



Spectral Light Absorption of Ambient Aerosols in Urban Beijing during Summer: An Intercomparison of Measurements from a Range of Instruments

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ABSTRACT

Aerosol light absorption is important to radiation balance, but it is difficult to accurately quantify using measurements. An intercomparison experiment for the measurement of the aerosol absorption coefficient (b_{ap}) was performed at an urban site in Beijing during the summer of 2012, including the filter-based particle soot absorption photometer (PSAP) and aethalometer (AE-31), and the reference photoacoustic extinctions (PAX), CRDS-Neph (cavity-ring down spectroscopy/nephelometer) system, and multi-angle absorption photometer (MAAP). The CRDS-Neph system and PAX performed poorly due to unexpected reasons. The corrected b_{ap} of the PSAP agreed well with the reference values determined by the MAAP, implying the applicability of this correction scheme as well as the credibility of the reference b_{ap} of the MAAP. A new conversion factor with a value of $\sim 7.1 \pm 0.05 \text{ m}^2/\text{g}$ at $\sim 530 \text{ nm}$ was established by regressing the reference b_{ap} against the AE-31 recorded black carbon (BC) concentrations, which is lower than the previously used value ($8.28 \text{ m}^2/\text{g}$).

Accordingly, the absorption Ångström exponent (α_{ap}) was estimated as 0.85 ± 0.21 on average. It was ~ 1 on clean days but significantly lower during pollution episodes, implying the main contributor to aerosol light absorption is freshly-emitted BC on clean days but aged BC during pollution. BC core sizes and the coating are likely to have a great impact on the α_{ap} , which needs further investigation. The mass absorption efficiency of BC was estimated by regressing the b_{ap} against the filter-analyzed elemental carbon (EC) concentrations, resulting in a mean of $9.2 \pm 0.5 \text{ m}^2/\text{g}$ at 670 nm . It was remarkably higher during pollution episodes than on clean days, implying a high variation of aerosol properties, such as the mixing state, with pollution levels.

Keywords: Ambient aerosol; Black carbon; Spectral light absorption.

INTRODUCTION

Aerosol light absorption is important not only for its direct influence on radiation balance (Charlson *et al.*, 1992; Jacobson, 2001) but also for its semi-direct effect on the enhanced dissipation of clouds by heating the vicinal atmosphere (Ackerman *et al.*, 2000). Recent research reported the total climate forcing of black carbon (BC), the dominant light-absorbing aerosol species in the visible spectrum, may

be equal to $+1.1 \text{ W/m}^2$ ($+0.17$ to $+2.1 \text{ W/m}^2$), about two-thirds that of carbon dioxide (Bond *et al.*, 2013). However, light absorption by atmospheric aerosols is relatively poorly characterized due to the highly varied chemical and physical properties of aerosols in time and space, as well as the lack of reliable measurements.

Filter-based aerosol absorption instruments, such as the particle soot absorption photometer (PSAP) and aethalometer (AE), have been commonly employed for their ease of operation and maintenance. However, aerosol absorption coefficients (b_{ap}) determined from filter-based techniques by measuring the optical attenuation through an aerosol-laden filter have inherent systematic errors that need to be corrected (Moosmüller *et al.*, 1998; Bond *et al.*, 1999; Weingartner *et al.*, 2003; Arnott *et al.*, 2005; Virkkula *et*

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al., 2005; Schmid *et al.*, 2006; Coen *et al.*, 2010). Multiple scattering by the filter in which particles are embedded will increase the optical path and as a result enhance the attenuation. Meanwhile, scattering by aerosols embedded in the filter will further enhance the light attenuation. In contrast, the increase in attenuation can be suppressed by increased aerosol loading within the filter, reducing the optical path – a phenomenon known as the “shadowing effect” (Weingartner *et al.*, 2003). To reduce the uncertainties in measurements caused by the multiply light scattering within the filter, and the scattering induced by embedded aerosols, a new filter-based instrument, the multi-angle absorption photometer (MAAP), has been developed to detect the backscattered light at two angles at the same time as when the transmission is measured. The detected intensity of the backscattered light is then put into a radiative transfer scheme, together with that of the transmitted light, to obtain the b_{ap} (Petzold and Schönlinner, 2004; Petzold *et al.*, 2005). Having treated the scattering effects that commonly exist in filter-based measurements, the b_{ap} determined using the MAAP should be more accurate compared with those determined using the AE or PSAP, and are therefore sometimes considered as a reference value.

Instruments based on the photoacoustic technique can measure the suspended particles directly in the chamber and produce reliable b_{ap} without the influence of the filter (Truex and Anderson, 1979; Arnott *et al.*, 1999), such as the commercial photoacoustic soot spectrometer (PASS) and photoacoustic extinctionmeter (PAX). Without considering the slight mass losses induced by cell heating, the photoacoustic method is also considered as a reference for aerosol absorption measurements. Besides, the b_{ap} can also be determined indirectly by subtracting the scattering coefficient (b_{sp}) from the aerosol extinction coefficient (b_{ep}). Thus, accurate measurements of the b_{ep} (e.g., as measured by cavity-ring down spectroscopy, CRDS) (O’Keefe and Deacon, 1988) and the synchronous b_{sp} (e.g., as measured by an integrating nephelometer, Neph) (Anderson *et al.*, 1996) can also provide reference values for b_{ap} .

Although these reference instruments can provide more reliable b_{ap} , it is not feasible for them to be widely used in long-term monitoring studies because of their high cost and/or the difficulty involved in their operation and maintenance, especially at remote sites. Additionally, they usually only provide information on aerosol absorption at a single wavelength (e.g., ~530 nm) and cannot indicate the light absorption spectral dependence of aerosols, which is also important in climate models (Bond, 2001).

In China, filter-based instruments, especially AEs, are commonly used operationally to monitor the b_{ap} and BC concentration ($[BC]$) because of their automated technology. Empirical or theoretical correction is needed to convert the recorded $[BC]$ to the reliable b_{ap} . This paper compares the results of b_{ap} calculated from the measurements of a range of instruments at an urban site in Beijing during the summer of 2012. Suitable empirical conversion schemes and factors for filter-based methods are provided according to the comparative measurements. The spectral absorption properties of aerosols during the experiment are also

discussed, as derived from the corrected measurements of the filter-based instruments at multiple wavelengths. Because of the high spatial variation in aerosol properties, our work is meaningful for the acquisition of relatively accurate aerosol absorption properties in this region.

EXPERIMENTAL PROCEDURES

Measurement Site and Study Period

The measurements to be compared were taken on the roof of a two-story building in the Tower Division of the Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP, CAS) during a summer period from 28 May through 1 July 2012. The site lies between the North 3th and 4th Ring Road in Beijing and is mainly surrounded by residential areas. It can therefore be considered as a typical urban site in Beijing. A detailed description of the site has been provided in previous work (Jing *et al.*, 2015; Tian *et al.*, 2015), and the meteorological conditions during the study period have been reported in Tian *et al.* (2015).

Absorption Measurements

A range of commercial absorption measurement instruments were employed in this study to produce the b_{ap} for comparison, including two AEs (Model AE-31, Magee Scientific, USA), two MAAPs (Model 5012, Thermo Fisher, USA), one 3-wavelength PSAP (Radiance Research, USA), and one PAX with wavelength of 532 nm (Droplet Measurement Technologies, USA). In addition, a combined system with one self-developed CRDS (Li *et al.*, 2011, 2013) series connected by one Neph (Model 3563, TSI, USA) was also utilized to measure the b_{ap} indirectly (i.e., $b_{ap} = b_{ep} - b_{sp}$). A diagram of the experimental setup is shown in Fig. 1. The operation principle and correction scheme of the b_{ap} determination for each instrument was described in detail in the supplementary material file. The b_{ap} determined from the PSAP, AE, MAAP, PAX and CRDS-Neph system were marked as b_{PSAP} , b_{AE} , b_{MAAP} , b_{PAX} and $b_{C\&N}$, respectively.

