



Review

Overview and Perspectives on Emissions of Polybrominated Diphenyl Ethers on a Global Basis: Evaporative and Fugitive Releases from Commercial PBDE Mixtures and Emissions from Combustion Sources

Farran Mack Redfern¹, Wen-Jhy Lee¹, Ping Yan^{2**}, John Kennedy Mwangi¹, Lin-Chi Wang^{3*}, Chih-Hsuan Shih¹

¹ Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan

² School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, China

³ Department of Civil Engineering and Geomatics, Cheng Shiu University, Kaohsiung 83347, Taiwan

ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants, but are of concern due to their potential health risks. PBDEs are ubiquitous in the environment and their occurrence in polar regions highlights the importance of atmospheric transport. As yet, most researches emphasized evaporative and fugitive releases of PBDEs during production, use and waste management phases. However, the recent studies have uncovered the importance of the combustion sources when considering the release of PBDEs into the atmosphere. Nevertheless, complete PBDE emission inventories are lacking, and no global PBDE emissions from combustion sources have been estimated. Therefore, this study estimated the global PBDE emissions from combustion sources and illegal open burning of waste electrical and electronic equipment (WEEE) and e-waste, as well as evaporative and fugitive releases from commercial PBDE mixtures. We found that combustion sources and illegal open burning of e-waste globally emit PBDEs at 6.75 and 0.255–5.56 tonnes year⁻¹, and are important PBDE emitters. The effectiveness of reducing human exposure to PBDEs will be minimized and delayed if mitigation of PBDE emissions from combustion sources is ignored. Control of PBDE emissions from combustion sources should be taken along with the ban of commercial PBDE mixtures.

Keywords: Inventory; Review; PBDEs; Dioxin; Open burning; E-waste.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) constitute an important group of brominated flame retardants (BFRs) that have been produced in significant quantity and are used extensively as additives in numerous everyday commercial and industrial products, such as plastics, building materials, electronic appliances, furnishings and textiles in many countries. The three most commonly used commercial PBDE mixtures, are penta-, octa- and deca-BDE, which differ in their degree of bromination. Penta-BDE has been most widely used in furniture (polyurethane foam), octa-BDE in wire and cable insulation (styrene copolymers) and deca-BDE in electronics and computers (high-impact polystyrene)

(Alaee *et al.*, 2003; La Guardia *et al.*, 2006).

The PBDE congener profiles of these three commercial PBDE mixtures are illustrated in Fig. 1 (Wang *et al.*, 2011). The most abundant congeners of commercial penta-BDE mixtures are from tetra- to hexa-BDE congeners (BDE-47, -99, -100, -154, -153), and those of the commercial octa-BDE mixtures are hexa- to deca-BDE (BDE-153, -183, -197, -196, -207, or BDE-183, -197, -203, -207, -206, -209). For the commercial deca-BDE, BDE-209 is the sole predominant congener and other highly brominated congeners (BDE-206, -207, -208) usually comprise well below 5% (Hoh and Hites, 2005; La Guardia *et al.*, 2006).

There is growing concern about the toxicity of these commercial PBDE mixtures, their persistence in the environment and their tendency to bioaccumulate in the food chain (Kelly *et al.*, 2007; Gebbink *et al.*, 2008). Due to these health risks, the commercial penta-BDE and octa-BDE mixtures were banned within the European Union in 2004, and no new manufacture or import was allowed in U.S. after January 1, 2005 (U.S. EPA, 2009). Therefore, the commercial penta-BDE and octa-BDE mixtures have not been manufactured globally since 2004, and have already

* Corresponding author.

Tel.: +886-7-7351275; Fax: +886-7-7332204

E-mail address: lcwang@csu.edu.tw

** Corresponding author.

E-mail address: y9621227@126.com

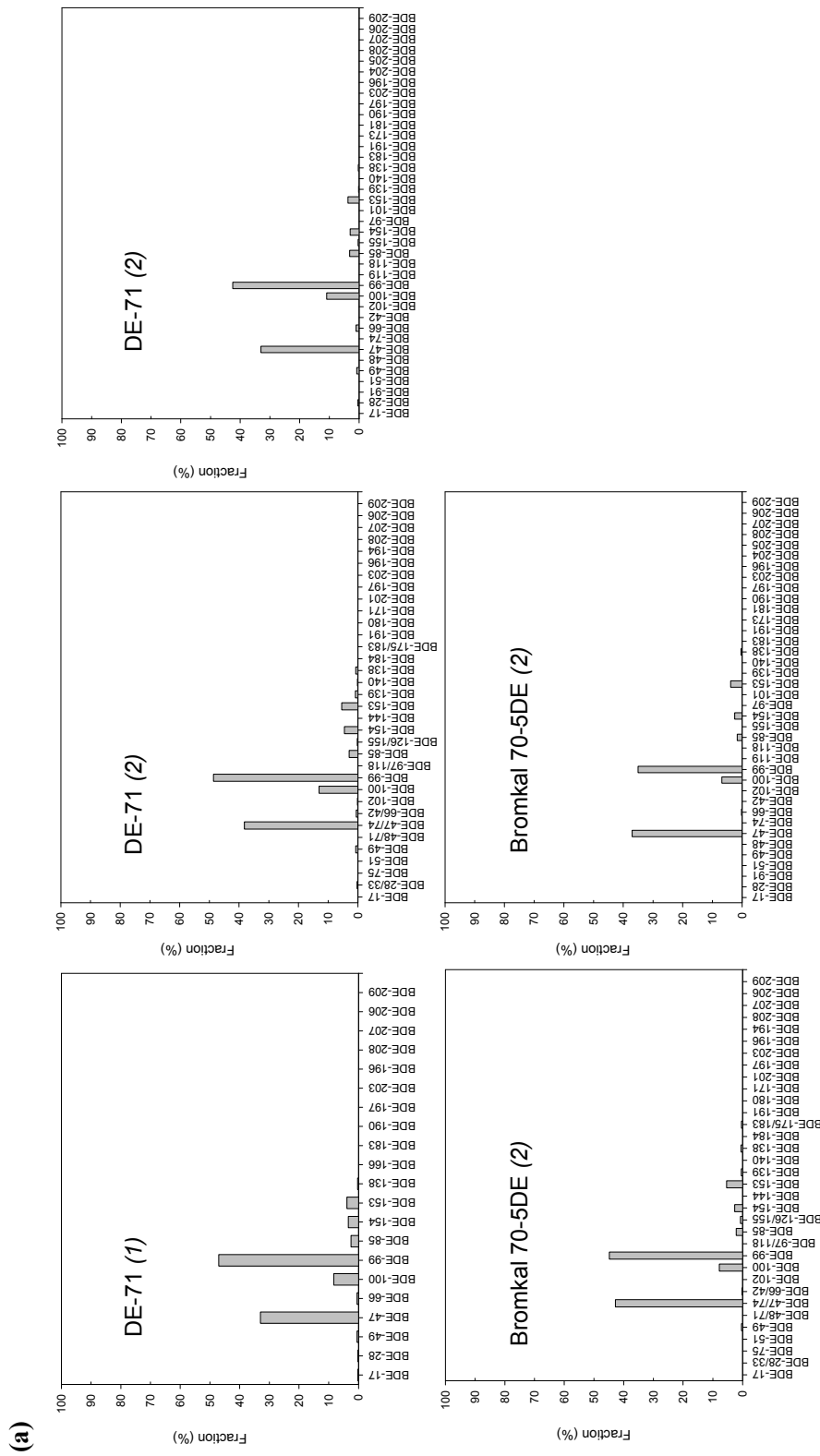


Fig. 1. PBDE congener profiles in commercial (a) penta-, (b) octa- and (c) deca-BDE mixtures (Wang et al., 2011). Note: (1) (Hoh and Hites, 2005), (2) (La Guardia et al., 2006).

