THE DISTRIBUTION CHARACTERISTICS OF PCDD/FS, DIOXIN-LIKE PCBS, CBZS AND THE LEACHING TOXICITY OF FLY ASH FROM TYPICAL MSWIS IN CHINA

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Introduction

At present, incineration is one of the major treatment methods for municipal solid waste (MSW) disposal in China. According to the data of National Bureau of Statistics of 2018, China, the incineration ratio of MSW treat capacity has reached to 43.8% and the number of MSW incinerators plants is 286 in 2017[1]. Many fly ashes were produced during the MSW incineration process. Fly ash produced from municipal solid waste incinerators contains many pollutants, such as, heavy metals and polychlorinated-p-dioxins and furans(PCDD/Fs), which was considered as hazardous solid waste in many countries. However, other chlorinated compounds, for example, chlorinated benzenes(CBzs) and dioxin-like polychlorinated biphenyls(PCBs) are also existed in the fly ash. In the paper, PCDD/Fs, dl-like PCBs, CBzs distribution characteristics and the leaching toxicity of fly ashes from two kinds of typical MSW incinerators in China were investigated and the correlation between chlorinated compounds were also determined.

Materials and methods

The fly ash samples were all collected from the bag filters of MSW incinerators. The basic information of MSW incinerators was seen in Table 1. For fluidized bed incinerators, coal was added as supplement fuel. The ratio of MSW/coal was 8.5:1,5.35:1,9:1 and 19:1 for FA5 to FA8 respectively.

Table 1 Basic information of MSW incinerators

Sample No	Furnace type	Capacity(ton/d)	Air pollution control device
FA1	Grate	330	[a]SNCR+Semi-dry absorber +[b]AC+Bag filter+AC absorbtion tower
FA2	Grate	500	SNCR+Semi-dry absorber+AC+Bag filter+ Wet scrubber
FA3	Grate	500	SNCR+Semi-dry absorber+Dry sorbent injection +AC+Bag filter+[c]SCR
FA4	Grate	500	SNCR+Semi-dry absorber+Dry sorbent injection +AC+Bag filter+SCR
FA5	Fluidized bed	350	SNCR+Semi-dry scrubber+AC+Bag filter
FA6	Fluidized bed	350	SNCR+Semi-dry scrubber+AC+Bag filter
FA7	Fluidized bed	420	SNCR+Semi-dry scrubber+AC+Bag filter
FA8	Fluidized bed	450	SNCR+Semi-dry scrubber+AC+Bag filter

[a]SNCR: selected non-catalytic reduction.

[b]AC: activated carbon.

[c]SCR: selected catalytic reduction.

Headspace-gas chromatography/ mass spectrometry was used to detect mono-chlorinated benzene. Dichlorobenzene to hexachlorobenzene were analyzed by GC/MS. PCDD/Fs and dl-like PCBs were detected by HRGC/HRMS. The heavy metal leaching toxicity of fly ash samples were analyzed by ICP-AES, except Cr(Ⅵ),which was determined by spectrophotometric method. The detail analysis processes were referred to the standards of China.

Results and discussion:

Concentration of PCDD/Fs and PCBs in the fly ash samples

The concentrations of PCDD/Fs and WHO-TEQ value in the fly ash samples are shown in Table 2. The average WHO-TEQ value of PCDD/Fs in the fly ash samples from grate-type and fluidized bed MSW incinerators are 0.35 and 6.02 ng TEQ/g, respectively. It seems that fluidized bed furnace produces more toxic fly ash than the grate-type one does. This trend is consistent with the result reported by Pan[2]. All the PCDD/Fs levels of fly ash produced from fluidized bed MSW incinerators exceeded the Chinese landfill acceptance criteria for wastes (3.0 ng TEQ/g). So the fly ash should be treated properly before being landfilled. Furthermore, the distributions of PCDD/F congeners in the fly ash samples from grate-type and fluidized bed MSW incinerators are different

(Figure 1). Among all of the PCDD/F congeners, 2,3,4,7,8-PeCDF was the most important contributor to the I-TEQ value, which was in accordance with other fly ash samples (Cobo et al. 2009; Tabata et al. 2013). As to PCBs, 3,3',4,4'-TeCB (#77) and 3,3',4,4',5-PeCB (#126) were dominant PCBs in all the fly ash samples.

