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Characteristic of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in fly ash from incinerators in china

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Abstract

Fly ash from municipal solid waste (MSW), medical waste (MW) and electrical power plant (EPP) incinerators were analyzed for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). The study showed that the PCDD/F levels in fly ash were EPP < MSW < MW. The homologue profiles of PCDD/Fs in fly ash produced from waste incinerators were similar. However, the homologue profiles of PCDD/Fs in fly ash from electrostatic precipitator (ESP) of electrical power plant were different from that from waste incinerator. The strong correlation was found between the concentration of 2,3,4,7,8-PeCDF and the I-TEQ value of fly ash regardless of the different fly ashes sources.

Keywords: Fly ash; Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs); Municipal solid waste (MSW); Medical waste; Incinerator; Electrical power plant

1. Introduction

Landfill is the dominant municipal solid waste (MSW) disposal method in China, which accounts for more than 80% of the MSW disposal [1]. However, the number of large-scale MSW incinerator plants has gradually increased in developed cities in China recently. Up to July 2002, the capacity of the constructed MSW incinerators was 13,155 tons waste/day [2]. For example, nine MSW incineration plants have been constructed in Zhejiang Province, which can dispose 4400 tons MSW/day. Twelve others are under construction, which are designed to dispose 6600 tons MSW/day [3]. A preliminary investigation of over 15 typical incineration facilities for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) emission from flue gas has shown that half data exceed 1.0 ng I-TEQ/Nm^3 at 11%O_2, which is the standard of PCDD/F emission regulation for MSW incinerator in China and calculated based on the International Toxicity Equivalency Factor (I-TEF) [4].

In 2003, "the National Plan for Construction of Facilities for Disposal of Hazardous Wastes and Medical Wastes" was officially replied by the State Council, which was established by National Development and Reform Commission and State Environmental Protection Administration of China. According to the plan, Chinese government will invest 15 billion Renminbi to construct 31 hazardous wastes and 300 medical wastes central disposal plants until 2006 [5]. Incineration was the priority disposal method for flammable hazardous wastes and medical wastes in the plan. An assessment of PCDD/Fs pollution in different type of medical waste incinerators was carried out by Zhejiang Environmental Monitoring Center. It showed that the emission levels of PCDD/Fs in flue gas ranged from 5.93 to 67.52 ng I-TEQ/Nm^3, which was in the range of 7.76–166 times higher than the standard limit for medical waste (MW) incinerator (0.5 ng I-TEQ/Nm^3) [6].

Until now there are only two standards for PCDD/Fs control emitted from flue gas produced from MSW and MW incineration in China. However, regulations for PCDD/Fs in fly ash have not been launched. PCDD/Fs could be emitted not only from flue gas but also from fly ash collected by air pollution control devices, such as bag filter. A dioxin balance in the post-combustion zone of an incinerator demonstrated that stack gas, filter cake and elec-

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trostatic precipitator (ESP) fly ashes accounting for about 11.8, 22.7 and 56.7% of the total PCDD/F output, respectively [7]. Abad et al. [8] also invested a dioxin mass balance in a Spanish MSWI. They found the PCDD/F emission from stack gas and fly ash was 0.0048, 2.6 g I-TEQ/year, respectively. Therefore, the PCDD/Fs in fly ash should also be considered in China.

At present, PCDD/F emissions from MSW, hazardous wastes or MW combustion process have been widely studied. However, scare information about big incinerators as coal-fired power plants is available [9]. Nowadays, over 70% of electricity in China is generated from coal [10]. The power plants exhaust large quantities of combusted waste in the form of bottom ash, fly ash or slag [11]. Heavy metals and its leaching behavior in fly ash were the focus for many studies. In this paper, five, one and three fly ash samples were collected from MSWIs, MWI and EPPIs, respectively. The levels and homologue profiles of PCDD/Fs in fly ash were studied to realize the status of PCDD/Fs in fly ash in China, which will help establish PCDD/F emission standard in fly ash. The correlation between the concentration of 2,3,4,7,8-PeCDF and the total I-TEQ value of fly ash was also presented.

