Emission estimation and congener-specific characterization of polybrominated diphenyl ethers from various stationary and mobile sources

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A R T I C L E   I N F O

Article history:
Received 24 April 2010
Received in revised form 21 June 2010
Accepted 28 June 2010

Keywords:
PBDEs
Dioxin
Combustion sources
Stack flue gases

A B S T R A C T

Here we show that combustion sources, including waste incinerators, metallurgical processes, power-heating systems and so on, are also important emitters of polybrominated diphenyl ethers (PBDEs) to the atmosphere. Geometric mean PBDE concentrations in the stack flue gases of the combustion sources ranged from 8.07 to 469 ng/Nm³. The sinter plants (24.7 mg/h), electric arc furnaces (EAFs) (11.3 mg/h) and power plants (50.8 mg/h) possessed the largest PBDE emission rates, which were several orders higher than those of the other reported sources. The occurrences of the PBDEs in the flue gases of the power plants and vehicles, as well as their PBDE concentrations statistically highly correlated with combustion-originated PCDD/Fs, revealing that PBDEs should be the products of combustion. The ranking of major PBDE emission sources in Taiwanese PBDE inventory for combustion sources was power plants (30.85 kg/year), vehicles (14.9 kg/year) and metallurgical processes (5.88 kg/year).

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1. Introduction

Polybrominated diphenyl ethers (PBDEs), structurally similar to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated diphenyls (PCBs), have been extensively used as brominated flame retardants (BFRs) in furniture, electronic goods and other consumer items. PBDEs with high octanol–water partition coefficients (KOW > 10³) and high octanol–air partition coefficients (KOA > 10⁶) can biomagnify in water-respiring and air-breathing organisms (Kelly et al., 2007). Even for BDE-209, its human biomagnification factor can still reach 8 (Kelly et al., 2007).

Due to these health risks, the commercial penta-BDE and octa-BDE mixtures were banned within the European Union in 2004. Meanwhile, the European Court of Justice ruled against the exemption of deca-BDE from the RoHS directive and decided that its use must be phased out by July 1, 2008 (European Court of Justice, 2008). Furthermore, no new manufacture or import of the commercial penta-BDE and octa-BDE mixtures is allowed after January 1, 2005, without a 90-day notification to U.S. EPA for evaluation (U.S. EPA, 2009). However, PBDEs are now not only ubiquitous in the environment (Hoh and Hites, 2005; Kohler et al., 2008; Mandalakis et al., 2008; Zhu and Hites, 2005), but also highly accumulated in humans (Voorspoels et al., 2007) and top predators, such as polar bears (Gebbink et al., 2008), dolphins (Litz et al., 2007) and birds of prey (Chen et al., 2007). After the ban on PBDEs, their levels did not follow any consistent pattern in milk from primiparous women in Sweden, with decreases in BDE-47 and -99, an increase in BDE-153, and no change in BDE-100 (Lignell et al., 2009). For California peregrine falcon, the PBDE contents were even found to be increasing in their eggs (Park et al., 2009).

Schenker et al. (2008) calculated global PBDE discharges from production, use and waste-management, however, they believed that their calculated global PBDE emissions were underestimated, because the model’s predicted PBDE concentrations in ambient air and environmental media were at least one order of magnitude lower than field data from environmental measurements (Schenker et al., 2008). PBDE emissions from combustion sources to the atmosphere were not included in Schenker et al. (2008), maybe because these emissions were believed to be much smaller compared to the fugitive emissions from PBDE-containing products (Prevedouros et al., 2004; Sakai et al., 2006). However, incinerators...
and metallurgical processes were recently identified as PBDE emission sources to the atmosphere (Odabasi et al., 2009; Wang et al., 2010a,b). Consequently, PBDE contributions from combustion emission sources to the atmosphere should not be ignored and need further comprehensive investigation.

