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Emissions of polycyclic aromatic hydrocarbons from coking industries in China

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ABSTRACT

This study set out to assess the characteristics of polycyclic aromatic hydrocarbon (PAH) emission from coking industries, with field samplings conducted at four typical coke plants. For each selected plant, stack flue gas samples were collected during processes that included charging coal into the ovens (CC), pushing coke (PC) and the combustion of coke-oven gas (CG). Sixteen individual PAHs on the US EPA priority list were analyzed by gas chromatography/mass spectrometry (GC/MS). Results showed that the total PAH concentrations in the flue gas ranged from 45.776 to 414.874 $\mu g/m^3$, with the highest emission level for CC (359.545 $\mu g/m^3$). The concentration of PAH emitted from the CC process in CP1 (stamp charging) was lower than that from CP3 and CP4 (top charging). Low-molecular-weight PAHs (i.e., two- to three-ring PAHs) were predominant contributors to the total PAH contents, and Nap, AcPy, Flu, PhA, and AnT were found to be the most abundant ones. Total BaP_{eq} concentrations for CC (2.248 $\mu g/m^3$) were higher than those for PC (1.838 $\mu g/m^3$) and CG (1.082 $\mu g/m^3$), and DbA was an important contributor to carcinogenic risk as BaP in emissions from coking processes. Particulate PAH accounted for more than 20% of the total BaP_{eq} concentrations, which were significantly higher than the corresponding contributions to the total PAH mass concentration (5%). Both particulate and gaseous PAH should be taken into consideration when the potential toxicity risk of PAH pollution during coking processes is assessed. The mean total-PAH emission factors were 346.132 and 93.173 $\mu g/kg$ for CC and PC, respectively.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are extremely harmful to human health and the environment because of their high toxicity, persistence in the environment and bioaccumulation through the food chain. Once released into the environment, they can be transported and distributed on a global scale by the grasshopper effect and global fractionation (Gouin, Mackay, Jones, Harner, & Meijer, 2004; Wania, 2003). Most PAHs are generated by incomplete combustion and pyrolysis of organic substances during industrial production, transportation, waste incineration and so on (Bai et al., 2007; Harrison, Smith, & Luhana, 1996; Tekasakul, Furuuchi, Tekasakul, Chomanee, & Otani, 2008). Controlling and regulating the emission of PAHs from key sources is one of the most effective measures for protection of the environment and human health (Ravindra, Sokhi, & van Grieken, 2008; Zhang et al., 2009). Many studies have focused on PAHs emission from mobile sources, but there is limited information on stationary sources, especially on the emissions from industrial stacks (Chen et al., 2007; Pisupati, Wasco, & Scaroni, 2000; Yang, Lee, Chen, & Lai, 1998).

Metallurgical coke is produced by the destructive distillation of coal in coke ovens. In 2007, the global output reached about 558 million tons. China is the largest coke-producing country in the world, accounting for about 60% of global coke production in 2007, and many coke plants use a variety of scales and techniques (Liu, Zheng, et al., 2009). In addition, coking is a well-known source of PAHs (Mastral & Callén, 2000). Coking accounted for 17.9% of the total annual PAH emission in China, much higher than that in the United States (Zhang & Tao, 2009). Accurate characterization of PAHs emission from coking is sorely needed.

Abbreviations: Nap, naphthalene; AcPy, acenaphthylene; Acp, acenaphthene; Flu, fluorene; PhA, phenanthrene; AnT, anthracene; FLuA, fluoranthene; Pyr, pyrene; BaA, benzo[*a*]anthracene; Chr, chrysene; BbF, benzo[*b*]fluoranthene; BkF, benzo[*k*]flouranthene; BaP, benzo[*a*]pyrene; DbA, dibenz(a,h)anthracene; BghiP, benzo[*ghi*]perylene; IND, indeno(1,2,3-cd)pyrene; APCD, air pollution control device; CC, charging coal; CG, combustion of coke-oven gas; DCM, dichloromethane; GFF, glass fiber filter; HMW, high molecular weight; LMW, low molecular weight; MMW, middle molecular weight; PAHs, polycyclic aromatic hydrocarbons; PC, pushing coke; PUF, polyurethane foam.

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During coking, PAHs can be released from various production stages, such as coal charging, coke pushing and combustion of gas in the battery flues. According to the classification scheme of the International Agency for Research on Cancer (IARC), coal tar-rich volatiles containing PAHs resulting from coke production are carcinogenic, and evidence of carcinogenicity to human beings in relation to the operation of the coking industry has been provided (IARC, 2002). As estimated from an epidemiologic study, there is a high incidence of lung cancer among human beings exposed to PAHs in the vicinity of coke ovens (Lloyd, 1971). Review of the epidemiologic evidence for the standard of the Occupational Safety and Health Act (USA) indicated a relatively excessive risk of lung cancer, as high as 16-fold, for workers at topside coke ovens with 15 years or more of exposure (Redmond, 1983). PAH concentrations in soil collected at the site of a former coke plant ranged from 6.27 to 40.18 mg/kg dry weight (Li, Chen, Wu, & Piao, 2010). Total PAH concentrations in wastewater ranged from about 2000 μg/L in ammonia still influent to 5–120 μg/L in the biological oxidation effluent (Walters & Luthy, 1984). Although some efforts have been devoted to investigating the concentrations and characteristics of PAHs in soil, waste water and air in coke plants or their vicinities, as far as we know, no studies have focused on PAH emission from coking industries with different technologies, particularly emission characteristics from different production stages, PAH phase distributions and carcinogenic potencies.

