Influence of different types of coals and stoves on the emissions of parent and oxygenated PAHs from residential coal combustion in China ☆

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ABSTRACT

To evaluate the influence of coal property and stove efficiency on the emissions of parent polycyclic aromatic hydrocarbons (pPAHs) and oxygenated PAHs (oPAHs) during the combustion, fifteen coal/stove combinations were tested in this study, including five coals of different geological maturities in briquette and chunk forms burned in two residential stoves. The emission factors (EFs) of pPAHs and oPAHs were in the range of 0.129—16.7 mg/kg and 0.059—0.882 mg/kg, respectively. The geological maturity of coal significantly affected the emissions of pPAHs and oPAHs with the lower maturity coals yielding the higher emissions. The chunk-to-briquette transformation of coal dramatically increased the emissions of pPAHs and oPAHs during the combustion of anthracite, whereas this transformation only elevated the emissions of high molecular weight PAHs for bituminous coals. The influence of stove type on the emissions of pPAHs and oPAHs was also geological-maturity-dependent. High efficiency stove significantly reduced the emissions of PAHs from those relatively high-maturity coals, but its influences on low-maturity coals were inconstant.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of the toxic organic pollutants of heightened concern all over the world. The derivatives of parent PAHs (pPAHs), such as nitrated PAHs (nPAHs) and oxygenated PAHs (oPAHs), are also persistent and mobile in environment and tend to be equally or even more toxic or mutagenic than pPAHs (Albinet et al., 2008; Wang et al., 2011; Shen et al., 2012). nPAHs and oPAHs are mainly formed from primary fuel combustion and/or through the reactions of pPAHs with atmospheric oxidants (Wang et al., 2011).

Coal combustion is considered as one of the most important sources of pPAHs, nPAHs, and oPAHs in the developing countries (Shen et al., 2012), such as in China. Although, the Chinese government is trying to change the energy consumption patterns, coal combustion was still the primary energy consumption accounting for ~66% of the total consumption in 2013 based on the China Statistical Yearbook of 2014. Coal combustion is also an important source of indoor pollutants for their widely usage for cooking and heating in the residence. Domestic coal combustion produced approximately 19.6% of the total PAH emissions in China (Xu et al., 2006), and contributed significantly to severe indoor air pollution and exposure risk in China as well (Zhang and Smith, 2007; Zhang

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et al., 2009; Shen et al., 2012).

To estimate the emissions of PAHs and their derivatives, the emission factors (EFs) are needed. EF is the mass of emitted pollutant per unit energy consumed. It varies with the fuel properties (type, rank, size, shape, and moisture), combustion facilities (residential or industrial stoves), burning conditions (combustion temperature or efficiency), and experimental methods (laboratory or field measurements) (Jenkins et al., 1996; McDonald et al., 2000; Johansson et al., 2004; Shen et al., 2011b). Chen et al. (Chen et al., 2005) studied the impact of geological maturity to the emission factors (EFs) of PAHs from coal combustion and found that the combustion of bituminous coal with vitrinite reflectance (R_O, a measure of the geological maturity of coal) around 0.9% produced the highest EFs of particulate matter, elemental carbon, organic carbon, and PAHs. Shen et al. (Shen et al., 2013a) studied the influence of volatile matter (VM) content on the emissions of PAHs and found that medium volatile bituminous coal emitted relatively large quantities of PAHs in comparison with low and high volatile bituminous coals. Meanwhile, the studies of Simoneit (Simoneit, 2002) and Shen et al. (Shen et al., 2013a) suggested that the fast burning of low moisture biomass fuel forms an oxygen deficient atmosphere yielding high pollutant emissions, whereas the burning of high moisture fuel requires extra energy to vaporize water reducing combustion temperature and efficiency, and hence increased emissions of incomplete combustion products, such as PAHs and their derivatives. However, the mechanism of the effects of coal properties on the production and emission of PAHs are still not well understood. Moreover, few studies (Zhang and Smith, 1999; Shen et al., 2013b) have drawn specific attention to the influence of different types of domestic stove on the emissions of PAHs and their derivatives. Their results showed that the emissions of contaminants were dependent not only on the fuel type but also on the stove type and the improved stove caused more emissions than the traditional stove. Studies (Liu et al., 2009; Shen et al., 2011a, 2013abib_Shen_et_al_2013a) on the emission of pPAHs and their derivatives from the residential combustion of coals with different shapes, such as honeycomb briquettes and raw chunk coals, are also limited.

The purpose of this research is (i) to determine the EFs of pPAHs and oPAHs from different types of residential coal combustion, (ii) to investigate the possible reasons for the influence of coal properties, forms, and stove types on the emissions of PAHs and their derivatives. For the lack of data, the result will lead to a better understanding of PAH emissions from the residential sources in China.

