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Emission factors and light absorption properties of brown carbon from household coal combustion in China

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Abstract. Brown carbon (BrC) draws increasing attention due to its effects on climate and other environmental factors. In China, household coal burned for heating and cooking purposes releases huge amounts of carbonaceous particles every year; however, BrC emissions have rarely been estimated in a persuasive manner due to the unavailable emission characteristics. Here, seven coals jointly covering geological maturity from low to high were burned in four typical stoves as both chunk and briquette styles. The optical integrating sphere (IS) method was applied to measure the emission factors (EFs) of BrC and black carbon (BC) via an iterative process using the different spectral dependence of light absorption for BrC and BC and using humic acid sodium salt (HASS) and carbon black (CarB) as reference materials. The following results have been found: (i) the average EFs of BrC for anthracite coal chunks and briquettes are 1.08 ± 0.80 and $1.52 \pm 0.16\,\mathrm{g\,kg^{-1}}$, respectively, and those for bituminous coal chunks and briquettes are 8.59 ± 2.70 and $4.01 \pm 2.19\,\mathrm{g\,kg^{-1}}$, respectively, reflecting a more significant decline in BrC EFs for bituminous coals than for anthracites due to briquetting. (ii) The BrC EF peaks at the middle of coal's geological maturity, displaying a bell-shaped curve between EF and volatile matter (V_{daf}). (iii) The calculated BrC emissions from China's residential coal burning amounted to 592 Gg ($1\,\mathrm{Gg} = 10^9\,\mathrm{g}$) in 2013, which is nearly half of China's total BC emissions. (iv) The absorption Ångström exponents (AAEs) of all coal briquettes are higher than those of coal chunks, indicating that the measure of coal briquetting increases the BrC / BC emission ratio and thus offsets some of the climate cooling effect of briquetting. (v) In the scenario of current household coal burning in China, solar light absorption by BrC (350–850 nm in this study) accounts for more than a quarter (0.265) of the total absorption. This implies the significance of BrC to climate modeling.

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1 Introduction

The past decade saw increased interest in brown carbon (BrC) due to its effects on atmospheric chemistry, air quality, health, and particularly climate (Andreae and Gelencsér, 2006; Saleh et al., 2014; Forrister et al., 2015; Laskin et al., 2015). BrC refers to the fraction of organic carbon (OC) that can absorb light (Yan et al., 2014; Zhi et al., 2015; Jo et al., 2016; Wang et al., 2016). Compared with black carbon (BC), which has usually been considered the strongest light-absorbing aerosol carbon, with an absorption Ångström exponent (AAE) of around 1.0, light absorption by BrC is weaker, but more strongly wavelength dependent (Kirchstetter and Novakov, 2004; Hoffer et al., 2006; Cai et al., 2014). In other words, the light absorption efficiency of BrC increases more than that of BC toward short wavelengths. Recent advances in BrC research revealed its abundances and properties in a number of regions and highlighted the importance of including BrC in the accurate modeling of aerosol radiative forcing (RF) (Mohr et al., 2013; X. Zhang et al., 2013; Chakrabarty et al., 2014; Du et al., 2014; Kirillova et al., 2014; Forrister et al., 2015; Liu et al., 2015; Washenfelder et al., 2015; Cheng et al., 2016). For example, Feng et al. (2013) used a global chemical transport model and a radiative transfer model, finding that the strongly absorbing BrC contributes up to $+0.25\,\mathrm{W\,m^{-2}}$ or 19 % of the absorption by anthropogenic aerosols; meanwhile, the RF at the top of the troposphere may change from $-0.08\,\mathrm{W\,m^{-2}}$ (cooling) to $0.025\,\mathrm{W\,m^{-2}}$ (warming) in some areas when BrC data are considered in the RF model. Park et al. (2010) combined a 3-D global chemical transport model (GEOS-Chem) with aircraft and ground-based observations, finding that the averaged RFs of BrC aerosol were $0.43\,\mathrm{W\,m^{-2}}$ at the surface and $0.05\,\mathrm{W\,m^{-2}}$ at the top of the atmosphere (TOA), respectively, both of which accounted for more than 15 % of their respective total RFs (2.2 and $0.33\,\mathrm{W\,m^{-2}}$) for absorbing aerosols.

The sources of BrC can be defined in two categories: primary emission and secondary formation. The former relates to the incomplete (even smoldering) combustion of either fossil fuels (coal, petroleum, natural gas, etc.) or biomass–biofuels (wood, agricultural residues, bioethanol, etc.), during which BrC is generated and released into the atmosphere as pollutants (Liu et al., 2014; Oris et al., 2014; Washenfelder et al., 2015; Zhi et al., 2015). The latter involves complex chemical reactions taking place in the atmosphere between various precursors, forming secondary organic aerosols (SOAs), some of which are light-absorbing (Laskin et al., 2014; Lee et al., 2014; Smith et al., 2014; Tóth et al., 2014; Martinsson et al., 2015; Yan et al., 2015; Zhao et al., 2015). The SOA precursors of anthropogenic origin are usually dominated by hydrocarbons like aromatics and aliphatics, and those of natural origin are mainly biogenic volatile organic compounds (BVOCs) like isoprene and monoterpene (Updyke et al., 2012; Faiola et al., 2014; Fu et al., 2014; Liu et al., 2014). Examples of characterization of the two BrC source categories are relatively rare, which is unfavorable for the accurate understanding of BrC in terms of sources and effects (Laskin et al., 2015; Zhi et al., 2015). In addition, there is a more pressing need to characterize BrC emissions from sources related to human activities so as to gain direct insight into the influence of anthropogenic emissions on global change.

