



Characterization of Persistent Organic Pollutants in Ash Collected from Different Facilities of a Municipal Solid Waste Incinerator

Mao-Sung Wang¹, Shui-Jen Chen^{1*}, Yi-Chieh Lai^{2,3}, Kuo-Lin Huang¹, Guo-Ping Chang-Chien^{2,3}

¹ Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, 1 Shieh-Fu Rd., Nei Pu 91207, Pingtung, Taiwan

² Department of Chemical and Materials Engineering, Cheng Shiu University, 840 Chengcing Rd., Niasong Township, Kaohsiung County 833, Taiwan

³ Super Micro Mass Research & Technology Center, Cheng Shiu University, 840 Chengcing Rd., Niasong Township, Kaohsiung County 833, Taiwan

ABSTRACT

This study investigated five persistent organic pollutants (polychlorinated and polybrominated dibenzo-*p*-dioxins (PCDDs/PBDDs), dibenzofurans (PCDFs/PBDFs), biphenyls (PCBs/PBBs), and diphenyl ethers (PBDEs)) in ash collected from several units (super heater (SH), heat economizer (HE), semi-dryer absorber (SDA), bag-house filter (BF), and fly ash pit (FAP), and bottom ash (BA) discharger) of a large-scale municipal solid waste incinerator (MSWI). Data on levels and emission factors of the five target compounds in the different units of the MSWI were first reported. The PCDD/Fs were found in high content in the HE, mainly because of the operating temperature range (250–400°C) which is favorable for PCDD/F formation through de novo synthesis. High concentrations PCBs and PBBs were detected in the BF. The highest concentrations of PBDD/Fs and PBDEs were observed in the BA. A significant correlation existed between content of PCDD/F and PCB in individual ash and corresponding operating temperature, while the content of ash-bound PBDD/Fs and PBDEs chiefly related to feeding wastes that contained brominated flame retardants. The emission of the five pollutants in the MSWI was primarily from fly ash. Further treatment is necessary for ash collected from the HE and BF because the ash had total-PCDD/F content exceeding the regulation limit (1 ng I-TEQ/g) in Taiwan.

Keywords: Municipal solid waste incinerators; Brominated flame retardants; Persistent organic pollutants; Emission factors; Distribution.

INTRODUCTION

Persistent organic pollutants (POPs), a very heterogeneous group of substances including chlorinated and brominated aromatics, have been of great concerns in the global environment. Human health hazards from these pollutants are associated with their persistence in the environment and their bioaccumulation potential in the food chain (Jones *et al.*, 1993; Birnbaum *et al.*, 2003).

Polychlorinated dibenzo-*p*-dioxin/dibenzofurans (PCDD/Fs) are well-known POPs, mostly found in fly ash and stack gases generated by municipal solid waste incinerators (MSWIs) (Rappe, 1993; Lee *et al.*, 2004a; Lee *et al.*, 2004b; Wang *et al.*, 2005; Kao *et al.*, 2006; Lin *et al.*, 2008). In general, the majority of PCDD/F formation occurs in the

post-combustion zone of a MSWI at low temperatures and fly ash can act as a heterogeneous catalyst in the synthesis of PCDD/Fs (Addink *et al.*, 1996; Wang *et al.*, 2009b). The formation of PCDD/Fs in incinerator units has been identified by Hung and Buekens (1995). They found that PCDD/F content in filter cakes, electrostatic precipitator ash, boiler ash, and bottom ash were 6, 4, 0.2, and 0.03 ng I-TEQ/g, respectively. MSWIs have been identified as the largest contributors to the environmental levels of PCBs due to the wide use and application of the PCBs mixtures (Jones *et al.*, 1993; Chang *et al.*, 1999). Polybrominated diphenyl ethers (PBDEs) and biphenyls (PBBs), common additive of brominated flame retardants (BFRs). The BFRs are usually used in arrays of commercial and industrial applications for the purpose of fire prevention (WHO, 1994). The structural likenesses of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) with PCDD/Fs results in similarity of formation mechanisms during thermal treatment via de novo synthesis and/or thermolysis of precursor compounds (e.g., brominated aromatic compounds) (Weber and Kuch, 2003). It has been

* Corresponding author. Tel.: +886-8-7740263;
Fax: +886-8-7740256
E-mail address: chensj@mail.npust.edu.tw

reported that PBDD/Fs can be generated in some production and waste incineration processes involving plastics containing BFRs (Vehlow *et al.*, 2000; Sakai *et al.*, 2001). Some commercial mixtures of PBDEs were found to contain PBDFs (~257 to 49,600 ng/g) as impurities, revealing that the use of PBDE mixtures may possibly contribute to the direct emission of PBDFs into the environment (Söderström and Marklund, 2000; Hanari *et al.*, 2006). It was reported that the pyrolysis of waste printed circuit boards at 850 and 1200°C in a pilot-scale melting system generated PBDD/Fs (0.231–0.490 ng I-TEQ/g) in residues (Lai *et al.*, 2007).

However, very little is known about how the BFRs in the feeding materials affect the emissions of chlorinated and brominated pollutants from MSWIs. Moreover, the data on levels of BFRs (e.g., PBDD/F, PBDE, and PBB) along with PCB and PCDD/F levels in different units of MSWIs have not been reported yet in literature. The purpose of this study was to characterize the levels of five persistent organic pollutants (including 2,3,7,8-substituted PCDD/Fs and PBDD/Fs, PBDEs, PCBs and PBBs) in ash obtained from different units (super heater (SH), heat economizer (HE), semi-dryer absorber (SDA), bag-house filter (BF), and fly ash pit (FAP), and bottom ash (BA) discharger) of a large-scale continuous MSWI. The relationship between operating temperature and content of POPs in ash from the different incinerator units were examined. Emission factors and distribution ratios of the five POPs were assessed.

EXPERIMENTAL

Sampling

Ash samples were collected from a large-scale MSWI in southern Taiwan. The MSWI has the capacity of 1350 tons/day and is equipped with air pollution control devices (APCDs) such as dry scrubber (250–230°C), activated carbon injector, and bag filter (250–230°C).

Ash from the six units (SH, HE, SDA, BF, FAP and BA) of MSWI was collected twice daily for 3 days to obtain representative samples. Sampling was done following the Taiwan's regulation (NIEA R118.02B) and the Minnesota regulation 7035.2910 in the US. For each sampling unit, approximately 200 g of ash was collected in every 12 h sampling interval; as a result, totally 1.2 kg of ash was collected for 3-day sampling. The ferrous/non-ferrous metals, glasses, and stones were removed. After mixing and diagonal sectioning, 600 g of each ash sample was retained. Samples were then spread out on a clean aluminum foil and dried naturally to avoid the effect of the ambient air and moisture on samples. Ash samples were ground for homogenization and then extracted for the analyses of five persistent organic compounds (PCDD/Fs, PBDD/Fs, PBDEs, PCBs, and PBBs).

Extraction, Cleanup and GC/MS Analysis

All chemical analyses in this study were carried out at the Super Micro Research and Technology Center at Cheng Shiu University — an accredited laboratory in

Taiwan for analyzing contents of PCDD/Fs, PBDD/Fs, PBDEs, PCBs, and PBBs in ash. Essentially, ¹³C-labeled internal standards (including PCDD/Fs, PBDD/Fs, PBDEs and PCBs) were added to samples that were then extracted for 24 h in Soxhlet extractors with toluene. The extract was concentrated by rotary evaporation and N₂ gas stream, followed by its transfer to a vial. Then, the simultaneous sample cleanup procedures by combining multiple (silica, alumina, and active carbon) columns were applied to measure the five persistent pollutants from one sample at the same time. The preparation of the samples in this study was based on the standard procedures for PCDD/Fs with modification for the analysis of brominated compounds. The method has been validated by analyses of blank and spiked samples. Under the optimized column and elution solvent conditions, presented in our previous study (Wang *et al.*, 2009a), the simultaneous sample cleanup procedures by combining multiple columns were applied.

