



PBDD/F impurities in some commercial deca-BDE

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PBDD/Fs can be formed as contaminants in the commercial DBDE production.

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ABSTRACT

The study presented the concentrations and distributions of polybrominated dibenzo-*p*-dioxins and polybrominated dibenzofurans (PBDD/Fs) as impurities in some commercial decabromodiphenyl ether (DBDE) mixtures that were produced by several manufacturers. The total concentrations of 12 2,3,7,8-substituted tetra- to octa-BDD/F congeners were found to be in the range of 3.4–13.6 (mean 7.8) µg/g, averagely accounting for 99% of total PBDD/Fs. OBDF was the prevailing congener, followed by 1,2,3,4,6,7,8-HpBDF. In addition, OBDD and 1,2,3,4,7,8-HxBDF were also obviously detectable. The total concentrations of PBDD/Fs varied both between the manufacturers and between the lots. On the basis of the global demand for the commercial DBDE in 2001, the annual potential emissions of PBDD/Fs were calculated coarsely to be 0.43 (range: 0.21–0.78) tons. The major dioxin congeners, OBDF and 1,2,3,4,6,7,8-HpBDF, presenting in DBDE, were estimated to be formed from BDE-209, BDE-206, and/or BDE-207 via an intramolecular elimination of Br₂/HBr.

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1. Introduction

Polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) are considered as a group of toxic environmental contaminants. The physicochemical properties and toxicity of PBDD/Fs are similar to those of PCDD/Fs (WHO, 1998). Concerns of PBDD/Fs have increased because brominated flame retardants (BFRs) are extensively added in polymers, paints, textiles and other materials in electrical equipments, furnishings and vehicles. PBDD/Fs have recently been detected to be widespread in environmental and biological samples (Litten et al., 2003; Terauchi et al., 2009; Jogsten et al., 2010; Sepúlveda et al., 2010). The high atmospheric concentrations of PBDD/Fs around an electronic waste dismantling area at Guiyu, China, and around an electronic industry park in Shanghai, were speculated to be from BFRs (Li et al., 2007, 2008). Also, the high level of PBDD/Fs in sediment in the Shima River might be attributed to the use of BFRs in the electrical and electronics industries (Ren et al., 2009). Analysis of profiles of PBDD/F congeners in commercial BFRs may fingerprint sources of PBDD/Fs in the environment. However, very few data are available concerning the amounts and characteristics of PBDD/F impurities in these chemicals. Thus, the estimation of the amount of PBDD/F emission from them is difficult.

Polybrominated diphenyl ethers (PBDEs) are major BFRs used in textiles, electronic equipment, and plastics to prevent these products from burning. PBDEs have been marketed as penta-, octa-, and deca-brominated mixtures, and deca-BDE (DBDE) represents the major product in all market, accounting for approximately 80% of the total PBDE production worldwide (BSEF, 2000). An Directive 2003/11/EC (2003), relating to marketing and use of dangerous substances, effectively banned the use of octa-BDE and penta-BDE, yet DBDE was exempted. However, in 2008, the European Court of Justice held that European Commission acted illegally when it exempted DBDE from an EU ban on several brominated flame retardants, including PBDEs, in electronic and electrical equipments, and that DBDE should not be used where suitable replacements were available (European Court of Justice, 2008). Many electronics firms have already eliminated or committed to eliminating DBDE in accordance with the EU RoHS, including Philips, Electrolux, Sony, Dell, Intel, Sharp, Apple and Hewlett Packard. However, DBDE is still being extensively used in many countries including China due to the exempt from the RoHS of these countries (Betts, 2008). The production of DBDE increased substantially from 10,000 to approximately 25,000 tons between the years 2000 and 2004 in China (Mai et al., 2005). It is important to study PBDD/Fs in commercial DBDE mixtures especially those that were made by China, for an increasing production of DBDE in China, yet data of PBDD/Fs in the Chinese products were unavailable until now.

