Interactive comment on **"Emission factors and light absorption properties of brown carbon from household coal combustion in China"** ***by*** **Jianzhong Sun et al.**

J. Sun et al. (Comments in black, Response in red)

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Reply to Referee 1#

General comment:

The manuscript "Emission factors and light absorption properties of brown carbon from household coal combustion in China" by Sun et al., presents valuable measurements of the emission factors and optical properties of brown carbon and black carbon fractions resulting from household coal burned for heating/cooking purposes in China. An optical method using an integrating sphere was applied to analyze several coals burned in typical stoves at both chunk and briquette styles. The method is not new but it is applied to an interesting study. The protocols are sufficiently well described, the study has been done carefully and the interpretation makes sense. The results are potentially interesting for other researchers engaged in aerosol studies. The paper is adequate to the journal scope, it is well formatted and presents a valuable experiment, so it deserves publication in the ACP. Except for some small technical corrections, I have only one major concern about reference Sun et al., 2016. Please see below.

Response:

Thanks a lot for the positive comments and recommendation for publication in ACP. We noticed that the reviewer has only one major concern, which is on the reference "Sun et al., 2016". We will specifically address such concern in our response to "**Comment 5**" below.

Comment 1:

Page 5 line 17: L/min should be l/min;

Response:

We have changed "L/min" to "l/min" in revised version (page 5 line 17).

Comment 2:

Page 5 line 18: "... into the PFS-4000..." should be "...into a FPS-4000...";

Response:

Thanks for reminder. We have changed "into the PFS-4000" to "into a FPS-4000" in revised version (page 5 line 18).

Comment 3:

Page 9 line 18: something is missing in the sentence starting with "It’s interesting that...";

Response:

The sentence is a complex sentence with “it” as the formal subject and the “that-clause” as the logic subject (page 10 line 12, revised version). With this sentence, we intend to show that the absorption Ångström exponent (AAE) comes lowest in the coals of medium V_{daf}, which happens to be opposite to that EF_{BC} and EF_{BrC} comes highest in the coals of medium V_{daf}. This can be seen by comparison of our two figures in the manuscript (Figure 3, Figure 5). In fact, some of our previous studies (e.g., Chen et al., 2006; Zhi et al., 2008, 2009) have repeatedly concluded that the maximal EF_{BC} occurs in medium maturity coals around V_{daf} =30%.

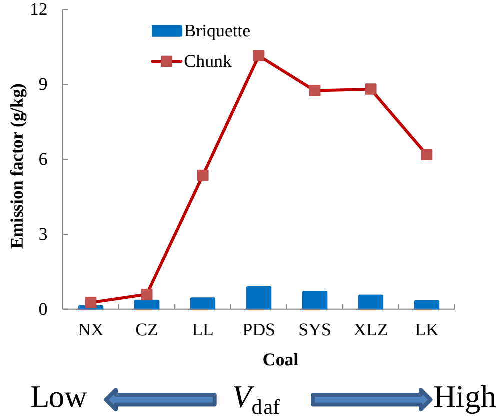

Fig. 3. “bell-shape” for EF_{BC} against V_{daf}

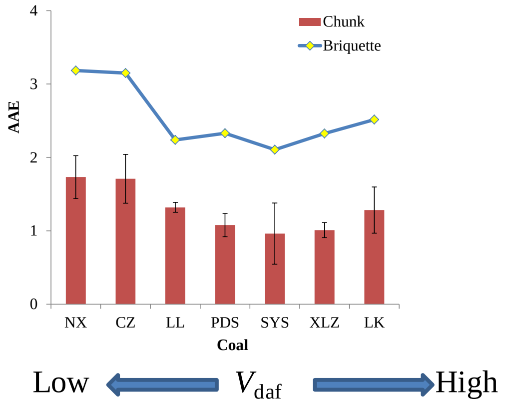

Fig. 5. “U-shape” for AAE against V_{daf}

Comment 4:

Please complete captions of figures and tables to make them more informative, for example, describing the meaning of the abbreviations used;

Response:

Thank you. We have examined all figures and tables and tried to make their captions more informative by explaining the meaning of the abbreviations, as follows:

(1) Page 21 revised version, Table 1: We added the full names of the coal mine locations of the 7 coals (at the end of the table).

(2) Page 22 revised version, Table 2: We added the full names of the 4 coal stoves (at the end of the table).

(3) Page 23 revised version, Figure 1: add “PTFE means Polytetrafluoroethylene” to the caption.

(4) Page 24 revised version, Figure 2: change “CarB (diamonds, squares) and HASS (forks, triangles)” to “CarB (carbon

black, diamonds, squares) and HASS (humic acid sodium salt, forks, triangles)".

(5) Page 25 revised version, Figure 3: "BC and BrC" have changed to "black carbon (BC) and brown carbon (BrC)".

(6) Page 26 revised version, Figure 4: add "The 4 stoves are respectively Wanjia brand briquette stove (WJ), Simple Chunk stove (SC), Huanding brand chunk stove (HD), and Laowan brand chunk stove (LW)" to the caption.

(7) Page 27 revised version, Figure 5: change "of AAEs" to "of AAEs (absorption Ångström exponents)" in the caption.

Comment 5:

Reference Sun et al., 2016 is an unpublished work and, based only on the title; it appears to have a significant overlap with the present manuscript, so authors should explain what part of the work is done in each manuscript.

Response:

The reference "Sun et al., 2016" is indeed our unpublished work. Different from the present work that focuses on household coal in terms of BrC emissions, "Sun et al., 2016" had intended to focus on household biomass in terms of BrC emissions. The same method (i.e., the integrating sphere, IS) had been planned for these twin papers. However the "Sun et al., 2016" paper (on biomass) has so far not been finished and submitted, which makes our reference senseless. In this case we have to cancel the reference to "Sun et al., 2016" throughout our revised version.

By the way, the planned paper "Sun et al., 2016" is close to being finished and will in return refer to the current paper (on coal) regarding IS method.

Thanks again for the careful and constructive reviewing.

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Chen, Y., Zhi, G., Feng, Y., Fu, J., Feng, J., Sheng, G., and Simoneit, B. R. T.: Measurements of emission factors for primary carbonaceous particles from residential raw-coal combustion in China, Geophys. Res. Lett., 33 (20), 1-4, 10.1029/2006gl026966, 2006.

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Zhi, G., Peng, C., Chen, Y., Liu, D., Sheng, G., and Fu, J.: Deployment of coal briquettes and improved stoves: possibly an option for both environment and climate, Environ. Sci. Technol., 43 (15), 5586-5591, 10.1021/es802955d, 2009.

Reply to Referee 2#

General Comment:

Black carbon (BC) and Brown carbon (BrC) have significant impacts on regional climate change and residential coal combustion is a major source of these pollutants. Emission data of BC and BrC from residential solid fuel combustion, depending on coals and stove types are still limited, though more and more studies are available during the last several years (most reported BC and/or elemental carbon). The present study measured emissions of BC and BrC from residential coal combustion in 7 different coals burnt in 4 different stoves in China. The study provided firsthand data on pollutant emission factors from residential coal combustion that would be interesting and helpful for emission inventory, air quality modelling and also control policies on raw coal combustion in the country. Overall the experiments are well conducted and the manuscript is clearly present.