2. Experimental

2.1. Sample pretreatment

Nine fly ash samples were collected from bag filters or ESPs, being listed in Table 1. Four different types of incinerators were investigated. For each incinerator 10 g fly ash samples were dried and transferred to the glass thimble of the Soxhlet extractor and spiked with a mixture of ^{13}C-labeled PCDD/Fs internal standards, which was supplied by Wellington Laboratories, Canada. The spiked samples were extracted for 24 h with 250 ml toluene. The extract was concentrated by a rotary evaporator until 1–2 ml approximately prior to the cleanup process. After concentration, a labeled cleanup standard was spiked into the extract, which is then cleaned up using different methods. The extract should be treated using back-extraction with sulfuric acid and base if the color of the extract was visible.

Cleanup of samples were conducted using two different methods: S1– S6 samples cleanup employed an automated cleanup system (Power-Prep Trade Mark, Fluid Management Systems Inc.) and S7–S9 samples cleanup used conventional manual chromatography columns including multi-silica gel column, alumina column and florisil column. After cleanup the extract was concentrated again then transferred to a vial. Then the remaining solvent in the vial was reduced to about 20 μl by a gentle stream of nitrogen.

^{13}C-labeled PCDD/Fs recovery standard mixture was spiked prior to HRGC/HRMS analysis.

2.2. HRGC/HRMS analysis

The analyses was performed by HRGC/HRMS on a 6890 Series gas chromatograph (Agilent, USA) and coupled to a JMS-800D mass spectrometer (JEOL, Japan). A DB-5ms (60 m × 0.25 mm I.D., 0.25 μm film thickness) capillary column was used for separation of the PCDD/F congeners. The GC temperature program was optimized as follows: splitless injection of 2 μl at 150 °C, initial oven temperature of 150 °C for 1 min, then increased at 25 °C/min to 190 °C, finally increased at 3 °C/min to 280 °C and held for 20 min. Helium was used as the carrier gas. The mass spectrometer was operated in the electron impact ionization mode using selected ion monitoring (SIM). Electron energy was set to 38 eV. Source temperature was 280 °C. The mass system was tuned to a minimum resolution of 10,000 (10% valley) using perfluorokerosene (PFK) as lock mass. The detailed quantitative determination of PCDD/Fs was referred to US EPA method 1613 [12]. Tetra- through octa-CDD/Fs was detected in this study.

3. Results and discussion

3.1. PCDD/Fs distribution in fly ash

PCDD/Fs concentrations in fly ash samples were summarized in Table 2. The total PCDD/Fs concentrations were from 0.059 to 2918 ng/g, showing a wide range for different fly ash sources. The large difference between the homologue distribution and concentration of PCDD/Fs in S1 and S2, which were all collected from bag filters of stoker incinerators, may be due to the different MSW composition, combustion efficiency of the two incinerators. Although OCDD was the predominant homologue among the MSWI and MWI fly ash samples except S1, in which TCDF

Table 1
Fly ash sources

Sample no.	Incinerator	Furnace type	Capacity	Air pollution control device
S1	MSWI	Stoker	350 t/d × 3 units	Semidry scrubber + bag filter
S2	MSWI	Stoker	350 t/d × 3 units	Semidry scrubber + bag filter
S3	MSWI	Stoker	288 t/d × 3 units	Semidry scrubber + electrostatic precipitator
S4	MSWI	CFB	200 t/d × 2 units + 300 × 1 unit	Semidry scrubber + bag filter
S5	MSWI	CFB	200 t/d × 2 units	Semidry scrubber + bag filter
S6	MWI	RC + CFB	10 t/d × 1 unit	Semidry scrubber + bag filter
S7	EPPI		300 MW	Electrostatic precipitator
S8	EPPI		300 MW	Electrostatic precipitator
S9	EPPI		300 MW	Electrostatic precipitator

CFB: circulated fluidized bed; RC: rotary kiln; The fuel used for CFB was MSW and coal. The ratio of MSW/coal was 8:2. S7, S8 and S9 fly ash samples were collected from the three different ESPs of one incinerator.

