

Emission of PAHs, NPAHs and OPAHs from residential honeycomb coal briquette combustion

Wei Huang,^{†,‡} Bo Huang,^{†,‡} Xinhui Bi,^{*,†} Qin hao Lin,^{†,‡} Ming Liu,^{†,‡} Zhaofang Ren,^{†,‡} Guohua Zhang,^{†,‡} Xinming Wang,[†] Guoying Sheng,[†] and Jiamo Fu[†]

[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, People's Republic of China

[‡]Graduate University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

S Supporting Information

ABSTRACT: Coal combustion is one of the most significant sources of air pollution in China. In this study, emission factors (EFs) of 15 polycyclic aromatic hydrocarbons (PAHs), 26 nitrated PAHs (NPAHs) and 6 oxygenated PAHs (OPAHs) were determined in five different coals with different geological maturity (vitrinite reflectance $R_O = 0.77\text{--}1.88\%$) burned in the form of honeycomb briquettes. The total EFs ranged from 9.82 to 215 mg kg⁻¹ for PAHs, 0.14 to 1.88 mg kg⁻¹ for NPAHs and 4.47 to 20.8 mg kg⁻¹ for OPAHs. Measured EFs and gas-particle partitioning varied depending on the geological maturity. The lowest EFs were found in anthracite. The proportion of PAHs, NPAHs and OPAHs in gaseous phase increasing with increased geological maturity. The coal with higher geological maturity produced more 3-ring PAHs. On the basis of the statistical analysis for the residential sector of China in 2008, PAHs, NPAHs and OPAHs emitted from residential honeycomb coal briquettes were 4.36 Gg, 0.03 Gg and 0.47 Gg in 2007, respectively. By 2020, the emission would decrease to 2.18 Gg, 0.02 Gg and 0.24 Gg for PAHs, NPAHs and OPAHs due to the increasing usage of new energy resources. If only anthracite is used as the residential coal, 93% PAHs, 87% NPAHs and 71% OPAHs would be reduced in 2020.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have been extensively studied due to their well-known carcinogenic and mutagenic properties.^{1–4} Recently, more attention has been paid to nitrated (NPAHs) and oxygenated PAHs (OPAHs) due to their toxicity.^{5–8} Some NPAHs have been suggested to be more mutagenic and carcinogenic than unsubstituted PAHs.⁹ OPAHs, such as polycyclic aromatic quinones, have been found to generate reactive oxygen species (ROS), resulting in oxidative stress that can lead to allergic diseases.^{10,11} NPAHs and OPAHs can be emitted during incomplete combustion processes,^{1,2,12} similar to unsubstituted PAHs and also are produced from the reactions between gas-phase PAHs and oxidants in the atmosphere.^{1,13,14}

Coal combustion is one of the most important sources of PAHs, NPAHs and OPAHs in most developing countries,² especially in China, where coal accounts for approximately 70% of the total primary energy consumption in 2009, according to the official figures in the National Bureau of Statistics.¹⁵ It was estimated that domestic coal combustion contributed to approximately 20% of total PAH emissions in China.¹⁶ Among different combustion forms of coal, residential honeycomb coal briquettes are widely used for cooking and heating in China and they are potentially an important source of PAHs in the atmosphere. The emission characteristics of residential coal combustion have been studied.^{17–22} The results showed that the combustion of bituminous coal with vitrinite reflectance (R_O) around 0.9% produced the highest emission factors (EFs) of particulate matter (PM), elemental carbon (EC), organic carbon (OC) and PAHs. Anthracite, the cleanest available residential coal fuel, is therefore the favored choice for

domestic combustion from the viewpoint of both climate change and health effects. Tao's group has scored lots of achievements in wood, crop residues and coals combustion in China.^{2,12,23–30} However, due to different geological maturity in various coals and their different burning styles, the studies on the emission of PAHs, NPAHs and OPAHs from the residential combustion of honeycomb coal briquettes are still limited in China.^{2,12,23,27}

The purpose of this study is (1) to determine EFs for PAHs, NPAHs and OPAHs from residential honeycomb coal briquette combustion, (2) to discuss the effects of geological maturity of the coal on the emissions, the profiles and the gas-to-particle partitioning of freshly emitted PAHs, NPAHs and OPAHs and (3) to estimate PAHs, NPAHs and OPAHs emissions from the residential combustion of honeycomb coal briquettes based on the EFs data in this study.

2. EXPERIMENTAL SECTION

2.1. Coals and Stove and Sampling Systems. Five different types of coals were investigated in this study, which covered a wide range of geological maturity, including bituminous coal from Ping Ding Shan (PDS, $R_O = 0.77\%$), Xuan Wei (XW, $R_O = 1.20\%$), Lin Fen (LF, $R_O = 1.35\%$) and Qin Yuan (QY, $R_O = 1.51\%$) and anthracite from Jin Cheng (JC, $R_O = 1.88\%$). The analysis of the coals is presented in Table 1. These raw coals were powdered and intermixed with 40% of clay to produce honeycomb briquettes. The briquettes were 12 hole columns with a height of 6 cm and diameter of 9 cm. The

Received: September 22, 2013

Revised: November 17, 2013

Published: December 4, 2013

Table 1. Ultimate and Proximate Analysis of Raw Coal

raw coal	JC	QY	LF	XW	PDS
proximate analysis (wt %, on air-dry (ad) basis)					
moisture (M_{ad})	0.66	0.68	0.63	1.16	0.74
ash (A_{ad})	16.4	19.0	5.8	37.7	38.3
volatile (V_{ad})	6.87	20.8	22.4	27.8	39.5
fixed carbon (FC_{ad})	76.1	59.6	71.2	33.4	21.4
total S ($S_{t,ad}$)	2.82	2.98	0.44	0.86	1.11
ultimate analysis (wt %, on dry ash-free (daf) basis)					
C_{daf}	83.3	80.1	76.2	74.9	73.2
H_{daf}	3.46	4.08	3.86	3.99	5.65
N_{daf}	0.91	1.32	1.16	1.23	1.32
O_{daf}	5.19	4.45	4.78	5.47	8.41
virtual reflectance (R_O (%))	1.88	1.52	1.34	1.20	0.77

combustion experiments were conducted in a clean room simulating the cooking and heating practice in a honeycomb briquette stove, which is commonly used in China and purchased from the market in Guang Zhou city. Details of the stove was described in previous study.¹⁷ Briefly, the stove is a 27 × 21 cm cylinder with a 12.5 cm diameter inner, metallic outer cover and the thermal barrier between the inner and the cover. Near the bottom, a 6 cm diameter hole is used for controlling the air supply. The pictures of the honeycomb coal

briquettes and the stove are presented in Figure S1 of the Supporting Information (SI). In this room, the ambient temperature and relative humidity were 24–26 °C and 55–60%, respectively. The temperature in sampling tunnel was 25–31 °C. The schematic diagram of the experimental setup is shown in the Figure S2 of the SI.

