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Characterization of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans of the Flue Gases, Fly Ash and Bottom Ash in a Municipal Solid Waste Incinerator

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ABSTRACT

The emissions factors of PCDD/Fs from the stack flue gas, bottom ash and fly ash of a municipal solid waste incinerator (MSWI) were analyzed in this study. The congner profiles of PCDD/F mass were dominant in OCDD and OCDF; however, those of PCDD/Fs-TEQ were mainly 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD in all samples. The PCDD/F emission factors of MSWI per metric ton of waste incinerated from the stack flue gas, bottom ash and fly ash were at an averaged of 0.0919, 7.20 and 12.8 µg PCDD/Fs-WHO$_{2005}$-TEQ ton^{-1}, respectively. Futhermore, the emission factor of MSWI in the unit of electricity produced averaged 0.185, 14.5 and 26.3 µg PCDD/Fs-WHO$_{2005}$-TEQ (MWh)$^{-1}$, respectively. As the results shown in this study, the majority of total PCDD/Fs-WHO$_{2005}$-TEQ were mainly in both bottom ash and fly ashes. From long-term perspective, the disposal of both bottom and fly ashes should pay more attention to this issue. The results of this study provide useful information for both further studies and environmental control strategies aimed at persistent organic compounds (POPs).

Keywords: PCDD/Fs; Municipal solid waste incinerator; Fly ash; Bottom ash; Flue gas.

INTRODUCTION

With the development of the economy and the growth of industry, incineration has become one of the major pathway for treatment of municipal solid wastes, due to its advantages in terms of volume reduction, energy recovery, pathogen elimination and chemical-toxicity destruction (Dempsey and Oppelt, 1993). Since polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) were first discovered in the flue gases and fly ash of municipal solid waste incinerators (MSWIs) in 1977 (Olie *et al.*, 1977), PCDD/Fs have been of wide concern due to their extreme toxicity and adverse implications for human health. The characteristics of being semi-volatile and hydrophobic enhance the PCDD/Fs ability to accumulate in the environment (Chi *et al.*, 2016), especially in organic carbon-rich media such as soil and sediment (Schuhmacher *et al.*, 1997; Chao *et al.*, 2007). Pollution issues related to the incineration process have drawn much more attention, even though the wastes have been reduced and stabilized. The chlorine content of the wastes and the temperature of the combustion process usually play a major role in the formation of PCDD/Fs (Lee *et al.*, 2003; Wang *et al.*, 2003; Li *et al.*, 2007; Wang *et al.*, 2010). Human activities are the major sources of PCDD/F emissions, including industrial and heat-treatment processes (Oh *et al.*, 1999; Baker and Hites, 2000; Tame *et al.*, 2007; Xu *et al.*, 2009; Cheruiyot *et al.*, 2015; Cheruiyot *et al.*, 2016; Redfern *et al.*, 2017). Previous studies suggested that there are processes in the post-furnace stage which by de novo synthesis or precursor synthesis can generate lots of PCDD/Fs, and the operating conditions include the flue gas temperature profile, air supply, carbon and metal contents in fly ash and so on, which are the major factors that affect the PCDD/Fs formation rates (Dickson *et al.*, 1992; Stieglitz *et al.*, 1993; Gullett *et al.*, 1994; Addink and Olie, 1995a, b; Stieglitz, 1998; Chang and Huang, 2000). Combustion experments suggest that most of the PCDDs and PCDFs are generated at temperatures higher than 650°C, but the process of condensation of CPhs (Chlorinated phenols) usuall produce more PCDDs, and generally more PCDFs are produced by a low- or non-chlorinated precursor followed by further chlorination

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reactions (Wikström and Marklund, 2000). MSWIs are a significant source for the transformation of PCDD/Fs to the atmosphere. In recent years, the levels of PCDD/Fs emitted by MSWIs and into the ambient air have often been used to evaluate the atmospheric concentrations of these pollutants near such facilities (Lorber *et al*., 1996; Abad *et al*., 1997; Koblantz *et al*., 1997; Fielder, 1999a, b; Oh *et al*., 1999). PCDD/F emissions result in subsequent aerial deposition onto soil and vegetation.

For MSWIs, as the incineration temperature increase, the concentrations of PCDD/Fs from flue gases will also rise (Han *et al*., 2017). Fly ash has the highest dioxin concentration produced by MSWIs, and it acts as a heterogeneous catalyst that is important for the synthesis of PCDD/Fs in the MSWIs (Karasek and Dickson, 1987; Goldfarb, 1989; Altwicker *et al*., 1992; Huang and Buekens, 1995; Lin *et al*., 2008). Previous studies have suggested that the PCDD/F emissions during start-up are a large source of emissions from MSWIs (Neuer-Etscheidt *et al*., 2006). PCDD/Fs released from the MSWIs (include stack flue gas, bottom ash and fly ash) can spread through the media of air, soil and water, eventually enter animal and human bodies through atmospheric deposition (Du *et al*., 2011; Chandra Suryani *et al*., 2015; Chang *et al*., 2016; Chen *et al*., 2017; Zhu *et al*., 2017a, b).

Because of Taiwan's high population density, incineration has become the major method to treat municipal solid wastes in the country. At present, there are 23 large MSWIs in operation in Taiwan, which has a very strict PCDD/F emission standard (0.1 ng I-TEQ Nm^{-3}) for MSWIs.

The congener profiles and emission factors of PCDD/Fs in the stack flue gas, bottom ash and fly ash produce when using unit waste and electricity generation, respectively, were investigated. This study provides useful information for the control strategies of MSWIs.

MATERIAL AND METHODS

Sampling

From January 2010 to December 2015, a number of stack flue gas, bottom ash and fly ash samples were collected from an MSWI, located in southern Taiwan. The air pollution control devices (APCDs) which are commonly believed to be the most effective techniques for PCDD/Fs control are the most widely used such devices in MSWIs in Taiwan (Wang *et al*., 2009).

Flue gas samples from the stack were collected with an isokinetic sampler (KNJ, Korea) according to US EPA modified Method 23. XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes before sampling, and the sampling lasted for ~3 h. The bottom ash samples were collected directly from each furnace. The fly ash samples were collected by the bag filters. To ensure the collected samples were free from contamination, one trip blank and one field blank were also taken during the field sampling.