After extraction, the treatment with concentrated sulfuric acid was conducted in the first cleanup stage. For the next, extract samples dissolved in 5 mL of hexane were added to an acid silica gel column with two additional 5 mL rinses. An alumina column was used in the third step. The concentrated eluate was sequentially eluted with hexane (10 mL) followed by 15 mL of dichloromethane (DCM)/hexane (4/96, v/v). The eluate was collected and concentrated to near dryness by N₂ gas, and by this way, non-planar fractions of PCB and PBB congeners were prepared for further analysis. Following the above stage, the column was eluted again with 25 mL of dichloromethane (DCM)/hexane (40/60, v/v) and then transferred to an activated carbon column for the separation of PBDD/Fs and PBDEs. The extracts were eluted with 5 mL of toluene/methanol/ethyl acetate/hexane (5/5/10/80, v/v/v/v) for PBDEs and planar PCBs/PBBs, followed by 40 mL toluene extraction for PBDD/Fs. The final extracts were then concentrated using N₂ gas before analysis. Detailed sample clean-up method for the analysis of PCDD/Fs, PBDD/Fs, PBDEs, PCBs and PBBs are given in our previous work (Wang *et al.*, 2003a; Wang *et al.*, 2003b; Chen *et al.*, 2004; Wang *et al.*, 2009a).

Instrumental analysis of five target compounds was performed separately by using a high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS). The HRGC (Hewlett-Packard 6970 Series gas, CA) was equipped with a silica capillary column (J&W Scientific, CA) and with a splitless injection, while the HRMS (Micromass Autospec Ultima, Manchester, UK) had a positive electron impact (EI+) source. Detailed instrumental analysis conditions of target compounds are given in our previous work (Wang *et al.*, 2009a).

Quality Assurance and Quality Control (QA/QC)

Identification of the target compounds in the ash samples was performed with the following criteria: relative retention time (RRT) of target compounds matching with the corresponding authentic standards (tolerance RRT = ±0.5%); the limit of detection (LOD) was defined as a signal-to-noise (S/N) ratio greater than three; isotope ratio

of at least two characteristic ions meeting the theoretical values within 15% deviation. Quantification of the target compounds was determined by analyzing calibration mixtures containing isotopically labeled internal standards. The $^{13}\text{C}_{12}$ -labeled internal standards as noted previously were spiked into the stack flue samples prior to the sample preparation and GC/MS analysis. Method detection limits (MDLs) of target compound analyses were determined via the standard deviations obtained from the analyses of seven matrix-spiked samples. The limit of quantification (LOQ) was determined based on an S/N greater than ten.

Method performance was evaluated with the accuracy and precision of the approach, blank and spiked samples with known standards. The spiked samples with 1.0, 2.0, and 5.0 ng PBDEs precision and recovery (PAR) stock standards, and with 40, 200, and 400 pg PBDD/Fs were used to evaluate recovery and reproducibility. The average recoveries of PBDEs PAR stock standards were 91–136%, with the exception of BDE 7 (39%), while those of PBDD/Fs PAR stock standards were 92–114%, both falling within the required range, 60–140%. The recoveries of PCDD/Fs PAR stock standards for the tetra- to octa-chlorinated homologues were between 100% and 122%, satisfying the criterion for PCDD/Fs (within 70–130%). Those of PCBs and PBBs were 104–116% and 69–113%, respectively, both fulfilling the requirement of being within 60–140%. Accordingly, simultaneous preparation using multiple columns was highly efficient and yielded good recovery for the determination of five persistent organic compounds in one single sample extraction procedure. Detailed evaluation results are given in our previous work (Wang *et al.*, 2009a).

Quantitative recoveries of target compounds in ash were conducted before the extraction and cleanup procedures by adding $^{13}\text{C}_{12}$ -labeled internal standards. Recoveries of $^{13}\text{C}_{12}$ -labeled internal standards and surrogate standards for PCDD/Fs were within the control limits of 40–130% and 70–130%, respectively. Recoveries of $^{13}\text{C}_{12}$ -labeled PBDEs and PCBs ranged 38–127% (RSD = 7.5–37%) and 64–139% (RSD = 5.6–9.3%), respectively, whereas those of $^{13}\text{C}_{12}$ -labeled PBDD/Fs were 28–146% with RSD of

5.9–28%. The obtained recoveries met the acceptance criteria for PBDEs, PCBs, and PBDD/Fs specified by the US-EPA methods 1614-draft (25–150%), 1668A (25–150%) and 1613B (17–185%), respectively. Due to limited availability of individual PBB standards, their recoveries could not be provided. Moreover, the method detection limits (MDLs) of ash samples for PBDD/Fs, PBDEs, PCDD/Fs, PCBs, and PBBs were 0.070–25.7, 0.262–333, 0.202–6.27, 0.189–6.29, and 0.0731–8.3 pg, respectively.

RESULTS AND DISCUSSION

Concentrations of Five Persistent Pollutants in Different Ash Samples

Table 1 presents the mean concentrations of persistent pollutants in ash samples from different units in the MSWI. The contents of PCDD/Fs in BA and SH (7.75 and 14.7 WHO-TEQ/g) were lower among different facilities, while that of HE (1297 WHO-TEQ/g) was the highest. The probable reason is that the HE was operated at around 374°C which is within the temperature range (250–400°C) and was thus favorable for PCDD/F formation through de novo synthesis. The similar PCDD/F result had been reported by our previous study (Wang *et al.*, 2010a) which revealed that the economizer is the source of PCDD/F formation in the MSWIs. Economizers with shorter residence time for the flue gas and higher heat exchange efficiency could effectively decrease PCDD/F formation in the MSWIs. The duration of operation for BF was longer than those of other investigated units in the MSWI, resulting in relatively high PCDD/F content in the BF. This result is similar to those presented in other researches (Giugliano *et al.*, 2002; Abad *et al.*, 2003; Lin *et al.*, 2008). The congener profiles of seventeen PCDD/Fs detected from different ash of the selected MSWI were shown in Fig. 1. Each selected congener was normalized by the total weight of all 2,3,7,8-congeners. The concentrations of 2,3,7,8-PCDD/Fs homologues increased with an increasing chlorine substitution level; in other words, higher chlorinated congeners dominated in all samples. Similar phenomena has been reported by our previous study (Wang *et al.*, 2003c)

Table 1. Mean concentrations of five persistent pollutants in ash samples from different units in the MSWI.

Persistent Pollutants		BA	SH	HE	SDA	BF	FAP
PCDD/Fs	Total (pg/g)	262	205	62851	4306	27463	27184
	Total TEQ (pg WHO ₉₈ -TEQ/g)	7.75	14.7	1297	107	1069	836
	Total TEQ (pg I-TEQ/g)	7.36	13.3	1210	99.4	981	781
PCBs	Total (pg/g)	114	37.7	1554	154	3097	1544
	Total TEQ (pg WHO ₉₈ -TEQ/g)	0.828	0.626	33.5	3.09	64.5	30.9
PBDD/Fs	Total (pg/g)	1648	0.482	9.12	60.5	4.87	32.5
	Total TEQ (pg WHO ₉₈ -TEQ/g)	6.32	0.000482	0.00985	0.00605	0.176	0.000383
PBBs	Total (pg/g)	11.4	2.78	53.3	29.0	229	38.3
PBDEs	$\sum_{2-8\text{ Br}}$ BDEs (pg/g)	7817	10.0	927	269	365	62.9
	$\sum_{9-10\text{ Br}}$ BDEs (pg/g)	70256	72.0	2064	33657	4253	110
	Total (pg/g)	78073	81.9	2991	33926	4618	173