Emission factors have been used for different applications, providing an easy estimation of emission rate and concentration of emitted pollutants (Chen et al., 2007; Zhao, Wang, Nielsen, Li, & Hao, 2010), and are of great significance in developing national environmental policies and protection strategies. In particular, to ensure that expenses on pollution control measures are properly targeted and warranted, it is important that emission factors be based on the latest and most accurate data (Yang et al., 1998). However, no study to date has reported the emission factors of PAHs from coking in China.

In the present study, PAH emissions from coking in China were quantified. Emission levels and characteristics are presented and discussed for different units (coke pushing, coal charging and combustion of coke-oven gas) in the coking process. Emission factors of PAHs from the processes including coke pushing and coal charging were also derived. These data are helpful for understanding the contribution of PAHs from the coking industry and developing an emission inventory of PAHs.

2. Experimental

2.1. Sampling

During coking, prepared coal is charged into the ovens, which are then subjected to external heating to approximately 1000 °C in an oxygen-free atmosphere. The coke is then removed and quenched, mainly with water. Formation and emission of PAHs might occur during charging of coal (CC), pushing of coke (PC) and combustion of coke-oven gas (CG) in the coking process. Although there are hundreds of coke plants in China, many plants are not suitable for field sampling of CC, PC and CG. In this study, four typical coke plants (CP1 to CP4) in China were selected. All these plants were found with a mean annual capacity of 652,055 t, and the coking time ranged from 23 to 26 h. Stamp charging and top charging was applied in coal charging for CP1 and CP2, CP3 and CP4, respectively. For these plants, two separate air-pollution-control devices (Baghouse filter, BF) were installed to remove particulate matter from the stack flue gases during CC and PC. For a few coke plants (CP) in China, such as CP2, special techniques are used for CC, and hardly any waste gas is released. Therefore, no stack was built for conducting the gas released when the coal is charged into the ovens. In each selected plant, coke oven gases were combusted to heat the coal. We found that no air-pollution-control device was installed for CG. The basic information about the four coke plants is described in Table 1.

Table 1
Basic information about the investigated coke plants.

Denotation	CP1	CP2	CP3	CP4
Annual capacity ($\times 10^3$ t)	251.85	863.96	556.41	936
Technique for coal charging	SC[a]	SC	TC[b]	TC
Height of oven (m)	3.20	4.30	4.30	6.00
Air pollution control device	BF[c]	BF	BF	BF
Coking time (h)	24	24	26	23
Output rate (t/d)	690	2376	1524.4	2564
Sampling point	A[d], B[e] & C[f]	B, C	A, B & C	A, B & C

[a] Stamp charging.
[b] Top charging.
[c] Baghouse filter.
[d] Exhaust gas emitted during charging of coal.
[e] Exhaust gas emitted during pushing of coke.
[f] Exhaust gas emitted during combustion of coke-oven gas.

The stack gas samples were collected isokinetically by the PAH-sampling system (PSS) (Fig. 1), the design of which was based on the sampling system adopted by Chen, Bi, Mai, Sheng, and Fu (2004). The PSS consisted of a sampling probe, a cooling device (a long curved pipe 5 cm in diameter) and a sampler. One connector was made to connect the sampler with the end of the pipe. All the parts were made of stainless steel, and Teflon was used for all gaskets to avoid organic contamination. The sampler (Tianhong Intelligent Instrument Plant of Wuhan, China) used in this study, can simultaneously collect particulate and gaseous organic compounds using glass fiber filters (GFF, 20.3 cm × 25.4 cm) and polyurethane foam (PUF, 6.25 cm diameter × 8 cm height), respectively. The GFFs were baked at 500 °C for 5 h and stored in aluminum foil packages until used, and the PUFs were Soxhlet pre-extracted in dichloromethane (DCM) for 48 h.

All parts of the sampling system in contact with the flue gas were cleaned thoroughly before sampling and were checked for leakage after assembly. During sampling the probe was put into the proper stack sampling point, and the nozzle size of the probe was adjusted to make the sampling velocity similar to the flue velocity. The curved pipe was immersed in cool water, which further dropped the emission flue to ambient temperature. Little deposit was observed in the pipes (less than 1% of the total particles). The actual temperature of the stack flue gas was recorded every 10 min, and the average temperature of the sampled gas was 25 °C.