2. Materials and methods

2.1. Coals and stoves

Five different types of coals from five locations, including Yulin (YL) in Shaanxi province, Cixian (CX) in Hebei province, Zhongyang (ZY) in Shanxi province, Changzhi (CZ) in Shanxi province, and Anyang (AY) in Henan province, were tested in two forms (honeycomb briquette and raw chunk coal) in this study. Each coal sample included three subsamples collected from the same batch of coal. The three subsamples were homogenized before test. Their volatile matter content (V_{daf}), ranks, and other characteristics are summarized in Table S1 in the Supporting Information (SI). Briefly, these coals cover a wide range of geological maturity and can be classified into one high-volatile bituminous coal (HVB), two medium-volatile bituminous coals (MVB), one low volatile bituminous coal (LVB), and one semi-anthracite coal (SA). The sizes of various coal chunks were similar (3–5 cm in diameter). Honeycomb briquettes for each coal were manufactured by a machine after intermixing coal powders (powdered from corresponding raw coal chunk) with clean clay (coal: clay = 2: 1 for bituminous coal and 1:1 for anthracite), and the briquettes were 16-hole (1.5 cm diameter each) columns with a height of 8 cm, a diameter of 12.5 cm, and a weight of ~300 g. The manufacturing process and the proportion of clay were identical to those of honeycomb briquettes sold on market.

Two commonly used household coal-stoves in China were selected, including a low-efficiency stove (LES) and a high-efficiency stove (HES). LES stove can only use raw coal chunk, whereas HES stove can use both honeycomb briquette and raw coal chunk. For comparison of burning efficiency of two stoves and two forms of coals, small raw coal chunks (3–5 cm in diameter) for the five coals were burned separately in the LES and HES stoves, while briquettes for the five coals were burned in the HES stove. Totally, fifteen coal/stove combinations were tested in this study. A duplicate sample was run randomly for every five coal/stove combinations to check the repeatability of this study. The relative standard deviations for these duplicate samples were <5%, which suggested that the data were reliable.

2.2. Sampling and analysis

The dilution sampling system and the emission sampling procedure has been described in detail elsewhere (Chen et al., 2005, 2015bib_Chen_et_al_2015). Briefly, the sampling system included four parts (Fig. S1, SI): a hood for gathering emissions from stoves, a long curved pipe for cooling flue gas to ambient temperature, an end pump for drawing flue gas through the sampling system at a flow rate of ~12 m³/min, and a branched pipe upstream the end pump for ducting part of exhaust to the high-volume particle sampler (quartzfiber filter, i.e. QFF, Whatman) at a flow rate of ~65 L/min with a split ratio of ~0.005.

Before sampling, a few anthracite coals were burned to heat the inner chamber of the stove to a high temperature, and then used to ignite the experimental coal chunks or briquettes from the bottom. The sampling procedure started when briquettes or chunks were added into the stove and ignited by preburned charcoals, and ended when the coals burned out under natural conditions without any disturbance, which ensured that the entire combustion process was sampled. The flow rate was calibrated and the system was cleaned before each combustion experiment. The disturbance of background (accounting for 1–4% of coal emission) can be neglected due to the significantly high emission compared with background pollution level.

The QFF sample was spiked with the deuterium-labeled surrogate standard, consisting of naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12, and then Soxhlet extracted with dichloromethane (DCM) for 24 h. After solvent exchange with hexane and concentration to ~0.5 mL using a rotary evaporator, each extract was cleaned by passing through a silica gel-alumina column containing baked anhydrous sodium sulfate (1 cm), neutral silica gel (3 cm, 3% deactivated), and neutral alumina (3 cm, 3% deactivated) from the top to the bottom using an eluent of 20 mL hexane/DCM (1:1, v/v). The 5 raw coal samples were also Soxhlet extracted and purified as shown above. These extracts were concentrated to approximately 0.5 mL using a gentle stream of N_2 prior to the instrumental analysis.

All samples were analyzed using an Agilent 7890GC-5975MS supplied with a DB5-MS column (30 m × 0.25 mm × 0.25 μm). The mass spectrometer was operated in electron impact ion (EI) mode for pPAHs, and electron capture negative ion (ECNI) mode for oPAHs. Sixteen pPAHs and six oPAHs were analyzed in this study. More details are provided in the SI and our previous study (Chen et al., 2015).

The EFs of PAHs and their derivatives are calculated as follows:

$$EF = \frac{m_{PAHs}}{M \times R} \qquad (1)$$

where m_{PAHs} means the weight (mg) of individual PAH congener emitted from coal combustion; R means the split ratio; M means the weight (kg) of consumed coal. For the calculation of EFs of honeycomb briquette, the weight of clay in the briquette was excluded.