In China, coal plays a dominant role in the energy structure. In 2013, coal consumption reached 4300 Tg ($1\,\mathrm{Tg} = 10^{12}\,\mathrm{g}$), accounting for approximately 70 % of China's total primary energy, 93 Tg of which was burned for household heating and cooking purposes (NBSC, 2014). Because burning raw coal in residential cooking and heating stoves has the potential to release pollutants that consist of up to 10 % of the fuel mass due to poor combustion conditions and control facilities (Zhang and Smith, 2007), huge emissions of carbonaceous particles including OC, BrC, and BC are expected in this sector. Our previous studies have shown that the emission factors (EFs) of BC for residential coal burning are closely related to coal rank (bituminous or anthracite) and processing style (raw coal chunk or coal briquette), but they never addressed BrC that is released concurrently with BC (Chen et al., 2006, 2009a; Zhi et al., 2008, 2009). Meanwhile, the optical properties of BrC from coal combustion have almost never been addressed by researchers, possibly because studies regarding BrC emissions have focused preferentially on the observed physical or chemical properties, particularly optical absorption (e.g., AAE) of ambient aerosols for an overall characterization of radiative impacts of BrC in the atmosphere, in a certain region, or from specific burning activities (Chakrabarty et al., 2013; Feng et al., 2013; Lack and Langridge, 2013; Wu et al., 2013; X. Zhang et al., 2013; Zheng et al., 2013; Du et al., 2014; Washenfelder et al., 2015; Yan et al., 2015; Zhao et al., 2015; Cheng et al., 2016). This is not conducive to the understanding of China's primary BrC emission characteristics, especially BrC from the residential sector, the largest contributor of primary carbonaceous particles in China (Streets et al., 2013; Cai et al., 2014; Zhi et al., 2015).

The general motivation of this study is to investigate the emissions and optical characteristics of BrC emitted by China's household coal burning. A group of coals jointly covering geological maturity from low to high were burned in various stoves as both chunk and briquette styles, accompanied by collecting particulate emissions on quartz fiber filters (QFFs). The optical integrating sphere (IS) approach was used to distinguish BrC from BC on the filters (Hitzenberger et al., 1996; Wonaschütz et al., 2009; Montilla et al., 2011), followed by the calculation of EFs of BrC and other particulate components. The calculated BrC emissions and light-absorbing contributions add to the importance of China's household coal burning in both climate and air quality.

2 Experimental section

2.1 Coals and stoves

Seven coals were prepared in the present study (Table 1). These coals cover a wide range of geological maturity and can be classified into one anthracitic coal (AN), one semi-anthracitic coal (SA), one low-volatile bituminous coal (LVB), one medium-volatile bituminous coal (MVB), and three high-volatile bituminous coals (HVB). Each coal was prepared in two styles: raw-coal chunk and honeycomb briquette. The raw-coal chunks were 3–6 cm in size and the honeycomb briquettes were made by intermixing coal powder with clay (25 %) into a 12-hole column, 6 cm in height and 9.5 cm in diameter (Chen et al., 2005, 2015a; Zhi et al., 2008).

Four household coal stoves were selected to represent the most popular stove patterns used in northern China: one of them is specifically for honeycomb briquettes (WJ) and the other three are for raw-coal chunks (SC, HD, and LW). Detailed information on these stoves regarding shape, size, and characteristic structure is presented in the Supplement (Fig. S1) and will be described here briefly. The briquette stove WJ and chunk stove SC are of a traditional style widely used especially in past decades for heating rooms through direct thermal radiation in Chinese households. HD and LW are actually mini-boilers of a low-pressure type used for heating rooms by heated water circulating through a piping system. Compared to HD, the LW stove has an additional iron baffle vertically fixed before the flue pipe so as to lengthen the time of heat exchange between hot flue gas and circulating water.

2.2 Coal combustion and sample collection

Since the briquettes of the seven coals were only burned in the WJ stove and the chunks of all seven coals were burned in the three chunk stoves (SC, HD, LW) one by one, there was a total of 28 coal and stove combinations for the emission test. At first, two or three anthracite briquettes (ca. 600 g each) were ignited outdoors using solid alcohol until the carbon burning stage of coal was reached to minimize the interferences of igniting alcohol and anthracite briquettes in subsequent coal tests. Then the stove was moved into the preset position of the burning sampling system. A batch of coal briquettes (1–3 briquettes) or chunks (0.5–3 kg) were put into the stove and were ignited from the bottom by preburned anthracite briquettes. When the combustion began to fade (the first burning cycle, 1–2 h), a new batch of test coal briquettes or chunks were added into the stoves until completely burned (the second burning cycle, 1–2 h). Some coals (especially AN and SA) were burned for a third cycle (1–2 h) to ensure enough particle sampling.

Samples were collected through a diversion–dilution sampling system (Supplement Fig. S2). Coal burning emissions were released into the air through a 3 m long iron chimney.

Table 1. Coals used in this study.