Response:

Many thanks for the positive comments on the significance of our research and the quality of our manuscript. We would further improve our manuscript according to the comments of reviewer.

Comment 1:

The study used optical integrating sphere method to quantify BC and BrC amounts. The quantification is based on calibration curves using CarB and HASS as standards. Chemical compositions and properties could be different between BrC and HASS (Page 6 lines 20-25). In fact, these two terms (BC and BrC) are initially defined based on the light properties while chemical composition of BrC is still not well characterized. So in my opinion although the difference here is out of this study scope it might be necessary and important to highlight in the paper that results reported here is probably different from others in literature reporting BC and/or BrC using other measurement techniques, which should be considered in the generation of results. What reported here are more likely a CarB-equivalent and HASS-equivalent carbon emissions. Interesting to know whether the authors had BC data from typical BC measurement instruments or BrC data from carbon analysis, and are the results comparable if you have the data?

Response:

(1) Integrating Sphere (IS) method was utilized in this study to separate the contributions of BrC and BC in terms of light absorption. Considering that preferred reference materials were often carbon black (CarB) for BC and humic acid sodium salt (HASS) for BrC (Heintzenberg, 1982; Hitzenberger et al., 2006; Reisinger et al., 2008; Wonaschütz et al., 2009), we carried over this philosophy to the current study. This implies our consent to the assumption that BC and BrC in our samples collected for household coal smoke have the same light-absorbing properties of CarB and HASS, respectively and what reported here are essentially CarB-C-equivalent and HASS-C-equivalent. 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 HULIS) (Duarte et al. 2007; Lukács, et al. 2007; Baduel et al. 2009, 2010), in view of both BC and BrC being method-defined.

In the revised version, we highlighted above opinion (page 6 lines 27-30).

(2) We noticed the reviewer's interest in whether we had BC data from typical BC measurement instruments or BrC data from carbon analysis, and whether the results are comparable. Actually in the current study we have both BC data from thermal/optical reflectance (TOR) carbon analysis method (expressed as“elemental carbon”, EC) and BC data from IS method. BC-EC paired data are given here as well as in the Supporting Information (see Table S1 and Figure S3, data are for coal briquette in WJ stove and for coal chunk in averaged 3 stoves, SC, HD, and LW). Although IS-BC is somewhat higher than TOR-EC in most cases, they are correlated significantly.

We briefly describe this relationship in our revised manuscript (page 8 lines 20-22 in subsection 3.1).

Table S1. Comparison between IS-based EF_{BC} and TOR-based EF_{EC}

Coal	**Chunk (Average voer 3 Chunk stoves)**	
	EF_{BC}	**EF_{EC}**
NX	0.26	0.12
CZ	0.59	0.29
LL	5.35	4.25
PDS	10.15	8.09
SYS	8.75	10.50
XLZ	8.81	6.80
LK	6.18	4.06
	Briquette (WJ stove)	
NX	0.10	0.08
CZ	0.32	0.07
LL	0.41	0.27
PDS	0.86	0.41
SYS	0.68	0.80
XLZ	0.52	0.71
LK	0.31	0.21

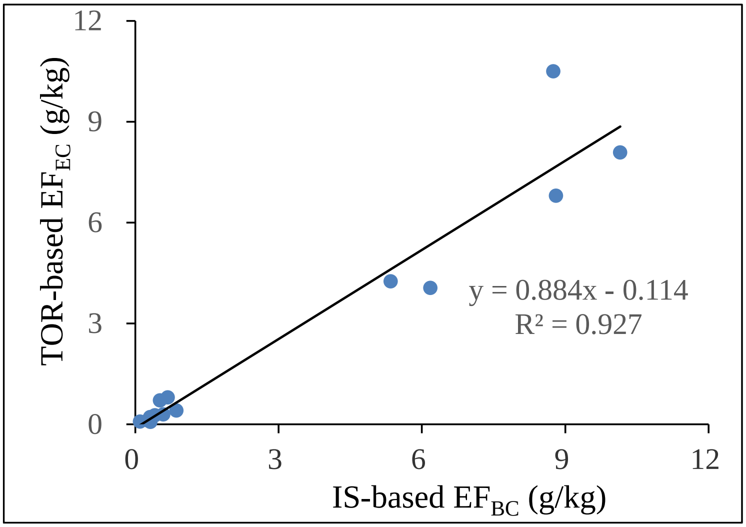

Figure S3. The correlation of EFs between IS-based EF_{BC} and TOR-based EF_{EC}

Comment 2:

Section 3.1 influence of briquetting, and Figure 3: are the results for chunk coals from traditional SC stove, or averaged from all three chunk stoves? Note that briquettes were burned in WJ stove while raw chunk coals were burned in another three stoves, therefore differences observed here are resulting from not only coal briquetting but also stove types. Can the author evaluate difference among different stoves, for example, emissions from chunk between traditional SC stove and HD/LW stoves?

Response:

The reviewer's description is right. In Section 3.1 and Figure 3, the emission factors (BC and BrC) for briquettes are the results from WJ stove (for briquette only), while those for chunks are the results from averaging over another three chunk-stoves (SC, HD, and LW). Because the WJ stove burned briquettes only and all the 3 chunk stoves burned coal chunks only, it is improper to compare the EFs between WJ and the other 3 chunk stoves. However, it is reasonable if we compare EFs among the three chunk stoves (SC/HD/LW). We take the advantage of Figure 4, finding that, among the 3 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 HD stove performs the best and the LW stove, the worst. As mentioned in subsection 2.1, stove SC is of traditional style widely used especially in past decades in China’s households for heating rooms through direct radiation of coal-burning whereas HD and LW are actually household mini-boilers of low pressure type used for heating rooms by a water piping/radiating system. The above order of LW>SC>HD 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 leads to a decline of EFs.

In the revised version, we described above notion briefly in subsection 3.2 (page 9 lines 14-21).

Comment 3:

As only two repeats for each experiment, it is inappropriate to calculate standard deviations. In Table 2, suggest to put all data for each coal. The overall means with standard deviations for anthracite and bituminous are fine. Also replace means with standard deviations by ranges in text if only two numbers.

Response:

We accept the suggestion and put all data we have got for each coal into Table 2. We also replaced "mean±standard deviation" manner in text with "ranges" manner (revised version, subsection 3.2 page 9 lines 8-10).

Comment 4:

As the research group had published a series of BC emission data from coal combustion, it is suggested to compare and discuss the results here and the previous studies, taking differences (if any) of coal types and stoves in the consideration. Will the overall means of BC for anthracite and briquettes change when taking more data into account, and how much the variation would be?

Response:

Thanks for the knowledge of a series of our previous studies of BC emission data from coal combustion. It is a good idea to compare and discuss the results of this study and the previous ones, taking differences of coal types and stoves in the consideration. We brought all of the directly measured BC emission factors in our previously published articles (Chen et al., 2005, 2006, 2015; Zhi et al., 2008, 2009) into the following Table S2, together with the emission factors measured in this study. Comparison between previous and current studies shows that the means of the emission factors 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, etc. 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). As an example, in our response to Comment 1, we showed that IS-BC is generally higher than TOR-EC. Moreover, we know TOR-EC is almost always higher than thermal/optical transmittance EC (TOT-EC) (Chow et al., 2001; Zhi et al., 2011) and our EC values in our previous studies were mostly originated from TOT protocol (NIOSH), which further enlarges the difference between this study and previous ones.