2.3. QA/QC

All QFF filters were baked at 450 °C for 4 h and equilibrated in a desiccator. Procedural blanks were run along with the sample extracts to assess potential contamination during the analysis. No target compound was detected in the blanks, except for Nap, Flu, and Phe. The average recoveries of the surrogate Nap-D$_8$, Ace-D$_{10}$, Phe-D$_{10}$, Chr-D$_{12}$, and perylene-D$_{12}$ in QFF samples were 74.5 ± 5.9%, 80.8 ± 4.8%, 89.1 ± 5.1%, 89.9 ± 4.0%, and 81.5 ± 7.3%, respectively. The results reported in the study were corrected for the blanks but not corrected for the surrogate recoveries.

3. Results and discussion

3.1. EFs of pPAHs and oPAHs

The measured EFs for individual pPAHs and oPAHs from both the raw coal chunk and the honeycomb briquette combustion of five different coals in two types of stoves are presented in Table 1. The results showed that EFs varied widely among different coals and stoves. EFs of total pPAHs were in the range of 0.129–16.7 mg/kg with an average of 3.36 ± 3.99 mg/kg. EFs of total 7 carcinogenic PAHs ranged from 0.051 to 8.47 mg/kg with an average of 1.20 ± 2.06 mg/kg. The highest emission of pPAHs was the combustion of honeycomb briquette from YL (HVB) using the HES stove, while the lowest emission of pPAHs was the combustion of raw coal chunk from AY (SA) using the HES stove. The EFs of pPAHs in this study were approximately an order of magnitude lower than those measured by Chen et al. (Chen et al., 2005) and Huang et al. (Huang et al., 2014). The relatively low EFs of pPAHs in our study compared with other studies may due to the different types of coals.

Fuel combustion is considered as the primary emission of oPAHs (Walgraeve et al., 2010). EFs of total 6 oPAHs were in the range of 0.059–0.882 mg/kg with an average of 0.462 ± 0.266 mg/kg. The lowest emission of oPAHs was also the combustion of raw coal chunk from AY (SA) using the HES stove, while the highest emission of oPAHs was the combustion of raw coal chunk from YL (HVB) using the HES stove. The EFs of total oPAHs were about an order of magnitude lower than those of pPAHs. The relatively high EFs of ΣoPAHs were because of the radical chain reactions between PAHs and O· or OH· during the combustion process (Huang et al., 2014). The EFs of oPAHs from coal combustion in this study were lower than the results of Huang et al. (Huang et al., 2014), but they were comparable with the results of Shen et al. (Shen et al., 2011a). Phe, Fla, Pyr, Chr, and BbF were the most dominant congeners of pPAHs, while 9FlO and 6H-BcdPO were the most dominant oPAH congeners (Fig. 1).

3.2. Factors affecting EFs of pPAHs and oPAHs

The factors, which can affect the coal combustion, can also influence the emissions of pPAHs and oPAHs, including different coal properties, coal shapes, stove types, and air supply (Shen et al., 2013a).

3.2.1. Coal properties

Coal structure can be simplified as two components, including a macromolecular network (insoluble) and a "mobile" phase (soluble), which both contain pPAHs (Haenel, 1992; Laumann et al., 2011). The pPAHs in the "mobile" phase are of particular concern because they are easier to be released into the environment than those interlinked with the macromolecular network (Haenel, 1992; Laumann et al., 2011) during the transportation, storage, and consumption. The emission of pPAHs from the coal combustion includes both the pPAHs released from the coal itself and the pPAHs formed during the combustion process. The extracted pPAHs ("mobile" phase) from the raw coals also varied widely (Table 1), because the PAH concentration and composition within coal itself normally depends on the biogenic precursor material, geological settings, coal rank, and coal's origin (Stout and Emsbo-Mattingly, 2008; Achten and Hofmann, 2009; Wang et al., 2010; Laumann et al., 2011). The extracted concentrations of low molecular weight (LMW) PAH congeners (2–3 rings) from raw coal first increased and then decreased with the coal geological maturities, whereas the extracted high molecular weight (HMW) PAHs decreased with the geological maturities all the time (Table 1). The result of Zhao et al. (Zhao et al., 2000) also suggested that the extracted LMW PAHs (2–4 rings) of eight bituminous coals first increased and then decreased with coal carbon content. Variations of the concentrations and compositions of PAHs in the extractable fraction ("mobile" phase) is a consequence of reactions during the coalification, such as condensation, aromatization, demethylation, and dehydroxylation. Those reactions can cause a decrease of the concentrations of extractable PAHs and an increase in the concentration of low molecular weight (2–3 ring) PAHs in the coals (Stout and Emsbo-Mattingly, 2008). Compared with the emission factor of total pPAHs from coal combustion, the extraction rates from raw coals were 4–49 times higher, which implied that the emissions from coal combustion had less toxicity than the raw coal extracts. However, most PAHs within raw coal were consumed during the combustion, while only a few PAHs were volatilized into emission flue (Chen et al., 2004).

