



Characterization of PAHs and PCBs in Fly Ashes of Eighteen Coal-Fired Power Plants

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ABSTRACT

For the management of coal fly ashes (CFAs) from coal-fired power plants (CFPPs), characterization of PAHs and PCBs in CFAs is imperative. The 18 PAH and 86 PCB congeners in CFAs collected from 18 large-scale CFPPs in China were detected using GC/MS system. The PAH concentrations were in the range of 5.51–70.9 ng g⁻¹ for 16 CFPPs with individual block power capacity as 600 MW (IBPC-600), significantly lower than 886–916 ng g⁻¹ for 2 CFPPs with IBPC as 200 and 300 MW (IBPC-200/300). Both PAH and PCB congeners for 18 CFPPs were dominated by low molecular weight ones. The 3- and 2-ring PAHs, di-, tri- and tetra-PCBs were the predominant homologs. PAH profiles for 16 CFPPs with IBPC-600 were significantly different from other industrial stacks based on higher coefficients of divergence. The BaP-based toxic equivalency (BaP_{eq}) concentration and BaP-based equivalent carcinogenic power (BaPE) for 16 CFPPs with IBPC-600 were 0.834 ng g⁻¹ and 0.570, much lower than corresponding 20.5 ng g⁻¹ and 15.4 for 2 CFPPs with IBPC-200/300. No difference existed for Σ₈₆PCBs between CPFFs with IBPC-600 and -200/300, which ranged from 9.60 to 32.1 ng g⁻¹. Higher mean carcinogenic PAH concentrations for 2 CFPPs with IBPC-200/300 and PCBs-TEQ concentration for 18 CFPPs indicated the application of CFAs as soil amendment should be prohibited. The PAH concentrations for 18 CFPPs were well correlated with the total organic carbon (TOC) values, while PCB concentrations showed not this trend, indicated the different formation mechanism between PCBs and PAHs.

Keywords: PAHs; PCBs; Coal fly ash; Coal-fired power plant.

INTRODUCTION

China is the world-largest coal producer and consumer, which consumed 50.2% of the world coal in 2012 (Yao *et al.*, 2015). The huge quantity of CFAs produced from burning process of pulverized coal in CFPPs can be a problematic solid waste (Skousen *et al.*, 2013; Ram and Masto, 2014). CFA would be recognized as environmental pollutant if not put to beneficial use (Blissett and Rowson, 2012). In China, CFPPs accounted for 78% of the total power generation in 2012. Pandey and Singh (2010) reported as many as 100 million tons were generated in China for 2005 and only 45% of them were utilized. In China the same installed capacity as those for the whole 20th century would be completed in next 20 years (Shaheen *et al.*, 2014). Although the part of this increased demand would be met by renewable resources,

coal is still the dominant fuel for power generation in China and India (Lior, 2010). Annual CFAs generation in China has been increased during 2001–2015 and is still increasing. The predicted 580 million tons should be reached in 2015 (Yao *et al.*, 2014). Clearly the more and more CFAs must be disposed in future China.

Some recycling methods of CFA have been reported in recently documents (Blissett and Rowson, 2012; Shaheen *et al.*, 2014). The CFAs can be used as a soil amendment, catalysts and catalyst supports, or used in concrete and cement manufacturing. However, these applications only consume a small proportion of the CFAs. The rest more than half of CFAs have to be disposed in landfills (Sahu *et al.*, 2009; Yao *et al.*, 2015). The CFAs were often stockpiled in open area before landfill or storing in lagoons in the present China, and the large amounts of pollutants in CFAs could easily entered into different environmental medias. Higher unintentionally produced persistent organic pollutants (UP-POPs) levels have been found in CFAs from CFPPs (Ba *et al.*, 2009). The UP-POPs contained in CFAs could contaminate the soil, air and ground water if not treated properly (Yao *et al.*, 2015). The work burden of CFA disposal

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is becoming heavier due to its steadily risen production and uncertain properties in China. For the large-scale environmental safe use and disposal of CFAs, the detailed study on UP-POPs in CFAs is imperative (Sun *et al.*, 2006; Wang *et al.*, 2013).

PAHs are belong to POPs and have been a concern for their threats to people's health (Zhang *et al.*, 2009; Kong *et al.*, 2011; Wu *et al.*, 2014; Tiwari *et al.*, 2015; Huang *et al.*, 2016; Pongpiachan *et al.*, 2016), mainly originated from burning and pyrolytic processes (Chen *et al.*, 2014; Li *et al.*, 2014). Coal burning for power generation has been considered one of the most significant anthropogenic source of PAHs by some researchers (Mastral and Callén, 2000; Liu *et al.*, 2002; Arditoglou *et al.*, 2004; Sahu *et al.*, 2009). PCBs are a kind of classic POPs due to their high lipophilicity, toxicity and difficulty of degradation (Guo *et al.*, 2014; Liu *et al.*, 2014). Although CFPPs is a known PCBs emission sources (Jansson *et al.*, 2011; Li *et al.*, 2011, 2015), the PCBs emission characteristics in CFAs from CFPPs has not been studied extensively as other POPs in China. The significant difference of PCB profiles existed among the flue gases, CFAs and Aroclor mixtures, possibly resulted from different formation mechanisms, so the systematically research on PCBs in CFAs is needed (Jansson *et al.*, 2011). Sahu *et al.* (2009) reported the PAHs and PCBs levels in CFAs of CFPPs based on 5 Indian power plants. However, the data are not available for CFPPs in present China.

In present China, the CFPPs with lower IBPC are planned replaced by higher IBPC as 600 or 1000 MW in order to work

economically and protect environment effectively. IBPC-600 is becoming the mainstream unit in China and account for 39% of present CFPPs and this ratio will increase in future (Zhu *et al.*, 2014). The main aims of this study are to systematically investigate the PAHs and PCBs in CFAs from CFPPs with different IBPC in China.

The CFAs were collected from 18 CFPPs including 16 CFPPs with IBPC-600 with and 2 CFPPs with IBPC-200/300 across China. The 18 PAHs were detected in this study such as naphthalene (NaP), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[123-*cd*]pyrene (Ind), benzo[*ghi*]perylene (BghiP) and dibenz[*ah*]anthracene (DBA). The 86 PCB congeners including 12 dioxin-like PCBs (dl-PCBs) were detected in this study. The total organic carbon (TOC) was detected for each CFA sample to investigate the formation mechanisms of PAHs and PCBs.

MATERIALS AND METHODS

CFA Sample Collection and Preparation before Extraction

As the Fig. 1, the sampling locations for 18 CFPPs covered essentially the whole Chinese territory. Along with the rapid economic development and strict requirement for environmental protection in China, higher IBPC is becoming



Fig. 1. Sampling sites distribution map in China.

the mainstream generation units for Chinese CFPPs. In present China, IBPC-600 is the mainly representative generation unit and accounts 39% of all the coal-fired power generation units. The samples from 16 CFPPs with IBPC-600 were FA1-4 and FA7-18. The CFA samples of FA5 and FA6 were collected from 2 CFPPs with IBPC-200 and -300, respectively.

The CFA samples were collected systematically from 18 large-scaled CFPPs in China during January to October, 2015. The same systematic sampling method as Sahu *et al.* (2009) was adopted in this study. The samples were collected using a stainless spoon from the bottom piles of the electrostatic precipitators and then stored in sealed polyethylene bags. About 1 kg of sample for each CFPP was stored in amber glass jars pre-cleaned using solvents. Each sample was dried using a vacuum freeze dryer and weighed.

Sample Extraction for PAHs Analysis

The sample extraction and analysis procedures were used according to the EPA method TO-13A and detailed described in Kong *et al.* (2011). The 30 g fly ashes were ultrasonically extracted with dichloromethane, concentrated using a rotary evaporator, purified using a silica gel column and re-concentrated using a rotary evaporator. The HP6890 GC/5973i MS system with selected ion mode (SIM) was used to PAHs analysis. The chromatographic condition, temperature climbing program, PAH identification and quantification method were all same as Kong *et al.* (2011).

GC/MS system was processed using selected ion monitoring (SIM) mode with m/z as 129, 127 for NaP, 153, 152 for Acy, 151, 153 for Ace, 165, 167 for Fl, 179, 176 for Phe and Ant, 101, 203 for Flu and Pyr, 229, 226 for BaA, 226, 229 for Chr, 256, 126 for BbF and BkF, 253, 126 for BaP and BeP, 138, 227 for Ind, 139, 279 for DBA, 138, 227 for BghiP, 150, 301 for COR, respectively. The m/z values as 128, 154, 152, 166, 178, 178, 202, 202, 228, 228, 252, 252, 252, 252, 276, 278, 276, 300 were selected to quantify the PAHs as NaP, Acy, Ace, Fl, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, BeP, Ind, DBA, BghiP and COR, respectively.