Table S2. The collection of the directly measured BC (EC) emission factors in our previous articles

	Anthracite		**Bituminous**	
	Raw chunk	**Briquette**	**Raw chunk**	**Briquette**

1	Chen et al, 2005		0.004		0.096 0.675 0.523 0.064
2	Zhi et al, 2008	0.035 0.005	0.012 0.001	0.13 0.73 16.9 10.3 28.5 4.35 1.48	0.009 0.014 0.076 0.016 0.080 0.034 0.019
3	Chen et al，2006	0.007 0.002		0.20 5.34 10.10 10.12 12.67 6.97 0.48	
4	Chen et al, 2015	0.02	0.06	1.71 2.38 3.46 0.61	0.67 1.3 1.28 0.07
5	Zhi et al, 2009			0.042 0.51 1.23 2.89 0.18 0.083 0.23 4.83 10.02 11.17 5.77 0.55	0.011 0.054 0.085 0.16 0.034 0.018 0.044 0.52 0.64 0.47 0.31 0.084
Mean		**0.014**	**0.019**	**5.34**	**0.27**
sd.		**0.014**	**0.028**	**6.36**	**0.37**
6	This study	0.26 0.59	0.1 0.32	5.35 10.15 8.75 8.81 6.18	0.41 0.86 0.68 0.52 0.31
Mean		**0.43**	**0.21**	**7.85**	**0.56**
sd.		**0.23**	**0.16**	**2.00**	**0.22**

Because our manuscript focuses on BrC instead of BC, we put this table in our Supporting Information (Table S2) and meanwhile add a new paragraph in our revised version (subsection 3.2, page 9 lines 22-29).

Comment 5:

Lab experiments are easier to be controlled and repeatable, but more and more studies suggested that lab studies may fail to simulate high emissions and be difficult to capture high variations in real field. Both methods have advantage and disadvantage. The limitation and consequent impacts on the generation of these lab-experimental data should be briefly discussed in main text.

Response:

We totally agree to the comment on lab experiments and field tests. Generally laboratory experiments allow investigators to repeat the process under controlled conditions for investigating the effects of a specific influencing factor on the emissions (Jenkins et al., 1996; Roden et al., 2009; Zhang et al., 2011; Jetter et al., 2012). In this study, with lab experiment methodology, we could test the briquetting effects or coal rank effects by fixing some other conditions (using the same 7 coals, identical combustion manipulation, and consistent sampling system). However this is anyway not so realistic as in field circumference with random conditions that are difficult to reproduce in laboratory (Roden et al., 2006; Johansson et al., 2008; Christian et al., 2010). Just as the reviewer mentioned, "Both methods have advantage and disadvantage", depending on what purpose you prefer to pursue.

In our revised manuscript we described the limitation and consequent impacts on the generation of these lab-based data in the subsection 2.2 (page 5 lines 32-33 and page 6 lines 1-4).

Some specific comments:

Comment 6:

Page 5 line 23, "PFS-4000" not "FPS"

Response:

FPS is the acronym of "Fine Particle Sampler". There are only 2 cases in our manuscript and both of them exist in subsection 2.2 (page 5 lines 18, 22, revised version).

Comment 7:

Page 7 line 10-15, the information should be shortened and moved to the section 2.4.

Response:

The paragraph in page 7 lines 11-14 (initial version) has been deleted. This means the second paragraph in the initial version would become the first paragraph in the new version. We added a new sentence to begin this paragraph, as "The calculated emission factors of BrC and BC for the coal/stove combinations are presented in Table 2" (page 7 line 19, revised version).

Comment 8:

Page 8 line 25-30, high emissions from medium-volatile content coals are also found in PAHs emissions. Therefore, it appears that this type of coals should be eliminated in use.

Response:

It is true that high emissions from medium-volatile content coals were also found in PAHs emissions (Shen et al., 2013). We added a sentence in subsection 3.2 at page 9 lines 12-13 (revised version).

Comment 9:

Page 9 line 11, delete "either"

Response:

Thanks for reminder. The "either" in our initial submission is useless and is due to carelessness. We deleted it in our revised version (Page 10 line 5).

Comment 10:

Page 9 line 25, please note that 20% briquettes probably underestimated, though no reliable statistical data available so far. Suggest to add a discussion on uncertainties of these estimated emissions, due to fractions of briquettes and variations of EFs.

Response:

In terms of the share of briquettes in total household coal consumption, the percentage "20%" has been used for more than 10 years (Chen et al., 2005; Zhi et al., 2008). This percentage is now seriously challenged by a more complicated situation in China. On the one hand, Chinese government has long since promoted the use of coal briquettes to achieve cleaner emission target, which helps increase the share of briquettes (Chen et al., 2015); on the other hand, the increasing reliance on burning raw-chunks for room heating (through circulating hot-water) in northern China is ridding briquettes of but bringing chunks into households, which results in a declined briquette share (Zhi et al., 2017). As a result, it is difficult to establish whether the assigned "20%" in this study 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.

Thus, we kept unchanged the "20%" for China's briquette share in household coal total and added a new paragraph for the discussion of uncertainty (subsection 3.4, page 10 lines 26-32, page 11 lines 1-2).

Comment 11:

Page 9 line 30, "less than BrC emissions from residential coal combustion in the same period"?

Response:

Yes, it is true that "the calculated BC emissions from household coal burning were…less than BrC emissions in the same period" (revised version, page 10 lines 22-24). This results from the higher EF_{BrC} than EF_{BC} (See Table 2 in subsection 3.1). However, it doesn't follow that BrC is more potent in light-absorption than BC in view of the far lower light absorption efficiency for BrC than for BC. In the subsection 3.4, we revealed 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".

Comment 12:

Table 1, can the authors provide heating values of these coals? And, are these properties like moisture and ash content changed when briquetting?

Response:

Regrettably we don’t have the heating values of coals used in the experiment. The properties like moisture and ash content were unavoidably changed by briquetting. We actually tried to equal the changes in moisture and ash content to even up the impacts of briquetting on EFs.

Thanks again for the careful and constructive reviewing.

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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 fields. In China, household coal burned for heating/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 7 coals jointly covering geological maturity from low to high were burned in 4 typical stoves at both chunk and briquette styles. The optical integrating sphere (IS) method was applied to measure the e~~E~~mission f~~F~~actors (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. It is found that (i) the average EFs of BrC for anthracite coal chunks and briquettes are (1.08±0.80) g/kg and (1.52±0.16) g/kg, respectively, and those for bituminous coal chunks and briquettes are (8.59±2.70) g/kg and (4.01±2.19) g/kg, respectively, reflecting a more significant decline of 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 Gg=10^9 g) in 2013, which is nearly half of China's total BC emissions, (iv) absorption Ångström exponent (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, and (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.

