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Emission of unintentionally produced persistent organic pollutants (UPOPs) from municipal waste incinerators in China

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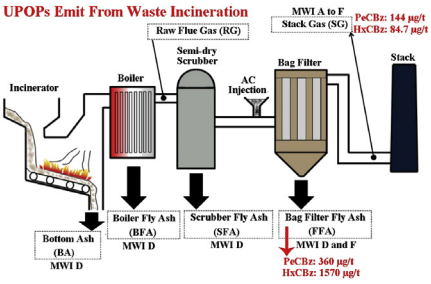
HIGHLIGHTS

- Level of PCDD/Fs, PCBs, PeCBz, and HxCBz in flue gas from MWI in China was reported.
- Emission factors of PeCBz (144 μg/t) and HxCBz (84.7 μg/t) in flue gas from MWI were given.
- Profiles of PCBs and dl-PCBs in both gaseous and fly ash phase were stated.
- Removal efficiencies of PCDD/Fs, PCBs, PeCBz, and HxCBz by air pollution control device were evaluated.

GRAPHICAL ABSTRACT



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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz), which are listed in the Stockholm Convention, are commonly known as unintentionally produced persistent organic pollutants (UPOPs). As municipal waste incinerators (MWIs) have burgeoned in China, the emission of UPOPs is of great concerns. Compared to the extensive studies of PCDD/Fs emission, not much information of non-dioxin UPOPs (i.e., PCBs, HxCBz, and PeCBz) is available. In the present study, samples from raw gas (RG) after boiler, stack gas (SG) after air pollution control devices (APCDs) and fly ash (FA) samples were collected from typical MWIs in China. The analyses of SG samples indicate that PCDD/Fs are the major contributor to TEQ value, but non-dioxin UPOPs are the dominant compounds in terms of mass concentration. The mean emission factors of dl-PCBs, PeCBz, and HxCBz in SG are 0.372, 144, and 84.7 μg/t, respectively. In contrast with gaseous samples, FA contains higher mass concentration of PCDD/Fs and PCBs than that of PeCBz and HxCBz. In terms of homologues distribution of PCBs, di- to tetra-CBs were the predominant species in both SG and FA samples. PCB-126 is the major contributor to the TEQ concentration. The comparison of UPOPs composition in SG and RG samples shows that activated carbon adsorption process is capable of removing most PCDD/Fs, but less efficient for the removal of non-dioxin UPOPs.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), pentachlorobenzene (PeCBz)

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and hexachlorobenzene (HxCBz) are categorized as unintentionally produced persistent organic pollutants (UPOPs) due to their toxicities, long range transport and bioaccumulation and are therefore listed in the Stockholm Convention. Previous studies have shown that UPOPs could be formed and emitted from thermal processes like municipal waste incinerator (MWI) (Fiedler, 2007; Hung et al., 2016; Liu and Zheng, 2013; Olie et al., 1977; U.S. EPA, 2006; Wallerstein, 1999) and from chemical manufacturing processes (Lysychenko et al., 2015; Weber et al., 2008). According to China Statistical Yearbook 2014 (NBS, 2014), as of 2013, 166 large-scale MWIs were in operation and their disposal capacities reached 4.63×10^7 t/a. More incinerators are currently under construction or in planning stage to combat the increasing amount of municipal waste. As MWIs have burgeoned in China, the emission of UPOPs receives great attention and concerns due to their adverse impact in environment.

In the past decades, the emission level and profile of PCDD/Fs have been extensively studied (Chi et al., 2005; Jansson and Andersson, 2012; Ni et al., 2009; Šyc et al., 2015; Weber and Hagenmaier, 1999; Yan et al., 2006; Zhang et al., 2013). However, not much attention has been paid on the non-dioxin UPOPs (i.e., PCBs, HxCBz, and PeCBz). Studies have shown that their existence are favorable for the formation of PCDD/Fs in flue gas (Liu et al., 2013; Nie et al., 2011) and could be indicator of PCDD/Fs (Hung et al., 2013; Kaune et al., 1996; Lavric et al., 2005; Öberg and Bergström, 1985).

The emissions of PCBs in flue gas from MWIs have been reported in Japan (Kim et al., 2004; Sakai et al., 2001; Sakurai et al., 2003), Korean (Shin et al., 2006), and the EU (Dyke et al., 2003; Šyc et al., 2015). Recently, a few studies have focused on the emissions of PCBs in other sources, including iron ore sintering plant (Tian et al., 2012), metallurgical process (Nie et al., 2011, 2012), and medical waste incineration (Chen et al., 2015) in China. Unfortunately, studies on PCB emissions from MWIs in China are extremely limited (Yan et al., 2010). As for PeCBz and HxCBz, some valuable studies on the basis of full scale (Kaune et al., 1996; Weber and Hagenmaier, 1999) and pilot scale (Fangmark et al., 1993, 1994) are available, which calls for more in-depth researches based on full-scale incinerator.

