Polychlorinated biphenyls in fly ashes collected from five coal-fired power plants in North China

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Abstract. The 5 coal fly ash samples (CFA) were systematically collected from 5 coal-fired power plants (CFPPs) in North China for analysis of 86 PCB congeners. The predominant PCB congeners were PCB-6, -4/10, -28, -18, -19 and -16/32, which belonged to lighter molecular weight (LMW) congeners. The $\Sigma_{86}$PCBs for 5 CFPPs ranged from 10.93 to 32.06 ng/g with the mean value as 16.01 ng/g. The PCBs in CFA were dominated by LMW-PCBs with 2-, 3- and 4-Cl PCBs contributed 34.80%, 39.18% and 9.21% to the $\Sigma_{86}$PCBs. The TEQ concentrations for 5 CFPPs was 42.54 pg/g higher than 4 pg/g designed by Canada for soil quality, indicated the using of CFA as soil amendment should be cautioned.

1. Introduction

China is the largest coal consumer in world and consumed 50.2% of world coal consumption in 2012 [1]. The CFPPs have the 78% of total power capacity in China. The large amounts of coal fly ashes (CFA) were emitted from the coal-fired power plants (CFPPs), which would beidentified as pollutants if without proper disposed [2, 3]. Some researchers reviewed the utilization methods of CFA such as used as a soil amendment, used in glass and ceramics manufacturing, zeolites and mesoporous materials productions, geopolymers, synthesis, catalysts and catalyst supports [4, 5]. Although some recycling disposal methods of CFA were adopted recently, only 45% of CFA was utilized, the rest was often stockpiled before landfill and storing in lagoons [6]. Coal is likely to be the dominant fuel for power generation in energy intensive country such as China in the future [7]. The CFA generation in China has been increased from 2001 to 2015, and has reached 580,000,000 tons in 2015 [8]. Clearly more and more CFA need to be disposed in future China as the highest CFA generation in the world. At the same time, large amounts of unintentionally pollutants such as heavy metals, organic pollutants entered the soil, atmosphere and water, had threat to human health [9]. These pollutants in CFA significantly make the utilization of CFA limited. As a result, the investigation of unintentionally organic pollutants in CFA is imperative before it was environmental friendly utilized. For example, the organic toxic compounds and trace elements in CFA restrict the using of CFA as soil remediation agent.

Polychlorinated biphenyls (PCBs) are environmental persistent organic pollutants (POPs) have been studied extensively in recent years characterized by high lipophilicity, extreme toxicity and high resistance to environmental degradation process [10, 11]. The CFA has been identified as the important source of PCBs to atmosphere, water and soil [10]. So the study on emission profiles of PCBs in CFA is very imperative work. Sahu et al. (2009) studied the PAHs and PCBs in CFA from...
Indian five CFPPs and indicated the restriction of using of CFA as soil amendment [9]. But the data of PCBs in CFA from CFPPs were not available in China.

Along with the rapid development of economy and the strict requirement for environment protection in China, the CFPPs with higher individual block power capacity (IBPC) are becoming the mainstream power generation units in China. In present China, IBPC as 600 MW is the mainly representative generation unit and accounted 39% of all the coal-fired power generation units [12]. The CFA samples from 5 CFPPs with IBPC as 600 MW were collected during March to November, 2015 for the analysis of 86 PCB congeners.

The main aims of this study were to investigate: 1) the concentrations and homolog distribution of PCBs in CFA from 5 CFPPs in North China with individual block power capacity (IBPC) as 600 MW; 2) the toxic equivalency (TEQ) concentration of PCBs in CFA to evaluate the using of CFA as soil amendment.

2. Experiment Methods

2.1. CFA Sample collection and preparation before extraction
The CFA samples were collected systematically from 5 large-scaled CFPPs in North China during March to November, 2015. These 5 CFPPs were all with the individual block of power capacity as 600 MW, which was the mainstream generation unit in China. The systematic sampling procedure lasting a month was adopted to obtain the representative samples. Every sample were collected for two days interval and the representative sample was consisted these samples. The samples were collected using a stainless spoon from the hoppers of the electrostatic precipitators used to clean the emissions [9]. The collected samples were stored immediately in sealed polyethylene bags to prevent contamination and weathering. The 1kg of each CFA sample was transported to the laboratory in solvent rinsed amber glass jars with Teflon lined aluminium caps. Before analysis, each sample was homogenized using coning and quartering. Each sample was weighed after being dried in a vacuum freeze dryer to remove the moisture.

2.2. Sample extraction for PCBs analysis
Three groups of PCB standards with the catalog numbers as C-IADN-01, 02 and 03 (containing 84 congeners) and PCB-157 and -189 (Accustandard, Inc.) were used in this study. PCB-14, 65, 166 were used as surrogate standards, 2,4,5,6-tetrachloro-m-xylene and PCB-209 were used as internal standards. Other solvents including n-hexane and acetone (pesticide grade, Fisher Scientific, Inc. Fair Lawn, New Jersey) were also used to the analysis of PCBs.