Table 2 Concentrations (ng/g) and TEQ values (ng TEQ/g) of dioxins and PCBs in the fly ash samples

	FA1	FA2	FA3	FA4	FA5	FA6	FA7	FA8
2,3,7,8-TeCDD	0.017	0.021	0.086	0.0053	0.70	0.34	0.48	0.33
1,2,3,7,8-PeCDD	0.029	0.083	0.17	0.0073	1.2	0.75	0.96	1.0
1,2,3,4,7,8-HxCDD	0.021	0.099	0.22	0.0076	0.87	0.48	0.81	1.1
1,2,3,6,7,8-HxCDD	0.045	0.27	1.2	0.015	1.3	0.58	2.0	3.4
1,2,3,7,8,9-HxCDD	0.033	0.15	0.57	0.012	1.1	0.52	1.5	2.5
1,2,3,4,6,7,8-HpCDD	0.34	1.6	9.8	0.12	7.8	2.3	14	18
OCDD	0.59	2.0	22	0.21	11	2.0	20	14
Total PCDDs	1.08	4.22	34.05	0.38	23.97	6.97	39.75	40.33
2,3,7,8-TeCDF	0.078	0.11	0.23	0.022	4.3	2.5	1.9	0.98
1,2,3,7,8-PeCDF	0.096	0.18	0.28	0.025	5.5	3.7	2.8	2.4
2,3,4,7,8-PeCDF	0.072	0.25	0.35	0.022	7.1	5.5	5.2	5.5
1,2,3,4,7,8-HxCDF	0.075	0.22	0.26	0.019	5.4	4.4	3.9	4.2
1,2,3,6,7,8-HxCDF	0.087	0.24	0.38	0.024	6.4	5.0	5.0	6.0
1,2,3,7,8,9-HxCDF	0.011	0.027	0.093	0.004	0.63	0.51	0.66	0.77
2,3,4,6,7,8-HxCDF	0.062	0.30	0.63	0.023	5.1	4.2	5.7	6.4
1,2,3,4,6,7,8-HpCDF	0.18	0.62	0.88	0.050	10	7.2	10	10
1,2,3,4,7,8,9-HpCDF	0.025	0.089	0.34	0.019	1.9	1.3	2.6	3.0
OCDF	0.085	0.20	0.52	0.037	2.9	1.9	3.7	3.1
Total PCDFs	0.771	2.236	3.963	0.245	49.23	36.21	41.46	42.35
Total (PCDDs+PCDFs)	1.361	4.236	25.963	0.455	60.23	38.21	61.46	56.35
3,4,4',5-TeCB (#81)	0.005	0.085	0.042	0.002	0.81	0.18	0.80	1.0
3,3',4,4'-TeCB (#77)	0.017	0.18	0.091	0.0071	2.3	0.54	1.7	1.2
3,3',4,4',5-PeCB (#126)	0.021	0.30	0.11	0.0064	2.4	0.72	2.0	3.0
3,3',4,4',5,5'-HxCB (#169)	0.011	0.14	0.063	0.0032	0.76	0.26	0.75	1.9
Total non-ortho	0.054	0.71	0.31	0.019	6.3	1.7	5.3	7.1
2',3,4,4',5-PeCB (#123)	0.0037	0.042	0.022	0.0013	0.27	0.13	0.34	0.62
2,3',4,4',5-PeCB (#118)	0.0094	0.069	0.041	0.0027	0.74	0.30	0.67	0.79
2,3,3',4,4'-PeCB (#105)	0.010	0.13	0.065	0.0036	0.99	0.46	1.6	1.7
2,3,4,4',5-PeCB (#114)	0.0029	0.033	0.026	0.0011	0.29	0.11	0.37	0.47
2,3',4,4',5,5'-HxCB (#167)	0.007	0.056	0.025	0.002	0.46	0.20	0.58	1.2
2,3,3',4,4',5-HxCB (#156)	0.010	0.14	0.047	0.0034	0.87	0.36	1.3	2.1
2,3,3',4,4',5'-HxCB (#157)	0.011	0.13	0.065	0.0035	0.68	0.29	1.3	2.4
2,3,3',4,4',5,5'-HpCB (#189)	0.013	0.14	0.058	0.0034	0.67	0.26	1.1	3.2
Total mono-ortho	0.067	0.74	0.35	0.021	5.0	2.1	7.3	12
Total DL-PCBs	0.12	1.4	0.66	0.040	11	3.8	13	20
Total PCDD/Fs	1.481	5.636	26.623	0.495	71.23	42.01	74.46	76.35
Total TEQ	0.12	0.38	0.86	0.035	7.2	4.9	5.7	6.3