Sample Extraction for PCBs Analysis

The standard solutions of PCBs and organic solvents used in this study were same as Li *et al.* (2015). The detailed sample analysis procedure was described in previous studies (Li *et al.*, 2011, 2015). The 60 g of sample was Soxhlet extracted with acetone: n-hexane (v:v = 1:1) for 24 h, concentrated by rotary vacuum evaporation, purified by a silica gel column and re-concentrated to 0.5 ml under a gentle N₂ stream before analysis. PCB-14, 65, 166 were spiked to samples before extraction as surrogate standards, 2,4,5,6-tetrachloro-m-xylene and PCB-209 were used as internal standards.

GC/MS system was processed using SIM mode with m/z as 222, 224 for di-PCBs, 256, 258 for tri-PCBs, 290, 292 for tetra-PCBs, 326, 328 for penta-PCBs, 360, 362 for hexa-PCBs, 394, 396 for hepta-PCBs, 428, 430 for octa-PCBs, 462, 464 for nona-PCBs and 498 for deca-PCBs, respectively. The

ions as 222, 256, 292, 326, 360, 394, 428, 464 498 were selected to quantify the homologs as di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and deca-PCBs, respectively.

Quality Control and Quality Assurance

For both PAH and PCB analyses, a procedural blank, a matrix-spiked sample, a sample duplicate and a solvent blank were processed every 5 samples. No any target compounds were detected in the procedural and solvent blank.

For PAH analysis, the method detection limits (MDLs) of 18 PAH congeners ranged from 0.05 for BaP to 0.60 ng g⁻¹ for NaP with the mean value as 0.16 ng g⁻¹. The recoveries for 18 PAH congeners in 4 matrix-spiked samples were in the range of 79–115% and the relative standard deviation (RSD) was lower than 12%. The recoveries for surrogate standard of 14-deuterium substituted terphenyl and 4-bromo-2-fluorobiphenyl were 97.20 ± 12.22% and 89.36 ± 11.66%, respectively. The method detection limits for 18 PAH congeners were ranged from

For PCB analysis, the recoveries for surrogate standard of PCB-14, 65, and 166 were 93 ± 15%, 89 ± 10 and 88 ± 13%, respectively. The recoveries for 86 PCB congeners in 4 matrix-spiked samples were all within 85–110% and the RSD was lower than 9%. The standard deviations for 4 pairs of repeated samples were all lower than 11%. The MDLs for 86 PCB congeners ranged from 2 to 33 pg g⁻¹ with the mean values as 7.54 pg g⁻¹.

RESULTS AND DISCUSSION

PAHs Concentrations in CFA Samples for 18 of Chinese CFPPs

The total amounts of 18 PAH congeners were ranged from 5.51 to 70.9 ng g⁻¹ (mean: 26.94 ng g⁻¹) for CFPPs with IBPC-600, and ranged from 886 to 916 ng g⁻¹ (mean: 901 ng g⁻¹) for CFPPs with IBPC-200/300 (Table 1). The results indicated the influence of different combustion condition, dust removal technique, the burn-up of feed coal among CFPPs with different IBPC values (Mastral *et al.*, 2000; Yang *et al.*, 2002; Kong *et al.*, 2011; Masto *et al.*, 2015).

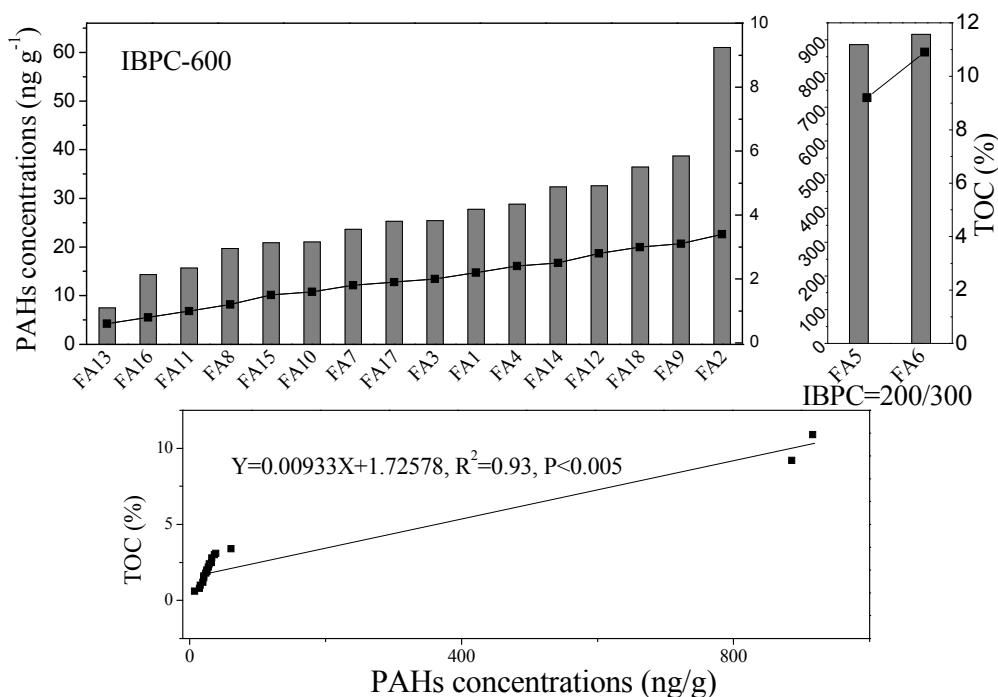
Sloss and Smith (1993) reported three formation mechanisms for PAHs during combustion process: 1) the penetration of feed coal containing-PAHs through combustion area without being destroyed; 2) reformation of ring structures; 3) de novo synthesis of PAHs via oligomerisation and cyclisation of acetylenes formed as a consequence of incomplete combustion.

The combustion temperature of coal among the 18 CFPPs were similar, the TOC concentration was the main reason result in this difference. The TOC and PAH concentrations for 18 CFPPs were well correlated ($R^2 = 0.93$, $p < 0.005$), indicated that the incompletely combustion of coal is the main formation mechanism of PAH in CFAs from CFPPs (Fig. 2). Wang *et al.* (2013) also reported they were well correlated ($R^2 = 0.96$) for PAH congeners in fly and bottom ashes of a Huainan CFPP in China. The unburned organic carbon was known as a stronger sorbent for PAHs than minerals (Karapanagioti *et al.*, 2000). The operating conditions of

Table 1. Statistic concentration values (ng g^{-1}) of individual PAH congener for 18 CFA samples.

PAH congener	CFPPs (FA1-4 and 7-18) IBPC-600				CFPPs (FA5 and 6) IBPC-200/300			
	Minimum	Maximum	Mean	SD ^a	Minimum	Maximum	Mean	SD ^a
Nap	0.920	30.2	8.31	6.91	151	647	400	350
Acy	n.d.	2.27	0.740	0.650	15.1	50.5	32.8	25.0
Ace	n.d.	1.97	0.850	0.280	17.3	27.5	22.4	7.19
Fl	0.600	5.73	2.49	0.850	43.0	51.4	47.2	5.94
BghiP	n.d.	0.780	0.280	0.121	0.200	38.8	19.5	27.3
Ind	n.d.	0.530	0.260	0.142	0.220	17.0	8.59	11.9
DBA	n.d.	0.330	0.200	0.0840	0.17	2.30	1.24	1.51
BbF	0.100	4.02	1.340	1.04	3.12	79.0	41.1	53.6
Phe	1.78	14.2	6.52	2.52	95.9	154.6	125.3	41.5
Ant	0.380	1.84	0.860	0.291	13.1	22.1	17.6	6.37
Flu	0.310	2.71	1.51	0.552	6.52	93.6	50.1	61.6
BaA	n.d.	0.670	0.510	0.148	1.83	44.2	23.0	30.0
Chr	0.630	1.64	1.04	0.251	3.77	46.0	24.9	29.9
Pyr	0.340	1.56	0.880	0.243	9.01	90.2	49.6	57.4
BaP	0.170	0.710	0.290	0.164	0.330	17.5	8.89	11.4
BkF	0.110	0.430	0.240	0.108	1.09	8.07	4.58	4.93
BeP	0.170	0.680	0.400	0.0910	2.97	34.1	18.5	22.0
COR	n.d.	0.600	0.230	0.122	n.d.	11.3	5.71	7.96
Total	5.51	70.9	26.9	14.6	886	916	901	21.6
LMW-PAHs	3.91	54.4	19.8	11.6	404	886	645	341
MMW-PAHs	1.63	5.24	3.94	0.922	21.1	274	148	179
HMW-PAHs	1.45	5.40	3.24	1.23	9.18	208	109	141

^aSD: standard deviation.

