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Emission Characteristics of Carbonaceous Particles from Various Residential Coal-Stoves in China

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China is thought to be the most important contributor to the global burden of carbonaceous aerosols, and residential coal combustion is the greatest emission source of black carbon (BC). In the present study, two high-efficiency household coal-stoves are tested together with honeycomb-coal-briquettes and raw-coal-chunks of nine different coals. Coal-burning emissions are collected onto quartz fiber filters (QFFs) and analyzed by a thermal-optical transmittance (TOT) method. Emission factors (EFs) of particulate matter (PM), organic carbon (OC), and elemental carbon (EC) are systematically measured, and the average EFs are calculated by taking into account our previous data. For bituminous coal-briquette and -chunk, EFs of PM, OC, and EC are 7.33, 4.16, and 0.08 g/kg and 14.8, 5.93, and 3.81 g/kg, respectively; and for anthracite-briquette and -chunk, they are 1.21, 0.06, and 0.004 g/kg and 1.08, 0.10, and 0.007 g/kg, respectively. Annual estimates for PM, OC, and EC emissions in China are calculated for the years of 2000 and 2005 according to the EFs and coal consumptions, and the results are consistent with our previous estimates. Bituminous coal-chunk contributes 68% and 99% of the total OC and EC emissions from household coal burning, respectively. Additionally, a new model of Aethalometer (AE90) is introduced into the sampling system to monitor the real-time BC concentrations. On one hand, AE90 provides a set of EFs for optical BC in parallel to thermal-optical EC, and these two data are generally comparable, although BC/EC ratios vary in different coal/stove combinations. On the other hand, AE90 offers a chance to observe the variation of BC concentrations during whole burning cycles, which demonstrates that almost all BC emits into the flue during the initial period of 15 min after coal addition into household stoves.

Introduction

Carbonaceous aerosol has acquired more and more scientific attention due to its importance on global warming in recent years (e.g., refs *1–3*), especially the fossil-fuel black carbon (BC) fraction that may rival methane in climate forcing (*1, 4*) and may be considered into post-Kyoto climate treaties (*5*). China is thought to be the largest contributor to global BC burden (*6, 7*), and fuel consumption for household heating and/or cooking contributes the main section of BC emissions in China (*5, 8*). For example, according to the estimates by Streets et al. (*8*), residential coal and biofuel combustion contributed 45 and 38%, respectively, of the 1.34 Tg BC emissions from China in 1995. However, there are still very few measurements on emission factors (EFs) of carbonaceous particles from household sector based on experiments (*9–11*), resulting in large uncertainties in the estimates for global and regional carbonaceous emissions and notable differences among them (*6–8, 12, 13*).

In our previous studies, a few coals were tested in both honeycomb-coal-briquette and raw-coal-chunk styles in a small domestic stove for measuring EFs of carbonaceous particles (*10, 11*). Great variations were observed among EFs of BC and organic carbon (EF_{BC} and EF_{OC}) from coals with different geological maturity, and averaged EF_{BC} values of bituminous coals were 3.32 and 0.22 g/kg for chunk and briquette, respectively, whereas those of anthracite coals were only 0.004 g/kg for both chunk and briquette, respectively. These values were unexpectedly comparable with the data calculated by Streets et al. (*8*). However, besides the small coal-stove mentioned, there are other stove types with larger volume and higher thermal efficiency that are ubiquitously used for heating in small residences in northern China, where emissions from residential coal-stoves are the most important pollution source of indoor and outdoor air. Although these stoves are originally designed for the increase of thermal efficiency, they may also have effects on emissions. The present study focuses on the measurement of EFs for carbonaceous particles from these improved coal-stoves.

In addition to elemental carbon (EC) determination by the thermal-optical protocol adopted in our previous studies (*10, 14*), a filter-based optical BC measurement method (Aethalometer) was incorporated into the sampling system (*15*). This method could not only produce a set of optical BC data paralleling with EC, but also provided the possibility to look into the variation of BC concentrations during fuel burning cycles.

Experimental Section

Stoves and Coals. Two high-efficiency household coal-stoves were selected in this study, which represent the commonly used ones in northern China: one is for honeycomb-coal-briquette (HEB) and the other for raw-coal-chunk (HEC) (Figure 1). The HEB stove is 52 cm high (chimney excluded) by 31 cm wide and has an upper lid and a galvanized flue pipe, which direct the smoke completely through the chimney. Above the ceramic chamber is a cast iron ring for heat exchange purpose. The HEC stove is 57 cm high (chimney excluded) by 38.5 cm wide, and also contains an upper lid and a flue pipe. The HEC stove is equipped with an iron casing and a clay-lined chamber, and water can circulate around the chamber and the chimney for heating.