The experimental period was divided into two sub-periods: one from 28 May to 27 June (before 17:00 LST), and the other from 27 June (after 17:00 LST) to 1 July. The main part of the intercomparison was conducted in the first sub-period, and the second sub-period was primarily used for checking the instruments’ stability during their operation. A particular flow rate was set for each instrument to make the total flow rate meet the required value of the 2.5 μm cyclone inlets (see Fig. 1). Thus, only particulate matter with size less than 2.5 μm in aerodynamic diameter ($\text{PM}_{2.5}$) was measured, within which range fell most of the absorbing material (e.g., BC). Regular calibration of the flow rate for each instrument was performed with a model 4141 (0.01–20 L/min) mass flowmeter (TSI, USA). Fluctuation of the flow rate was considered negligible during the whole period. Calibration for certain instruments was conducted before the experiment, such as signal calibration for the PAX (see Sect. S4 in the supplement) and gas calibration for the Neph. In order to distinguish between the same model instruments, the two AEs were marked as AE31-B and AE31-W, respectively, while the two MAAPs were marked as MAAP-C and

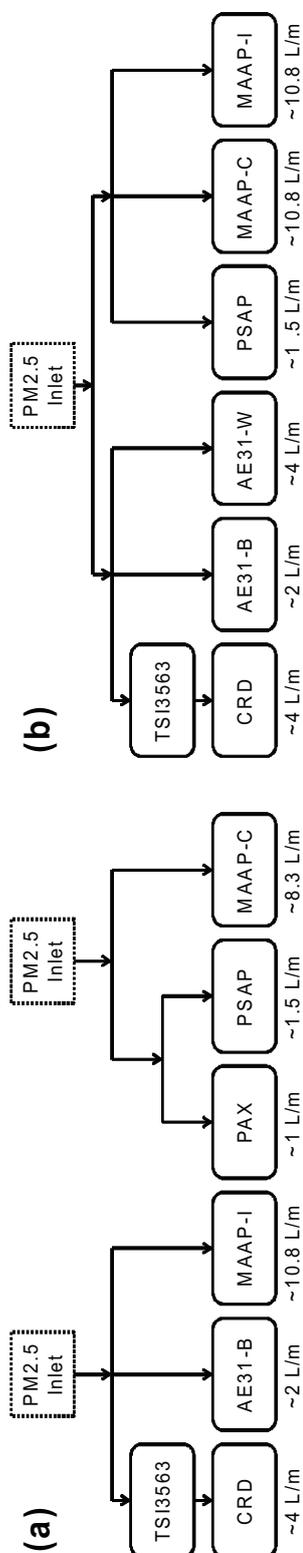


Fig. 1. Experimental setup for the intercomparison measurements.

MAAP-I, respectively. Drying was not employed before the sample air entered the instruments, except for the CRDS-Neph system. Thus, ‘ambient’ (the term ‘non-dried’ is more accurate due to slightly elevated instrument temperatures) b_{ap} was measured in this experiment.

Sampling and Chemical Analysis

Daily $PM_{2.5}$ samples were collected on the quartz filter during the campaign. These samples were weighed and further analyzed chemically for water soluble ions (e.g., SO_4^{2-} , NO_3^- , and NH_4^+), elemental carbon (EC) and organic carbon (OC). The methods and processes used for the sampling and chemical analysis have been described in detail previously by Tian *et al.* (2015).

Data Pretreatment

Raw data were recorded at 1-min intervals for the PSAP, MAAPs, PAX and Neph, at 5-min intervals for the AE-31s, and ~6-second intervals for the CRDS. To compare at the same time resolution, raw data at different intervals were hourly averaged before analysis. Hourly data were further daily averaged from 09:00 LST to 09:00 LST of the following day when compared with the sampling data.

Stability CHECKS

As shown in Fig. 1(b), two AE-31s and two MAAPs were set in the same frame during the second sub-period of the experiment to check the stability of the instruments. Although the two AE-31s were operated at different flow rates (2 L/m for AE31-B and 4 L/m for AE31-W), the [BC] measurements were highly consistent (Fig. S1(a)). The measurements of the two MAAPs were also consistent, with the overall discrepancy (~8%) lower than the inherent bias ($\pm 10\%$) between different units of MAAP reported by the manufacturer (solid triangles in Fig. S1(b)). The measurement consistency, both in the two AE-31s and in the two MAAPs, suggests that the two types of instruments worked in a stable manner during the experiment.

Measurement stability was also checked by setting the two MAAPs into different branches during the main part of the intercomparison experiment (see Fig. 1(a)). No significant divergence was found from the [BC] recorded by the two MAAPs at different flow rates (10.8 L/m for MAAP-I and 8 L/m for MAAP-C), which indicated that the influence of pipe losses in different branches, as well as the variation in flow rates, can be ignored in this study (open circles in Fig. S1(b)). Thus, considering the unchanged flow rate throughout the whole experiment, MAAP-I was chosen as the representative MAAP to compare with the other types of instruments during the below analysis.

INTERCOMPARISON OF ABSORPTION MEASUREMENTS

Intercomparison of the Reference Methods

As mentioned above, the MAAP, PAX and CRDS-Neph system can be considered as reference methods for the b_{ap} measurements. Thus, intercomparison measurements of these three reference methods are firstly presented. Plotting the

b_{PAX} against the $b_{C\&N}$ shows that the measurements of the PAX correlated poorly with those of the CRDS-Neph system (Fig. 2(a)). Uncertainties in both the measurements of the b_{ep} by the CRDS and the b_{sp} by the Neph might result in a large $b_{C\&N}$ bias. Additionally, particle losses in the cell of the Neph and connecting pipe before entering the measurement cell of the CRDS might also increase the bias in the indirectly determined $b_{C\&N}$. Thus, series connection of the CRDS and Neph should be used with caution when determining the b_{ap} . Synchronous but individual measurements of CRDS and Neph might produce more accurate b_{ap} , which warrants further study.

Although the variation of b_{PAX} was highly consistent with that of the $[BC]$ recorded by the MAAP ($R^2 = 0.98$, Fig. 2(b)), the slope (with a value of ~ 5.9 m^2/g) seems much lower than expected. As mentioned above when introducing the operation principle of the MAAP, a conversion factor with a value of 6.6 m^2/g was employed as the slope in the linear relationship between the b_{ap} at 670 nm and the recorded $[BC]$ of the MAAP. Considering the wavelength dependence of the b_{ap} (greater than zero in general), the value of the slope should be greater than 6.6 m^2/g when comparing the b_{ap} at ~ 532 nm with the recorded $[BC]$. Although there is no substantial evidence to evaluate the reliability of the b_{MAAP} or b_{PAX} , the close agreement between the two MAAPs seems to imply the reliable measurement of the MAAP. Previous studies have shown that strong negative biases of the photoacoustic b_{ap} commonly exist at high relative humidity (RH) (Langridge et al., 2013). During our campaign, which was conducted in summer, $\sim 65\%$ of the ambient RH values were greater than 50% , with a mean value of 59% . Therefore, underestimation of the b_{PAX} can be expected. Thus, measurements of the MAAP-I are chosen as the reference throughout this study when comparing the measurements of the other two filter-based instruments, PSAP and AE-31.