**Fig. 2.** PAH concentrations and TOC values for each CFA sample.

CFPPs such as combustion efficiencies and excess oxygen were the key factors controlling PAH emissions, more important than type of coal and plant design (Revelta *et al.*, 1999; Cheruiyot *et al.*, 2015).

Significant variation existed in PAH compositions among

the different combustion processes (Yang *et al.*, 2002; Kong *et al.*, 2011). Sohu *et al.* (2009) reported the mean value of $\Sigma_{14}\text{PAHs}$ for 5 Indian CFPPs was 355 ng g^{-1} , which was compared to that for FA5 (886 ng g^{-1}) and FA6 (917 ng g^{-1}) in this study, much higher than mean value for 18 CFPPs

with IBPC-600 (26.9 ng g^{-1}). The difference among IBPC values, combustion temperature, combustion technique and feed coal would be the explanation. The 26.9 ng g^{-1} for IBPC-600 was similar to the 32.1 ng g^{-1} for a CFPP with IBPC-600 located at Unchahar, India (Verma *et al.*, 2015) and 9.78 ng g^{-1} for a CFPP with IBPC-620 in Belgrade (Pergal *et al.*, 2014).

As for CFPPs with IBPC-200, the 916 ng g^{-1} was lower than that ($766 \mu\text{g g}^{-1}$) of PM_{10} fraction from a CFPP with IBPC-200 for heating in Liaoning province, China (Kong *et al.*, 2011), possibly resulted from the shorter residence time and larger surface of PM_{10} . Arditoglou *et al.* (2004) and Wang *et al.* (2015) also reported the reverse relationship between PAH levels and particle size of CFAs. Li *et al.* (2014) also reported higher PAH concentrations in fine particles were related to their long residence time in combustion area and high surface area.

The PAH levels of CFPPs were significantly lower than those of biomass fired power plants (BFPPs). Mastro *et al.* (2015) reported the concentrations of total 16 PAH congeners were $0.19\text{--}12.3 \text{ mg kg}^{-1}$ in fly ashes from 4 Indian BFPPs, which suggested the influence of IBPC values and biomass fuels on PAH concentrations.

For the individual PAH congener (IPC), Nap, Phe, Fl and Flu were the predominant congeners in CFAs from 18 CFPPs and accounted for 69.9% of $\Sigma_{18}\text{PAHs}$ (Table 1).

This IPC distribution possibly resulted from the different temperature of flue gas at the different part of boiler. For example, the flue gas temperature were 500°C for coal saving device, $800\text{--}900^\circ\text{C}$ for superheater, and $1200\text{--}1400^\circ\text{C}$ for boiler chamber, respectively. The highest concentration for each IPC appeared at a specific temperature. For examples, Ace at 700°C , NaP, Flu, Chr and BaP at 800°C and the others at 900°C . Ant, Phe and Flu increased when the temperature rise from 800 to 900°C (Peng *et al.*, 2016). Peng *et al.* (2016) reported the top congeners were Phe and Ant during the coal combustion process. Sahu *et al.* (2009) reported they were Fl, NaP, BaA, DBA and Flu for 5 Indian power

plants. Kong *et al.* (2011) reported they were Ant, Flu and Phe for PM_{10} collected from FA of a coal-fired power plant in Liaoning aim to provide heating for local residents using a re-suspension sampler. Singh *et al.* (2013) reported they were Ant, Flu, Pyr and BaA in the fly ash from combustion of rural used biomass fuel in Indo-Gangetic plains of India. The difference of IPC profiles possibly result from the combustion condition (such as turbulence, temperatures and residence time), fuel composition, and air flow (Sloss and Smith, 1993; Cheruiyot *et al.*, 2015; Košnař *et al.*, 2016; Peng *et al.*, 2016; Wen *et al.*, 2016).

Composition of PAH Homologs with Different Number of Rings

The PAH congeners were often divided to three classes including low, media and high molecular weight congeners, named as LMW-, MMW- and HMW-PAHs. The 2- and 3-ring congeners were belong to LMW PAHs, 4-ring congeners belong to MMW PAHs, and 5-, 6- and 7-ring congeners belong to HMW PAHs (Chen *et al.*, 2007; Kong *et al.*, 2011). Contents of LMW-, MMW- and HMW-PAHs were 19.8 ± 11.6 , 3.94 ± 0.920 , $3.24 \pm 1.23 \text{ ng g}^{-1}$ for 16 CFPPs with IBPC-600, 645 ± 341 , 148 ± 179 , $109 \pm 141 \text{ ng g}^{-1}$ for 2 CFPPs with IBPC-200/300. The LMW-, MMW- and HMW-PAHs accounted for 70.1%, 16.3% and 13.7% of the total PAHs among 18 CFPPs (Table 1). Previous studies also reported the LMW-PAHs were the major contributors in CFAs from CFPPs (Mastral *et al.*, 2000; Sahu *et al.*, 2009). The PAHs in CFAs from 18 CFPPs were dominated by 3- and 2-ring PAHs, accounted for 40.5% and 29.6% of the $\Sigma_{18}\text{PAHs}$, respectively (Fig. 3). The same conclusion was drawn for the PAHs in fly ashes from 4 Indian BFPPs (Mastro *et al.*, 2015). Among 18 CFPPs, FA5 and FA10 were dominated by 3- and 4-ring PAHs, the same homolog compositions were reported for PAHs in CFAs from a CFPP in Anhui, China (Li *et al.*, 2014). While the fly ashes from municipal solid waste and coal co-combustion process dominated by 3- and 4-ring PAHs (Peng *et al.*, 2016). The

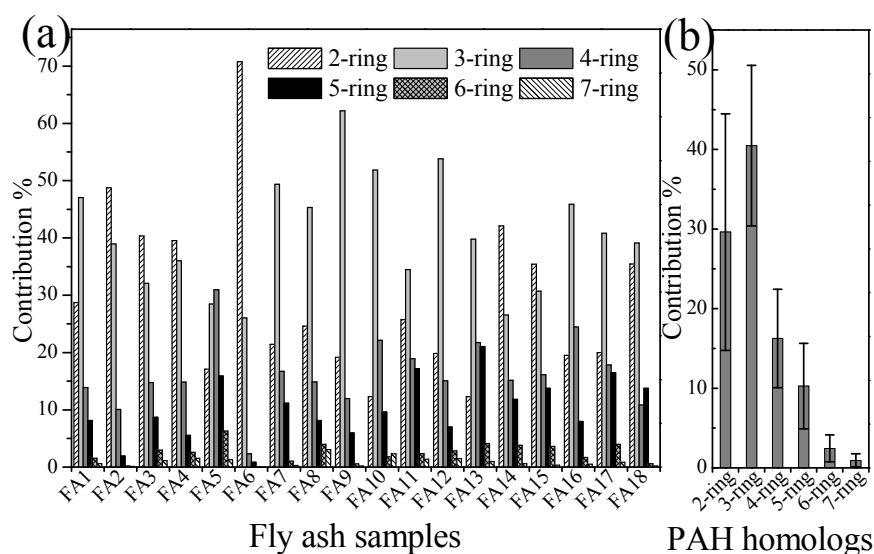


Fig. 3. Composition profiles of PAHs by ring size for a) individual fly ash samples and b) all the fly ash samples

difference of PAH homolog compositions reflected the difference among fuels, IBPC values and combustion conditions (Cheruiyot *et al.*, 2015; Masto *et al.*, 2015; Peng *et al.*, 2016).

