CHARACTERISTICS OF POLYBROMINATED DIPHENYL ETHERS (PBDES) AND POLYBROMINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS (PBDD/FS) IN THE BOTTOM AND FLY ASHES OF MUNICIPAL SOLID WASTE INCINERATORS

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Abstract

As yet, very little is known about the characteristics of of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) in the ashes of municipal solid waste incinerators (MSWIs). In this study, the ashes in different units of two MSWIs were sampled to measure the PBDEs, PBDD/Fs and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). Bottom ashes (BA) exhibited much higher PBDD/F (8.11 – 52.2 pg TEQ/g) and PBDE contents (20.4 – 186 ng/g) than those of fly ashes (0.0932 – 2.02 pg TEQ/g, and 0.332 – 25.5 ng/g), revealing that PBDD/Fs and PBDEs in the feeding waste may not be completely destroyed. In addition, PBDE contents in BA were one to three orders higher than those found in contaminated site soils or reference soils. The reutilization of BA of MSWIs for beneficial purpose, however, might add PBDEs to the environmental loading, which should not be ignored while developing a PBDE inventory.

Introduction

Polybrominated diphenyl ethers (PBDEs) are extensively used as brominated flame retardants (BFRs) in many daily-use articles, to meet the regulatory requirements aiming at reducing damage and fatal risks from fires. On the other hand, there is a raising concern about polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), in view of the likely formation of PBDD/F during processing of PBDE-containing plastics or incineration of wastes which contains BFRs (*1, 2*). It is noted that, products containing PBDEs and PBDD/Fs sooner or later will have to be treated by municipal solid waste incinerators (MSWIs) or metal recycling plants, therefore worthy a track-down of their fate..

Unlike fly ashes, bottom ashes are usually considered as non-hazardous materials. Many countries, such as the USA, Germany, France, Sweden, Denmark, UK, the Netherlands, Switzerland, Taiwan and Japan, encourage or legalize the reutilization of BA from MSWIs. The contained pollutants, usually chlorine salts, heavy metals and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), in this case, must be evaluated before BA's further use as the raw material in road sub-base, cement aggregate, and so on. Nevertheless, PBDEs and PBDD/Fs generally are not considered to be serious pollutants in the BA. In this study, the ashes in different units of two MSWIs are sampled to measure the PBDEs, PBDD/Fs and PCDD/Fs. With a better understanding of the PBDE and PBDD/F characteristics in the ashes of MSWIs, appropriate control strategies can be developed and implemented to reduce the relevant toxics emitted from MSWIs.

Materials and Methods

The continuously operating MSWIs (MSWI1 and MSWI2) in southern Taiwan were investigated in 2008. Both MSWIs co-treated municipal and industrial wastes. The municipal vs. industrial wastes handled were 40% vs. 60% for MSWI1, and 80% vs. 20% for MSWI2. The capacity of each furnace of MSWI1 and MSWI2 was 450 and 300 tonnes/day, respectively. Each furnace was of two-stage, starved-air modular type complete with its own heat recovery system (superheater and economizer), dry scrubber, activated carbon injection, fabric filter and stack.

Different ashes, including BA, and fly ashes from a superheater (SA), economizer (EA), dry scrubber (DA), fabric filter (FA) and ash storage pit (PA), were sampled, and three and four repeat sampling runs were performed for each of MSWI1 and MSWI2. Fifty grams of both BA and SA were collected for PBDD/F analyses, while 20 g of the other ashes were sampled. The same was done for the PBDE analyses. For PCDD/F analyses, 5 g of BA and SA, and 2 g of the other ashes were sampled.

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. As for PBDEs, the samples were analyzed for 30 PBDE congeners. Detailed analytical procedures of PCDD/Fs and PBDD/Fs are described in our previous work (*3, 4*). PBDE analyses were done following the U.S. EPA Method 1614. A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for PCDD/F, PBDD/F and PBDE analyses. Detailed instrumental analysis parameters of PBDD/Fs and PCDD/Fs are given in our previous work (*3*).