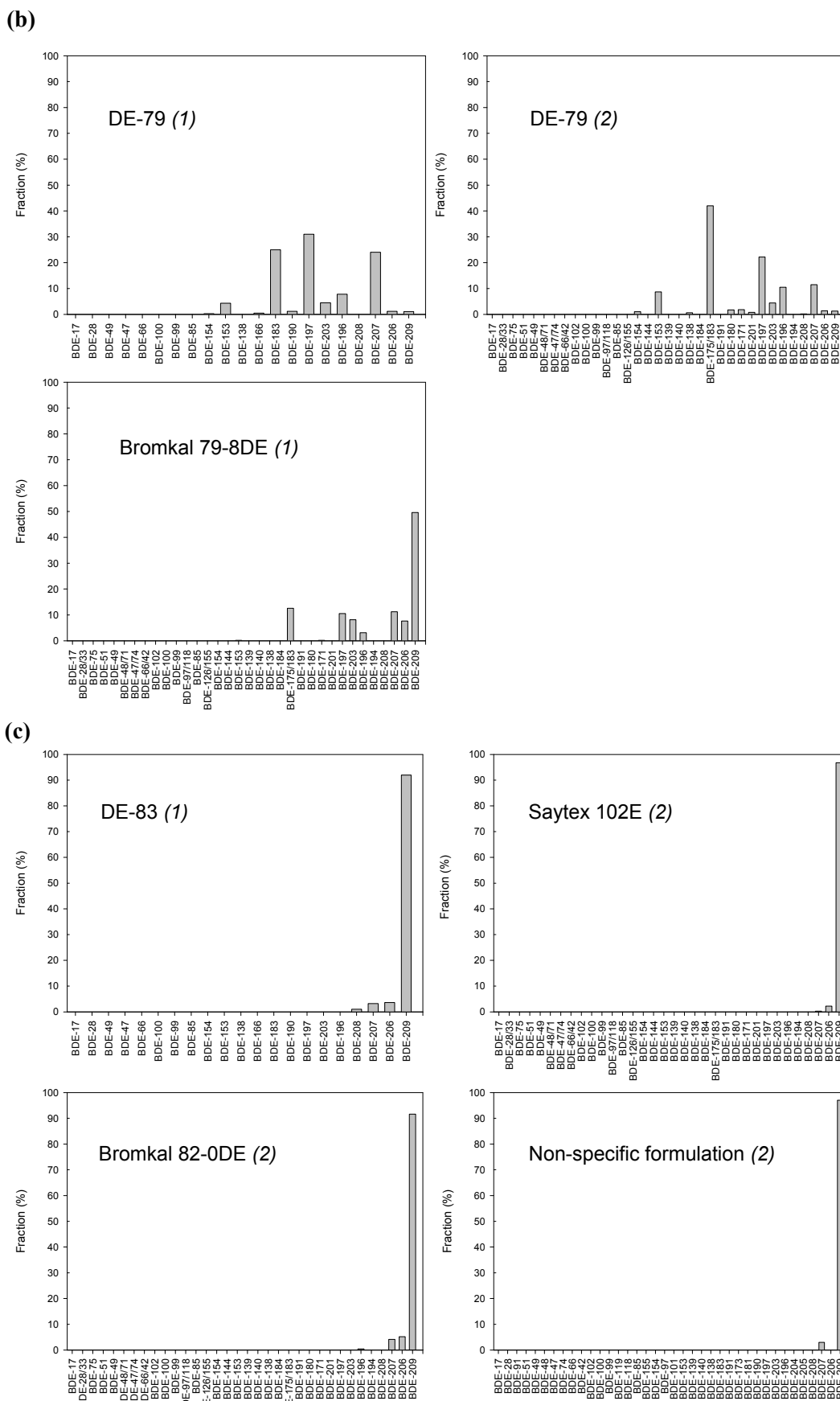


Fig. 1. (continued).

been added to Annex A of the Stockholm Convention in 2009. As for commercial deca-BDE mixtures, their use in electrical and electronic equipment was phased out within EU on July 1, 2008 (European Court of Justice, 2008). The major producers and importers in the U.S. voluntarily phased out the production of deca-BDE mixtures by December 2012, and its use stopped by the end of 2013 (Wyrzykowska-Ceradini *et al.*, 2011; Earnshaw *et al.*, 2013). However, the commercial deca-BDE mixtures are still produced and widely used in other regions.

PBDEs are ubiquitous in the environment and their occurrence in polar regions highlights the importance of atmospheric transport (Wang *et al.*, 2011; Chao *et al.*, 2014; Kuo *et al.*, 2015; Mwangi *et al.*, 2016). Emissions related to the commercial PBDE mixtures can occur during production, processing, use of products containing PBDEs, and waste management (e.g., from landfills, incineration, and open burning) (Prevedouros *et al.*, 2004; Sakai *et al.*, 2006; Schenker *et al.*, 2008; Earnshaw *et al.*, 2013). So far, researches related to PBDE emission inventory and estimation mostly emphasized their evaporative and fugitive releases during production, use, and waste management phases.

However, the recent studies have uncovered the importance of the combustion sources when considering the release of PBDEs into the atmosphere (Odabasi *et al.*, 2009; Wang *et al.*, 2010b, c, 2011; Drage *et al.*, 2014). Some studies even indicated that PBDEs can be formed during combustion (Sakai *et al.*, 2001; Wang *et al.*, 2010b; Artha *et al.*, 2011; Ni *et al.*, 2016) and measured in the flue gas of combustion sources that their fuels contained no commercial PBDE mixtures (Wang *et al.*, 2010b; Chang *et al.*, 2014b, c; Chen *et al.*, 2017). PBDE emissions from combustion sources were not included in the mentioned PBDE inventory and estimation, maybe because these emissions used to be believed to be much smaller than the evaporative releases from PBDE-containing products (Prevedouros *et al.*, 2004; Sakai *et al.*, 2006).

Therefore, this study estimated the global PBDE emissions from combustion sources and illegal open burning of waste electrical and electronic equipment (WEEE) and e-waste, as well as evaporative and fugitive releases from commercial PBDE mixtures. The PBDE emissions from these sources were compared and discussed in order to provide important information to establish effective control strategies and policies to minimize PBDE releases on a global basis.