In addition, most of the reported data are mainly based on stack gas samples, which is strongly affected by APCDs. In contrast, information from RG samples collected before APCDs could truly reflect the emission pattern and is also important for the evaluation of APCDs performance. However, such information is rarely provided. Moreover, aside from flue gas, the emission pattern of non-dioxin UPOPs in fly ash has not been fully investigated yet.

In this study, in addition to stack gas samples, also raw gas and fly ash samples were collected from MWIs in China. The emission factors as well as emission pattern of non-dioxin UPOPs in different matrix were reported. The performance of APCDs on removing non-dioxin UPOPs was evaluated. The results are not only important supplements for UPOPs emission inventory, but also provide guidance to the improvement of APCDs.

2. Materials and methods

2.1. MWI description

Six MWIs were selected in this study with plant A, B, C, D, and E locating in southern China, while plant F in northern China. All MWIs were equipped with modern APCDs, including semi-dry scrubber, activated carbon (AC) injection and bag filter units. The operating parameters are listed in Table S1 of Supplementary material.

As illustrated in Fig. 1, SG samples were collected after APCDs treatment from all six MWIs. RG samples, taken from sampling vent between boiler and semi-dry scrubber, were collected from MWI D and F. Bottom ash (BA), boiler fly ash (BFA), scrubber fly ash (SFA), and bag filter fly ash (FFA) were collected from MWI D. As for MWI F, only FFA samples were available.

2.2. Sampling

Gas sampling was performed according to the procedure outlined in HJ 77.2−2008 (Ministry of Environmental Protection of China), with the aids of automatic isokinetic sampler (TECORA, Italy). Gas sampler consisted of a glass fiber filter, and a water-cooled XAD-2 adsorbing trap (SUPELCO, U.S.). The XAD-2 was initially spiked with internal standard ($^{13}C_{12}$-1,2,3,7,8-PeCDF) before sampling. RG sampling was conducted on plant D and F. In order to collect more samples and in particular to prevent the clogging of the filter paper (particle concentration from 1850 to 2140 mg/m^3 in two plants based on-line measurements), the replacement of filter was performed every half hour in our automatic isokinetic sampler (total 3 m^3). Thus a total of 6 filters were used for overall sampling duration of 3 h. All filters were placed together for subsequent pre-treatment and eventually UPOPs analysis. SG sampling was conducted on all six MWIs. Triplicate samples were collected from all of the MWIs.

2.3. Analysis

The analysis of gas and ash samples follow those procedures in HJ 77.2−2008 of China and U.S. EPA Method 1613, respectively. Each gas sample contains the extract from filter, XAD-2 resin, and condensed water. XAD-2 resin was extracted by 24 h Soxhlet extraction with toluene. The filter was washed with hydrochloric acid before extraction. The condensed water and rinse of filter washing were extracted by dichloromethane, and the extract was combined with the Soxhlet extracted toluene. Fly ash samples were treated with hydrochloric acid and then subjected to Soxhlet extraction. The washing solution was extracted with dichloromethane and added into toluene as well.

All samples were spiked with 17 $^{13}C_{12}$-labeled PCDD/Fs, 12 $^{13}C_{12}$-labeled dl-PCBs, $^{13}C_{12}$-labeled HxCBz and $^{13}C_{12}$-labeled PeCBz (Cambridge Isotope Laboratories, U.S.) internal standards before Soxhlet extraction. The extract was concentrated by rotary evaporation and divided into four parts by volume for UPOPs analysis: 25% for PCDD/Fs and dl-PCBs, 25% for total-PCBs, 10% for HxCBz and PeCBz and another 40% was kept as a reserved sample.

For PCDD/Fs and dl-PCBs analysis, the extract was treated by sulfuric acid, followed by multilayer silica gel column purification and activated carbon silica gel column separation. The procedures for total-PCBs extraction is the same as for PCDD/Fs and dl-PCBs, without the activated carbon column separation. Analyses of PCDD/Fs, dl-PCBs and total-PCBs were performed by a high-resolution gas chromatograph coupled with a high-resolution mass spectrometry (HRGC-HRMS, Agilent 6890N/JEOL JMS-800D) equipped with a DB-5ms (60 m, 0.25 mm i.d., 0.25 μm film thickness) capillary column. The HRMS was operated in the selected ion monitoring (SIM) mode, with the ionization energy of 38 eV and a resolution over 10,000.

As for HxCBz and PeCBz analysis, the extract was purified in Florisil column with hexane. Finally, the extract was concentrated to 0.5 mL by rotary evaporation and a gentle stream of nitrogen gas. HxCBz and PeCBz were analyzed by GC-MS (Agilent 7890A) with DB-5ms capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness). The MS was operated in the SIM mode.