



# Size-segregated emission factors and health risks of PAHs from residential coal flaming/smoldering combustion

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## Abstract

Residential coal combustion is one of the main sources of ambient polycyclic aromatic hydrocarbons (PAHs). Updating its emission estimation is limited by the shortages of emission factors, especially for them in different particle sizes and from different combustion conditions. PAH emission factors (EFs) for nine size-segregated particle segments emitted from smoldering and flaming combustion of residential coals (four kinds of raw coals (RCs) and three kinds of honeycomb coal briquettes (HCBs)) were obtained in China, using a dilution sampling system. EFs of PAHs for the flaming and smoldering of HCB ranged from 1.32 to 2.04 mg kg<sup>-1</sup> and 0.35 to 5.36 mg kg<sup>-1</sup>, respectively. The EFs of PAHs for RC flaming combustion varied from 0.50 to 218.96 mg kg<sup>-1</sup>. About 53.5–96.4% and 47.4–90.9% of PAHs concentrated in PM<sub>2.1</sub> and PM<sub>1.1</sub>, respectively. Different fuel types and combustion conditions strongly affected the PAH EFs. The PAH EF for the RC was 0.3 times that for HCB in Guizhou, which implied that PAH EFs for RC combustion were not always higher than those from HCB burning. For different combustion conditions, the PAH EFs from flaming were more than 2.5 times higher than those from smoldering for HCB except in the Anhui region. Results indicated that current PAH EFs may not be universal, which may bias the establishment of control policies for toxic pollutants emitted from domestic coal burning. On average, 73.2 ± 15.5% of total PAH potential toxicity risks were concentrated in submicron particles. More size-segregated PAH EFs for residential coal combustion should be investigated considering combustion conditions with a uniform sampling method in China.

**Keywords** Residential coal · Polycyclic aromatic hydrocarbon · Emission factor · Toxic risk · Smoldering and flaming burning · Particle size

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## Introduction

Coal still accounts for 62.0% of China's energy consumption and the consumption amount was 2.70 trillion tons with 12.4% consumed by residential sector in 2016 (NBSC 2018). Large amounts of residential coal consumption were found in some coal production provinces, such as Guizhou, where 2.45 times more residential coals were consumed compared with Beijing (Lin et al. 2014). Domestic coal is always burned directly without pollutant control, which is why it is one of the most important contributors to primary particles and associated toxic chemical components. Previous research indicated that coal burning contributed about 10.9–18.6% of PM<sub>2.5</sub>, 45% of carbonaceous aerosols, and 38.9–49.2% of sulfate in multiple northern Chinese cities (Ni et al. 2018; Dai et al. 2019; Xu et al. 2019). Furthermore, coal combustion contributed 25% of black carbon (BC) and 47% of polycyclic

aromatic hydrocarbons in China (Inomata et al. 2012; Zhang et al. 2015). The pollutants emitted from domestic coal burning can lead to severe regional air pollution especially for winter heating period in China (Shang et al. 2018).

Toxic pollutants emitted from residential coal combustion can also pose adverse impact on human health and can cause serious diseases like lung cancer (Mumford et al. 1987; Lee et al. 2010; Barone-Adesi et al. 2012). Polycyclic aromatic hydrocarbons (PAHs) are a group of organic matter compounds containing multiple aromatic rings which are generated from incomplete combustion, and some PAHs are identified as toxic organic pollutants due to their great teratogenicity, carcinogenicity, and mutagenicity (Boström et al. 2002; Lu et al. 2009; Kim et al. 2013). Research on PAHs emitted from residential coal combustion has been continuously reported in the last decade (Chen et al. 2004; Liu et al. 2009; Shen et al. 2011; Wang et al. 2016). PAH emission inventories for China (Xu et al. 2006; Zhang et al. 2007, 2008), northeast Asia (Inomata et al. 2012), and global (Zhang and Tao 2009; Shen et al. 2013a) have been established. However, the emission factors (EFs) of residential coal combustion sector of China employed in these studies were mostly from the test by Chen et al. (2005), and few studies have involved the EFs from Liu et al. (2009). The uncertainty of emission inventories has been considered to be mostly caused from variation of EFs (Zhang et al. 2008).

PAH EFs from residential coal are impacted by coal types and properties, combustion conditions, stove types, gas-particulate partitioning and particle size, etc. (Chen et al. 2005; Liu et al. 2009; Shen et al. 2011). Former studies also found that honeycomb coal briquettes yield higher PAH emissions than raw coals (Chen et al. 2015) and most particulate PAHs emitted from residential coal combustion were concentrated in fine particles (Shen et al. 2010). Submicron and fine particles have adverse impacts on human health (Yu et al. 2000). Former studies indicated that the particles with aerodynamic diameter less than 0.49  $\mu\text{m}$  accounted for 88% of the mass of the particles emitted from residential coal combustion (Chen et al. 2004). Previous study has shown that 89% of particulate phase PAHs emitted from coal combustion process were found in  $\text{PM}_{2.5}$ , which makes an increase of the hazard of  $\text{PM}_{2.5}$  to human beings (Shen et al. 2010).