Analysis of PCDD/Fs

The US EPA Modified Method 23 was used for the analyses of the stack flue gas samples, while the US EPA Method 1613B was used for the the analyses of bottom and fly ash samples (US EPA, 1994, 1996).

All chemical analyses were measured in the Super Micro Mass Research and Technology Centre of Cheng Shiu University, which has passed the international intercalibration standards test for PCDD/Fs in fly ash, sediment, mother's milk, human blood, and cod liver. A known amount of the internal standard was spiked in each sample, which was then extracted for 24 hours. The extract was treated with concentrated sulfuric acid, and then a series of sample cleanup and fractionation procedures. Sample cleanup was done using an acidic silica-gel column, an alumina column, and an activated carbon column. Consequently, the elution was concentrated to around 1 mL, and further concentrated to near dryness with a nitrogen stream. Before PCDD/Fs analysis, each sample was added to the standard solution to ensure recovery during the analysis process (Shih *et al*., 2006). We used high-resolution gas chromatographs/high-resolution mass spectrometers (HR-GC/ HR-MS) for the PCDD/F analysis. The HRGC (Hewlett-Packard 6970 Series gas, CA) was equipped with a DB-5 fused silica capillary column (L = 60 m, ID = 0.25 mm, film thickness = 0.25 µm) (J&W Scientific, CA) with a splitless injection, while the HR-MS (Micromass Autospec Ultima, Manchester, UK) had a positive electron impact (EI+) source. Selected ion monitoring with the resolving power of 10,000 was used for the analyzer mode. The electron energy and source temperature were specified at 35 eV and 250°C, respectively. In addition, the oven temperature program was set as follows: initially at 150°C (held for 1 min), then increased by 30°C min^{-1} to 220°C (held for 12 min), and finally increased by 1.5 °C min^{-1} to 310°C (held for 20 min). Helium was used as the carrier gas. The analysis process strictly followed the protocol for quality analysis/quality control (Wang and Lee, 2010).

RESULTS AND DISCUSSION

Basic Information of the MSWI

The basic information of the MSWI investigated in this study is presented in Tables 1 and 2, which shows the weight of monthly MSW treated from 2009 to 2015 is in the range between 19,917 and 22,173 ton $month^{-1}$ and with an average of 20,886 ton $month^{-1}$. Table 2 present the monthly electric energy production per ton of MSW treated from 2009 to 2015, which ranged from 459 and 523 kWh ton^{-1}, and averaged 490 kWh ton^{-1}.

Furthermore, from 2010 to 2015, the monthly average gas flow rate in the stack flue gas ranged between 1225 and 1639 Nm^3 min^{-1}, and averaged 1460 Nm^3 min^{-1}. The operational time of MSWI ranged from 599 to 665 hr $month^{-1}$, and averaged 629 hr $month^{-1}$. From 2010 to 2015, the monthly generation rate of bottom ashes varied from 1360 to 7380 ton $month^{-1}$, and averaged 4700 ton $month^{-1}$; as for the fly ash, ranged from 1270 to 2630 ton $month^{-1}$, and averaged 1830 ton $month^{-1}$. The mean PCDD/F mass contents in bottom ash were between 0.0455 and 4.85 ng g^{-1}, and averaged 1.48 ng g^{-1}, and those of fly ash were between 0.0121 and 19.69 ng g^{-1}, and averaged 2.56 ng g^{-1},

Table 1. Monthly MSW treated during 2009–2015 (Unit: Metric ton).

Month	2009	2010	2011	2012	2013	2014	2015
Jan.	20956	18647	21641	20210	20056	20906	16329
Feb.	17941	20477	17726	11922	18387	14082	18133
Mar.	18559	20855	21043	12704	20089	22467	22856
Apr.	14704	21843	22124	23039	21630	16891	15772
May.	23370	20823	19002	26477	16058	12298	11909
June.	21069	23034	24958	22504	17629	23365	23600
July.	20640	22935	26138	19181	26278	24741	23063
Aug.	29235	21288	23259	21035	23173	16510	25449
Sep.	20296	26835	24120	20801	24752	25715	22317
Oct.	20172	24776	22169	23963	22597	23249	22798
Nov.	17865	20859	21314	23094	22119	17998	20618
Dec.	19472	20876	22577	20924	21190	20787	19195
Mean	**20357**	**21937**	**22173**	**20488**	**21163**	**19917**	**20170**
Annual	**244279**	**263246**	**266071**	**245854**	**253960**	**239010**	**242040**

Table 2. Monthly electric energy production per ton of MSW treated during 2009–2015 (Unit: kWh ton^{-1}).

Month	2009	2010	2011	2012	2013	2014	2015
Jan.	512	538	558	462	507	531	517
Feb.	490	508	536	397	553	516	569
Mar.	484	483	527	453	504	586	463
Apr.	410	476	480	480	448	523	506
May.	492	450	475	473	449	483	385
June.	484	422	459	417	499	487	510
July.	444	457	449	424	546	517	540
Aug.	474	485	488	453	484	469	512
Sep.	475	453	486	478	462	544	527
Oct.	489	504	476	508	517	540	516
Nov.	484	499	471	480	475	541	519
Dec.	454	503	460	484	504	543	547
Mean	**474**	**481**	**489**	**459**	**496**	**523**	**509**

respectively, and the corresponding PCDD/Fs-WHO$_{2005}$-TEQ levels for bottom ash ranged from 0.001 to 0.138 ng PCDD/Fs-WHO$_{2005}$-TEQ g^{-1} and averaged 0.038 ng PCDD/Fs-WHO$_{2005}$-TEQ g^{-1}, and those for fly ash were from 0.0002 to 0.900 ng PCDD/Fs-WHO$_{2005}$-TEQ g^{-1} and averaged 0.111 ng PCDD/Fs-WHO$_{2005}$-TEQ g^{-1}. The average value of PCDD/F content in the fly ash was approximately 2.92 times higher than that of bottom ash. The total PCDD/Fs-WHO$_{2005}$-TEQ contents in both bottom and fly ashes were all lower than the regulated standard (1.0 ng WHO$_{2005}$-TEQ g^{-1}). However, the total PCDD/Fs-WHO$_{2005}$-TEQ content in a certain fly ash sample was as high as up to 0.900 ng PCDD/Fs-WHO$_{2005}$-TEQ g^{-1}, and thus needs more attention. The great variation in PCDD/F content in both the bottom and fly ashes indicated that the feeding wates, particularly those related to the chlorine content, may vary to a great extent.