There were several possible sources of PBDD/Fs. They can be formed by chemical, photochemical, or thermal reactions

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(Weber and Kuch, 2003; Ebert and Bahadir, 2003; Ren et al., 2008). PBDD/Fs can be formed from brominated organic chemicals by chemical reaction (e.g. PBDEs, Hanari et al., 2006), from brominated organic chemicals via photochemical degradation (e.g. UV, Eriksson et al., 2004), and from flame-retarded plastic materials under thermal stress (e.g. shredders in recycling processes, extruders, burning of waste plastics containing PBDEs) (Luijk et al., 1992; Wang and Chang-Chien, 2007).

Widespread occurrence of DBDE and PBDD/Fs in the environment, and ongoing usage of DBDE, are causes for concern. Some attentions have been paid on the environmental health and safety (EH&S) effects of PBDD/Fs impurities in the final consumer products because PBDD/Fs would contaminate the products when using secondary raw material containing those PBDEs. For example, Brominated furans were important contributors to dioxin-like activity in Japanese indoor dust and products such as TV casing containing BFRs were likely to be the potential sources (Suzuki et al., 2010). Airborne Hepta-BDFs positively were detected in automobile cabins (Mandalakis et al., 2008). Analysis of the composition and content of PBDD/Fs in commercial DBDE is important if we need to understand the sources of the emissions, to estimate global inventories of PBDD/Fs, and to accurately evaluate toxic effects of DBDE.

In this study, PBDD/F impurities in commercial DBDE mixture were analyzed. Samples from three large manufacturers were used to elucidate the differences in concentrations and compositions of PBDD/Fs among the manufacturers. Two different lots were analyzed to examine the lot-to-lot variations. Based on the global production level of commercial DBDE in 2001, potential annual environmental release of PBDD/Fs from the commercial DBDE was estimated. Finally, the formation mechanisms of PBDD/Fs were discussed.

2. Materials and methods

2.1. Samples

Four samples of commercial DBDE were obtained from a large chemical engineering market in Guangdong. Sample 1 and sample 2 were two different lots, produced by Zhongyi Corporation (Weifang, Shandong, China), sample 3 was made by Haiwan Corporation (Weifang, Shandong, China), and sample 4 was made by Albemarle Corporation (Richmond, VA, USA).

2.2. Chemical analysis

Because PBDD/Fs can be formed from the photolysis of DBDE (Hagberg et al., 2006), it is necessary to separate DBDE from PBDD/Fs. A new analytical method was successfully used in this study to separate trace PBDD/Fs from DBDE, which was helpful to lower the detection limits of PBDD/Fs and to avoid the influence of the unwanted formation of PBDD/Fs from the thermodegradation of DBDE in the capillary chromatography column during determination. A flowchart of the analytical procedure is shown in Fig. 1. About 0.1 g of DBDE sample was dissolved in toluene. The solvent was concentrated and exchanged to hexane using a rotary evaporator. Then the hexane solution was concentrated. As the solubility of the higher brominated BDEs was low in hexane, most ether could be separated from dioxins through several replications of concentration, precipitation and separation with hexane. The remaining ether was further separated with a 5 g of Florisil (activated at 140 °C for 24 h) column, eluting sequentially with 80 mL 95:5 (v/v) hexane/dichloromethane to separate interferences, and 150 mL dichloromethane to collect dioxins.

Identification and quantification were performed with HRGC/HRMS (Trace GC 2000 and Finnigan MAT 95 XP). The mass spectrometer was operated in positive electron impact (40 eV energy), selected ion monitoring (SIM) mode at the resolution >10,000. A DB-5 ms capillary column (J&W Scientific, CA, 30 m, 0.25 mm ID, 0.1 mm film) was used. As the thermolysis of the higher brominated furans was likely to occur, it was difficult to quantify them precisely (Hagberg, 2003). To avoid the unwanted degradation as far as possible, two programs of oven temperature were used to respectively analyze the lower and higher brominated congeners. For tetra- to hexa-BDD/Fs (not including hexa-BDF) analysis, the oven temperature program was as follows: from 120 °C to 160 °C at a rate of 40 °C/min, then to 240 °C (4 min) at a rate of 16 °C/min, finally to 300 °C (6 min) at a rate of 10 °C/min. For hexa- to octa-BDD/Fs (including hexa-BDF) analysis, the oven temperature program was as follows: from 120 °C to 200 °C at a rate of 40 °C/min, then to 310 °C (14 min) at a rate of 20 °C/min.