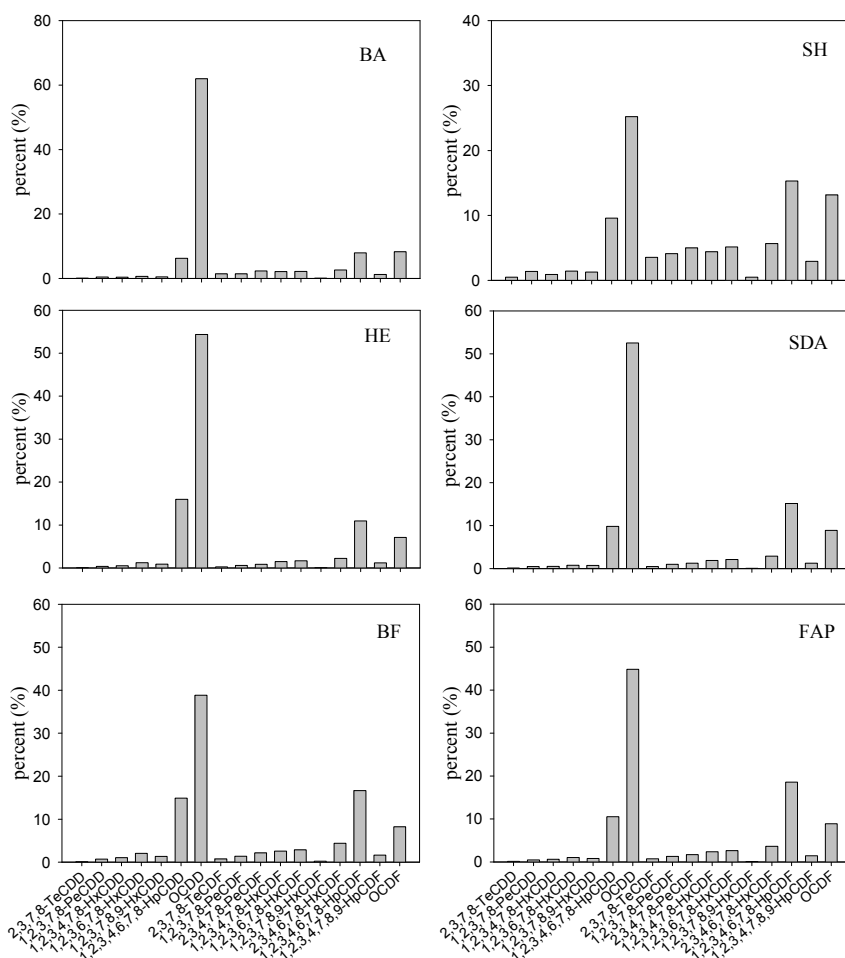


Fig. 1. Congener profiles of 17 PCDD/F species in ash samples from different units in the MSWI.

which investigated the effect of chlorine content in feeding wastes on the PCDD/F characteristics in the stack gases of incinerators. The OCDD was predominant in all ash from the BA, SH, HE, SDA, BF, and FAP.

In general, ash generated from different incinerator units was collected and then transported to FAPs for being reused as road sub-bases or secondary building materials. The total-PCDD/F content of ash from the BA, SH and SDA were all lower than the limit (1 ng I-TEQ/g) of hazardous waste regulations in Taiwan (Table 1), so such ash can be collected and transferred to the FAP for the reuse purpose. However, the total PCDD/F content in ash from HE (1.297 ng I-TEQ/g) and BF (1.069 ng I-TEQ/g) exceeded the Taiwan's regulation limit. It is suggested that such HE and BF ash should be separately collected and controlled by sodium hypophosphite before being landfilled (Wang *et al.*, 2006).

The PCB congeners represented by their IUPAC (International Union of Pure and Applied Chemistry) numbers and TEQ concentrations were calculated using WHO-TEF values (Van den Berg *et al.*, 1998). The total-PCB content in ash from BA and SH were very low (0.828 and 0.626 pg WHO98-TEQ/g) due to the high temperatures used in the combustion chamber (around 961°C) and super heater (477°C). It has been noted that PCBs may

be formed together with PCDD/Fs in the de novo synthesis (Hell *et al.*, 2001; Pekárek *et al.*, 2001); as expected, high PCB content (33.5 pg WHO98-TEQ/g) was found in the HE ash. Moreover, PCBs were captured by the activated carbon adsorption, and the duration of fly ash in BF was longer than those in other investigated units of the MSWI, thus causing an increase of PCB content in the BF. PBBs were also found in high content in the BF (229 pg/g). PCB congener profiles in different ash from the MSWI were shown in Fig. 2. Accounting for 29.3–32.3% to total PCBs, PCB 77 was found to be the predominant species of BA and SH ash, while PCB-126 dominated (18.8–20.2%) in HE, SDA, BF and FAP ash. For BA and SH ash, the predominant PBB species was PBB-153 (60.4–64.1%), while that for HE, SDA, BF and FAP ash was PBB-15 (Fig. 3).

Only twelve 2,3,7,8-PBDD/Fs congeners were quantified because of limitation of standard compounds. Due to the incomplete research on the toxic effects of PBDD/Fs, there is still no complete toxicity equivalency factor (TEF) value. For the present survey of several biological and toxicological parameters for animals, 2,3,7,8-TeBDD and 2,3,7,8-TeBDF were equipotent to 2,3,7,8-TeCDD and 2,3,7,8-TeCDF. To assess the toxicologically relevant information on PBDD/Fs, WHO (1998) recommends the use of the same TEF values for PBDD/Fs as described for the chlorinated analogues.

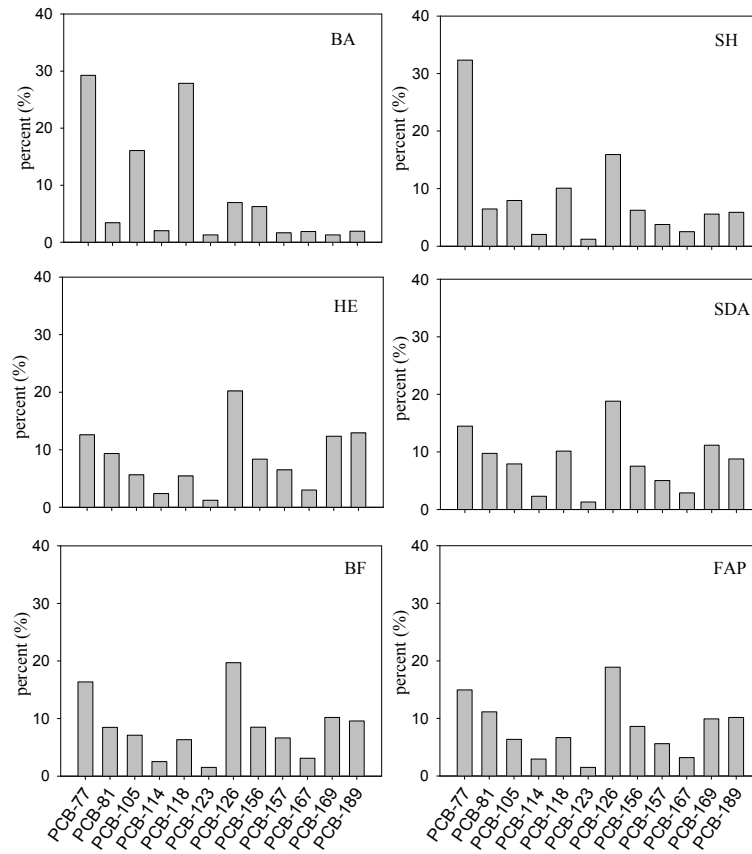


Fig. 2. Congener profiles of 12 PCB species in ash samples from different units in the MSWI.