After sampling, all the filter samples were wrapped in baked aluminum foil, and the PUF plugs were stored in brown glass jars to minimize contamination and loss. At the end of the sampling trip, the samples were immediately transferred to a refrigerator, and stored frozen at −20 °C for a maximum period of 1 week before analysis. All the experiments for each sampling point in every plant were repeated at least four times to make sure that the results were reproducible.

2.2. Chemical analysis

All PUF and filter samplers were extracted for 48 h with DCM in a Soxhlet apparatus, and surrogate deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) were added prior to extraction. The organic extracts were then concentrated on a rotary evaporator and fractionated on a silica gel column. The PAH fraction was further concentrated to 1.0 mL with nitrogen. Internal standard pyrene-d_{10}

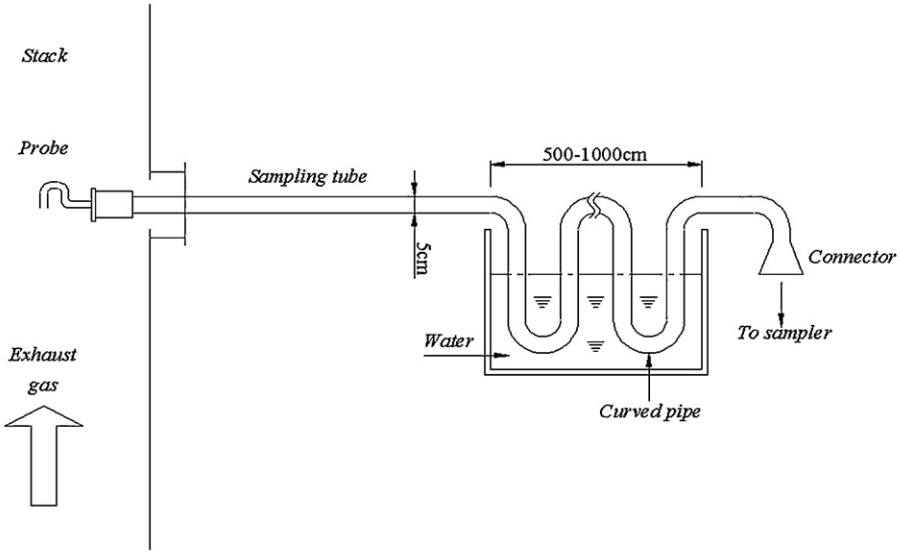

Fig. 1. PAH sampling system.

was added for quantification of individual PAHs. The PAH analyses were performed on a gas chromatograph equipped with a mass-selective detector (Thermo Fisher, Focus GC/DSQII) and a computer workstation. The capillary chromatographic column (DB-5MS) was 30 m × 0.25 mm inner diameter × 0.25 μm film thickness. This GC/MS was operated under the following conditions: injection volume 1 μL, splitless injection at 250 °C, ion source temperature at 300 °C; oven heating from 50 °C (3 min) to 200 °C at 15 °C/min, 200 °C (5 min) to 310 °C at 3 °C/min, and then constant at 310 °C for 10 min. The masses of primary and secondary ions of PAHs were determined in the scan mode. Quantitation of PAH was performed in the selected ion monitoring (SIM) mode.

The concentrations of the following 16 PAH species were determined in this study: 2-ring including naphthalene (Nap); 3-ring including acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PhA), anthracene (AnT); 4-ring including fluoranthene (FLuA), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr); 5-ring including benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*a*,*h*]anthracene (DbA); 6-ring including indeno[1,2,3-*cd*]pyrene (IND), benzo[*ghi*]perylene (BghiP). The concentration of total PAHs was defined as the sum of the concentrations of the above 16 PAH species for both particle and gaseous phases. To understand the distribution of PAH homologues for each collected sample, PAHs were also classified into three categories based on their molecular weights: low molecular weight (LMW-PAHs; containing two- to three-ring PAHs), middle molecular weight (MMW-PAHs; containing four-ring PAHs), and high molecular weight (HMW-PAHs; containing five- to six-ring PAHs).

2.3. Quality control

Surrogate deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) were added to all the samples prior to extraction to monitor procedural performance and matrix effects. The total recovery efficiencies of the PAHs ranged from 78.8% to 107.3%, averaging 92.1%, and mean relative standard deviation (%) of recovery efficiencies was up to 18%. Blank tests for PAHs were accomplished using the same procedure as the recovery-efficiency tests without adding the known standard solution before extraction. Analyses of field blanks including GFF and PUF revealed no detectable contamination.

Three breakthrough tests were investigated by adding an additional GFF and 1/3 PUF separately during the sampling processes. The additional GFF and 1/3 PUF were analyzed individually. The results showed that no significant PAH mass was collected in the additional GFF and PUF.