GLOBAL EVAPORATIVE AND FUGITIVE EMISSIONS FROM COMMERCIAL PBDE MIXTURES

Prevedouros *et al.* (2004) have estimated a European consumption and emission inventory into air for penta-BDE for the period 1970–2000. A peak BDE-47 atmospheric emission of 22–31 tonnes occurred around 1997 was estimated, with a decline of ~20% in 2000. The total of both indoor and outdoor BDE-209 atmospheric emissions for Japan were estimated by Sakai *et al.* (2006) to be 170

kg yr⁻¹ using data from field studies, including contributions from textile processing (0.18 kg yr⁻¹), plastics processing (0.28 kg yr⁻¹), dismantling and crushing of home appliances (27 kg yr⁻¹), deca-BDE production (84 kg yr⁻¹), and house dust (54–120 kg yr⁻¹). Earnshaw *et al.* (2013) developed a dynamic substance flow analysis model of deca-BDE and the predicted BDE-209 atmospheric emissions peak in 2004 at 10 tonnes year⁻¹. The dominant BDE-209 contributions to the atmosphere during its life cycle are volatilization and particle bound emissions from landfills during waste management phase. To the best of our knowledge, no comprehensive global PBDE estimations which included evaporative and fugitive emissions from penta-BDE, octa-BDE and deca-BDE mixtures have been reported.

In this study, we follow the methods proposed by Prevedouros *et al.* (2004) and Schenker *et al.* (2008) to use the statistical data from global bromine production during 1996–2016, the fractions of BFR production and the fractions of the three main commercial PBDE mixtures to estimate global PBDE production. With the amounts of global PBDE production, we then can use emission factor approach to estimate global PBDE emissions from production, use and waste management phases.

We targeted on year 2016 in this study, and assumed 10 years of product service life to estimate PBDE evaporative and fugitive releases during production, use and waste management phases after the ban on commercial penta-BDE and octa-BDE mixtures worldwide.

Global Production of the Three Commercial PBDE Mixtures

Table S1 lists the amounts of global bromine production for 2003–2016 (USGS National Minerals Information Center). By using the global bromine production, the production amounts of global BFR can be estimated by the percent values of BFR production to bromine production derived from references, which were 49% in 2007 and 46% in 2013 (HIS Markit, 2014). The percent of PBDE production amounts to all BFR in 1999 was 32.85% which was derived from the data in Alae *et al.* (2003). We also used the data in Lassen *et al.* (2014) to calculate the percentage for 2011, and found it decreased to 10.6% due to the ban on PBDEs. The percentages between 2000 and 2010 were obtained by linear interpolations of literature values, and the values after 2011 were assumed to be the same as 2011. As of 2007, penta-BDE mixtures were not manufactured in Europe, Japan, Canada, Australia and the U.S., but no information on the status of production in China was available (Lassen *et al.*, 2014). We assumed the remaining commercial PBDE mixture were only octa-BDE and deca-BDE, and derived their proportions to the total PBDE mixtures to be 1.45% and 98.55% using the data reported in Lassen *et al.* (2014). From the above values and assumptions, the global production of commercial PBDE mixtures for 2007–2016 can be obtained and are listed in Table 1. Our estimated global deca-BDE production in 2011 is 30582 tonnes, which is in the range (25000–50000 tonnes) of global consumption of BFR for deca-BDE reported in Lassen *et al.* (2014).

Table 1. Global production of PBDEs for 2007–2016.

year	World bromine production (tonne y ⁻¹)	BFR Bromine production (%)	PBDE production/ BFR production (%)	PBDE mixtures/ production (%)	deca-BDE mixture (%)	octa-BDE mixture (%)	penta-BDE mixture (%)	Global deca-BDE mixture production (tonne)	Global octa-BDE mixture production (tonne)	Global penta-BDE mixture production (tonne)
2007	658000	49 ^a	18.0 ^d	98.55 ^f	1.45 ^f	0 ^f	0 ^f	57246	840	0
2008	658000	48.5 ^c	16.2 ^d	98.55	1.45	0	0	50829	745	0
2009	544000	48 ^c	14.3 ^d	98.55	1.45	0	0	36817	540	0
2010	614000	47.5 ^c	12.5 ^d	98.55	1.45	0	0	35791	525	0
2011	623000	47 ^c	10.6 ^e	98.55	1.45	0	0	30582	449	0
2012	600000	46.5 ^c	10.6	98.55	1.45	0	0	29139	427	0
2013	632000	46 ^b	10.6	98.55	1.45	0	0	30363	445	0
2014	652000	46	10.6	98.55	1.45	0	0	31324	459	0
2015	585000	46	10.6	98.55	1.45	0	0	28105	412	0
2016	634000	46	10.6	98.55	1.45	0	0	30460	447	0

a: data from http://www.bromine.chem.yamaguchi-u.ac.jp/library/L02_Global%20Bromine%20Industry.pdf.

b: data from HIS Markit (2014), and assuming keeping the same value after 2013.

c: linear interpolations of literature values for 2008–2012.

d: linear interpolations of literature values in 1999 (Alaee et al., 2003) and 2011 (Lassen et al., 2014) for 2000–2010.

e: derived from the data in Lassen et al. (2014), and assuming keeping the same value after 2011.

f: derived from the data in Lassen et al. (2014).

The Global Cumulative Use of the Three Commercial PBDE Mixtures

The three commercial PBDE mixtures contain different PBDE congeners, as shown in Fig. 1. To simplify the emission estimation, the following calculations use their homologue compositions, instead of detailed congener compositions. PBDEs are used into two streams of product groups: polymers (75%) and textiles (25%) (Schenker *et al.*, 2008; Earnshaw *et al.*, 2013). The PBDE emission factors of polymer materials and textiles are different, therefore, their PBDE emissions during use and waste management phases were separately evaluated. The cumulative PBDE production for ten years (2007–2016) and their cumulative use in polymers and textiles (2007–2016) are listed in Table S2.

The Cumulative PBDE Amounts in Landfills

From the substance flow analysis model in Earnshaw *et al.* (2013), PBDE-containing products may go to different waste management processes, such as landfill, recycling, incineration (open burning and controlled incineration) and sewerage, after the end of their service life. It is still impossible to obtain the activity data of these waste management processes, especially on a global scale. Therefore, we adopted the transfer factor approach reported in Schenker *et al.* (2008) to calculate the PBDE amounts in waste management phase. The transfer factor of PBDEs in use phase to landfill is 0.9, while that for use phase to open burning and controlled incineration are 0.002–0.1 and 0.05–0.1, respectively, depending on the human development index in different countries (Schenker *et al.*, 2008). It should be noted that we only estimate PBDE evaporative and fugitive emissions in this section, and PBDE emissions related to combustion are discussed in the following section of this study.