Coal	M_{ad}^{a}	A_{ad}^{b}	V_{daf}^{c}	F_{Cad}^{d}	Rank[e]
NX	1.00	17.59	7.61	74.22	AN
CZ	0.91	10.69	12.59	77.26	SA
LL	0.79	7.95	19.35	73.60	LVB
PDS	0.39	10.06	26.25	65.63	MVB
SYS	2.22	22.33	33.20	50.40	HVB
XLZ	2.70	12.77	38.58	51.92	HVB
LK	22.56	11.51	49.39	33.34	HVB

[a] Moisture on air-dry basis (%). [b] Ash on air-dry basis (%). [c] Volatile matter on a dry and ash-free basis (%). [d] Fixed carbon on air-dry basis. [e] Rank by ASTM standard classification of coal (American Society for Testing and Material, 2004). HVB is for high-volatile bituminous coal, MVB is for medium-volatile bituminous coal, LVB is for low-volatile bituminous coal, SA is for semi-anthracite, and AN is for ordinary anthracite. In addition, the seven coals were produced in Ningxia Hui Autonomous Region (NX), Changzhi in Shanxi Province (CZ), Lüliang in Shanxi Province (LL), Pingdingshan in Henan Province (PDS), Shuangyashan in Heilongjiang Province (SYS), Xinglongzhuang Coal Mine in Shandong Province (XLZ), and Longkou in Shandong Province (LK), respectively.

A small flue gas stream (ca. 1–3 L min^{-1}) was diverted from the chimney mainstream into a FPS-4000 (Dekati) dilution device. The side opening of the chimney for stream diversion was 50 cm above the stoves. The dilution ratio in this study ranged from 30 to 180, depending on the envisaged emission intensity of each combination as well as on burning conditions. For example, emissions from the two anthracites (AN, SA) were less diluted by clean air than those from bituminous coals due to a lower emission concentration expected for the former than for the latter. There were six outlets at the end of the FPS-4000 that could be used to connect to different sampling and monitoring instruments, including at least a particle sampler (Φ90 mm Pallflex QFFs) for future BrC determination using the IS approach (Wonaschütz et al., 2009). In addition, the flue gas temperature, flow velocity, and composition were all simultaneously monitored by a digital thermocouple, a Kurz flowmeter, and a flue gas analyzer, respectively, throughout sampling so that the combustion processes could be characterized as fully as possible.

For each coal–stove combination, sampling started when the first batch of coal was put into the stove and ended when combustion was over (Zhi et al., 2008; Chen et al., 2015a, b). QFFs used for sample collection were baked at 450 °C in a muffle furnace for 6 h to get rid of any organics adsorbed on the filters. The combustion experiment for each coal–stove combination was done twice to check for reproducibility. Blanks were also tested to correct for the influences of whole procedures and anthracite briquettes used for initial igniting.

It should be noted that we chose to perform our study through lab experiments rather than real field tests because the former is easier to control and repeat than the latter, which allowed us to test the briquetting effects or coal rank effects

by fixing other conditions (the same seven coals, identical combustion manipulation, and consistent sampling system) (Jenkins et al., 1996; Roden et al., 2009; Zhang et al., 2011; Jetter et al., 2012). However, more and more studies suggested that lab studies may fail to simulate high emissions and it may be difficult to capture high variations in real field tests (Roden et al., 2006; Johansson et al., 2008; Christian et al., 2010). Thus, future study using field tests is proposed.

2.3 Measurement of BrC with IS method

The IS method was utilized in this study to separate the contributions of BrC and BC in terms of light absorption. A 150 mm integrating sphere (manufactured by Labsphere, Inc.) was built in a UV-Vis-NIR spectrophotometer (Perkin Elmer Lambda 950). The sphere is coated internally with polytetrafluoroethylene (PTFE), which reflects > 99 % of the incident light in the wavelength range of 0.2–2.5 µm (Wonaschütz et al., 2009). Using the full-scan mode, we scanned through the wavelength range of 350–850 nm to measure the light absorption of samples. A transparent quartz cuvette was specially customized and placed in the center of the sphere to hold filter samples for optical measurement. Inside the cuvette was 3 mL of a 1 : 1 mixture of acetone and an 80 : 20 mixture of water and isopropanol in which a filter punch (rectangle punch, 30 × 8 mm) could be immersed. Around the quartz cuvette was a specially customized cuvette holder coated with PTFE to hold the quartz cuvette in the sphere center. The sketch diagram of the IS measurement principle is shown in Fig. 1.

As discussed by Hitzenberger and Tohno (2001) and Wonaschütz et al. (2009), samples are put into the liquid mixture for the following consideration. Non-absorbent coatings on light-absorbing particles lead to appreciably enhanced absorption efficiencies. In the liquid, soluble coatings are removed. Typical insoluble coatings of aerosol particles (mainly organic material) have refractive indices around 1.4 (D'Almeida et al., 1989), which is similar to that of the liquid mixture (1.35). The resulting relative refractive index is small enough (1.04) to render the absorption enhancement by the coating negligible.