This paper is the first one of the series, with a focus on the PBDE emission characteristics of the combustion sources and estimation of their PBDE emission quantities. On the sequent study, the PBDE congener profiles of the ambient air samples were compared to those of indoor air, the commercial PBDE mixtures and combustion sources to support the contention that combustion is important PBDE emission source. In the present study, a total of 110 stack flue gas samples from stationary sources and 17 tailpipe exhaust samples from diesel and gasoline motor vehicles were examined for both PBDE and PCDD/F concentrations, emission rates and emission factors to clarify the relationship between PBDEs and combustion-originated PCDD/Fs. Furthermore, a Taiwanese PBDE inventory for combustion sources was established to offer the useful information for PBDE control strategies.

2. Materials and methods

2.1. Basic information concerning the combustion sources

The combustion sources investigated in this study included waste incinerators, metallurgical processes, and power-heating systems. The waste incinerators can be divided into large-scale municipal solid waste incinerators (MSWIs) and number to sampled facilities, m = 16; n: number of successfully analyzed samples, n = 47, batch MSWI (m = 1, n = 3), medical waste incinerators (MWIs) (m = 2, n = 4), and industrial waste incinerators (IWIs) (m = 4, n = 10). The metallurgical processes can be classified into six plants (m = 4, n = 11), electric arc furnaces (EAFs) (m = 6, n = 18), and secondary aluminum smelters (secondary AlSs) (m = 4, n = 9). The power-heating systems are further separated into power plants (m = 3, n = 7), boiler (m = 1, n = 1), unladen gas-fueled vehicles (UGFVs) (m = 12, n = 12), and diesel-fueled vehicles (DFVs) (m = 5, n = 5). The basic and operational information of these combustion sources is described in Table S1.

2.2. Sampling procedures

All the stack flue gas samplings as well as chemical analyses in this study were carried out in 2007–2008 by our accredited laboratory, which specializes in PCDD/F samplings and analyses in Taiwan. The stack flue gas samples were collected isokinetically following U.S. EPA Modified Method 23 using U.S. EPA Modified Method 5 sampling trains. The sampled flue gas volumes were normalized to dry condition of 760 mmHg and 273 K, and denoted as Nm3. Three stack flue gas samples were collected for each facility, and the collection time for each sample lasted for about three hours. For EAFs and secondary ALs, each stack gas sampling time combined three whole batch operating processes.

Exhausts of mobile sources (vehicular tailpipes) were sampled directly and isokinetically during the entire testing cycle. UGFVs were operated following a standard chassis dynamometer (Schenck CA). For PCDD/Fs, the HRGC was equipped with a DB-5HT capillary column (l = 60 m, i.d. = 0.25 mm, film thickness = 0.1 μm) (J&W Scientific, CA). For PCDD/Fs, the HRGC was equipped with a DB-SMS fused silica capillary column (l = 60 m, i.d. = 0.25 mm, film thickness = 0.25 μm) (J&W Scientific, CA). The HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI) source. The analyzer mode of the selected ion monitoring (SIM) was used with a resolving power of 10,000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. The detailed instrumental analysis parameters of PBDEs and PCDD/Fs are given in our previous works (Wang et al., 2010a, 2003a). The quality assurance and quality control (QA/QC) are described in the Supporting Information, which included field and laboratory blanks, as well as the recoveries of the surrogate and internal standards (Table S2).