3. Results and discussion

3.1. PAH emission levels

Table 2 shows that the average concentration of total PAHs emission from coking process was 236.795 μg/m^3. The result was significantly higher than that found in the air near the coke plant (24.52 μg/m^3) (Khalili, Scheff, & Holsen, 1995), which is attributed to the discrepancies in sample characteristics (i.e., stack flue gas versus aerosol samples, the latter was collected 100 m directly downwind of a coke plant). Nap, AcPy, Flu, PhA and AnT were found to be the most abundant species in this study, accounting for 54.58%, 7.14%, 12.76%, 9.16% and 10.93% of the total PAH mass, respectively. NaP was identified as the most prominent PAH in the flue gas from coking. The reason may be that NaP has the lowest boiling point and the highest stability among the PAHs, allowing it to avoid decomposition during the coking process. The dominance of NaP has also been reported in ash from municipal solid waste incineration (Johansson & Bavel, 2003). Among the PAHs, BaP is usually considered an indicator because of its strong and direct carcinogenicity (Shen et al., 2010). In this investigation, the concentrations of BaP in the flue gases for CC, PC and CG were 0.736, 0.724 and 0.290 μg/m^3, respectively, which were higher than that emitted from the pyrolysis of scrap tires (Chen et al., 2007).

The total PAH concentration in the stack flue gas for CC (359.545 μg/m^3) was higher than those emitted from PC (124.197 μg/m^3) and CG (226.644 μg/m^3) (see Table 2). It is known that when the coal is discharged from the hoppers of the lorry car into the oven, substantial amounts of air are emitted from the carbonization chamber. The higher value of PAHs from CC may be attributed to incomplete combustion of the coal during charging. Liu, Zheng, et al. (2009) and Liu et al. (2010) also confirmed that the emissions of dioxin-like contaminants (i.e., PCDD/Fs, PCBs and PCNs) from CC were higher than those from PC, showing plausibleness of the results obtained from the present study. In addition, it should be noted that substantial amounts of PAHs were

Table 2
Concentrations of individual PAHs and BaP_{eq} for samples collected from all the studied stacks of coking processes (in μg/m^3, $n = 9$).

PAH	Mean concentration				BaP_{eq} concentration			
	PC	CC	CG	Average	PC	CC	CG	Average
NaP	61.928	158.344	167.456	129.243	0.062	0.158	0.167	0.129
AcPy	10.916	32.744	7.041	16.900	0.011	0.033	0.007	0.017
AcP	3.414	2.001	4.100	3.172	0.003	0.002	0.004	0.003
Flu	10.672	67.723	12.233	30.209	0.011	0.068	0.012	0.030
PhA	14.548	35.412	15.103	21.688	0.015	0.035	0.015	0.022
AnT	12.740	49.981	14.918	25.880	0.127	0.500	0.149	0.259
Pyr	2.352	4.915	2.046	3.104	0.002	0.005	0.002	0.003
FLuA	1.339	2.530	1.167	1.679	0.001	0.003	0.001	0.002
Chr	0.596	0.632	0.318	0.515	0.006	0.006	0.003	0.005
BaA	0.666	0.607	0.334	0.536	0.067	0.061	0.033	0.054
BbF	1.222	1.324	0.397	0.981	0.122	0.132	0.040	0.098
BkF	1.317	1.132	0.427	0.959	0.132	0.113	0.043	0.096
BaP	0.724	0.736	0.290	0.583	0.724	0.736	0.290	0.583
IND	0.610	0.590	0.243	0.481	0.061	0.059	0.024	0.048
DbA	0.488	0.332	0.287	0.369	0.488	0.332	0.287	0.369
BghiP	0.667	0.542	0.283	0.497	0.007	0.005	0.003	0.005
Total	124.197	359.545	226.644	236.795	1.838	2.248	1.082	1.723

emitted during the process of CG. In general, CO concentration can be used as a surrogate indicator for combustion efficiency. He (2006) reported that the levels of CO in exit gases from two coke plants were 14.3 and 776.9 mg/m^3, indicating that the combustion conditions were not very good in some coke plants. Thus, higher concentrations of PAHs from CG may be attributed to the incomplete combustion of coke-oven gases. Moreover, coke-oven gas may leak through damaged oven walls and mix with the combustion gases to increase emissions.

Fig. 2 shows that the total PAH concentration for CC in CP1 (292.438 μg/m^3) was significantly lower than that in CP3 (414.874 μg/m^3) and CP4 (371.322 μg/m^3), maybe due to different techniques of coal charging applied in these coke plants (stamp charging in CP1, top charging in CP3 and CP4). For stamp charging, the prepared coal is tamped into large briquettes before charging into the ovens, while for top charging, small pulverized coal particles containing free PAH, may be entrained by the steam and crude gases. Because of this, it is not so surprising to see that the mean total PAH concentration for CC in CP1 was lower than those in CP3 and CP4. However, it should be noted that total PAH emission ranking for PC among these coke plants (CP1 > CP2 > CP3 > CP4) was quite different from that for CC (CP3 > CP4 > CP1). The different PAH emission levels for PC may be attributed to the specified coking conditions at different coke plants (as listed in Table 1). Finally, we also found that PAH levels in the stack flue gas for CG varied significantly among these plants because of the differences in combustion condition of the coke-oven gases.