2.2. Sampling Procedure. The first honeycomb coal briquette was ignited at the bottom of the stove using charcoal. The second coal briquette was added after the first one had burned for 1 h, subsequently, the charcoal ash was cleared out. The third briquette was added after the second had burned for 1 h. Then the stove was put into the burning chamber and the sampling started instantly. During the sampling, a fraction of smoke was collected using a quartz fiber filter (QFF, Whatman, 25.4 cm length × 20.3 cm width) for particulate compounds and a polyurethane foam (PUF, Whatman, 6.5 cm diameter × 8 cm height) for gaseous compounds with a flow rate of 32 L min⁻¹. The sampling lasted for 1 h. The weights of the honeycomb coal briquettes before and after combustion were recorded to obtain the actual weight of coal burned, which varied from 0.21 to 0.30 kg. It should be noted that the disturbance of background can be neglected due to the front filter of the blower and the significantly high emission compared with background pollution level. The reproducibility of the experiment was checked in two separate combustions and collecting procedures for LF and PDS, the whole procedure for ignition and burning to sampling. The relative deviations (RD) of PAHs, NPAHs and OPAHs were 11.1%, 7.2% and 17.1%, respectively, and a set of experiment results were used in the following discussion.

Table 2. EFs of PAHs, NPAHs and OPAHs Including Particulate and Gaseous Phases in Residential Coal Combustion

	abbreviation	JC	QY	LF	XW	PDS		abbreviation	JC	QY	LF	XW	PDS
NPAHs ($\mu\text{g kg}^{-1}$)							PAHs (mg kg^{-1})						
1-nitronaphthalene	1-NNap	38.3	24.0	9.04	7.36	30.3	acenaphthylene	Acy	0.03	0.35	0.97	0.53	1.46
2-nitronaphthalene	2-NNap	30.3	24.0	9.75	8.08	9.12	acenaphthene	Ace	0.02	0.15	0.91	0.30	1.89
3-nitrobiphenyl	3-NBip	0.52	2.70	1.44	1.33	1.61	fluorene	Fl	0.57	16.1	17.6	12.5	22.9
4-nitrobiphenyl	4-NBip	3.25	7.38	7.44	15.5	289	phenanthrene	Phe	5.91	54.8	53.1	42.3	56.5
2-nitrobiphenyl	2-NBip	27.0	755	96.9	18.5	604	anthracene	Ant	0.41	6.36	7.67	8.74	19.2
1,5-dinitronaphthalene	1,5-DNNap	0.06	0.42	0.15	0.58	0.44	fluoranthene	Flu	0.64	8.65	7.55	7.35	10.8
1,3-dinitronaphthalene	1,3-DNNap	0.62	0.55	3.42	4.70	7.03	pyrene	Pyr	0.56	8.93	9.54	12.2	19.1
3-nitrodibenzofuran	3-NBFur	0.26	4.69	4.45	9.74	122	benz[a]anthracene	BaA	0.14	11.6	8.87	10.2	13.7
5-nitroacenaphthene	5-NAce	4.81	130	18.6	29.9	82.5	chrysene	Chr	0.62	24.2	20.5	18.5	22.1
2,2'-dinitrobiphenyl	2,2'-NNBip	0.09	0.63	0.11	0.16	4.14	benzo[b]fluoranthene	BbF	0.62	14.7	9.38	6.87	8.05
2-nitrofluorene	2-NFl	4.33	19.7	7.19	7.85	3.74	benzo[k]fluoranthene	BkF	0.03	1.76	1.13	1.15	1.88
9-nitroanthracene	9-NAnt	2.32	22.7	26.5	38.8	73.9	benzo[a]pyrene	BaP	0.05	5.80	4.69	6.84	12.4
1,8-dinitronaphthalene	1,8-NNap	2.67	21.5	30.8	46.8	71.5	indeno[1,2,3-cd]pyrene	IncdP	0.06	3.59	2.10	2.47	3.14
1-amino-4-nitronaphthalene	1A-4-NNap	0.01	0.05	ND	0.22	0.65	dibenzo[ah]anthracene	DahA	0.04	4.53	2.00	2.04	2.45
2-nitroanthracene	2-NAnt	6.03	27.6	35.3	49.0	28.9	benzo[ghi]perylene	BghiP	0.13	7.59	8.01	12.2	19.4
2-nitrodibenzothiophene	2-NDBthp	3.61	35.6	82.2	73.0	89.9	OPAHs (mg kg^{-1})						
9-nitrophenanthrene	9-NPhe	1.37	1.25	2.27	2.28	10.5	9-fluorenone	9-FIO	4.10	9.94	14.9	8.28	8.69
3-nitrophenanthrene	3-NPhe	1.37	1.84	0.02	8.49	60.5	anthraquinone	AntO	0.23	3.41	2.65	3.22	4.97
9,10-dinitroanthracene	9,10-DNAnt	ND	0.92	1.31	1.04	5.35	cyclopenta[def]phenanthrene-4-one	CPO	0.05	0.27	0.21	0.24	0.50
3-nitrofluoranthene	3-NFlu	9.55	29.7	9.43	17.6	42.2	benzanthrone	BZO	0.01	0.21	0.61	0.67	1.70
1-nitropyrene	1-NPyr	0.43	55.9	34.4	45.3	106	benz(a)anthracene-7,12-dione	BaAO	0.08	0.57	0.22	0.24	0.40
2,7-dinitrofluorene	2,7-DNFl	0.17	9.28	33.0	41.7	32.6	6H-benzo[c,d]pyrene-6-one	6H-BcdPO	ND	1.59	1.26	1.67	4.56
2,8-dinitrodibenzothiophene	2,8-DNBthp	0.90	5.96	14.0	24.6	116	total (mg kg^{-1})						
7-nitrobenz[a]anthracene	7-NBaA	0.44	7.23	12.2	25.0	77.8	\sum PAHs		9.82	169	154	144	215
6-nitrochrysene	6-NChr	0.37	12.6	2.61	17.3	7.29	\sum NPAHs		0.14	1.20	0.44	0.50	1.88
6-nitrobenz(a)pyrene	6-NBap	2.97	2.45	1.92	1.73	7.65	\sum OPAHs		4.47	16.0	19.9	14.3	20.8

*Not detected.