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) that 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; Zhang et al., 2013a; 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 $W\cdot m^{-2}$ or 19% of the absorption by anthropogenic aerosols; meanwhile the RF at the top of the troposphere may change from -0.08 $W\cdot m^{-2}$ (cooling) to 0.025 $W\cdot m^{-2}$ (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/ground based observations, finding that the averaged RFs of BrC aerosol were 0.43 $W\cdot m^{-2}$ at the surface and 0.05$W\cdot m^{-2}$ at the top of atmosphere (TOA), respectively, both of which accounted for more than 15% of their respective total RFs (2.2 $W\cdot m^{-2}$ and 0.33 $W\cdot m^{-2}$) for absorbing aerosols.

The sources of BrC can be defined into two categories: primary emission and secondary formation. The former relates to the incomplete (even smoldering) combustion of either fossil fuels (coal, petroleum and natural gas, etc.) or biomass/biofuels (wood, agricultural residues and bio-ethanol, 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 on characterization of the two BrC source categories are relatively rare, which is unfavorable to 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 seek 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 Tg=10^{12} g), accounting for approximately 70% of China's total primary energy, 93 Tg of which was burned for household heating/cooking purposes (NBSC, 2014). Because burning raw coal in residential cooking/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 e~~E~~mission f~~F~~actors (EFs) of BC for residential coal burning are closely related to coal's ranks (bituminous or anthracite) and processed styles (raw coal chunk or coal briquette), but never addressed BrC that is released concurrently with BC (Chen et al., 2006, 2009; Zhi et al., 2008, 2009). Meanwhile, the optical properties of BrC from coal combustion have almost never been addressed by researchers around the world, possibly because studies regarding BrC emission have focused preferentially on the observed physical or chemical properties, particularly optical absorption (e.g., ~~absorption Ångström exponent (~~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; Zhang et al., 2013a; Zheng et al., 2013; Du et al., 2014; Washenfelder et al., 2015; Yan et al., 2015; Zhao et al., 2015; Cheng et al., 2016). These are not conducive to the understanding of China's primary BrC emission characteristics, especially BrC from 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 at 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~~; Sun et al., 2016~~), 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-anthracite 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 into two styles: raw-coal chunk and honey-comb 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~~b~~; 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 Supporting Information (Figure S1) and will be described here briefly. The briquette stove WJ and chunk stove SC are of traditional style widely used especially in past decades in China's households for heating rooms through direct thermal radiation. HD and LW are actually mini-boilers of 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 7 coals were only burned in stove WJ and the chunks of 7 coals all were burned in the 3 chunk stoves (SC, HD, LW) one by one, there were a total of 28 coal/stove combinations for the emission test. At first, two or three anthracite-briquettes (ca. 600 g each) were ignited outdoors by 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) or chunks (0.5-3 kg) were put into the stove and were ignited from the bottom by pre-burned 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 being burned completely (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 (Supporting Information Figure S2). Coal burning emissions were released to the air through a 3m-long iron-chimney. A small flue gas stream (ca. 1-3 l/min) was diverted from the chimney mainstream into ~~the~~ a FP~~F~~S-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 6 outlets at the end of the FPS-4000, which could be used to connect to different sampling/monitoring instruments including at least a particle sampler (Φ90mm Pallflex QFFs) for future BrC determination by the IS approach (Wonaschütz et al., 2009~~; Sun et al., 2016~~). 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~~; Zhi et al., 2008~~). QFFs used for sample collection were baked at 450 ^{o}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 is because the former is easier to be controlled and repeatable than the latter, which allowed us to test the briquetting effects or coal rank effects by fixing other conditions (the same 7 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 be difficult to capture high variations in real field (Roden et al., 2006; Johansson et al., 2008; Christian et al., 2010). In this sense, future study is proposed to go to real field manner.

2.3 Measurement of BrC with IS Method~~.~~

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 1:1 mixture of acetone and a 80:20 mixture of water/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 Figure 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-absorbing 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~~; Sun et al., 2016~~). 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 proxies 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 HULIS) (Duarte et al. 2007; Lukács, et al.

2007; Baduel et al. 2009, 2010). Even if~~Although~~ this assumption is anyway 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.

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 nm and 365 nm. The reason why 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 (Zhang et al., 2013a; Du et al., 2014; Yan et al., 2014~~; Yan et al~~., 2015; Zhi et al., 2015). Figure 2 shows the calibration curves for BrC and BC at both 365 nm 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 4 calibration curves in Figure 2, filter samples were analyzed for BrC and BC with the IS method.

2.4 Calculation Methods~~.~~

Details of the methods for calculating EFs (for BrC and BC), absorption Ångström exponent (AAEs), wavelength dependent BrC contribution to light absorption ($f_{BrC}(\lambda)$) and average BrC contribution to solar light absorption (F_{BrC}) in the range of 350-850 nm are given in the Supporting Information.

3 Results and Discussion~~.~~

3.1 Influence of Coal Briquetting on the EFs of BrC~~.~~

~~A series of emission factors of BrC and BC for the coal/stove combinations were calculated according to the methods described in the Supporting Information. Briefly, EFs were obtained after taking into account the masses of BrC and BC on the QFFs measured by the IS approach, the ratios of sampled to total emissions, and the actually burned masses of coal (Table 2).~~

The calculated emission factors of BrC and BC for the coal/stove combinations are presented in Table 2. Based on Table 2, Figure 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 9th five-year-plan period (1995-2000) (Cheng et al., 1998; Chen et al., 2009; Zhi et al., 2009). Our previous studies showed that briquetting reduces emissions of BC and some other pollutants (e.g., OC, particle matter (PM)~~PM~~) drastically, making briquetting possibly an option for both climate and environmental protection (Zhi et al., 2009; Shen et al., 2014). The effect of reducing BC emissions is seen also in the present study. As shown in Figure 3a and Table 2, the average EFs of BC for chunk- and briquette- anthracites are (0.43±0.23) g/kg and (0.21±0.16) g/kg, respectively, indicating a more than 50% drop due to briquetting of anthracites; meanwhile the average EFs of BC for chunk- and briquette- bituminous coals are (7.85±2.00) g/kg and (0.56±0.22) g/kg, respectively, reflecting a more than 90% drop due to briquetting of bituminous coals. It is believed that the structure (multihole for ventilation and burning) and composition (including 1/3 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 (Figure 3b), no significant decline in EFs is seen for anthracite briquetting (EF is (1.08±0.80) g/kg for chunks, and (1.52±0.16) g/kg for briquettes), but a notable decline in EFs is observed for bituminous coals (EF is (8.59±2.70) g/kg for chunks, and (4.01±2.19) g/kg 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 (more than 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 accounting for the difference. According to Pöschl (~~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 process instead. According to the authors, PAHs are formed through two inter-linked 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 on the different effects of briquetting on BrC and BC emissions are needed.

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

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 Figure 4 for comparing the overall influence of coal's rank on BrC emissions. Each EF for bituminous coal is the average over 5 bituminous coals and similarly each EF for anthracite coal is the average over 2 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 reactant in producing the final emissions. This also suggests that burning anthracite coals instead of bituminous coals in residential sector results in lower emissions of light-absorbing carbon BrC and BC, which favors climate protection.