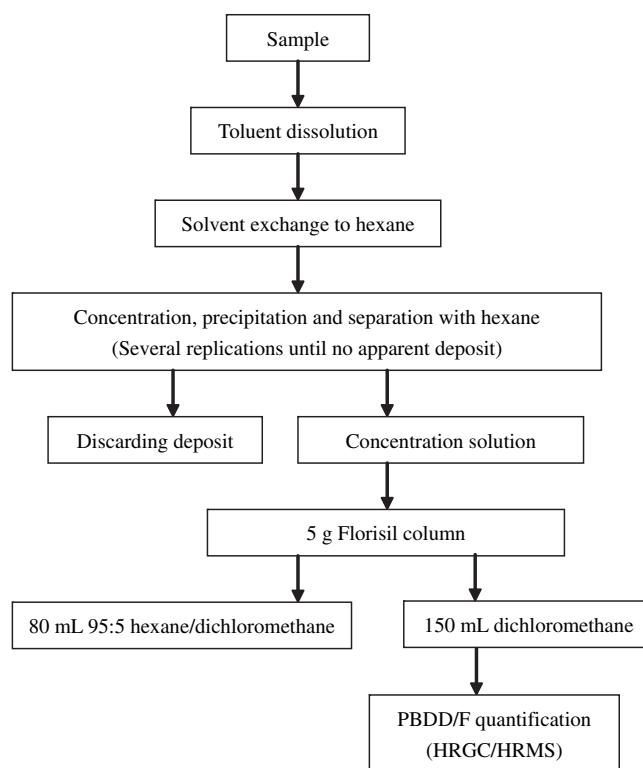


Fig. 1. Flowchart of analytical procedure.

Standards from Cambridge Isotope Laboratories (CIL; Andover, MA) were used, such as $^{13}\text{C}_{12}$ -labeled PBDD/Fs (EDF-5071), recovery standard (ED-5073), and native standards including OBDF (EF-5263), a mixture standard of 8 components (EDF-5074) and a mixture standard of 11 components (EDF-5059). PBDD/F congeners were divided into two groups to be determined, to match the significantly different orders of concentrations of PBDD/F congeners in the actual samples, and to avoid as much as possible the degradation of higher brominated congeners with a suitable oven program. One group was tetra- to hexa-BDD/Fs (not including hexa-BDF) with the low concentrations of standard (EDF-5074). The other group was hexa- to octa-BDD/Fs (including hexa-BDF) with the relatively high concentrations of standard solutions (EF-5263 and EDF-5059). 12 2,3,7,8-substituted PBDD/F congeners (including 2,3,7,8-TBDF, 2,3,7,8-TBDD, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,7,8-PeBDD, 1,2,3,4,8,9-HxBDF, 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD, 1,2,3,4,6,7,8-HpBDF, OBDF and OBDD) were quantified based on the response factors obtained from the corresponding standards. Other non-2,3,7,8-substituted congeners were quantified with the average response factors of the isomers with the same degree of bromination. Quality control criteria for positive identification of target compounds included signal-to-noise ratio exceeding 3, abundance ratios of the two monitored ions for each congener falling within 15% of the theoretical ratios, and compounds eluting at the same retention time (± 2 s) as the standards. Recoveries of $^{13}\text{C}_{12}$ -labeled PBDD/Fs through the analytical procedure varied from 70% to 110%. Procedure blanks did not contain quantifiable concentrations of the target compounds.

The concentration of the remaining DBDE in the last exact solution (20 μL) was determined with HRGC/HRMS to be about 10 ng/ μL , indicating that the clean-up procedure in this study was complete and it was helpful to lower the detection limits of PBDD/Fs. For example, the detection limits of HxBDD and HpBDD were 30 pg/g of DBDE, which were far below 100–200 ng/g reported elsewhere (Hanari et al., 2006). The potential formation of PBDD/Fs from the thermolysis of DBDE in the capillary column under high temperature was examined by HRGC/HRMS with DBDE standard solution. The results showed that PBDD/Fs were undetectable in a standard solution of 50 ng/ μL of DBDE, which was higher than the concentrations of DBDE in the last extracts of samples. Therefore, the influence of the unwanted formation of PBDD/Fs from DBDE was negligible.