We assume the residence times of PBDEs in the landfills during waste management phase to be 10 years (Schenker *et al.*, 2008). Then the cumulative PBDEs in the landfills for 2007–2016 can be derived from the global PBDE production during 1997–2006 (Schenker *et al.*, 2008) (assuming product service life to be 10 years), and are listed in Table S3.

Waste Electrical and Electronic Equipment (WEEE) and E-waste

The quantities of WEEE (e.g., air conditioners, refrigerators, washing machines) and e-waste (discarded electronic goods, such as computers and mobile telephones) are on the increase globally. Global generation of WEEE and e-waste around 2005 was estimated as 35 million tonnes (20–50 million tonnes) (Breivik *et al.*, 2014). The trade and transport of WEEE and e-waste from developed to developing regions (China, India, and five West African countries) have received considerable attention. Telecommunication equipment seems to be the dominant e-waste being generated in Africa and in the poorer regions of Asia and South America (Ongondo *et al.*, 2011; Breivik *et al.*, 2014).

Although it is difficult to give a generalized material composition for the WEEE and e-waste, studies reported that iron and steel account for half of the total weight of WEEE, and plastics are the second largest component,

representing 21% of WEEE (Ongondo *et al.*, 2011). Dismantling activities release coarse particles containing BFR into the atmosphere. Illegal dismantling and open burning recycling activities even result in the formation of PCDD/Fs, PBDD/Fs and PBDEs, and cause extremely high health risks (Sepúlveda *et al.*, 2010).

PBDE Emission Factors during Production, Use and Waste Management Phases

PBDE emission factors during production, use and waste management phases are listed in Table S4. These emission factors obtained from scientific publications were used to estimate global PBDE evaporative and fugitive emissions (excluding emissions from combustion treatments or open burnings) to the atmosphere. The penta-BDE evaporative emission factors during the use phase of polymer and textile products have been estimated as 2.7×10^{-4} and 3.3×10^{-4} , respectively (Alcock *et al.*, 2003; Morf *et al.*, 2007; Schenker *et al.*, 2008). Nevertheless, those of deca-BDE during the use phase of polymer and textiles had more than three orders discrepancy and were 3.9×10^{-8} (Schenker *et al.*, 2008) and 9.5×10^{-5} (Stevens *et al.*, 2004), respectively. The deca-BDE emission factors (9.5×10^{-5}) adopted for textiles seemed too large.

BDE-47 and -99 emission factors had been reported as 8.17×10^{-3} and 7.00×10^{-4} based on vapor pressure, and 5.64×10^{-5} and 1.28×10^{-5} based on octanol-air partition coefficient (K_{OA}) (Prevedouros *et al.*, 2004). The emission factors derived by vapor pressure approach are one to two orders higher than those derived by K_{OA} approach. Emission factors based on vapor pressure of PBDEs have been applied in several studies (Wyrzykowska-Ceradini *et al.*, 2011; Earnshaw *et al.*, 2013). Besides vapor pressure approach, in this study we also use emission factors based on the K_{OA} of PBDEs to estimate PBDE emissions. The emission factor for deca-BDE was 1.06×10^{-8} , calculated by using K_{OA} data reported in Wang *et al.* (2008). The reason for using K_{OA} approach is because a much smaller difference in emission factors between congeners can be obtained, and their results are more consistent with field atmospheric PBDE concentrations (Prevedouros *et al.*, 2004). In contrary, if PBDEs are evaporated as functions of vapor pressure values, BDE-47 in the atmosphere will be at least an order higher than those of BDE-99, which is not in line with the observation in indoor and outdoor air (Prevedouros *et al.*, 2004; Batterman *et al.*, 2009; Wang *et al.*, 2011).

For dismantling and crushing during recycling, Sakai *et al.* (2006) reported the deca-BDE emission factors per unit weight of PBDE entering the recycling process ranged from 8×10^{-9} to 5×10^{-6} (median: 3×10^{-8}) by conducting flue gas samplings of seven home appliance recycling facilities. However, the emission factors of other PBDE congeners were not measured in their study. Here we assume that deca-BDE mixtures are the only BFR used in electronics and computers (high-impact polystyrene) (Alaee *et al.*, 2003; La Guardia *et al.*, 2006).

Global PBDE Evaporative and Fugitive Emissions

Table 2 lists the global PBDE evaporative and fugitive

Table 2. Global PBDE evaporative and fugitive emissions (tonnes) from production, use and waste management phases (landfill and dismantling and crushing during e-waste recycling) based on year 2016.

	deca-BDE mixture	octa-BDE mixture	penta-BDE mixture	Total PBDE mixtures
tri-BDE	0	0	0.00171	0.00171
tetra-BDE	0	0	0.0581	0.0581
penta-BDE	0	0	0.0975	0.0975
hexa-BDE	0	0.0216–0.0900	0.0137	0.0353–0.104
hepta-BDE	0	0.0721–0.245	0	0.0721–0.245
octa-BDE	0	0.0531–0.155	0	0.0531–0.155
nona-BDE	0.0896–0.545	0.0155–0.0377	0	0.105–0.583
deca-BDE	2.01–13.6	0.00141–0.00317	0	2.01–13.6
Total PBDEs	2.10–14.2	0.164–0.531	0.171	2.43–14.9

emissions from the production, use and waste management phases of the three commercial PBDE mixtures. These PBDE homologue emissions are estimated based on year 2016 by using the global PBDE production in 2016, assuming 10 years of product service life and assuming 10 years of the residence times in landfill. As for the fugitive PBDE emissions from dismantling and crushing during e-waste recycling, we use the upper values of global e-waste generation in 2005, 50 million tonnes (Breivik *et al.*, 2014), as the global e-waste amounts in 2016. Then by assuming collection percentage as 70%, (60% of e-waste generated in China was collected and passed into recycling processes (Zeng *et al.*, 2013)), 21% of WEEE weight (Ongondo *et al.*, 2011) as plastic parts, and 20% of the plastic parts as the added deca-BDE mixtures (Hale *et al.*, 2002), we estimated global fugitive PBDE emissions from dismantling and crushing to be 0.0441 tonnes in 2016 by using the emission factor, 3×10^{-8} , reported in Sakai *et al.* (2006).

Estimated global PBDE evaporative and fugitive emissions in 2016 were 2.43–14.9 tonnes (Table 2), and the deca-BDE mixture was responsible for 86.2–95.3% of total emissions (Table 3). Landfill is the dominant source (65.4%) of PBDE evaporative and fugitive emissions and the production ranks second (32.2%) when our established emission factors for PBDE uses in textile materials are applied. But the dominant source will be changed to PBDE uses in textile materials (83.4%) if the emission factor reported in literatures is used, as shown in Table S5. It should be noted that the choice of the emission factors make great difference on total emissions and contribution percentage of different sources. Nevertheless, current studies are too limited to provide

convincing data for these emission factors.

