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Short communication

# Mass absorption efficiency of elemental carbon for source samples from residential biomass and coal combustions

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ABSTRACT

Optical properties of particulate matter are of growing concern due to their complex effects on atmospheric visibility and local/regional climate change. In this study, mass absorption efficiency (MAE) of elemental carbon (EC) was measured for source emission samples obtained from the residential combustions of solid fuels using a thermal-optical carbon analyzer. For source samples from residential wood, crop straw, biomass pellet and coal combustions, MAE of EC measured at 650 nm, were 3.1 (2.4–3.7 as 95% Confidence Interval), 6.6 (5.5–7.6), 9.5 (6.7–12), and 7.9 (4.8–11) $m^2\ g^{-1}$, respectively. MAE of EC for source sample from the wood combustion was significantly lower than those for the other fuels, and MAE of EC for coal briquette appeared to be different from that of raw chunk. MAE values of the investigated source emission samples were found to correlate with OC/EC ratio, and a significantly positive correlation was found between MAE and particle-bound polycyclic aromatic hydrocarbons (pPAHs), though pPAHs contributed a relatively small fraction of OC.



## 1. Introduction

Mass absorption efficiency (MAE, also referred to as mass absorption cross section) is a widely used parameter characterizing the optical properties of light absorbing particles (Bond and Bergstrom, 2006; Cheng et al., 2011). MAE values of light absorbing particles are widely used by climate modelers to determine solar radiation absorption, and it is also an important parameter used to measure elemental carbon mass concentration with photometric methods (Bond and Bergstrom, 2006; Chung et al., 2012; Liousse et al., 1993; Ram and Sarin, 2009). The term of light-absorbing carbon (LAC) was suggested by Malm et al. (1994) and adopted by Bond and Bergstrom (2006) in their review to avoid conflict with operationally based definition. In practice, the light absorbing component has several names, among which, "Black Carbon (BC)" is the most widely used for climate modelers, and "Elemental Carbon (EC)" is widely used in air quality and source apportionment studies by atmospheric chemists (Bond et al., 2004; Bond and Bergstrom, 2006). BC is defined optically, implying that the aerosols have strong absorption across a wide spectrum of wavelengths, and EC is an operational definition based on the thermal stability of carbon.

MAE reported in the literature vary dramatically depending on the source types (e.g., biomass burning or diesel exhaust), particle properties (e.g., size and mixing state) and even measurement methods (e.g., filter-based or not) (Bond and Bergstrom, 2006; Kanaya et al., 2008; Lan et al., 2013; Ram et al., 2012; Snyder and Schauer, 2007; Weingartner et al., 2003). Once emitted into the atmosphere, MAE values would change obviously (increased in most cases) due to particle coagulation and aggregation, change in mixing status during the aging (Bond and Bergstrom, 2006; Lan et al., 2013; Ram et al., 2010), and also influenced by ambient meteorological conditions like relative humidity (Cheng et al., 2008; Wehner et al., 2009). Bond and Bergstrom (2006) reviewed published MAE data in the literature, and found that after correction for the measurement wavelength and scattering processes in the filter medium, most of the reported results for freshly emitted light-absorbing carbon fell in a narrow range of 6.3–8.6 $m^2\ g^{-1}$ ($n = 21$), and the variability in MAE for ambient LAC is generally greater. Recent, Lan et al. (2013) reported MAE of black carbon measured at 532 nm averaged at $6.5 \pm 0.5\ m^2\ g^{-1}$ in South China where main emission source was vehicular emissions, rather than biomass burning. Schwarz et al. (2008) reported a high MAE value

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($13 \pm 3$ $m^2$ $g^{-1}$) with thicker coatings for biomass burning black carbon in comparison with that for urban aerosol mainly from vehicle emissions ($7.5 \pm 2$ $m^2$ $g^{-1}$). However, Cheng et al. (2011) found that MAE values of ambient EC were much lower in the regions heavily impacted by biomass burning. Using source emission samples, Cheng et al. (2011) also found that MAE values of diesel exhaust were higher than those of biomass burning. While a large number of studies so far work on light absorption property of ambient aerosol, to the best of our knowledge, measurements on MAE for source emission samples are much fewer (Bond et al., 1999; Cheng et al., 2011; Schnaiter et al., 2003).

MAE is usually calculated from the light absorption coefficient ($b_{abs}$) divided by the simultaneous but independent measured mass concentration of elemental carbon (EC). In most cases, optical measurement instruments, like Aethalometer (filter-based), Particle soot absorption photometer (PSAP, filter-based), and Photoacoustic spectrometer (PAS, which can measure light absorption directly on airborne particles), were used to measure the light attenuation (ATN) and $b_{abs}$, while thermal-optical (or thermal) instruments, like Sunset semi-continuous carbon analyzer and DRI model thermal/optical carbon analyzer, are used to measure the mass concentration of EC. In this method, two instruments are often required, and the light absorption and EC measurements are usually conducted for not exactly the same samples. The use of a thermal-optical carbon analyzer to determine both light attenuation and EC concentration has been introduced in the literature, and provided a reliable and effective measurement (Cheng et al., 2011; Ram and Sarin, 2009). It was reported in the literature that ATN values measured using a Sunset carbon analyzer agreed well with those measured using PSAP ($R^2 = 0.93$, Sciare et al., 2003) or Aethalometer ($R^2 = 0.82$, Ram and Sarin, 2009).