Intercomparison of the PSAP with the Reference

The b_{ap} determined by the PSAP was corrected according to Bond et al. (1999), regardless of the wavelength. Although the correction scheme is provided for a single wavelength

in the PSAP (565 nm), the corrected b_{PSAP} of the 3-wavelength instrument also agrees well with the reference values determined by the MAAP once the filter transmittance (Tr) is greater than 0.3 , with a correlation coefficient (R^2) of 0.97 and slope of 0.96 (Fig. 3). The slope is well within the inherent bias ($\pm 6\%$) between individual PSAPs reported by Bond et al. (1999). Note that the b_{PSAP} at 670 nm was estimated from the measured values at 530 and 660 nm according to the wavelength dependence of the b_{PSAP} . High consistency between the b_{PSAP} and b_{MAAP} implies good applicability in our study of the correction scheme developed by Bond et al. (1999), and also credibility of the reference values of the MAAP measurements. As suggested by the manufacturer and previous work (e.g., Bond et al., 1999; Virkkula et al., 2005; Schmid et al., 2006), the b_{PSAP} with $Tr < 0.5$ is unavailable due to the large biases. However, the b_{PSAP} in our study is adequate until Tr drops to 0.3 .

The wavelength dependence of the b_{ap} (i.e., the absorption Ångström exponent (α_{ap}) calculated from Eq. (S15) in the supplementary file by replacing b_{sp} with b_{ap}) was estimated from the corrected b_{PSAP} at 467 and 660 nm. To access with more data, all data of the b_{PSAP} with $Tr > 0.3$ were employed. Overall, the mean α_{ap} was 0.85 ± 0.21 during this experiment, lower than the commonly used value (~ 1) of freshly emitted BC particles (Bond and Bergstrom, 2006). Despite discussion in previous work for different situations, the cause of an α_{ap} lower than one is still unclear, but may result from the measurement uncertainties or larger values of the imaginary part of the refractive index at longer wavelengths (Bergstrom et al., 2007). Gyawali et al. (2009) also reported a minimum value of α_{ap} (~ 0.88) in the afternoon and ascribed it to the greater enhancement of absorption by coating at longer wavelengths.

Intercomparison of the AE with the Reference

The variation of the b_{MAAP} (at 670 nm) agrees well with that of the $[BC]$ recorded by AE-31 (at 880 nm), with a correlation coefficient of $R^2 = 0.96$ (open circles in Fig. 4). The value of the slope ($\sim 5.8 \pm 0.04$ m^2/g) can be regarded as the mass absorption efficiency (MAE) at 670 nm of the recorded $[BC]$ of AE-31, which can be used as the

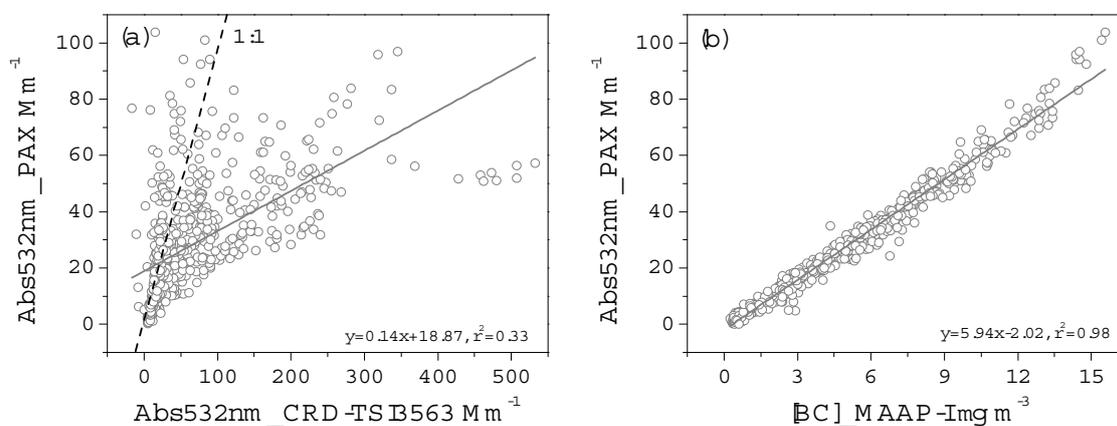


Fig. 2. Scatter plots of the aerosol absorption coefficients at 532 nm determined by the PAX against (a) those determined by the CRDS-Neph system, and (b) the BC concentrations recorded by the MAAP.

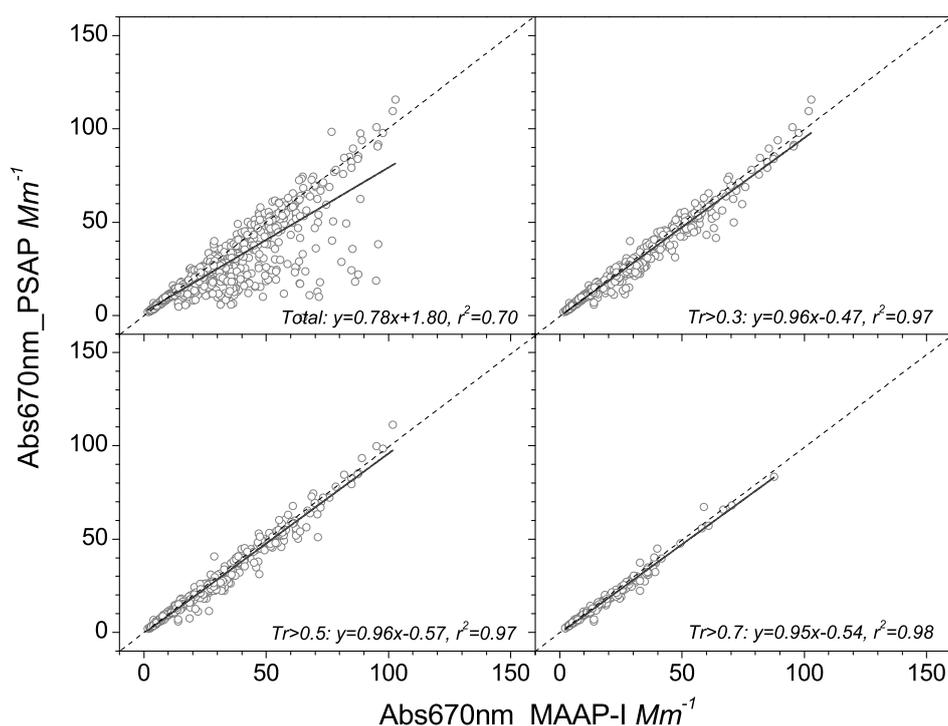


Fig. 3. Scatter plots of the aerosol absorption coefficients at 670 nm determined by the PSAP against those determined by the MAAP. Comparisons at different transmissions are shown in the four different panels.