Reference materials need to be used as calibration standards to link the measured optical signals to the amounts of absorbing materials. Available reference materials were usually carbon black (CarB) (e.g., Elftex 570, Cabot Corporation) for BC and humic acid sodium salt (HASS) (e.g., Acros Organics, no. 68131-04-4) for BrC (Heintzenberg, 1982; Reisinger et al., 2008; Wonaschütz et al., 2009). For example, in the study of Medalia et al. (1983), CarB was used as the proxy of BC in diesel exhaust, and in the study of Wonaschütz et al. (2009), HASS was used as a proxy for BrC from wood combustion. We carry over this philosophy to the current study, with an assumption that BC and BrC in household coal smoke have the same light-absorbing properties of CarB and HASS, respectively. Consequently, it is not surprising that the results obtained here are probably different from others in literature reporting BC and/or BrC using other measurement techniques (e.g., thermal–optical method or aethalometer) (Chen et al., 2006; Zhi et al., 2008, 2009; Shen et al., 2013, 2014; Aurell and Gullett, 2013) or reference materials (e.g., fulvic acid, humic acid, or humic-like substances) (Duarte et al., 2007; Lukács, et al., 2007; Baduel et al., 2009, 2010). Even if this assumption is not perfect because the properties of CarB and HASS may never be completely the same as BC and BrC released from either wood, diesel, or coal, researchers can still use them to link and compare the emission characteristics of BC and BrC from various sources.

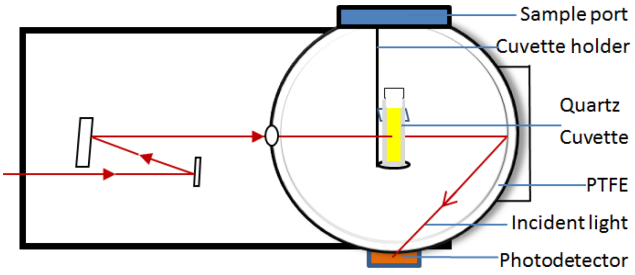

Figure 1. The sketch of the integrating sphere (IS) method. PTFE means polytetrafluoroethylene.

Calibration curves were obtained for a series of CarB masses of 1.5–90 µg and HASS masses of 3–240 µg at wavelengths of 650 and 365 nm. The reason we used two wavelengths is the different spectral dependence of the absorptive characteristics of BrC and BC, based on which a gradual separation of BrC from BC could be realized through iteration procedures. Different from CarB that is composed of almost pure carbon, HASS contains only 47 % carbon by weight. For this reason, all measured HASS-equivalent values based on such a calibration curve must be multiplied by 0.47 to obtain real BrC. The separation method of BC and BrC was generally similar to that by Wonaschütz et al. (2009), except that 405 nm was replaced by 365 nm because 365 nm is more preferred by researchers in BrC research and because the strong spectral dependence of absorption by BrC enables a better separation of the contributions of BC and BrC at this wavelength (X. Zhang et al., 2013; Du et al., 2014; Yan et al., 2014, 2015; Zhi et al., 2015). Figure 2 shows the calibration curves for BrC and BC at both 365 and 650 nm. At 650 nm, HASS gives only about 3 % of the signal of an equal mass of CarB, yet at 365 nm, HASS gives 24 % of the signal of an equal mass of CarB. With the four calibration curves in Fig. 2, filter samples were analyzed for BrC and BC using the IS method.

2.4 Calculation methods

Details of the methods for calculating EFs (for BrC and BC), AAE, wavelength-dependent BrC contribution to light ab-

sorption ($f_{BrC}(\lambda)$), and average BrC contribution to solar light absorption (F_{BrC}) in the range of 350–850 nm are given in the Supplement.

3 Results and discussion

3.1 Influence of coal briquetting on the EFs of BrC

The calculated emission factors of BrC and BC for the coal–stove combinations are presented in Table 2. Based on Table 2, Fig. 3 is derived to show the influence of coal briquetting on the EFs for BC and BrC. Turning coal powder into briquette is considered one of the effective approaches to reduce emissions of many pollutants and has been vigorously promoted by the Chinese government since its ninth 5-year-plan period (1995–2000) (Cheng et al., 1998; Chen et al., 2009b; Zhi et al., 2009). Our previous studies showed that briquetting drastically reduces emissions of BC and some other pollutants (e.g., OC; particulate matter, PM), making briquetting a possible option for both climate and environmental protection (Zhi et al., 2009; Shen et al., 2014). The effect of reducing BC emissions is also seen in the present study. As shown in Fig. 3a and Table 2, the average EFs of BC for chunk and briquette anthracites are 0.43 ± 0.23 and $0.21 \pm 0.16\,g\,kg^{-1}$, respectively, indicating a >50 % drop due to briquetting of anthracites; meanwhile, the average EFs of BC for chunk and briquette bituminous coals are 7.85 ± 2.00 and $0.56 \pm 0.22\,g\,kg^{-1}$, respectively, reflecting a >90 % drop due to briquetting of bituminous coals. It is believed that the structure (multi-hole for ventilation and burning) and composition (including one-third clay) of coal briquettes help the complete combustion of coal, and thereby less BC is released by the burning of briquettes than that of coal chunks (Bond et al., 2004; Zhi et al., 2009).