Total PCDD/Fs-TEQ Concentration in the Stack Flue Gas

From 2010 to 2015, the total PCDD/Fs mass concentration in the stack flue gas ranged between 0.363 and 2.077 ng Nm^{-3} and averaged 0.917 ng Nm^{-3}; and the corresponding total PCDD/Fs-WHO$_{2005}$-TEQ values were between 0.00808 and 0.0711 ng PCDD/Fs-WHO$_{2005}$-TEQ Nm^{-3}, and averaged 0.0343 ng PCDD/Fs-WHO$_{2005}$-TEQ Nm^{-3}. These results show that the total PCDD/Fs-WHO$_{2005}$-TEQ concentrations in the stack flue gas were all lower than the PCDD/F emission standard (0.1 ng PCDD/Fs-I-TEQ Nm^{-3}) for MSWIs, as regulated by the Taiwan EPA. The average result found in this study was lower than those of previous studies, which the mean total PCDD/Fs-I-TEQ concentrations were 0.0593 ng PCDD/Fs-I-TEQ Nm^{-3} (Wang *et al.*, 2005) and 0.0533 ng PCDD/Fs-I-TEQ Nm^{-3} (Lee *et al.*, 2003), respectively.

Congener Profiles of PCDD/Fs

The conger profiles of the PCDD/F mass and PCDD/Fs-TEQ in stack flue gas, bottom ash and fly ash are shown in Figs 1, 2 and 3, respectively. Each congener was normalized by the sum of the seventeen PCDD/F congeners. In the stack flue gas, the congener profiles of PCDD/F mass are predominant in highly chlorinated congeners, like OCDD (42.1%), 1,2,3,4,6,7,8-HpCDD (18.8%), 1,2,3,4,6,7,8-HpCDF (9.38%) and OCDF (6.64%). The congener profiles of PCDD/F mass in stack flue gas in this study are similar to those in previous studies (Lee *et al.*, 2003, 2004; Wang *et al.*, 2005). However, the congener profiles of PCDD/Fs-TEQ are dominanted by 2,3,4,7,8-PeCDF (21.0%),

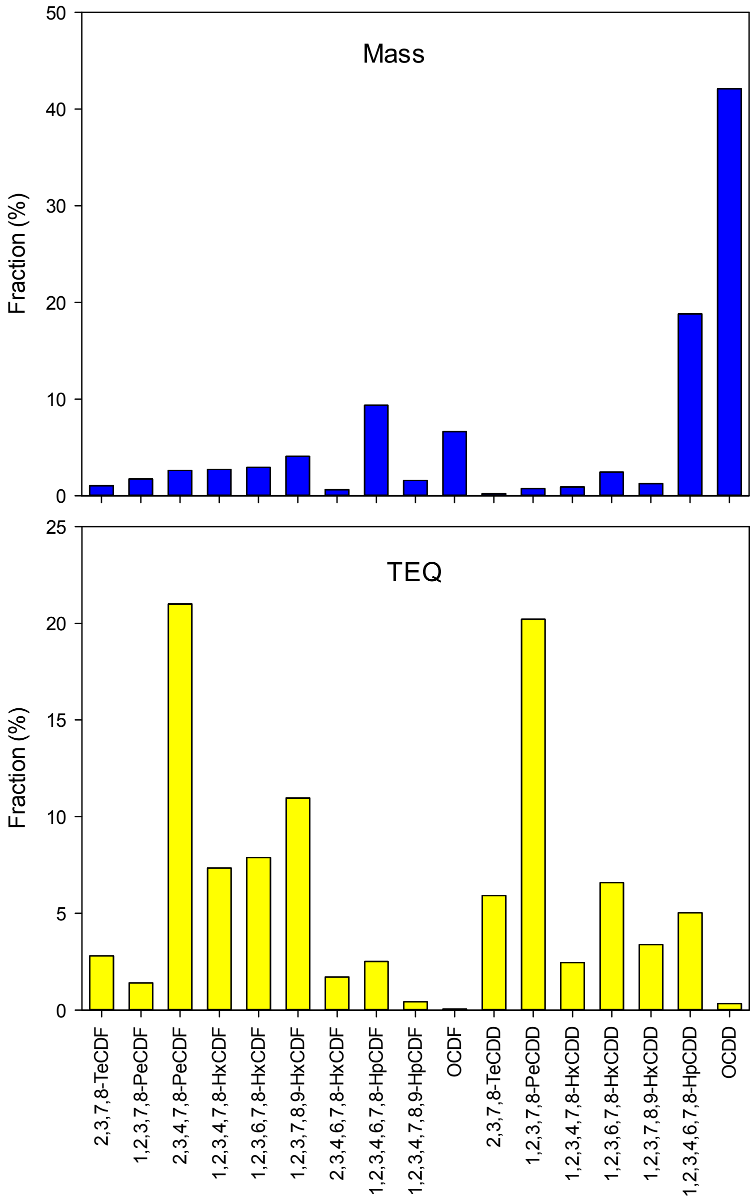

Fig. 1. Congener profiles of total PCDD/F mass and total-PCDD/Fs-WHO$_{2005}$-TEQ in the stack flue gas.

1,2,3,7,8-PeCDD (20.2%), 1,2,3,7,8,9-HxCDF (11.0%) and 1,2,3,6,7,8-HxCDF (7.89%). This is very similar to the congener profiles of PCDD/Fs-TEQ in the ambient air in central Taiwan (Chen *et al.*, 2017). Very few previous studies report the congener profiles of PCDD/Fs-TEQ in stack flue gases. The major impact of PCDD/Fs is due to their toxicity rather than their mass. Therefore, we need pay more attention to those PCDD/F congeners with higher fractions of PCDD/Fs-TEQ.