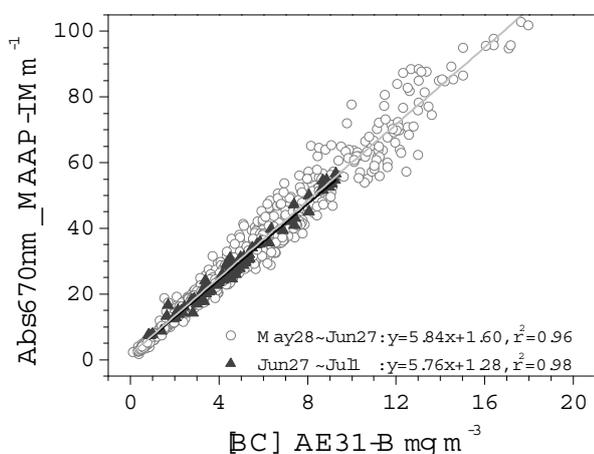


Fig. 4. Scatter plots of the aerosol absorption coefficients at 670 nm determined by the MAAP against the BC concentrations recorded by AE-31 at 880 nm.

conversion factor in Eq. (S5) to evaluate the b_{AE} indirectly. The result is also confirmed by the comparison of the b_{MAAP} against the recorded $[BC]$ of AE-31 during the check period (solid triangles in Fig. 4). Employing the mean wavelength dependence of the b_{ap} derived from the measurement of the PSAP ($\alpha_{ap} = 0.85$), the estimated conversion factor at ~ 530 nm is approximately $7.1 \pm 0.05 \text{ m}^2/\text{g}$, which is much lower than the previously used value ($8.28 \text{ m}^2/\text{g}$; Yan *et al.*, 2008; He *et al.*, 2009). This implies a large discrepancy in aerosol properties between North and South China. Accordingly, previous studies on aerosol absorption in North China

(especially in urban Beijing) based on the measurements of AE-31 using the indirect method and original conversion factor with value of $8.28 \text{ m}^2/\text{g}$ might have overestimated the light absorption of aerosol by $\sim 17\%$, if the temporal variation of the conversion factor was not considered. Because a factor with a value of $6.6 \text{ m}^2/\text{g}$ is used to convert the recorded $[BC]$ of the MAAP to the b_{MAAP} , the value of the slope ($\sim 5.8 \pm 0.04 \text{ m}^2/\text{g}$) of the linear relationship between the b_{MAAP} and the $[BC]$ recorded by AE-31 also implies that the $[BC]$ recorded by AE-31 is systematically higher than that recorded by the MAAP (by $\sim 14\%$ in this study).

The indirect method using an empirical conversion factor can only evaluate the b_{AE} at a certain wavelength of the reference instrument, e.g., 670 nm in this study. Although based on a similar operation principle to the PSAP, there is no mature and commonly accepted method to directly obtain the b_{AE} at multiple wavelengths from the raw measurements of AE-31 (i.e., the measured light attenuation). Even though Eq. (S7) provides a general correction scheme, the identified correction factors (i.e., C and R in Eq. (S7)) are difficult to obtain. However, previous work reported that the artifact of the filter-based method (e.g., AE-31) had an ignorable influence on the wavelength dependence of aerosol absorption (Bond, 2001; Weingartner *et al.*, 2003). Thus, the wavelength dependence of the light attenuation coefficient (α_{ATN}) was calculated to estimate the α_{ap} of AE-31. The mean α_{ATN} between 470 and 660 nm was 0.88 ± 0.13 during the whole experiment, close to the mean value of α_{ap} determined by the PSAP (0.85 ± 0.21). Furthermore, although more uncertainties existed when evaluating the spectral dependence, the α_{ATN} of AE-31 also correlated well

with the α_{ap} of the PSAP ($R^2 = 0.62$). The commonly low α_{ATN} and α_{ap} values imply that spectral dependence lower than one should not be only derived from the measurement uncertainties, which might also relate to the chemical/physical properties of the measured aerosols.

SPECTRAL AEROSOL ABSORPTION PROPERTIES

Aerosol Absorption Magnitude

Inter-day variations of mass concentrations of PM_{2.5}, EC and OC, as well as the b_{ap} (i.e., b_{MAAP} at 670 nm), are shown in Fig. 5(a). The b_{ap} varied significantly with aerosol loading, with the daily mean ranging from 7.0 Mm⁻¹ during clean periods to 67.6 Mm⁻¹ under heavily polluted conditions. The value of the MAE of PM_{2.5} at 670 nm was 0.20 ± 0.02 m²/g, which was estimated as the slope of the linear regression of the b_{ap} against the PM_{2.5} mass concentration. Even considering the wavelength dependence, the MAE of PM_{2.5} (~ 0.25 m²/g at 525 nm) in our study was much lower than previously reported values. Jing *et al.* (2015) reported a value of MAE = 0.78 m²/g at 525 nm at the same site during 2009–2010. However, the b_{ap} in their study was indirectly estimated from the [BC] recorded by AE-31 using the empirical conversion factor of 8.28 m²/g, which will overestimate the b_{ap} as mentioned above. Additionally, the filter-based gravimetric method used in our study usually gives higher PM_{2.5} concentrations than the tapered element oscillating microbalance (TEMO) method utilized in their work (Ayers *et al.*, 1999; Charron *et al.*, 2004). Besides the inherent bias in measurement, a higher portion of scattering composition, such as secondary species, in our study diluted

the light absorption in PM_{2.5} resulting in the low MAE. Three primary secondary inorganic ions (i.e., SO₄²⁻ + NO₃⁻ + NH₄⁺) accounted for 43% of PM_{2.5} during this campaign (Tian *et al.*, 2015), while they accounted for 34% in urban Beijing in July 2009 (Zhang *et al.*, 2013).

The daily b_{ap} showed a highly synchronous temporal variation with EC concentrations ($R^2 = 0.92$, Fig. 5(a)), implying a dominant contribution of EC to aerosol light absorption. As expected, OC was also low on clean days and high during pollution episodes. Meanwhile, the ratio of OC to EC (OC/EC) showed a similar temporal variation, as well as the ratio of secondary inorganic ions to EC (SII/EC) (Fig. 5(b)). Higher ratios of OC and secondary inorganic ions to EC during pollution periods likely significantly influenced the spectral aerosol light absorption, which is discussed below.

Wavelength Dependence

The α_{ap} was 0.85 ± 0.21 averaged over the whole experiment and varied significant. The daily α_{ap} (calculated from the daily b_{PSAP} at 467 nm and 660 nm) seems to show an opposite variation with the b_{ap} and EC concentration, being higher on clean days but lower during pollution episodes (Fig. 5). The values of α_{ap} during clean periods were near 1, the widely adopted value for fresh BC particles (Bond and Bergstrom, 2006), implying freshly emitted BC contributed mostly to light absorption. However, it is very interesting that lower α_{ap} (e.g., < 1) was commonly observed during polluted periods (Fig. 5(b)). The value of α_{ap} was mostly reported close to or higher than the unit for ambient aerosol because of the existence of other light absorbing species besides BC, such as brown carbon (BrC)

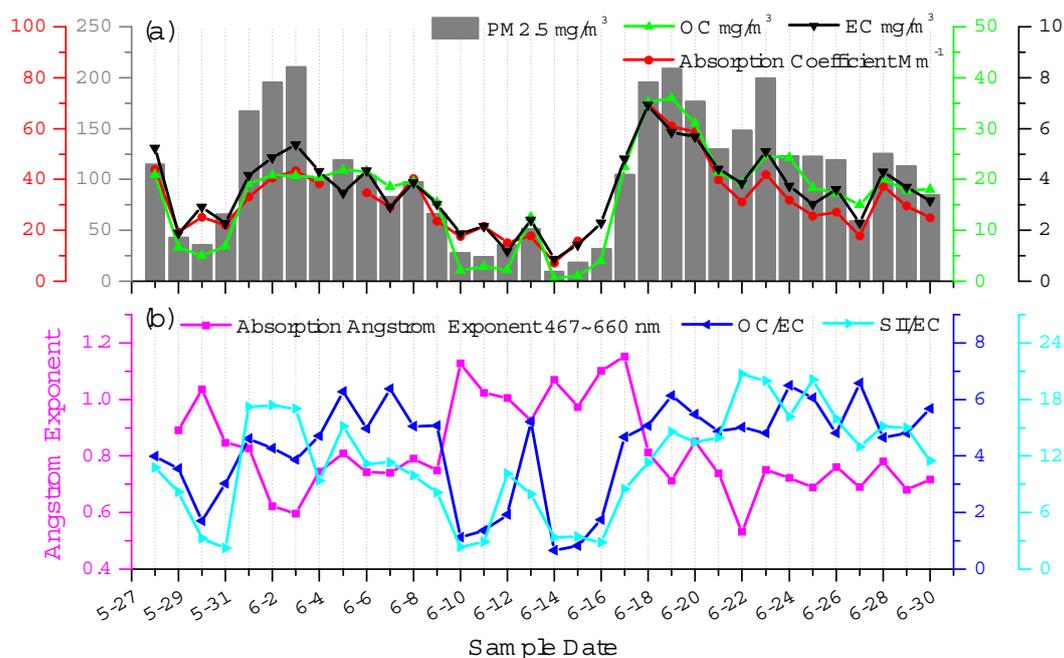


Fig. 5. Time series of daily (a) PM_{2.5}, OC and EC mass concentrations, and absorption coefficients at 670 nm, and (b) absorption Ångström exponents between 467 and 660 nm, and mass ratios of OC and secondary inorganic ions (SO₄²⁻ + NO₃⁻ + NH₄⁺) to EC.