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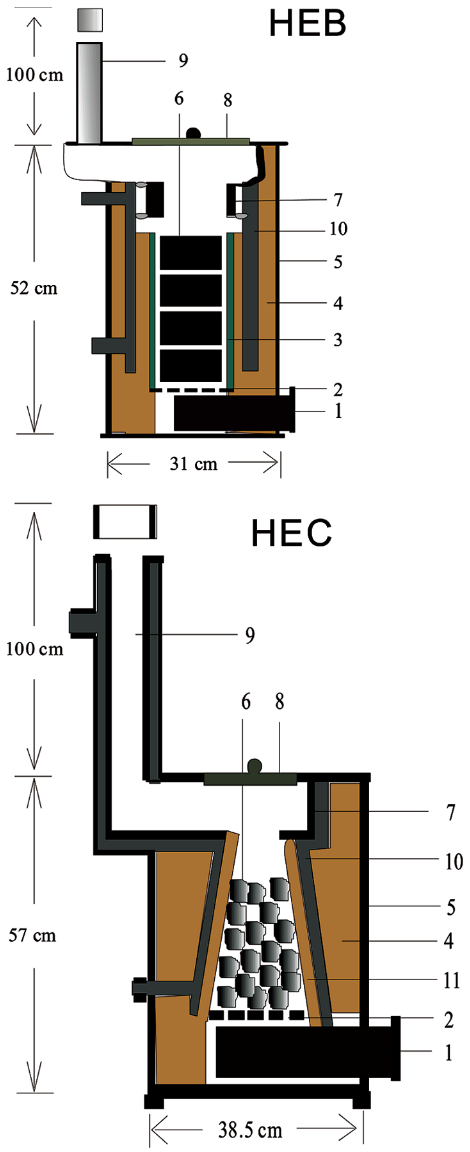

FIGURE 1. Cross sections of the selected Chinese household coal-stoves. HEB, high-efficiency briquette stove; HEC, high-efficiency chunk stove; 1, air inlet and/or dust bin; 2, steel grates; 3, ceramic cylinder; 4, ceramic fiber for heat insulation; 5, iron casting; 6, fuel; 7, cast iron conductor; 8, removable lid; 9, flue; 10, circulation water; 11, clay coating.

In either of the stoves, a steel grate lies underneath the combustion chamber to separate the burning space from the ash holding and air-inlet area.

Nine coals were tested in the present study, whose volatile matter content (V_{daf}) and ranks were tabulated in a previous paper (*11*) and are summarized in Table 1. Briefly, these coals cover a wide range of geological maturity and can be classified into two high-volatile bituminous coals (HVB), three medium-volatile bituminous coals (MVB), two low-volatile bituminous coals (LVB), and two semianthracites (SA). Honeycomb briquettes for each coal were manufactured by a machine after intermixing coal powders with clay, and the briquettes were 12 hole columns 6 cm in height and 9.5 cm in diameter. Briquettes and small raw-coal chunks (3–5 cm in diameter) for the nine coals were burned separately in HEB and HEC stoves. For intercomparison of burning efficiency between these two stoves, one bituminous coal (DT) and one semianthracite (YQ) were tested in a HEB stove in chunk style as well.

Sampling and Analysis. The dilution sampling system has been described in detail elsewhere (*10, 11*). Briefly, it is made up of four main parts: a hood for gathering emissions from stoves and clean air around, a long curved pipe immersed in water for cooling flue gas to ambient temperature, an end pump for drawing the flue gas through the pipe system at a flow rate of about 1 m^3/min and blowing outside the sampling room, and a branched pipe upstream the end pump for ducting a portion of exhaust to two samplers. The dilution ratio for this study ranges from 5 to 20, depending on the combination of stove/coal and burning conditions, for example, emissions from chimney-equipped stoves (HEB, HEC) are less diluted by clean air due to higher burning rate in these stoves than in a simple one. One sampler collects particles at a flow rate of 5–20 L/min onto a quartz-fiber filter (QFF, Whatman) for thermal-optical carbon analysis; the other is an Aethalometer AE90 (described in detail below) that measures real-time BC concentrations (1 min of time base) at a flow rate of 2 L/min. To raise the hood above the chimney outlet of coal-stoves, a slender stainless-steel pipe (5 cm in diameter) is used to connect the hood with the curved pipe instead of the previously used large-size pipes (30 cm in diameter). A digital thermocouple is inserted 10 cm into the chimney outlet to measure real-time–temperature throughout the sampling period.