In bottom ash, the congener profiles of PCDD/F mass are also predominant in higher chlorinated PCDD/Fs congeners, like OCDD (36.0%), OCDF (26.5%), 1,2,3,4,6,7,8-HpCDF (12.8%) and 1,2,3,4,6,7,8-HpCDD (7.57%), with these results very similar to previous studies (Lin *et al.*, 2010). However, the congener profiles of PCDD/Fs-TEQ are mainly dominated by 2,3,4,7,8-PeCDF (25.5%), 1,2,3,7,8-PeCDD (16.2%), 2,3,4,6,7,8-HxCDF (12.6%) and 1,2,3,6,7,8-HxCDF (8.80%).

In fly ash, the congener profiles of PCDD/F mass are also mainly dominated by higher chlorinated PCDD congeners, like OCDD (34.8%), 1,2,3,4,6,7,8-HpCDF (13.8%), 1,2,3,4,6,7,8-HpCDD (13.2%) and OCDF (11.1%); the congener profiles of PCDD/Fs-TEQ are predominated by 2,3,4,7,8-PeCDF (22.9%), 1,2,3,7,8-PeCDD (20.7%), 2,3,4,6,7,8-HxCDF (11.4%) and 1,2,3,6,7,8-HxCDF (8.97%). The congener profiles of mass PCDD/Fs found in this work are similar to those of previous studies (Lin *et al.*, 2010; Wei *et al.*, 2016).

The results indicated that the mass fraction of higher chlorinated PCDD/F congeners are higher than those of lower chlorinated ones. The congener profiles of PCDD/Fs-TEQ in all samples show that 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD are the most dominant congeners, due to the product of their relatively high toxic equivalency factor (TEF) and PCDD/F concentration.

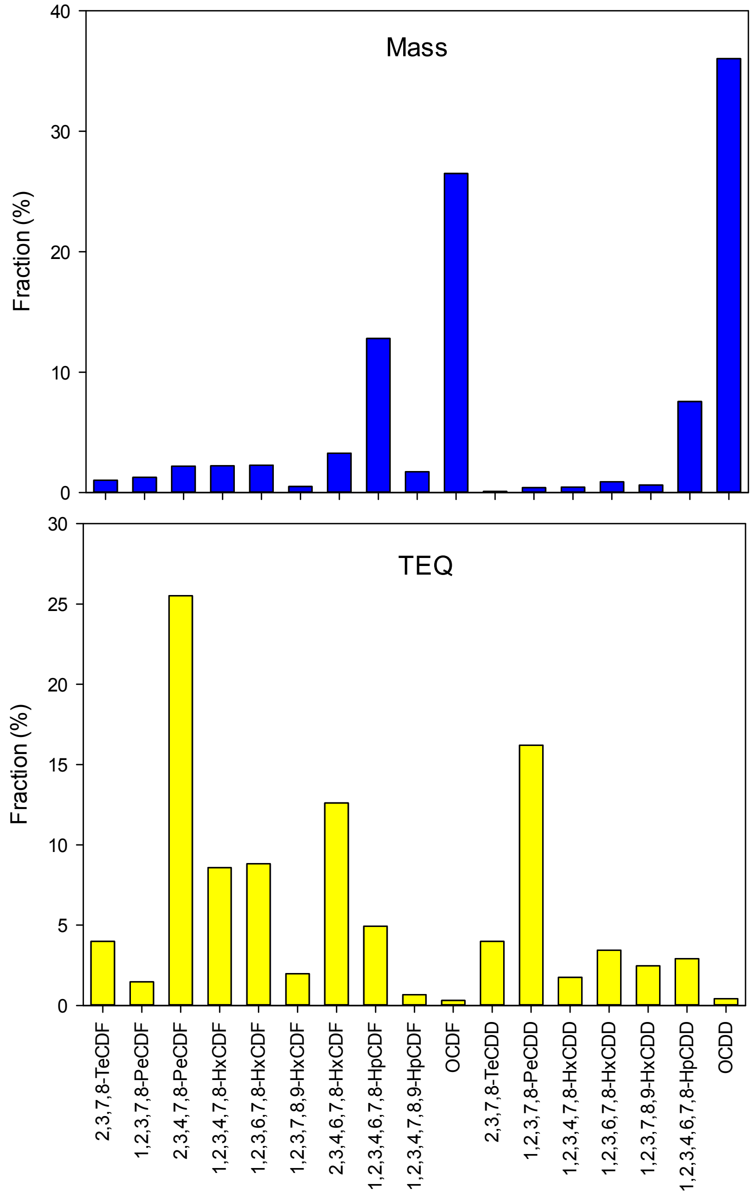

Fig. 2. Congener profiles of total PCDD/F mass and total-PCDD/Fs-WHO_{2005}-TEQ in the bottom ash.

Emission Factors

The emission factors are important information to establish a PCDD/F inventory and develop a control strategy. Figs. 4, 5 and 6 show the emission factors of total PCDD/Fs-TEQ by the unit ton of MSW treated from the stack flue gas, bottom ash and fly ash, respectively.

From 2010 to 2015, the PCDD/F emission factors of MSWI (EF) by the unit ton of MSW treated from stack flue gas are shown in Fig. 4, and these reveal that between 2011 and 2014, the EF ranged from 0.0583 to 0.0673 µg PCDD/Fs-WHO_{2005}-TEQ ton^{-1}; while the EF in 2010 (0.148 µg PCDD/Fs-WHO_{2005}-TEQ ton^{-1}) and 2015 (0.153 µg PCDD/Fs-WHO_{2005}-TEQ ton^{-1}) were similar, and much larger than those from 2011 to 2014. Overall, the EF of total PCDD/Fs-TEQ in the stack flue gas are in the range of 0.0583–0.153 µg PCDD/Fs-WHO_{2005}-TEQ ton^{-1}, with an average of 0.0919 µg PCDD/Fs-WHO_{2005}-TEQ ton^{-1}. These values are similar to those in Wang *et al.* (2003), which ranged from 0.0475 to 0.187 µg PCDD/Fs-I-TEQ ton^{-1} and averaged 0.0939 µg PCDD/Fs-I-TEQ ton^{-1}; however, they are lower than the results of Lin *et al.* (2010), which aveaged 0.149 and 0.220 µg PCDD/Fs-I-TEQ ton^{-1} in MSWI-A and MSWI-B, respectively. The variation of PCDD/Fs-TEQ EF may due to the variations in feeding wastes and the use of different air control devices (Wang *et al.* 2003). The above results reveal that the stack flue gas of MSWIs is one of the major emission sources of PCDD/Fs.