It should be also noted that residential coal combustion occurred in low heat mode at night and high heat mode at daytime in rural China (Shen et al. 2010). In rural China, the domestic coal burning always can be classed as two modes: flaming (cooking period for breakfast, lunch, and dinner, with stove door opened) and smoldering burning (non-cooking period, especially for night period with stove door closed wholly). The PAH species, size distribution, and emission factors should be quite different and the human exposure risks should also be varied for the two burning conditions. Therefore, the investigation of PAH EFs for smoldering (low heat mode) and

flaming combustion (high heat mode) is important to reflect the real emission. Studies considering size-segregated PAH EFs under flaming/smoldering burning conditions for raw and honeycomb coal burning are still limited.

With a dilution sampling system utilized, this study intends to (1) obtain the PAH EFs for different types of residential coal combustion, (2) determine the difference of PAH emissions from smoldering combustion and flaming combustion, (3) identify the size distribution of particulate PAHs in different combustion conditions, and (4) evaluate the health risks of PAHs emitted from residential coal burning. The results are expected to be an important supplement for the current PAH EF database, which is helpful for updating PAH emission inventories of different burning conditions and particle size, and also helpful for policy development in view of human health.

## Materials and experiments

### Coal collection and properties

Coal mines are widely distributed in China. Coals have a wide range of geological maturity and the coals utilized in previous studies were mostly purchased from Beijing, Shanxi, and Shaanxi (Liu et al. 2009; Shen et al. 2010). For making a supplement of current EF dataset, seven types of coals including four kinds of raw coals (RCs) and three kinds of honeycomb coal briquettes (HCBs) were purchased in the markets of Anhui (AH), Guizhou (GZ), Inner Mongolia (NM), and Xinjiang (XJ) and tested in this study. The HCBs had 12 holes except that GZ HCB had 15 holes. Two combustion conditions, flaming combustion and smoldering combustion, were considered to reflect the actual residential coal combustion conditions. A total of ten groups of experiments were carried out, including seven groups of flaming phase combustion experiments and three groups of smoldering combustion phase experiments. The coal properties are shown in Table 1.

### Combustion and sampling

A white iron stove purchased from a local market was used. The dimensions of the coal stove were 30 cm outer diameter, 12 cm inner diameter, and 43 cm high. The initial mass of the fuel and the mass of the fuel residue after combustion were recorded. For flaming and smoldering burning, the stove air inlet cap was entirely opened and closed, respectively, which reflected the real cooking and non-cooking situation in China. Each time, a piece of RC was ignited with an electric stove and put at the bottom of stove when no obvious smoke can be found, then another 0.3 kg RC was added for the test, and sampling was stopped when the 0.3 kg coal was completely consumed, with no obvious fire and the stove was gradually

**Table 1** Coal properties in this study

Type	Market location	Moisture (%)	Ash (%)	Volatile (%)	Fixed carbon (%)	Rank
Honeycomb coal briquettes (HCB)	AH	2.7	48.3	8.9	40.1	–
	GZ	1.1	42.9	10.7	45.3	–
	NM	2.1	59.5	15.4	23.0	–
Raw coals (RC)	AH	1.7	4.3	8.7	85.3	Anthracite
	GZ	3.5	4.0	9.7	82.8	Anthracite
	NM	12.8	4.0	28.5	54.7	Bituminous
	XJ	14.1	3.3	47.2	35.4	Lignite

AH Anhui province, GZ Guizhou province, NM Inner Mongolia, XJ Xinjiang province

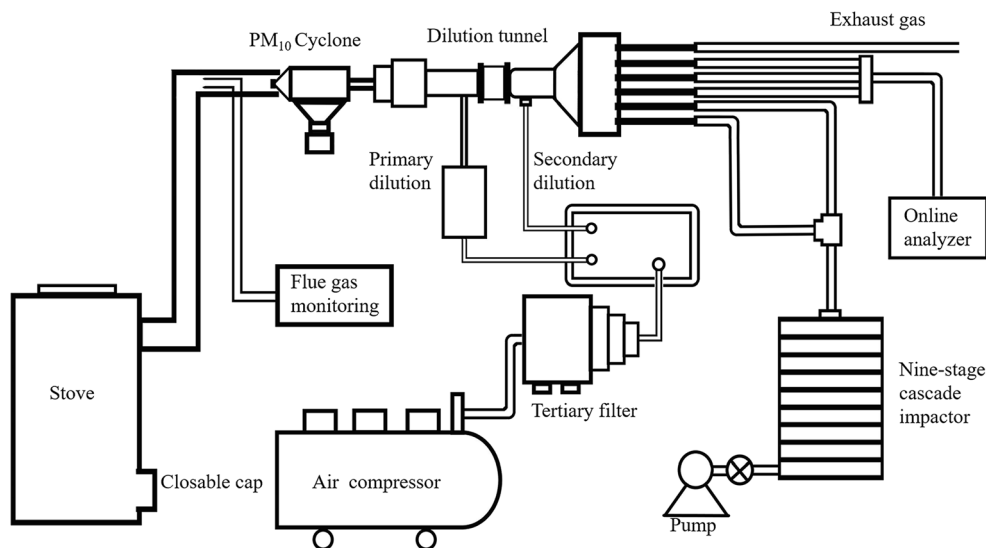
cooled for about half an hour (Yan et al. 2017; Yang et al. 2018). Due to time/equipment limitation, RC in this study was only burned in flaming mode. Each HCB burning test used three pieces of honeycomb briquettes for overlapping combustion. One briquette coal was ignited firstly by charcoal, and then another two pieces of briquettes were quickly added. The flue gases were sampled after diluted about 30 times by a dilution sampling system (Dekati FPS-4000, Finland). The particles in the flue gases were firstly selected by a PM<sub>10</sub> cyclone, which was put in a hole in the stack, about 1.5 m higher than the flame (Kong et al. 2014). Then part of the flue gas was drawn isokinetically into the dilution tunnel. Flue gases were diluted by clean air which was pre-purified with 95% of 0.01 μm particles removed by the air filter system (Kong et al. 2013). The flue gas flow for each type of coal burning was tested three times at the beginning, middle, and burning out periods and the averaged flue gas flow was adopted for calculating emission factors. An FA-3 nine-stage cascade impactor was used to collect particulate matter from the flue gas onto quartz fiber media (diameter of 80 mm), and the nine particle size segments were < 0.43, 0.43–0.65, 0.65–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.5, 5.5–9.0, and 9.0–