Besides the pPAHs within the coal, the emission of PAHs during the combustion can also be affected by coal properties. Previous studies (Chen et al., 2009; Huang et al., 2014) showed that the geological maturity of coals can significantly influence the EFs of organic carbon or PAHs. The emissions of ΣpPAHs from the bituminous coals (YL, CX, ZY, and CZ) in this study were 3–25 times higher than those from the anthracite (AY), while the emissions of ΣoPAHs from the bituminous coals were 2–15 times higher than those from the anthracite. The EFs of ΣpPAHs and ΣoPAHs decreased noticeably with the increasing geological maturity. It was suggested that coal with the vitrinite reflectance around 0.9% yields the most particulate matter and PAHs (Chen et al., 2005). However, significant negative correlations were only found between the vitrinite reflectance of coals and the EFs of ΣpPAHs ($p = 0.02$) or ΣoPAHs ($p = 0.005$) from the raw coal chunk combustion using the HES stove in this study. This suggested that the emission of PAHs from coal combustion may be controlled by many factors besides the vitrinite reflectance of coal. The compositions of pPAHs and oPAHs also varied significantly with geological maturity (Fig. 1). Generally, the combustion of relatively high volatile coals (YL, CX, and ZY with a volatile matter >20%) yielded higher percentage of LMW PAHs (2–3 rings) than that of low volatile coals (CZ and AY with a volatile matter <20%), because the combustion of low volatile coals can lead to a high-temperature pyrolysis processes and emit higher HMW PAHs (Mostert et al., 2010).

Moisture was also suggested to be an important factor that influences the EFs of coals (Fitzpatrick et al., 2007; Shen et al., 2012), since an appreciable amount of energy is consumed to vaporize the

Table 1
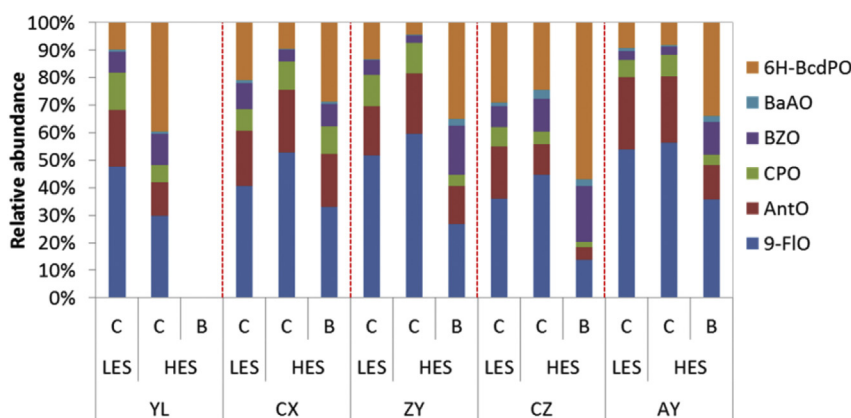EFs of pPAHs and oPAHs from different residential coal combustion.