Results and Discussion

PCDD/F, PBDD/F and PBDE contents in the ashes.

Figure 1 illustrates the PCDD/F, PBDD/F and PBDE contents measured in the ashes from the different units of MSWIs (n=7 for each compound in each unit). The international toxic equivalency factors (I-TEFs) of PCDD/Fs were used as tentative TEFs for PBDD/Fs to evaluate their toxicity (*2*). Both MSWI1 and MSWI2 exhibited similar trends of PCDD/F, PBDD/F and PBDE contents in the ashes. For PCDD/Fs, when the temperature decreased to 339 °C – 396 °C in the economizers, which is within the region (250 °C – 450 °C) of optimal PCDD/F formation, the PCDD/F contents in the EA dramatically increased to 0.719 – 1.02 ng I-TEQ/g. The PCDD/F contents in the FA increased again to 1.95 – 2.08 ng I-TEQ/g owing to gas-phase PCDD/F adsorption by activated carbon injected. The PCDD/F trend in the ashes 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 PBDD/F and PBDE content trends were similar between the two, but different from the PCDD/F trend based on the whole MSWI system. BA exhibited the highest PBDD/F (434 – 2620 pg/g, 8.11 – 52.2 pg TEQ/g) and PBDE (20.4 – 186 ng/g) contents of all the other ashes (6.59 – 39.1 pg/g, 0.0932 – 2.02 pg TEQ/g for PBDD/Fs, and 0.332 – 25.5 ng/g for PBDEs). The elevated PBDE contents in the BA showed that the PBDEs in the feeding waste may not be completely destroyed, although Sakai et al. (*5*) reported that PBDEs were destroyed by more than 99.9% in a laboratory scale incinerator.

Less than 10% of PBDD/Fs in the input materials had been found undestroyed in the combustion tests by means of a PBDD/F mass balance calculation (*6*). The elevated PBDD/F contents in the BA, which could be similar to PBDEs in the BA, were from PBDD/F-containing wastes incompletely destroyed. Another reason that PBDD/Fs exist in the BA could be the pyrolysis and thermolysis of BFR-containing wastes in the furnaces. However, the dominant BDE-209 in the BA suggested that the formation of the highly brominated-substituted PBDD/Fs (see Fig. 2) from PBDEs was not favorable due to "steric crowding" of bromine atoms (*1*).

The PBDE contents in BA (20.4 – 186 ng/g) were one to three orders higher than those in contaminated site soils or reference soils, which were low and ranged from 0.038 – 3.8 ng/g (BDE-209 included) (*7, 8*). It is possible, therefore, that the reutilization of BA of MSWIs would contribute PBDEs to the environmental loadings. This pathway should not be ignored while developing an overall PBDE inventory. It is noted, however, that the PBDE leaching behavior of BA is still unclear, and the PBDE risk assessment on reutilization of BA has never been investigated.

The phenomenon of higher PBDD/F (two- to five-fold) and PBDE (two- to six-fold) contents in the EA than the SA can also be observed for PCDD/Fs. This result suggests that de novo syntheses could also occur among PBDD/Fs and PBDEs. The above results showed that appropriate control strategies for PBDD/Fs and PBDEs in the MSWIs not only

can prevent high PBDE-contained wastes being fed into incinerators but also can decrease de novo syntheses of PBDD/Fs and PBDEs among the economizers.

Emission factors of PCDD/Fs, PBDD/Fs and PBDEs.

Table 1 lists the PCDD/F, PBDD/F and PBDE emission factors of routes of bottom residues (BA and SA) and fly ashes (EA, DA and FA). The TEQ contributed by PBDD/Fs was only 0.05% of the PCDD/F I-TEQ based on fly ash route, but their output toxicity from BA was comparable (5.31 μg I-TEQ/tonne-waste vs. 4.43 μg TEQ/tonne-waste). The PBDE emission factors of the BA route were 104 and 66 times higher than PCDD/F and PBDD/F emission factors, respectively.