Regarding BrC emissions (Fig. 3b), no significant decline in EFs is seen for anthracite briquetting (EF is $1.08 \pm 0.80\,g\,kg^{-1}$ for chunks and $1.52 \pm 0.16\,g\,kg^{-1}$ for briquettes), but a notable decline in EFs is observed for bituminous coals (EF is $(8.59 \pm 2.70)\,g\,kg^{-1}$ for chunks, and $(4.01 \pm 2.19)\,g\,kg^{-1}$ for briquettes), displaying a reduction of 53 % due to briquetting. On the one hand, we are convinced that coal briquetting can generally lower BrC emissions, particularly for the bituminous coals (a 53 % reduction) that are more widely used in China than anthracite coals; on the other hand, the magnitude of BrC decrease for bituminous coals is significantly less than that for BC (>90 % reduction for bituminous coals). The lesser decline of BrC compared to that of BC due to briquetting of bituminous coals may be due to the different formation mechanisms of BrC and BC. Although such mechanisms have never been specifically addressed, evidence regarding the influence of briquetting in polycyclic aromatic hydrocarbons (PAHs) may indirectly contribute to the difference. According to Pöschl (2003), BrC aerosols are optically colored organics and thermochemically refractory organics, some of which are polycyclic aromatics. Chen et al. (2015b) observed that the EFs of 16 parent PAHs, 26 nitrated PAHs, 6 oxygenated PAHs, and 8 alkylated PAHs for coal briquettes were higher than those for coal chunks, corroborating the difference in formation mechanisms between BrC and BC. The authors tried a tentative insight into the enhancement of PAH emissions and speculated that PAHs are not affected as much by combustion efficiency as BC and might be more greatly affected by pyrolytic processes instead. According to the authors, PAHs are formed through two interlinked processes: pyrolysis and pyrosynthesis (Bjorseth and Ramdahl, 1985; Barbella et al., 1990; Bonfanti and Theodosis, 1994; Mastral et al., 1996, 1999, 2000). Turning the mixture of coal powder and clay into briquette favors the pyrosynthesis (Chen et al., 2015b). Here, with the example of PAHs, we attempt to show that BrC (including PAHs) behaves differently from BC and that further investigations into the different effects of briquetting on BrC and BC emissions are needed.

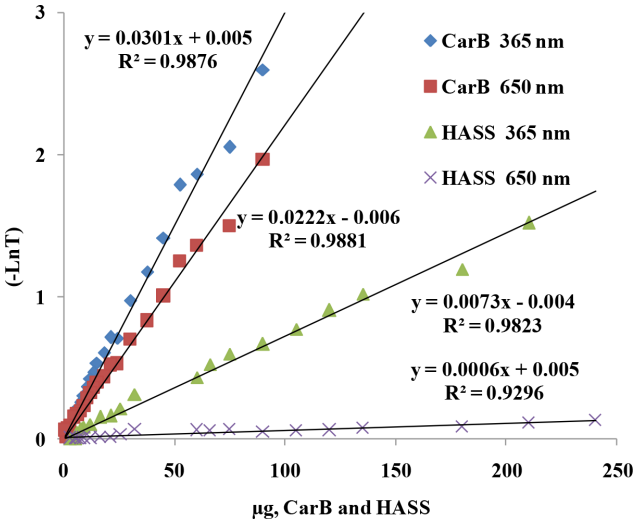

Figure 2. The calibration curves for CarB (carbon black; diamonds and squares) and HASS (humic acid sodium salt; crosses and triangles) at 365 and 650 nm. T is the transmittance of incident light through calibration solution.

In addition to the BC data from the IS method here, we also have elemental carbon (EC) data from the thermal optical reflectance (TOR) carbon analysis method. BC–EC paired data are given in the Supplement (Table S1 and Fig. S3). Although IS BC is somewhat higher than TOR EC in most cases, they are significantly correlated.

3.2 The dominant role of coal ranks in the EFs for BrC

Based on Table 2, the emission factors for BrC and BC from bituminous and anthracite coals burned in the same four stoves are plotted in Fig. 4 for comparing the overall influence of coal's rank on BrC emissions. Each EF for

Table 2. Measured emission factors (g kg^{-1}) of BrC and BC for China's household coal combustion.

	Briquette in WJ stove		Chunk in SC stove		Chunk in HD stove		Chunk in LW stove		Average over chunks	
Coal	EF_{BrC}	EF_{BC}	EF_{BrC}	EF_{BC}	EF_{BrC}	EF_{BC}	EF_{BrC}	EF_{BC}	EF_{BrC}	EF_{BC}
Anthracite										
NX	1.31	0.095	0.12	0.036	0.39	0.16	0.93	0.55	0.51	0.26
	1.51	0.10	0.098	0.024	0.58	0.16	0.95	0.65		
CZ	1.87	0.36	0.82	0.34	0.48	0.16	4.09	0.92	1.65	0.59
	1.40	0.28	1.43	0.47	0.45	0.16	2.61	1.50		
Mean of anthracites	1.52	0.21	0.62	0.22	0.48	0.16	2.15	0.91	1.08	0.43
Standard deviation	0.16	0.16	0.72	0.27	0.01	0.00	1.70	0.43	0.80	0.23
Bituminous										
LL	2.85	0.44	6.08	9.29	1.63	1.60	9.67	6.19	5.51	5.35
	2.10	0.38	4.24	7.22	2.28	1.32	9.15	6.48		
PDS	8.13	0.75	9.41	13.93	5.28	2.17	9.98	10.72	8.69	10.15
	4.71	1.00	7.65	17.88	7.42	3.46	12.36	12.70		
SYS	6.88	0.65	6.05	5.85	9.20	8.21	20.05	10.66	11.49	8.75
	5.81	0.71	6.04	4.07	10.02	6.30	17.55	17.34		
XLZ	3.36	0.51	12.15	8.95	13.18	8.46	8.06	8.62	11.02	8.81
	2.53	0.53	14.14	10.30	10.69	7.09	7.92	9.47		
LK	1.77	0.31	6.80	7.30	2.95	1.18	9.31	7.91	6.26	6.18
	1.97	0.31	5.24	7.38	3.07	1.54	10.01	11.80		
Mean of bituminous coals	4.01	0.56	7.78	9.21	6.59	4.14	11.41	10.20	8.59	7.85
Standard deviation	2.19	0.22	3.25	4.10	4.23	3.15	4.29	2.87	2.70	2.00

Notes: the four stoves are Wanjia brand briquette stove (WJ), simple chunk stove (SC), Huanding brand chunk stove (HD), and Laowan brand chunk stove (LW).