The detailed analyzed method was shown in references [11]. The 60 g of CFA sample was Soxhlet extracted with acetone: n-hexane. The extracts were concentrated by rotary vacuum evaporation and purified by a silica gel column. When the extracts passed through this column, PCBs fractions were eluted with n-hexane. The collected eluents were concentrated by a rotary evaporator and then reduced to 0.5 mL under a gentle N₂ stream for analysis. The extracts were analyzed using a HP 6890GC/5973i MS system equipped with a DB-5 fused silica capillary column (60 m×0.25 mm i.d.). The GC condition adopted was same as references [10] and [11]. GC/MS system was processed using selected ion monitoring 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.

2.3. Quality control and quality assurance
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 90% to 118% and the standard deviation was lower than 8%. The standard deviations for 4 pairs of repeated samples were all lower than 10%. The method detection limits for 86 PCBs ranged from 2 to 33 pg/g (mean: 7.5 pg/g)
3. Results and Discussion

3.1. Individual PCB congener in CFA from 5 CFPPs

As shown in Table 1, 47 PCB congeners among 86 PCBs were detectable in this study. The predominant PCBs in CFA for 5 CFPPs in north China were PCB-6, -4/10, -28, -18, -19 and -16/32, which accounted for 43.80% to 80.82% (61.91±15.32) of total PCBs and correlated well with total PCBs (R²=0.96, p<0.005).

Table 1. Statistic values of individual PCB congener in CFA from 5 CFPPs (pg/g)

| PCBs     | Min   | Max   | Mean±SD | PCBs     | Min   | Max   | Mean±SD |
|----------|-------|-------|---------|----------|-------|-------|---------|
| PCB4/10  | 7089.47 | 2922.53±1930.51 | PCB83     | n.d. | n.d. | n.d. |
| PCB7/9   | 1729.33 | 435.74±747.08 | PCB97     | n.d. | n.d. | n.d. |
| PCB6     | 6810.26 | 3942.81±1113.20 | PCB88     | 30.24 | 90.25 | 60.36±20.44 |
| PCB5/8   | n.d. | n.d. | PCB87     | 23.54 | 139.41 | 51.98±36.66 |
| PCB19    | 501.24 | 3289.66 | PCB85     | n.d. | n.d. | n.d. |
| PCB12/13 | 1464.86 | 462.87±321.45 | PCB77     | n.d. | n.d. | n.d. |
| PCB18    | 182.83 | 5689.45 | PCB110    | n.d. | n.d. | n.d. |
| PCB15    | n.d. | n.d. | PCB144/135 | n.d. | n.d. | n.d. |
| PCB17    | 325.45 | 86.40±89.12 | PCB123    | 9.82 | 46.71 | 66.17±43.57 |
| PCB16/32 | 2695.93 | 1056.92±942.63 | PCB149    | n.d. | n.d. | n.d. |
| PCB26    | 700.56 | 491.56±132.09 | PCB118    | 304.02 | 460.01 | 375.94±58.04 |
| PCB28    | 1160.21 | 2559.39±1651.08 | PCB114    | 197.95 | 303.34 | 103.49±193.94 |
| PCB31    | n.d. | n.d. | PCB131    | n.d. | n.d. | n.d. |
| PCB33/53 | 300.01 | 119.02±152.36 | PCB153/132 | n.d. | n.d. | n.d. |
| PCB22    | 1489.40 | 491.56±371.83 | PCB105    | 96.58 | 375.46 | 204.83±46.54 |
| PCB45    | 172.25 | 37.65±44.24 | PCB138/163 | n.d. | n.d. | n.d. |
| PCB52    | 800.41 | 1128.42±826.18 | PCB126    | 198.25 | 300.84 | 220.01±33.56 |
| PCB49    | 164.59 | 36.12±71.82 | PCB128    | n.d. | n.d. | n.d. |
| PCB47+48 | 18.73 | 8.95±5.47 | PCB167    | 73.55 | 100.25 | 79.20±11.63 |
| PCB44    | n.d. | n.d. | PCB174    | n.d. | n.d. | n.d. |
| PCB37+42 | 504.12 | 404.70±108.65 | PCB171/202 | n.d. | n.d. | n.d. |
| PCB41+71+64 | 540.70 | 404.70±108.65 | PCB156    | 11.13 | 4.23±3.86 |
| PCB100   | n.d. | n.d. | PCB157    | 319.77 | 721.21 | 474.20±167.71 |
| PCB74    | n.d. | n.d. | PCB172    | n.d. | n.d. | n.d. |
| PCB76+70 | n.d. | n.d. | PCB180    | n.d. | n.d. | n.d. |
| PCB66+95 | n.d. | n.d. | PCB201    | n.d. | n.d. | n.d. |
| PCB91    | n.d. | n.d. | PCB169    | 550.99 | 910.66 | 681.86±141.27 |
| PCB56+60 | n.d. | n.d. | PCB170/190 | n.d. | 85.00 | 44.40±40.61 |
| PCB92    | 154.77 | 54.54±61.13 | PCB199    | 48.09 | 10.42±21.06 |
| PCB84    | 60.12 | 153.98 | PCB189    | 125.00 | 412.21 | 249.60±124.94 |
| PCB89    | 22.65 | 488.79 | PCB207    | n.d. | 88.18 | 44.78±27.76 |
| PCB101   | n.d. | n.d. | PCB194    | 360.03 | 72.81±111.38 |
| PCB99    | 82.94 | 18.99±35.75 | PCB205    | n.d. | n.d. | n.d. |
| PCB119   | n.d. | n.d. | PCB206    | n.d. | n.d. | n.d. |