2.3. Analytical Methods. Detailed information on the extraction and instrumental analyses has been published elsewhere.^{3,31,32} Briefly, the surrogate standard consisting of 5-nitroacenaphthene-D9, 9-nitroanthracene-D9, 3-nitrofluoranthene-D9, 6-nitrochrysene-D11, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12, was added to the samples prior to extraction. The PUFs were Soxhlet extracted with 200 mL of dichloromethane (DCM)/methanol (2:1, v:v) for 48 h. The QFF samples were ultrasonically extracted with 3 × 20 mL DCM/methanol (2:1, v:v) for 30 min. The extracts were filtered, concentrated and then purified by 2:1 silica–alumina columns. The fraction containing parent PAHs, NPAHs and OPAHs was collected, reduced almost to dryness and then dissolved in *n*-hexane. Prior to an instrumental analysis, known quantities of internal standards, hexamethylbenzene (for PAHs) and 2-nitrofluorene-D9 (for NPAHs and OPAHs) were added to the samples. All samples were analyzed using gas chromatography/mass spectrometer (GC/MS). The mass spectrometer was operated in electron impact ion (EI) mode and selected ion monitoring (SIM) for parent PAHs, and electron capture negative ion (ECNI) mode and SIM for NPAHs and OPAHs. The instrumental conditions for individual PAHs, NPAHs and OPAHs are provided in the Supporting Information. Fifteen PAHs, twenty-six NPAHs and six OPAHs were quantified in this study. These target compounds and their abbreviations are given in Table 2.

2.4. Quality Control (QC) and Quality Assurance (QA). Before the sampling, PUFs were pre-extracted with DCM for 48 h each. QFFs were baked at 550 °C in a muffle furnace for 4 h. The reproducibility of the collecting procedure was checked in two separate experiments for the filter/PUF samplers. Surrogate standards were spiked to the samples for monitoring the analytical procedural performance and matrix effects. Instrumental detection limits of the PAHs, NPAHs and OPAHs ranged from 1.22×10^{-7} to 1.52×10^{-7} mg, 1.54×10^{-8} to 4.87×10^{-8} mg and 1.11×10^{-8} to 2.91×10^{-8} mg, respectively. Laboratory analysis method detection limits ranged from 1.46×10^{-7} to 1.95×10^{-7} mg mL⁻¹, 1.91×10^{-8} to 5.91×10^{-8} mg mL⁻¹ and 1.55×10^{-8} to 3.56×10^{-8} mg mL⁻¹. The mean recoveries for the target compounds were in the range from 73% to 117%, except naphthalene-D8 (less than 50%). The results of naphthalene, therefore, have not been discussed in this study.

3. RESULTS AND DISCUSSION

3.1. EFs of PAHs, NPAHs and OPAHs. The individual EFs for PAHs, NPAHs and OPAHs for both particulate and gaseous phases from the honeycomb briquette combustion of five different coals are presented in Table 2. The formula to calculate EFs is provided in the Supporting Information. The results showed that the \sum EFs varied widely among these fuels, and bituminous coals yielded the higher emission than the anthracite.

The highest EF of \sum PAHs (EF_{PAHs}) for bituminous coal was 215 mg kg⁻¹ (PDS) and the anthracite (JC) yielded the lowest emission (9.82 mg kg⁻¹). This result was consistent with the study by Tao et al., which reported that the EFs of the total 16 PAHs were in the range from 6.25 mg kg⁻¹ (anthracite) to 253 mg kg⁻¹ (bituminous) for residential coal combustion in a rural area in China.²⁹ The EF_{PAHs} reported in other literatures for the coal combustion varied from 14 to 341 mg kg⁻¹ in vigorous combustion conditions.^{12,18}

PAHs diagnostic ratios have been used as a tool for identifying and assessing pollution emission sources.^{26,33} Ratios of Ant/(Ant + Phe), Flu/(Flu + Pyr), BaA/(BaA + Chr) and IncdP/(IncdP + BghiP) in this study ranged from 0.06–0.25, 0.36–0.53, 0.18–0.38 and 0.14–0.32, respectively (Table 3). Compared with previous studies,^{18,26,34,35} the values of these ratios fell in the range for the coal combustion and biomass burning.

Table 3. PAHs Diagnostic Ratios from the Emission of Coal Combustion

coal	JC	QY	LF	XW	PDS
virtual reflectance (R_o (%))	1.88	1.52	1.34	1.20	0.77
Ant/(Ant + Phe)	0.06	0.10	0.13	0.17	0.25
Flu/(Flu + Pyr)	0.53	0.49	0.44	0.38	0.36
BaA/(BaA + Chr)	0.18	0.32	0.30	0.36	0.38
BbF/(BbF + BkF)	0.95	0.89	0.89	0.86	0.81
IncdP/(IncdP + BghiP)	0.30	0.32	0.21	0.17	0.14

The EFs for \sum NPAHs were approximately 2 orders of magnitude lower than those of \sum PAHs. They ranged from 0.14 mg kg⁻¹ (JC) to 1.88 mg kg⁻¹ (PDS). The NPAHs could be produced by the reaction of PAHs with the NO₂.^{14,36} The lower EF_{NPAHs} might be attributed to the lower contents of element N (0.91–1.32% of original coals) and inactive N₂ in the air.² Similar to the PAH emissions, bituminous coals combustion produced much more NPAHs than anthracite. The results in this study were in the same range of coal combustion reported by Shen et al.,¹² in which NPAHs varied from 0.16 to 2.4 mg kg⁻¹ for vigorous coal combustion. However, only 9 NPAHs including 1-NNap, 2-NNap, 5-NAce, 2-NFl, 9-NAnt, 9-NPhe, 3-NPhe, 3-NFlu and 1-NPyr were analyzed in the previous studies.^{2,12} The 9 NPAHs accounted for 22.2–65.4% of \sum NPAHs, and additional 17 NPAHs were reported in this study.