and dust, which absorb stronger in shorter wavelength ranges (e.g., UV spectrum) (Andreae and Gelencsér, 2006; Bergstrom *et al.*, 2007). Even BrC in eastern Asia outflow has been reported as absorbing highly at long wavelengths (e.g., visible and near-infrared spectrum), the α_{ap} of which is also considered to be much higher than 1 (e.g., ~ 1.7 presented by Chung *et al.*, 2012; ~ 1.5 by Alexander *et al.*, 2008). Therefore, lower α_{ap} should not only be attributed to the coexistence of BrC or dust with BC, even though the ratio of organic OC to EC showed a significantly negative correlation with the α_{ap} ($R = -0.70$, Fig. 5(b)).

Besides chemical composition, particle size and morphology also have a great impact on the α_{ap} . A plot of the variation in theoretical α_{ap} with BC core sizes without coating based on Mie theory (Bohren and Huffman, 1998) is shown in Fig. 6(a). Obviously, the α_{ap} decreases sharply once the diameter of the BC core becomes larger than 100 nm, regardless of the complex refractive index ($n-ki$, with n being the real part and k the imaginary part of the refractive index). Previous observations of ambient BC particles have shown the BC core to peak at 150–230 nm in volume equivalent diameter (Huang *et al.*, 2012 and references therein). Considering the size range, the theoretical α_{ap} of non-coated BC particles varies sharply from near 1 to less than 0.4. Although unpublished, our own observations in urban Beijing during January 2013 using a single particle soot photometer (SP2), which can determine the BC core size directly according to the incandescence signal, also showed that the BC core diameter peaked at ~ 200 nm. Moreover, our preliminary analysis revealed that the BC core diameter under clear conditions was significantly lower than that during pollution periods, with a peak at ~ 175 nm compared to ~ 205 nm in volume equivalent diameter. Therefore, there is evidence that lower α_{ap} during pollution can be partly explained by the larger BC core sizes.

Although there is no conclusive evidence certifying the influence of coating on the α_{ap} , a few theoretical (Gyawali

et al., 2009) and laboratory (Schnaiter *et al.*, 2005) studies have shown that modest coating by non-absorbing matter can reduce the α_{ap} of BC. Fig. 6(b) illustrates the variation of the Mie-theoretical α_{ap} as a function of the ratios of coating thickness to BC core radius. Two BC core sizes were evaluated, with diameters of 175 and 205 nm representing the typical BC core size under clean and pollution conditions, respectively. Obviously, thick coating (e.g., shell thickness/core radius > 0.5) by non-absorbing matter will reduce the α_{ap} to some extent (see lines with circles in Fig. 6(b)). However, if coated by weakly absorbing matter (e.g., $n = 1.5$, and $k = 0.002$ at 467 nm, while $k = 0$ at 660 nm), the α_{ap} shows a more complex relationship with the ratio of shell thickness to core radius (see lines with triangle in Fig. 6(b)). Generally, for the two BC core sizes (i.e., 175 nm and 205 nm in diameter), the α_{ap} decreased under modest shell thickness conditions (e.g., $0.5 < \text{shell thickness/core radius} < 1.5$) and increased with much thicker coating (e.g., shell thickness/core radius > 2). The increase of the α_{ap} in the much thicker coating conditions might be related to the great increase in the abundance of the weakly absorbing species with a high α_{ap} , which offset the decrease of the α_{ap} induced by the coating effect. According to our observations at this site during January 2013, BC tended to be thickly coated by other species on haze days (70% on haze vs. 37% on non-haze days). Thus, moderately thick coating might account for the decrease in α_{ap} during pollution periods to some extent.

Although these calculations were performed with monodisperse particles, the lower α_{ap} during pollution is nevertheless greatly related to the BC core size and its coating thickness. Further investigation of the BC core size and coating thickness under different conditions is needed to advance our understanding of aerosol radiation properties.

Absorption Efficiency of BC

The slope of the linear relationship between b_{ap} and EC

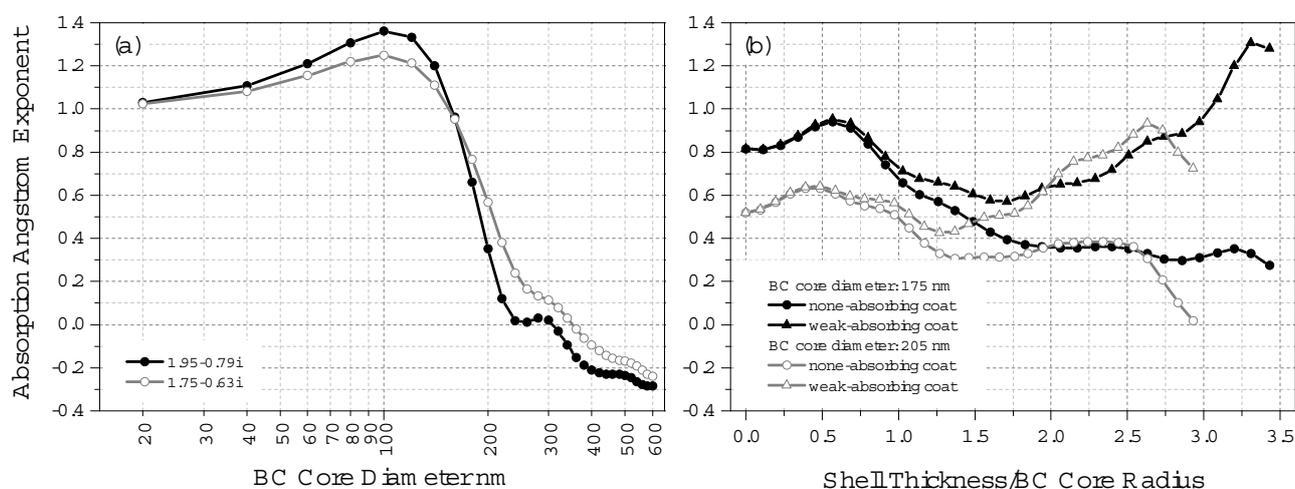


Fig. 6. (a) Variation of the absorption Ångström exponents of non-coated BC particles as a function of the BC core diameters; (b) variation of the absorption Ångström exponents of coated BC with the identical core size as a function of the ratios of shell thicknesses to BC core radius. The refractive index with a value of 1.75–0.63i was selected as representative of the BC core in (b).