The sampling procedure is similar to the descriptions in our previous studies (*10, 11*). Briefly, after the burning chamber of the coal-stove was preheated, a batch of small coal-chunks or -briquettes were put into the stove for ignition from the bottom by preburned charcoal and were left burning without any disturbance. When the combustion began to fade (the first burning cycle, 1–2 h), a new batch of coal-chunks or briquettes were added into the stoves and left until burned out (the second burning cycle, 1–4 h). The sampling procedure started when the first batch of coal was put into the stove and lasted for 2–6 h until combustion completely ended. The weights of all coals before and after combustion were recorded, and duplicate samples for each coal were collected to check the reproducibility. As in our earlier work (*16*), backup filters were used to correct for positive adsorption artifacts.

A new model of one-wavelength Aethalometer AE90 (also named "stack tester") (Magee Scientific Company, Berkeley, California) was introduced into the sampling system to measure real-time optical BC concentration in the flue gas. The AE90 operates on principles similar to a traditional Aethalometer such as AE16 (*15*), but it is specifically designed for determination of high BC concentrations in combustion sources such as engine tailpipes, smoke plumes, and industrial stacks. By adopting a time-fractioning function, AE90 can directly measure BC concentration up to 100 mg/m^3, compared to the range of 0.1–10 μg/m^3 for typical Aethalometer instruments (*17*).

In parallel to the sampler that collects particulate emissions onto QFFs, a fraction of emissions from the branched pipe was drawn into the AE90 at a flow rate of 2 L/min, and the time base of each reading was set to 1 min. Optical BC concentrations were measured by the AE90 using a laser with the wavelength of 880 nm, and the specific absorption cross section (σ, attenuation coefficient) used in this study for the calculation of BC was 16.6 m^2/g, as recommended by the manufacturer. QFFs were analyzed for EC and OC using a thermal−optical transmission carbon analyzer (TOT, Sunset Laboratory Inc., Forest Grove, Oregon) with a $\lambda = 680$ nm laser. The temperature protocol for ECOC analysis was similar to the National Institute of Occupational Safety and Health (NIOSH) method 5040 (*14*), as follows: in a He atmosphere, 250 °C, 60 s; 500 °C, 60 s; 650 °C, 60 s; 850 °C, 90 s; and in an O_2−He mixture atmosphere, 550 °C, 45 s; 650 °C, 60 s; 750 °C, 60 s; 850 °C, 40 s; 870 °C, 40 s.

TABLE 1. Emission Factors (g/kg) for PM, OC, and EC of Residential Coal Combustion Based on Burned Dry and Ash-Free Coal Weight

			honeycomb-coal-briquette/HEB stove					raw-coal-chunk/HEC stove				
coal	V_{daf}[a]	rank[b]	EF_{PM}	EF_{OC}	EF_{EC}	EC/OC	OM[c]/PM	EF_{PM}	EF_{OC}	EF_{EC}	EC/OC	OM[c]/PM
bituminous coal												
ZG	38.42	HVB	1.43	0.56	0.009	0.02	0.51	1.95	0.73	0.13	0.18	0.49
YL	37.34	HVB	6.61	4.88	0.041	0.01	0.96	14.1	5.71	7.03	1.23	0.53
XW	30.83	MVB	6.71	5.07	0.076	0.01	0.98	23.8	5.43	16.9	3.11	0.30
DT	30.36	MVB	11.7	8.27	0.160	0.02	0.92	24.0	7.12	10.3	1.45	0.39
CX	30.08	MVB	11.8	8.75	0.180	0.02	0.96	46.6	11.4	28.5	2.49	0.32
XA	20.74	LVB	7.11	2.32	0.034	0.01	0.42	17.2	5.20	4.35	0.84	0.39
CZ	16.00	LVB	3.06	1.23	0.019	0.02	0.52	5.41	2.58	1.48	0.57	0.62
geomean of bituminous coals			5.68	3.12	0.047	0.02	0.71	13.2	4.24	4.34	1.02	0.42
total average for bituminous coal[d]			7.33	4.16	0.082	0.02	0.74	14.8	5.93	3.81	0.64	0.52
semianthracite coal												
YQ	12.19	SA	2.20	0.36	0.012	0.03	0.21	1.47	0.13	0.035	0.27	0.11
AY	8.09	SA	0.60	0.04	0.001	0.03	0.09	1.54	0.42	0.005	0.01	0.35
geomean of anthracites			1.15	0.12	0.003	0.03	0.14	1.50	0.23	0.013	0.06	0.20
total average for anthracite[d]			1.21	0.06	0.004	0.06	0.07	1.08	0.10	0.007	0.07	0.12