3. Results and discussion

3.1. Concentrations of PBDD/Fs

Representative chromatograms of major PBDD/F congeners in commercial DBDE from Haiwan Corporation are shown in Fig. 2.

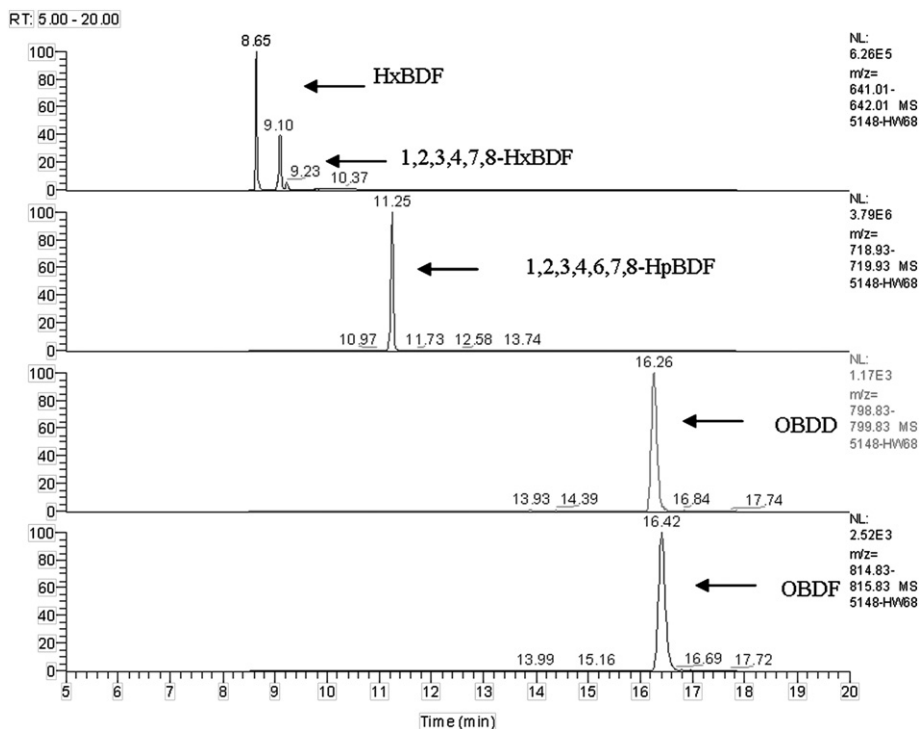


Fig. 2. Selected HRGC-HRMS chromatograms of major PBDD/F congeners in commercial DBDE.

Concentrations of PBDD/Fs in the commercial DBDE mixtures are shown in Table 1. The total concentrations of 12 2,3,7,8-substituted tetra- to octa-BDD/F congeners (total 2,3,7,8-PBDD/Fs, or \sum 12 PBDD/Fs) were in the range of 3.4–13.6 $\mu\text{g/g}$, and the total concentrations of tetra- to octa-BDD/Fs (total PBDD/Fs) were in the range of 3.4–13.9 $\mu\text{g/g}$. The total concentration of 2,3,7,8-PBDD/Fs

was averagely accounted for 99% of that of PBDD/Fs, indicating that the major congeners were 2,3,7,8-substituted (Fig. 2). The average concentration of total PBDD/Fs in DBDE commercial mixture in our study was 7.9 $\mu\text{g/g}$, 5 times lower than that from Great Lakes Chemical Corporation (Hanari et al., 2006). Among the four samples, the level of PBDD/Fs in sample 3 was the highest, about 4 times as high as that in sample 4. There was also a distinct difference between the two lots, sample 1 and sample 2, which respectively contained 3.7 and 8.9 $\mu\text{g/g}$ of total 2,3,7,8-substituted PBDD/Fs and varied by approximately 2-fold. The change of concentrations suggested an influence of production conditions on the byproduct formation of PBDD/Fs.

Table 1
Concentrations of PBDD/Fs in some commercial DBDE ($\mu\text{g/g}$).