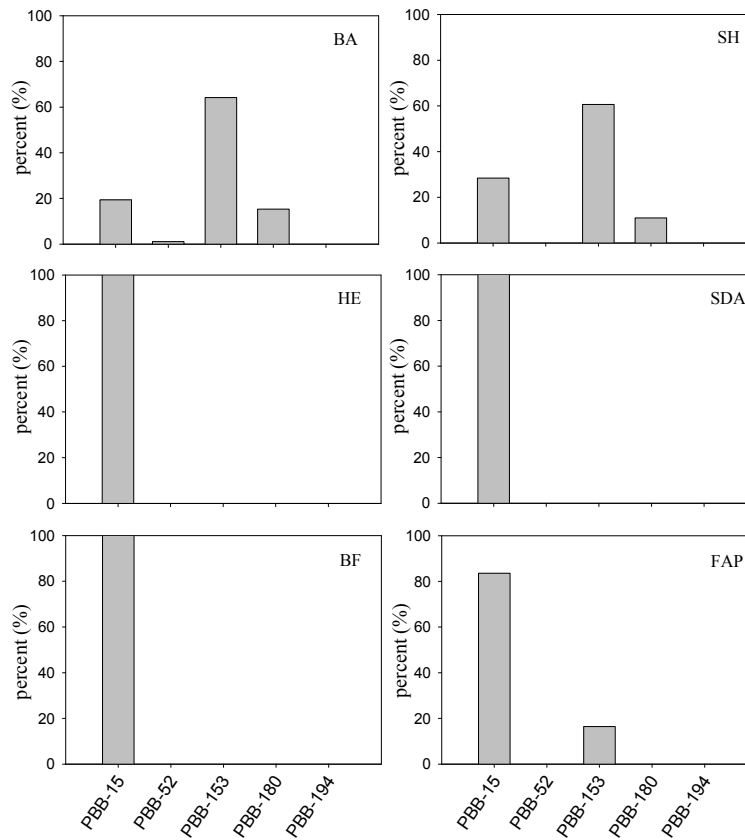


Fig. 3. Congener profiles of 5 PBB species in ash samples from different units in the MSWI.

According to this criterion, we calculate the I-TEQ value for PBDD/Fs by using the concentrations of seven 2,3,7,8-brominated substitutes and the TEF of their chlorinated analogues. The total PBDD/F (sum of twelve tetra–hexa congeners) and PBDE (sum of thirty BDEs) content in BF ash were 1648 pg/g (6.32 pg WHO₉₈-TEQ/g) and 78073 pg/g, respectively (Table 1). The highest concentrations of PBDD/Fs and PBDEs in bottom ash related mainly to the feeding materials containing BFRs. It is possible that BFR mixtures remained as incineration residue without being decomposed (Sakai *et al.*, 2001), but some of such compounds were debrominated in the process of incineration of BFR-containing wastes (Wang *et al.*, 2010a).

Fig. 4 shows the congener profiles in mass fractions of 12 PBDD/F species in ash from different incinerator units. Compared to the PCDD/Fs, which had 17 congeners reported, only 12 of the possible 17 2,3,7,8-substituted PBDD/F congeners were reported due to the lack of a standard. For PBDD/Fs, PBDF was dominant in all samples and the top two abundant congeners were 1,2,3,4,6,7,8-HpBDF and OBDF, accounting for around 35.7% and 64.3% of the total-PBDD/F mass, respectively. Responsible for more than 61% of total-PBDE mass, BDE 209 was the most predominant PBDE congener, followed by BDE 206 and

BDE 207 (Fig. 5). The dominant PBDE congeners in the ash were comparable to our previous findings (Wang *et al.*, 2010a), possibly because the feeding wastes contain more commercial deca-BDE mixtures. BDE-209 is the main congener of the commercial deca-BDE mixtures (Agrell *et al.*, 2004) and has a larger production volume than other commercial PBDE mixtures; therefore, the dominant concentration of BDE 209 was present in both the flue gas and residue of the MSWI. Moreover, BDE-209 can undergo long-range transport and metabolically or photocatalytically degrade to lower brominated congeners with enhanced toxicity and greater ability to bioaccumulate relative to the parent (Stapleton *et al.*, 2006). BDE-209 has been found to be relatively abundant in some ambient air samples in the east-central United States (Hoh and Hites, 2005) and China (Chen *et al.*, 2006).

Relationship between Temperature and Content of Five Persistent Pollutants

The content of total PCDD/Fs and PCBs in individual ash was closely related to their corresponding operating temperatures of units, while this tendency was not observed for PBDD/Fs, PBDEs and PBBs in ash (Fig. 6). This finding is consistent with the fact that PCDD/Fs and PCBs were

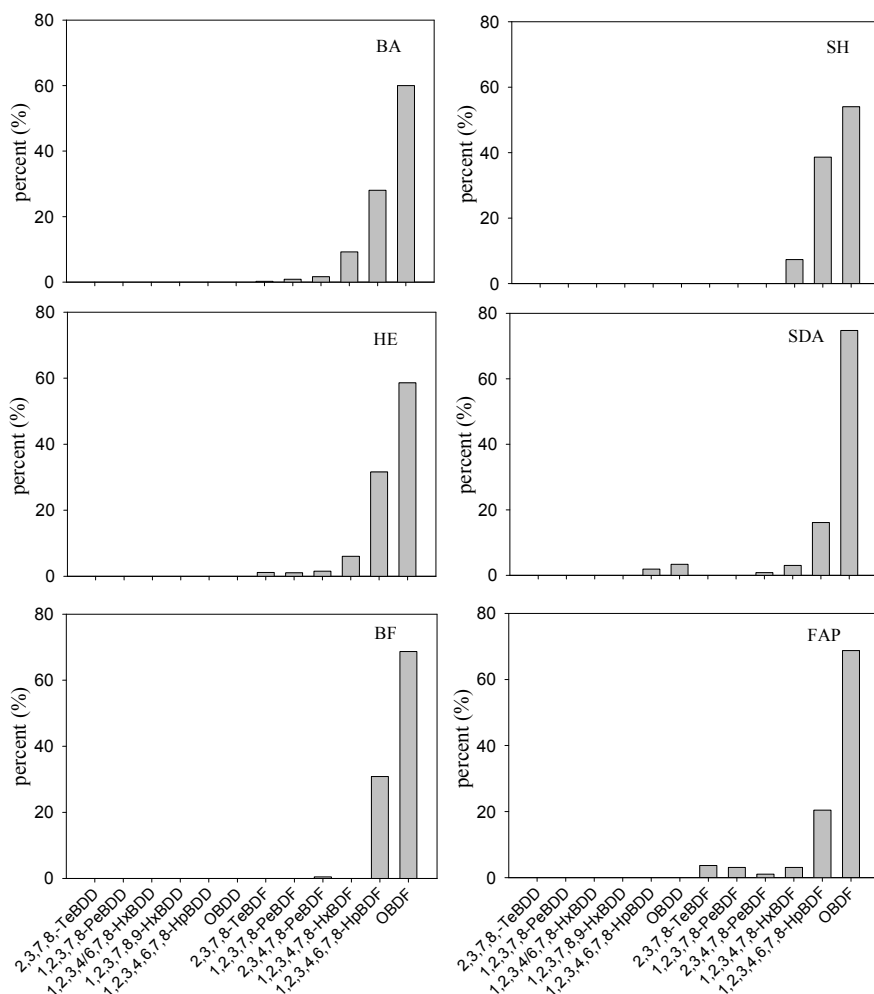


Fig. 4. Congener profiles of 12 PBDD/F species in ash samples from different units in the MSWI.