[a] Volatile matter on dry and ash-free basis (%). [b] 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, and SA is for semianthracite. [c] Organic matter, calculated as OC × 1.3. [d] Totally geometric mean by taking account of the present data and previous results published in refs *10* and *11*.

Results and Discussion

EFs for Coal-briquette Burning. The emission factors of particulate matter (EF_{PM}), EC (EF_{EC}), and OC (EF_{OC}) for honeycomb-briquette combustion of the nine tested coals in the HEB stove are presented in Table 1. All results are calculated according to the masses of PM, EC, and OC collected on the quartz-fiber filters (QFFs), the ratios of sampled to total emissions, as well as the actually burned coal weights (on dry and ash-free bases). The volatile matter content and rank classification of each coal are also included in Table 1, because the geological maturity of coal has been found to be related to the significant variations of all EFs for residential coal combustion (*9–11*). These relations are confirmed here that the plot of EF_{PM} versus V_{daf} looks like a bell curve with the medium V_{daf} having the highest emissions. For example, among the bituminous coals, CX (MVB, $V_{daf} = 30.1\%$) has the highest EFs, and its EF_{OC} (8.75 g/kg) and EF_{EC} (0.18 g/kg) are 16 and 20 times that of ZG coal (HVB, $V_{daf} = 38.4\%$), respectively, and are 7 and 9 times that of CZ coal (LVB, $V_{daf} = 16.0\%$), respectively (Table 1).

The geometric means of EF_{PM}, EF_{OC}, and EF_{EC} for the seven bituminous coals are 5.68 g/kg, 3.12 g/kg, and 0.047 g/kg, respectively. By comparison, the averaged EFs for the other four bituminous coals burned in a small coal-stove are 11.5, 6.89, and 0.22 g/kg, respectively (*10*). These marked reductions of various EFs from these different stoves, especially for EF_{EC}, which decreases by about 5 times, may derive from higher combustion efficiency of the HEB stove. However, under residential combustion conditions, the diminutions resulting from the improvement of coal-stoves cannot cover the wide variations of EFs resulting from thermal maturities of coals, as mentioned above.

For anthracite coals, the geometric means of EF_{PM}, EF_{OC}, and EF_{EC} from HEB stoves are 1.15, 0.12, and 0.003 g/kg, respectively. These values are close to those from the small stove (1.33, 0.02, and 0.004 g/kg for EF_{PM}, EF_{OC}, and EF_{EC}, respectively) (*10*). Of the two semianthracites in the present study, YQ coal has more similar characteristics to bituminous coals such as ZG and CZ, whereas AY coal is close to the anthracite (YX) previously tested (Table 1).

Because both the HEB and small coal-stoves are used ubiquitously in Chinese kitchens, comprehensively averaged EFs for residential coal-briquette combustion can be calculated by combination of all coals tested in these two stoves. As can be seen in Table 1, the averaged EF_{PM}, EF_{OC}, and EF_{EC} values for briquetted bituminous coals are 7.33, 4.16, and 0.08 g/kg, respectively, whereas for anthracites they are 1.21, 0.06, and 0.004 g/kg, respectively. Although bituminous coal has an EF_{PM} value that is only several times the value of anthracite, their EFs for OC and EC differ by 70 and 20 times, respectively. Actually, much higher percentages of organic matter (OM, 1.3 × OC) in PM are observed in emissions of bituminous coals than of the anthracites (Table 1).

EFs for Coal-chunk Burning. The nine coals were also burned in raw-coal-chunk style in the HEC stove. As presented in Table 1, the averaged EF_{PM}, EF_{OC}, and EF_{EC} values for coal-chunk combustion of bituminous coals are 13.2, 4.24, and 4.34 g/kg, respectively. It is unexpectedly observed that EC concentrations in these emissions are often greater than those of OC, and EF_{EC} values from this stove even exceed those from the small stove (3.32 g/kg) (*11*). The same case occurs for the anthracites; EF_{PM}, EF_{OC}, and EF_{EC} from the HEC stove are 1.50, 0.23, and 0.013 g/kg, respectively, which are higher by several times than the previous measurements from the small stove (0.78, 0.04, and 0.004 g/kg, respectively) (*11*).