10.0 μm, respectively. The sum of <0.43, 0.43–0.65, and 0.65–1.1 is regarded as PM<sub>1.1</sub> (submicron particle) and the sum of <0.43, 0.43–0.65, 0.65–1.1, and 1.1–2.1 is defined as PM<sub>2.1</sub> (fine particle). The coarse particles (PM<sub>2.1–10</sub>) included 2.1–3.3, 3.3–4.7, 4.7–5.5, 5.5–9.0, and 9.0–10.0 μm. For each test, the sampling flow rate was set at 28.3 L min<sup>-1</sup>. The structure of the experiment system is shown in Fig. 1.

**PAH analysis**

The analytical procedures were shown in our former study (Kong et al. 2015) and briefly described here. Eighteen PAHs were analyzed including naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbFA), benzo(k)fluoranthene (BkFA), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), dibenz(a,h)anthracene (DBahA), benzo(e)pyrene (BeP), benzo(g,h,i)perylene (BghiP), and coronene (COR). The samples were ultrasound extracted with dichloromethane solvent. After concentration and purification, the extract was

**Fig. 1** Structure of the burning and dilution sampling system



analyzed with a trace 2000 GC-MS (Thermo Finnigan, USA). The quality assurance and quality control were implemented during the sampling experiment and PAH analysis. The samples were stored under  $-20\text{ }^{\circ}\text{C}$  and the recovery experiment was performed. The recoveries for individual PAHs ranged from 86 to 95%. Blank filters were analyzed with every 10 samples. Detection limits for the 18 kinds of PAHs were in the range of 3.0–10.0 ng.

### Emission factors and health risks of PAHs

The emission factors were calculated according to following formula:

$$EF_{ij} = \frac{v \times m_{ij} \times n}{v_1 \times M_j} \quad (1)$$

$EF_{ij}$  was the emission factor ( $\text{mg kg}^{-1}$ ) of the  $i$ -type PAHs of the  $j$ th fuel combustion;  $v$  was the flue gas flow ( $\text{L min}^{-1}$ );  $v_1$  was the sampling flow ( $\text{L min}^{-1}$ );  $m_{ij}$  was the mass of the  $i$ -type PAHs in the filter of the  $j$ th fuel combustion (mg);  $n$  was the dilution ratio;  $M_j$  was the  $j$ th fuel consumption mass (kg).

The health risks were calculated by the method in former studies (Chen et al. 2004; Geng et al. 2014; Lin et al. 2016; Yang et al. 2017).  $\Sigma\text{PAH}_7$  was the sum of EFs of seven carcinogenic PAHs, and BaP-equivalent carcinogenic power (BaPE) and 2,3,7,8-tetrachlorodibenzo-p-dioxin-based total toxicity potency (TEQ) were calculated by formulas (2) and (3), respectively.

$$\text{BaPE} = \sum EF_i \times \text{REF}_i \quad (2)$$

$$\text{TEQ} = \sum EF_i \times \text{IEF}_i \quad (3)$$

where  $EF_i$  was the emission factor of PAH, and  $\text{REF}_i$  and  $\text{IEF}_i$  were relative potency factors of BaP (Lin et al. 2016) and 2,3,7,8-tetrachlorodibenzo-dioxin induction equivalently factor (Geng et al. 2014; Yang et al. 2017), respectively.

## Results and discussion

### PAH emission factors

The PAH EFs in three particle size segments ( $\text{PM}_{1.1}$ ,  $\text{PM}_{2.1}$ , and  $\text{PM}_{10}$ ) for all experiments were summarized in Tables S1, S2, and S3, respectively. EFs of total PAHs fell in the range of 0.35–219  $\text{mg kg}^{-1}$ . The results were much lower than those EFs published in the literature (13–1434.8  $\text{mg kg}^{-1}$ ). Coal/stove properties, burning conditions, sampling/analyzing methods, and particle sizes could be the reasons for the large variation (Oanh and Dung 1999; Chen et al. 2005; Liu et al. 2009; Shen et al. 2013b). EFs for HCB smoldering combustion were 5.36  $\text{mg kg}^{-1}$  (AH), 0.35  $\text{mg kg}^{-1}$  (GZ), and 0.44  $\text{mg kg}^{-1}$  (NM), respectively, which were about 2.74,

0.22, and 0.35 times than those of flaming combustion. It seemed that flaming combustion cannot reduce the PAH emission as we expected (Liu et al. 2017). For the four types of raw coal flaming burning, the EF of coal from NM was highest at 218.96  $\text{mg kg}^{-1}$ , which was 2–3 magnitude order higher than those of lignite (2.15  $\text{mg kg}^{-1}$  for XJ) and anthracites burning (2.08  $\text{mg kg}^{-1}$  for AH and 0.50  $\text{mg kg}^{-1}$  for GZ). Raw bituminous was determined to be the dirtiest one among all fuels, and the EFs for anthracites were found to be the lowest. Similar results were also obtained in former study (Wang et al. 2016).