3.2. PAH composition profile

Fig. 3 demonstrates the distribution of PAH homologues from the coking process. It can be seen that PAH compositions in the stack flue gas for CC, PC and CG were consistently dominated by LMW-PAHs (accounting for 95.9%, 91.8% and 96.6% of total PAHs, respectively). The above results are not so surprising because either thermal decomposition or combustion was involved in these processes. However, it should be noted that instead of 2-ring PAH, which was a major contributor to LMW-PAHs for PC and CG, the 3-ring species was dominant for CC. He, Huang, Han, Li, and Li (2009) investigated the distribution characteristics of 16 PAHs in several typical coking coals used in China and reported that 3–5-ring PAHs were dominant (accounting for 83% of the total PAHs). Therefore, the relatively high contribution of 3-ring PAHs for CC found in the present work could be related to free PAHs trapped in coking coal.

Different PAH ratios for different catalogued sources may provide information helpful in identifying the specific sources of PAHs

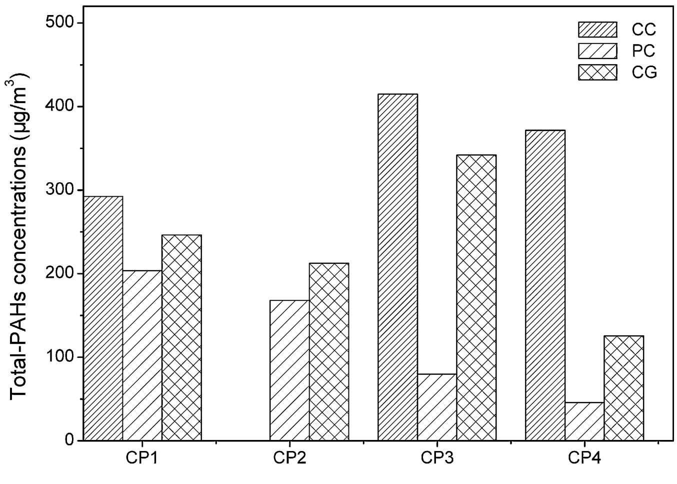

Fig. 2. PAH concentrations in flue gas emitted from different coking stages in different coke plants.

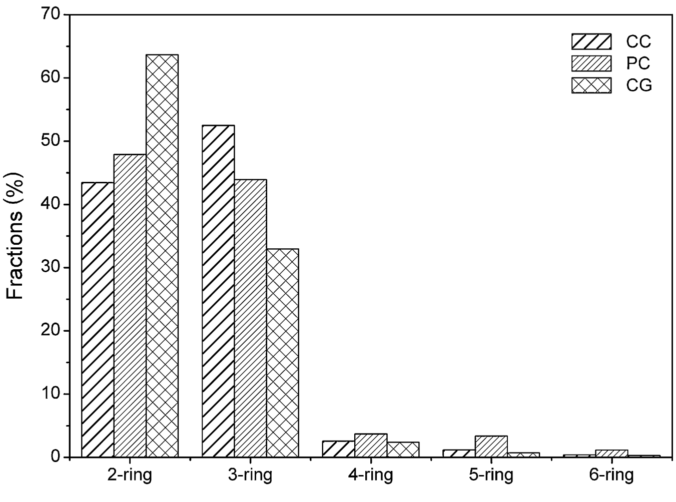

Fig. 3. PAH-homologue distributions from three emission stages in coke plants.

Table 3
PAH characteristic ratios for ashes from various industrial stacks.

Diagnostic ratio	CC[a]	PC[a]	CG[a]	Coal/coke	Coal burning	Cement production[i]	Bronze smelter[i]	Iron smelting[j]	Coke making[j]
BaP/BghiP	1.20	1.06	1.12	>1.25[c,g]	0.9–6.6[c,h]	0.85	0.59		1.14
BaA/Chr	1.15	1.32	1.44					0.74	0.9
Ant/(Ant + PhA)	0.43	0.49	0.43		0.24[c,e]			0.59	0.59
FluA/(FluA + Pyr)	0.40	0.41	0.50	0.53[b,c]	0.57[c,f]	0.50	0.32	0.69	0.62
IND/(IND + BghiP)	0.48	0.45	0.47	0.33[c,d]	0.56[c,g]	0.90	0.69	0.69	0.63
BaA/(BaA + Chr)	0.53	0.56	0.58	0.5[c,d]	0.46[c,f]	0.30	0.39	0.39	0.45

[a] This study.
[b] Saarnio et al. (2008).
[c] Kong et al. (2010).
[d] Tang et al. (2005).
[e] Guo et al. (2003).
[f] Galarneau (2008).
[g] Ravindra et al. (2008).
[h] Akyüz and Çabuk (2008).
[i] Manoli, Kouras, and Samara, 2004.
[j] Kong et al. (2011).