There are no comparable studies related to global PBDE evaporative and fugitive emissions. Sakai *et al.* (2006) estimated total BDE-209 atmospheric emissions to be 170 kg year⁻¹ in Japan with stock in use of deca-BDE mixture giving emission of 54 kg year⁻¹. Earnshaw *et al.* (2013) estimated BDE-209 atmospheric emissions peak in 2004 at 10 tonnes year⁻¹ in Europe, and the emissions from the stock in use of deca-BDE mixture peak in 2003 at 0.5 kg. Similar to the result when our emission factor is applied, landfills are responsible for the majority of atmospheric emissions. Compared to the emission estimation for 1993 when penta-BDE had not been banned yet, Prevedouros *et al.* (2004) have estimated a peak BDE-47 emission in 1993 of 74 tonnes from stock of 3200 tonnes.

GLOBAL PBDE EMISSIONS FROM VARIOUS COMBUSTION SOURCES

Schenker *et al.* (2008) developed a PBDE emission inventory which included PBDE discharges from production, use and waste management, to calculate environmental PBDE concentrations and mass fluxes. However, the authors believed that they underestimated PBDE emissions, because their model's predicted 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). It should be noted that PBDE emissions from stationary and mobile combustion sources to the atmosphere were not included in the PBDE inventory of Schenker *et al.* (2008).

Table 3. Percentage contribution of PBDE emissions from production, use and waste management phases (landfill and dismantling and crushing during e-waste recycling) to total PBDE emissions (%) based on year 2016.

	deca-BDE mixture	octa-BDE mixture	penta-BDE mixture	Total PBDE mixtures
tri-BDE	0	0	0.01–0.07	0.01–0.07
tetra-BDE	0	0	0.4–2.4	0.4–2.4
penta-BDE	0	0	0.7–4.0	0.7–4.0
hexa-BDE	0	0.6–0.9	0.09–0.6	0.7–1.5
hepta-BDE	0	1.6–3.0	0	1.6–3.0
octa-BDE	0	1.0–2.2	0	1.0–2.2
nona-BDE	3.7	0.3–0.6	0	3.9–4.3
deca-BDE	82.5–91.6	0.02–0.06	0	82.6–91.6
Total PBDEs	86.2–95.3	3.6–6.7	1.1–7.0	100

Recent studies have reported the occurrence of PBDEs in flue gases of various combustion sources, including waste incinerators, sinter plants, electric arc furnaces (EAFs) converter steelmaking plants, secondary aluminum smelters (secondary ALSs), fly ash treatment plants, power plants, boilers, vehicles, diesel-engine generators, and even in ambient air affected by open rice straw biomass burning (Odabasi *et al.*, 2009; Wang *et al.*, 2010a, b, c; Wyrzykowska-Ceradini *et al.*, 2011; Liao *et al.*, 2012; Chang *et al.*, 2013b, 2014b, c; Drage *et al.*, 2014; Li *et al.*, 2015; Tsai *et al.*, 2016; Chen *et al.*, 2017; Li *et al.*, 2017). Combustion sources possess high PBDE concentrations in the flue gases/exhaust (one to three orders higher than those in indoor and workplace air), huge flue gas flow rates and numerous amounts (e.g., vehicles), revealing their importance on contributing significant PBDEs to the atmosphere (Wang *et al.*, 2010b). In fact, the PBDE emission rates of sinter plants (24.7 mg hr^{-1}), EAFs (11.3 mg hr^{-1}) and power plants (50.8 mg hr^{-1}) were much higher than or equivalent to those of plastics processing ($0.00799\text{--}0.704 \text{ mg hr}^{-1}$) and the dismantling and crushing of home appliances ($0.0433\text{--}25.5 \text{ mg hr}^{-1}$) in the Japanese BDE-209 inventory (Sakai *et al.*, 2006; Wang *et al.*, 2010b).

Furthermore, elevated atmospheric PBDE concentrations in the vicinity of EAFs or in metallurgical complex than those in urban and residential areas have been reported (Cetin and Odabasi, 2008; Choi *et al.*, 2008; Wang *et al.*, 2011). The PBDE concentrations were highly correlated ($r = 0.871$, $p < 0.001$) with the PCDD/F concentrations in the atmosphere, which are combustion-originated, revealing that PBDEs are likely the products of combustion, and combustion sources are one of the PBDE sources in the ambient air (Wang *et al.*, 2011).

A comprehensive emission inventory that presents sources of pollutions and environmental releases can provide important information for the authority to establish effective control strategies and policies. Many countries established their PCDD/F inventories to promulgate relevant PCDD/F regulations and emission standards on main PCDD/F sources, and obtained quite apparent outcomes (Cheruiyot *et al.*, 2016). Nevertheless, complete PBDE emission inventories are lacking, and no global PBDE emissions from combustion sources have been estimated.

Survival and Formation of PBDEs in Combustion System

PBDEs can be released to the atmosphere or environment due to incomplete destruction in the feeding waste/materials in combustion systems. The PBDE output/input research (Chang *et al.*, 2013a) showed that the very good PBDE destruction efficiencies ($> 93.5\%$) in an industrial boiler can be reached, which co-combusted woodchip and industrial-wastewater-treatment sludge having high PBDE contents. Drage *et al.* (2014) carried out PBDE mass balances study at a full scale sinter plant, and found PBDEs in the raw materials were mostly destroyed during the sintering process (79–96%). Likewise, most of the PBDEs in the feedstock of fly ash were depleted in a fly ash thermal treatment plants (Liao *et al.*, 2012). Although high PBDE destruction efficiencies in the combustion system can be obtained, the

residues of PBDEs could still cause some environmental issues. For instance, in the study of Wang *et al.* (2010a), the PBDE contents in the bottom ashes ($20.4\text{--}186 \text{ ng g}^{-1}$) of municipal solid waste incinerators (MSWIs) were much higher than those in the fly ashes ($0.332\text{--}25.5 \text{ ng g}^{-1}$) due to that PBDEs in the feeding waste were not completely destroyed, even though the operational temperatures in the combustion chamber can reach 950°C . The PBDE contents in the bottom ashes could reach three orders higher than those in the reference soils, and pollute the environment via the reutilization of bottom ashes (Wang *et al.*, 2010a; Lin *et al.*, 2014).

On the other hand, PBDEs can be formed in the combustion systems, such as power plants and vehicles, that their fuel contains bromine, but no commercial PBDE mixtures (Wang *et al.*, 2010b; Chang *et al.*, 2014b, c; Chen *et al.*, 2017). Although the detailed formation mechanisms of PBDEs still need to be further investigated, several studies from different research groups do report similar PBDE formations in the combustion system.