For an explanation of the higher EFs of carbonaceous particles from the HEC stove than from the small stove, apart from more burning cycles and coal masses tested in the HEC stove, the improved coal-stove may only pursue higher heat transfer efficiency but sacrifice combustion efficiency. Zhang et al. (*18*) also reported greater EFs for particles and some carbonaceous gases from improved stoves than from traditional stoves. Therefore, future designs for high-efficiency stoves should optimize both energy transfer and environmental concerns.

TABLE 2. Emission Estimates of PM, OC, and EC from Residential Coal Combustion during the Years of 2000 and 2005 in China

		bituminous coal		anthracite		
year		chunk	briquette	chunk	briquette	total
2000	consumption, Tg	37.04	24.69	8.34	5.56	75.62
	emissions estimate, Gg					
	PM	550.13	181.07	9.00	6.70	746.90
	OC	219.76	102.73	0.80	0.35	323.63
	EC	141.06	2.03	0.06	0.02	143.16
2005	consumption, Tg	40.94	27.29	9.21	6.14	83.58
	emissions estimate, Gg					
	PM	608.02	200.12	9.95	7.41	825.50
	OC	242.88	113.54	0.88	0.38	357.68
	EC	155.90	2.24	0.06	0.02	158.23

TABLE 3. Comparison of EFs (g/kg) for BC and EC from Residential Coal Combustion

Coal	EF_{BC}	EF_{EC}	BC/EC	EC/TC	OM/PM
Honeycomb-Coal-Briquette/HEB Stove					
ZG	0.016	0.009	1.77	0.02	0.51
YL	0.053	0.041	1.29	0.01	0.96
XW	0.138	0.076	1.82	0.01	0.98
XA	0.071	0.034	2.09	0.01	0.42
CZ	0.029	0.019	1.51	0.02	0.52
geomean of bituminous coal	0.047	0.028	1.67	0.02	0.64
AY	0.003	0.001	2.63	0.02	0.09
Raw-Coal-Chunk/HEC Stove					
ZG	0.08	0.13	0.61	0.15	0.49
XW	9.51	16.9	0.56	0.76	0.39
XA	2.11	4.35	0.48	0.46	0.62
CZ	0.97	1.48	0.65	0.36	0.42
geomean of bituminous coal	1.12	1.94	0.58	0.36	0.47
AY	0.005	0.005	1.05	0.01	0.35

The EFs for the same nine coals from the HEB and HEC stoves offer the possibility to compare the burning efficiencies of two kinds of residential coal burning styles, i.e., honeycomb-briquettes versus chunks. As showed in Table 1, all EFs for coal briquettes burned in the HEB stove are several times lower than those for coal chunks in HEC, especially the EF_{EC} for bituminous coals, which declines by almost 2 orders of magnitude. A direct comparison of these two high-efficiency stoves was also performed in this study. Two coals (DT and YQ) were burned in chunks in both HEB and HEC stoves, and the corresponding EFs from two coal-stoves are quite close (data are not present here). Therefore, it can be concluded that the geological maturity of coal is the most important factor that affects EFs for carbonaceous aerosol from residential coal combustion, followed by burning style (molded or not) combined with corresponding stove.

The comprehensively averaged EFs for PM, OC, and EC for household coal-chunk combustion were calculated from the present values together with the measurements in the small coal-stove (*11*), as shown in Table 1. The geometric means of EF_{PM}, EF_{OC}, and EF_{EC} for bituminous coal chunks are 14.8, 5.93, and 3.81 g/kg, respectively, and for anthracite chunks they are 1.08, 0.10, and 0.007 g/kg, respectively. Except for the EF_{EC} value for bituminous coal, all EFs from both chunk and briquette styles differ by less than a factor of 2. For comparison, Bond et al. compiled EF_{PM} values as 7.7 ± 6.5 and 12 ± 8 g/kg of bituminous coals for residential cooking and heating, respectively (*6*); Streets et al. summarized EF_{EC} values of 0.12 g/kg for briquette or anthracite and 3.7 g/kg for raw bituminous coal (*8*). All these data are comparable to some extent.