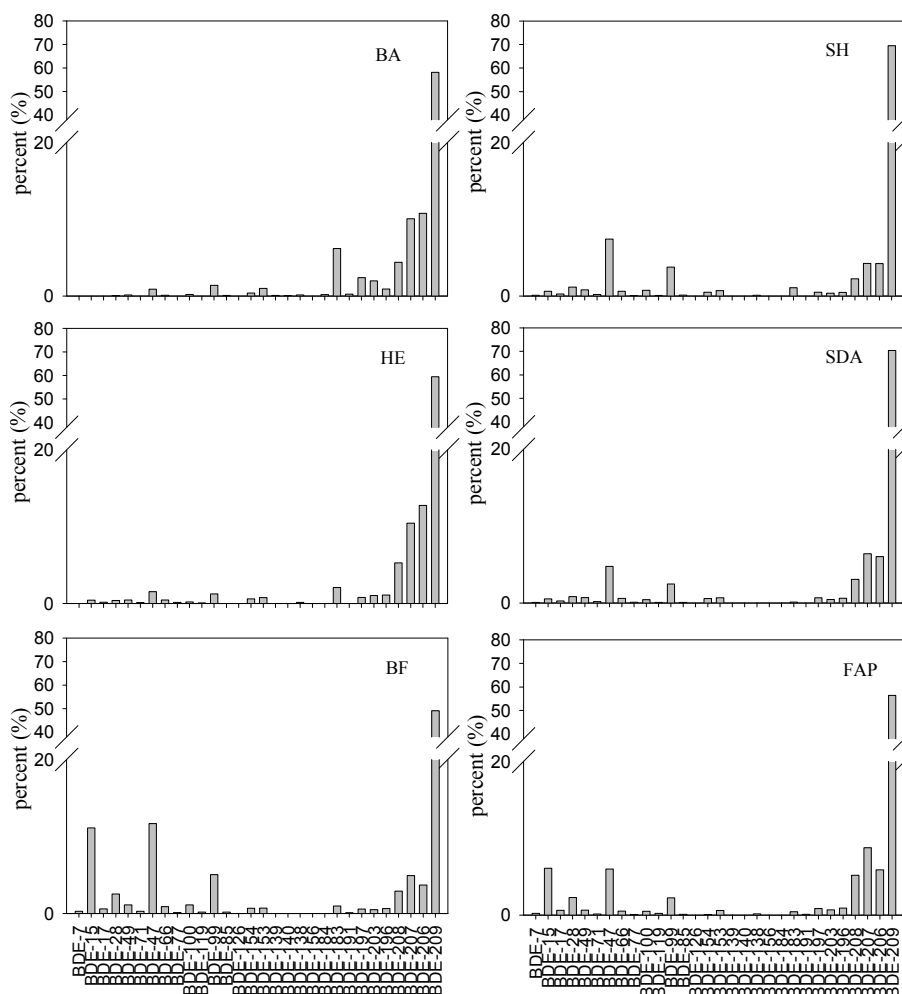


Fig. 5. Congener profiles of 30 PBDE species in ash samples from different units in the MSWI.

formed together in the de novo synthesis (Hell *et al.*, 2001; Pekárek *et al.*, 2001), resulting in high content of PCDD/Fs and PCBs in the HE (374°C). Although the SDA was operated at 245°C, within the temperature range (250–400°C) favorable for the formation of PCDD/Fs and PCBs, the content of PCDD/F and PCB in the SDA was not so high as that in the HE, mainly because the operating temperature was relatively higher for the SDA than for the HE and calcium carbonate was added to the flue gas to dechlorinate and dilute chlorine-containing species (Lin *et al.*, 2008). The off-gas from the combustion chamber of an incineration plant usually passes through a cooling unit and then a particle collecting device (i.e., bag house filter) before being emitted from the stack. Fly ash in the off-gas provide active surface for the reactions of PCDD/F formation (Addink *et al.*, 1996). The duration of fly ash was longer in the BF than in other units, and thus caused increasing downstream levels of PCDD/F and PCB (except the SDA). Therefore, the operating temperature of incinerator equipments should not be in the range of 250–400°C (favorable for PCDD/F formation) to lower the emission of PCDD/Fs.

As for PBBs, the total content in ash samples from BA and SH was very low due to the high temperatures in the combustion chamber (around 961°C) and super heater

(477°C). The trend of total PBB content was comparable to that of PCDD/F and PCB in the ash of different incinerator units. Among these units, the BF had the highest total PBB content (~229 µg/g).

Emission Factors (EFs) of Five Persistent Pollutants in the Whole MSWI

The investigated POPs may be emitted from the MSWI to the environment through (1) ash from the combustion chamber and super heater (BA+SH), (2) ash from the heat economizer, semi-dryer absorber, and bag-house filter (HE+SDA+BF), and (3) the stack flue gas. Therefore, to evaluate the potential of POP emissions from incineration processes, the emission factors (EFs) of five target compounds were divided into three parts: EF sum of ash from the BA and the SH (BA+SH), EF sum of ash from the HE, SDA, and BF (HE+SDA+BF), and EF of stack flue gas (Table 2). The EFs (µg/ton-waste) of five target compounds in different ash were calculated using $A \times C/W$, where A is the ash amount generated in incineration of municipal solid waste, C is the content of target compounds in different ash, and W is the waste amount combusted in the incineration of the MSWI. A POP EF of stack flue gas was obtained by multiplying the actual POP

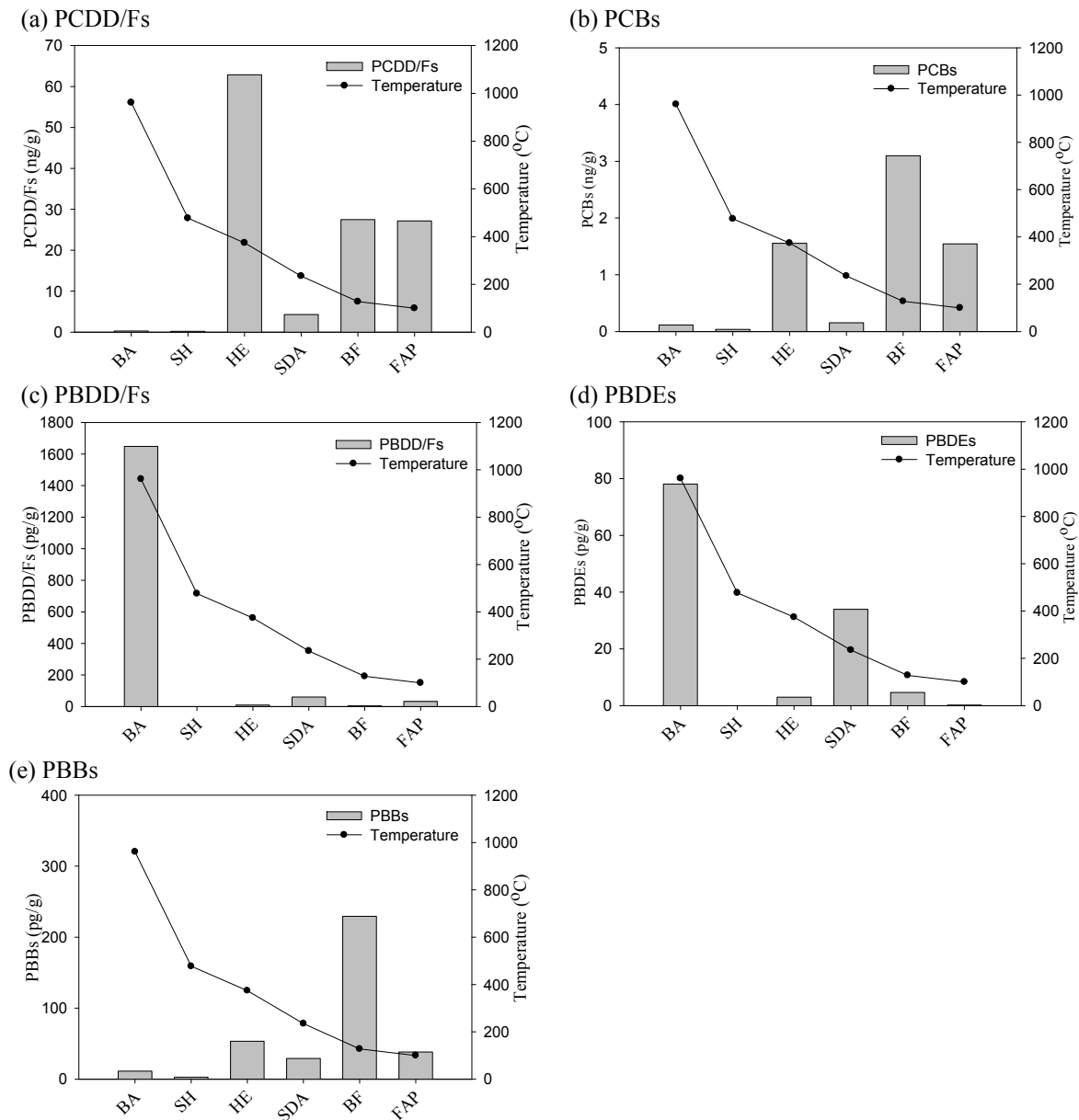


Fig. 6. The relationship between operating temperature of unit and content of persistent pollutants in ash samples from different units in the MSWI.