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 7 coals, from left to right in Figure 3a and Figure 3b, are arranged for increasing V_{daf}. The bell shape profile of BC is maintained, with the coal PDS (V_{daf} =26.25%) having the highest EFs (0.75-1.00~~0.86~~ g/kg for briquettes and 10.15 g/kg for chunks; Figure 3a). Meanwhile as shown in Figure 3b, the bell-shape profile reappears for BrC EFs, with EFs for coal briquettes and chunks peaking respectively in coal PDS (V_{daf}=26.25%, $\mathrm{EF}_{\mathrm{BrC}}$=4.71-8.13~~6.40~~ g/kg) and SYS (V_{daf} =33.20%, $\mathrm{EF}_{\mathrm{BrC}}$=11.49 g/kg). 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. 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 in household purpose.

We take additional advantage of Figure 4, finding that, among the 3 chunk stoves, both $\mathrm{EF}_{\mathrm{BrC}}$ and $\mathrm{EF}_{\mathrm{BC}}$ of coal chunks are in the order of LW>SC>HD, regardless of bituminous coal or anthracite coal, reflecting that HD stove performs the best and the LW stove, the worst. As stove SC is of traditional style widely used especially in past decades in China's households for heating rooms through direct radiation of coal-burning whereas the stoves HD and LW are actually household mini-boilers of low pressure type used for heating rooms by a water piping/radiating system (see subsection 2.1), The above order 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 leads to a decline of 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 Supporting Information (Table S2). Comparison between previous and current studies shows that the means of the emission factors 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, etc. 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 c~~C~~alculated AAE values for China's residential coal combustion are shown in Figure 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 a 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 Gelencser, 2006; Chen and Bond, 2010; Kirchstetterand 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 ~~either~~ both BC and BrC emissions (as shown in Figure 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, Figure 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 Figure 5). It's interesting that this relationship profile is by and large in contrast to the "bell-shape" for the relationship between EF_{BC} and V_{daf} (The maximal 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 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 Gg=10^9 g), which is nearly half of China's BC emissions (Cao et al., 2006a, 2006b, 2011; Wang et al., 2012; Zhang et al., 2013b; Zhang et al., 2015). Chakrabarty et al. (2014) reported a BrC emission of 92 Gg from funeral pyres in South Asia, which is less than 1/6 of our figure for China's household coal burning. We also notice that the calculated BC emissions from household coal burning were 482 Gg in 2013, less than BrC emissions in the same period, suggestive of the relatively high BrC emissions from China's residential coal burning and deserving 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 China's households. On the one hand, Chinese government has long since promoted the use of coal briquettes to achieve 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 briquettes of, but bringing chunks into, households, 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's optical properties and climate consequences compared to BrC's, 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 $f_{BrC}(\lambda)$ 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 Supporting Information for the method to calculate $f_{BrC}(\lambda)$). The results of $f_{BrC}(\lambda)$ were plotted in Figure 6 for coal briquette, coal chunk and the average over briquette and chunk weighted by their consumption shares. According to Figure 6, the values of $f_{BrC}(\lambda)$ 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, Figure 6 demonstrates a significantly higher $f_{BrC}(\lambda)$ 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) (Figure 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 Supporting Information 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).

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

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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

Notes： [a]Moisture on air-dry basis (%); [b]Ash on air-dry basis (%); [c]Volatile matter on 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 7 coals were produced in Ningxia Hui Nationality Autonomous Region (NX), Changzhi City of Shanxi Province (CZ), Lvliang City of Shanxi Province (LL), Pingdingshan City of Henan Province (PDS), Shuangyashan City of Heilongjiang Province (SYS), Xinglongzhuang Coal Mine of Shandong Province (XLZ), and Longkou City of Shandong Province (LK), respectively.

Table 2. Measured ~~Emission~~ emission ~~Factors~~ factors (g/kg) 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 4 stoves are respectively Wanjia brand briquette stove (WJ), Simple Chunk stove (SC), Huanding brand chunk stove (HD), and Laowan brand chunk stove (LW).

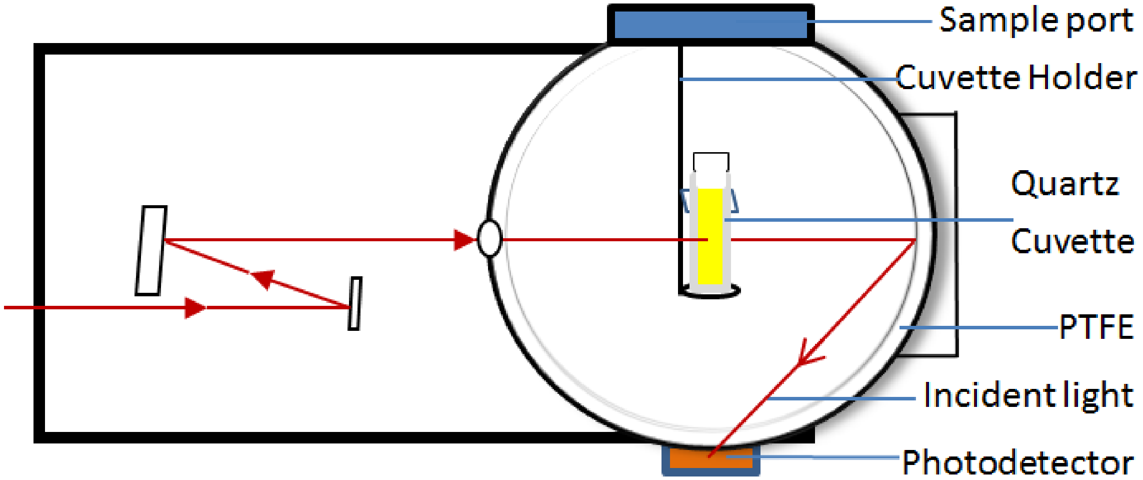

Figure 1. The sketch of integrating sphere (IS) method. PTFE means Polytetrafluoroethylene.

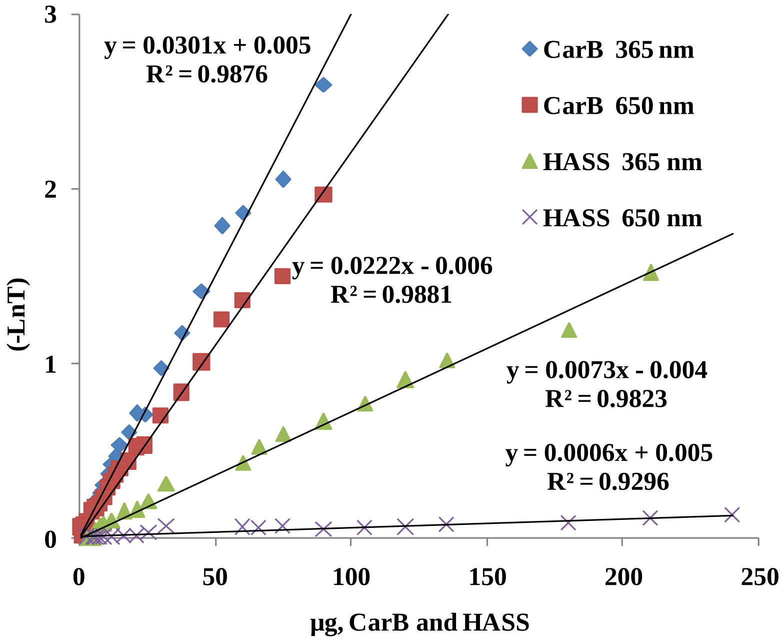

Figure 2. The ~~Calibration~~ calibration curves for CarB (carbon black, diamonds, squares) and HASS (humic acid sodium salt, forks, triangles) at 365 and 650 nm. T is the transmittance of incident light through calibration solution.