Sample No.	Sample 1	Sample 2	Sample 3	Sample 4
Manufacturer	Zhongyi	Zhongyi	Haiwan	Albemarle
2,3,7,8-TBDF	54	37	88	12
1,2,3,7,8-PeBDF	1128	703	1429	244
2,3,4,7,8-PeBDF	475	237	754	110
1,2,3,4,7,8-HxBDF	18,793	7528	120,481	4530
1,2,3,4,6,7,8-HpBDF	117,189	2,740,385	6,993,818	410,141
OBDF	3,506,315	6,165,662	6,324,915	2,977,453
2,3,7,8-TBDD	15	8	12	2
1,2,3,7,8-PeBDD	68	40	82	0
1,2,3,4,7,8/1,2,3,6,7,8-HxCDD	0	0	0	0
1,2,3,7,8,9-HxBDD	0	0	0	0
OBDD	9742	13,884	138,999	1877
TBDF	366	267	570	341
PeBDF	12,557	5998	14,866	3186
HxBDF	119,995	58,088	381,518	16,588
HpBDF	117,189	2,740,385	6,993,818	410,141
TBDD	39	19	29	9
PeBDD	1164	597	638	0
HxBDD	0	0	0	0
HpBDD	0	0	0	0
\sum 12 PBDD/Fs ($\mu\text{g/g}$)	3.7	8.9	13.6	3.4
Total PBDD/Fs ($\mu\text{g/g}$)	3.8	9.0	13.9	3.4
\sum 8 PBDD/Fs (ng/g)	1.7	1.0	2.4	0.4
TEQ (ng/g)	6.9	35	89	7.6

\sum 8 PBDD/Fs was the total concentration of 8 tetra- to hexa-2,3,7,8-BDD/F congeners (not including 123478-HxBDF); HxBDD and HpBDD congeners were not detected, at a detection limit of 30 $\mu\text{g/g}$.

Because the toxic equivalency factors (TEFs) have not been determined for PBDD/Fs, the I-TEFs of PCDD/Fs were used for the corresponding congeners of PBDD/Fs to calculate their toxicity, which was suggested by WHO (WHO, 1998). It should be noted that this conversion of exposure values for PBDD/F to TCDD toxicity equivalents is only an estimate and is by no means accepted. The TEQ concentrations of PBDD/Fs in commercial DBDE were estimated to be in the range of 6.9–89 ng/g, with an average concentration of 39 ng/g.

Among the 12 2,3,7,8-substituted tetra- to octa-BDD/F congeners, the lower brominated congeners were generally more toxic and more stable than the higher brominated congeners, so they were of more concern. In addition, because few standard solutions of higher brominated dioxins were available in the past, relatively more reports were correlated with the eight 2,3,7,8-substituted tetra- to hexa-BDD/F congeners (\sum 8 PBDD/Fs, not including 1,2,3,4,7,8-HxBDF). Analyzing the eight congeners would be helpful to identify the comprehensive fingerprint of the sources. In this study, some tetra- to hexa-BDD/Fs in commercial DBDE were detectable, yet they were not detectable in the previous report possibly due to the high detection limits (Hanari et al., 2006). The concentrations of \sum 8 PBDD/Fs in commercial DBDE varied from 0.4 to 2.4 ng/g, equivalent to 0.08–0.5 I-TEQ ng/g.