Estimates of Carbonaceous Emissions from Chinese Household Coal Burning. According to the EFs measured in our studies and the statistical data for coal consumption, emission estimates for PM, OC, and EC from household coal combustion in China can be made. In the years of 2000 and 2005, total coal consumptions in the residential sector are 79.07 and 87.39 Tg (teragrams), respectively (*19*). Although the actual percentages of anthracite and bituminous coal in total consumption are unavailable, their ratios in the total production of raw coal (17.6 and 78.1%, respectively, and the remainder is lignite coal) can be referenced. Another assumption is about the ratio of honeycomb-briquette to raw-coal-chunk in the residential sector. Although it was reported that only about 10% of total coal consumption was burned in briquettes (*19*), we followed the previous assumption that this ratio is 40% (*10, 11*).

As presented in Table 2, annual emissions of PM, OC, and EC from Chinese household coal consumption are 746.9, 323.6, and 143.2 Gg (gigagrams), respectively, for the year 2000, and are 825.5, 357.7, and 158.2 Gg, respectively, for the year 2005. It was illustrated that bituminous coal for residential stoves dominates the total carbonaceous emissions in this sector in China; bituminous coal-chunk contributes 68 and 99% of the total OC and EC emissions from household coal burning, respectively, whereas bituminous coal-briquette contributes almost the residues; the contribution from anthracite of both styles can be omitted due to their relatively low EFs.

The present estimates of PM, OC, and EC for the year 2000 are consistent with our previous study (*11*), although their EFs have been updated. However, these estimates differ greatly from other published data, for example, 605.4 Gg of EC emissions for the year 1995 by Streets et al. (*8*) and 1332.8 Gg of OC and 520.8 Gg of EC for the year 2000 by Cao et al. (*13*). Because our EF_{EC} for bituminous coal-chunk (3.81 g/kg) coincides with that (3.7g/kg) used in Streets et al. (*8*), and because bituminous-chunk burning dominates the estimate of BC emissions (99%), the striking disagreement in estimates should mainly be attributed to the different statistics of coal consumption adopted by different researchers. For example, Streets et al. (*8*) adopted 184 Tg (personal communication) as the residential coal consumption for 1995, and Cao et al. (*13*) adopted 213.4 Tg as the residential coal consumption for 2000, several times higher than the figure adopted in this paper (79.09 Tg, China Statistical Yearbook 2003); in addition, the briquette ratio in residential coal was assumed to be only 6% by Streets et al. (*8*) for 1995, which is approximately 6 times lower than our assumption (40%) for 2000. It can be affirmed that carbonaceous emissions from Chinese residential coal burning will decrease greatly as the percentages of briquette and anthracite increase in total coal consumption.

Implication of Measurements by the AE90. The intro-

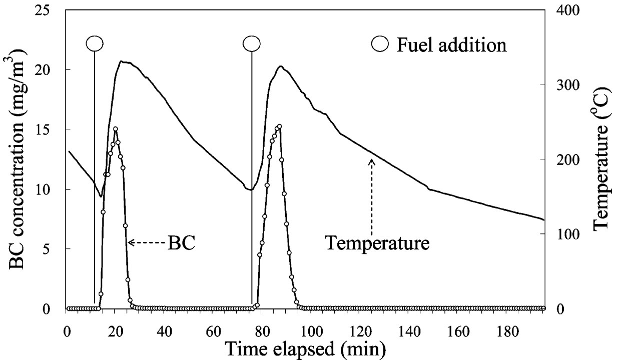

FIGURE 2. Real-time BC concentrations observed by the Aethalometer AE90 during two burning cycles. (Using XA coal-chunk burned in the HEC stove as the example.)

duction of AE90 into this experiment enables us to acquire a set of emission factors for optical BC (EF_{BC}) paralleling thermal-optical EC determination from residential coal combustion. In the present study, real-time BC concentration in the diluted emissions from coal-stove was measured by AE90 every minute (i.e., time base was set to 1 min), and the duration covered whole burning cycles. The BC concentrations of each reading were averaged for each coal/stove combination, and then its EF_{BC} value was calculated with the similar method for EF_{EC}.

As shown in Table 3, the EFs for BC and EC are generally comparable in the present measurements. Averaged EF_{BC} values for briquettes of bituminous coal and anthracite are 0.047 and 0.003 g/kg, respectively, and those for chunks are 1.12 and 0.005 g/kg, respectively. It should be noted that only 6 coal-briquettes and 5 coal-chunks were measured for optical BC, whereas some coals (such as CX and DT), which possess the highest EFs, are excluded due to difficulties of operation of the AE90, and this is the reason for the lower averaged EF_{EC} values in Table 3 than in Table 1.