EF	Raw coal chunk										Honeycomb coal briquette					Raw coal				
	LES					HES					HES					No combustion				
mg/kg	YL	CX	ZY	CZ	AY	YL	CX	ZY	CZ	AY	YL	CX	ZY	CZ	AY	YL	CX	ZY	CZ	AY
pPAHs																				
Nap	0.113	0.084	0.484	0.047	0.015	0.097	0.167	0.207	0.036	0.005	0.109	0.197	0.101	0.028	0.025	1.61	2.21	8.39	4.55	1.27
Acy	0.069	0.073	0.132	0.028	0.012	0.074	0.091	0.156	0.020	0.006	0.076	0.059	0.074	0.020	0.018	0.30	1.09	0.50	0.13	0.05
Ace	0.060	0.054	0.114	0.021	0.008	0.042	0.072	0.072	0.015	0.004	0.059	0.053	0.058	0.016	0.013	0.46	1.11	1.84	0.21	0.13
Flu	0.151	0.129	0.343	0.054	0.022	0.160	0.294	0.247	0.037	0.012	0.167	0.162	0.187	0.043	0.039	1.00	3.44	4.95	3.46	0.25
Phe	1.10	0.172	1.44	0.067	0.019	0.739	0.762	0.669	0.077	0.009	0.551	1.61	0.851	0.076	0.037	9.68	10.5	15.4	10.3	1.18
Ant	0.161	0.067	0.171	0.028	0.010	0.097	0.106	0.121	0.021	0.006	0.158	0.063	0.088	0.025	0.018	2.64	0.12	0.85	0.59	0.06
Fla	0.650	0.611	0.816	0.346	0.038	0.484	0.401	0.384	0.163	0.018	3.60	0.836	0.621	0.204	0.067	14.2	0.74	0.79	0.55	0.09
Pyr	0.569	0.503	0.608	0.146	0.030	0.347	0.260	0.319	0.143	0.012	2.71	0.341	0.241	0.141	0.048	8.65	1.48	1.40	0.84	0.14
BaA	0.073	0.183	0.121	0.065	0.011	0.118	0.087	0.063	0.030	0.007	1.73	0.125	0.237	0.227	0.049	6.78	0.64	0.55	0.29	0.22
Chr	0.065	0.218	0.104	0.097	0.009	0.131	0.061	0.042	0.032	0.005	1.96	0.150	0.295	0.348	0.071	6.54	2.82	3.45	3.35	0.45
BbF	0.098	0.295	0.210	0.168	0.015	0.196	0.117	0.080	0.052	0.010	2.08	0.297	0.397	0.581	0.170	8.20	2.73	2.67	2.16	1.28
BkF	0.057	0.100	0.110	0.051	0.009	0.092	0.069	0.049	0.022	0.006	0.585	0.089	0.108	0.085	0.033	1.53	0.17	0.13	0.21	0.07
BaP	0.044	0.102	0.085	0.024	0.006	0.059	0.053	0.040	0.018	0.004	0.979	0.046	0.061	0.029	0.013	2.72	0.54	0.44	0.28	0.07
IcdP	0.104	0.168	0.177	0.089	0.017	0.150	0.129	0.100	0.039	0.011	0.975	0.145	0.178	0.136	0.035	1.70	0.41	0.36	0.37	0.26
DahA	0.087	0.112	0.138	0.054	0.013	0.079	0.106	0.083	0.030	0.009	0.159	0.071	0.101	0.031	0.022	0.48	0.49	0.43	0.44	0.15
BghiP	0.066	0.166	0.123	0.074	0.011	0.109	0.083	0.061	0.031	0.007	0.815	0.113	0.148	0.184	0.022	1.67	2.12	1.38	1.57	0.64
oPAHs																				
9-FlO	0.159	0.212	0.394	0.123	0.054	0.263	0.315	0.237	0.091	0.033	/	0.257	0.203	0.068	0.088	/	/	/	/	/
AntO	0.069	0.104	0.136	0.065	0.026	0.106	0.136	0.087	0.022	0.014	/	0.149	0.103	0.023	0.031	/	/	/	/	/
CPO	0.045	0.040	0.088	0.023	0.006	0.057	0.061	0.045	0.010	0.005	/	0.079	0.033	0.010	0.009	/	/	/	/	/
BZO	0.026	0.051	0.041	0.026	0.003	0.101	0.026	0.010	0.024	0.002	/	0.063	0.135	0.100	0.029	/	/	/	/	/
BaAO	0.002	0.005	0.003	0.004	0.001	0.006	0.002	0.001	0.007	0.000	/	0.008	0.018	0.012	0.005	/	/	/	/	/
6H-BcdPO	0.033	0.109	0.101	0.099	0.009	0.350	0.056	0.018	0.049	0.005	/	0.224	0.265	0.284	0.083	/	/	/	/	/
ΣpPAHs	3.46	3.04	5.18	1.36	0.245	2.98	2.86	2.69	0.765	0.129	16.7	4.36	3.75	2.17	0.681	68.1	30.6	43.5	29.2	6.30
ΣoPAHs	0.334	0.521	0.763	0.341	0.100	0.882	0.596	0.397	0.202	0.059	/	0.779	0.756	0.498	0.246	/	/	/	/	/
ΣPAHs$_{car}$[a]	0.529	1.179	0.946	0.548	0.079	0.825	0.622	0.457	0.222	0.051	8.47	0.922	1.38	1.44	0.393	28.0	7.80	8.03	7.09	2.49
LMW%	47.6	19.0	51.9	18.0	35.1	40.7	52.2	54.7	26.9	32.3	6.7	49.2	36.3	9.6	22.1	23.0	60.3	73.3	65.6	46.5
HMW%	52.4	81.0	48.1	82.0	64.9	59.3	47.8	45.3	73.1	67.7	93.3	50.8	63.7	90.4	77.9	77.0	39.7	26.7	34.4	53.5

/ Means not available.