Bottom ash is a highly heterogeneous burnt-out mixture. The PCDD/Fs EF by the unit ton of MSW treated in bottom ash are presented in Fig. 5, which show the EF of total PCDD/Fs-WHO_{2005}-TEQ in bottom ash ranged between 1.83 and 12.9 µg WHO_{2005}-TEQ ton^{-1} and averaged 7.20 µg WHO_{2005}-TEQ ton^{-1} (Fig. 5); that of 2014 (12.9 µg WHO_{2005}-TEQ ton^{-1}) was approximately 7.0 times greater

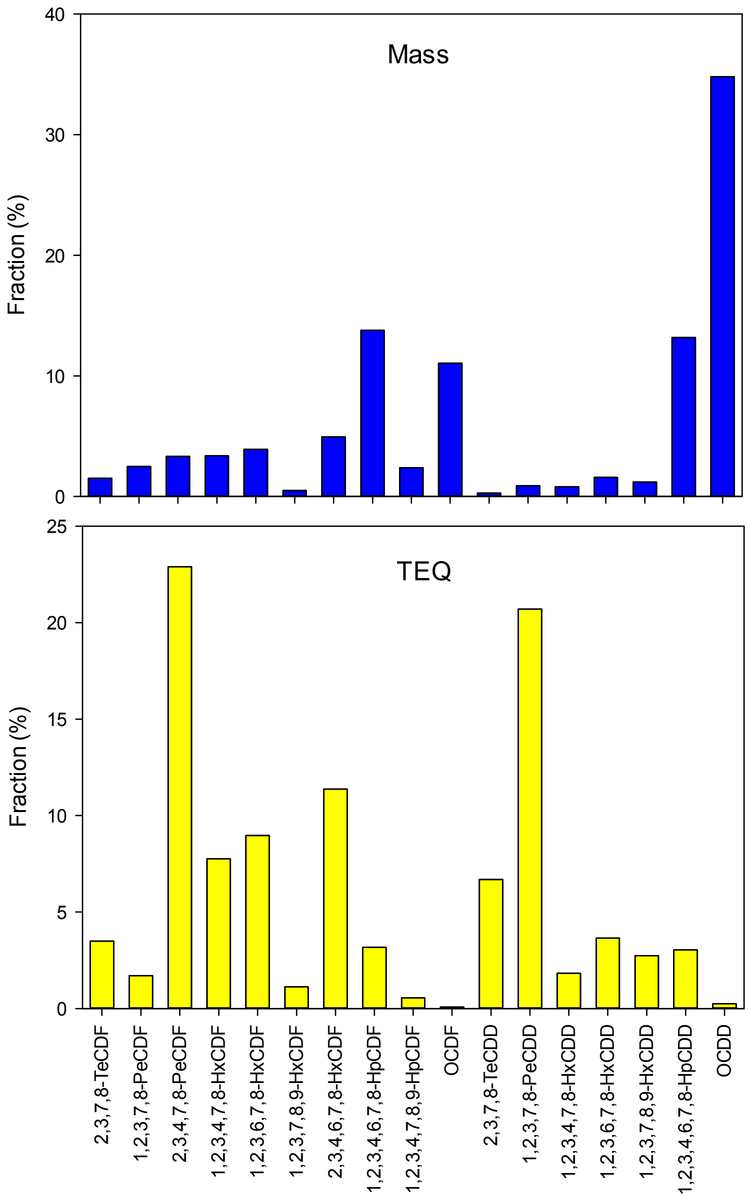

Fig. 3. Congener profiles of total PCDD/F mass and total-PCDD/Fs-WHO_{2005}-TEQ in the fly ash.

than that of 2011 (1.83 µg WHO_{2005}-TEQ ton^{-1}). The overall trend of PCDD/F EF in bottom ash increased year by year from 2011 to 2014, and decreased in 2015. These values are higher than those in Lin *et al*. (2010) with regard to bottom residues, which were 1.91 and 2.05 µg PCDD/Fs-I-TEQ ton^{-1} in MSWI-A and MSWI-B, respectively.

The PCDD/Fs EF by the unit ton of MSW treated in fly ash are shown in Fig. 6. The change in trends of EF in fly ash are different from those in bottom ash. The overall trend shows a decrease from 2010 to 2015. The PCDD/Fs EF in fly ash are in the range of 2.41–31.2 µg WHO_{2005}-TEQ ton^{-1}, with an average of 12.8 µg WHO_{2005}-TEQ ton^{-1}. The amoun of PCDD/Fs EF in fly ash (averaged 12.8 µg WHO_{2005}-TEQ ton^{-1}) is higher than that in bottom ash (averaged 7.20 µg WHO_{2005}-TEQ ton^{-1}).

The PCDD/F EF in the stack flue gas, bottom ash and fly ash in the unit of electricity produced (MWh) are presented in Figs. 7, 8 and 9, respectively. As Fig. 7. shows, from 2011 to 2014 the EF of the stack fule gas are similar and ranged from 0.119 to 0.140 µg PCDD/Fs-WHO_{2005}-TEQ $(MWh)^{-1}$; while in 2010 (0.307 µg PCDD/Fs-WHO_{2005}-TEQ $(MWh)^{-1}$ and 2015 (0.297 µg PCDD/Fs-WHO_{2005}-TEQ $(MWh)^{-1}$, the EF are similar, but much larger than those seen during 2011 and 2014. From 2010 to 2015, the emission factor of total-PCDD/Fs -WHO_{2005}-TEQ in stack flue gas produced by the unit electricity produced ranged between 0.119 and 0.307 µg WHO_{2005}-TEQ $(MWh)^{-1}$ and averaged 0.185 µg WHO_{2005}-TEQ $(MWh)^{-1}$.