Comparing the emission factors of MSWI1 and MSWI2 (see Table 2), MSWI1 with similar operational units but fed with a larger percentage of the industrial waste obviously exhibited higher PCDD/F, PBDD/F and PBDE emission factors. For PCDD/Fs and PBDD/Fs, the higher emission factor ratios of MSWI1 to MSWI2 were observed only on the BA+SA route of PBDD/Fs, and ranged at 5.7 – 6.1, revealing that the feeding wastes was an influential factor affecting the PBDD/Fs in BA, while the operational factors of MSWIs determine the PCDD/Fs and PBDD/Fs in the fly ashes. For PBDEs, the divergence between MSWI1 and MSWI2 was more apparent, and the ratios of emission factors ranged from 6.2 to 8.4, revealing that the compositions in the feeding waste also influence the PBDEs in fly ashes. This may be because the undestroyed PBDEs after waste combustion could condense onto the fly ashes.

Congener profiles of PCDD/Fs, PBDD/Fs and PBDEs.

The PCDD/F, PBDD/F and PBDE congener profiles in the BA and FA of MSWIs are illustrated in Fig. 2. The BA and FA of MSWIs contained abundant highly chlorinated-substituted congeners, like OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF. The most dominant PBDE congeners in the BA are highly brominated-substituted congeners, possibly because the feeding wastes contain more commercial deca-BDE mixtures. Similarly, the abundant highly brominated-substituted congeners, 1,2,3,4,6,7,8-HpBDF, OBDF in the BA may be the side compounds in the commercial deca-BDE mixtures (*9*).

Acknowledgments

We would like to thank the National Science Council of Taiwan for supporting this research work under Grant NSC 97-2221-E-230 -013.

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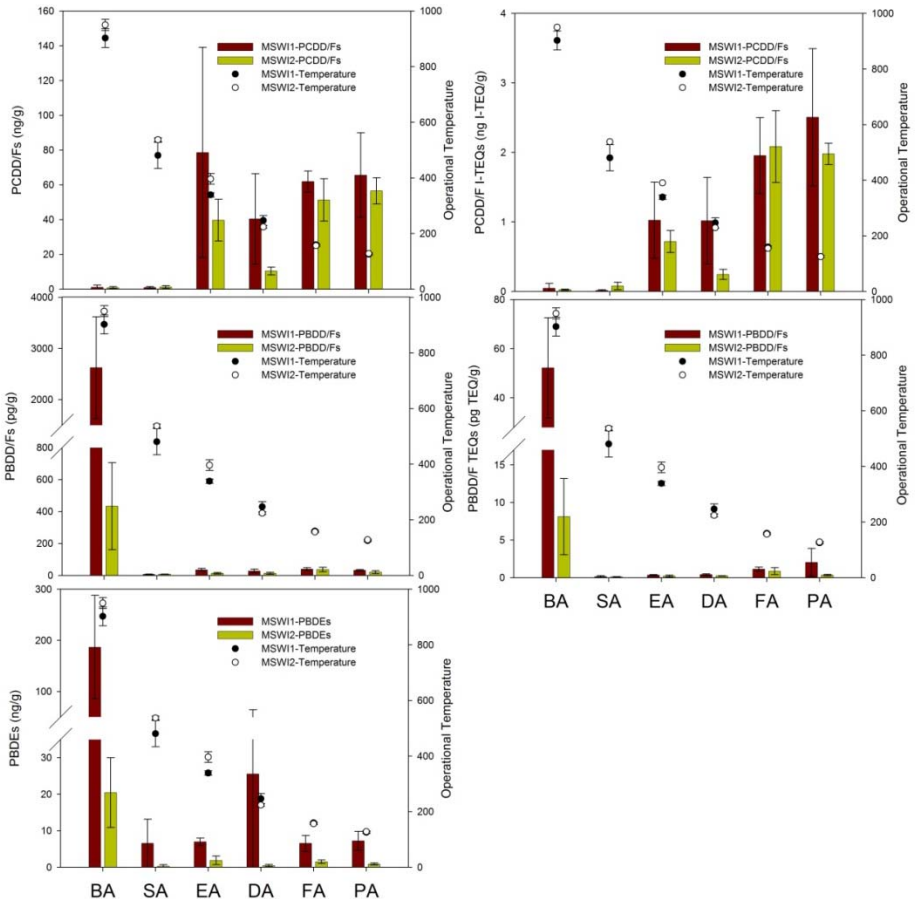

Figure 1 PCDD/F, PBDD/F and PBDE contents (mean ± SD) in the ashes from different units of MSWIs.