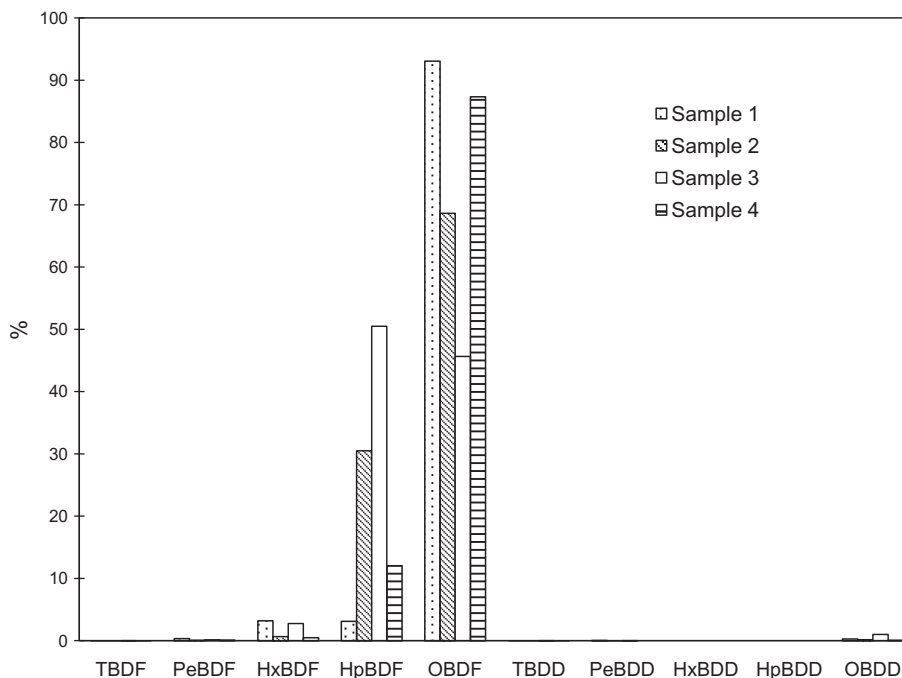


Fig. 3. Relative proportions of individual PBDD/F homologue groups in commercial DBDE from Zhongyi (sample 1 and sample 2), Haiwan (sample 3) and Albemarle (sample 4).

3.2. Profiles of PBDD/Fs

The profiles of PBDD/Fs in commercial DBDE mixtures were characterized by as follows (Figs. 3 and 4). (1) PBDFs were obviously found much more abundant than PBDDs. (2) The concentrations of the higher brominated congeners (e.g. OBDF, 1,2,3,4,6,7,8-HpBDF) were generally higher than the lower brominated congeners (e.g. 2,3,7,8-TBDF, 1,2,3,7,8-PeBDF). (3) OBDF was the dominant congener, followed with 1,2,3,4,6,7,8-HpBDF, respectively accounting for 46–93% (mean 71%, RSD 31%) and 3.1–50% (mean 26%, RSD 79%) of the total concentrations of PBDD/Fs. In addition, OBDD, 1,2,3,4,7,8-HxBDF and another HxBDF congener were relatively abundant. Very low levels of TBDD and PeBDD were detected, and HxBDD and HpBDD were found to be lower than the deletion limit of 30 pg/g. (4) Among the 8 lower brominated congeners, the major congeners were 1,2,3,7,8-PeBDF and 2,3,4,7,8-PeBDF, averagely accounting for

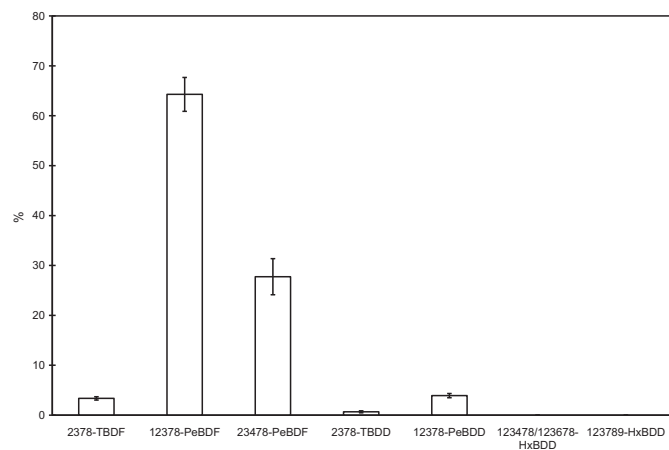


Fig. 4. Relative proportions of individual 2,3,7,8-substituted PBDD/F congeners in commercial DBDE without consideration of higher brominated congeners.

64% (RSD 5%) and 28% (RSD 13%) respectively, and PBDFs contributed 95% of total 2,3,7,8-PBDD/Fs. (5) It was found that the variation of profiles between manufacturers was larger for the higher brominated homologues than the lower, which was consistent with the relatively more instability of the higher brominated homologues.