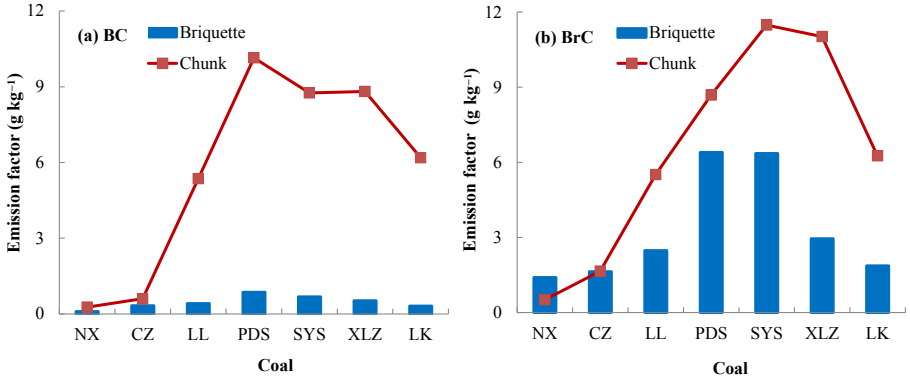

Figure 3. Effects of coal briquetting on black carbon (BC) and brown carbon (BrC) emissions.

bituminous coal is the average over five bituminous coals, and similarly each EF for anthracite coal is the average over two anthracites. It is very clear that both BrC and BC have higher EFs for bituminous coals than for anthracites, indicating that anthracites are always cleaner than bituminous coals, either for BC or BrC emissions from either briquettes or chunks. This confirms our previous recognition that coal's geological maturity (represented by V_{daf} value) plays a decisive role in the pollutant emission factors for residential coal burning because emissions from residential stoves are essentially the result of incomplete combustion of volatile matter in coal (Zhi et al., 2008, 2009). The lower combustion efficiency in household stoves leads to markedly incomplete combustion of volatile matter contained in raw coal, which acts as a reactant in producing the final emissions. This also suggests that burning anthracite coals instead of bituminous coals in the residential sector results in lower emissions of light-absorbing BrC and BC, which favors climate protection.

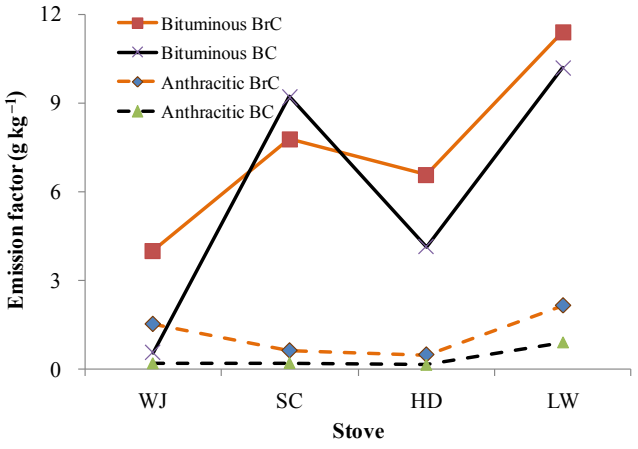

Figure 4. Comparison of emission factors between bituminous and anthracitic coals. The four stoves are Wanjia brand briquette stove (WJ), simple chunk stove (SC), Huanding brand chunk stove (HD), and Laowan brand chunk stove (LW).

It is interesting that although anthracite coals have been found to have lower EFs for BrC than bituminous coals in general, the EFs do not increase monotonically with V_{daf} but rather display a "bell shape". Previous studies proposed a bell-shaped curve with a maximum EF at V_{daf} around 30 % to describe the variation of BC EFs versus coal V_{daf} when coal is burned in household stoves (Zhi et al., 2008, 2009). In this study, the seven coals, from left to right in Fig. 3a and b, are arranged by increasing V_{daf}. The bell-shaped profile of BC is maintained, with the PDS coal ($V_{daf} = 26.25$ %) having the highest EFs (0.75–1.00 g kg^{-1} for briquettes and 10.15 g kg^{-1} for chunks; Fig. 3a). Meanwhile, as shown in Fig. 3b, the bell-shaped profile reappears for BrC EFs, with EFs for coal briquettes and chunks peaking respectively in PDS ($V_{daf} = 26.25$ %, $EF_{BrC} = 4.71$–8.13 g kg^{-1}) and SYS ($V_{daf} = 33.20$ %, $EF_{BrC} = 11.49$ g kg^{-1}) coal. The findings of this study indicate that in order to reduce emissions of light-absorbing carbon (BC and BrC), the use of middle-maturity coal in residential stoves should be minimized. A similar trend was also found by Shen et al. (2013) for the emissions of particle-bound PAHs (the medium-volatile bituminous coals are most productive), which prompts us to propose a ban on this type of coals for household purposes.