in the environment (Bzdusek, Christensen, Li, & Zou, 2004; Guo, Lee, Ho, Wang, & Zou, 2003; Ravindra et al., 2006). The estimated values for the most common ratios of particle PAHs are listed along with some literature values in Table 3. In general, the ratios obtained in the present study were similar to those reported by Kong et al. (2011) for coke processing course. The BaP/BghiP (1.20, 1.06 and 1.12 for CC, PC and CG, respectively), IND/(IND + BghiP) (0.48, 0.45 and 0.47 for CC, PC and CG, respectively) and BaA/(BaA + Chr) (0.53, 0.56 and 0.58 for CC, PC and CG, respectively) ratios obtained in the present study were similar to those for coal combustion. This conclusion is consistent with that of Zhu, Wang, Liu, and Zhu (2001), who documented that the pollution from coking was similar to that from coal combustion and rather different from those of other sources in terms of PAH ratios. Galarneau (2008) indicated that PAH isomer ratios showed substantial intra-source variability and inter-source similarity, and it was unlikely that any single ratio obtained from the literature will be representative of a source in different parts of the world emitting under different conditions. Therefore, diagnostic ratio method should be applied based on characteristic sources for specific regions.

3.3. Phase distribution of PAHs

PAHs exist in both vapor and particulate phases, and their distribution depends on temperature, properties of the adsorption surface, adsorption surface available, molecular weight and vapor pressure of the PAHs (Masclet, Mousier, & Nikolaou, 1986). As shown in Fig. 4, total PAHs in the gas phase for CC, PC and CG were 94.69%, 93.43% and 96.01%, respectively. These results agree well with previous observations (Yang et al., 1998; Yang, Lai, Hsiech, Hsueh, & Chi, 2002), indicating that the total PAHs were mostly present in the gas phase (92%) for various industrial stack gases. The higher percentage of gaseous PAHs may be due to the high temperatures involved in these industrial processes.

Baghouse filter (BF) is a commonly used device designed primarily to reduce the emission of air pollutants (especially PM). In the present study, all the coke plants are known to use BF for air-pollution control. However, a considerable mass fraction of PAH (94.71%) that existed in the gas phase revealed that although the air pollution control devices (APCD) used in these coke plants could be helpful in reducing the emission of particulate PAHs, they were not effective in controlling the emission of gaseous PAHs. Other studies have also demonstrated that the removal efficiency of gaseous PAHs by electrostatic precipitator and cyclone is far lower than that of particulate PAHs (Lee, Liow, Tsai, & Hsieh, 2002; Yang, Jung, Wang, & Hsieh, 2005). Teng, Wey, Chen, and Lu (2002) concluded that modifying the desulfurization sorbents with surfactants can improve the removal efficiency of PAHs. Therefore, it may be possible to decrease PAH emission by improving the dust removal condition of APCD in the coking process.

Fig. 5 shows the individual PAH fractions distributed in gas and particulate phases. LMW-PAHs (such as NaP, AcPy, Acp, Flu, PhA, AnT, Pyr, and FLuA) were dominant in the gas phase, while HMW-PAHs (such as BbF, BkF, BaP, IND, DbA, and BghiP) had relatively high contents in the particulate phase in the stack flue gas. A significant positive correlation was found between the proportion in the particulate phase and the molecular weight of the PAHs ($r = 0.866$, $P < 0.01$). The difference reveals that LMW-PAHs vaporize easily and exist predominantly in the gas phase, while the HMW-PAHs are less likely to vaporize and are instead adsorbed by particulates. In addition, it should be noted that the partition of HMW-PAHs between gaseous and particulate phase found in the present study strongly shifted towards the gaseous phase as compared with literature data on HMW-PAHs distribution in ambient air (Bi et al., 2003). The higher percentage of HMW-PAHs in the gas phase in this study may be due to the high temperature during coking processes. In addition, PAHs in the gas and particle phase might not be

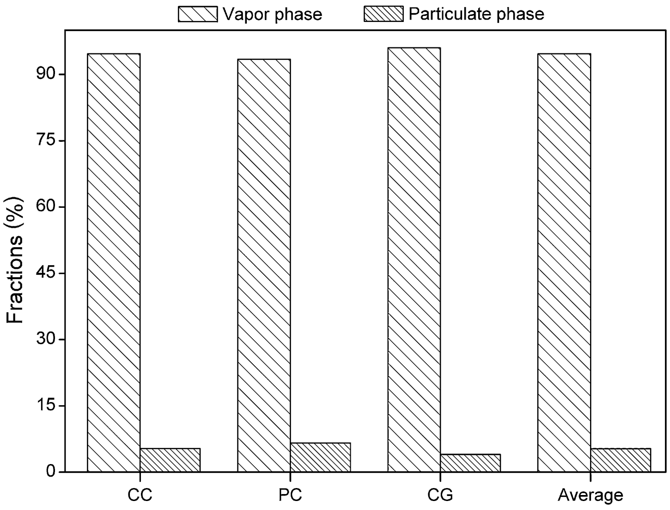

Fig. 4. Distributions of total-PAH contents in both gas and particulate phases for samples collected during coking processes.