Sakai *et al.* (2001) incinerated three types of waste samples containing BFR, and found increases of PBDE concentrations in more than half of the runs, suggesting possible PBDE formations occurred during the flue gas cooling process. Ni *et al.* (2016) selected five plastic wastes to investigate BFR emission behaviors during open burning, and found the formation and survival of PBDEs exceeded their decomposition during the burns, that is, output/input mass ratios > 1 . However, similar phenomenon can not be observed in the experiments for hexabromocyclododecanes (HBCDs). The thermal formation of PBDEs also occurred by heating fly ashes under different temperatures in a laboratory furnace (Artha *et al.*, 2011). Similar to the distribution of PCDD/Fs in the MSWIs, PBDD/F and PBDE contents in the ashes of the economizers ($339^\circ\text{C}\text{--}396^\circ\text{C}$) were six times higher than those in the ashes of the superheater ($480^\circ\text{C}\text{--}537^\circ\text{C}$), suggesting that formations of PBDD/Fs and PBDEs occur in the post combustion area of MSWIs (Wang *et al.*, 2010a). BDE-77, -126, -156, -169, and -180, are brominated analogues of dioxin-like PCBs, and thus structurally resemble PCDD/Fs. Wyrzykowska-Ceradini *et al.* (2011) found that these dioxin-like PBDEs were detected in the flue gases mostly during the transients of MSWI, and suggested that these dioxin-like PBDEs can be a product of the dimerisation or condensation of brominated precursors in the flue gas.

Even rice straw open burning resulted in the formation of PBDEs, and increased the atmospheric PCDD/F and PBDE concentrations by six to twenty times (Chang *et al.*, 2014a). Although rice straw do contain PBDEs (934 ng kg^{-1}) and PCDD/Fs (48.9 ng kg^{-1}), the higher ratio of PBDEs to PCDD/Fs emission factors compared to rice straw contents indicate that formation of PBDEs occurred during rice straw burning, and not from the thermal release from their original content (Chang *et al.*, 2014a). Odabasi *et al.* (2015) measured PAHs, PCBs, PCNs and PBDEs in tree ring samples in pine samples collected at industrial and background sites in Turkey. Historical trends of all POP concentrations indicated an increase with time in industrial

and background sites. Surprisingly, PBDEs were also present in tree-ring sections which represent 1900s, quite long time before the 1970s when the commercial PBDE mixtures were first produced. This indicated that similar to PCBs and PCNs, combustion emissions are the sources of PBDEs in stem samples before the industrialization in the study area (Odabasi *et al.*, 2015). Similarly, PBDEs unexpectedly presented in the components of raw sinter mix used in the iron ore sintering process, including iron ores (ca. 992 ng kg⁻¹), coke breeze (ca. 4891 ng kg⁻¹) and flux samples such as limestone and olivine (ca. 240 ng kg⁻¹) (Drage *et al.*, 2014).

Chen *et al.* (2017) corrected the effects of sampling artifacts on the partitioning of gas- and particle-phase POPs, including PAHs, PCDD/Fs, PCBs, PBDD/Fs, and PBDEs, in the exhaust of a diesel engine, and found that 89.7–100% of POPs in the raw exhausts were in gas-phase. This demonstrated that similar to PCDD/Fs, the formation mechanism of PBDEs in diesel engines is mainly through homogeneous gas-phase formation, rather not through *de novo* synthesis. The PBDEs in the raw exhausts were dominated by highly brominated congeners, such as BDE-209, -208, -207, and -206, revealing that these highly brominated congeners may be preferentially formed during combustion processes.

From the aforementioned researches, we can conclude that the fate of PBDEs in combustion is the competition result between formations and destructions. When high PBDEs are inputted into combustion system, the destruction of PBDEs is dominant (Wang *et al.*, 2010a; Liao *et al.*, 2012; Chang *et al.*, 2013a; Drage *et al.*, 2014), whereas when the input of PBDEs is fewer, the formation of PBDEs is more apparent (Wang *et al.*, 2010b; Chang *et al.*, 2014a, b, c; Chen *et al.*, 2017). Similar phenomena are observed with PAHs (Cheruiyot *et al.*, 2015). The fate of PAHs is depletion in the combustion in engines due to high PAH contents in gasoline and diesel fuels (Mi *et al.*, 1996; Chang *et al.*, 2014b, c), while PAHs are formed in biomass open burnings (Hays *et al.*, 2005; Yang *et al.*, 2006).

PBDE Emission Factors of Combustion Sources

Table 4 lists PBDE emission factors of major combustion sources which can be divided into different categories, including waste incinerators, metallurgical processes, power and heating facilities, vehicles, and non-controlled combustion sources. These combustion sources also have been identified by various countries across the globe as important PCDD/F emission sources (Wang *et al.*, 2003a, b; Lee *et al.*, 2004; Wu *et al.*, 2014; Xu *et al.*, 2014; Mwangi *et al.*, 2015; Wang *et al.*, 2015; Cheruiyot *et al.*, 2016). We can also categorize these combustion sources into two groups. The first group is their feeding waste or raw materials contain commercial PBDE mixtures, such as MSWIs, medical waste incinerators (MWIs), industrial waste incinerators (IWIs), electric arc furnaces (EAFs), secondary aluminum smelters (secondary ALS), and plastic waste open burnings. The other group is their feeding materials or fuels contain no plastic materials or commercial PBDE mixtures, such as sintering plants, fly ash treatment plants, power plants,

boilers, vehicles and biomass open burnings. It should be noted that even though their feeding materials contain no plastics, PBDEs do exist in some of their feeding materials or fuels as the forms of environmental pollutant accumulations, such as PBDEs in rice straw (Chang *et al.*, 2014a), woodchips (Chang *et al.*, 2013a), inner cross section of pine stem (Odabasi *et al.*, 2015), coal and iron ores (Drage *et al.*, 2014).

Since the available PBDE emission factors are very limited, many source categories only have one data. But this data may be the mean values of significant sample numbers, for instance, the PBDE emission factor of MSWIs in Table 4 was the geometric mean value of 47 stack flue gas samples from 16 MSWIs. The levels of these PBDE emission factors can be affected by many factors, such as PBDE contents in the feeding materials and fuels, combustion conditions, operation type (continuous or intermittent operation), operational parameters, and the equipped air pollution control devices (APCDs) (Wang *et al.*, 2010a, b, c; Cheruiyot *et al.*, 2016). In general, the PBDE emission factors of non-controlled combustion sources were three to five orders higher than those of combustion sources under good combustion practices, for instance, rice straw open burning vs. woodchip-fueled boilers; plastic waste open burning vs. waste incinerators.

Furthermore, for combustion sources that feeding materials or fuels contain no plastic materials or commercial PBDE mixtures, such as sintering plants, power plants and vehicles, their PBDE behaviors (formation and removal processes) are more similar to PCDD/Fs, and can be found that the total PBDE concentrations were highly correlated with total PCDD/Fs mass and I-TEQ concentrations (r ranged from 0.481 to 0.779 and $p < 0.05$) (Wang *et al.*, 2010b).

In the study of Drage *et al.* (2014), the authors did not report their PBDE emission factors of sintering plants, but it seems that PBDE emission factors of sintering plants in the United Kingdom were much higher compared to those in other studies (Wang *et al.*, 2010b, c; Li *et al.*, 2017), because their PBDE concentrations in the stack flue gases (295 ng Nm⁻³, BDE-209 not measured) were one order higher than others (22.2 ng Nm⁻³, BDE-209 included) in Wang *et al.* (2010b).