These characteristics were expected to be useful to trace the source of PBDD/Fs in environmental and biological matrices. PBDD/Fs and PBDEs in ash-laden runoff samples collected from Hudson River were reported; 1,2,3,4,7,8-HxBDF, 1,2,3,7,8-PeBDF and 2,3,4,7,8-PeBDF accounted for the relatively high percentage of the total 2,3,7,8-substituted tetra- to hexa-BDD/Fs, which was similar to the profile of PBDD/Fs in our study; and DBDE constituted 71% of the total PBDEs (Litten et al., 2003). The congener profile of 2,3,7,8-substituted tetra- to hexa-BDD/Fs (not including HxBDF) was characterized by the relatively high abundance of 2,3,7,8-TBDF, 1,2,3,7,8-PeBDF and 2,3,4,7,8-PeBDF in sediments from the East River (Ren et al., 2009), in air in Guiyu Town (Li et al., 2007), and in nine Swedish human adipose tissue samples (Jogsten et al., 2010).

Table 2

Global demand for commercial DBDE in 2001 (BSEF, 2001) and estimated content (kg) of PBDD/Fs as impurities.

	USA	EU	Asia	Rest of world	Total
DBDE (ton)	24,500	7600	23,000	1050	56,150
PBDD/Fs (kg)	93–341	29–106	87–320	4–15	213–780
(range, average)	193	60	181	8.3	434

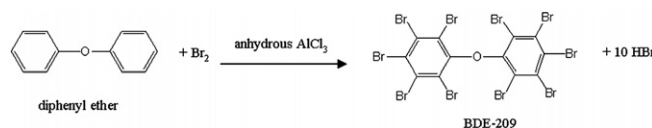


Fig. 5. Process of synthesizing DBDE.

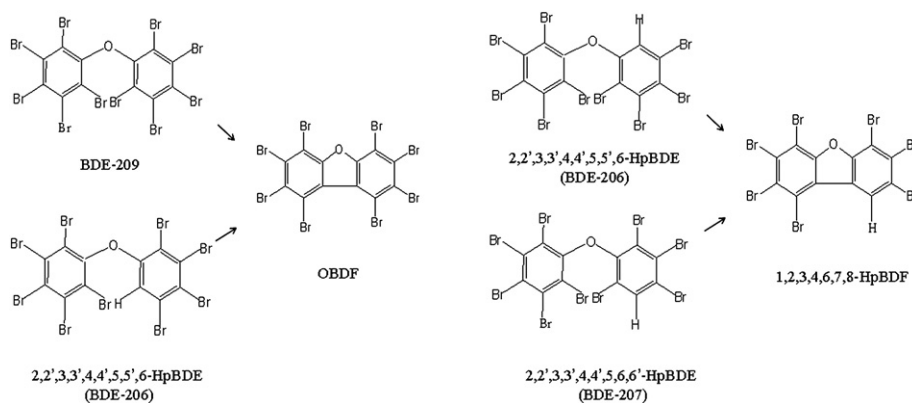


Fig. 6. Formation of major PBDD/F impurities in commercial DBDE mixture.

More fingerprints of PBDD/F sources were needed to be considered when tracing the sources. The measurable concentrations of PBDD/Fs in commercial DBDE, the ongoing use of PBDE-containing products and the continuing use of DBDE together suggest that human and environmental exposures to PBDD/Fs are likely to increase in the further. Further studies are needed to monitor the distribution and trends of PBDD/Fs in the environment.

3.3. Content estimation

To estimate PBDD/F amount released potentially from the DBDE, we multiplied the total global demand for the commercial DBDE mixture in 2001 (BSEF, 2001) by the concentrations of PBDD/Fs that were found in this paper, the lower, upper and the average estimated content (kg) PBDD/Fs of PBDD/Fs as impurities are listed in Table 2. Approximately 0.43 (RSD: 68%, range: 0.21–0.78) tons of total PBDD/Fs could have been released from the usage, recycling and combustion of DBDE-containing products in 2001, equivalent to 2.2 (RSD: 111%, range: 0.4–5.0) kg TEQ. It should be noted that this estimation is only coarse and is by no means accepted, for the concentrations of PBDD/Fs varied both between manufacturers and between lots. With the increasing production of DBDE in the world, especially, in China in recent year, it could be expected that the potential emission of PBDD/Fs from DBDE would also increase.