PAH emissions from coal combustion are highly dependent on coal properties. However, the EFs of coals from the same origin may vary greatly in different studies. For example, Geng et al. (2014) and Yang et al. (2017) measured the PAH EFs of coals from Yinchuan, Dongsheng, Datong, and Zhijin, but the PAH EFs calculated by the former were 4.75–17.58 times those of the latter. Therefore, there are still other factors affecting PAH EFs. The PAH EFs for residential coal combustion of China in the literature were summarized in Table S4. Huge variation of PAH EFs (varied from 0.014–1413.8  $\text{mg kg}^{-1}$ ) for residential coal combustion could be found (Chen et al. 2004; Liu et al. 2009; Wang et al. 2016). It suggested more studies are needed to update the EF database continuously.

Factors impacting PAH emission also involved the fuel volatile content, ash content, and coal heat values (Chen et al. 2004; Shen et al. 2010). Moderate volatile content of coal leads to high emissions of PAHs (Chen et al. 2005). The original PAHs in coals can reflect the emission characteristics of PAHs emitted after coal combustion (Chen et al. 2004). Coals with two structures including macromolecular network and mobile phase contain PAHs, and the PAHs in the mobile phase are easier to release into environment than the PAHs in macromolecular network (Wang et al. 2016). Moreover, PAH emissions can be governed by other combustion co-products, such as CO, BC, and organic carbon (OC) (Shen et al. 2010). A large amount of OC emissions from RC in NM has also been detected ( $\text{OC}_{\text{EF}}$  for RC from NM was 5647  $\text{mg kg}^{-1}$ , while it was 79.2–434.0  $\text{mg kg}^{-1}$  for other groups) (Yang et al. 2018), which may be the reason for the high PAH EFs in this study. Experiment facilities are also one of the factors determining PAH emissions. It was believed that PAH EFs for field measurement were higher than those of laboratory experiments (Shen et al. 2013b). Other parameters of the experiments like the dilution ratio and residence time of dilution sampling method can contribute to the differences in PAH emissions (Chen et al. 2004; Geng et al. 2014). The PAH EFs tests are still important as currently the main uncertainty in emission inventories is mainly attributed to the variation in EFs (Zhang et al. 2008). However, as discussed above, the emissions of household coal burning are too complex to be characterized by a single group of EFs. Therefore, before



updating PAH emission inventory, more accurate and comprehensive EFs involving different types of coals, combustion conditions, and experimental methods should be tested and compiled firstly.

### Comparison of PAH EFs

#### HCB versus RC

Coal size was believed to be one of the factors affecting pollutant emissions, and an increase of coal size from 1 to 10 cm may result in a decrease of PM by 80% for certain applications (Li et al. 2016). Huge variation of PAH EFs between coals and briquettes had been detected (Shen et al. 2013b). As a coal clean technology, HCB has twice the combustion efficiency and reduces a majority of pollution emissions compared with those of RC (Chen et al. 2015). HCB will reduce the emission of particulate matter, but the addition of oxidants, binders, and clay can result in an increase in the emissions of heavy metals (Yan et al. 2017). Therefore, HCB still needs to be evaluated for the emissions of certain pollutants. It has been found that HCB will increase the emission of PAHs (Chen et al. 2015), while these HCBs were manufactured in a laboratory by simulated briquetting and were not the local used HCBs. The comparison of PAH EFs between RC and HCB is shown in Fig. 2a. For coals from AH, the combustion of HCB yield almost the same emission of PAHs as that from RC burning, but RC burning generated 3.7 times higher PAH emission in the particles with diameter less than <math>0.43\ \mu\text{m}</math> size segment. It means that HCB of AH can reduce the PAH emissions in ultrafine particles but increase the emission of PAHs in larger size of particles. AH HCB may contain amounts of hydrophilic components, and fine particles generated from AH HCB would condensate under high moisture contents. Then emitted PAHs would condense in larger particles. For coals from GZ, the PAH emissions of each size segment from RC burning were lower than those of HCB burning. High emission may be caused by irregular hole distribution of HCB. There were 15 holes of HCB from GZ, and the others have 12 holes. The