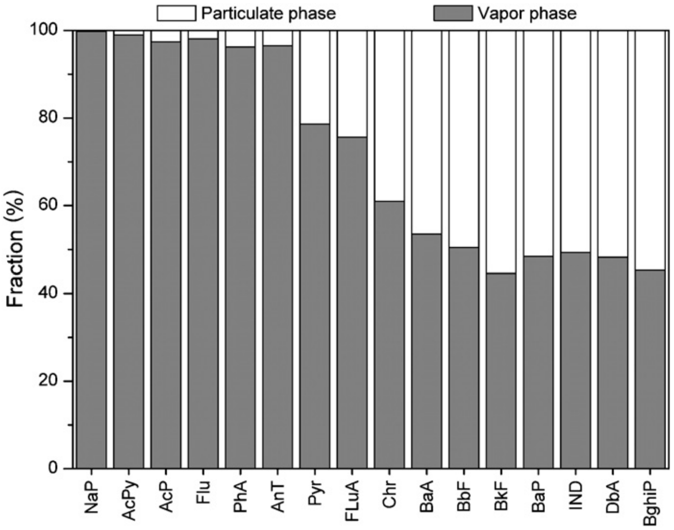

Fig. 5. Distributions of individual PAH fractions in gas and particulate phases.

in equilibrium in the present study, which could also be the reason of the higher percentage of HMW-PAHs in the gas phase.

3.4. Evaluation of BaP-equivalent carcinogenicity

The toxic equivalent factors (TEFs) estimated by Nisbet and LaGoy (1992) were adopted in the present study to obtain the toxic potency (with respect to that of BaP, benzo[*a*]pyrene) of each PAH species. The carcinogenic potency of the total PAHs (i.e., total BaP_{eq}) was estimated as the sum of individual BaP_{eq} of the 16 PAH compounds. Listed in Table 2 are the total BaP_{eq} concentrations in coking flue gases. It can be found that total BaP_{eq} concentrations for CC (2.248 $\mu g/m^3$) were markedly higher than that for PC (1.838 $\mu g/m^3$) and CG (1.082 $\mu g/m^3$), a result that is consistent with what we have found on total PAH mass concentrations in stack flue gases emitted from the three stages. The higher total BaP_{eq} concentrations emitted from the charging of coal indicate the importance of assessing PAH exposures for workers in coke plants in the future. As has been discussed, the fraction of HMW-PAHs contained in the stack flue gas for PC was higher than that emitted from CG (Fig. 3). It should also be noted that PAHs with higher molecular weights are known to have higher carcinogenic potencies. Based on this, it can be recognized that total BaP_{eq} concentrations for PC were higher than that exhausted from CG (Table 2). Furthermore, because of its high TEF value compared with the other PAH congeners, it is not so surprising to see that BaP was the most predominant toxic contributor for coking. In addition to BaP, DbA was also an important contributor to carcinogenic risk in emissions from coking process, which was consistent with the findings in the combustion of different residential coals (Liu, Dou, et al., 2009).

As shown in Fig. 6, the contributions of total particulate PAHs differed greatly among the three emission stages (34.59%, 35.98% and 18.72% for CC, PC and CG, respectively). However, it should be noted that contributions of particulate PAHs to the total BaP_{eq} concentrations for individual stages were significantly higher than the corresponding contributions to the total PAH mass concentrations. The above results can be explained as follows: (a) PAHs with higher molecular weights are known to have higher carcinogenic potencies and (b) the PAHs of high molecular weight are mainly in the particulate phase (see Fig. 5). The above result suggested that particle-bound PAHs did play an important part in total BaP_{eq} concentrations from the viewpoint of health-risk assessment. However, it should be noted that more than 60% of total BaP_{eq} concentrations resulted from the contributions of gaseous-phase PAHs for all studied sites. Therefore, the conclusion could be made that both particulate and gaseous PAHs should be taken into consideration when the potential toxicity risk of PAH pollution is assessed for coking processes.

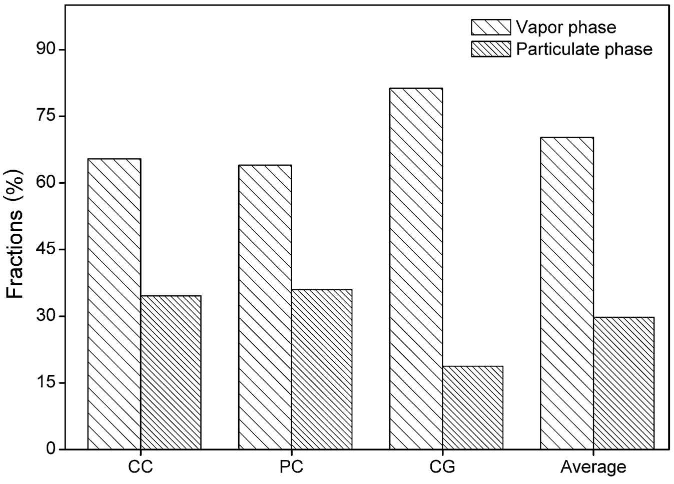

Fig. 6. Distributions of total BaP_{eq} concentrations in both gas and particulate phases in the flue gases.