It's not very clear that the potential emission of PBDD/Fs as contaminants in commercial DBDE is whether high or low compared with other sources, due to the lack of the global inventories of PBDD/Fs for other sources. Nonetheless, according to the similarity of PBDD/Fs and PCDD/Fs, the potential emission could be evaluated approximately by comparing PBDD/Fs to PCDD/Fs. For example, a global emission of 3000 kg of PCDD/Fs was estimated by Brzuzy and Hites (1996), approximately equivalent to 50 kg TEQ (divided by 60). Considering the similar toxicity of PCDD/Fs and PBDD/Fs, we suggested a potential emission of 0.43 tons of PBDD/Fs (2.2 kg TEQ) as impurities in commercial DBDE was not low and should not be neglected.

3.4. Formation mechanism of major dioxin congeners

Laboratory experiments have demonstrated the formation of PBDD/Fs through a simple intra-molecular elimination of Br₂ or HBr during the pyrolysis PBDEs (Luijk and Govers, 1992; Weber and Kuch, 2003; Hagberg et al., 2006). Our study indicated that PBDD/Fs could also be formed in the production process of DBDE. PBDD/Fs in commercial DBDE mixture were characterized with the dominant OBDF and 1,2,3,4,6,7,8-HpBDF. These characteristics could be due to the production process in which DBDE was synthesized by

brominating diphenyl ether in the presence of Friedel Crafts catalyst and excess bromine (Fig. 5). 2,2',3,3',4,4',5,5',6-HpBDE (BDE-206) and 2,2',3,3',4,4',5,6,6'-HpBDE (BDE-207) were the most abundant byproducts (Alaee et al., 2003). OBDF was speculated to be formed from BDE-209 by an intra-molecular elimination of Br₂, and also from BDE-206 by an intra-molecular elimination of HBr. 1,2,3,4,6,7,8-HpBDF was speculated to be formed from BDE-206 and BDE-207 by an intra-molecular elimination of Br₂ (Fig. 6).

PBDDs have been found by the thermolysis of DBDE in the presence of metal (tin, iron, copper or zinc). In the procedure, PBDEs were degraded to form polybrominated phenols and polybrominated benzenes, and PBDDs were formed by a dimerisation of polybrominated phenols (Lenoir et al., 1994). PBDDs could also be formed via an intra-molecular oxygen insertion during the thermolysis of DBDE in the presence oxygen (Buser, 1986). In our study, PBDDs were all at small level, which was consistent with the fact of the lack of the suitable conditions such as higher temperature, oxygen, and/or metal.

4. Conclusions

- (1) PBDD/Fs were found as impurities in commercial DBDE mixtures. The total concentrations of 12 2,3,7,8-substituted tetra- to octa-BDD/Fs in commercial DBDE mixtures were in the range of 3.4–13.6 (mean 7.8) µg/g, averagely contributing 99% of total PBDD/Fs. OBDF is the most abundant, followed by 1,2,3,4,6,7,8-HpBDF, respectively accounting for 46–93% (mean 71%) and 3.1–50% (mean 26%) of total PBDD/Fs. Without consideration of the higher brominated congeners such as HxBDFs, HpBDD/Fs and OBDD/Fs, 1,2,3,7,8-PeBDF and 2,3,4,7,8-PeBDF were the major congeners, averagely accounting for 64% (RSD 5%) and 28% (RSD 13%) of \sum 8 2,3,7,8-PBDD/Fs, respectively. OBDF and 1,2,3,4,6,7,8-HpBDF were speculated to be formed from BDE-209, BDE-206 and/or BDE-207 through an intra-molecular elimination of Br₂ and/or HBr in the production process of DBDE.
- (2) Although there is no general legislation concerning PBDD/Fs in the commercial DBDE, it does not mean the industrial usage of DBDE is environmental safety. A potential annual emission of 0.43 (RSD: 68%, range: 0.21–0.78) tons of PBDD/Fs was found as impurities in commercial DBDE mixtures, based on the total global demand for the commercial DBDE mixture in 2001. The results showed that commercial DBDE was an important source for PBDD/Fs. Exposure to PBDD/Fs brought by the usage of the final products such as electronic products, furniture and toys which contain BDEs and PBDD/F impurities might cause a potential impact on human health, especially on young

children. The EH&S effect of PBDD/Fs impurities should be of great concern and need a further investigation.

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