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Characteristics of dioxins content in fly ash from municipal solid waste incinerators in China

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HIGHLIGHTS

- Fly ash was divided into four groups according to profile characteristics of dioxins.
- Low-chlorinated PCDD/F homologs were dominated in the fly ash.
- The concentration of 3,3′,4,4′-TePCB was highest among 12 dioxin-like PCBs.
- The main contribution to the TEQ was from 1,2,3,7,8,-PeCDD and 2,3,4,7,8-PeCDF.

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ABSTRACT

MSWI fly ashes sampled from 15 large-scale commercial municipal solid waste incineration plants in China were analyzed for seventeen polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDFs) as well as twelve dioxin-like polychlorinated biphenyls (dl-PCBs). The concentration of PCDD/PCDFs and dl-PCBs in fly ash samples ranged from 2.8 to 190 ng g^{-1}, and 59.6 ng g^{-1} on average. The toxic equivalent (TEQ) ranged from 34 to 2500 ng WHO(2005)-PCDD/PCDF-PCB-TEQ kg^{-1}, and 790 ng WHO(2005)-PCDD/PCDF-PCB-TEQ kg^{-1} on average. For PCDDs, hexa-chlorinated homolog was the dominant compound except two fly ash samples. Tetra-chlorinated homolog was dominant for PCDFs except one sample. The ratio of PCDDs/PCDFs ranged from 0.32 to 2.44 (average 0.97). The contribution of dl-PCBs to total concentration and TEQ was relatively minimal. Correlation between the concentration of three congeners and total TEQ values of fly ashes was also established. The findings obtained in this work provided overview information on the PCDD/PCDF-PCB content characterization of MSWI fly ash in China, which can be available for MSWI fly ash management in the environment.

1. Introduction

Over 150 million tons of municipal solid wastes (MSWs) are produced in China annually with a growing rate of 8–10%. Disposal of MSW has become a serious environmental challenge encountered in China. Incineration brings many advantages, such as significant volume reduction from about 80–90%, mass reduction of about 70–80%, and recovery of useful biomass resources for heating and power generation. The percentage of MSWs treated by incineration attained to 12% in 2011. A total of over 160 MSWs incineration plants were in operation in 2011, treating approximately 50000 tons of MSWs per day. It is expected that incineration will play an increasingly prominent role in MSW disposal in the coming decade in China.

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs) are typically found in flue gas, bottom ash and fly ash generated by municipal solid waste incinerators (MSWIs) (Olie, 1977; Hiraoka et al., 1987; Sakai et al., 1993). MSWIs have been identified as one of the largest contributor to the emissions of dioxins in Europe (Caserini and Monguzzi, 2002). MSWIs equipped with advanced air pollution control devices (APCDs) produce approximately 200000 tons of fly ash per year in China (Nie, 2008), which contains PCDD/Fs at high levels. Previous reports (Chang and Huang, 2000) indicated that PCDD/Fs from the flue gas could be effectively removed by APCD and transferred into fly ash. Dioxins are high toxicity persistent chemicals and widespread environmental pollutants (Mari et al., 2009; Davoli et al., 2010). Therefore, the MSWI fly ash is classified as hazardous waste.

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As a hazardous waste, the management of MSWI fly ash is a crucial issue, and before its disposal into final landfill MSWI, fly ash required further detoxifying treatment (Ling and Hou, 1998).

The content distributions and characteristics of dioxins in the fly ash depend on the constituents of incinerated MSW, the varieties of incineration facilities including their APCDs, and incineration technique, etc. The content characteristics of dioxins in MSWI fly ash could be concluded that OCDD was dominant, the major source of PCDD/F toxicity comes from the PeCDD/F homolog, and the concentration of dl-PCBs was relatively low (Chang and Huang, 2000; Minomo et al., 2010; Chang et al., 2011). Dioxins in the fly ash have received little attention in China, and there is relatively little information on the characteristics of MSWI fly ash from China.

Different from most of previous surveys with region-limited data, MSWI fly ash samples were collected from 15 different municipal solid waste incineration plants covering almost whole of China in this paper. Distribution and characteristics of PCDD/Fs and dl-PCBs content were investigated to understand the status of dioxins in fly ash in China. The relationship between the value of PCDD/Fs and dl-PCBs, furnace type, capacity of the municipal solid waste incinerators, and the type of air pollution control device was analyzed. The correlation between the concentration of indicative congeners and total TEQ value of PCDD/Fs and dl-PCBs in fly ash was also presented.

2. Experimental methods

2.1. Sample collection

Fly ashes researched in this study came from 15 different municipal solid waste incineration plants located in different Chinese cities. These fly ashes were designated by notations indicating the respective sample of origin (FA1, FA2···and FA15). Fly ash mixture was collected at a weight of 2 kg from fly ash hoppers or pits. This fly ash was then reduced down to about 20 g by well cross-mixing for laboratory analysis. The basic information and parameters of the 15 MSWIs were listed in Table 1.