3. Results and discussion

3.1. PCDD/F concentrations, emission rates and emission factors

The measured PCDD/F concentrations, emission rates and emission factors of stationary source emissions and motor vehicle exhausts are detailed in Tables S3–S12 of the Supporting Information. To prevent the mean values being skewed too much by the high values, geometric means (GM) of the concentrations, emission rates and emission factors for each kind of the emission sources are listed in these tables besides the arithmetic means (AM). Fig. 1 illustrates the PCDD/F concentrations, emission rates and emission factors of the combustion sources with horizontal lines representing the 10th, 50th, and 90th percentiles, and the boxes representing the 25th to 75th percentiles. The PCDD/F-I-TEQ concentrations of the stationary emissions were all lower than Taiwanese PCDD/F emission limits (MSWIs: 0.1 ng I-TEQ/Nm3; batch MSWIs and EAFs: 0.5 ng I-TEQ/Nm3; others: 1 ng I-TEQ/Nm3); except for 3 MSWIs, 1 IW and 2 EAFs, indicating that most of the investigated facilities were operated in good condition. For stationary sources, the PCDD/F-I-TEQ concentrations and emission factors were comparable to or lower than other reported results (Hofstädler et al., 2000; Lee et al., 2005; Lin et al., 2007; Wang and Chang-Chien, 2007; Wang et al., 2003b).

PCDD/F emission factors of UGFVs (0.111 ng I-TEQ/km) and DFVs (0.134 ng I-TEQ/km) obtained in this study (see Table S12) were about one order higher than those from other studies (Dyke et al., 2007; Gullett and Ryan, 2002; Ryan and Gullett, 2000). This may due to the shorter sampling durations (30 min) of this study than those (6–8 h) of other studies (Dyke et al., 2007; Gullett and Ryan, 2002), and short sampling durations may give a higher weight to cold starts that may have a higher PCDD/F emission.

3.2. PBDE concentrations, emission rates and emission factors

Fig. 2 illustrates the measured PBDE concentrations, emission rates and emission factors of stationary source emissions and motor vehicle exhausts, with the values detailed in Tables S3–S12 of the Supporting Information. Horizontal lines represent the 10th, 50th, and 90th percentiles, and the boxes represent the 25th to 75th percentiles. The GM PBDE concentrations measured from stack flue gases of municipal, medical and industrial waste incinerators ranged from 8.07 to 469 ng/Nm3. In addition, the GM PBDE concentrations of the other combustion sources were 22.2 ng/Nm3 for sinter plants, 19.4 ng/Nm3 for EAFs, 45.0 ng/Nm3 for secondary ALs, 33.5 ng/Nm3 for power plants, 46.7 ng/Nm3 for UGFVs, and 29.1 ng/Nm3 for DFVs. There was only one data for wood chips boiler, and its PBDE concentration was 16.8 ng/Nm3. It is interesting that while no commercial PBDE mixtures are added to the feeding materials or fuels of the power plants, industrial boilers and motor vehicles,
PBDEs were still found in their flue gases and exhausts. Our recent studies concerning incinerators and metallurgical processes suggested that PBDEs could form or survive from the PBDE-contaminated feeding materials in the combustion system (Wang et al., 2010a,b). The occurrences of the PBDEs in the flue gases and exhausts of the power plants and vehicles further confirm PBDE formation during the combustion processes. Bromine contents in the fuels and coals (Marklund et al., 1990; Pecherer et al., 1950) could be one of the bromine sources for the formation of PBDEs.

As for PBDE emission rates, similar to the results of PCDD/Fs, the GM values of the sinter plants (24.7 mg/h), EAFs (11.3 mg/h) and power plants (50.8 mg/h) were the largest, which is attributed to their huge flow rates of stack flue gases. Batterman et al. (2009) monitored 12 U.S. houses and garages and combined PBDE measurements in air and settled dust, air exchange rates, and other information to estimate in-use releases from building materials. Their measured indoor PBDE concentrations are at the high end of the literature, which is consistent with many other studies reporting higher PBDE levels in North American air and dust samples compared with Europe and elsewhere (Harrad and Hunter, 2006; Prevedouros et al., 2004; Sakai et al., 2006). However, the PBDE concentrations in the stack and exhaust emissions obtained in this study are one to three orders higher than those in indoor and industrial workplace air (see Table S12). Combustion sources possess high PBDE concentrations, huge flow rates of stack flue gases and numerous amounts, revealing that they could contribute significant PBDEs to the atmosphere. In other words, combustion sources are not only major PCDD/F emission sources, but also important sources of PBDEs. Furthermore, fugitive emission of house or workplace dust mainly affects indoor environments (Jones-Otazo et al., 2005; Wilford et al., 2005), and thus combustion sources are probably more important PBDE contributors to outdoor air levels and have more influence on the food chain, which is one of the major routes for human and wildlife PBDE exposure. Consequently, the PBDE emission quantities from global combustion sources need to be further evaluated, and compared to those from global fugitive emissions in order to adopt appropriate global control strategies for PBDEs.