(simply equivalent to BC hereafter) concentrations illustrates the absorption efficiency of BC, which is usually called the MAE of BC. The bulk MAE of BC in our study is $9.2 \pm 0.5 \text{ m}^2/\text{g}$ at 670 nm (Fig. S2), equivalent to $\sim 10.9 \pm 0.6 \text{ m}^2/\text{g}$ at $\sim 550 \text{ nm}$ when considering the mean α_{ap} of 0.85, which is higher than previously reported for the measurements of aerosols at other urban sites, although different methods to determine the b_{ap} or BC concentrations were used (e.g., Lan *et al.*, 2013 and references therein). However, this mean value is close to that ($\sim 11.3 \text{ m}^2/\text{g}$ at 550 nm) reported by Yang *et al.* (2009), whose work was conducted near Beijing. Cheng *et al.* (2011) also presented a similar MAE of BC in Beijing ($\sim 9.4 \text{ m}^2/\text{g}$ at 632 nm during summer). Previous research has shown that particle absorption would be amplified by coating with scattering components (Shiraiwa *et al.*, 2008, 2010). Thus, a higher MAE of BC might be related to more coating in this region. Although there is no direct evidence from our measurements, the high percentage of secondary inorganic aerosols as well as OC (see Tian *et al.*, 2015) increase the probability of coated BC, resulting in a high MAE of BC. The MAE during pollution periods was significantly greater than that on clean days, with means of $10.9 \text{ m}^2/\text{g}$ against $6.5 \text{ m}^2/\text{g}$ at 670 nm, respectively. BC tends to be coated by other scattering compositions on haze days leading to a higher MAE. The MAE under clean conditions ($\sim 7.7 \text{ m}^2/\text{g}$ at 550 nm) was close to that of typically less-coated, fresher urban BC particles suggested by Bond and Bergstrom (2006) ($7.5 \pm 1.2 \text{ m}^2/\text{g}$ at 550 nm) and Schwarz *et al.* (2008) ($7.9 \text{ m}^2/\text{g}$ at 530 nm), indicating a dominant contribution of fresh BC emitted to aerosol light absorption.

CONCLUSION

Aerosol light absorption is important to radiation balance, but it is difficult to accurately quantify using measurements. The widely used filter-based methods (e.g., PSAP and AE) encounter inherent bias when used to determine the b_{ap} , such as the scattering and loading effects induced by the filter. Although the b_{ap} measured by the photoacoustic technique (e.g., PASS and PAX) or determined as $b_{ep} - b_{sp}$ (e.g., the CRDS-Neph system) is generally accurate and close to true values, the high cost and difficulty in maintaining such instruments limits their application in the long-term monitoring of aerosol absorption. Having treated the scattering effects in the filter-based measurements, the b_{ap} determined by the MAAP was closer to true values. However, the spectral absorption properties, which are also important to climate modeling, could not be derived via this method, in which only the b_{ap} at a single wavelength is measured. Thus, filter-based aerosol light-absorbing measurements are still recommended, but need to be corrected for the inherent bias. An experiment that compared the measurements of b_{ap} using a range of instruments was performed at an urban site in Beijing during the summer of 2012. The instruments included the filter-based PSAP and AE-31, and the reference PAX, CRDS-Neph system, as well as the advanced filter-based MAAP.

Differences were found between the reference methods; the b_{ap} determined by the CRDS-Neph was poorly correlated

with that of the PAX or MAAP. Series connection in the CRDS and Neph should be used with caution for measuring the b_{ap} indirectly, owing to the likely growth of measurement error in both instruments, as well as particle losses in the system. The b_{ap} determined by PAX was greatly influenced by the ambient RH and the pre-measurement calibration. Although the measurements of the PAX and MAAP were closely correlated ($R^2 = 0.98$), the recorded b_{ap} of the PAX seemed to be systematically underestimated in this study. Aerosol drying should be considered when using the photoacoustic instrument as the reference of the aerosol absorption measurements. The b_{ap} determined by the MAAP was used as the reference to compare with those measured by the PSAP or AE-31.

The corrected b_{ap} of the PSAP according to Bond *et al.* (1999) agreed well with the reference values determined by the MAAP, implying the applicability of this correction scheme as well as the credibility of the reference b_{ap} of the MAAP. A new conversion factor with a value of $5.8 \pm 0.04 \text{ m}^2/\text{g}$ was established by regressing the reference b_{ap} at 670 nm against the recorded $[BC]$ of AE-31, equivalent to $\sim 7.1 \pm 0.05 \text{ m}^2/\text{g}$ at $\sim 530 \text{ nm}$, which is much lower than the previous value ($8.28 \text{ m}^2/\text{g}$) used in the indirect method to estimate the b_{ap} from the recorded $[BC]$ of AE-31. This finding indicates that the use of the single value of $8.28 \text{ m}^2/\text{g}$ may cause bias as this value is dependent on the sources of aerosols, meteorological conditions and may vary with location and season. Long-term synchronous observation of the AE and the reference method, such as the MAAP, is needed to provide a more reliable conversion factor which suitable for the aerosol in urban Beijing.

Spectral absorption properties were discussed based on the corrected filter-based b_{ap} . The wavelength dependence of b_{ap} (i.e., α_{ap}) was 0.85 ± 0.21 on average during the whole experiment; importantly, this is lower than 1, the widely used value for freshly emitted BC. The α_{ap} was close to 1 on clean days but significantly lower than 1 during pollution episodes, implying the main contributor to aerosol light absorption is freshly emitted BC on clean days but aged BC with different properties during pollution episodes. BC core sizes have a great impact on the α_{ap} ; lower α_{ap} values might be related to larger BC cores during pollution. Besides, the coating of BC cores might also influence the α_{ap} to some extent. Further investigation of the BC core size and the coating thickness is needed to explore this phenomenon more clearly. The MAE of BC was estimated by regressing the b_{ap} against the daily EC concentrations. Considering the wavelength dependence, the mean MAE ($9.2 \pm 0.5 \text{ m}^2/\text{g}$ at 670 nm) was relatively high in this study, which might be related to more coating. Moreover, the MAE during pollution was remarkably higher than during clean conditions, further implying the variation in aerosol properties such as the mixing state.

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SUPPLEMENTARY MATERIALS

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

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Supplementary materials for manuscript entitled “Spectral light absorption of ambient aerosols in urban Beijing during summer: an intercomparison of measurements from a range of instruments”

Introduction of the operation principle and correction scheme of aerosol absorption measurements for each instrument

(S1) PSAP

The PSAP is a widely used instrument for the real-time measurement of aerosol absorption. The 3-wavelength PSAP employed in our study measures the light absorption at three wavelengths of 467, 530 and 660 nm. Considering the magnification of absorption by the filter medium or nonlinearities in the response of the unit as the filter is loading, the absorption coefficients reported by PSAP ($b_{PSAP,raw}$) are empirically described as

$$b_{PSAP,raw} = b_{ap,raw}/f(Tr) \quad (S1)$$

and

$$f(Tr) = 1.0796 \cdot Tr + 0.71, \quad (S2)$$

where $b_{ap,raw}$ is the raw derived absorption coefficient according to Beers Law, as well as the practical flow rate and sample spot area, which is similar to the b_{ATN} of the AE (see Eq. S4), and $f(Tr)$ is the transfer function based on filter transmittance (Tr , $Tr=1$ for an unloaded filter). The transfer function is incorporated in the software.

Bond *et al.* (1999) calibrated the single-wavelength PSAP (565 nm) with pure nogrosin and ammonium sulfate particles as well as internal mixtures of both by comparing with reference measurements. The adjustments to the PSAP can be summarized as (Bond *et al.*, 1999; Schmid *et al.*, 2006)

$$b_{PSAP} = \frac{b_{PSAP,raw} \cdot K_Q \cdot K_A - K_1 \cdot b_{sp}}{K_2}, \quad (S3)$$

where K_Q and K_A are the correction factors for flow rate and sample spot area, respectively; K_1 and K_2 are aerosol-scattering-related calibration constants given by $K_1=0.02\pm0.02$ and $K_2=1.22\pm0.2$, respectively; and b_{sp} is the aerosol scattering coefficient at the same wavelength. The uncertainty of the corrected b_{PSAP} can be estimated as $\sim 23\%$ using the uncertainties of K_Q , K_A , K_1 and K_2 (Schmid *et al.*, 2006). The spot sizes varied less in this experiment with the average diameter of 5 mm. Therefore, a mean value of 0.96 ($= (5/5.1)^2$ where 5.1 is the spot diameter of the reference PSAP calibrated by the manufacturer) for K_A was utilized in this work. Besides, regular flow rate checks for PSAP showed good consistency between the internal set value and the true flow rate during the experiment. Thus, K_Q was not involved in this study.