Potential Toxicity Risk Assessment for PAHs

The values of BaP-based toxic equivalency concentration (BaP_{eq}), total carcinogenic PAHs (C-PAHs), BaP-based equivalent carcinogenic power (BaPE) and 2,3,7,8-tetrachlorodibenzodioxin (TCDD)-based toxic equivalency concentration (TEQ), are often calculated and used to evaluate the potential health risk of PAHs to human beings in previous studies (Chen *et al.*, 2004, 2007; Liu *et al.*, 2009; Kong *et al.*, 2011, 2013; Cheruiyot *et al.*, 2015). The calculated results of potential toxicity risk of PAHs in this study were shown in Table 2. The 16 CFPPs with IBPC-600 have a lower mean BaP_{eq} as 0.834 ng g⁻¹ than 20.5 ng g⁻¹ for 2 CFPPs with IBPC-200/300 due to higher PAH levels for CFPPs with IBPC-200/300. The significantly difference among ratios of BaP_{eq} of each PAH to that of BaP existed between CPFFs with IBPC-600 and -300/200, resulted from the difference of IPC concentrations and their BaP-based equivalent factors. DBA and BbF had the highest ratios as 77.5%, 46.6% for CPFFs with IBPC-600, while the ratios of BbF and Flu were 43.7% and 26.7% for CFPPs with IBPC-200/300. The total BaPE were 0.570 and 15.4 for CFPPs with IBPC-600 and -200/300, respectively. The incompletely combustion of coal in CFPPs with IBPC-200/300 possibly resulted in these difference.

As an indicator PAH, BaP was the most carcinogenic congener (Kong *et al.*, 2011). Its contents in this study

ranged from 0.170 to 0.710 ng g⁻¹ for CFPPs with IBPC-600, 1.33 to 17.46 ng g⁻¹ for CPFFs with IBPC-200/300, respectively. According to the commonly used PAH criterions for sensitive land use designated by the Swedish EPA as 0.3 mg kg⁻¹ for carcinogenic PAHs (Sun *et al.*, 2006; Zhao *et al.*, 2008; Kong *et al.*, 2011), the 3.88 ng g⁻¹ of carcinogenic PAHs for CFPPs as IBPC-600 was significantly lower than 0.3 mg kg⁻¹, while the corresponding value of 0.11 mg kg⁻¹ for CFPPs with IBPC-200/300 was comparable to 0.3 mg kg⁻¹. Therefore, the utilization of CFAs as soil amendment from CFPPs with IBPC-200/300 should be prohibited (Table 2).

Source Profiles of PAHs

To our knowledge, the data of PAH source profiles in CFAs from CFPPs across China were not available. Similarities between the PAH profiles in fly ashes from different industrial stacks were compared based on coefficient of divergence by previous documents, a self normalizing parameter to check the data points expansion for two data groups. The parameter was calculated as follows.

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2} \quad (1)$$

where j and k are referred to the two profiles for different emission sources, p was the number of detected PAH congeners, and x_{ij} and x_{ik} were the mean mass concentrations of compound i for j and k (Wongphatarakul *et al.*, 1998; Kong *et al.*, 2011).

Table 2. BaP_{eq} and BaPE for CFPPs with different IBPC and BaP_{eq} ratios for individual PAH congener.

PAHs	TEF ^b	BaP _{eq} (%) ^a	
		CFPPs with IBPC-600	CFPPs with IBPC-200/300
Phe	0.005	11.4	6.67
Ant	0.005	1.50	0.934
Flu	0.05	26.4	26.7
Pyr	0.001	0.306	0.528
BaA	0.005	0.889	1.23
Chr	0.03	10.9	7.95
BbF	0.1	46.6	43.7
BkF	0.05	4.18	2.44
BaP	1.0	100	100
Ind	0.1	9.20	9.15
DBA	1.1	77.5	14.5
BghiP	0.02	1.98	4.15
Total C-PAHs ^c (ng g ⁻¹)		3.88	113
BaP _{eq} concentration (ng g ⁻¹)		0.834	20.5
BaPE ^d		0.570	15.4

^a The ratio of BaP based toxic equivalency concentration for individual PAH (i) to that of BaP (BaP_{eq}, %) is derived as

$$\text{followed: } BaP_{eq,i} (\%) = \frac{PAH_{i,TEF} \times PAH_{i,EF}}{PAH_{BaP,TEF} \times PAH_{BaP,EF}}$$

^b BaP based toxic equivalent factors are referred to Liu *et al.* (2009) and Kong *et al.* (2011).

^c C-PAHs: carcinogenic PAHs including BaA, Chr, BbF, BkF, BaP, Ind and DBA.

^d The BaP-equivalent carcinogenic power (BaPE) for the total PAHs: BaPE = BaA × 0.06 + B[b,k]F × 0.07 + BaP + DBA × 0.6 + Ind × 0.08 (Chen *et al.*, 2004; Liu *et al.*, 2009; Kong *et al.*, 2011).

Source profiles of j and k were similar if the CD_{jk} approaches zero and they were significantly different if it approaches one (Wongphatarakul *et al.*, 1998). Wongphatarakul and Kong thought the CD of 0.269 and < 0.3 suggested the similarity between two source profiles in their studies (Wongphatarakul *et al.*, 1998; Kong *et al.*, 2011).

In this study, the CD_{jk} were calculated for CFAs from 16 CFPPs with IBPC-600 and fly ashes from other industrial stacks (Sahu *et al.*, 2009; Kong *et al.*, 2011). They were 0.645 for CFPPs vs. coke production, 0.674 for CFPPs vs. iron smelting process, 0.587 for CFPPs vs. 5 India CFPPs and 0.608 for CFPPs vs. BFPPs, respectively. These higher CD_{jk} values indicated the significantly difference existed between the Chinese CFPPs with mainstream IBPC and other industrial stacks. As shown in Fig. 4, the difference among the mass concentrations of Nap, Phe and Fl possibly resulted in higher CD_{jk} values.

PAH Diagnostic Ratios

The diagnostic ratios (DRs) were often used to identify the PAH emission sources and the use and selection of DRs in PAH source apportionment was described elsewhere

(Ravindra *et al.*, 2008; Tobiszewski and Namiesnik, 2012). The DRs were used to replace the PAHs profiles for emission sources although the PAHs profiles were always different among PAHs sources, to eliminate the effect of chemical reactions with other atmospheric pollutants. The DRs widely used to investigate PAH origins were calculated and listed in Table 3.

The PAH DRs for CFPPs with IBPC-600 and -200/300 were generally similar. The PAHs DRs for different industrial stacks varied significantly each other. The values of Ant/(Ant + Phe), Flu/(Flu + Pyr), Ind/(Ind + BghiP), BaP/BghiP, BaA/(BaA + Chr) in this study were similar with the corresponding reported values for coal burning (Guo *et al.*, 2003; Akyüz and Çabuk, 2008; Galarneau *et al.*, 2008; Ravindra *et al.*, 2008; Kong *et al.*, 2010; Finardi *et al.*, 2015). The ratios of Ind/(Ind + BghiP) and BaP/BghiP for CFPPs in this study were different from those of cement production (Manoli *et al.*, 2004). The ratios of BaP/BghiP, Pyr/BaP and BaA/BaP for Chinese 18 CFPPs were significantly different from Indian 5 CFPPs (Sahu *et al.*, 2009). Also the ratios of BaA/Chr, BbF/BkF, BaP/BghiP and BaA/BaP for Chinese 18 CFPPs were significantly different from those of an Indian BFPP (Masto *et al.*, 2015).