The PCDD/F EF from bottom ash in the unit of electricity produced (MWh) are presented in Fig. 8., which shows the annual average EF increased year by year from 2011 to 2014, and ranged between 3.76 and 24.52 µg WHO_{2005}-TEQ $(MWh)^{-1}$; while the EF in 2010 and 2015 were 9.04 and 9.45 µg PCDD/Fs-WHO_{2005}-TEQ $(MWh)^{-1}$, respectively, and

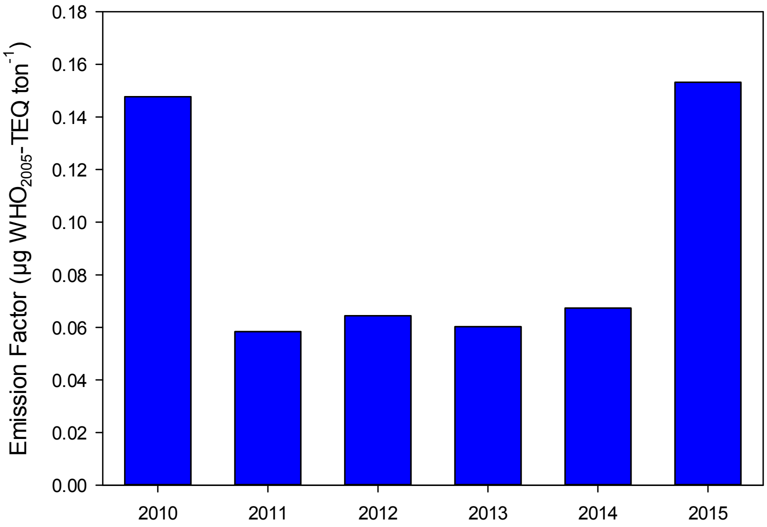

Fig. 4. The emission factor of total-PCDD/Fs-WHO-TEQ from the stack flue gas in the unit weight of MSW treated.

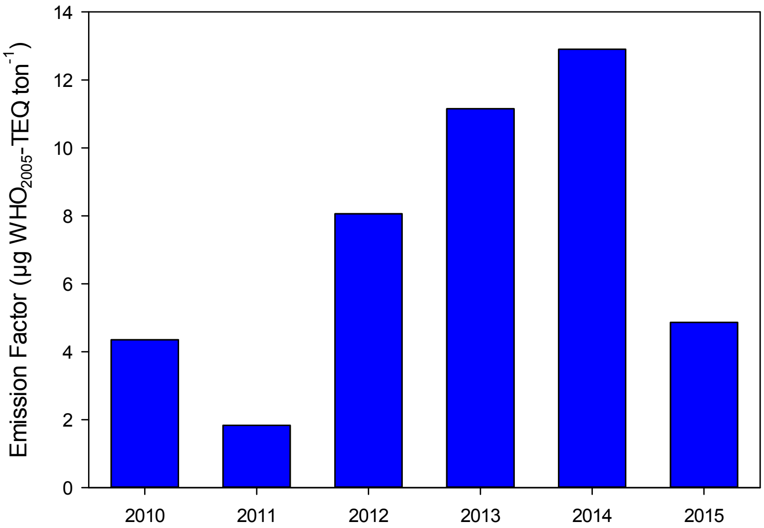

Fig. 5. The emission factor of total-PCDD/Fs-WHO-TEQ from the bottom ash in the unit weight of MSW treated.

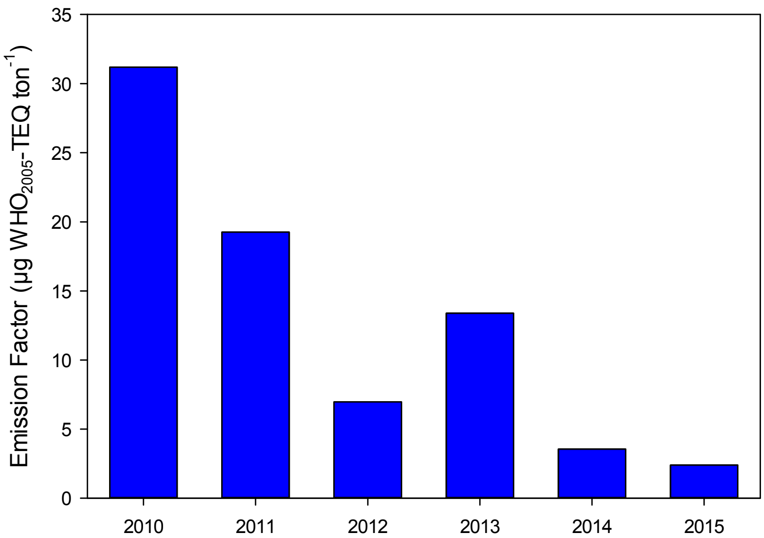

Fig. 6. The emission factor of total-PCDD/Fs-WHO-TEQ from the fly ash in the unit weight of MSW treated.

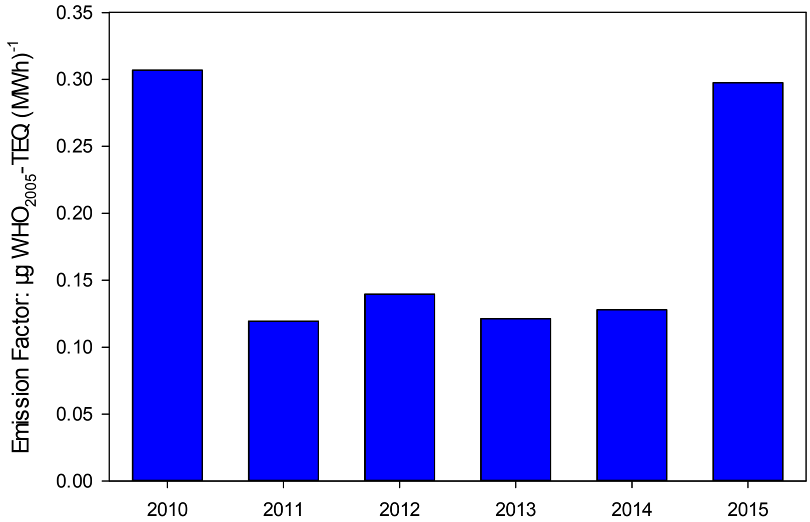

Fig. 7. The emission factor of total-PCDD/Fs -WHO$_{2005}$-TEQ from the stack flue in the unit of electricity produced.