Global PBDE Emissions from Combustion Sources

Similar to the PCDD/F inventory, global annual PBDE emissions from combustion sources can be estimated theoretically by the combinations of multiplying the PBDE emission factors and the activity at national level for each country. Although the developments of PCDD/F inventory have become a legal obligation in international treaties, the information of activity for individual combustion source category is not always offered in PCDD/F inventories in the scientific publications and government reports. Therefore, it is very difficult to use the emission factor approach to estimate global PBDE emissions from combustion sources.

On the other hand, Wang *et al.* (2010b) applied the geometric mean (GM) of PBDEs:PCDD/Fs I-TEQ ratios to estimate PBDE emissions from combustion sources based on Taiwanese PCDD/F inventory, and found the emission

Table 4. PBDE emission factors of major combustion sources.

Important combustion sources	PBDE Emission Factor	Reference
Waste incinerators		
MSWIs	0.153 mg tonne-waste ⁻¹	(Wang et al., 2010b)
Batch MSWIs	1.77 mg tonne-waste ⁻¹	(Wang et al., 2010b)
MWIs	0.103 mg tonne-waste ⁻¹	(Wang et al., 2010b)
IWIs	0.0844 mg tonne-waste ⁻¹	(Wang et al., 2010b)
Metallurgical process		
Sintering plants	0.0907 mg tonne-product ⁻¹	Average from Wang et al. (2010b) (0.0702 mg tonne-product ⁻¹ ; recalculate by basing on product) and Wang et al. (2010c) (0.067 and 0.135 mg tonne-product ⁻¹) (Li et al., 2017)
Sinter plants	0.107 mg tonne-product ⁻¹	109 ng WHO-TEQ tonne ⁻¹ (2.47 µg t ⁻¹)
EAFs	0.207 mg tonne-product ⁻¹	Average from Wang et al. (2010b) (0.239 mg tonne-product ⁻¹ ; recalculate by basing on product) and Wang et al. (2010c) (0.0870 and 0.296 mg tonne-product ⁻¹) (Wang et al., 2009)
Ferrous foundries	0.663 mg tonne-feedstock ⁻¹	(Li et al., 2015)
Converter Steelmaking Processes	0.00636–0.0766 mg tonne-product ⁻¹	(Wang et al., 2010c)
Secondary ALs	0.544 mg tonne-feedstock ⁻¹	(Wang et al., 2010c)
Fly ash treatment plants	0.428 mg tonne-feedstock ⁻¹	(Wang et al., 2010b)
Power and heating facilities		
Power plants (coal)	0.407 mg tonne-coal ⁻¹	Average from coal power plants (Wang et al., 2010b)
Power plants (fuel)	0.348 mg tonne-fuel ⁻¹	Average from fuel power plants (Wang et al., 2010b)
Boilers (wood chips)	0.346 mg tonne-fuel ⁻¹	(Wang et al., 2010b)
Boilers (wood chips)	0.0397 mg tonne-fuel ⁻¹	(Chang et al., 2013)
Boilers (wood chips + sludge)	0.0785 mg tonne-fuel ⁻¹	(Chang et al., 2013)
Diesel-engine generator	90.9–91.8 ng L-fuel ⁻¹ 45–69.4 ng kWh ⁻¹	(Tsai et al., 2016)
Vehicles non-controlled combustion sources		
Road transport	92.3 ng km ⁻¹	Average from UGFV and DFV emissions (Wang et al., 2010b)
Rice straw open burning	26.5 mg tonne-waste ⁻¹	recalculate the emission factors in Chang et al. (2014a) by using the ultimate analysis data (C: 44.2%) in Worasuwannarak et al. (2007)
Plastic waste open burning	775 mg tonne-plastic waste ⁻¹	(Ni et al., 2016)

difference between emission factor approach (52.6 kg year⁻¹) and GM PBDEs:PCDD/Fs I-TEQ ratio approach (28.6 kg year⁻¹) was much less than an order. Applying the PBDEs:PCDD/Fs I-TEQ ratios to estimate PBDE emissions from widely available PCDD/F inventories is suggested as a preliminary and easier method for evaluating global PBDE emissions from combustion sources (Wang *et al.*, 2010b).

Table S6 lists the PBDE emissions from combustion sources estimated by GM PBDE/PCDD/F I-TEQ ratios approach using worldwide available PCDD/F inventories. The major categories of PCDD/F emission sources in the PCDD/F inventories of various countries were waste incineration (controlled and uncontrolled), biomass burnings including backyard and wood combustion, metallurgical processes, and power plants. More comprehensive investigations on these combustion sources for their PBDE emissions are needed, especially burning with minimal control and uncontrolled combustion sources, such as open burning of municipal or agricultural wastes, because they are not only PCDD/Fs but also major PBDE emitters in many countries. The initial estimation of global PBDE emissions from combustion sources is approximately 6.75 tonnes year⁻¹.

It is needed to mention that some important PBDE combustion emission sources do not have commercial PBDE mixtures in their fuel or feeding materials, such as agricultural residue burning, residential combustion, power plants and road transport, but PBDEs are emitted due to formation or incomplete destruction of their original PBDE contents.

Another important PBDE emission source related to combustion is illegal open burning recycling activities of WEEE and e-waste in developing regions, such as China, India, and five west African countries (Sepúlveda *et al.*, 2010; Ongondo *et al.*, 2011; Breivik *et al.*, 2014). This type of PBDE emission source is not included or truly reflected in the PCDD/F inventory, and should be considered separately as its PBDE emission characteristics are extremely different to other combustion sources.

To estimate global PBDE emissions from illegal open

burning of WEEE and e-waste, we use 50 million tonnes (Breivik *et al.*, 2014) as the global e-waste amounts in 2016, the same amount as our estimation on fugitive PBDE emissions from dismantling and crushing during e-waste recycling. Then assuming 21% of WEEE weight as plastic parts (Ongondo *et al.*, 2011), transfer factor of BFR in use phase to open burning as 0.05 (Schenker *et al.*, 2008), and the percentage of PBDE production to all BFR (10.6%) (Lassen *et al.*, 2014) as the percentage of using commercial PBDE mixtures as BFR in plastic parts, we estimate that the plastic amounts of global PBDE-containing e-waste treated by illegal open burning was 55600 tonnes in 2016.

Two studies reported PBDE emission factors of open burning of plastic wastes and high-impact polystyrene under thermal stress (Ortuño *et al.*, 2015; Ni *et al.*, 2016), and the PBDE emission factors were 4586.8 mg tonne-plastic⁻¹ waste (Ni *et al.*, 2016) and 70000–130000 mg tonne-plastic⁻¹ waste (Ortuño *et al.*, 2015), respectively, which ranged in one-order difference. We estimated the range of global PBDE emissions from illegal open burning recycling activities to be 0.255–5.56 tonnes in 2016 by using the emission factors, 4586.8 mg tonne-plastic⁻¹ waste (Ni *et al.*, 2016) and 100000 mg tonne-plastic⁻¹ waste (mean value) (Ortuño *et al.*, 2015).