The main objective of this study is to measure MAE of EC of source emission samples from residential combustions of various solid fuels that are commonly found in rural China by using a thermal-optical carbon analyzer. In this study, EC is defined as the carbon fraction measured in an oxygen/helium atmosphere at elevated temperature.

## 2. Method

Four types of solid fuels including wood, crop straw, coal and biomass pellets were combusted in residential cooking stoves in rural China. Detailed information about the fuel combustion and sampling procedure can be found elsewhere in which the emission factors of incomplete pollutants, including carbonaceous particles and polycyclic aromatic hydrocarbons (PAHs) were measured for crop straw (Shen et al., 2010a, 2011), wood (Shen et al., 2012a, 2012b), coal (Shen et al., 2010a, 2010b) and biomass pellets (Shen et al., 2012c). Briefly, particles in the combustion exhaust were collected using quartz fiber filters. Organic carbon and elemental carbon were analyzed using a Sunset EC/OC analyzer (Sunset Lab, USA). The temperature protocol used is listed in Table S1. Briefly, the oven temperature was increased to 600 (90 s), 840 °C (90 s) in a pure helium atmosphere for OC detection, and then 550 (35 s), 650 (45 s) and 870 (90 s) °C in an oxygen/helium atmosphere to analyze EC (Shen et al., 2010a, 2012a). Pryolyzed OC formed in pure helium when temperature increased was subtracted from EC according to the initial transmitted light signal. It's noted that different temperature protocols could result in varied EC values (Cavalli et al., 2010; Cheng et al., 2011), indicating cautions in the direct comparison of measured EC concentration and calculated MAE of EC. Light attenuation was monitored at 650 nm and calculated automatically according to the Beer–Lambert's law. It was proved that the Lambert–Beer law was valid down to transmission of $10^{-5}$ (Horvath, 1993).

MAE ($m^2$ $g^{-1}$) is calculated according to the following equation:

$$\mathrm{MAE} = \frac{\mathrm{ATN}}{\mathrm{ECs} \cdot C \cdot R(\mathrm{ATN})}$$

where ATN is the light attenuation (a unit less parameter), ECs is the EC mass loading on the filter (μg $cm^{-2}$), $C$ and $R$(ATN) are two empirical factors that are often used to correct the artifacts in filter based measurement due to the multiple scattering and shadowing effects, respectively. Detailed calculation process can be found in the Appendix (Section A1).

ATN values for filter blank and clean filter spiked with glucose standard (42.07 μg) were $0.002 \pm 0.002$ ($n = 30$) and $0.008 \pm 0.007$ ($n = 12$), respectively, suggesting the light attenuation of particle-loaded filter was mainly induced by the present of sampled light-absorbing particles (Cheng et al., 2011; Yang et al., 2009). Measured ATN values strongly correlated with EC mass loading on the filter (Table S2), but the linearity ceased at high EC loadings (Figure S1). And hence, the outliers were excluded in the calculation of MAE of EC. In the present study, C of 2.14 was used for the freshly emitted samples measured near the combustion source and collected using the quartz fiber filter (Bond and Bergstrom, 2006; Schmid et al., 2006). It is realized that a constant C correction may be inappropriate, especially for particles with abundant organic fraction (Cappa et al., 2008; Schmid et al., 2006; Weingartner et al., 2003). Moreover, the use of correction values applied for other optical instruments could lead to an increased uncertainty. The analytical data, applied correction factors and associated uncertainty analysis are present in the Appendix Section A3 and Table S3 in detail. By assigning uncertainties of 7% in ATN, 10% in ECs, 40% in C and 84% in $R$(ATN), the propagated error in calculated MAE was 94%. *Stastistica* (v5.5, StatSoft) was used in data statistical analysis with a significance level of 0.05.

## 3. Results and discussion

Fig. 1 shows the frequency distributions of calculated MAE and log-transformed MAE values. It appears that MAE for combustion sources may follow a log-normal distribution, better than a normal distribution. As a small sample size in the present study, to better understand the distribution of MAE of EC for combustion sources, more data available are needed.

Average MAE values for the combustion of wood, crop straw, pellet and coal were 3.1 (2.4–3.7 as 95% Confidence Interval), 6.6 (5.5–7.6), 9.5 (6.7–12), and 7.9 (4.8–11) $m^2$ $g^{-1}$, respectively, as shown in Fig. 2. The result of variance analysis showed that the difference among these four type fuels was statistically significant ($p = 5.7 \times 10^{-12}$). Moreover, MAE of EC from the wood combustion was significantly lower than those for the other fuels based on a multiple comparison analysis (Table S4). The reason for such difference was not clear and requires further study. Bond and Bergstrom (2006) tabulated reported MAE data in the literature, and suggested an average value of $7.5 \pm 1.2$ $m^2$ $g^{-1}$ for freshly emitted particles measured at 550 nm. Cheng et al. (2011) reported an MAE value of 3.0–3.2 $m^2$ $g^{-1}$ of EC from crop straw burning when EC was measured by a DRI thermal/optical carbon analyzer using an IMPROVE temperature protocol with transmittance correction of carbon charring, and ATN was monitored at 632 nm. In a previous study on carbonaceous particle emissions from residential coal combustion in rural China, EC and BC contents were measured by a Sunset EC/OC analyzer and an Aethalometer instrument, respectively (Zhi et al., 2008). Based on the reported results, calculated MAE values of EC for coal samples from residential cooking stoves were in the range of 8.1–50 $m^2$ $g^{-1}$ varying obviously among different coal types. Since different methods used