The EFs of individual NPAHs were over two orders of magnitude lower than those of their corresponding parent PAHs. The ratios of EF_{NPAH} to their corresponding parent EF_{PAH} varied from 4.3×10^{-7} (3-NPhe/Phe, LF coal) to 0.06 (6-NBap/Bap, JC coal) (Table 4), which were different from

Table 4. Ratios of the Individual EF_{OPAH} and EF_{NPAH} to Their Corresponding Parent EF_{PAH}

coal	JC	QY	LF	XW	PDS
NPAH/PAH					
2-NFl/Flu	7.55	1.22	0.41	0.63	0.16
2,7-DNFl/Flu	0.30	0.58	1.87	3.35	1.42
9-NPhe/Phe	0.23	0.02	0.04	0.05	0.19
3-NPhe/Phe	0.23	0.03	0.0004	0.20	1.07
2-NAnt/Ant	14.8	4.34	4.60	5.61	1.50
9-NAnt/Ant	5.70	3.58	3.45	4.44	3.84
9,10-DNAnt/Ant	NA ^a	0.14	0.17	0.12	0.28
3-NFlu/Flu	15.0	3.44	1.25	2.40	3.91
1-NPyr/Pyr	0.77	6.26	3.60	3.72	5.55
7-NBaA/BaA	3.25	0.63	1.37	2.44	5.67
6-NChr/Chr	0.60	0.52	0.13	0.94	0.33
6-NBap/Bap	60.7	0.42	0.41	0.25	0.62
OPAH/PAH					
9-FIO/Flu	7.14	0.62	0.84	0.66	0.38
AntO/Ant	0.57	0.54	0.35	0.37	0.26
BaAO/BaA	0.60	0.05	0.03	0.02	0.03

^aNot available.

the values for wood and coal combustion reported by Shen et al.,¹² ranging from 5.7×10^{-5} for 3-NPhe/Phe to 0.095 for 9-NAnt/Ant. The differences might be attributed to the different content of element N in fuels and the combustion conditions. The relationship between the ratios of EF_{NPAH} to their corresponding parent EF_{PAH} and the contents of element N in five different coals was investigated in this study. A weak

correlation between them was observed. The N contents in coals ranged from 0.91% to 1.32% in mass with the order of PDS > QY > XW > LF > JC, but the order of the ratios of EF_{NPAH} to their corresponding parent EF_{PAH} was JC > PDS > XW > QY > LF. Therefore, the N contents in coals might not be involved in the NPAH formation during combustion directly. The previous studies found that the particulate NPAHs from direct emissions were formed from a high temperature electrophilic nitration of PAHs by NO_2 during combustion processes.^{14,36} Therefore, a possible reason for the divergence between the different studies for these ratios might be diverse contents of active N such as NO_2 in ambient air.

The EFs of $\sum OPAHs$ ranged from 4.47 (JC) to 20.8 $mg\ kg^{-1}$ (PDS) and they were approximately an order of magnitude lower than those of $\sum PAHs$. The EFs of $\sum OPAHs$ were higher than that of $\sum NPAHs$ because the OPAHs may be produced by reaction of PAHs with $O\cdot$ or $OH\cdot$, which are produced continuously by the radical chain reactions during the combustion.³⁷ Bituminous coals yielded 3–4 times OPAHs than anthracite. EF_{9-FIO} and EF_{AntO} were in the same order of magnitude as EF_{Fl} and EF_{AntP} whereas the EFs of BZO and BaAO were much lower than that of their parent compound BaA. The ranges for FIO/Fl, AntO/Ant, BZO/BaA and BaAO/BaA were 0.38–7.14, 0.26–0.57, 0.02–0.12 and 0.02–0.60, respectively (Table 4). The FIO/Fl (4.3) and BaAO/BaA (0.025) ratios for coal briquette combustion reported by Shen et al.¹² fell in the range of this study. It is worth noting that the wood combustion showed similar values of FIO/Fl (0.79) and AntO/Ant (0.42), and lower BaAO/BaA when compared to those from coal combustion, with an average of 0.020.¹² Therefore, BaAO/BaA might be used for identifying pollution emission sources.

To explore the formation mechanism of PAHs, NPAHs and OPAHs, their contents in the raw coals were measured. The results show that the PAHs, NPAHs and OPAHs contained in the raw coal accounted for 5.17–39.9%, 1.21–12.1% and 0.91–13.5% of the EF_{PAHs} , EF_{NPAHs} and EF_{OPAHs} , respectively. The profile of PAHs, NPAHs and OPAHs existed in the raw coal were different from that in the combustion smoke. For example, Phe was most abundant species in smoke whereas BbF was the most in JC raw coal, and most of NPAHs were not detected in raw coals. Therefore, the PAHs, NPAHs and OPAHs in the emission may be yielded during the combustion, and/or volatilize from the raw coals. The individual PAHs, NPAHs and OPAHs in the raw coal are presented in Table S1 of SI.

3.2. Profiles of PAHs, NPAHs and OPAHs. The profiles of PAHs, NPAHs and OPAHs were significantly different among the anthracite and bituminous coals (Figure S3). For anthracite, Phe was the most abundant species, accounting for 60.2% of $\sum PAHs$, followed by Chr, Fl, BbF and Flu, which accounted for 6.31–14.3%. For bituminous coals, PAHs showed a similar profile. Phe was still the most abundant species; however, it had lower contribution to $\sum PAHs$ (26.3–32.4%). The contributions of Fl and Chr from anthracite were lower than those from bituminous coals (8.65–11.5% and 12.8–14.3%), and Flu did not vary greatly among the tested coals. A similar PAH profile was reported for the coal combustion.^{12,18}

Compared with other emission sources,^{26,38,39} the coal combustion emitted less 3-ring PAHs (44.6–70.6% of $\sum PAHs$) and more 4-ring PAHs (around 30%) than vehicle emission, in which 3- and 4-ring PAHs contributed 79.8–93.9%

and 3.6–10.3% to $\sum PAHs$, respectively. Biomass burning emitted similar 4-ring PAHs but less 5-ring PAHs (1.9–7.18%) than coal combustion (7.57–15.8%). Nevertheless, coal combustion emitted more 6-ring PAHs than the other sources (around 2%), particularly the bituminous coals emitting more 6-ring PAHs (around 10.5%).