It is found that the ratio of EF_{BC} to EF_{EC} varies with different coal/stove combination (Table 3). For example, when coals are burned in briquettes in the HEB stove, their EF_{BC} values are notably greater than EF_{EC} (BC/EC ratios vary in 1.3–2.6), but when bituminous coals are combusted in chunks in the HEC stove, BC/EC ratios are less than 1 (ranged in 0.48–0.65 and averaged 0.58); anthracite chunks are the exception, whose ratio is close to 1. If various EF_{BC} values were calibrated according to the EF_{EC} data in Table 1 and BC/EC ratios, then the total BC emission estimate in China will be 84.6 Gg for the year 2000, only 60% of total EC emission (143.2 Gg).

The reason for the large variation of BC/EC ratios may derive from the different constituents in the emissions, such as the EC or OC fractions in total carbon (TC, sum of EC and OC) and the content of metal oxides. It is well-known that some organic compounds (e.g., polycyclic aromatic hydrocarbons) can absorb light and disturb the measurements of optical BC (*20, 21*), and higher OC fractions in TC are observed for all briquettes and anthracite chunks than for bituminous coal chunks (Table 3). Additionally, some inorganic material (e.g., metal oxides) in aerosol may result in significant overestimation of BC values by Aethalometer instruments (*22*), and greater concentrations of inorganic material are contained in the emissions from anthracites than from bituminous coals, as mentioned above. Finally, the absorption efficiency of EC can be enhanced if EC concentrations are very low (*23*), and EC/PM ratios for all briquette samples are extremely low (below 0.02, Table 1).

The measurement of the AE90 also exhibits real-time variation of BC concentrations in the emissions from residential coal burning. By taking XA coal-chunk burned in the HEC stove as the example, Figure 2 demonstrates the significant variation of BC concentration as well as temperature in the diluted flue gas during the two burning cycles. When fuel was added into the coal-stove, the combustion bloomed almost at once, which was indicated by the soaring temperature of the flue gas, and BC concentration ascended swiftly at the same time. Both temperature and BC concentration peaked during 5–15 min after the coal addition, and then BC concentration descended quickly toward baseline while temperature of the flue gas dropped slowly. This process can be simply explained as follows. When coal was put into the stove and heated, volatile materials were abundantly produced and emitted into the combustion zone, where poor air mixture with the fuel resulted in a high BC concentration. After this period, the remaining charcoal began to contact oxygen and steadily burned, and fewer BC particles were formed under such condition. As showed in Figure 2, almost all BC emissions (about 99%) were produced during the initial period of 15 or 20 min after coal addition. This suggests that optimization of design for clean combustion coal-stove should be emphasized on the air supply and mixture conditions during the beginning period of coal combustion.

Acknowledgments

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Supporting Information Available

A figure comparing the average EFs of the different stove/coal combinations is provided. This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Jacobson, M. Z. Climate response of fossil fuel and biofuel soot, accounting for soot's feedback to snow and sea ice albedo and emissivity. *J. Geophys. Res.* **2004**, *109*, D21201. doi: 10.1029/2004JD004945.

(2) Hansen, J.; Sato, M.; Ruedy, R.; Nazarenko, L.; Lacis, A.; Schmidt, G. A. Efficacy of climate forcings. *J. Geophys. Res.* **2005**, *110*, D18104. doi: 10.1029/2005JD005776.

(3) Ramanathan, V.; Chung, C.; Kim, D.; Bettge, T.; Buja, L.; Kiehl, J. T.; Washington, W. M.; Fu, Q.; Sikka, D. R.; Wild, M. Atmospheric brown clouds: impacts on south Asian climate and hydrological cycle. *Proc. Natl. Acad. Sci. USA.* **2005**, *102*, 5326–5333.

(4) Chung, S. H.; Seinfeld, J. H. Climate response of direct radiative forcing of anthropogenic black carbon. *J. Geophys. Res.* **2005**, *110*, D11102. doi: 10.1029/2004JD005441.

(5) Streets, D. G.; Aunan, K. The importance of China's household sector for black carbon emissions. *Geophys. Res. Lett.* **2005**, *32*, L12708. doi: 10.1029/2005GL022960.

(6) Bond, T. C.; Streets, D. G.; Yarber, K. F.; Nelson, S. M.; Woo, J.-H.; Klimont, Z. A technology-based global inventory of black and organic carbon emissions from combustion. *J. Geophys. Res.* **2004**, *109*, D14203. doi: 10.1029/2003JD003697.