*SD: Standard deviation

3.2. PCBs levels and homolog compositions for five CFPPs

As shown in Figure 1(a), the Σ86PCBs for 5 CFPPs ranged from 10.93 ng/g to 32.06 ng/g with the mean value as 16.01 ng/g. The PCBs congeners were classified into two categories including low molecular weight (LMW) PCBs (2- to 4-Cl substituted PCB congeners) and high molecular weight (HMW) PCBs (the chlorine atoms higher than 5). As shown in Figure 1(b), the PCBs in CFA were dominated by LMW-PCBs with 2-, 3- and 4-Cl substituted PCBs contributed 34.80%, 39.18% and 9.21% to the Σ86PCBs.

Seven indicator PCB congeners (PCBs) including PCB-28, 52, 101, 118, 138, 153, and 180 were commonly measured and often compared in PCBs analysis [10]. Among seven IPCBs, PCB-101, -138,
-153 and -180 were all not detected in 5 CFA samples. The sum of 7 IPCBs was 4.06 ± 2.32 ng/g and not correlated with total PCBs. Li et al. (2011) also reported the 7 IPCBs were not correlated with total PCBs in surface soils of Tianjin due to the emission of PCBs from industrial sources [10]. The 7 IPCBs were mainly existed in conventional PCB products, the emissions from industrial stacks resulted this lower correlation coefficient.

![Graph](a)

**Figure 1.** a) PCBs concentrations in CFA from 5 CFPPs and b) the contribution of PCB homologs with different chlorine atoms to total PCBs

![Graph](b)

**Figure 2.** Mean TEQ concentration for each dl-PCBs for 5 CFPPs

3.3. Toxic equivalency concentrations of PCBs in CFA from five CFPPs

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 TEQ concentration for each dl-PCB was calculated by multiplying its concentration and WHO 2005 toxic equivalent factor (TEF) [10, 11].

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\text{TEQ} = (\text{mass concentration of PCB}) \times \text{TEF}
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The TEF values for 12 dl-PCBs were 0.0001, 0.0003, 0.00003, 0.00003, 0.00003, 0.00003, 0.1, 0.00003, 0.00003, 0.00003, 0.03 and 0.00003 for PCB-77, -81, -105, -114, -118, -123, -126, -156, -
157, -167, -169 and -189, respectively. The sum of 11 dl-PCBs for 5 CFPPs ranged from 2.24 to 2.92 ng/g with the mean value as 2.57 ng/g. The value of 2.57 ng/g was higher than 1.65 ng/g for 15 Chinese large-scale municipal solid waste incinerators (MSWIs) and 0.5-2.3 ng/g for 4 Chinese MSWIs [13, 14], much lower than 8.972 ng/g for a MSWI in Medellin, Colombia [15]. These differences possibly resulted from the different combustion condition, feed fuel among different industrial stacks. The TEQ concentrations for 5 CFPPs ranged from 37.60 pg/g to 46.59 pg/g with the mean as 42.54 pg/g. PCB -126 and -169 have the higher TEQ concentrations due to their higher TEF values as 0.1 and 0.03. The TEQ for PCB-126 and -169 were 22.00±3.36 and 20.45±4.24 pg/g (see Figure 2). The TEQ concentrations for 18 CFPPs in the range of 38.71-78.55 pg/g (mean:52.63 pg/g), significantly higher than 4 pg/g designated by Canada for soil quality [16], which did not supports their suitability for soil amendment.

4. Conclusions
The 5 CFA samples were collected from 5 CFPPs in North China for analysis of 86 PCB congeners. The predominant PCB congeners were PCB-6, -4/10, -28, -18, -19 and -16/32. The mean value of Σ86 PCBs for 5 CFPPs was 16.01 ng/g. The PCBs in CFA were dominated by LMW-PCBs with 2-, 3- and 4-Cl PCBs. The mean value of sum of 12 dioxin-like PCBs for 5 CFPPs was 2.57 ng/g. The TEQ concentrations for 5 CFPPs was higher than that designed by Canada for soil quality, indicated the using of CFA as soil amendment should be cautioned.

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