Table 2. Emission factors of five persistent pollutants from the BA + SH ash, HE + SDA + BF ash, and stack flue gas of MSWI.

Persistent Pollutants		BA + SH	HE + SDA + BF	Stack flue gas
PCDD/Fs	Total ($\mu\text{g}/\text{ton-waste}$)	3.94	2399	9.10
	Total TEQ ($\mu\text{g WHO}_{98}\text{-TEQ}/\text{ton-waste}$)	0.164	81.9	0.336
PCBs	Total ($\mu\text{g}/\text{ton-waste}$)	1.16	180	1.71
	Total TEQ ($\mu\text{g WHO}_{98}\text{-TEQ}/\text{ton-waste}$)	0.0107	3.65	0.0204
PBDD/Fs	Total ($\mu\text{g}/\text{ton-waste}$)	12.6	0.873	0.925
	Total TEQ ($\mu\text{g WHO}_{98}\text{-TEQ}/\text{ton-waste}$)	0.258	0.0251	0.00750
PBBs	Total ($\mu\text{g}/\text{ton-waste}$)	0.139	11.2	1.05
PBDEs	$\sum_{2-8 \text{ Br}}$ BDEs ($\mu\text{g}/\text{ton-waste}$)	90.8	29.0	8.57
	$\sum_{9-10 \text{ Br}}$ BDEs ($\mu\text{g}/\text{ton-waste}$)	611	399	75.9
	Total ($\mu\text{g}/\text{ton-waste}$)	702	428	84.5

concentration in stack gas and the gas flow rate on a dry basis divided by the feeding rate.

The EFs of PCDD/Fs from BA+SH, HE+SDA+BF, and stack flue gas were 3.94 $\mu\text{g}/\text{ton-waste}$ (0.164 $\mu\text{g WHO}_{98}\text{-TEQ}/\text{ton-waste}$), 2399 $\mu\text{g}/\text{ton-waste}$ (81.9 $\mu\text{g WHO}_{98}\text{-TEQ}/\text{ton-waste}$) and 9.10 $\mu\text{g}/\text{ton-waste}$ (0.310 $\mu\text{g WHO}_{98}\text{-TEQ}/\text{ton-waste}$), respectively; furthermore, the highest EF was that from HE+SDA+BF. The EFs of PCDD/Fs from different incinerator units and flue gas of this study are slightly higher than the values in southern Taiwan reported by Lin *et al.* (2007) and Lin *et al.* (2008). This difference between their and our observations is probably because of various compositions of feeding wastes used and different APCDs equipped. The PCB EFs from BA+SH, HE+SDA+BF, and stack flue gas were 1.16, 180, and 1.71, respectively (corresponding to 0.0107, 3.65, and 0.0204 $\mu\text{g WHO}_{98}\text{-TEQ}/\text{ton-waste}$, respectively). The HE+SDA+BF also exhibited the highest PCB EF.

The highest emission factors of PBDD/Fs and PBDEs were from BA+SH, mainly because the bottom ash had abundant PBDD/Fs and PBDEs from feeding wastes containing BFRs (Table 2). Around 93% of the total PBDD/Fs are adsorbed on the ash from BA+SH. Lai *et al.* (2007) found that ~83% of the total PBDD/Fs adsorbed on the surface of bottom ash and the left 17% PBDD/Fs was present in flue gas; additionally, this phenomenon is associated with the fact that PBDD/Fs have higher molecular weights and lower vapor pressures than PCDD/Fs. The EF of PBDEs in flue gas (84.5 $\mu\text{g}/\text{ton-waste}$) estimated in this study were 2 to 21 times lower than that determined from e-waste (e.g., waste TV housing) incineration processes in Japan (1200 to 1800 $\mu\text{g}/\text{ton}$) and were rather small when compared to those from other processes (including manufacturing of PBDEs, dismantling and crushing, textile processing, and plastics processing) (Sakai *et al.*, 2006). Furthermore, PBDEs were identified in the stack flue gases of sinter plants revealed that PBDEs can form during the combustion processes through the similar formation conditions of PCDD/Fs (Wang *et al.*, 2010b). It has been indicated that the metallurgical facilities are not only important PCDD/F but also significant PBDD/F and PBDE emission sources to the environment. Since the total emission factor of PBB in the whole MSWI (12.4 $\mu\text{g}/\text{ton-waste}$) was lower than those from the processes mentioned above, the influence of PBB emissions from the investigated MSWI to the environment should be minor.

Distributions of Five Persistent Oollutants in the Whole MSWI

Fig. 7 presents the distribution ratios ($\mu\text{g}/\text{ton-waste}$) of POPs in the MSWI (excluding the FAP). Mass distribution ratios of PCDD/Fs in $\mu\text{g}/\text{ton-waste}$ from BA, SH, HE, SDA, BF, and stack were 0.06%, 0.14%, 19.9%, 1.6%, 78.0% and 0.3%, respectively (Fig. 7(a)). The results reveal that the main PCDD/F source was from the ash of bag-house filter and the PCDD/F contribution of flue gas was negligible in the MSWI. Similar distributions of total PCDD/Fs were observed by Giugliano *et al.* (2002), and they found that the percentages of total PCDD/F flux in

ash and stack gas were approximately 98.3% and 1.7%, respectively. For PCBs, the distribution ratios of different units were 0.45% for BA, 0.15% for SH, 7.0% for HE, 0.7% for SDA, 90.7% for BF, and 1.0% for flue gas (Fig. 7(b)). The PBBs in ash were contributed mostly by BF, accounting for around 86.3% of total-PBB (Fig. 7(e)), indicating that the primary emission sources of PCBs and PBBs were the fly ash collected from the BF.

Figs. 7 (c) and (d) show that PBDD/Fs and PBDEs were most present in incineration residues, and the distribution ratios of PBDD/Fs and PBDEs in $\mu\text{g}/\text{ton-waste}$ of bottom ash were approximately 89.0% and 56.3%, respectively. With adequate combustion control and flue gas treatment, the amount of brominated pollutants released from the flue gas was lower than that from incineration residues (from combusting feeding material containing BFRs). Obviously, the main POP source in the MSWI was the fly ash. Therefore, further treatment of ash from the MSWI (especially from dust control units such as the HE and BF) needs to be considered.