Table 5 compares the global PBDE emissions from fugitive releases from commercial PBDE mixtures, from illegal open burning of WEEE and e-waste, and from combustion sources. The homologue distributions of the PBDE emissions from illegal open burning were derived based on the averaged values of homologue distributions in the emission factors from the study of Ortuño *et al.* (2015) and Ni *et al.* (2016). As for combustion sources, the homologue distributions are calculated based on the homologue in the flue gases of various combustion sources and their relative contributions. Therefore, the homologue distributions of the PBDE emissions from global combustion sources are skewed to those of treated flue gases by APCDs, and the homologue distributions of uncontrolled combustion sources, such as uncontrolled domestic waste burning and landfill fires, have not reflected in the calculation. Their PBDE homologues should be partly contributed by thermal desorption from commercial PBDE mixtures present in the wastes.

Table 5. Global PBDE emissions from evaporative and fugitive releases from commercial PBDE mixtures, from illegal open burning of WEEE and e-waste, and from combustion sources (tonnes yr⁻¹).

Homologue	Global evaporative and fugitive emissions from commercial PBDE mixtures (tonnes yr ⁻¹)	Global emissions from illegal open burning of WEEE and e-waste (tonnes yr ⁻¹)	Global emissions from combustion sources (tonnes yr ⁻¹)
di-BDE	-	-	0.00766
tri-BDE	0.00171	0.00577–0.835	0.0156
tetra-BDE	0.0581	0.00604–0.233	0.0855
penta-BDE	0.0975	0.00962–0.354	0.0686
hexa-BDE	0.0353–0.104	0.0114–0.647	0.0320
hepta-BDE	0.0721–0.245	0.00171–0.588	0.0361
octa-BDE	0.0531–0.155	0.0890–0.407	0.110
nona-BDE	0.105–0.583	0.0328–0.593	0.854
deca-BDE	2.01–13.6	0.0989–1.91	5.54
Total PBDEs	2.43–14.9	0.255–5.56	6.75

COMPARISON OF PBDE EMISSIONS BETWEEN FUGITIVE RELEASES FROM COMMERCIAL PBDE MIXTURES AND DISCHARGE FROM COMBUSTION SOURCES

The global PBDE emissions from evaporative and fugitive releases from commercial PBDE mixtures, from illegal open burning of WEEE and e-waste, and from combustion sources were 2.43–14.9, 0.255–5.56 and 6.75 tonnes year⁻¹ (Table 5), and deca-BDE was the most contributed PBDE congener among these three PBDE emission sources. This may be the reason why the higher levels and relative abundance of BDE-209 in lichens, soils, and ornithogenic soils of the Antarctic coastal environment were observed in recent study than earlier works (Mwangi *et al.*, 2016).

Table 5 also shows that combustion sources which include illegal open burning of WEEE and e-waste are more important PBDE emitters than evaporative and fugitive emissions from commercial PBDE mixtures, or at least at equal importance if the uncertainties are considered. With the global trend of phasing out commercial deca-BDE mixtures, the contribution of PBDE emissions from combustion sources will be even more significant. Furthermore, fugitive emission of house dust mainly affects indoor environments (Jones-Otazo *et al.*, 2005; Wilford *et al.*, 2005; Gou *et al.*, 2016), and thus combustion sources are probably more important PBDE contributors to outdoor air levels, and have more influence on the food chain which is the major route for human PBDE exposure. Consequently, PBDE contributions from combustion emission sources to the atmosphere should not be ignored and need further comprehensive investigation.

Table 5 also reveals that the percentages of nona-BDE homologue (i.e., BDE-206, -207, and -208) in the emissions from combustion sources were higher than that from evaporative and fugitive emissions from commercial PBDE mixtures. The nona- and deca-BDE homologues in commercial Deca-BDE mixtures were dominated by sole congener, BDE-209. BDE-208 was a very minor component, and only comprised 0.06%–0.07% of the commercial Deca-BDE mixtures (La Guardia *et al.*, 2006; Wyrzykowska-Ceradini *et al.*, 2011). Therefore, higher percentage of nona-BDE homologue in the atmosphere could be an indication of influence from combustion sources. In the study of Wang *et al.* (2011), the result of correspondence analysis showed the atmospheric PBDEs of the heavy steel and metals complex areas were associated with BDE-209, -203, -207, and -208, indicative of combustion source contributions (Wang *et al.*, 2010b, c).

It is worthwhile to mention that the properties of BDE-209 lean to metabolically and 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; Stapleton *et al.*, 2006; Huwe and Smith, 2007).

UNCERTAINTIES

Many emission factors used to estimate PBDE evaporative

and fugitive emissions from commercial PBDE mixtures during use and waste management phases in this study were derived from physicochemical properties of PBDEs. This does not consider the emission variations in real situations, and creates uncertainties, for instance, the temperature in the environments and the working temperatures of products both may increase or reduce PBDE evaporative emissions during use phases, even during landfill in waste management phase. Furthermore, PBDE-containing products may degrade with time, which then results in higher fugitive emission in the later lifetime. It is important to mention that using different kinds of physicochemical properties of PBDEs (vapor pressure and K_{OA}) can result in emission factors ranging in up to three-order differences. Therefore, the experimental and field measurements for these emission factors are needed for better estimation.

As for the estimation on PBDE emissions from various combustion sources, one of the uncertainties comes from that the PBDE emission factors of some important combustion sources are still lacking or insufficient, especially the uncontrolled combustion sources, such as open burning of municipal or agricultural wastes, and illegal open burning of WEEE and e-waste. Although the PBDE emission factors of some industrial combustion sources were derived from sufficient field stack flue gas samples, their geographical coverage was very limited, and most available PBDE emission factors of combustion sources were from Taiwan. Furthermore, due to the difficulty on collecting the activity information of combustion sources on a global basis, PBDEs:PCDD/Fs I-TEQ ratios approach was applied in this study. However, bias may come from the fact that the correlation between PBDEs and PCDD/Fs is not proportional, and some emissions do not exhibit a correlation between PBDEs and PCDD/Fs (Wang *et al.*, 2010b), such as waste incinerators and secondary ALS, because their PBDE emissions are not only from formation during combustion, but also from undestroyed PBDEs in the feed wastes/materials. Based on the above discussion, the uncertainties of the estimation on PBDE emissions in this study are still high, and the obtained results should be considered as preliminary ones.

CONCLUSIONS

Commercial deca-BDE mixtures are slated for elimination, but this study indicates that the effect of reducing human exposure by controlling PBDE mixtures in commercial products will be minimized and delayed if mitigation of PBDE emissions from combustion sources is ignored. Thus the related global control strategies for PBDEs require significant changes to be effective, and the action to reduce PBDE emissions from combustion sources should be taken along with the ban of commercial deca-BDE mixtures.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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