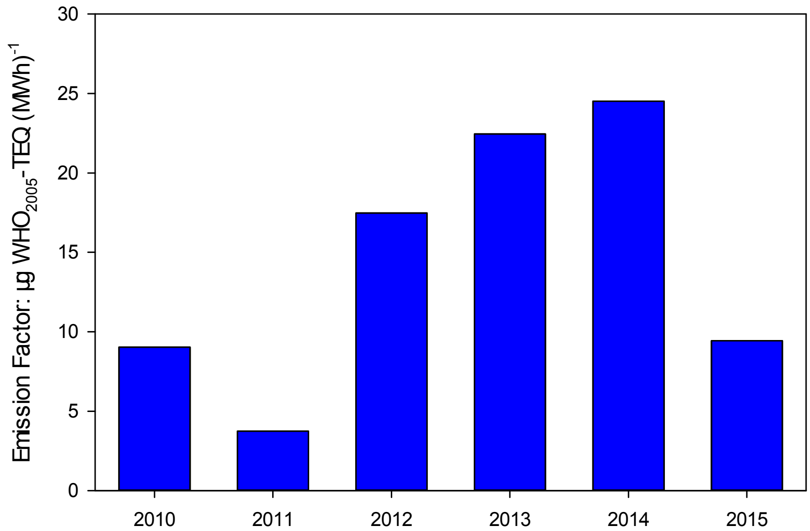

Fig. 8. The emission factor of total-PCDD/Fs-WHO$_{2005}$-TEQ from the bottom ash in the unit of electricity produced.

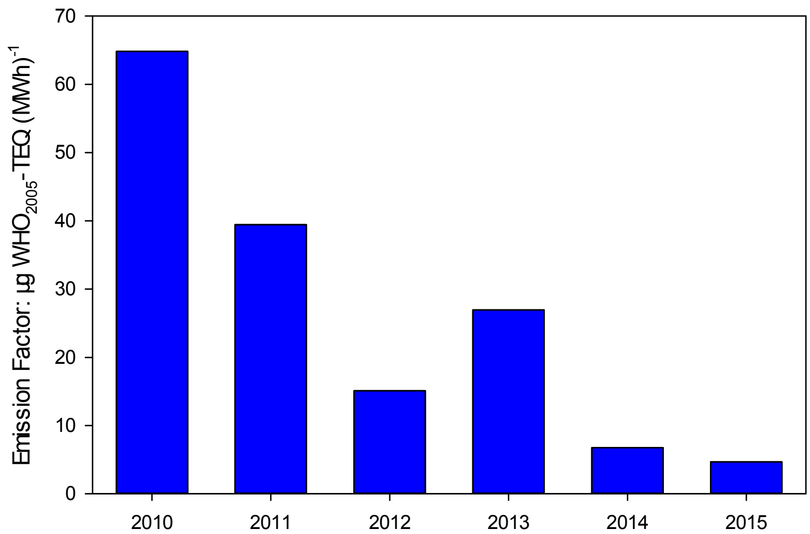

Fig. 9. The emission factor of total-PCDD/Fs-WHO$_{2005}$-TEQ from the fly ash in the unit of electricity produced.

are similar. Overall, during 2010–2015, the PCDD/F EF in bottom ash ranged between 3.76 and 24.5 µg WHO_{2005}-TEQ $(MWh)^{-1}$ and averaged 14.5 µg WHO_{2005}-TEQ $(MWh)^{-1}$.

The PCDD/F EF from fly ash are presented in Fig. 9 in the unit of electricity produced (MWh), and the results are different to those for bottom ash. The EF from fly ash increased from 2010 to 2015, which ranged from 4.68 to 64.8 µg WHO_{2005}-TEQ $(MWh)^{-1}$ and averaged 26.3 µg WHO_{2005}-TEQ $(MWh)^{-1}$.

From 2010 to 2015, the fraction of the PCDD/F mass contributed by stack flue gas was the lowest, which ranged from 0.19% to 2.08% and averaged 0.48% (Table 3); while the fraction of corresponding PCDD/Fs-WHO_{2005}-TEQ contributed by the stack flue gas ranged between 0.24% and 2.06% and averaged 0.45% (Table 3). For the bottom ash, the fraction of PCDD/F mass contributed by it, in general, increased year by year from 2010 to 2015, which ranged from 26.6% (2010) to 72.8% (2014) and averaged 43.61%; while the fraction of corresponding PCDD/Fs-WHO_{2005}-TEQ contributed by the bottom ash ranged from 8.68% (2011) to 78.0% (2014) and averaged 34.71%. When compared with the bottom ash, the opposite trend was found in the fly ash. The fraction of the PCDD/F mass contributed by fly ash decreased year by year from 2010 to 2015, and ranged from 26.3% (2015) to 73.1% (2010) and averaged 55.91%; while the fraction of corresponding PCDD/Fs-WHO_{2005}-TEQ contributed by the fly ash ranged from 21.6% (2014) to 91.1% (2011) and averaged 64.84%. As the results show in this study, the majority of total PCDD/Fs-WHO_{2005}-TEQ were mainly in both bottom ash and fly ash. Landfill is a major disposal method for the MSWI ashes in Taiwan. From a long-term perspective, such landfills will cause serious environmental problems, since the ashes (bottom and fly) contain very high amounts of POPs (Lee *et al.*, 2003; Neuer-Etscheidt *et al.*, 2006; Lin *et al.*, 2010; Wang *et al.*, 2010; Cheruiyot *et al.*, 2016; Redfern *et al.*, 2017).

Scenario Analysis

From 2010 to 2015, the mean annual content of the PCDD/Fs in stack flue gas was 0.34 ng WHO_{2005}-TEQ Nm^{-3}. Actually, the contents of the PCDD/Fs in stack flue gas are usually underestimated. A simple model describing the accumulation of PCDD/Fs in stack flue gas was used in this study. The model is employed to predict the contribution of PCDD/Fs in stack flue gas to total PCDD/Fs from MSWI. Scenario A is the case when the total PCDD/Fs from bottom and fly ash are constant, while the total PCDD/Fs TEQ concentrations in the stack flue gas are 0.01, 0.05, 0.1, 0.5. 1.0, 5.0, 10.0, 20.0, and 50.0 ng WHO_{2005}-TEQ Nm^{-3}. The results of the modeled fraction of the PCDD/F contributed by stack flue gas, bottom ash and fly are presented in Table 4. The model suggests that the fractions of PCDD/Fs from stack flue gas are increase greatly, and ranged from 0.14%–87.25%.