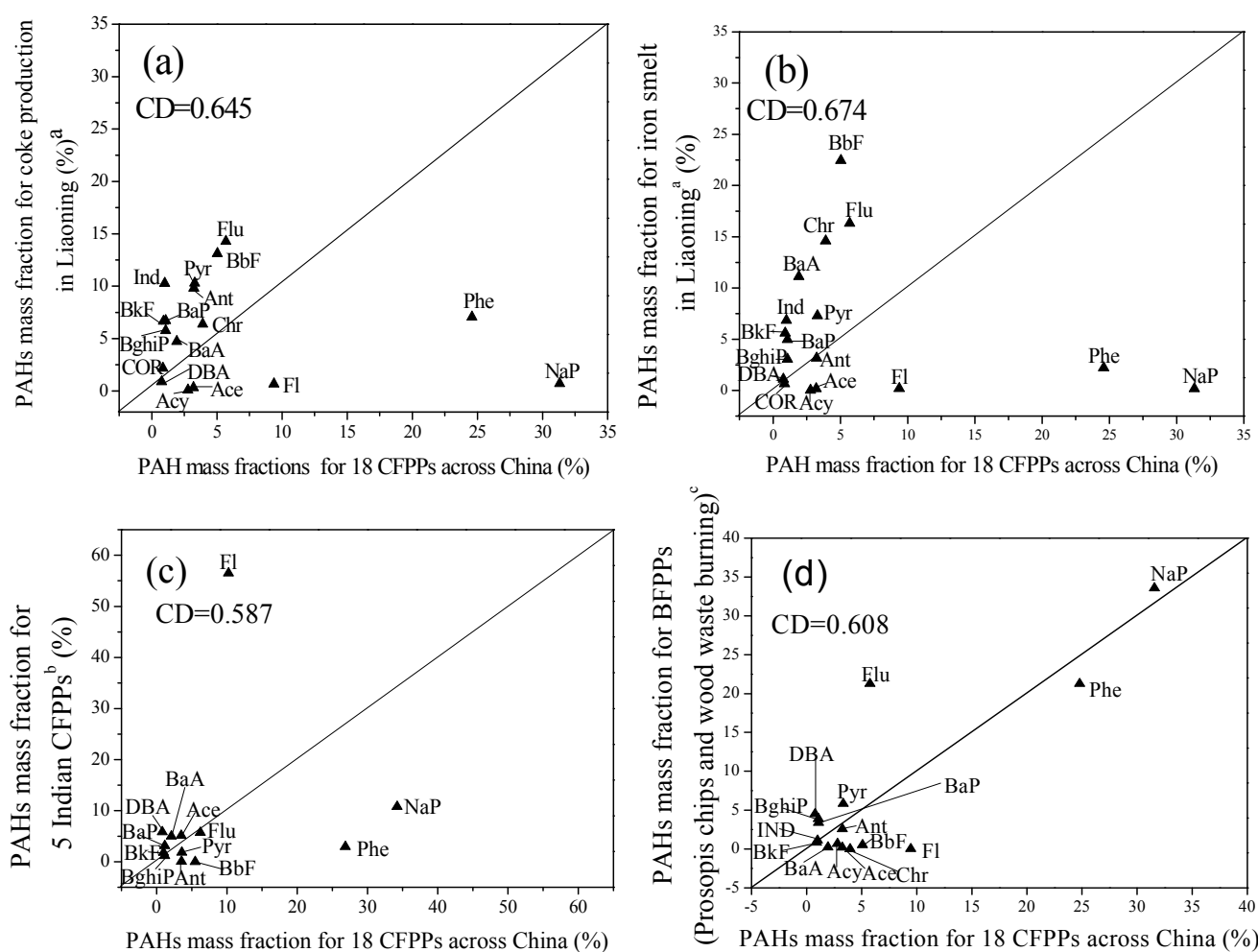


Fig. 4. Similarity comparison of PAH profiles in fly ashes for different industrial stacks (^a Kong *et al.*, 2011; ^b Sahu *et al.*, 2009; ^c Masto *et al.*, 2015).

Table 3. Diagnostic ratios for several PAHs for ashes from various industrial stacks.

Diagnostic ratios	CFPPs 600 MW (this study)	CFPPs 200/300 MW (this study)	Coal burning	Cement Production ^g	BFPP 18 MW ^h	BFPP 7.5 MW ^h	Indian 5 CFPPs ⁱ
Ant/(Ant + Phe)	0.14 ± 0.08	0.12 ± 0.00	0.24 ^{a,b}	--	0.11	0.09	0.03
Flu/(Flu + Pyr)	0.69 ± 0.08	0.59 ± 0.10	0.57 ^{b,c}	0.50	0.78	0.53	0.75
BaA/Chr	0.53 ± 0.10	0.72 ± 0.14	--	--	1.24	--	--
BbF/BkF	6.56 ± 1.12	6.32 ± 1.54	--	--	0.64	2.04	--
Ind/BghiP	1.34 ± 0.41	0.76 ± 0.46	--	--	0.29	--	--
Ind/(BghiP + Ind)	0.53 ± 0.09	0.41 ± 0.05	0.56 ^{b,d} , 0.5–0.7 ^e	0.90	0.22	--	--
BaP/BghiP	1.70 ± 0.69	1.05 ± 0.04	0.9–6.6 ^f	0.85	0.87	--	2.67
BaP/COR	1.96 ± 0.48	2.96 ± 0.50	--	--	--	--	--
Pyr/BaP	3.96 ± 2.33	5.98 ± 1.14	--	--	1.72	241.91	0.59
BaA/(BaA + Chr)	0.33 ± 0.06	0.41 ± 0.11	0.35–0.5 ^e	0.30	--	0.55	--
BaA/BaP	2.46 ± 0.41	2.08 ± 0.91	--	--	0.07	5.57	0.59
BaP/(BaP + Chr)	0.21 ± 0.05	0.27 ± 0.01	--	--	--	0.18	--

^a Guo *et al.*, 2003; ^b Kong *et al.*, 2010; ^c Galarnau, 2008; ^d Ravindra *et al.*, 2008; ^e Finardi *et al.*, 2015; ^f Akyüz and Çabuk, 2008; ^g Manoli *et al.*, 2004; ^h Mastro *et al.*, 2015; ⁱ Sahu *et al.*, 2009.

Concentrations, Toxic Equivalency, and Homolog Compositions of PCBs from CFPPs

As shown in Fig. 5(a), the Σ_{86} PCBs for 18 CFPPs ranged from 9.60 ng g⁻¹ for FA10 to 32.1 ng g⁻¹ for FA11 with the mean value as 16.0 ng g⁻¹. There were no significantly differences for PCBs levels existed between CFPPs with IBPC-200/300 and IBPC-600. Among 86 PCB congeners, 34 PCBs were not detectable in all the 18 CFPPs (Table 4). As shown in Table 4, the top PCB congeners for all the 18 CFPPs were PCB-4/10, -28, -6, 118, -169 and -52, the average concentration of these congeners for 18 CFPPs was 9.36 ng g⁻¹. As shown in Fig. 5(b), The CFAs from 18 CFPPs were dominated by LMW-PCBs with di-, tri- and tetra-PCBs, which contributed 28.7%, 35.6% and 10.2% to Σ_{86} PCBs.

Seven indicator PCB congeners (IPCBs) including PCB-

28, 52, 101, 118, 138, 153, and 180 were commonly measured and often compared in PCBs analysis (Li *et al.*, 2011). In this study, the Σ IPCBs ranged from 1.72 for to 6.09 ng g⁻¹ with a mean value as 2.75 ng g⁻¹, which were weak correlated with total PCBs ($R^2 = 0.16$). The lower correlation coefficient was possibly attributed to the formation mechanism of PCBs in coal combustion process, while the IPCBs were mainly contained in the conventional PCB products. Li *et al.* (2011) also reported this lower coefficient for atmospheric PCBs in east Tianjin due to the PCB emissions from new sources.

The 11 dioxin-like PCBs (dl-PCBs) except PCB-77 such as PCB-81, -105, -114, -118, -123, -126, -156, -157, -167, -169 and -189 were all detected in this study, and the TEQ was calculated for each dl-PCB. The toxic equivalency (TEQ) concentration was calculated for each dl-PCB through multiplying its concentration by its WHO 2005 toxic

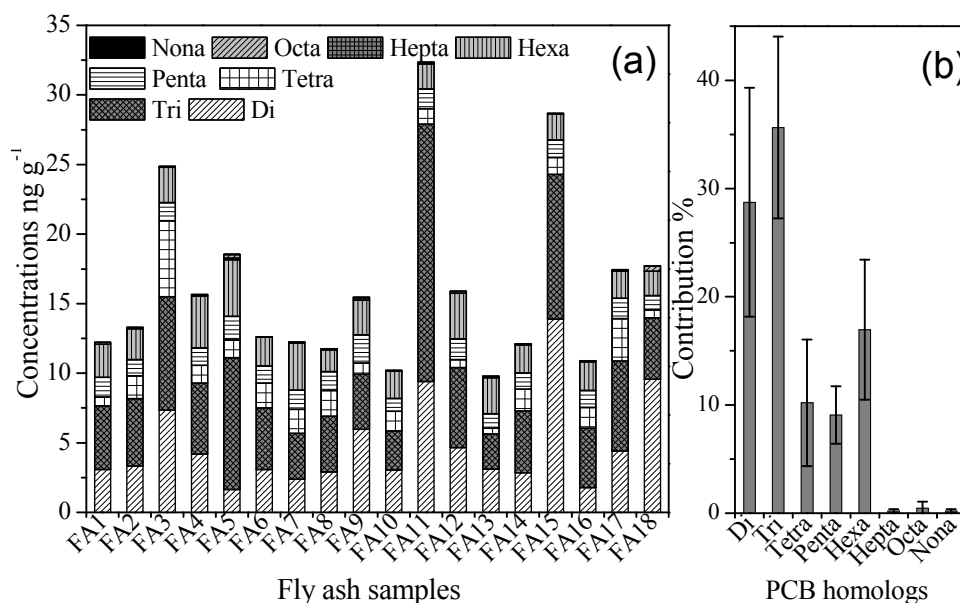


Fig. 5. (a) Concentrations of PCBs with different chlorine atoms and total PCBs in CFA from each CFPP and (b) PCB homologs distribution in CFA from 18 CFPPs.