(7) Streets, D. G.; Bond, T. C.; Carmichael, G. R.; Fernandes, S. D.; Fu, Q.; He, D.; Klimont, Z.; Nelson, S. M.; Tsai, N. Y.; Wang, M. Q.; Woo, J.-H.; Yarber, K. F. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. *J. Geophys. Res.* **2003**, *108* (D21), 8809. doi: 10.1029/2002JD003093.

(8) Streets, D. G.; Gupta, S; Waldhoff, S. T.; Wang, M. Q.; Bond, T. C.; Bo, Y. Black carbon emissions in China. *Atmos. Environ.* **2001**, *35*, 4281–4296.

(9) Bond, T. C.; Covert, D. S.; Kramlich J. C.; Larson, T. V.; Charlson, R. J. Primary particle emissions from residential coal burning: Optical properties and size distributions. *J. Geophys. Res.* **2002**, *107* (D21), 8347. doi: 10.1029/2001JD000571.

(10) Chen, Y.; Sheng, G.; Bi, X.; Feng, Y.; Mai, B.; Fu, J. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environ. Sci. Technol.* **2005**, *39*, 1861–1867.

(11) Chen, Y.; Zhi, G.; Feng, Y.; Fu, J.; Feng, J.; Sheng, G.; Simoneit, B. R. T. Measurements of emission factors for primary carbonaceous particles from residential raw-coal combustion in

China. *Geophys. Res. Lett.* **2006**, *33*, L20815. doi: 10.1029/2006GL026966.

(12) Cooke, W. F.; Liosse, C.; Cachier, H.; Feichter, J. Construction of a 1° × 1° fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model. *J. Geophys. Res.* **1999**, *104*, 22137–22162.

(13) Cao, G. L.; Zhang, X. Y.; Wang, D.; Zheng, F. C. Inventory of black carbon and organic carbon emissions from China. *Atmos. Environ.* **2006**, *40*, 6516–6527.

(14) Birch, M. E. Analysis of carbonaceous aerosols: Interlaboratory comparison. *Analyst* **1998**, *123*, 851–857.

(15) Hansen, A. D. A.; Rosen, H.; Novakov, T. The Aethalometer-an instrument for the realtime measurement of optical absorption by aerosol particles. *Sci. Total Environ.* **1984**, *36*, 191–196.

(16) Chen, Y.; Bi, X.; Mai, B.; Sheng, G.; Fu, J. Emission characterization of particulate/gaseous phases and size association for polycyclic aromatic hydrocarbons from residential coal combustion. *Fuel* **2004**, *83*, 781–790.

(17) Zhi, G.; Chen, Y.; Hansen, A. D. A.; Sheng, G.; Fu, J. *Evaluation of a new model Aethalometer–AE90 (stack tester) by comparison of BC values with AE42 and thermal-optical transmittance EC measurements.* **2008**, In preparation.

(18) Zhang, J.; Smith, K. R.; Uma, R.; Ma, Y.; Kishore, V. V. N.; Lata, K.; Khalil, M. A. K.; Rasmussen, R. A.; Thorneloe, S. T. Carbon monoxide from cookstoves in developing countries: 1. Emission factors. *Chemosphere: Global Change Science* **1999**, *1*, 353–366.

(19) Department of Industry and Transport Statistics, National Bureau of Statistics, PRC; Energy Bureau, National Development and Reform Commission, PRC. *China Energy Statistical Yearbook 2006*. China Statistics Press: Beijing, 2007.

(20) Bond, T. C.; Anderson, T. L.; Campbell, D. C. Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols. *Aerosol Sci. Technol.* **1999**, *30*, 582–600.

(21) Arnott, W. P.; Hamasha, K.; Moosmüller, H.; Sheridan, P. J.; Ogren, J. A. Towards aerosol light-absorption measurements with a 7-wavelength Aethalometer: Evaluation with a photoacoustic instrument and 3-wavelength nephelometer. *Aerosol Sci. Technol.* **2005**, *39* (1), 17–29.

(22) Li, Y.; Zhang, X.; Gong, S.; Che, H.; Wang, D.; Qu, W.; Sun, J. Comparison of EC and BC and evaluation of dust aerosol contribution to light absorption in Xi'an, China. *Environ. Monitor. Assess.* **2006**, *120*, 301–312.

(23) Seinfeld, J. H.; Pandis, S. N. In *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, New York, 1998.

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