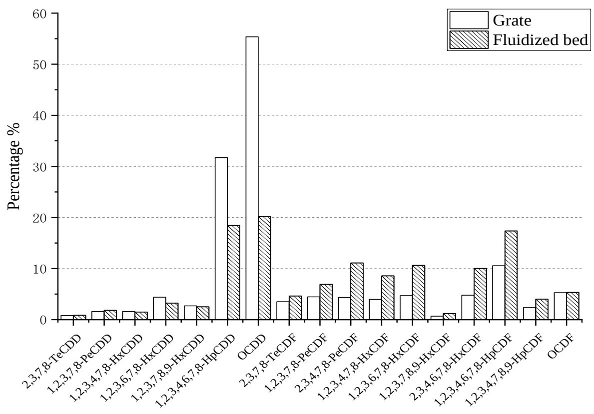

Figure 1 The congener distribution of PCDD/Fs in the fly ash samples

Concentration of heavy metal in the leaching solution of the fly ash samples

The concentration and limit of heavy metal in the leaching solution of the fly ash samples are shown in Figure 2 and Figure 3. The concentrations of Hg in all the leaching solution of the fly ash samples from grate-type MSW incinerator exceed the national standard value. For some heavy metals such as Cr, As and Se, it seems that grate-type furnace aggregated more of them in the fly ash than the fluidized bed type. However, higher concentrations of Cu were found in the leaching solution of the fly ash samples from fluidized bed MSW incinerator. This is the main reason contributed to the higher concentration of PCDD/Fs formed in the fly ash samples from fluidized bed MSW incinerator since Cu is one of the most important catalytic metal for PCDD/F formation.

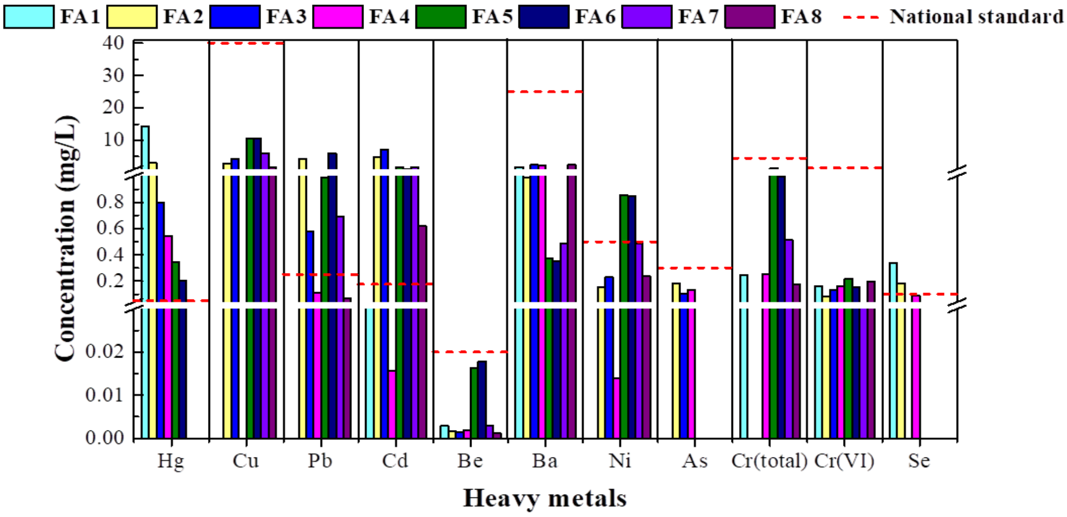

Figure 2 The concentration of heavy metal in the leaching solution of the fly ash samples

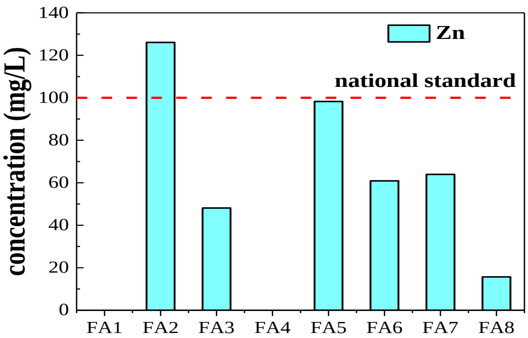

Figure 3 The concentration of Zn in the leaching solution of the fly ash samples

Concentration of chlorobenzene in the fly ash samples

The concentrations of chlorobenzene in the fly ash sample are shown in Figure 4. The levels of CBzs in the fly ash were from 89 to 1189 μg/kg, with the average value of 314 μg/kg. More higher chlorinated CBzs were found, which is in accordance with the results obtained by other researchers[5]. Incomplete combustion conditions are also an important factor because they can provide main source to form CBzs. In general, the yield of CBzs in the MSW incinerator could increase when the temperature decrease.