Among the 26 detected NPAHs in this study, 1-NNap was the most abundant species for anthracite, accounting for 27.0% of $\sum NPAHs$ with the EFs of 0.04 $mg\ kg^{-1}$, followed by 2-NNap, 2-NBip and 3NFlu accounting for 21.4%, 19.1% and 6.74%, respectively. The mean of 2-NBip was the most abundant species for bituminous accounting for 3.72–62.8% of $\sum NPAHs$ with the EFs of 0.02–0.75 $mg\ kg^{-1}$, followed by 2-NDBthp, 5-NAce and 1-NPyr, accounting for 2.96–14.7%, 6.01–10.7% and 4.65–9.13%, respectively. Although 26 NPAHs were detected in this study, only 9 NPAHs were chosen for the profile comparison because the data for the other compounds was not available in the literature. Among the selected 9 NPAHs, 1-NNap was the most abundant species for anthracite accounting for 41.2% of 9 NPAHs with the EFs of 0.04 $mg\ kg^{-1}$, followed by 2-NNap, 3-NFlu and 5-NAce accounting for 32.7%, 10.3% and 5.19%, respectively. 5-NAce was the most abundant species for bituminous coals accounting for 18.0–41.9% with the EFs of 0.02–0.13 $mg\ kg^{-1}$, followed by 1-NPyr, 9-NAnt and 3-NFlu, accounting for 18.2–29.4%, 7.4–23.4% and 8.1–10.6%, respectively. These profiles were different from the study by Shen et al.,¹² in which 9-NAnt and 9-NPhe were the most abundant two species accounting above 70.6% and 10% of the total 9 NPAHs, respectively. In this study, 9-NAnt and 9-NPhe only accounted for 0.41–23.4% of the total 9 NPAHs. The difference may be attributed to the different coals tested and the different combustion conditions. Geological maturity of the coal was not available in the study by Shen et al. Compared with the biomass burning, a similar NPAHs profile was observed in anthracite, for which 1-NNap and 2-NNap were the largest contributors to $\sum NPAHs$ (greater than 50%). Different profiles were found for bituminous coals, in which 1-NNap and 2-NNap contributed less than 16% (Figure S3b).

Four OPAHs, 9-FIO, AntO, BZO and BaAO were chosen for the profile comparison, which accounted for 75.8–98.9% of $\sum OPAHs$. 9-FIO contributed 55.1–92.7% to the total 4 OPAHs, followed by the AntO, BZO and BaAO. The most remarkable difference between coals and biomass burning was the contribution of BZO, which accounted 0.159–10.8% for coal combustion and 15.4–39.6% for biomass burning (Figure S3c). The contribution of 9-FIO for the coal combustion (55.1–92.7%) was higher than that for the biomass burning (41.9–44.2%).

3.3. Impact of Geological Maturity. In the previous study, the geological maturity of the coals showed significant effects on the EF_{EC} and EF_{OC} under the residential burning conditions.²⁰ In this study, the EFs and profiles of PAHs, NPAHs and OPAHs and their gas-particle distribution were also found to be dependent on the geological maturity of the coals.

The EFs of $\sum PAHs$, $\sum NPAHs$ and $\sum OPAHs$ decreased noticeably with geological maturity increasing. Briefly, bituminous coal (PDS, $R_O = 0.77\%$) had the highest values of EFs, followed by XW ($R_O = 1.20\%$), LF ($R_O = 1.35\%$) and QY ($R_O = 1.51\%$). Anthracite (JC, $R_O = 1.88\%$) yielded 1–2 orders of magnitude lower than the bituminous coals. The previous studies showed that bituminous coal formed more tar,

PM, EC, OC and PAHs than anthracite, particularly the bituminous coal, with a value of R_o around 0.9%.^{18,20,40,41}

From Table 5, it can be seen that 3-ring PAHs were the most species in the coal combustion emission in which Phe

Table 5. Species of PAHs from the Emission of Coal Combustion

Coal	JC	QY	LF	XW	PDS
virtual reflectance (R_o (%))	1.88	1.52	1.35	1.20	0.77
3-ring	70.6	46.0	52.1	44.6	47.4
4-ring	19.9	31.5	30.1	33.5	30.6
5-ring	7.57	15.8	11.2	11.7	11.5
6-ring	1.94	6.61	6.56	10.2	10.5

accounted for a large percentage, and it decreased with the decreasing geological maturity. Higher ring (6-ring) PAHs showed an increased tendency with decreasing geological maturity, but no trend was found for the other PAHs. Compared with coal combustion, the combustion of diesel and gasoline with higher geological maturity, which can be obtained from the methyphenanthrene distributions, produced much more 3-ring PAHs and less 4-ring, 5-ring and 6-ring PAHs.^{38,39}

In addition to the EFs, the distribution between the gaseous and particulate phases was also influenced by the geological maturity of the coals. The EFs of individuals PAHs, NPAHs and OPAHs in the gaseous and particulate phases are presented in Table S2–S7 (SI). Generally, compounds with relatively low molecular weight (MW) and high volatility are dominated in the gaseous phase, whereas those with relatively high MW and low volatility tend to stay in particulate phase.^{4,23} In Figure 1, it is noticeable that the contributions of the gaseous phase to the

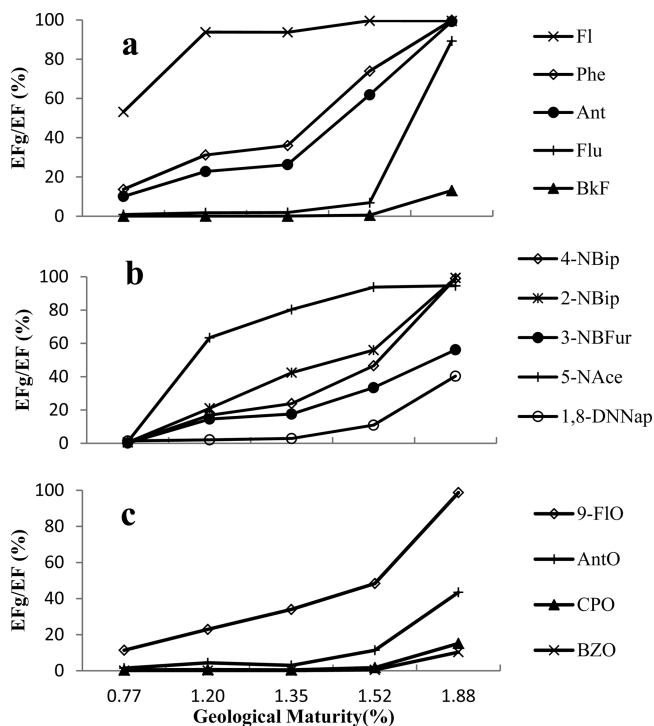


Figure 1. Proportion of part of PAHs (a), NPAHs (b) and OPAHs (c) in gas phase impacted by geological maturity for five selected coal combustions.