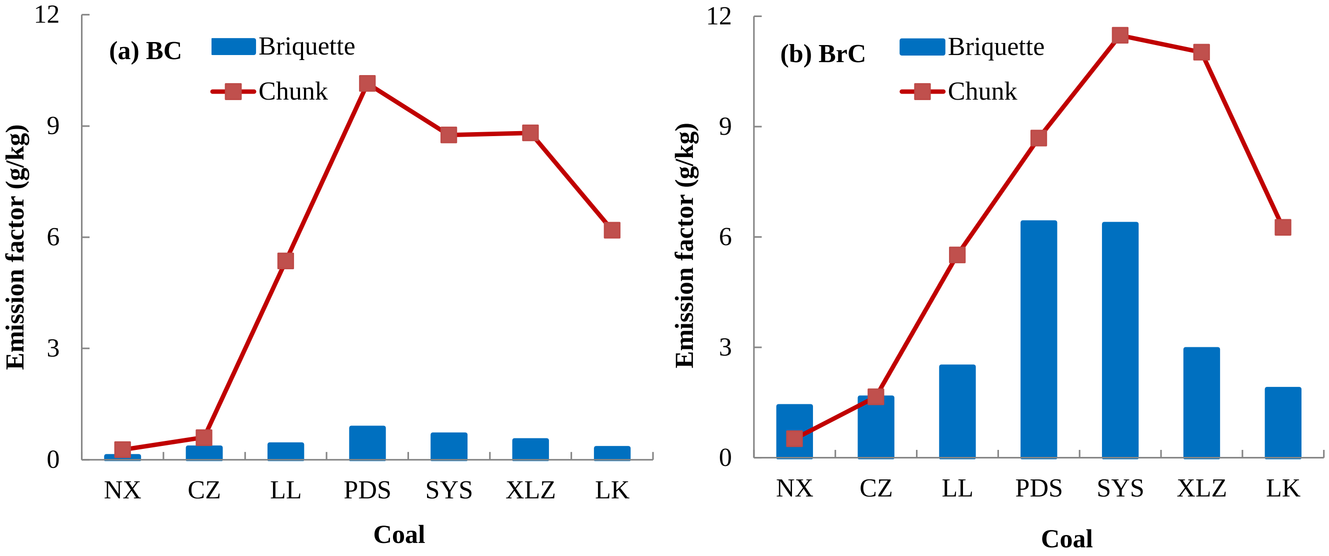

Figure 3. Effects of coal briquetting on black carbon (BC) and brown carbon (BrC) emissions.

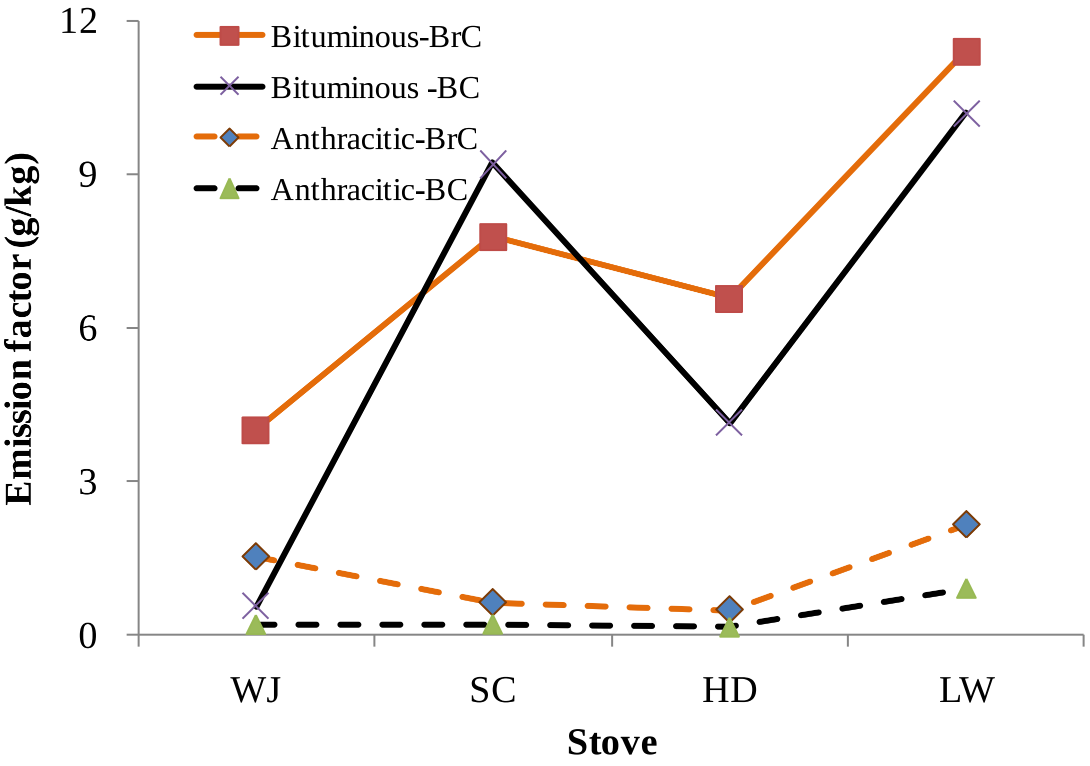

Figure 4. Comparison of emission factors between bituminous and anthracitic coals. The 4 stoves are respectively Wanjia brand briquette stove (WJ), Simple Chunk stove (SC), Huanding brand chunk stove (HD), and Laowan brand chunk stove (LW).