(S2) AE-31

The operation principle of the AE is very similar to that of the PSAP, both of which belong to the category of filter-based transmittance measurements. The AE is a self-contained, automatic instrument and requires no calibration other than periodic checks of the airflow meter response. The model AE-31 measures the attenuation (ATN) of incident light at seven wavelengths (370, 470, 520, 590, 660, 880, and 950 nm) transmitted through a particle-laden quartz filter (Hansen *et al.*, 1984). The absorption coefficient of the filtered aerosol particles (referred to as the attenuation coefficient, b_{ATN}) can be determined as the change in attenuation (ΔATN) during the time interval (Δt) and given by

$$b_{ATN} = \frac{A \Delta ATN}{Q \Delta t}, \quad (S4)$$

where A is the area of the filter spot and Q is the volumetric flow rate. The measured attenuation coefficient at each wavelength is converted into the corresponding BC mass concentration ($[BC]$), which is directly presented by the instrument according to

$$[BC] = \frac{b_{ATN}}{\sigma_{ATN}} \quad (S5)$$

and

$$\sigma_{ATN} = 14625 / \lambda, \quad (S6)$$

where σ_{ATN} (units: $\text{m}^2 \text{g}^{-1}$) is the spectral mass specific attenuation cross-section at wavelength of λ (units: nm). The b_{ATN} is commonly higher than the true absorption coefficient of ambient aerosol because of the effect of the filter. Thus, correction for the AE-31-derived aerosol absorption coefficient (b_{AE}) is necessary. Empirical or theoretical correction for the b_{AE} has been presented in previous research (e.g., Weingartner *et al.*, 2003; Arnott *et al.*, 2005; Schmid *et al.*, 2006), and was also reviewed by Coen *et al.* (2010). Although there are differences between these correction methods, the general scheme of correction can be expressed as

$$b_{AE} = \frac{b_{ATN}}{C \cdot R(ATN)}, \quad (S7)$$

where the factor C corrects for scattering effects within the filter and $R(ATN)$ accounts for the “shadowing” effect due to filter loading, which is related to the ATN .

Since light absorption can be attributed solely to BC in the near-infrared channel, the $[BC]$ recorded by the AE at the wavelength of 880 nm is usually used to simply determine the b_{AE} by multiplying an appropriate factor (i.e., mass absorption efficiency):

$$b_{AE} = \sigma \cdot [BC], \quad (S8)$$

where σ is the indirect conversion factor which can be determined empirically from linear regression of $[BC]$ against the b_{ap} from a reference method. The value of $\sigma=8.28 \text{ m}^2 \text{ g}^{-1}$ (corresponding to b_{AE} at 532 nm), which was obtained based on the result of an

intercomparison experiment conducted in southern China, is commonly used in the indirect conversion of AEs in China (e.g., Yan *et al.*, 2008; He *et al.*, 2009). However, the value of σ is greatly affected by the physical and chemical properties of the light absorbing matter, which vary spatially and temporally, and so the value obtained in southern China is not completely suitable for application in northern China. Thus, a new value of the conversion factor, which should be more reliable for aerosol absorption research in northern China, is presented in this study, also established via intercomparison experiments.

(S3) MAAP

Although the MAAP is also a filter-based instrument, it determines the b_{ap} via the simultaneous measurement of light transmitted through and backward-scattered from the particle-laden filter. It operates at two detection angles (130° and 165°) to resolve the influence of light scattering aerosol components on the angular distribution of the back-scattered radiation (Petzold and Schönlinner, 2004; Petzold *et al.*, 2005). The b_{ap} of the MAAP (b_{MAAP}) can be determined from the final parameter combination through iterative calculation and expressed as

$$b_{MAAP} = -\frac{A}{V}(1 - SSA_L^{(f)}) \cdot LOD^{(f)}, \quad (S9)$$

where SSA_L and LOD are the single scattering albedo (ratio of light scattering to extinction) and total optical depth ($LOD = \ln T_L$, T_L is the transmission) of the aerosol-filter layer, respectively, and A and V refer to the active filter area and sampled volume, respectively. The superscript (f) represents the final value of the iterative process to the below equations:

$$\frac{P_F}{P_F^{(0)}} = \frac{T_L + F_L}{1 - B_L^* B_M} \quad (S10)$$

and

$$\frac{B_F}{B_F^{(0)}} = P_L^* \frac{T_L + F_L}{1 - B_L^* B_M} + \frac{B_L}{B_M}, \quad (S11)$$

where the parameters F , B , and T are the fractions of forward-scattered, back-scattered, and transmitted radiation; P is the total fraction of radiation passing through a layer ($P = T + F$); and the subscripts L , M and F represent the particle-loaded aerosol-filter layer, the particle-free filter matrix, and the composite system consisting of the aerosol-filter layer and the particle-free filter matrix, respectively.

The MAAP records $[BC]$ directly, which is determined by dividing the measured b_{MAAP} by the manufacturer-provided conversion constant (i.e., the mass absorption efficiency, $6.6 \text{ m}^2 \text{ g}^{-1}$). Thus, b_{MAAP} can be simply calculated by the recorded $[BC]$ multiplied by this conversion constant:

$$b_{MAAP} = 6.6 \cdot [BC], \quad (S12)$$

where $[BC]$ is in units of $\mu\text{g m}^{-3}$ corresponding to b_{MAAP} in units of Mm^{-1} . According

to the instrument's manual, the central wavelength of the incident light is close to 670 nm. Thus, the b_{MAAP} at wavelength of 670 nm were determined from the measurements.

(S4) PAX

The main principle of the photoacoustic technique is to determine aerosol light absorption based on the conversion of the absorbed energy into an acoustic wave which is then detected by a sensitive microphone (Truex and Anderson, 1979). Light absorption ($b_{PAX,raw}$) derived from this method can be expressed as (Arnott *et al.*, 1999, 2000; Schmid *et al.*, 2006)

$$b_{PAX,raw} = \frac{P_m}{P_L} \frac{\pi^2 A_{res} f_0}{Q(\gamma - 1)}, \quad (S13)$$

where A_{res} , f_0 , and Q are the cross-sectional area, resonance frequency, and dimensionless quality factor of the acoustic resonator, respectively; and P_m , P_L , and γ are the acoustic pressure from light absorption, the laser beam power, and the ratio of specific heats for the gas mixture, respectively. The b_{ap} recorded by PAX (b_{PAX}) is then determined as the measured light absorption ($b_{PAX,raw}$) subtracted by the background light absorption of particle-free air.

The PAX used in this study is a commercial product based on the photoacoustic method. As specified by the manufacturer, the PAX utilizes a Class 3B fiber-coupled laser module with wavelength of 532 nm. In addition to the measurement of b_{ap} , the PAX also simultaneously determines aerosol scattering coefficients (b_{sp}) through a wide-angle integrating reciprocal nephelometer. Details of the PAX's operation is available in the manufacturer's manual and so is not described in any further depth in this paper.