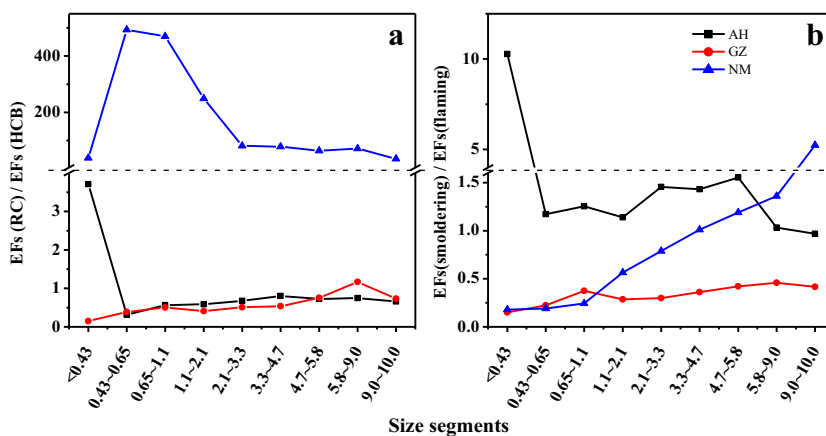
use of HCB in NM can reduce 99.4% of the PAH emissions compared to that of RC burning. In summary, the use of HCB needs to be adapted considering the real situation locally. HCB from AH cannot reduce total PAH emissions, but it can significantly reduce the ultrafine particulate-associated PAHs which have more adverse impact on human health. HCB in GZ still needs improvement to reduce its PAH emissions. NM HCB can effectively reduce PAH emissions and can be widely used instead of RC.

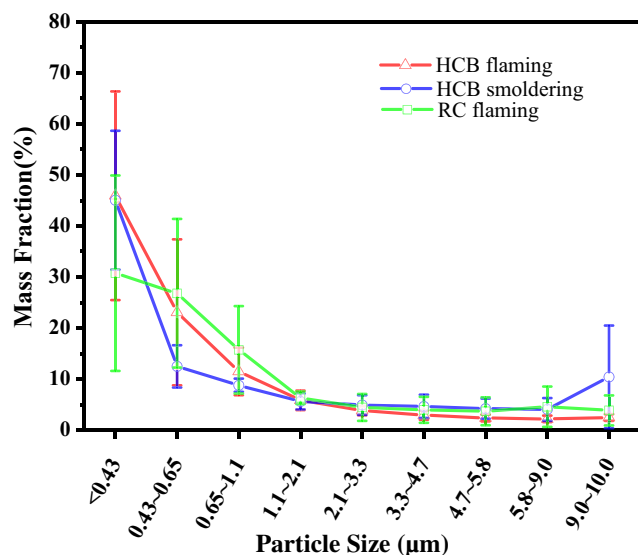
The process of grinding raw coal into powder in honeycomb coal briquette production increases the surface area of coal, and the subsequent process of pressing pulverized coal and clay additives into briquette decreases the contact area between coal and air. These processes will promote the pyrolysis of organic matter in raw coal and increase the emission of PAHs (Chen et al. 2015). In addition, other properties of briquette itself may also have an impact on PAH emission.  $\text{SiO}_2$  and bentonite clay additions were believed to have negative influence on PM emission of briquettes (Li et al. 2016). Properties of clay addition, the size of briquettes, and the diameter and the number of holes may affect the organic reactions during the combustion process. There were only preliminary studies of the factors affecting PAH emissions of honeycomb coal briquettes (Liu et al. 2009; Chen et al. 2015; Yang et al. 2017). Further research regarding the properties of HCB impacting PAH emission are still needed.

#### Smoldering versus flaming

Smoldering combustion with inadequate supply of air leads to low temperature of combustion (Liu et al. 2017), and it has been reported that the increase of temperature in the range of 200 to 700 °C leads to evident increase of PAH emission (Lu et al. 2009). Emission factors of PAHs varied widely between flaming and smoldering of HCBs, and the size distributions of PAHs for the two combustion phases were also difficult to evaluate. The comparison of PAH EFs under smoldering and flaming burning condition is shown in Fig. 2b.

**Fig. 2** Comparison of PAH EFs ( $\text{mg kg}^{-1}$ ) for different types (a) and different combustion conditions (b). HCB honeycomb coal briquette, RC raw coal

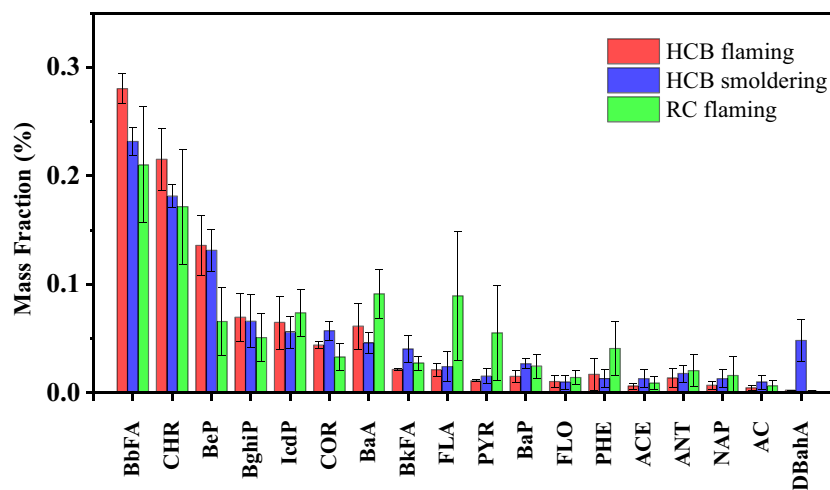




**Fig. 3** Averaged mass fraction of PAHs in different sizes of particles for residential honeycomb coal briquettes (HCBs) and raw coal (RC) burning in flaming and smoldering modes