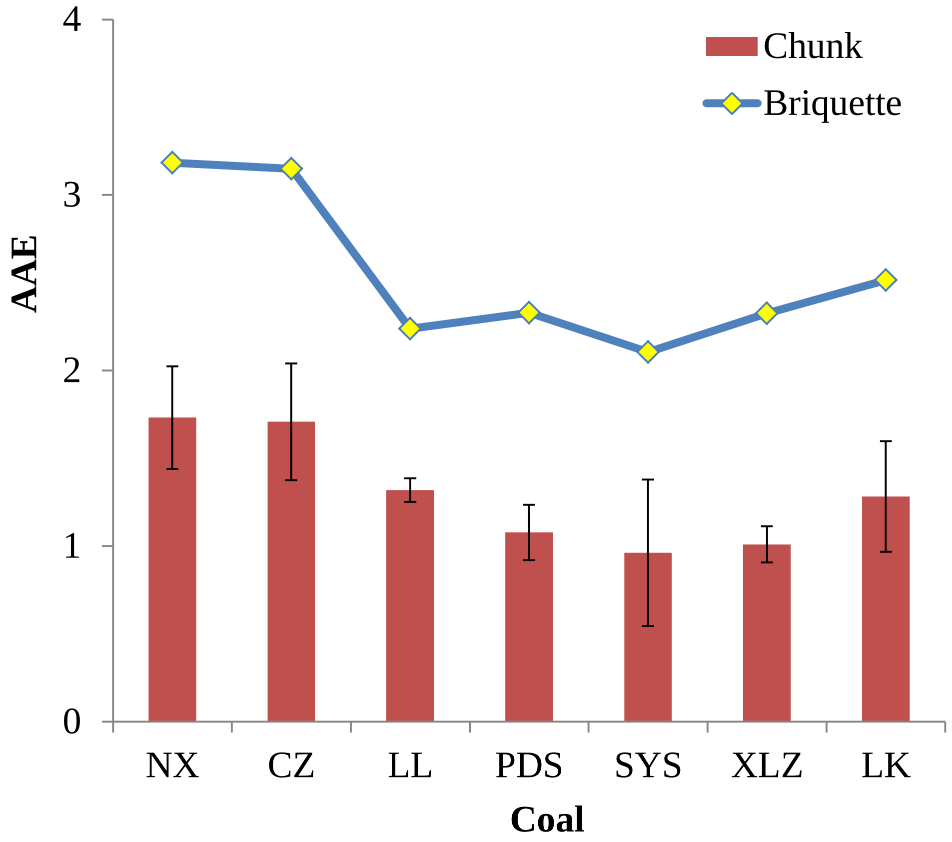

Figure 5. Comparison of AAEs (absorption Ångström exponents) **between briquette and chunk coals.**

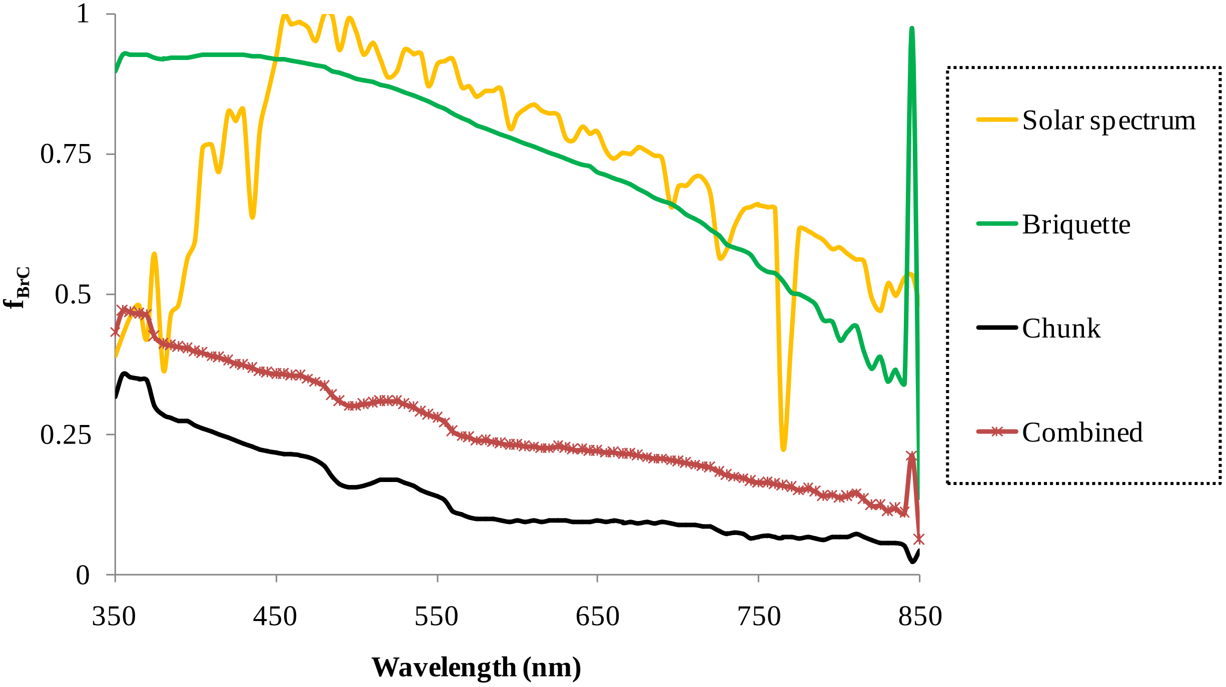

Figure 6. Fraction of light absorption by BrC in total absorption by BrC+BC from residential coal burning. The fraction is expressed as $f_{BrC}(\lambda)$ and was calculated in accordance with the method described in the Supporting Information. The yellow line is the clear sky air mass one global horizontal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

Supplement of

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

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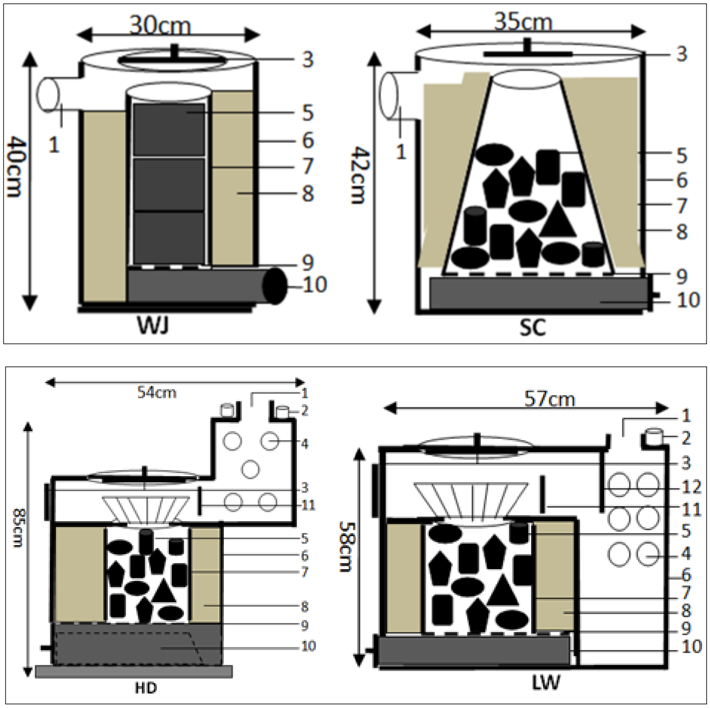

Figure S1. Cross sections of the selected Chinese residential coal-stoves~~.~~

Note: WJ, WanJia brand briquette stove; SC, Simple Chunk stove; HD, HuanDing brand chunk stove; LW, LaoWan brand chunk stove. 1, metal chimney; 2, circulation water; 3, removable lid; 4, circulation water; 5, fuel; 6, iron casting; 7, ceramic cylinder; 8, ceramic fiber for heating insulation; 9, steel grates; 10, air inlet and/or dust bin; 11, adjustable iron baffle; 12, fixed iron baffle.

Here are the dimensions of all 4 stoves (Chen et al., 2005; Zhi et al., 2008). Among them, WJ is specifically for honeycomb briquettes and the other three (SC, HD, and LW) are for raw-coal chunks. In addition, the briquette stove WJ and chunk stove SC are of traditional style widely used especially in past decades in China's households for heating rooms through direct thermal radiation. HD and LW are actually mini-boilers of low pressure type used for heating rooms by heated water circulating through a piping system (2, 4). 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.