The PAX was calibrated before the campaign using the highly concentrated pure scattering material (ammonia sulfate in this study) and standard soot particles (Aquadag in this study). The scattering signal of PAX was first calibration using the highly concentrated ammonia sulfate. The step by step procedures are listed below:

- ① First, particle-free air was measured for several minutes by adding a filter on the inlet. The average laser power (I_0) was recorded as well as the scattering coefficient (b_{sp}).
- ② Then, pure scattering particles with high concentration were generated and measured by the PAX for several minutes. The laser power during the period (I) was recorded as well as the b_{sp} .
- ③ The extinction coefficient during calibration (b_{ep}) can be calculated from the variation of laser power:

$$b_{ep} = -\frac{1}{0.354} \ln \frac{I}{I_0} \cdot 10^6 [Mm^{-1}], \quad (S14)$$

where the constant with value of 0.354 is the path length of the laser beam through the cavity in meters which is provided by the manufacturer.

④ The calculated b_{ep} was linear regressed against the recorded b_{sp} . The coefficient of the scattering signal was then modified by multiplying the slope of the linear regression.

The absorption signal was then calibrated based on the similar procedures but using the highly concentrated Aquadag particles instead of the pure scattering particles. The scattering coefficients (b_{sp}) and absorption coefficients (b_{ap}) were both recorded. The calculated b_{ep} according to the variations of laser power were subtracted by the recorded b_{sp} and then linear regressed against the recorded b_{ap} (i.e., $(b_{ep} - b_{sp})$ vs. b_{ap}). The slope was used to calibrate the coefficient of the absorption signal. The overall uncertainty of the photoacoustic absorption coefficient including that during the calibration is estimated to be ~5%.

(S5) CRDS and Neph

The aerosol extinction coefficient (b_{ep}) measured by the CRDS minus the b_{sp} measured by the Neph was chosen as another reference for the aerosol absorption measurement. The CRDS employed in this study is self-developed (Li *et al.*, 2011, 2013) based on the theory and scheme presented in previous work (e.g., O’Keefe and Deacon, 1988; Zalicki and Zare, 1995; Berden *et al.*, 2000; Moosmüller *et al.*, 2005). The principle of operation is based on the measurement of a decay rate of the intensity of the trapped pulse round tripping within the optical cell:

$$b_{ep} = \frac{L}{c \cdot l} \cdot \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right), \quad (\text{S15})$$

where L and l are the cavity length and the effective light path, respectively; τ and τ_0 are the ring-down time (i.e., the time taken for the intensity of light to fall to 1/e of the initial intensity) of the ambient air and particle-free air, respectively; and c is the speed of light in a vacuum. The ratio of L to l (i.e., L/l) should be a constant, which was determined and checked before the experiment using standard particles such as Polystyrene Latex Spheres (PSLs) with certain diameter.

The Neph is commonly used to determine the b_{sp} . The main principle of operation is based on the linear relationship between measured photo counts and scattering coefficients. The b_{sp} can be then determined by the corresponding scattering coefficients minus the scattering of zero gas (i.e., particle-free air). The Neph used in this study is a mature commercial product which is operable at three wavelengths (450, 550, 700 nm) (see Anderson *et al.* (1996) for a detailed description). Correction for angular nonidealities, including truncation error and the non-Lambertian distribution of illumination intensity, is needed to obtain accurate aerosol scattering coefficients from the measurements of the Neph. Anderson and Ogen (1998) found that the angular correction factor is closely related to the particle size, which can be roughly illustrated by the wavelength dependence of light scattering (i.e., the scattering Ångström exponent, α_{sp}). The α_{sp} is defined as the power-law relation between the b_{sp} and the wavelength (λ) of incident light (Ångström, 1964):

$$\alpha_{sp} = \frac{\ln b_{sp, \lambda_1} - \ln b_{sp, \lambda_2}}{\ln \lambda_1 - \ln \lambda_2}. \quad (\text{S16})$$

Analogous to α_{sp} , the absorption Ångström exponent (α_{ap}) is defined by replacing b_{sp} with b_{ap} . The empirical correction to obtain the true b_{sp} from that measured by the Neph ($b_{sp,Neph}$) is given as

$$b_{sp} = b_{sp,Neph} \cdot (a + b \cdot \alpha_{sp,Neph}), \quad (S17)$$

where a and b are the empirical correction parameters reported by Anderson and Ogen (1998) against no-cut and sub-micrometer particles, respectively; and $\alpha_{sp,Neph}$ is the scattering Ångström exponent calculated using the uncorrected Neph measurements of $b_{sp,Neph}$ at multiple wavelengths. Actually, ‘Mie theory’ combined with synchronous measurements of particle size distribution and reasonable assumption of particle optical parameters (e.g., refraction index) can provide a more accurate correction for the Neph (Heintzenberg *et al.*, 1996), which has been adopted in previous work (e.g., Cheng *et al.*, 2006; Ma *et al.*, 2011).

Since the wavelength of the incident light of CRDS is 532 nm, the b_{sp} at wavelength 532 nm was calculated from the corrected b_{sp} at 450 nm and 550 nm using the power-law relationship between b_{sp} and the wavelength of the light. As a result, the b_{ap} at wavelength 532 nm was determined from the combined system

$$b_{C\&N} = b_{ep} - b_{sp}, \quad (S18)$$

where $b_{C\&N}$ represents the b_{ap} determined from the CRDS-Neph system.

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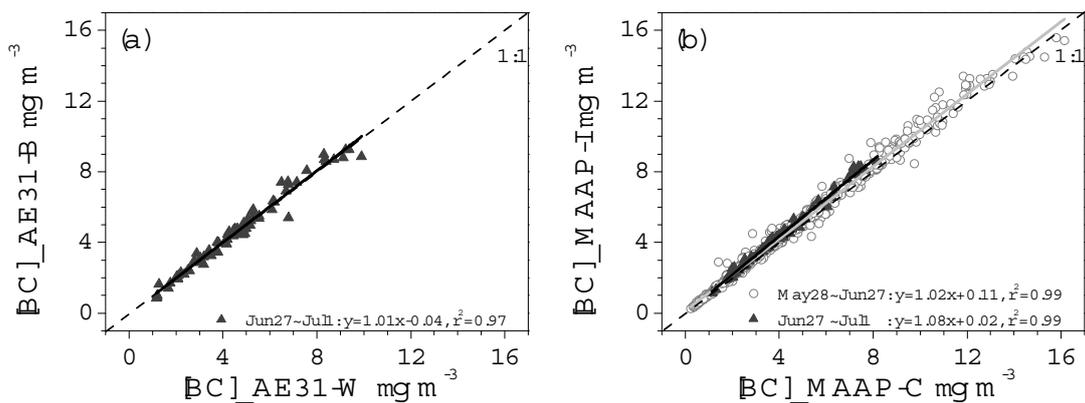


Fig. S1. Scatter plots of the BC concentrations recorded by (a) the two AE-31s and (b) the two MAAPs.

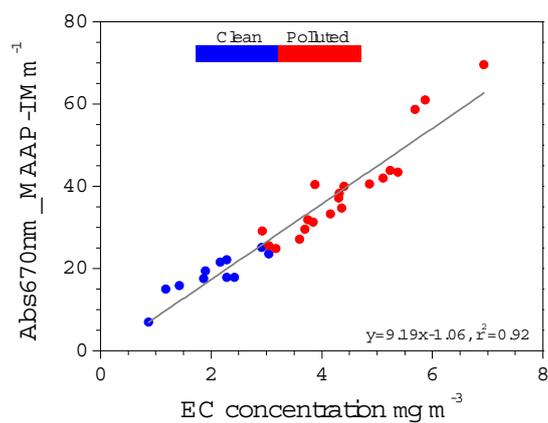


Fig. S2. Scatter plots of the daily absorption coefficients at 670 nm against EC concentrations.