There is a good correlation between the PAH emissions and the excess air. Excessive air supply may interfere with the heat balance in the boiler, resulting in lower boiler temperature and incomplete combustion, which causes more PAH emission (Mastral et al. 1998). In the current study, the PAH EFs under smoldering phase for AH HCB with low volatile content were 2.7 times of that for flaming phase. And smoldering combustion increased the PAH emissions (about 10.3 times) in the particles of  $<0.43 \mu\text{m}$  size segment, resulting in increased toxicity. But for HCB from GZ and NM, flaming combustion yielded 4.5 times and 2.9 times higher PAH emissions than smoldering, respectively. Smoldering combustion of NM HCB had reduced the PAH emission in fine particles and increased the emission for particles of size higher than  $3.3 \mu\text{m}$ . In theory, there is less volatile organic compound emissions during the flaming combustion process of residential coals (Liu et al. 2017), but there may be some mechanism

**Fig. 4** Composition profiles of PAHs in  $\text{PM}_{10}$  emitted from residential honeycomb coal briquettes (HCBs) and raw coal (RC) burning in flaming and smoldering modes



in the actual combustion process that is not accounted for in the theory. The high content volatiles of GZ and NM HCBs were slowly released during the smoldering process and converted into smaller molecular organics, resulting in low PAH EFs, while AH HCB with lower volatile content was less affected by this mechanism. Therefore, the effect of flaming condition on PAH emission reduction is not universal, which still needs more investigation. It is also suggested that considering the huge PAH EF variation among different combustion stages, emission inventories should be established with EFs fully demonstrating and representing the actual combustion situation.

### PAH size distribution

Measuring particle size distribution of particulate PAHs could provide valuable information for assessing the toxicity of particulate matter from residential coal combustion. PAH size distribution of residential coal combustion is shown in Fig. 3. 53.5–96.4% of PAHs emitted from coal combustion experiments were concentrated in  $\text{PM}_{2.1}$ , and 47.4–90.9% of PAHs concentrated in  $\text{PM}_{1.1}$ . Seven carcinogenic PAHs (BbFA, BkFA, BaA, CHR, IcdP, BaP, and DBahA) concentrated in  $\text{PM}_{1.1}$  accounted for 51.2–91.4% of their total emissions. PAHs generated from residential coal combustion were mostly concentrated in fine particles especially in  $\text{PM}_{1.1}$ , which means that most of PAHs can penetrate deep into the lung regions easily. Based on the char residue characteristic of coals, PAH size distribution of residential coal combustion had been shown to have the maximum fraction appearing in the  $<0.4 \mu\text{m}$  particle size segment or the maximum fraction appearing in  $0.7\text{--}2.1 \mu\text{m}$  particle size (Shen et al. 2010). A similar regular pattern has been detected in this study: the peak of PAH emissions from AH HCB flaming burning and RC from NM and XJ burning was concentrated in particles of  $0.67\text{--}2.1 \mu\text{m}$  and the PAH emission peaks of other groups including all smoldering tests were found for particles with

**Table 2** PAH isomer ratios for particles emitted from residential coal combustion

RC	Particle size (µm)	Burning condition	ANT/(ANT + PHE)	FLA/(FLA + PYR)	BaA/(BaA + CHR)	BbFA/(BbFA + BkFA)	IcdP/(IcdP + BghiP)	BaP/(BaP + BghiP)	Reference
RC	< 7.2	/	0.03	0.48	0.09	–	0.43	0.13	Chen et al. 2004
	/	Hheat	0.25–0.34	0.50–0.54	0.32–0.53	0.48–0.63	0.33–0.60	0.54–0.64	Liu et al. 2009
	/	Lheat	0.28–0.40	0.50–0.59	0.29–0.56	0.50–0.63	0.25–0.56	0.36–0.43	
	< 10	/	0.14–0.28	0.50–0.57	0.53–0.60	0.47–0.63	0.57–0.73	0.46–0.69	Shen et al. 2010
	/	LES	0.11–0.34	0.53–0.70	0.40–0.55	0.63–0.77	0.50–0.61	0.24–0.41	Wang et al. 2016
	/	HES	0.12–0.40	0.53–0.61	0.47–0.60	0.62–0.70	0.56–0.62	0.35–0.40	
	/	/	/	0.54–0.62	0.49–0.55	0.36–0.69	0.23–0.65	0.50–0.75	Yang et al. 2017
	< 10	Flaming	0.16–0.50	0.59–0.67	0.24–0.54	0.86–0.92	0.54–0.67	0.09–0.52	This study
	< 7.2	/	0.04	0.48	0.10	–	0.43	0.14	Chen et al. 2004
	< 7.2	/	0.03–0.24	0.48–0.74	0.09–0.37	–	0.23–0.47	0.13–0.48	Chen et al. 2005
HCB	/	Hheat	0.28	0.47–0.48	0.36–0.38	0.31	0.28–0.50	–	Liu et al. 2009
	/	Lheat	0.23	0.45	0.36	–	0.23	–	
	< 10	/	0.13–0.15	0.51–0.55	0.28–0.52	0.51–0.57	0.33–0.67	0.36–0.67	Shen et al. 2010
	/	/	0.14–0.26	0.36–0.49	0.17–0.38	0.81–0.95	0.14–0.32	0.24–0.43	Huang et al. 2014
	/	HES	0.04–0.33	0.57–0.72	0.39–0.47	0.77–0.87	0.43–0.61	0.14–0.55	Wang et al. 2016
	/	/	/	0.57	0.54	0.63	0.74	0.86	Yang et al. 2017
	< 10	Flaming	0.20–0.81	0.59–0.75	0.16–0.34	0.92–0.94	0.46–0.50	0.12–0.24	This study
	/	Smoldering	0.50–0.84	0.49–0.69	0.18–0.23	0.82–0.91	0.43–0.50	0.17–0.44	