3.3. PCDD/F and PBDE congener profiles

The PCDD/F congener profiles are illustrated in Fig. S1, and are comparable to those found in previous studies from Taiwan (Lee et al., 2003, 2004; Wang and Chang-Chien, 2007; Wang et al., 2003b) and elsewhere (Anderson and Fisher, 2002; Hofstadler et al., 2000; Kasai et al., 2001; U.S. EPA, 2006). Waste incineration and power-heating system emissions contain an abundance of (0.00799–0.704 mg/h) and the dismantling and crushing of home appliances (0.0433–25.5 mg/h) in the Japanese BDE-209 inventory (Sakai et al., 2006).
highly chlorinated-substituted congeners, like OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF. However, metallurgical processes tend to emit PCDD/F profiles containing an abundance of lighter chlorinated-substituted congeners, such as 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF (Lee et al., 2004). Cluster analysis of EAF PCDD/F congener profiles yielded two subcategories: EAFs-1 and EAFs-2 (see Fig. S1(b)). 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF contributed 56% of EAFs-2 but only 36% of EAFs-1 PCDD/Fs.

The PBDE congener profiles are illustrated in Fig. 3, and apart from the polystyrene IWI, the most abundant PBDE congeners of waste incineration and power-heating system emissions were highly brominated-substituted congeners, including BDE-209, -208, -207, -206, and -183. Among the low to medium brominated-substituted congeners, BDE-47 and BDE-99 were more abundant. The PBDE congener profile of the polystyrene IWI differs from those of others, with higher abundances of BDE-47 and BDE-99 (19.2% and 20.2%) that might be caused by the feedstock containing penta-BDE.

Unlike the waste incineration and power-heating systems, relatively higher fractions of lighter brominated substituents (e.g., BDE-47 and -99) characterized the emissions of the EAFs and secondary ALSs (Fig. 3(b)), although their PBDE congener profiles still comprise larger amounts of highly brominated-substituted congeners (BDE-209, -206, -207, and -208). As for sinter plants, the most dominant PBDE congeners were highly brominated-substituted congeners, similar to the abundances in the power-heating system profiles.

Although the wearing of flame-retardant materials from conveyor belts used in the iron and steel making plants was speculated as a possible source of PBDEs to the atmosphere (Choi et al., 2008), the conveyor belts of the sinter plants investigated in this study are made of steel, and contain no plastics or other materials. The sintered pellets were placed on the bottom of the conveyor belts, and the ambient air was pulled down through the conveyor belts. Furthermore, the move of the conveyor belts keeps them from continuously contacting the highest temperature zone (about 1300 °C). These measures all prevent the temperature being too high to damage the conveyor belts.

No raw materials containing PBDEs were fed into the power-heating systems and sinter plants, revealing that PBDE formation during the combustion processes prefer highly brominated congeners. Consequently, the abundant lighter brominated substituents (e.g., BDE-47 and -99) of the EAFs and secondary ALSs may be attributed to the thermal desorption of the commercial penta-BDE mixtures during stages of feeding, which were the impurities in the feeding scraps.

BDE-209 is usually the most abundant PBDE congener in the stack flue gases of the combustion sources. After being emitted from combustion sources, BDE-209 can be metabolically or photocatalytically degraded to lighter brominated congeners, resulting in enhanced toxicity, as they are more easily absorbed by animal tissues and thus subject to serious bio-accumulation (de Boer and Wells, 2006; Huwe and Smith, 2007; Stapleton et al., 2006).

