs,BrC}}$ and SOC (Fig. S4). As noted by Lambe *et al.* (2013), the extent of absorption by SOA is linked with the magnitude dependent on both precursor type and oxidation level.

CONCLUSIONS

This paper provides an improved AAE-based method of quantitatively estimating the light absorption by BrC in real-time based on multi-wavelength light absorption measurements. The analysis shows that the wavelength dependence of BC light absorption can be better approximated for higher (880–950 nm) wavelengths. Based on simultaneous measurements of σ_{abs} for both ambient and heated aerosols, $\text{AAE}_{880-950}$ was found to show a negligible response to the presence of BrC; thus, the application of $\text{AAE} = \text{AAE}_{880-950}$ (0.70 ± 0.07) for “pure” BC, instead of $\text{AAE} = 1$, should be more accurate for estimating the light absorption by BrC in the PRD region. However, the estimated AAE value of approximately 0.7 in this work cannot represent all kinds of situations, in particular, when the BrC absorption over longer wavelengths is non-negligible. BrC was estimated to contribute 37.4% to the light absorption at 370 nm by the developed method, and it was largely attributed to primary emissions. The contribution is > 20% larger on average than that estimated by assuming the AAE to be equal to 1. The results also suggest that the estimated contribution of BrC to the total light absorption at 370 nm based on the light absorption enhancement method might suffer from potential errors during high loadings of SOA, which might serve as evidence for the production of BrC when aerosols are heated—an aspect neglected in previous studies.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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