2.2. Chemical analysis of dioxins

Chemical analysis of PCDD/Fs and PCBs in fly ash samples were conducted at Center for Environmental Science in Saitama, Japan, which group has an accredited process to determine the amount of dioxin species. 20 g of the fly ash samples were treated. The extracts were treated H_2SO_4, and purified using $AgNO_3$/silica-gel column and active carbon–silica gel column. Concentrations of PCDD/Fs and dl-PCBs were determined by gas chromatography high resolution mass spectrometry (HRGC-HRMS; JMS-800D, JEOL, Tokyo, Japan). Tetra-Hexa PCDD/Fs were used "CP-Sil88 for dioxins", Hepta-Octa PCDD/Fs and dl-PCBs were used DB-5ms for capillary column.

3. Results and discussion

3.1. PCDD/Fs concentrations

PCDD/Fs and dl-PCBs were found in all fly ash samples. The concentrations of 17 individual toxic (2,3,7,8-substituted) PCDD/F congeners, homologs, 4 non-*ortho* and 8 mono-*ortho* dl-PCBs in the fly ash samples, along with their TEQs are summarized in Table 2. The concentration of PCDD/Fs and dl-PCBs in fly ashes ranged from 2.8 ng g^{-1} to 190 ng g^{-1}, and 59.6 ng g^{-1} on average. The ratio of PCDDs/PCDFs ranged from 0.32 to 2.44, and 0.97 on average. It was found that the PCDD/F content in the fly ash were from 9.07 to 46.68 ng g^{-1} in Taiwan (Chang et al., 2011). (Chen et al. (2008)) reported that PCDD/F contents in the fly ash were from 19.2 to 236 ng g^{-1}. Our result showed the same order of magnitude with those found in China.

Toxic equivalents (TEQs) were calculated based on the WHO-TEF 2005 (Van den Berg et al., 2006). TEQ concentrations of PCDD/Fs and dl-PCBs in the fly ash samples ranged from 34 to 2500 ng WHO(2005)-PCDD/PCDF-PCB-TEQ kg^{-1} (Table 2), and 790 ng WHO(2005)-PCDD/PCDF-PCB-TEQ kg^{-1} on average. The TEQ value of dioxins in FA1 (1800 ng WHO(2005)-PCDD/PCDF-PCB-TEQ kg^{-1}), FA7 (2500 ng WHO(2005)-PCDD/PCDF-PCB-TEQ kg^{1}) and FA13 (1300 ng WHO(2005)-PCDD/PCDF-PCB-TEQ kg^{-1}), exceeded 1000 ng-TEQ kg^{-1}, which is the environmental quality standards for soil in some countries (Germany, United States and Japan). These three samples were all collected from the municipal solid waste incineration plants with circulating fluidized bed furnace or fluidized bed incinerator. It seems that fluidized bed furnace produces more toxic fly ash than the grate-type one does, in which TEQ values of dioxins were from 340 to 1000 ng WHO(2005)-PCDD/PCDF-PCB-TEQ kg^{-1}. However, it was noticeable that the TEQ value of dioxins in FA2, which is also from a circulated fluidized bed plant, was 34 ng WHO(2005)-PCDD/PCDF-PCB-TEQ kg^{-1}. This lowest TEQ value in FA2 was probably due to that the load of feeding waste on incinerators was not full in CFB plant (FA2) and congener profiles of PCDD/PCDFs and

Table 1
Basic information and parameters concerning the 15 MSWIs.

Sample no.	Furnace type	Capacity (ton/d)	Air pollution control device	Location
FA1	[a]CFB	3 units × 200	Semidry purification system + bag filter	East of China
FA2	CFB	2 units × 260	Desulfurization purification treatment + bag filter	Northeast of China
FA3	Grate-type	2 units × 200	Semidry scrubber + [b]AC + bag filter	South of China
FA4	Grate-type	2 units × 400	Semidry purification system + AC + bag filter	East of China
FA5	Grate-type	2 units × 800	AC + bag filter	Northeast of China
FA6	Grate-type	2 units × 600	Semidry purification system	Middle of China
FA7	[c]FBI	300	Semidry scrubber + AC + bag filter	South of China
FA8	Grate-type	1000	Semidry scrubber + bag filter	East of China
FA9	Grate-type	2 units × 600	Semidry purification system + bag filter	South of China
FA10	Grate-type	3 units × 350	Semidry scrubber + AC + bag filter	East of China
FA11	Grate-type	1500	Urea + AC + hydrated lime + bag filter	East of China
FA12	Grate-type	1000	Semidry purification system + AC + bag filter	South of China
FA13	CFB	2 units × 400	Semidry neutralization reaction + AC + bag filter	East of China
FA14	Grate-type	600	Semidry reaction tower + bag filter	East of China
FA15	Grate-type	1200	Cooling + AC + bag filter	West of China

[a] CFB: circulating fluidized bed.
[b] AC: activated carbon.
[c] FBI: fluidized bed incinerator.