Table 2
PCDD/Fs concentrations in fly ash samples (ng/g)

	S1	S2	S3	S4	S5	S6	S7	S8	S9
TCDD	0.41	1.67	1.42	0.61	0.23	19.3	0.000	0.076	0.002
PeCDD	1.25	10.1	2.96	1.20	0.34	52.6	0.013	0.250	0.026
HxCDD	1.09	25.2	4.10	1.01	0.21	86.0	0.016	0.137	0.027
HpCDD	2.08	53.9	3.91	0.44	0.23	57.1	0.004	0.031	0.010
OCDD	2.19	79.4	19.8	0.86	17.0	2106	0.007	0.018	0.015
Total PCDDs	7.02	170	32.2	4.12	18.0	2321	0.040	0.512	0.080
TCDF	4.75	15.1	4.84	7.61	1.50	146	0.007	0.012	0.010
PeCDF	3.84	17.6	4.10	7.60	1.18	190	0.005	0.002	0.012
HxCDF	2.45	17.0	3.36	4.52	0.71	156	0.004	0.002	0.016
HpCDF	0.91	11.4	1.73	1.03	0.16	55.8	0.002	0.003	0.007
OCDF	0.25	4.53	0.77	0.22	0.14	48.9	0.001	0.005	0.017
Total PCDFs	12.2	65.6	14.8	21	3.69	597	0.019	0.024	0.062
Total PCDD/Fs	19.2	236	47	25.1	21.7	2918	0.059	0.536	0.142

was the dominant homologue. However, PeCDD and HxCDD were the dominant homologue for S7–S9 samples, which were obtained from ESPs of the EPP incinerator. The magnitude of PCDD/Fs concentrations in fly ash samples collected from different incinerators investigated was EPP < MSW < MW. The reason for lowest PCDD/Fs concentrations in S7–S9 samples probably related to the relatively high sulfur to chlorine (S/Cl) ratio of coal compared to MSW [13]. Compared to MSW, coal could be combusted more efficiency. Previous research had concluded that cofiring MSW with coal could remarkably decease the PCDD/Fs formation [14,15].

The homologue patterns of tetra- to octa-chlorinated PCDD/Fs in S1–S6 samples were shown in Fig. 1. They were similar from S1 to S6 samples despite of different types of incinerators, fuel composition, operation conditions, etc. Highly chlorinated homologues were dominant for PCDDs and the tendency was contrary for PCDFs, i.e., lowly chlorinated homologues were dominant expect S4 sample, which were also consistent with the results mentioned by Chang et al. [16]. Fig. 2 shows the homologue patterns of PCDD/Fs in S7–S9 samples. It was different from Fig. 1. The dominant homologues were PeCDD and HxCDD for all the three samples, which accounted for 37–72% of the total PCDD/Fs production. So the PCDD/Fs formation mechanism probably correlated with the type of fuel during combustion. In contrast to MSWI and MWI fly ash, the graphitic structure of the coal fly ash is much less active for PCDD/Fs formation. The concentrations of copper, iron and other metals, which are considered the PCDD/Fs formation catalysts, are also lower in coal fly ash than in MSWI and MWI fly ash [14].

3.2. I-TEQ values in fly ash samples

The I-TEQ values of 2,3,7,8-substituted PCDD/Fs were listed in Table 3. The TEQ values of PCDD/Fs in S2 (2.68 ng I-TEQ/g) and S6 (20.4 ng I-TEQ/g) exceeded 1 ng I-TEQ/g, which is a residential soil criteria for some countries, such as Germany, United States and Japan [17]. S6 fly ash was collected from bag filter of a MWI and the I-TEQ value was 20 times higher than the criteria. The disposal capacity of MWI is much smaller than that of MSWI. So, the unstable combustion in MWI caused more products of incomplete combustion, which might be the precursors of PCDD/Fs formation. Furthermore, medical waste contained more polyvinyl chloride (PVC) products compared with MSW. PVC plastic can also serve as PCDD/Fs precursors [18]. Accordingly, the PCDD/Fs levels are higher than that of MSWI, which is also seen in the introduction [6], that is the PCDD/Fs emissions from flue gas were all higher than the standard limit in China. So the fly ash produced from MWI should be treated properly before being landfilled.