Table 4. Statistic values of individual PCB congener in CFA from 18 CFPPs ($\mu\text{g g}^{-1}$).

PCBs	Min	Max	Mean \pm SD ^a	PCBs	Min	Max	Mean \pm SD ^a
PCB4/10	400	7090	2530 \pm 1640	PCB83	n.d.	n.d.	n.d.
PCB7/9	n.d.	1010	228 \pm 210	PCB97	n.d.	405	29.6 \pm 95.5
PCB6	300	6210	1490 \pm 1010	PCB81	34.8	100	50.0 \pm 18.5
PCB5/8	n.d.	299	93.3 \pm 88.6	PCB87	21.5	124	48.7 \pm 41.2
PCB19	601	4250	662 \pm 588	PCB85	n.d.	128	29.6 \pm 85.5
PCB12/13	n.d.	2260	521 \pm 321	PCB77	n.d.	n.d.	n.d.
PCB18	189	6130	1160 \pm 895	PCB110	n.d.	n.d.	n.d.
PCB15	n.d.	534	40.0 \pm 71.2	PCB144/135	n.d.	n.d.	n.d.
PCB17	n.d.	412	38.7 \pm 89.1	PCB123	9.82	150	103 \pm 49.4
PCB16/32	391	1300	793 \pm 553	PCB149	n.d.	n.d.	n.d.
PCB26	100	1130	461 \pm 232	PCB118	299	607	400 \pm 80.8
PCB28	1200	5420	2190 \pm 990	PCB114	n.d.	268	173 \pm 160
PCB31	n.d.	n.d.	n.d.	PCB131	n.d.	n.d.	n.d.
PCB33/53	n.d.	619	1910 \pm 197	PCB153/132	n.d.	n.d.	n.d.
PCB22	100	3290	356 \pm 772	PCB105	100	375	216 \pm 57.6
PCB45	n.d.	n.d.	n.d.	PCB138/163	n.d.	n.d.	n.d.
PCB52	181	5250	1270 \pm 1150	PCB126	196	301	211 \pm 32.3
PCB49	n.d.	n.d.	n.d.	PCB128	n.d.	n.d.	n.d.
PCB47+48	n.d.	n.d.	n.d.	PCB167	74.3	1450	223 \pm 324
PCB44	n.d.	n.d.	n.d.	PCB174	n.d.	n.d.	n.d.
PCB37+42	230	1140	419 \pm 225	PCB171/202	n.d.	90.2	15.3 \pm 28.0
PCB41+71+64	n.d.	n.d.	n.d.	PCB156	n.d.	44.9	9.11 \pm 13.7
PCB100	n.d.	n.d.	n.d.	PCB157	200	1200	301 \pm 500
PCB74	n.d.	n.d.	n.d.	PCB172	n.d.	n.d.	n.d.
PCB76+70	n.d.	n.d.	n.d.	PCB180	n.d.	n.d.	n.d.
PCB66+95	n.d.	n.d.	n.d.	PCB201	n.d.	n.d.	n.d.
PCB91	n.d.	n.d.	n.d.	PCB169	551	2350	1050 \pm 545
PCB56+60	n.d.	n.d.	n.d.	PCB170/190	n.d.	215	55.0 \pm 57.3
PCB92	n.d.	125	38.9 \pm 43.1	PCB199	n.d.	211	18.3 \pm 49.8
PCB84	n.d.	154	67.9 \pm 36.5	PCB189	325	1330	613 \pm 3983
PCB89	56.8	489	179 \pm 101	PCB207	n.d.	88.5	28.7 \pm 25.3
PCB101	n.d.	99.9	10.2 \pm 9.87	PCB194	n.d.	360	45.1 \pm 91.4
PCB99	n.d.	82.9	9.21 \pm 10.9	PCB205	n.d.	n.d.	n.d.
PCB119	n.d.	54.2	12.0 \pm 13.2	PCB206	n.d.	n.d.	n.d.

^a SD: Standard deviation.

equivalent factor (TEF) for human and mammals (Li *et al.*, 2011, 2015). The sum of 11 dl-PCBs ranged from 2.23 ng g^{-1} for FA8 to 6.52 ng g^{-1} for FA5 with the mean value as 3.35 ng g^{-1} , which were in the range of 0.00–13.8 ng g^{-1} for dl-PCBs in fly ashes from municipal solid waste incinerators (MSWI) in Korea reported by Shin and Chang (1999), higher than 1.65 ng g^{-1} for 15 large-scale MSWIs in China reported by Pan *et al.* (2013) and 0.52–2.3 ng g^{-1} for 4 MSWIs in China reported by Wu *et al.* (2016). While Cobo *et al.* (2009) reported the concentration of dl-PCBs as high as 49.0 ng g^{-1} for FA from a MSWI in Medellin, Colombia. These differences for dl-PCB concentrations were possibly resulted from the different combustion condition and fuel components among different incinerators. As shown in Fig. 6(a), the top dl-like PCBs were PCB-169, -189, -118 and -157, the corresponding concentrations were 1.05, 0.61, 0.40 and 0.30 ng g^{-1} , respectively. As shown in Fig. 6(b), PCB-169 and -126 have the higher TEQ concentrations as 31.5 and 21.1 pg g^{-1} due to their high concentration and TEF values, which contributed 59.8% and 40.1% to the total TEQ

concentration. The TEQ concentrations for 18 CFPPs in the range of 38.8–78.6 pg g^{-1} (mean: 52.6 pg g^{-1}), significantly higher than 4 pg g^{-1} designated by Canada for soil quality (CCME, 2007), which did not supports their suitability for soil amendment.

CONCLUSIONS

The 18 PAH and 86 PCB congeners in CFAs collected from 18 large-scale CFPPs across China were detected using GC/MS system. The $\Sigma 18\text{PAHs}$ ranged from 5.51 to 70.9 ng g^{-1} with the mean value as 26.9 ng g^{-1} for 16 CFPPs with IBPC-600 and from 886 to 916 ng g^{-1} with the mean value as 901 ng g^{-1} for 2 CFPPs with IBPC-200/300. The PAHs in CFAs from 18 CFPPs were dominated by 3- and 2-ring congeners, which accounted for 40.5% and 29.6%, respectively. For the individual PAH, Nap, Phe, Fl and Flu were the predominant congeners in CFAs from Chinese 18 CFPPs and accounted for 69.9% of $\Sigma 18\text{PAHs}$. PAH profiles for 16 CFPPs with IBPC-600 were significantly different

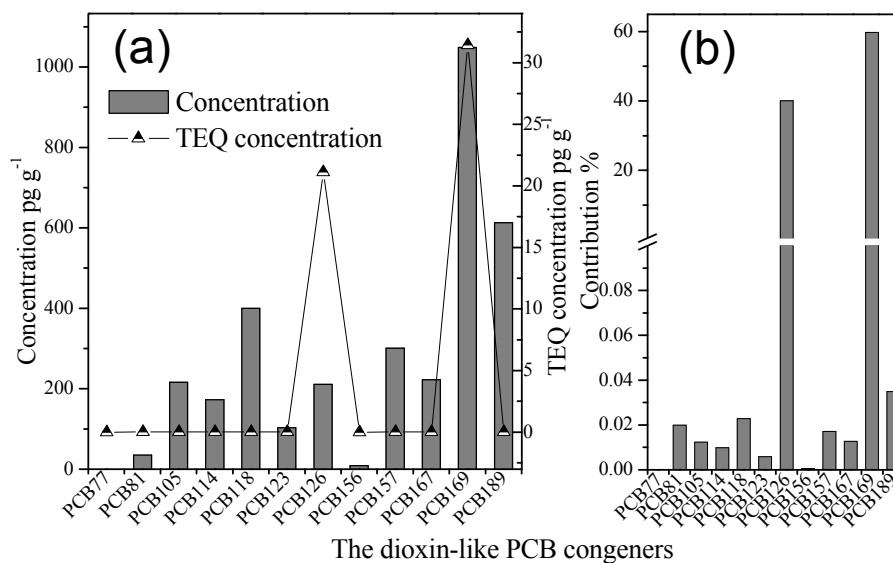


Fig. 6. (a) The concentration, TEQ concentration, and (b) TEQ contribution for 12 dioxin-like PCBs.

from the other industrial stacks such as coke production, iron smelting process, Indian 5 CFPPs and 4 BFPPs with higher coefficients of divergence as 0.645, 0.674, 0.587 and 0.608, respectively. The total BaP-based toxic equivalency (BaP_{eq}) concentration and BaP-based equivalent carcinogenic power (BaP_{eq}) for CFPPs with IBPC-600 were 0.834 ng g⁻¹ and 0.570, lower than corresponding mean values of 20.5 ng g⁻¹ and 15.4 for 2 CFPPs with IBPC-200/300. The diagnostic ratios (DRs) of CFPPs with IBPC-600 and -200/300 were generally similar. The DRs of Ant/(Ant + Phe), Flu/(Flu + Pyr), Ind/(Ind + BghiP), BaP/BghiP, BaA/(BaA + Chr) in this study were all similar with the corresponding reported values for coal burning. The DR values for different industrial stacks varied significantly each other, such as BaP/BghiP, Pyr/BaP and BaA/BaP for Chinese 18 CFPPs were significantly different from Indian 5 CFPPs.