We take additional advantage of Fig. 4, finding that, among the three chunk stoves, both EF_{BrC} and EF_{BC} of coal chunks are in the order of LW > SC > HD, regardless of bituminous coal or anthracite coal, reflecting that the HD stove performs the best and the LW stove the worst. The SC stove is of traditional style widely used, especially in past decades, in Chinese households for heating rooms through direct radiation of coal burning, whereas the HD and LW stoves are actually household mini-boilers of low-pressure type used for heating rooms by a water piping–radiating system (see Sect. 2.1). The order above of LW > SC > HD in terms of EFs implies that current transfer from stove type of direct coal combustion radiation (e.g., SC stove) to that of heated water piping–radiating system (e.g., LW and HD stoves) in households does not necessarily lead to a decline in EFs.

A collection of the directly measured BC (EC) emission factors in our previous articles (since 2005) (Chen et al., 2005, 2006, 2015a; Zhi et al., 2008, 2009) and in this study are given in the Supplement (Table S2). Comparison between previous and current studies shows that the means of the EFs for either anthracite coals or bituminous coals in either briquette or chunk styles in this study are somewhat higher than those in previous ones; however, the key findings in previous studies still stand in this study. For example, bituminous coals or raw chunks usually release more pollutants (including BC) than anthracites or briquettes, and BC emission factor usually peaks in medium-volatile bituminous coal. The differences in reported EFs are generally from a variety of factors, such as stoves, briquetting procedures, combustion manipulations, and even the quantification methods (Chow et al., 2001; Zhi et al., 2009, 2011).

3.3 Absorption Ångström exponent (AAE)

The calculated AAE values for China's residential coal combustion are shown in Fig. 5. It is very obvious that AAEs of all coal briquettes are higher than those of coal chunks. For coal briquettes, AAE values are in the range of 2.11–3.18, with the average of 2.55 ± 0.44, while for coal chunks, AAE values decline to 0.96–1.73, with an average of 1.30 ± 0.32, which is nearly half of that for coal briquettes. This may be attributed to the higher ratio of EF_{BrC} / EF_{BC} ($R_{BrC/BC}$) for coal briquettes (7.68 ± 3.16, derived from Table 2) than for coal chunks (1.46 ± 0.69, derived from Table 2) in view of the generally higher AAEs for BrC than for BC (Andreae amd Gelencsér, 2006; Chen and Bond, 2010; Kirchstetter and Thatcher, 2012; Cai et al., 2014; Yan et al., 2014; Martinsson et al., 2015; Chakrabarty et al., 2016; Wang et al., 2016). This reminds us that although briquetting can reduce both BC and BrC emissions (as shown in Fig. 3), BC is far more reduced than BrC, leading to an increased $R_{BrC/BC}$ after briquetting and consequently offsetting the climate cooling effect of briquetting (Zhi et al., 2009). In addition, in Cai et al. (2014)'s study, the AAEs of 10 samples of wheat straw open burning were measured, with an average of 3.02 ± 0.18, much higher than those for coals (chunk or briquette) in this study. The higher OC / TC ratio for biomass burning than for fossil fuel combustion possibly accounts for such a result (Novakov et al., 2005; Cai et al., 2014).

As for the relationship between coal's maturity (represented by V_{daf}) and AAE, Fig. 5 demonstrates that AAE values do not decrease monotonically with V_{daf} % but display a "U shape" pattern; the minimal AAEs occur in the coals of medium maturity (SYS) (2.11 for briquette and 0.96 for chunk, in Fig. 5). It is interesting that this relationship profile is by and large in contrast to the bell shape for the relation-

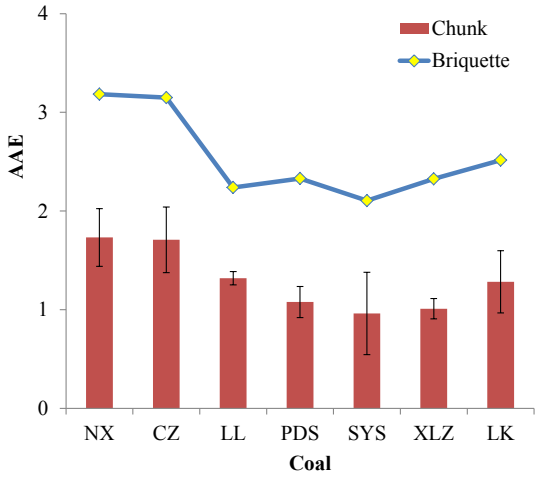

Figure 5. Comparison of AAEs (absorption Ångström exponents) between briquette and chunk coals.

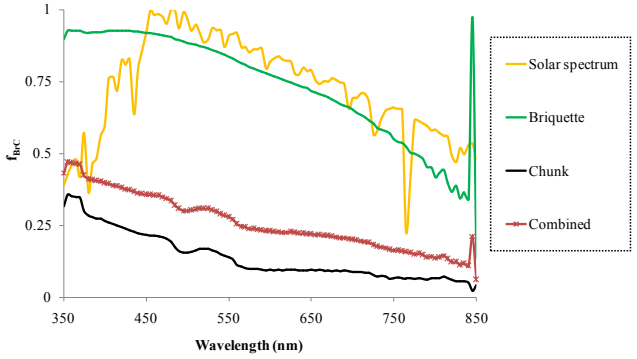

Figure 6. Fraction of light absorption by BrC in total absorption by BrC+BC from residential coal burning. The fraction is expressed as $f_{\mathrm{BrC}}(\lambda)$ and was calculated in accordance with the method described in the Supplement. The yellow line is the clear-sky air mass 1 global horizontal solar spectrum at the earth's surface in relative unit (Levinson et al., 2010).

ship between $\mathrm{EF_{BC}}$ and V_{daf} (the maximal $\mathrm{EF_{BC}}$ occurred in medium-maturity coals) (Zhi et al., 2008, 2009). The mechanism behind this contrast needs further investigation.