CONCLUSIONS

In this study, the simultaneous sample cleanup procedures by combining multiple columns were applied to concentrate five persistent organic compounds (PCDD/Fs, PBDD/Fs, PBDEs, PCBs and PBBs) in ash samples from SH, HE, SDA, BF, FAP and BA. The levels of five target compounds were first measured and their emission factors were estimated. The following conclusions were made:

1. PCDD/F was found in high concentration in the HE (1297 $\text{pg WHO}_{98}\text{-TEQ}/\text{g}$), mainly because the operating temperature (~374°C) was within the range (250–400°C) favorable for PCDD/F formation through the de novo synthesis. The PCBs were formed together with PCDD/Fs in the de novo synthesis, resulting in an increase of PCB content in the HE. The duration of fly ash in the BF was longer than those in the other units in the MSWI, so the ash of BF had the highest PCB content.
2. The BFRs in incinerator feeding materials led to the highest concentrations of PBDD/Fs and PBDEs in bottom ash.
3. The total content of PCDD/Fs and PCBs in individual ash were closely related to the operating temperatures of MSWI units, while those of PBDD/Fs and PBDEs relate mainly to the BFRs in feeding wastes.
4. The HE+SDA+BF ash exhibited higher emission factors of PCDD/Fs and PCBs than BA+SH ash and stack flue gas, whereas the emission factors of PBDD/Fs and PBDEs were greater for the BA+SH ash than for the HE+SDA+BF ash and stack flue gas. The total emission factor of PBB in the whole MSWI was 12.4 $\mu\text{g}/\text{ton-waste}$.
5. The primary emission source of five target pollutants in the MSWI was the fly ash. The total PCDD/F content in HE + BF ash exceeded the regulation limit (1 $\text{ng I-TEQ}/\text{g}$) in Taiwan. Such ash should be collected separately and treated properly before reutilization.

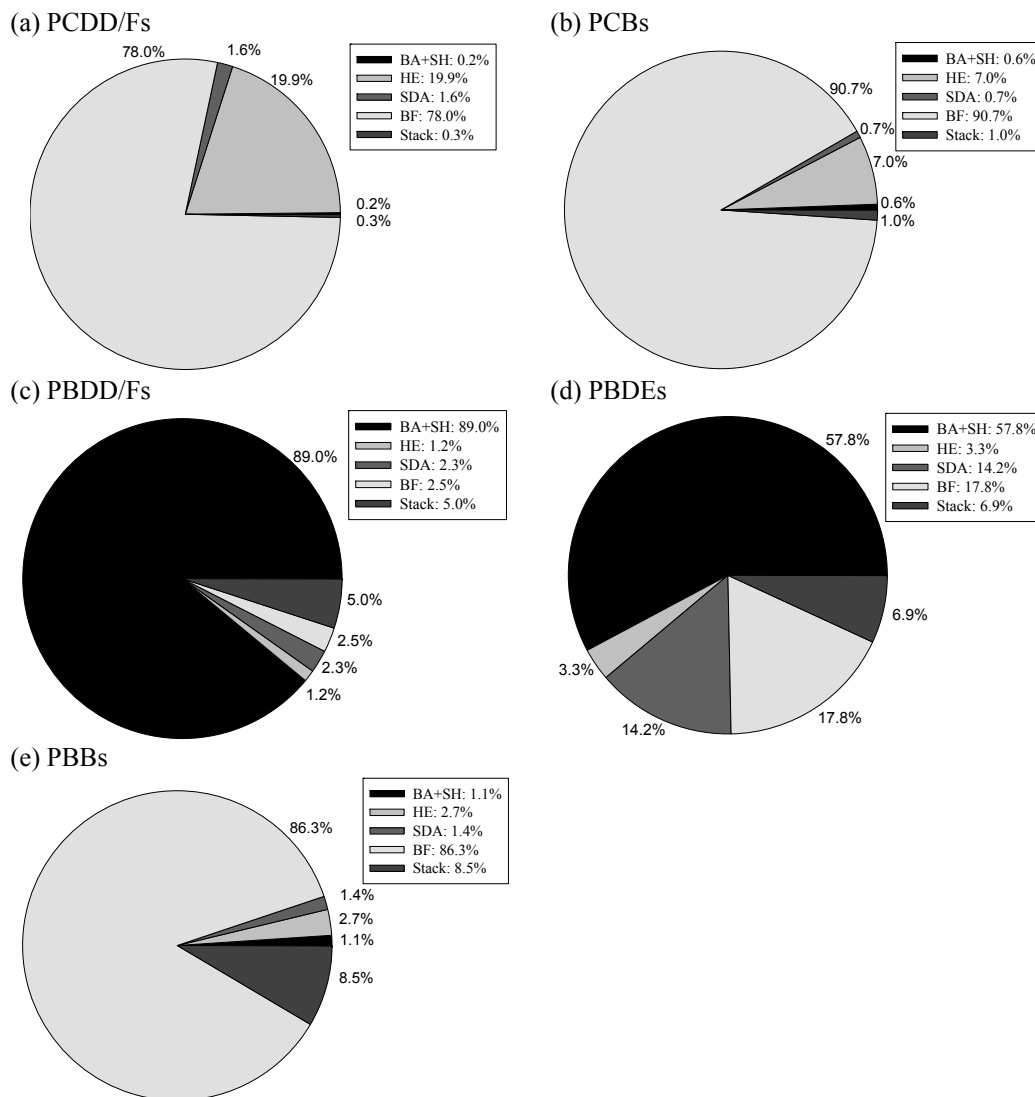


Fig. 7. Mass distributions (%) of persistent pollutants ($\mu\text{g}/\text{ton-waste}$) for the ash of units and stack flue gas of MSWI.

ACKNOWLEDGEMENTS

The authors would like to thank Professor Lin-Chi Wang at Cheng Shiu University for his insightful discussion on this article.

REFERENCES

- Abad, E., Caixach, J. and Rivera, J. (2003). Improvements in Dioxin Abatement Strategies at a Municipal Waste Management Plant in Barcelona. *Chemosphere* 50: 1175–1182.
- Addink, R., Paulus, R.H.W.L. and Olie, K. (1996). Prevention of Polychlorinated Dibenzop-dioxins/dibenzofurans Formation on Municipal Waste Incinerator Fly Ash Using Nitrogen and Aulfur Compounds. *Environ. Sci. Technol.* 30: 2350–2354.
- Agrell, C., ter Schure, A.F.H., Sveder, J., Bokenstrand, A., Larsson, P. and Zegers, B.N. (2004). Polybrominated Diphenyl Ethers (PBDES) at a Solid Waste Incineration Plant I: Atmospheric Concentrations. *Atmos. Environ.* 38: 5139–5148.
- Birnbaum, L.S., Staskal, D.F. and Diliberto, J.J. (2003). Health Effects of Polybrominated Dibenzop-dioxins (PBDDs) and Dibenzofurans (PBDFs). *Environ. Int.* 29: 855–860.
- Chang, Y.S., Kong, S.B. and Ikonomou, M.G. (1999). PCBs Contributions to the Total TEQ Released from Korean Municipal and Industrial Waste Incinerators. *Chemosphere* 39: 2629–2640.
- Chen, L.G., Mai, B.X., Bi, X.H., Chen, S.J., Wang, X.M., Ran, Y., Luo, X.J., Sheng, G.Y., Fu, J.M. and Zeng, E.Y. (2006). Concentration Levels, Compositional Profiles, and Gas-particle Partitioning of Polybrominated Diphenyl Ethers in the Atmosphere of an Urban City in South China. *Environ. Sci. Technol.* 40: 1190–1196.
- Chen, S.J., Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Kao, J.H. and Hu, M.T. (2004). Characterizing Polychlorinated Dibenzop-dioxins and Dibenzofurans in the Surrounding Environment and Workplace of a