total gaseous and particulate PAHs, most NPAHs and OPAHs declined with decreasing geological maturity. For example, the highest contribution of 9-FIO (98.7%) was found in JC ($R_o = 1.35\%$), followed by QY (48.3%, $R_o = 1.20\%$) LF (34.4%, $R_o = 1.35\%$), XW (22.9%, $R_o = 1.20\%$), and PDS (1.37%, $R_o = 0.77\%$). The EF_{PM} values for different coals were 2.21×10^3 mg kg^{-1} for JC, 1.20×10^4 mg kg^{-1} for QY, 1.35×10^4 mg kg^{-1} for LF, 1.37×10^4 mg kg^{-1} for XW and 7.03×10^4 mg kg^{-1} for PDS. The individual PAHs, NPAH and OPAHs tended to exist in the gaseous phase when a low number of particles was emitted, whereas they tended to be bound with particles when plenty of particles were emitted. The contributions of gaseous phase decreased exponentially with the increase of EF_{PM} (correlation coefficient R^2 ranging from 0.424 to 0.915) (Figure S4).

3.4. Estimates of PAHs, NPAHs and OPAHs Emission.

The estimation of the emission of PAHs, NPAHs and OPAHs from the residential honeycomb coal briquettes combustion in China was calculated. The total residential coal consumption in China from China coal industry yearbook 2008⁴² was about 81.1Tg (teragram) during 2007, in which 17.4% was anthracite and 76.8% was bituminous coals. Chen et al. reported that 40% of the residential coal was burned as honeycomb coal briquettes,¹⁸ and Streets et al. assumed a very close value (41%) for the year 2020.⁴³ In this study, 40.5% of the domestic coal was supposed to be burned in the honeycomb coal briquette form. Therefore, there were 5.72 Tg of anthracite and 25.2 Tg of bituminous coal burned as honeycomb coal briquettes in 2007. The estimated annual emission from honeycomb coal briquette combustion in 2007 was 4.36, 0.03, and 0.47 Gg (gigagram) for PAHs, NPAHs and OPAHs, respectively. Although bituminous coal accounted for 76.8% of the total coal consumption, it contributed much more PAHs (98.7%), NPAHs (97.7%) and OPAHs (94.6%). A previous study estimated 4.72 Gg PAHs emission form domestic honeycomb coal briquettes combustion,¹⁸ which was about 8.3% higher than that estimated by this study. An estimate by Xu et al. on the total emission of 16 PAHs in China was 25.3 Gg and they were from major sources including the using of coals, oil and firewood.¹⁶ On the basis of the estimation above, the emission from honeycomb coal briquettes contributed about 17.2% to the total PAHs. It was estimated that residential coal consumption in China would be 40 Tg by 2020,⁴⁴ thus, the estimated annual emission from honeycomb coal briquette combustion in China would be declining greatly, which would be 2.18, 0.02, and 0.24 Gg for PAHs, NPAHs and OPAHs, respectively. The emissions would be further reduced by 2050 because of the increased usage of new clean energy resources. If only anthracite is used as the residential coal, 93% PAHs, 87% NPAHs and 71% OPAHs would be reduced in 2020. It should be noted that NPAHs and OPAHs are more mutagenic and carcinogenic than unsubstituted PAHs even though their emissions are much lower than PAHs, and great attention should be taken of the negative effects of coal combustion on human health and the environment.

4. CONCLUSIONS

Emission characterizations of PAHs, NPAHs and OPAHs yielded from different honeycomb coal briquettes were studied. The results indicate that geological maturity of the coals may affect the emission characterization such as EFs, gas-particle partition and profiles of PAH species. Bituminous showed the highest EFs among the tested coals, whereas anthracite had the

lowest EFs. Therefore, priority should be given to anthracite when coal is used as residential fuel. Additionally, annual emissions of PAHs, NPAHs and OPAHs from the residential honeycomb coal briquettes combustion in China were estimated. The emissions would be decreased as the more new energy resources are used.

■ ASSOCIATED CONTENT

■ Supporting Information

Instrumental conditions, formula of EFs, schematic diagram of the experimental setup, the PAHs, NPAHs and OPAHs profiles and their composition in gaseous phase and particle phase. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*X. Bi. E-mail: bixh@gig.ac.cn. Tel.: + 86 20 85290195. fax: + 86 20 85290288.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Funding for this study was provided by the National Natural Science Foundation of China (41073077), "Strategic Priority Research Program (B)" of the Chinese Academy of Sciences (XDB05020205), and we also thank the support from State Key Laboratory of Organic Geochemistry (SKLOG2013A01). We are grateful to Mr. T. S. Xiang for his technical assistance in the GC/MS analysis. This is contribution from GIGCAS No. 1782.

■ REFERENCES

(1) Zhang, J. J.; Smith, K. R. Household air pollution from coal and biomass fuels in China: measurements, health impacts, and interventions. *Environ. Health Perspect.* **2007**, *115* (6), 848–55.

(2) Shen, G.; Tao, S.; Wei, S.; Zhang, Y.; Wang, R.; Wang, B.; Li, W.; Shen, H.; Huang, Y.; Chen, Y.; Chen, H.; Yang, Y.; Wang, W.; Wang, X.; Liu, W.; Simonich, S. L. Emissions of parent, nitro, and oxygenated polycyclic aromatic hydrocarbons from residential wood combustion in rural China. *Environ. Sci. Technol.* **2012**, *46* (15), 8123–8130.

(3) Wei, S.; Huang, B.; Liu, M.; Bi, X.; Ren, Z.; Sheng, G.; Fu, J. Characterization of PM_{2.5}-bound nitrated and oxygenated PAHs in two industrial sites of South China. *Atmos. Res.* **2012**, *109–110*, 76–83.