[a] Sum of 7 carcinogenic PAHs: BaA, Chr, BbF, BkF, BaP, IcdP, DahA, BghiP.
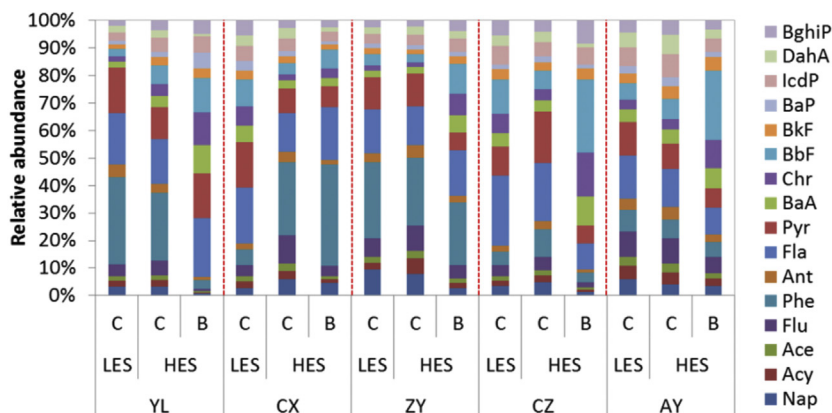
a Profiles of pPAHs

b Profiles of oPAHs

Fig. 1. Profiles of pPAHs and oPAHs originate from different coal combustion. (C means raw coal chunk; B means honeycomb briquette. Profile of oPAHs from YL briquette combustion was not available.)

water in the coals, which can reduce the combustion temperature and enhance the pollutant emissions (Simoneit, 2002). However, significantly positive correlation ($p < 0.05$) was only observed between EFs of pPAHs and moisture of briquette burned in HES stove. As we mentioned above, many factors, including moisture, can influence the PAH emissions from coal combustion. Thus, the correlations for different coals were inconsistent.

3.2.2. Coal shapes

Raw coal chunk and honeycomb briquette are two commonly used coal forms. The use of honeycomb briquettes has been sponsored by the Chinese government as a cleaner and more efficient source for heating (Liu et al., 2009). However, our results suggested that the emissions of ΣpPAHs and ΣoPAHs from honeycomb briquette combustion were generally 1.3–5.6 times higher than those from the corresponding raw coal chunk combustion (Table 2). Moreover, the influence of coal shape on the emission of PAHs varied with the individual PAH congener and the geological maturity (Fig. 1 and Table 2). For the anthracite (AY), the burning of briquettes yielded higher emissions of every pPAH and oPAH congeners (2–18 times) than the burning of raw coal chunks, especially for the HMW PAHs (≥4 rings, such as BaA, Chr, BbF, BkF, BZO, BaAO, and 6H-BcdPO). For the bituminous coals, the emissions of HMW PAHs from briquette combustion were generally higher than these

from raw coal chunk combustion, whereas the emissions of LMW PAHs (such as Nap, Acy, Ace, Flu, 9-FlO, and AntO) from briquette and chunk coals were comparable. The results suggested that the transformation of raw coal chunks into briquettes can increase the emission of PAHs, especially for the HMW congeners, during the combustion process. On the contrary, previous studies suggested that the emissions of pPAHs or oPAHs from chunk coals were higher than those from honeycomb briquettes (Shen et al., 2010, 2011abib_Shen_et_al_2011a). However, the honeycomb briquettes in their studies were not transformed directly from the same chunk coals. We suggested that the higher emissions of PAHs (both parent and oxygenated) from briquettes may be primarily attributed to clay in the briquettes, which can lead to less-severe or incomplete combustion compared to the chunk coals. During briquette combustion, the binding effect of clay may increases the transfer of pPAHs and oPAHs, and consequently generated higher emissions. Mastral et al. (Mastral et al., 1996) discovered that the PAH emissions primarily depended on the pyrolysis process instead of combustion efficiency. Although briquetting can improve coal combustion efficiency and decrease the carbon emission (Zhi et al., 2008, 2009bib_Zhi_et_al_2009), it can increase the emissions of PAHs, especially for the carcinogenic PAHs. This suggested that combustion efficiency was not the main factor influence PAH emissions from coal briquettes, and the influence of briquetting on

Table 2
Comparison of emissions of pPAHs and oPAHs from different combustion styles.