3.4. Relationship between PBDE and PCDD/F concentrations

After conducting Q-Q plots, both PBDE and PCDD/F concentrations in the stack flue gases and exhaust fumes have been found to possess log-normal distributions. Therefore, after using natural logarithm transformation processes and further Pearson correlation analyses, total PBDE concentrations were found to be statistically highly correlated (r ranged from 0.481 to 0.779 and p < 0.05) with those of total PCDD/Fs and total PCDD/F-I-TEQ for sinter plants, EAFs, power plants and vehicle exhausts (UGFVs and DFVs) (Table S14 and Fig. S2), revealing that PBDEs are likely to be combustion products.
with formation and removal processes similar to those of PCDD/Fs. We had not measured polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) in this study. However, PBDEs were indicated as precursors of PBDFs in combustion system (Wang et al., 2010b). Consequently, the formation of PBDEs and PBDD/Fs should be more related with each other comparing to their relation with PCDD/Fs, although both PBDD/Fs and PBDEs could form during the combustion processes through the similar formation conditions of PCDD/Fs (Wang et al., 2010b).

Non-significant correlations were found between PBDE and PCDD/F concentrations in MSWI, IWI and secondary ALS emissions, indicating that their PBDE emissions derive not only from formation, but also from undestroyed PBDEs in the feeding materials. Similar phenomena had been found on PBDD/F and PBDE emission factors of carbon steel EAFs much higher than those of stainless steel EAFs (Wang et al., 2010b), and MSWIs with a larger percentage of the industrial waste exhibited higher PBDD/F and PBDE emission factors (Wang et al., 2010a).

3.5. Taiwanese PBDE inventory for combustion sources

Taiwan EPA has established a PCDD/F inventory (Taiwan EPA, 2008), and estimated that 74.7 g I-TEQ PCDD/Fs were emitted into the atmosphere in 2008. The important PCDD/F emission sources in the inventory are listed in Table 1, and together contributed 62.6 g I-TEQ which accounted 84% of the total PCDD/F emissions. The PBDE emission factors of these important combustion sources could be derived from this study and our previous research (Wang et al., 2010b, 2009). After multiplying the PBDE emission factors by their corresponding activities, the annual PBDE emissions from these important combustion sources were obtained as 52.6 kg (see Table 1). The major PBDE emission sources were power plants (30.85 kg/year), vehicles (14.9 kg/year) and metallurgical processes (5.88 kg/year), such as EAFs (2.08 kg/year), ferrous foundries (2.05 kg/year) and sinter plants (1.20 kg/year). The ranking of PBDE emission sources is similar with that of PCDD/Fs, which is metallurgical processes, power plants and vehicles, in that order.
Fig. 3. (continued).
The GM PBDE concentrations in the stack flue gases of combustion sources, which was obtained by applying the GM of the PBDEs:PCDD/Fs I-TEQ ratios in the stack flue gases. The estimation (28.6 kg/year) was smaller than that (52.6 kg/year) obtained by using the emission factors, but the range was much less than an order. The estimation biases may come from the fact that the correlation between PBDEs and PCDD/Fs is not proportional, than an order. The estimation biases may come from the fact that the activities of combustion sources need to be further evaluated.

Table S15 presents another estimation of PBDE emissions from these combustion sources, which was obtained by applying the GM of the PBDEs:PCDD/Fs I-TEQ ratios in the stack flue gases. The estimation (28.6 kg/year) was smaller than that (52.6 kg/year) obtained by using the emission factors, but the range was much less than an order. The estimation biases may come from the fact that the correlation between PBDEs and PCDD/Fs is not proportional, than an order. The estimation biases may come from the fact that the activities of combustion sources need to be further evaluated.

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