RC raw coal, HCB honeycomb coal briquettes, Hheat high heat combustion, Lheat low heat combustion, LES low efficient stoves, HES high efficient stoves, / no information, – data is not available

**Table 3** Potential toxicity of PAHs emitted from residential coal combustion

		HCB flaming			HCB smoldering			RC flaming			
		AH	GZ	NM	AH	GZ	NM	AH	GZ	NM	XJ
$\Sigma$ PAHs <sub>7</sub>	PM <sub>1,1</sub>	1.01	0.87	0.75	3.11	0.15	0.14	1.11	0.19	94.5	0.99
	PM <sub>2,1</sub>	1.11	0.91	0.78	3.23	0.16	0.16	1.17	0.21	100.2	1.06
	PM <sub>10</sub>	1.28	1.05	0.86	3.48	0.22	0.28	1.29	0.32	103.4	1.30
BaPE	PM <sub>1,1</sub>	0.08	0.07	0.09	0.70	0.02	0.02	0.11	0.02	17.3	0.10
	PM <sub>2,1</sub>	0.09	0.08	0.09	0.71	0.02	0.02	0.11	0.02	18.2	0.11
	PM <sub>10</sub>	0.11	0.10	0.10	0.74	0.04	0.05	0.13	0.04	18.7	0.15
TEQ	PM <sub>1,1</sub>	3.7E-05	3.4E-05	2.2E-05	1.3E-04	4.5E-06	5.6E-06	2.8E-05	7.1E-06	2.9E-03	3.1E-05
	PM <sub>2,1</sub>	4.1E-05	3.6E-05	2.3E-05	1.3E-04	5.3E-06	6.5E-06	3.0E-05	8.4E-06	3.1E-03	3.5E-05
	PM <sub>10</sub>	4.8E-05	4.2E-05	2.7E-05	1.5E-04	8.6E-06	1.2E-05	3.7E-05	1.4E-05	3.1E-03	4.6E-05

$\Sigma$ PAHs<sub>7</sub> (mg kg<sup>-1</sup>): the sum of 7 carcinogenic PAH components (BaA, CHR, BbFA, BkFA, BaP, DBahA, IcdP) (Geng et al. 2014; Yang et al. 2017); BaPE (mg kg<sup>-1</sup>): BaP-equivalent carcinogenic power (Lin et al. 2016); TEQ (mg kg<sup>-1</sup>): the 2,3,7,8-tetrachlorodibenzo-p-dioxin-based total toxicity potency (Geng et al. 2014; Yang et al. 2017)

dynamic diameter less than 0.43  $\mu$ m. Moreover, the size distribution of PAHs was positively correlated with the particle size distribution of OC ( $p < 0.01$ ) (Yang et al. 2018). This may help to reveal the relationship between the PAH formation process and the OC content.

### PAH composition profiles

The PAH composition profiles are shown in Fig. 4. BkFA, CHR, and BeP were the most abundant species for HCB flaming/smoldering combustion and accounting for  $58.8 \pm 6.3\%$  of total PAHs. BkFA, CHR, and BaA dominated the PAH emission of RC combustion and accounting for  $47.3 \pm 7.9\%$  of the total emission. Seven carcinogenic PAHs account for more than half of PAH emissions, and the content of

carcinogenic PAHs slightly increased with particle size decreasing. Most PAHs with particulate phase emitted from residential coal combustion were high or median molecular weight PAHs (with 4–7 benzene rings). The profile of particulate PAHs in this study was similar with others in the literature (Shen et al. 2010; Yang et al. 2017). The distributions of individual PAHs emitted from briquette smoldering combustion were similar to those of briquette flaming combustion. Notably, DBahA accounted for more than 3% of PAH emission from smoldering phase of briquettes, but less than 0.3% for all other flaming groups. The extremely low vapor pressure, low-temperature combustion, and insufficient oxygen supply could be the reason of high emission of DBahA. Studies in the literature report FLA was the tracer of vehicle emission, incineration, and oil combustion in source

**Table 4** Potential toxicity risks of PAHs in particles emitted from domestic coal combustion in China

		RC		HCB	
		Average	Stand deviation	Average	Stand deviation
Particulate phase ( $n = 12^a$ )	$\Sigma$ PAH <sub>7</sub>	46.43	84.44	18.37	54.51
	BAPE	12.25	23.64	5.04	15.60
	TEQ	1.6E-03	3.1E-03	7.8E-04	2.3E-03
Gaseous phase ( $n = 33^b$ )	$\Sigma$ PAH <sub>7</sub>	0.32	0.52	0.28	0.52
	BAPE	0.40	0.38	0.24	0.33
	TEQ	1.8E-05	3.5E-05	2.1E-05	3.9E-05