No significant difference existed for total PCB concentrations between CFPPs with IBPC-600 and -200/300. The sum of 86 PCB congeners for 18 CFPPs ranged from 9.60 ng g⁻¹ for FA10 to 32.1 ng g⁻¹ for FA11 with the mean value as 16.0 ng g⁻¹. PCB-4/10, -28, -6, -18, -169, -52 were the predominant congeners for 18 CFPPs. The CFAs from 18 CFPPs were dominated by LMW-PCBs with di-, tri- and tetra-PCBs contributed 28.7%, 35.6% and 10.2% to Σ₈₆PCBs. PCB-169 and -126 have the highest TEQ concentrations as 31.5 and 21.1 pg g⁻¹, respectively. The PAHs concentrations were well correlated with the TOC ($R^2 = 0.934$, $p < 0.005$) and PCBs showed not this trend ($R^2 = 0.063$, $p < 0.005$), indicated the different formation mechanism between PCBs and PAHs.

Higher carcinogenic PAH levels for CFPPs with IBPC-200/300 and PCB TEQ concentrations for 18 CFPPs indicated the using of CFAs as soil amendment should be prohibited.

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REFERENCES

- Akyüz, M. and Çabuk, H. (2008). Particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey. *Sci. Total Environ.* 405: 62–70.
- Arditsoglou, A., Petaloti, C., Terzi, E., Sofoniou, M. and Samara, C. (2004). Size distribution of trace elements and polycyclic aromatic hydrocarbons in fly ashes generated in Greek lignite-fired power plants. *Sci. Total Environ.* 323: 153–167.
- Ba, T., Zheng, M.H., Zhang, B., Liu, W.B., Liu, K. and Xiao, L.F. (2009). Estimation and characterization of PCDD/Fs and dioxin-like PCBs from secondary copper and aluminum metallurgies in China. *Chemosphere* 75: 1173–1178.
- Blissett, R.S. and Rowson, N.A. (2012). A review of the multi-component utilization of coal fly ash. *Fuel* 97: 1–23.
- CCME (Canadian Council of Ministers of the Environment) (2007). Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health, Winnipeg.
- Chen, Y.J., Bi, X.H., Mai, B.X., Sheng, G.Y. and Fu, J.M. (2004). Emission characterization of particulate/gaseous phases and size association for polycyclic aromatic hydrocarbons from residential coal combustion. *Fuel* 83: 781–790.
- Chen, S.J., Su, H.B., Chang, J.E., Lee, W.J., Huang, K.L., Hsieh, L.T., Huang, Y.C., Lin, W.Y. and Lin, C.C. (2007). Emissions of polycyclic aromatic hydrocarbons (PAHs) from the pyrolysis of scrap tires. *Atmos. Environ.* 41: 1209–1220.
- Chen, W.H., Han, J., Qin, L.B., Furuuchi, M. and Mitsuhiro, H. (2014). The emission characteristics of PAHs during

- coal and sewage sludge co-combustion in a drop tube furnace. *Aerosol Air Qual. Res.* 14: 1160–1167.
- Cheruiyot, N.K., Lee, W.J., Mwangi, J.K., Wang, L.C., Lin, N.H., Lin, Y.C., Cao, J.J., Zhang, R.J., Guo, P. and Chang, C. (2015). An overview: Polycyclic aromatic hydrocarbon emissions from the stationary and mobile sources and in the ambient air. *Aerosol Air Qual. Res.* 15: 2730–2762.
- Cobo, M., Gálvez, A., Conesa, J.A. and de Correa, C.M. (2009). Characterization of fly ash from a hazardous waste incinerator in Medellín, Colombia. *J. Hazard. Mater.* 168: 1223–1232.
- Finardi, S., Radice, P., Cecinato, A., Gariazzo, C., Gherardi, M. and Romagnoli, P. (2015). Seasonal variation of pahs concentration and source attribution through diagnostic ratios analysis. *Urban Clim.* 2002: 873–874.
- Galarneau, E. (2008). Source specificity and atmospheric processing of airborne PAHs: Implications for source apportionment. *Atmos. Environ.* 42: 8139–8149.
- Guo, H., Lee, S.C., Ho, K.F., Wang, X.M. and Zou, S.C. (2003). Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmos. Environ.* 37: 5307–5317.
- Guo, C.J., Wang, M.S., Lin, S.L., Mi, H.H., Wang, L.C. and Chien, G.P.C. (2014). Emissions of PCDD/Fs and PCBs during the cold start-up of municipal solid waste incinerators. *Aerosol Air Qual. Res.* 14: 1593–1604.
- Huang, K.L., Wu, M.S., Tsai, J.H., Lin, D.Y., Chen, S.J. and Lee, W.J. (2016). Effect of operating conditions on PAHs emission from a single H₂-O₂ PEM fuel cell. *Aerosol Air Qual. Res.* 16: 2186–2197.
- Jansson, S., Lundin, L. and Grabic, R. (2011). Characterisation and fingerprinting of PCBs in flue gas and ash from waste incineration and in technical mixtures. *Chemosphere* 85: 509–515.
- Karapanagioti, H.K., Kleineidam, S., Sabatini, D.A., Grathwohl, P. and Ligouis, B. (2000). Impacts of heterogeneous organic matter on phenanthrene sorption: equilibrium and kinetic studies with aquifer material. *Environ. Sci. Technol.* 34: 406–414.
- Kong, S.F., Ding, X., Bai, Z.P., Han, B., Chen, L., Shi, J.W. and Li, Z.Y. (2010). A seasonal study of polycyclic aromatic hydrocarbons in PM_{2.5} and PM_{2.5-10} in five typical cities of Liaoning Province, China. *J. Hazard. Mater.* 183: 70–80.
- Kong, S.F., Shi, J.W., Lu, B., Qiu, W.G., Zhang, B.S., Peng, Y., Zhang, B.W. and Bai, Z.P. (2011). Characterization of PAHs within PM₁₀ fraction for ashes from coke production, iron smelt, heating station and power plant stacks in Liaoning Province, China. *Atmos. Environ.* 45: 3777–3785.
- Kong, S.F., Ji, Y.Q., Li, Z.Y., Lu, B. and Bai, Z.P. (2013). Emission and profile characteristic of polycyclic aromatic hydrocarbons in PM_{2.5} and PM₁₀ from stationary sources based on dilution sampling. *Atmos. Environ.* 77: 155–165.
- Košnář, Z., Mercl, F., Perná, I. and Tlustoš, P. (2016). Investigation of polycyclic aromatic hydrocarbon content in fly ash and bottom ash of biomass incineration plants in relation to the operating temperature and unburned carbon content. *Sci. Total Environ.* 563–564: 53–61.
- Li, Z.Y., Kong, S.F., Chen, L., Bai, Z.P., Ji, Y.Q., Liu, J.W., Lu, B., Han, B. and Wang, Q.W. (2011). Concentrations, spatial distributions and congener profiles of polychlorinated biphenyls in soils from a coastal city – Tianjin, China. *Chemosphere* 85: 494–501.
- Li, H., Liu, G.J. and Cao, Y. (2014). Content and distribution of trace elements and polycyclic aromatic hydrocarbons in fly ash from a Coal-Fired CHP plant. *Aerosol Air Qual. Res.* 14: 1179–1188.
- Li, Z.Y., Zhang, Y.L. and Chen, L. (2015). Seasonal variation and gas/particle partitioning of PCBs in air from central urban area of an industrial base and coastal city -Tianjin, China. *Aerosol Air Qual. Res.* 15: 1059–1071.
- Lior, N. (2010). Sustainable energy development: The present 2009. Situation and possible paths to the future. *Energy* 35: 3976–3994.
- Liu, K., Heltsley, R., Zou, D., Pan, W. and Riley, J.T. (2002). Polyaromatic hydrocarbon emissions in fly ashes from an atmospheric fluidized bed combustor using thermal extraction coupled with GC/TOF-MS. *Energy Fuels* 16: 330–337.
- Liu, W.X., Dou, H., Wei, Z.C., Chang, B., Qiu, W.X., Liu, Y. and Tao, S. (2009). Emission characteristics of polycyclic aromatic hydrocarbons from combustion of different residential coals in North China. *Sci. Total Environ.* 407: 1436–1446.
- Liu, D., Xu, Y., Li, J., Chaemfa, C., Tian, C.G., Liu, X., Luo, C.L. and Zhang, G. (2014). Organochlorinated compounds in the air at NAE0, an eastern background site in China: Long-range atmospheric transport versus local sources. *Aerosol Air Qual. Res.* 14: 1258–1268.
- Manoli, E., Kouras, A. and Samara, C. (2004). Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece. *Chemosphere* 56: 867–878.
- Masto, R.E., Sarkar, E.S., George, J., Jyoti, K., Dutta, P. and Ram, L.C. (2015). PAHs and potentially toxic elements in the fly ash and bed ash of biomass fired power plants. *Fuel Process. Technol.* 132: 139–152.
- Mastral, A.M. and Callén, M.S. (2000). A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. *Environ. Sci. Technol.* 34: 3051–3057.
- Mastral, A.M., Callén, M.S. and Garcia, T. (2000). Toxic organic emissions from coal combustion. *Fuel Process. Technol.* 67: 1–10.
- Pan, Y., Yang, L.B., Zhou, J.Z., Liu, J.Y., Qian, G.R., Ohtsuka, N., Motegi, M., Oh, K. and Hosono, S. (2013). Characteristics of dioxins content in fly ash from municipal solid waste incinerators in China. *Chemosphere* 92: 765–771.
- Pandey, V.C. and Singh, N. (2010). Impact of fly ash incorporation in soil systems. *Agric. Ecosyst. Environ.* 136: 16–27.
- Peng, N.N., Li, Y., Liu, Z.G., Liu, T.T. and Gai, C. (2016). Emission, distribution and toxicity of polycyclic aromatic hydrocarbons (PAHs) during municipal solid waste