(4) Albinet, A.; Leoz-Garziandia, E.; Budzinski, H.; Villenave, E.; Jaffrezou, J. L. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys - Part 1: Concentrations, sources and gas/particle partitioning. *Atmos. Environ.* **2008**, *42* (1), 43–54.

(5) Reisen, F.; Arey, J. Atmospheric reactions influence seasonal PAH and nitro-PAH concentrations in the Los Angeles basin. *Environ. Sci. Technol.* **2005**, *39* (1), 64–73.

(6) Tsapakis, M.; Stephanou, E. G. Diurnal cycle of PAHs, nitro-PAHs, and oxy-PAHs in a high oxidation capacity marine background atmosphere. *Environ. Sci. Technol.* **2007**, *41* (23), 8011–8017.

(7) Karavalakis, G.; Fontaras, G.; Ampatzoglou, D.; Kousoulidou, M.; Stournas, S.; Samaras, Z.; Bakeas, E. Effects of low concentration biodiesel blends application on modern passenger cars. Part 3: impact on PAH, nitro-PAH, and oxy-PAH emissions. *Environ. Pollut.* **2010**, *158* (5), 1584–1594.

(8) Ladji, R.; Yassaa, N.; Cecinato, A.; Meklati, B. Y. Seasonal variation of particulate organic compounds in atmospheric PM₁₀ in the biggest municipal waste landfill of Algeria. *Atmos. Res.* **2007**, *86* (3–4), 249–260.

(9) Durant, J. L.; Busby, W. F.; Lafleur, A. L.; Penman, B. W.; Crespi, C. L. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. *Mutat. Res., Genet. Toxicol.* **1996**, *371* (3–4), 123–157.

(10) Chung, S. W.; Chung, H. Y.; Toriba, A.; Kameda, T.; Tang, N.; Kizu, R.; Hayakawa, K. An environmental quinoid polycyclic aromatic hydrocarbon, acenaphthenequinone, modulates cyclooxygenase-2 expression through reactive oxygen species generation and nuclear factor kappa B activation in A549 cells. *Toxicol. Sci.* **2007**, *95* (2), 348–355.

(11) Sklorz, M.; Briede, J. J.; Schnelle-Kreis, J.; Liu, Y.; Cyrus, J.; de Kok, T. M.; Zimmermann, R. Concentration of oxygenated polycyclic aromatic hydrocarbons and oxygen free radical formation from urban particulate matter. *J. Toxicol. Environ. Health, Part A* **2007**, *70* (21), 1866–1869.

(12) Shen, G.; Tao, S.; Wei, S.; Chen, Y.; Zhang, Y.; Shen, H.; Huang, Y.; Zhu, D.; Yuan, C.; Wang, H.; Wang, Y.; Pei, L.; Liao, Y.; Duan, Y.; Wang, B.; Wang, R.; Lu, Y.; Li, W.; Wang, X.; Zheng, X. Field measurement of emission factors of PM, EC, OC, parent, Nitro- and Oxy- polycyclic aromatic hydrocarbons for residential briquette, coal cake, and wood in rural Shanxi, China. *Environ. Sci. Technol.* **2013**, *47* (6), 2998–3005.

(13) Atkinson, R.; Arey, J.; Zielinska, B.; Aschmann, S. M. Kinetics and nitro-products of the gas-phase OH and NO₃ radical-initiated reactions of naphthalene-D8, fluoranthene-D10, and pyrene. *Int. J. Chem. Kinet.* **1990**, *22* (9), 999–1014.

(14) Zhang, Y.; Yang, B.; Gan, J.; Liu, C.; Shu, X.; Shu, J. Nitration of particle-associated PAHs and their derivatives (nitro-, oxy-, and hydroxy-PAHs) with NO₃ radicals. *Atmos. Environ.* **2011**, *45* (15), 2515–2521.

(15) Li, R.; Leung, G. C. K. Coal consumption and economic growth in China. *Energy Policy* **2012**, *40*, 438–443.

(16) Xu, S. S.; Liu, W. X.; Tao, S. Emission of polycyclic aromatic hydrocarbons in China. *Environ. Sci. Technol.* **2006**, *40* (3), 702–708.

(17) Chen, Y. J.; Bi, X. H.; Mai, B. X.; Sheng, G. Y.; Fu, J. M. Emission characterization of particulate/gaseous phases and size association for polycyclic aromatic hydrocarbons from residential coal combustion. *Fuel* **2004**, *83* (7–8), 781–790.

(18) Chen, Y. J.; Sheng, G. Y.; Bi, X. H.; Feng, Y. L.; Mai, B. X.; Fu, J. M. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environ. Sci. Technol.* **2005**, *39* (6), 1861–1867.

(19) Chen, Y. J.; Zhi, G. R.; Feng, Y. L.; Fu, J. M.; Feng, J. L.; Sheng, G. Y.; Simoneit, B. R. T. Measurements of emission factors for primary carbonaceous particles from residential raw-coal combustion in China. *Geophys. Res. Lett.* **2006**, *33*, (20).

(20) Chen, Y. J.; Zhi, G. R.; Feng, Y. L.; Liu, D. Y.; Zhang, G.; Li, J.; Sheng, G. Y.; Fu, J. M. Measurements of black and organic carbon emission factors for household coal combustion in China: implication for emission reduction. *Environ. Sci. Technol.* **2009**, *43* (24), 9495–9500.

(21) Zhi, G. R.; Chen, Y. J.; Sun, J. Y.; Chen, L. G.; Tian, W. J.; Duan, J. C.; Zhang, G.; Chai, F. H.; Sheng, G. Y.; Fu, J. M. Harmonizing aerosol carbon measurements between two conventional thermal/optical analysis methods. *Environ. Sci. Technol.* **2011**, *45* (7), 2902–2908.

(22) Zhi, G. R.; Peng, C. H.; Chen, Y. J.; Liu, D. Y.; Sheng, G. Y.; Fu, J. M. Deployment of coal briquettes and improved stoves: possibly an option for both environment and climate. *Environ. Sci. Technol.* **2009**, *43* (15), 5586–5591.

(23) Shen, G.; Tao, S.; Wang, W.; Yang, Y.; Ding, J.; Xue, M.; Min, Y.; Zhu, C.; Shen, H.; Li, W.; Wang, B.; Wang, R.; Wang, W.; Wang, X.; Russell, A. G. Emission of oxygenated polycyclic aromatic hydrocarbons from indoor solid fuel combustion. *Environ. Sci. Technol.* **2011**, *45* (8), 3459–3465.