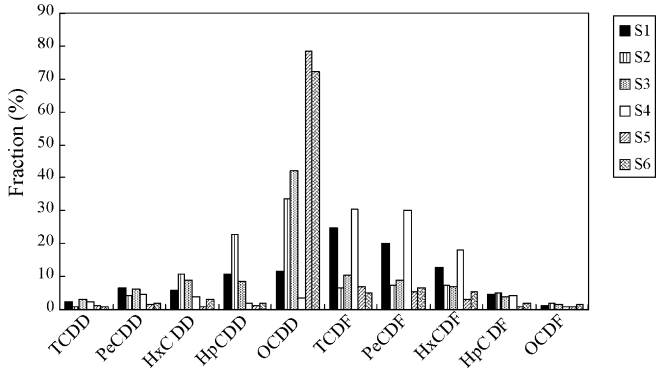

Fig. 1. Homologue patterns of tetra- to octa-chlorinated PCDD/Fs in S1–S6 samples.

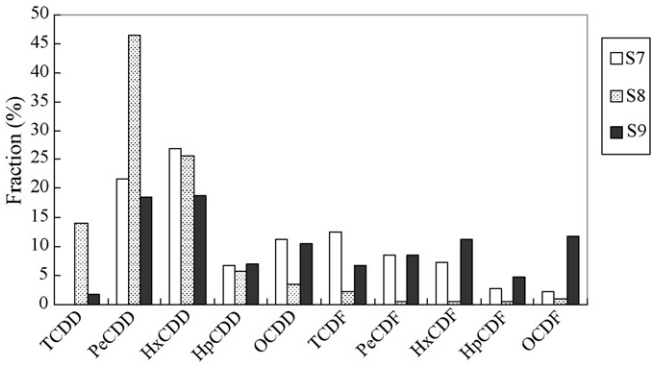

Fig. 2. Homologue patterns of tetra- to octa-chlorinated PCDD/Fs in S7 –S9 samples.

Table 3
The TEQ values in fly ash samples (pg I-TEQ/g)

	S1	S2	S3	S4	S5	S6	S7	S8	S9
2378TCDD	33.7	130	44.7	N.D.	8.31	830	N.D.	N.D.	N.D.
12378PeCDD	62.5	N.D.	N.D.	107	16.0	N.D.	N.D.	N.D.	N.D.
123478HxCDD	6.35	63.2	12.0	11.8	1.16	228	N.D.	N.D.	N.D.
123678HxCDD	13.5	180	24.4	82.1	1.73	380	0.089	0.686	0.239
123789HxCDD	3.47	82.3	13.6	0.561	1.01	547	0.073	0.422	0.139
1234678HpCDD	11.4	263	20.0	2.47	1.33	288	0.024	0.192	0.054
OCDD	2.19	79.3	19.8	0.857	17.0	2106	0.007	0.018	0.015
2378TCDF	24.8	72.3	20.3	41.9	4.23	N.D.	0.119	0.198	0.169
12378PeCDF	13.4	53.7	11.7	24.0	3.03	418	0.055	N.D.	N.D.
23478PeCDF	189	988	216	428	57.0	9666	0.704	0.627	1.31
123478HxCDF	24.9	170	30.6	55.4	7.09	1602	N.D.	0.139	0.423
123678HxCDF	28.0	182	35.7	59.4	7.73	1550	0.138	N.D.	0.465
234678HxCDF	28.1	254	46.3	59.8	8.67	1843	0.101	N.D.	0.296
123789HxCDF	8.54	79.0	13.5	16.4	2.27	485	0.054	N.D.	0.107
1234678HpCDF	5.22	64.9	9.00	6.42	0.989	355	0.017	0.020	0.060
1234789HpCDF	1.03	13.9	2.13	1.06	0.150	49.6	N.D.	N.D.	0.008
OCDF	0.252	4.53	0.766	0.217	0.139	48.9	0.001	0.005	0.017
PCDDs	133	798	135	205	46.5	4379	0.193	1.32	0.447
PCDFs	323	1882	386	692	91.3	16018	1.19	0.989	2.86
PCDDs/PCDFs	0.41	0.42	0.35	0.30	0.51	0.27	0.16	1.3	0.16

Note: N.D.: not detectable.