- (MSW) and coal co-combustion. *Sci. Total Environ.* 565: 1201–1207.
- Pergal, M.M., Relić, D., Tešić, Ž.L. and Popović, A.R. (2014). Leaching of polycyclic aromatic hydrocarbons from power plant lignite ash-influence of parameters important for environmental pollution. *Environ. Sci. Pollut. Res.* 21: 3435–3442.
- Pongpiachan, S. (2016). Incremental lifetime cancer risk of PM_{2.5} bound polycyclic aromatic hydrocarbons (PAHs) before and after the wildland fire episode. *Aerosol Air Qual. Res.* 16: 2907–2919.
- Ram, L.C. and Masto, R.E. (2014). Fly ash for soil amelioration: A review on the influence of ash blending with inorganic and organic amendments. *Earth Sci. Rev.* 128: 52–74.
- Ravindra, K., Sokhi, R. and Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmos. Environ.* 42: 2895–2921.
- Reuelta, C.C., De la Fuente Santiago, E. and Vázquez, J.R. (1999). Characterization of polycyclic aromatic hydrocarbons in emissions from coal-fired power plants: The influence of operation parameters. *Environ. Technol.* 20: 61–68.
- Sahu, S.K., Bhangare, R.C., Ajmal, P.Y., Sharma, S., Pandit, G.G. and Puranik, V.D. (2009). Characterization and quantification of persistent organic pollutants in fly ash from coal fueled thermal power stations in India. *Microchem. J.* 92: 92–96.
- Shaheen, S.M., Hooda, P.S. and Tsadilas, C.D. (2014). Opportunities and challenges in the use of coal fly ash for soil improvements-A review. *J. Environ. Manage.* 145: 249–267.
- Shin, K.J. and Chang, Y.S. (1999). Characterization of polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls, and heavy metals in fly ash produced from Korea municipal solid waste incinerators. *Chemosphere* 38: 2655–2666.
- Skousen, J., Yang, J.E., Lee, J.S. and Ziemkiewicz, P. (2013). Review of fly ash as soil amendment. *Geosyst. Eng.* 16: 249–256.
- Singh, D.P., Gadi, R., Mandal, T.K., Saud, T., Saxena, M.A. and Sharma, S.K. (2013). Emission estimates of PAH from biomass fuels used in rural sector of indo-gangetic plains of India. *Atmos. Environ.* 68: 120–126.
- Sloss, L. and Smith, I.M. (1993). *Organic Compounds from Coal Utilisation*, IEACR/63, IEA Coal Research, London.
- Sun, P., Weavers, L.K., Taerakul, P. and Walker, H.W. (2006). Characteristics of polycyclic aromatic hydrocarbons (PAHs) on lime spray dryer (LSD) ash using different extraction methods. *Chemosphere* 62: 265–274.
- Tiwari, M., Sahu, S.K. and Pandit, G.G. (2015). Inhalation risk assessment of PAH exposure due to combustion aerosols generated from household fuels. *Aerosol Air Qual. Res.* 15: 582–590.
- Tobiszewski, M. and Namiéńnik, J. (2012). PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* 162: 110–119.
- Verma, S.K., Masto, R.E., Gautam, S., Choudhury, D.P., Ram, L.C., Maiti, S.K. and Maiti, S. (2015). Investigations on PAHs and trace elements in coal and its combustion residues from a plant. *Fuel* 162: 138–147.
- Wang, R.W., Zhang, J.M., Liu, J.J. and Liu, G.J. (2013). Levels and patterns of polycyclic aromatic hydrocarbons in coal-fired power plant bottom ash and fly ash from Huainan, China. *Arch. Environ. Contam. Toxicol.* 65: 193–202.
- Wang, R., Liu, G. and Zhang, J. (2015). Variations of emission characterization of PAHs emitted from different utility boilers of coal-fired power plants and risk assessment related to atmospheric PAHs. *Sci. Total Environ.* 65: 1421–1433.
- Wen, X.Q., Yang, Y.L., Zeng, F.G. and Huang, D.M. (2016). Influence of temperature and airflow on polycyclic aromatic hydrocarbons (PAHs) by simulated self-combustion of coal partings. *J. Environ. Chem. Eng.* 4: 3601–3609.
- Wongphatarakul, V., Friedlander, S.K. and Pinto, J.P. (1998). A comparative study of PM_{2.5} ambient aerosol chemical databases. *Environ. Sci. Technol.* 32: 3926–3934.
- Wu, S.P., Yang, B.Y., Wang, X.H., Yuan, C.S. and Hong, H.S. (2014). Polycyclic aromatic hydrocarbons in the atmosphere of two subtropical cities in southeast china: seasonal variation and gas/particle partitioning. *Aerosol Air Qual. Res.* 14: 1232–1246.
- Wu, S., Zhou, J., Pan, Y., Zhang, J. and Zhang, L. (2016). Dioxin distribution characteristics and health risk assessment in different size particles of fly ash from MSWIs in China. *Waste Manage.* 50: 113–120.
- Yang, H.H., Lai, S.O., Hsieh, L.T., Hsueh, H.J. and Chi, T.W. (2002). Profiles of PAH emission from steel and iron industries. *Chemosphere* 48: 1061–1074.
- Yao, Z.T., Xia, M.S., Sarker, P.K. and Chen, T. (2014). A review of the alumina recovery from coal fly ash, with a focus in China. *Fuel* 120: 74–85.
- Yao, Z.T., Ji, X.S., Sarker, P.K., Tang, J.H., Ge, L.Q., Xia, M.S. and Xi, Y.Q. (2015). A comprehensive review on the applications of coal fly ash. *Earth Sci. Rev.* 141: 105–121.
- Zhang, Y., Tao, S., Shen, H. and Ma, J. (2009). Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population. *Proc. Natl. Acad. Sci. U.S.A.* 106: 21063–21067.
- Zhao, L.J., Zhang, F.S., Hao, Z.P. and Wang, H.L. (2008). Levels of polycyclic aromatic hydrocarbons in different types of hospital waste incinerator ashes. *Sci. Total Environ.* 397: 24–30.
- Zhu, Z.F., Wang, L.P., Qi, H., Zhang, C., Zhao, Y.C., Chen, G., Qiu, J.H. and Zhang, J.Y. (2014). Emission characteristics of fine particulate matters from a 660 MW coal-fired boiler. *J. Fuel Chem. Technol.* 42: 323–328 (in Chinese).

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