The combustion conditions were not considered. The particle diameters from the literature were 2.5  $\mu$ m, 10  $\mu$ m, and TSP, respectively. By adopting the particle and PAHs mass percentage ratios of the three sizes obtained from Ge et al. (2004) and Shen et al. (2013c), the toxicity values in the table were all converted for PAHs toxicity in PM<sub>10</sub>

<sup>a</sup> Data from Liu et al. (2009); Shen et al. (2010); Wang et al. (2016); Yang et al. (2017); and this study

<sup>b</sup> Data from Chen et al. (2004, 2005); Liu et al. (2009); Shen et al. (2010); Huang et al. (2014); Wang et al. (2016); Yang et al. (2017)



apportionment (Mishra et al. 2016; Wang et al. 2019), while in this study, high FLA emission was detected in raw coal combustion. This may suggest that some source apportionment may underestimate the contribution of coal combustion emissions to atmospheric PAHs.

### PAH isomer ratios

PAH isomer ratios (molecular diagnostic ratios) are convenient and concise in source apportionment (Ravindra et al. 2008). Based on the particulate phase PAH EFs obtained in this study and previous literature, the frequently used PAH isomer ratios were calculated for residential coal combustion (Table 2). Results showed that the isomer ratios of ANT/(ANT + PHE), FLA/(FLA + PYR), BaA/(BaA + CHR), BbFA/(BbFA + BkFA), IcdP/(IcdP + BghiP), and BaP/(BaP + BghiP) were in the ranges of 0.03–0.84, 0.36–0.75, 0.09–0.60, 0.31–0.95, 0.14–0.74, and 0.09–0.86, respectively. Due to the briquetting of coal, the isomer ratios of residential coal combustion have great fluctuation. It is suggested the diagnostic ratio of BaA/(BaA + CHR) > 0.35 can indicate coal combustion (Akyüz and Çabuk 2010), and the ratios of FLA/(FLA + PYR) > 0.5 and IcdP/(IcdP + BghiP) > 0.45 can indicate coal/biomass combustion (Wang et al. 2019). These values were quite different from the ratios obtained in this study. The application of isomer ratio may bias the contribution of coal combustion to atmospheric PAHs. Wang et al. (2016) also indicated that the applications of PAH isomer ratios were suspected to be problematic. It suggested that the PAH isomer ratios should be updated and used carefully, and it is better to establish local PAH source profiles and an isomer ratio database.

### Potential toxicity risk of PAHs

PAHs have carcinogenicity, teratogenicity, and genotoxicity to human beings (Kim et al. 2013). The sum of 7 carcinogenic PAH components ( $\Sigma$ PAH<sub>7</sub>, including BaA, CHR, BbFA, BkFA, BaP, DBahA, and IcdP), BaP-equivalent carcinogenic power (BaPE), and the 2,3,7,8-tetrachlorodibenzo-p-dioxin-based total toxicity potency (TEQ) are three frequently employed parameters used to estimate the toxicity risk of PAHs to human and environment (Nisbet and LaGoy 1992; Chen et al. 2004; Geng et al. 2014; Lin et al. 2016; Yang et al. 2017).

In this study, the PAH toxicity risks for residential coal combustion are shown in Table 3. The potential toxicity risks showed a similar variation trend as the EFs. Potential toxicity risk of RC was higher than that of HCB. Except for HCB from AH, the flaming combustion of briquettes exhibited higher potential toxicity risk than smoldering burning. For particulate phase PAHs,  $73.2 \pm 15.5\%$  potential toxicity risks were associated with PM<sub>1.1</sub>, on average. This means that most of the

PAH toxicity is associated with ultrafine particles, which can endanger human health. It is suggested that for the cooking period, human protection measures, such as ventilation, should be considered to avoid the exposure to PAHs in ultrafine particles.

From the literature, the PAH toxicity risks of residential coal combustion in China are summarized in Table 4. The toxicity of RC emission was obviously higher than HCB ( $p < 0.1$ ). On account of  $91.2 \pm 16.2\%$ , toxicity was related to particle phase PAHs (Liu et al. 2009; Shen et al. 2010; Yang et al. 2017). As the coal clean technology, HCB shows a positive effect on reducing toxicity.

### Conclusion

Based on dilution sampling, 18 PAH emission factors of residential coal flaming and smoldering combustion were investigated, with totally three kinds of honeycomb coal briquettes (HCBs) and four kinds of raw coals (RCs) tested. PAH EFs of residential coal combustion ranged from 0.35 to 218.96 mg kg<sup>-1</sup>. PAH EFs were strongly affected by combustion conditions and fuel categories. About 47.4–90.9% of PAH emissions and 73.2% of toxicity of PAHs concentrated in particles with diameter less than 1.1 μm from residential coal combustion. The current source apportionment results with PAH composition profiles and isomer ratio reported in the literature may bias the estimation of coal combustion contributions, which suggests the importance of more local testing on PAH emission in different particle sizes under various burning conditions of domestic coal. Coal briquetting as a clean technology shows a positive effect on reducing the PAH emission and toxicity; however, the effect of clay additives on PAH emissions in different particle sizes from HCB burning still needs further evaluation.

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