Scenario B is the case when the total PCDD/Fs from stack flue gas and fly ash are constant, while the total PCDD/Fs TEQ concentration in the stack flue gas are 0.01, 0.05, 0.1, 0.5. 1.0, and 4.8 ng WHO_{2005}-TEQ Nm^{-3}. The results of the modeled fraction of the PCDD/F contributed by stack flue gas, bottom ash and fly are presented in Table 5.

Table 3. The fraction of PCDD/F mass and total-PCDD/Fs-WHO_{2005}-TEQ contributed by bottom ash, fly ash and stack flue gas, respectively.

Year	Total PCDD/Fs Mass			Total PCDD/Fs-WHO_{2005}-TEQ		
	Bottom Ash (%)	Fly Ash (%)	Stack Flue Gas (%)	Bottom Ash (%)	Fly Ash (%)	Stack Flue Gas (%)
2010	26.60	73.07	0.33	12.19	87.40	0.41
2011	26.95	72.86	0.19	8.68	91.05	0.28
2012	50.13	49.40	0.47	53.42	46.15	0.43
2013	58.02	41.75	0.23	45.33	54.42	0.24
2014	72.80	26.27	0.92	78.04	21.55	0.41
2015	71.63	26.28	2.08	65.50	32.44	2.06
Mean	**43.61**	**55.91**	**0.48**	**34.71**	**64.84**	**0.45**

Table 4. The modeled fraction of the PCDD/F from stack flue gas, bottom ash and fly ash in scenario A.

Stack Flue Gas (ng WHO_{2005}-TEQ Nm^{-3})	Stack Flue Gas (Fraction: %)	Fly Ash (Fraction: %)	Bottom Ash (Fraction: %)
0.01	0.14	65.05	34.82
0.034	**0.45**	**64.84**	**34.71**
0.05	0.68	64.69	34.63
0.1	1.35	64.26	34.39
0.5	6.40	60.96	32.63
1	12.04	57.30	30.67
5	40.62	38.68	20.70
10	57.78	27.50	14.72
20	73.24	17.43	9.33
50	87.25	8.31	4.45

Table 5. The modeled fraction of the PCDD/F from stack flue gas, bottom ash and fly ash in scenario B.

Stack Flue Gas (ng WHO_{2005}-TEQ Nm^{-3})	Stack Flue Gas (Fraction: %)	Fly Ash (Fraction: %)	Bottom Ash (Fraction: %)
0.01	0.14	65.16	34.71
0.05	0.68	64.61	34.71
0.1	1.36	63.93	34.71
0.5	6.81	58.48	34.71
1	13.62	51.67	34.71
4.8	65.29	0	34.71

These show that when the PCDD/Fs from fly ash is 0 the total PCDD/Fs TEQ concentration in the stack flue gas is 4.8 ng WHO_{2005}-TEQ Nm^{-3}, and the fraction of PCDD/Fs from stack flue gas increase from 0.14% to 65.29%, while the fraction of PCDD/Fs from fly ash decreases from 65.16 to 0. The use of scenario analysis enables us to better understand possible problems in this context. The results of this study provided useful information for both further studies and environmental control strategies aimed at PCDD/F emissions from MSWIs.

CONCLUSION

1. The mass concentration of higher chlorinated PCDD/Fs congeners are higher than those of the lower chlorinated ones. The congener profiles of TEQ PCDD/Fs in all samples showed that 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were the major congeners, due to the relatively high Toxic Equivalency Factor (TEF) and PCDD/Fs concentration.
2. The PCDD/F emission factors by the unit ton of MSW treated from the stack flue gas of MSWI ranged between 0.0583 and 0.1532 µg WHO_{2005}-TEQ ton^{-1} and averaged 0.0919 µg WHO_{2005}-TEQ ton^{-1}.
3. The PCDD/F emission factors by the unit ton of MSW treated from the bottom ash of MSWI ranged between 1.83 and 12.9 µg WHO_{2005}-TEQ ton^{-1} and averaged 7.20 µg WHO_{2005}-TEQ ton^{-1}.
4. The PCDD/Fs emission factors by the unit ton of MSW treated from the fly ash ranged from 2.41 to 31.2 µg WHO_{2005}-TEQ ton^{-1} and averaged 12.8 µg WHO_{2005}-TEQ ton^{-1}.
5. The emission factor of total-PCDD/Fs-WHO_{2005}-TEQ from the stack flue gas in the unit of electricity produced ranged between 0.119 and 0.307 µg WHO_{2005}-TEQ $(MWh)^{-1}$ and averaged 0.185 µg WHO_{2005}-TEQ $(MWh)^{-1}$.
6. The emission factor of total-PCDD/Fs -WHO_{2005}-TEQ from the bottom ash in the unit of electricity produced in bottom ash range between 3.76 and 24.52 µg WHO_{2005}-TEQ $(MWh)^{-1}$, with an average of 14.5 µg WHO_{2005}-TEQ $(MWh)^{-1}$.
7. The emission factor of total-PCDD/Fs-WHO_{2005}-TEQ from the fly ash in the unit of electricity produced in fly ash range between 4.68 and 64.8 µg WHO_{2005}-TEQ $(MWh)^{-1}$, with an average of 26.3 µg WHO_{2005}-TEQ $(MWh)^{-1}$.
8. From 2010 to 2015, the fraction of the mass PCDD/Fs concentration from stack flue gas, bottom ash and fly ash range of 0.19–2.08%, 26.60–72.8% and 26.28–73.07%, respectively. While the corresponding fraction of the WHO_{2005}-TEQ PCDD/Fs concentration from stack flue gas, bottom ash and fly ash were in the ranges of 0.24%–2.06%, 8.68%–78.0% and 21.6–91.1% and averaged 0.45 %, 34.71% and 64.84%, respectively.
9. The fraction of PCDD/Fs from stack flue gas increased from 0.14% to 87.25% in scenario A. In scenario B, the fraction of PCDD/Fs from stack flue gas increased from 0.14% to 65.29%, while the fraction of PCDD/Fs from fly ash decreased from 65.16 to 0.
10. The results of this study provide valuable information for the emission factors of PCDD/Fs in stack flue gas, bottom ash and fly ash from MSWI. Which will be useful for the establishment of control strategies in the future.

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