	LES/HES					Briquette/Chunk				
	YL	CX	ZY	CZ	AY	YL	CX	ZY	CZ	AY
pPAHs										
Nap	1.2	0.5	2.3	1.3	2.7	1.1	1.2	0.5	0.8	4.6
Acy	0.9	0.8	0.8	1.4	2.2	1.0	0.6	0.5	1.0	3.3
Ace	1.4	0.7	1.6	1.4	2.0	1.4	0.7	0.8	1.1	3.2
Flu	0.9	0.4	1.4	1.5	1.9	1.0	0.6	0.8	1.2	3.3
Phe	1.5	0.2	2.2	0.9	2.1	0.7	2.1	1.3	1.0	4.2
Ant	1.7	0.6	1.4	1.3	1.7	1.6	0.6	0.7	1.2	3.0
Fla	1.3	1.5	2.1	2.1	2.2	7.4	2.1	1.6	1.3	3.8
Pyr	1.6	1.9	1.9	1.0	2.5	7.8	1.3	0.8	1.0	3.9
BaA	0.6	2.1	1.9	2.2	1.7	15	1.4	3.7	7.6	7.5
Chr	0.5	3.6	2.5	3.0	1.8	15	2.4	7.1	11	15
BbF	0.5	2.5	2.6	3.3	1.6	11	2.5	4.9	11	18
BkF	0.6	1.4	2.2	2.3	1.5	6.3	1.3	2.2	3.8	5.8
BaP	0.7	1.9	2.2	1.4	1.5	17	0.9	1.5	1.6	2.9
IcdP	0.7	1.3	1.8	2.3	1.5	6.5	1.1	1.8	3.5	3.2
DahA	1.1	1.1	1.7	1.8	1.5	2.0	0.7	1.2	1.0	2.4
BghiP	0.6	2.0	2.0	2.4	1.6	7.5	1.4	2.4	6.0	3.2
ΣpPAHs	1.2	1.1	1.9	1.8	1.9	5.6	1.5	1.4	2.8	5.3
ΣPAHscar[a]	0.6	1.9	2.1	2.5	1.6	10.3	1.5	3.0	6.5	7.7
oPAHs										
9-FlO	0.6	0.7	1.7	1.4	1.6	/	0.8	0.9	0.8	2.6
AntO	0.6	0.8	1.6	2.9	1.9	/	1.1	1.2	1.0	2.2
CPO	0.8	0.7	2.0	2.5	1.4	/	1.3	0.7	1.0	2.0
BZO	0.3	2.0	4.0	1.1	1.9	/	2.5	13	4.2	16
BaAO	0.4	2.4	3.6	0.6	2.9	/	3.9	22	1.8	15
6H-BcdPO	0.1	1.9	5.7	2.0	1.9	/	4.0	15	5.8	18
ΣoPAHs	0.4	0.9	1.9	1.7	1.7	/	1.3	1.9	2.5	4.2

/ Means not available.
[a] Sum of 7 carcinogenic PAHs: BaA, Chr, BbF, BkF, BaP, IcdP, DahA, BghiP.

the combustion emissions depends on many factors including the mixing ratio between coal and clay and the size of the coal particles (Bond et al., 2002). Moreover, coal briquetting can facilitate the pyrolytic process and lead to the increased PAH emissions, especially for these PAH formed from precursors via complex processes (Chen et al., 2015).

3.2.3. Stove efficiency

Different stoves can provide different amount of oxygen supply resulting in varied coal combustion efficiencies. Generally, the low-efficiency stove (LES) yielded the higher emissions (~1.5 times) of ΣpPAHs and ΣoPAHs than the high-efficiency stove (HES). However, the influence of stove efficiency (or styles) on emissions of pPAHs and oPAHs also varied widely with the individual congener and the geological maturity (Table 2 and Fig. 1).

For the coal with high vitrinite reflectance (R_O >1.0%, ZY, CZ, and AY), the use of high-efficiency stove can significantly reduce approximately half of the PAH emissions compared to the low-efficiency stove (Table 2). For the coal with with R_O around 1.0%, the use of high-efficiency stove can only reduce the emissions of HMW PAHs, such as Fla, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP, BghiP, BZO, BaAO, and 6H-BcdPO, but increase the emissions of LMW PAHs (Nap, Flu, and Phe). On the contrary, for the coal with relatively low R_O (<1.0%, YL), the use of high-efficiency stove can increase (rather than decrease) the emission of HMW pPAHs and oPAHs. Although, the design of high-efficiency stove can improve the heating efficiency and reduce the black carbon and organic carbon emissions, their influence on the emissions of PAHs and their derivatives is still uncertain. Previous studies (Zhi et al., 2008, 2009bib_Zhi_et_al_2009) have suggested that some improved stoves may even yield more emissions than the traditional stove, because those improved stoves may only pursue higher heat transfer efficiency instead of combustion efficiency. The influence of stove efficiency on the emissions of PAHs from coal combustion

are rather complicated, thus further study is needed for a better understanding.

3.3. Isomer ratios of pPAHs

PAH isomer ratios are often used as diagnostic signatures for source apportionment (Yunker et al., 2002). The average values of these commonly used isomer ratios, including Ant/(Ant + Phe), Fla/(Fla + Pyr), BaA/(BaA + Chr), and IcdP/(IcdP + BghiP) in this study were 0.21 ± 0.11, 0.60 ± 0.06, 0.49 ± 0.07, and 0.57 ± 0.05, respectively (Fig. 2). Compared with previous studies (Yunker et al., 2002; Zuo et al., 2007), the values of these ratios fell in the range for the coal combustion or pyrogenic sources, except for the Ant/(Ant + Phe) ratios obtained from the combustion of CX and ZY briquettes and the IcdP/(IcdP + BghiP) ratio from the combustion of CZ briquettes. These exceptions implied that the clay mixed in the briquette may change pyrolysis process, to some extent, and subsequently lead to a different composition of PAH emissions. This may also support the previous viewpoint that the applications of PAH isomer ratios were sometimes suspected (Zhang et al., 2005; Katsoyiannis et al., 2011; Wang et al., 2015). Therefore, the isomer ratios should be treated carefully in identifying and evaluating PAH sources.