3.5. PAH emission factors

Emission factor is an important parameter for estimating the total emission of a given pollutant from a given source and can be defined on the basis of the mass of PAH emitted per unit fuel consumed. The emission factor obtained in this study is calculated as follows:

$$\text{Emission factor} = \frac{\text{flow rate} \times \text{concentration} \times \text{emission time}}{\text{coal consumption}}.$$

The calculated emission factors for the investigated coke plants are listed in Table 4. For total PAHs, mean emission factors of 346.132 and 93.173 $\mu g/kg$ coal were found for CC and PC, respectively. Thus, the average emission factor for the sum of CC and PC was 439.305 $\mu g/kg$. It is interesting to compare emission factors of coking processes with those of other industries. It can be seen in Table 5 that the PAH emission factors (i.e., PC + CC) for coke plants

Table 4
Average PAH emission factors for the coke plants investigated (in $\mu g/kg$ coal charged, $n = 3$).

PAH	PC				CC		
	CP1	CP2	CP3	CP4	CP1	CP3	CP4
NaP	130.666	57.999	5.464	4.741	285.069	81.172	28.611
AcPy	17.520	9.146	2.955	0.795	116.905	6.501	6.251
AcP	4.208	3.779	0.703	0.355	4.641	0.815	0.377
Flu	16.537	8.631	3.941	0.331	164.269	38.584	8.501
PhA	18.455	14.240	5.621	0.350	81.047	15.474	6.362
AnT	18.284	14.073	3.645	0.335	79.168	35.147	6.309
Pyr	2.545	3.910	0.345	0.067	18.008	2.789	0.278
FLuA	1.639	2.106	0.181	0.046	10.165	1.359	0.120
Chr	1.254	0.476	0.053	0.066	4.368	0.066	0.023
BaA	1.250	0.728	0.047	0.057	4.185	0.064	0.022
BbF	2.723	1.161	0.058	0.096	9.509	0.087	0.045
BkF	2.437	1.076	0.073	0.217	7.641	0.098	0.058
BaP	1.502	0.527	0.062	0.096	4.925	0.073	0.037
IND	1.329	0.464	0.046	0.070	3.942	0.054	0.031
DbA	0.741	0.375	0.058	0.094	1.691	0.062	0.036
BghiP	1.250	0.532	0.059	0.098	3.355	0.069	0.037
ΣPAHs	222.340	119.224	23.313	7.813	798.882	182.415	57.098

Table 5
Emission factors of PAHs from various industrial sources (in μg/kg feedstock).

PAH source	Emission factor	Feedstock	Data source
Blast furnace	77.0	Coke	Yang et al. (1998)
Electric arc furnace	179	Waste steel	
Heavy oil plant	3970	Fuel oil	
Power plant	602	Bituminous coal	
Cement plant	132, 184	Cement raw or kiln feed	
Waste-tire pyrolysis	4000	Scrap tires	Chen et al. (2007)
Municipal waste incinerator	871	Municipal waste	Mi, Chiang, Lai, Wang, and Yang (2001)
Medical waste incinerator	24, 900, 85, 600	Medical waste	Lee et al. (2002)
Coking process (CC + PC)	439.305	Coal	This study

are significantly higher than those for various industrial stacks, except for the heavy oil plant and the power plant reported by Yang et al. (1998), but lower than those for waste-tire pyrolysis and waste incineration. These differences were mainly due to the differences in incoming fuel, manufacturing process and APCD. The emission factors obtained from the present study might be helpful in understanding the levels of PAH produced by the coking industry and in developing a PAH inventory.

4. Conclusions

Total PAH concentration in the stack flue gas for CC was higher than those collected from PC and CG, which was attributed to incomplete combustion of coal charged into the coke ovens. For the CC process stage, the concentration of PAHs emitted from CP1 (stamp charging) was lower than those from CP3 and CP4 (top charging). LMW-PAHs (Nap, AcPy, Flu, PhA, and AnT) were found to be the most abundant ones in the flue gases, and the fractions of MMW- and HMW-PAHs contained in the stack flue gas for PC were higher than those emitted from CC and CG. LMW-PAHs (such as NaP, AcPy, Acp, Flu, PhA, AnT, Pyr, and FLuA) were dominant in the gas phase, while HMW-PAHs (such as BbF, BkF, BaP, IND, DbA, and BghiP) had relatively significant mean concentrations in the particulate phase. The contribution of particulate PAHs to total $\mathrm{BaP_{eq}}$ concentrations (20%) was significantly higher than their contribution to the total PAH mass concentrations (5%). Emission factors of total PAHs in the investigated coke plants were 346.132 and 93.173 μg/kg coal for CC and PC, respectively.

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