3.3. Correlation between the concentration of 2,3,4,7,8-PeCDF and the I-TEQ value

There is a linear correlation between the concentration of 2,3,4,7,8-PeCDF and the toxic equivalent (TEQ) value in the flue gas [19,20]. Iino et al. proposed a TEQ (which is calculated by WHO-TEF) prediction equations based on PCDD/Fs isomer pattern prediction model. All the PCDF plots showed highly linear correlations ($R^2 > 0.99$) regardless of the different types of incinerators, temperature profiles and various chemical and physical properties of fuels [19]. It was found the contribution of 2,3,4,7,8-PeCDF to the I-TEQ value was stable. The positive correlation was obtained and it could be expressed by the following Eq. (1) for various incineration facilities [19].

$$[\text{I-TEQ of PCDD/Fs}] = 1.4[2, 3, 4, 7, 8\text{-PeCDF}], \quad r = 0.99 \tag{1}$$

The mentioned two results both concerned the concentration of the total PCDD/Fs in gas phase. Is there also correlation between the concentration of 2,3,4,7,8-PeCDF and the I-TEQ value in fly ash? Fig. 3 showed the relationship between the concentration of 2,3,4,7,8-PeCDF and the I-TEQ value in S1–S9. The positive correlation was also obtained and the Eq. (2) could be used to express the relationship.

$$[\text{I-TEQ of PCDD/Fs}] = 1.06[2, 3, 4, 7, 8\text{-PeCDF}], \quad R^2 = 0.999 \tag{2}$$

The good correlation between the concentration of 2,3,4,7,8-PeCDF and the I-TEQ value is due to the high toxicity (I-TEF is 0.5 for 2,3,4,7,8-PeCDF) and the high concentration of the congener, compared with the other 16 2,3,7,8-substituted congeners, which could be referred in Table 3.

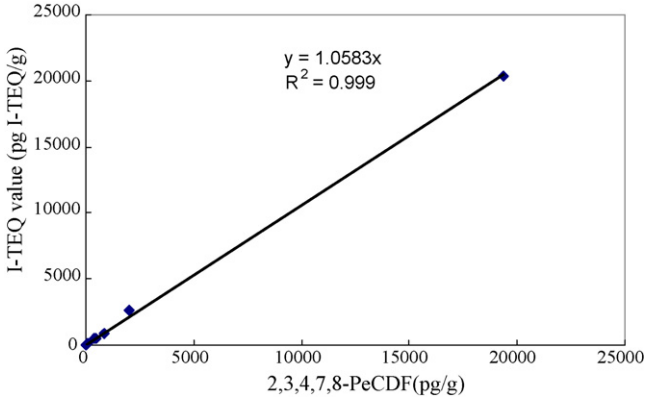

Fig. 3. Correlation between 2,3,4,7,8-PeCDF and I-TEQ in S1–S9.

4. Conclusions

The PCDD/Fs levels in fly ash samples collected from different incinerators were EPPI < MSWI < MWI. OCDD was the dominant homologue in the MSWI and MWI except S1, in which TCDF was the dominant homologue. PeCDD and HxCDD were the major homologue in fly ash collected from ESPs of an EPP incinerator.

The current China PCDD/Fs emission standards are only for PCDD/Fs from flue gas emission. Therefore, a regulation for MWI and MWI fly ash is needed.

The positive relationship between the concentration of 2,3,4,7,8-PeCDF and the I-TEQ value in the nine fly ash samples was obtained, which could be expressed by the following equation, i.e.

$$[\text{I-TEQ of PCDD/Fs}] = 1.06[2, 3, 4, 7, 8\text{-PeCDF}] \tag{3}$$

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