- Secondary Aluminum Smelter. *Atmos. Environ.* 38: 3729–3732.
- Giugliano, M., Cernuschi, S., Grosso, M., Miglio, R. and Aloigi, E. (2002). PCDD/F Mass Balance in the Flue Gas Cleaning Units of a MSW Incineration Plant. *Chemosphere* 46: 1321–1328.
- Hanari, N., Kannan, K., Miyake, Y., Okazawa, T., Kodavanti, P.R.S., Aldous, K.M. and Yamashita, N. (2006). Occurrence of Polybrominated Biphenyls, Polybrominated Dibenzo-*p*-dioxins, and Polybrominated Dibenzofurans as Impurities in Commercial Polybrominated Diphenyl Ether Mixtures. *Environ. Sci. Technol.* 40: 4400–4405.
- Hell, K., Stieglitz, L., Altwicker, E.R., Addink, R. and Will, R. (2001). Reactions of 2,4,6-trichlorophenol on Model Fly Ash: Oxidation to CO and CO₂ Condensation into PCDD/F and Conversion into Related Compounds. *Chemosphere* 42: 697–702.
- Hoh, E. and Hites, R.A. (2005). Brominated Flame Retardants in the Atmosphere of the East-central United States. *Environ. Sci. Technol.* 39: 7794–7802.
- Jones, P.H., de Gerlache, J., Marti, E., Mischer, G., Scherrer, M.C., Bontinck, W.J. and Niessen, H.J. (1993). The Global Exposure of Man to Dioxins: A Perspective on Industrial Waste Incineration. *Chemosphere* 26: 1491–1497.
- Kao, J.H., Chen, K.S., Chang-Chien, G.P. and Chou, I.C. (2006). Emissions of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans from Various Stationary Sources. *Aerosol Air Qual. Res.* 6: 170–179.
- Lai, Y.C., Lee, W.J., Li, H.W., Wang, L.C. and Chang-Chien, G.P. (2007). Inhibition of Polybrominated Dibenzo-*p*-dioxin and Dibenzofuran Formation from the Pyrolysis of Printed Circuit Boards. *Environ. Sci. Technol.* 41: 957–962.
- Lee, W.S., Chang-Chien, G.P., Chen, S.J., Wang, L.C., Lee, W.J. and Wang, Y.H. (2004a). Removal of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Flue Gases by Venture Scrubber and Bag Filter. *Aerosol Air Qual. Res.* 4: 27–37.
- Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Tsai, P.J., Wu, K.Y. and Lin, C. (2004b). Source Identification of PCDD/Fs for Various Atmospheric Environments in a Highly Industrialized City. *Environ. Sci. Technol.* 38: 4937–4944.
- Lin, L.F., Lee, W.J., Li, H.W., Wang, M.S. and Chang-Chien, G.P. (2007). Characterization and Inventory of PCDD/F Emission from Coal-fired Power Plants and other Sources in Taiwan. *Chemosphere* 68: 1642–1649.
- Lin, Y.S., Chen, K.S., Lin YC, Hung, C.H. and Chang-Chien, G.P. (2008). Polychlorinated Dibenzo-*p*-dioxins/dibenzofurans Distributions in Ash from Different Units in a Municipal Solid Waste Incinerator. *J. Hazard. Mater.* 154: 954–962.
- Pekárek, V., Grabic, R., Marklund, S., Punčochář, M. and Ullrich, J. (2001). Effects of Oxygen on formation of PCB and PCDD/F on Extracted Fly Ash in the Presence of Carbon and Cupric Salt. *Chemosphere* 43: 777–782.
- Rappe, C. (1993). Sources of Exposure, Environmental Concentration and Exposure Assessment of PCDDs and PCDFs. *Chemosphere* 27: 211–225.
- Sakai, S., Watanabe, J., Honda, Y., Takatsuki, H., Aoki, I., Futamatsu, M. and Shiozaki, K. (2001). Combustion of Brominated Flame Retardants and Behavior of its Byproducts. *Chemosphere* 42: 519–531.
- Sakai, S.I., Hirai, Y., Aizawa, H., Ota, S. and Muroishi, Y. (2006). Emission Inventory of Deca-brominated Diphenyl Ether (DBDE) in Japan. *J. Mater. Cycles Waste Manag.* 8: 56–62.
- Söderström, G. and Marklund, S. (2000). PXDD and PXDF from Combustion of Bromoflameretardant Containing MSW. *Organohalogen Compd.* 47: 225–228.
- Stapleton, H.M., Brazil, B., Holbrook, R.D., Mitchelmore, C.L., Benedict, R., Konstantinov, A. and Potter, D. (2006). In Vivo and in Vitro Debromination of Decabromodiphenyl Ether (BDE 209) by Juvenile Rainbow Trout Andcommoncarp. *Environ. Sci. Technol.* 40: 4653–4658.
- Van den Berg, M., Birnbaum, L., Bosveld, A.T.C., Brunström, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., van Leeuwen, F.X.R., Liem, A.K.D., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younse, M., Waern, F. and Zacharewski, T. (1998). Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife. *Environ. Health Perspect.* 106: 775–792.
- Vehlow, J., Bergfeldt, B., Jay, K., Seifert, H., Wanke, T. and Mark, F.E. (2000). Thermal Treatment of Electric and Electronic Waste Plastics. *Waste Manage. Res.* 18: 131–140.
- Wang, L.C., His, H.C., Wang, Y.F., Lin, S.L. and Chang-Chien, G.P. (2010a). Distribution of Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Dibenzo-*p*-dioxins and Dibenzofurans (PBDD/Fs) in Municipal Solid Waste Incinerators. *Environ. Pollut.* 158: 1595–1602.
- Wang, L.C., Wang, Y.F., His, H.C. and Chang-Chien, G.P. (2010b). Characterizing the Emissions of Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Dibenzo-*p*-dioxins and Dibenzofurans (PBDD/Fs) from Metallurgical Processes. *Environ. Sci. Technol.* 44: 1240–1246.
- Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P. and Tsai, P.J. (2003a). Characterizing the Emission of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans from Crematories and their Impacts to the Surrounding Environment. *Environ. Sci. Technol.* 37: 62–67.
- Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P. and Tsai, P.J. (2003c). Effect of Chlorine Content in Feeding Wastes of Incineration on the Emission of Polychlorinated Dibenzo-*p*-dioxins/dibenzofurans. *Sci. Total Environ.* 302:185–198.
- Wang, L.C., Lee, W.J., Tsai, P.J., Lee, W.S. and Chang-Chien, G.P. (2003b). Emission of Polychlorinated Dibenzo-*p*-dioxins/dibenzofurans from Stack Flue Gases of Sinter Plants. *Chemosphere* 50: 1123–1129.
- Wang, M.S., Chen, S.J., Huang, K.L., Lai, Y.C.,

- Chang-Chien, G.P., Tsai, J.H., Lin, W.Y., Chang, K.C. and Lee, J.T. (2009a). Determination of Levels of Persistent Organic Pollutants (PCDD/Fs, PBDD/Fs, PBDEs, PCBs, and PBBs) in Atmosphere near a Municipal Solid Waste Incinerator. *Chemosphere*, Minor Revision.
- Wang, M.S., Wang, L.C., Chang-Chien, G.P. and Lin, L.F. (2005). Characterization of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in the Stack Flue Gas of a Municipal Solid Waste Incinerator, in the Ambient Air, and in the Banyan Leaf. *Aerosol Air Qual. Res.* 5: 171–184.
- Wang, W., Gao, X., Zheng, L. and Lan, Y. (2006). Reductive Dechlorination of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in MSWI Fly Ash by Sodium Hypophosphite. *Sep. Purif. Technol.* 52: 186–190.
- Wang, Y.H., Lin, C. and Chang-Chien, G.P. (2009b). Characteristics of PCDD/Fs in a Particles Filtration Device with Activated Carbon Injection. *Aerosol Air Qual. Res.* 9:317–322.
- Weber, R. and Kuch, B. (2003). Relevance of BFRs and Thermal Conditions on the Formation Pathways of Brominated and Brominated-chlorinated Dibenzodioxins and Dibenzofurans. *Environ. Int.* 29: 699–710.
- World Health Organization (WHO). (1994). Polybrominated Diphenyl Ethers. Environmental Health Criteria (EHC) Monographs 162.
- World Health Organization (WHO). (1998). Polybrominated Dibenzo-*p*-dioxins and Dibenzofurans. *Environmental Health Criteria (EHC) Monographs* 205.

Received for review, January 1, 2010

Accepted, April 30, 2010