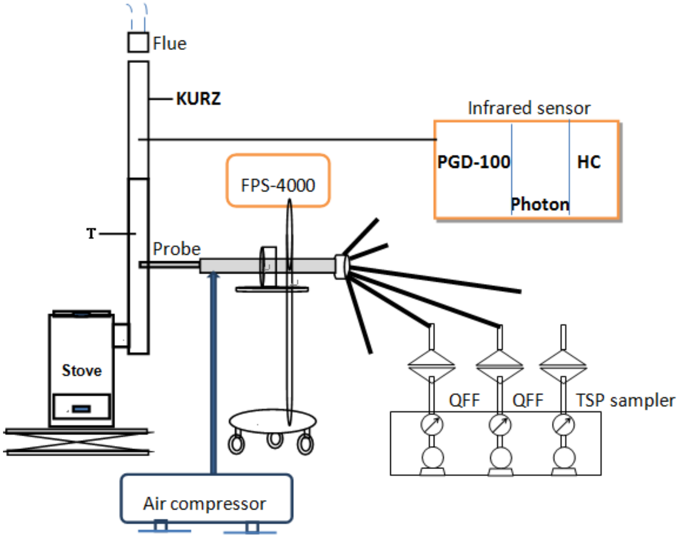

Figure S2. Diversion-dilution-sampling system.

Methods for calculation of EFs (BC and BrC), AAEs, $f_{BrC}(\lambda)$, and F_{BrC}

(A) EFs

Each EF (g/kg) of BC or BrC can be calculated as follows (Chen et al., 2005; Zhi et al., 2008):

$$EF = CF \times \rho \times A \times 10^{-6} / ((M1 - M2) \times f) \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where,

CF—conversion factor from measured equivalent of carbon black (CarB) to BC or from measured equivalent of humic acid sodium salt (HASS) to BrC. As described in our manuscript, CF is 1 for the former and is 0.47 for the latter

ρ—the mass of CarB equivalent or HASS equivalent per unit area of sampling filter (μg/cm^2)

A—the area of sampling filter (cm^2)

M1—the mass of coal before combustion (kg)

M2—the mass of coal after combustion (kg)

f—the fraction of sampled flue gas in total flue gas

(B) AAEs

Based on the light absorption at the wavelength pair of 365 and 650 nm measured by the IS method, AAEs are calculated as follows(Krivácsy et al., 2001~~; Chen and Bond, 2010~~; Sun et al., 2007; Lukács et al., 2007; Chen and Bond, 2010; Lack et al., ~~2012~~2013; Yuan et al., 2015; Forrister et al., 2015):

$$AAE = \frac{-\ln(A650/A365)}{\ln(650/365)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

(C) $f_{BrC}(\lambda)$ and F_{BrC}

The spectrally dependent absorbance by BrC ($ABS_{BrC}(\lambda)$) is obtained by subtracting the BC absorbance from the total absorbance (Kirchstetter et al., 2012; Chakrabarty et al., 2014):

$$ABS_{BrC}(\lambda) = ABS_{sum}(\lambda) - ABS_{BC}(\lambda) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Then, in each wavelength, the fraction of BrC absorbance in total absorbance ($f_{BrC}(\lambda)$) is calculated as:

$$f_{BrC}(\lambda) = ABS_{BrC}(\lambda)/ABS_{sum}(\lambda) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Finally, solar spectrum is considered. The average fraction of absorbed solar radiation by BrC relative to the combined absorption by BrC+BC over the wavelength range from 350 to 850 nm

$$F_{BrC} = \frac{\int_{350}^{850} fBrC(\lambda)\, k(\lambda) d\lambda}{\int_{350}^{850} k(\lambda) d\lambda} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Where k(λ) is the clear sky air mass one global horizontal solar spectrum at the earth's surface (Levinson et al., 2010).

Table S1. Comparison between IS-based EF_{BC} and TOR-based EF_{EC}

Coal	Chunk (Average voer 3 Chunk stoves)	
	EF_{BC}	EF_{EC}
NX	0.26	0.12
CZ	0.59	0.29
LL	5.35	4.25
PDS	10.15	8.09
SYS	8.75	10.50
XLZ	8.81	6.80
LK	6.18	4.06
	Briquette (WJ stove)	
NX	0.10	0.08
CZ	0.32	0.07
LL	0.41	0.27
PDS	0.86	0.41
SYS	0.68	0.80
XLZ	0.52	0.71
LK	0.31	0.21

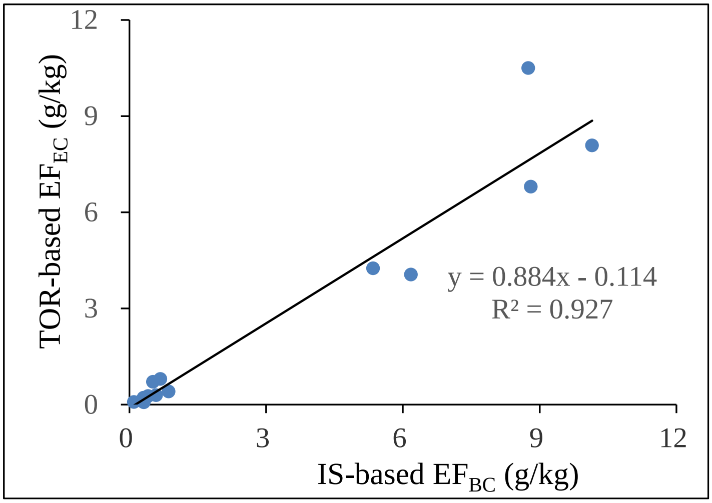

Figure S3. The correlation of EFs between IS-based EF_{BC} and TOR-based EF_{EC}

Table S2. The collection of the directly measured BC (EC) emission factors in our previous article

		Anthracite		Bituminous	
		Raw chunk	**Briquette**	**Raw chunk**	**Briquette**
1	Chen et al, 2005		0.004		0.096 0.675 0.523 0.064
2	Zhi et al, 2008	0.035 0.005	0.012 0.001	0.13 0.73 16.9 10.3 28.5 4.35 1.48	0.009 0.014 0.076 0.016 0.080 0.034 0.019
3	Chen et al, 2006	0.007 0.002		0.20 5.34 10.10 10.12 12.67 6.97 0.48	
4	Chen et al, 2015	0.02	0.06	1.71 2.38 3.46 0.61	0.67 1.3 1.28 0.07
5	Zhi et al, 2009			0.042 0.51 1.23 2.89 0.18 0.083 0.23 4.83 10.02 11.17 5.77 0.55	0.011 0.054 0.085 0.16 0.034 0.018 0.044 0.52 0.64 0.47 0.31 0.084
Mean		**0.014**	**0.019**	**5.34**	**0.27**
sd.		**0.014**	**0.028**	**6.36**	**0.37**
6	This study	0.26 0.59	0.1 0.32	5.35 10.15 8.75 8.81 6.18	0.41 0.86 0.68 0.52 0.31
Mean		**0.43**	**0.21**	**7.85**	**0.56**
sd.		**0.23**	**0.16**	**2.00**	**0.22**

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