(24) Shen, G.; Tao, S.; Wei, S.; Zhang, Y.; Wang, R.; Wang, B.; Li, W.; Shen, H.; Huang, Y.; Chen, Y.; Chen, H.; Yang, Y.; Wang, W.; Wei, W.; Wang, X.; Liu, W.; Wang, X.; Masse Simonich, S. L. Reductions in emissions of carbonaceous particulate matter and

polycyclic aromatic hydrocarbons from combustion of biomass pellets in comparison with raw fuel burning. *Environ. Sci. Technol.* **2012**, *46* (11), 6409–16.

(25) Shen, G.; Tao, S.; Wei, S.; Zhang, Y.; Wang, R.; Wang, B.; Li, W.; Shen, H.; Huang, Y.; Yang, Y.; Wang, W.; Wang, X.; Simonich, S. L. Retene emission from residential solid fuels in China and evaluation of retene as a unique marker for soft wood combustion. *Environ. Sci. Technol.* **2012**, *46* (8), 4666–4672.

(26) Shen, G.; Wang, W.; Yang, Y.; Ding, J.; Xue, M.; Min, Y.; Zhu, C.; Shen, H.; Li, W.; Wang, B.; Wang, R.; Wang, X.; Tao, S.; Russell, A. G. Emissions of PAHs from indoor crop residue burning in a typical rural stove: emission factors, size distributions, and gas–particle partitioning. *Environ. Sci. Technol.* **2011**, *45* (4), 1206–1212.

(27) Shen, G. F.; Wei, S. Y.; Zhang, Y. Y.; Wang, R.; Wang, B.; Li, W.; Shen, H. Z.; Huang, Y.; Chen, Y. C.; Chen, H.; Wei, W.; Tao, S. Emission of oxygenated polycyclic aromatic hydrocarbons from biomass pellet burning in a modern burner for cooking in China. *Atmos. Environ.* **2012**, *60*, 234–237.

(28) Shen, G. F.; Yang, Y. F.; Wang, W.; Tao, S.; Zhu, C.; Min, Y. J.; Xue, M. A.; Ding, J. N.; Wang, B.; Wang, R.; Shen, H. Z.; Li, W.; Wang, X. L.; Russell, A. G. Emission factors of particulate matter and elemental carbon for crop residues and coals burned in typical household stoves in China. *Environ. Sci. Technol.* **2010**, *44* (18), 7157–7162.

(29) Tao, S.; Shen, G. F.; Wang, W.; Yang, Y. F.; Zhu, C.; Min, Y. J.; Xue, M. A.; Ding, J. N.; Li, W.; Wang, B.; Shen, H. Z.; Wang, R.; Wang, X. L. Emission factors and particulate matter size distribution of polycyclic aromatic hydrocarbons from residential coal combustions in rural Northern China. *Atmos. Environ.* **2010**, *44* (39), 5237–5243.

(30) Guofeng, S.; Siye, W.; Wen, W.; Yanyan, Z.; Yujia, M.; Bin, W.; Rong, W.; Wei, L.; Huizhong, S.; Ye, H.; Yifeng, Y.; Wei, W.; Xilong, W.; Xuejun, W.; Shu, T. Emission factors, size distributions, and emission inventories of carbonaceous particulate matter from residential wood combustion in rural China. *Environ. Sci. Technol.* **2012**, *46* (7), 4207–4214.

(31) Bi, X.; Simoneit, B. R. T.; Wang, Z.; Wang, X.; Sheng, G.; Fu, J. The major components of particles emitted during recycling of waste printed circuit boards in a typical e-waste workshop of South China. *Atmos. Environ.* **2010**, *44* (35), 4440–4445.

(32) Bi, X. H.; Sheng, G. Y.; Peng, P.; Chen, Y. J.; Zhang, Z. Q.; Fu, J. M. Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. *Atmos. Environ.* **2003**, *37* (2), 289–298.

(33) Tobiszewski, M.; Namiesnik, J. PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* **2012**, *162*, 110–119.

(34) Oanh, N. T. K.; Albina, D. O.; Ping, L.; Wang, X. K. Emission of particulate matter and polycyclic aromatic hydrocarbons from select cookstove-fuel systems in Asia. *Biomass Bioenergy* **2005**, *28* (6), 579–590.

(35) Zhang, Y. X.; Schauer, J. J.; Zhang, Y. H.; Zeng, L. M.; Wei, Y. J.; Liu, Y.; Shao, M. Characteristics of particulate carbon emissions from real-world Chinese coal combustion. *Environ. Sci. Technol.* **2008**, *42* (14), 5068–5073.

(36) Nielsen, T. Reactivity of Polycyclic Aromatic-Hydrocarbons toward Nitrating Species. *Environ. Sci. Technol.* **1984**, *18* (3), 157–163.

(37) Warnatz, J.; Maas, U.; Dibble, R. W. *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*; Springer: Berlin, 2006.

(38) Mi, H. H.; Lee, W. J.; Chen, C. B.; Yang, H. H.; Wu, S. J. Effect of fuel aromatic content on PAH emission from a heavy-duty diesel engine. *Chemosphere* **2000**, *41* (11), 1783–1790.

(39) Yang, H.; Hsieh, L.; Liu, H.; Mi, H. Polycyclic aromatic hydrocarbon emissions from motorcycles. *Atmos. Environ.* **2005**, *39* (1), 17–25.

(40) Mitra, A.; Sarofim, A. F.; Barziv, E. The Influence of Coal Type on the Evolution of Polycyclic Aromatic-Hydrocarbons during Coal Devolatilization. *Aerosol Sci. Technol.* **1987**, *6* (3), 261–271.

(41) Radke, M.; Schaefer, R. G.; Leythaeuser, D.; Teichmüller, M. Composition of Soluble Organic-Matter in Coals - Relation to Rank and Liptinite Fluorescence. *Geochim. Cosmochim. Acta* **1980**, *44* (11), 1787–1800.

(42) Safety, S. A. o. C. M., China coal industry yearbook 2008; China Coal Industry Yearbook Press: Beijing, 2010.

(43) 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.: Atmos.* **2003**, *108* (D21), 8809.

(44) Alibaba, Analysis and prediction coal supply-demand of 2004–2020 in China 2012, <http://info.1688.com/detail/1024328639.html>.