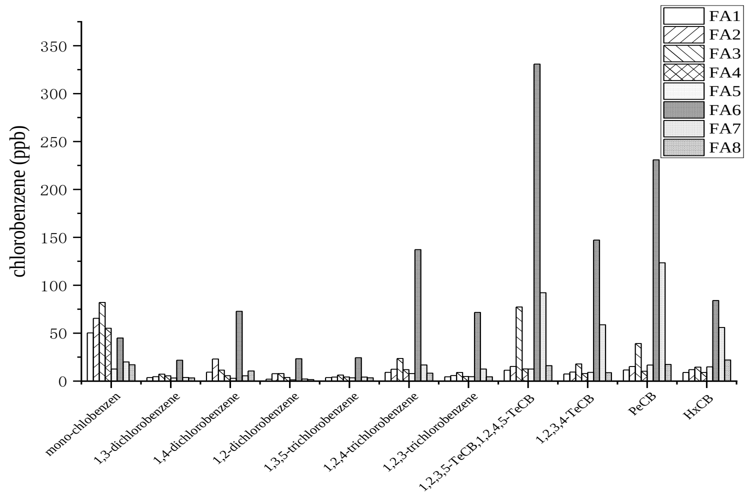

Figure 4 The distribution of chlorobenzene in the fly ash samples

Correlation between the TEQ value and the total concentration of chlorobenzene

As shown in Figure 4, the TEQ value correlated well with the total concentration of chlorobenzene in the grate-type MSW incinerator. The correlation coefficient value was up to 0.99. However, no correlation was found between the TEQ value and the total concentration of chlorobenzene in the fluidized bed MSW incinerator. Therefore, different formation routes of PCDD/Fs can be found in the fly ash from the grate-type and fluidized bed MSW incinerator.

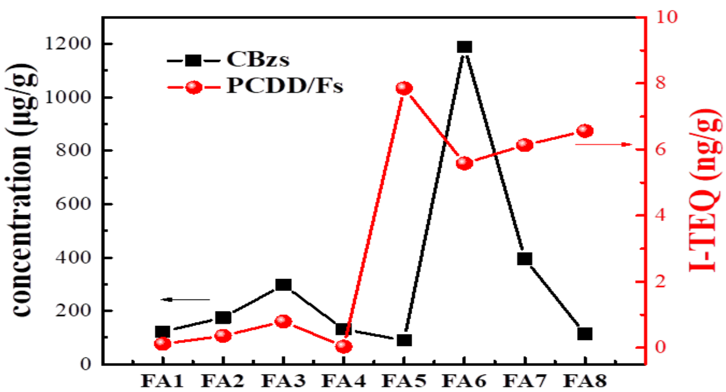

Figure 4 The correlation between the TEQ values and the total concentrations of chlorobenzene

Conclusion

The distribution characteristics of PCDD/Fs, dl-like PCBs, CBzs and the concentration of heavy metals in the leaching solution of fly ash samples from two kinds of typical MSW incinerators in China were studied. Several interesting results were obtained:

1. The TEQ concentrations of PCDD/Fs and dl-PCBs in the fly ash samples ranged from 0.035 to 7.2 ng WHO-PCDD/PCDF-PCB-TEQ/g. It seems that fluidized bed furnace produces more toxic fly ash than the grate-type one does. All the PCDD/Fs levels of fly ash produced from fluidized bed MSW incinerators exceeded the Chinese landfill acceptance criteria for fly ash samples (3.0 ng TEQ/g);
2. Some kinds of heavy metal, especilly Hg, Pd and Cr, in the leaching solution of the fly ash samples exceed the national standard value;
3. The levels of CBzs in the fly ash were from 89 to 1189 μg/kg, with the average value of 314 μg/kg. Correlation analysis showed that the TEQ value correlated well with the total concentration of chlorobenzene in the grate-type MSW incinerator.
4. The fly ash produced from MSW incinerators need to be further disposed before landfill.

Reference

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