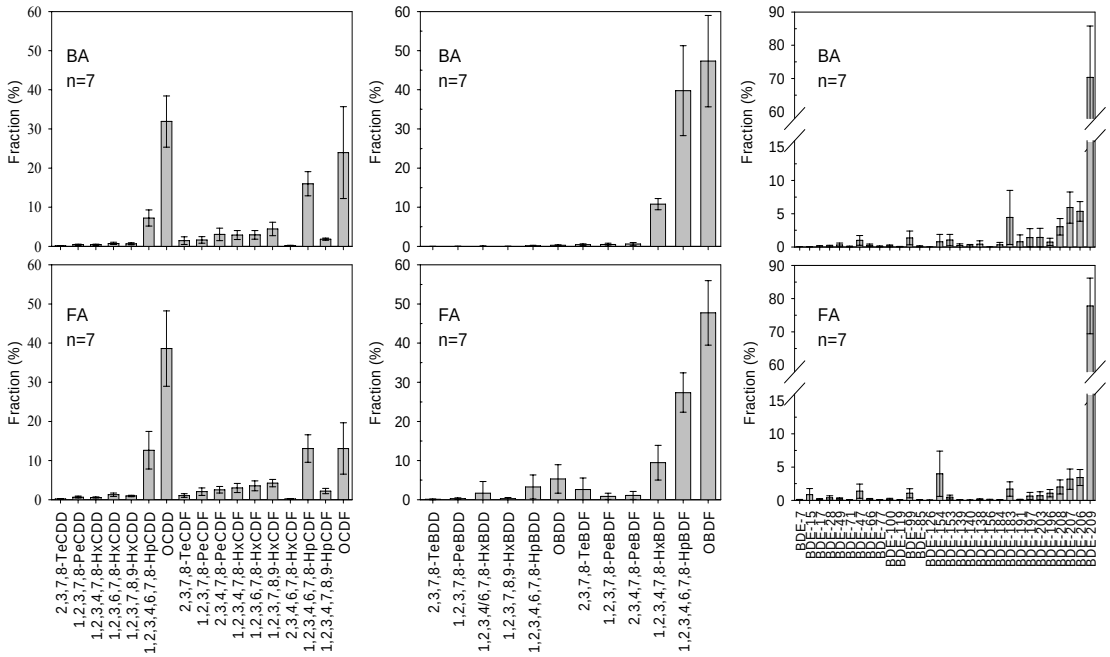

Figure 2 PCDD/F, PBDD/F and PBDE congener profiles in the BA and FA

Table 1 Mean PCDD/F, PBDD/F and PBDE emission factors

		Route I BA+SA	Route II EA+DA+FA
PCDD/Fs	mass (μg/tonne-waste)	143±132	2720±724
	I-TEQs (μg I-TEQ/tonne-waste)	5.31±6.38	96.5±26.3
PBDD/Fs	mass (μg/tonne-waste)	225±204	1.87±0.694
	TEQs (μg TEQ/tonne-waste)	4.43±4.13	0.0472±0.0201
PBDEs	mass (μg/tonne-waste)	14900±16300	208±198

Table 2 Ratios of PCDD/F, PBDD/F and PBDE emission factors of MSWI1 to MSWI2

		Route I BA+SA	Route II EA+DA+FA
PCDD/Fs	mass	1.1	1.5
	I-TEQs	1.8	1.2
PBDD/Fs	mass	5.7	1.3
	TEQs	6.1	1.6
PBDEs	mass	8.4	6.2