3.4. oPAHs/pPAHs ratios

Significant positive correlations ($p \leq 0.006$) were found between the individual oPAH congeners and their corresponding parent PAH congeners (Fig. S2, SI), suggested that the oPAHs were oxygenated from their pPAHs during the coal combustion (Walgraeve et al., 2010). The calculated ratios of 9-FlO/Flu, AntO/Ant, and BaAO/BaA from different combustion styles were shown in Fig. 3. These ratios differed with different coal/stove combinations. Generally, the CZ (LVB) and AY (SA) coal presented the relatively higher productivities of oPAHs than the other coals, which may attribute to the relatively high quality of the coals can result in high combustion temperatures and subsequently favorite the oPAH formation (Fitzpatrick et al., 2007). The oPAHs/pPAHs ratios in this studies were slightly higher than these of Shen et al. (Shen et al., 2012) and Huang et al. (Huang et al., 2014), which may be due to the relatively high temperature during the combustion in this study.
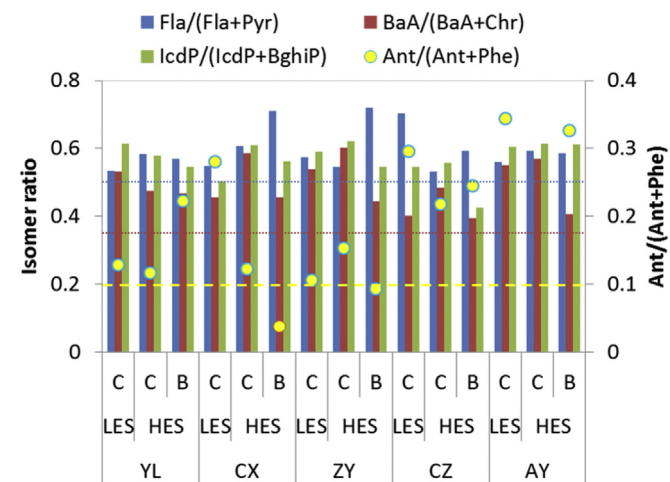

Fig. 2. The isomer ratios of pPAHs. (The ratios of Ant/(Ant + Phe) use the secondary Y-axis. C means raw coal chunk; B means honeycomb briquette.)
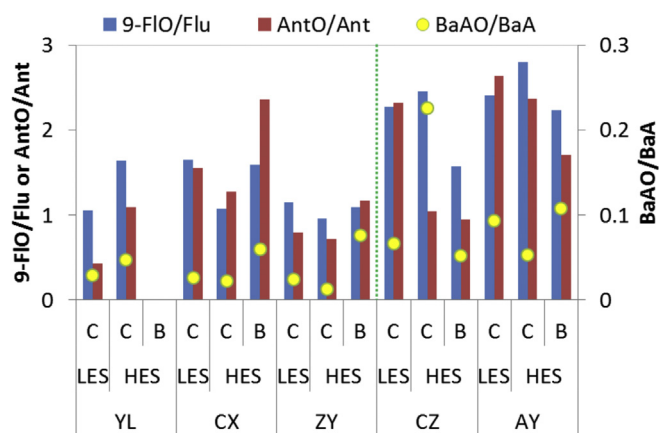
Fig. 3. The ratio of oPAHs/pPAHs. (The ratios of BaAO/BaA use the secondary Y-axis. C means raw coal chunk; B means honeycomb briquette.)

4. Conclusions

This study investigated the effects of coal property, coal shape, and stove efficiency on the productivities and emissions of parent and oxygenated PAHs. Results suggested that the geological maturity of coal is the most important factor that affects EFs of pPAHs and oPAHs from residential coal combustion, followed by coal shape (briquetting or chunk) and stove efficiency. The influences of coal briquetting and stove type on the emissions of PAHs were geological maturity-dependent. The transformation of coal chunk to briquette can significantly elevate the emissions of pPAHs and oPAHs for anthracite, whereas the transformation can increase the emissions of HMW PAHs for bituminous coals. The high efficiency stove can reduce the emissions of PAHs from the relatively high-maturity coals, but for low-maturity coals, the effects were uncertain. The improved stoves may even release more pollutants than traditional ones for the low-maturity coals, even though they have high combustion efficiencies. Given the severe air pollution situation in China, this finding may challenge the recommendation of replacing raw coal chunks with coal briquettes. However, considering the difference between the laboratory measurements and in situ emissions, the findings in the study should be treated carefully. For the uncertainties of the effects of briquetting and stove improvement on the different coal combustion, further detailed investigations are required.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.01.041.

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