3.4 Light absorption by BrC from household coal stoves

Based on the measured EFs in this study and China's yearly consumption of residential coal in the China Energy Statistical Yearbooks (CESYs) (NBSC, 2014), the emissions of BrC and BC from China's coal burning in household stoves can be calculated. According to CESY 2014, 92.90 Tg of coal was used in the residential sector in 2013. Assuming that 20 % of coal was anthracite and that 20 % of bituminous and anthracite coals were both made into briquettes (Chen et al., 2006; Zhi et al., 2008), the calculated BrC emissions from China's residential sector amounted to 592 Gg ($1\ \mathrm{Gg} = 10^9$ g), which is nearly half of China's BC emissions (Cao et al., 2006a, b, 2011; Wang et al., 2012; N. Zhang et al., 2013, 2015). Chakrabarty et al. (2014) reported a BrC emission of 92 Gg from funeral pyres in South Asia, which is less than one-sixth of our figure for China's household coal burning. We also notice that the calculated BC emissions from household coal burning was 482 Gg in 2013, less than BrC emissions in the same period, which is suggestive of the relatively high BrC emissions from China's residential coal burning. This deserves special attention and efforts.

Questions may arise regarding the share of briquettes in the total household coal consumption. The percentage 20 % has been used for more than 10 years in our studies (e.g., Chen et al., 2005; Zhi et al., 2008). This percentage is now being seriously challenged by a more complicated situation of coal consumption in Chinese households. On the one hand, Chinese government has long since promoted the use of coal briquettes to achieve a cleaner emission target, which helps increase the share of briquettes (Chen et al., 2015b); on the other hand, the increasing reliance on burning raw chunks for room heating (through circulating hot water) in northern China is ridding households of briquettes but bringing chunks into them, which results in a declined briquette share (Zhi et al., 2017). As a result, it is difficult to establish whether the assigned 20 % is higher or lower than the actual one, which adds uncertainty to the estimates of the emissions and optical effects for China's household coal burning.

The huge emissions of BrC from household coal burning suggest the importance of including BrC in calculations of the total light absorption of coal emissions for understanding the BrC-related global energy budget. Given the more established knowledge of BC optical properties and climate consequences compared to those of BrC, exploration of the light-absorbing relationship between BrC and BC helps to substantiate the importance of BrC in the current discussion of climate effects of light-absorbing carbonaceous aerosols. Here, $f_{\mathrm{BrC}}(\lambda)$ is used to quantitatively describe the fraction of BrC absorption in the combined light absorption of BrC+BC at each wavelength of the scanned solar spectrum (refer to the Supplement for the method to calculate $f_{\mathrm{BrC}}(\lambda)$). The results of $f_{\mathrm{BrC}}(\lambda)$ were plotted in Fig. 6 for coal briquette, coal chunk, and the average over briquette and chunk weighted by their consumption shares. According to Fig. 6, the values of $f_{\mathrm{BrC}}(\lambda)$ for briquette, chunk, and the average all increase towards short wavelengths, directly corroborating the conventional understanding that the light absorption by BrC increases more than that by BC from the green to violet spectral ranges due to the stronger spectral dependence of absorption by BrC than that by BC (Hoffer et al., 2006; Chakrabarty et al., 2010; Kirchstetter et al., 2012).

Moreover, Fig. 6 demonstrates a significantly higher $f_{\mathrm{BrC}}(\lambda)$ for briquettes (green line) than for chunks (black line), which corresponds to a higher BrC / BC ratio for briquettes (7.70 ± 3.28) than for chunks (1.45 ± 0.68) (based on

Table 2) and to a higher AAE for briquettes (2.55 ± 0.44) than for chunks (1.30 ± 0.32) (Fig. 5). In consideration of the share of briquette or anthracite in the total residential coal consumption, the calculated average $f_{BrC}(\lambda)$ (red line) over all residential coal consumption (including bituminous coals and anthracites in either chunk or briquette styles) is found to range from 0.061 (at 850 nm) to 0.470 (at 355 nm). Integration of $f_{BrC}(\lambda)$ and solar spectrum results in F_{BrC}, the fraction of absorbed solar radiance by BrC relative to the total absorption (refer to the Supplement for the method for calculating F_{BrC}). A value of 0.265 is obtained for F_{BrC} for the wavelength range from 350 to 850 nm. This means that in the scenario of current household coal burning in China, solar light absorption by BrC accounts for more than a quarter of the total absorption, while the other 73.5 % is attributable to BC. This implies that although BrC plays a less important role in solar light absorption than BC regarding light absorption by carbonaceous emissions from the residential sector, it is absolutely non-negligible. The recommendation of adding BrC to climate modeling merits serious consideration for better modeling-based climate predictions.

Data availability. The research data can be accessed on request to the corresponding author (zhigr@craes.org.cn).

The Supplement related to this article is available online at doi:10.5194/acp-17-4769-2017-supplement.

Competing interests. The authors declare that they have no conflict of interest.

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