Dietary exposure assessment of Chinese population to tetrabromobisphenol-A, hexabromocyclododecane and decabrominated diphenyl ether: Results of the 5th Chinese Total Diet Study

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ABSTRACT

Based on the 5th Chinese Total Diet Study (TDS) carried out in 2011, the dietary exposure of Chinese population to three currently used brominated flame retardants (BFRs), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) and decabrominated diphenyl ether (BDE-209), was estimated and the related health risks were assessed. Levels of the three BFRs were determined in 80 composite samples from four animal-origin food groups. The average levels of BFRs in various food groups ranged from 0.671 to 5.76 ng/g lipid weight (lw). The levels of TBBPA were lower than those of HBCD but higher than those of BDE-209. Moreover, average contamination levels of TBBPA and HBCD in TDS 2011 were found to be 3 to 30 times higher than those observed in TDS 2007 in the four food groups, indicating an increase in TBBPA and HBCD in the environment during 2007–2011. The average estimated daily intakes (EDIs) of TBBPA, HBCD and BDE-209 via food consumption for a "standard Chinese man" were 1.34, 1.51 and 0.96 ng/kg bw/day, respectively. Meat and meat products were found to be the major contributor to the daily dietary intake because the consumption of meat and meat products were significantly higher than that of other food groups in China. In comparison, the levels and EDIs of BFRs in this study were found to be higher than those in most studies worldwide. However, the large margin of exposure (MOE), with at least 1.1 × 10^5 calculated following the European Food Safety Authority (EFSA) approach, indicates that the estimated dietary exposure to these three BFRs is unlikely to raise significant health concerns. In addition, a comparison between the contamination levels of TBBPA, HBCD, BDE-209 and some novel BFRs in food samples from TDS 2011 indicated an obvious shift in the industrial production and usage pattern between PBDE and non-PBDE BFRs in China.

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1. Introduction

Brominated flame retardants (BFRs) are a series of chemicals normally used to inhibit or slow the propagation of fire. They have been widely used in electronics, foams, padding materials and so on. As “The World's Factory”, BFRs are mainly produced and consumed in China (Yu et al., 2016). In addition, obsolete electrical and electronic equipment (e-waste) from developed countries have brought new BFRs sources to China. According to "The Global E-waste Monitor 2014" reported by United Nations University, huge amounts of e-waste is imported into China for recycling; inevitably, many BFRs are emitted into the environment and present serious threats to the environment and human beings during the crude recycling of e-wastes (UNU, 2015). Sorts of BFRs with various physical and chemical properties are produced and used in the Chinese market. In those BFRs, tetrabromobisphenol-A (TBBPA), hexabromocyclododecane (HBCD) and polybrominated diphenyl ethers (PBDEs) are the three BFRs mainly used in China, which have been used since the 1970s and are called “legacy BFRs” (Covaci...
et al., 2011; Yu et al., 2016). TBBPA could be used as a reactive or additive BFR. Since the European Union reported that the use of TBBPA in circuit boards and plastics is unlikely to raise health risks, the production and application of TBBPA greatly increased (Liu et al., 2016). However, a recent study in rats has suggested that long-term exposure to TBBPA may lead to immunomodulatory changes that contribute to carcinogenic processes (Dunnick et al., 2017). PBDEs are additive BFRs and can therefore leach or volatilize from products and enter the environment. There are three types of commercial PBDEs: penta-BDE, octa-BDE and deca-BDE. Penta-BDE and octa-BDE have been phased out since they were listed as persistent organic pollutants (POPs) under the Stockholm Convention in 2009, whereas the production and application of deca-BDE (mainly composed of BDE-209) has continued in China. Commercial HBCD, as an additive BFR is composed of three main isomers (α-, β- and γ-HBCD), in which γ-HBCD is predominant, comprising 75–89% of the total HBCD (α-HBCD, 10–15%; β-HBCD, 1–12%). HBCD was added into the list of POPs in 2013 and has been phased out in many fields since 2016. However, the use of HBCD in special building materials, such as extruded polystyrene (XPS) and expanded polystyrene (EPS), is still permitted in China. Hence, the production and application of HBCD and TBBPA continues in China. Due to their long-term and wide usage, BFRs have been found to be ubiquitous in various environmental and biota matrices (Fromme et al., 2016; Yu et al., 2016). For example, PBDEs were found in seafood from Europe with high levels up to 108 μg/g, whereas levels of HBCD and TBBPA in seafood were relatively low (Cruz et al., 2017; Vandermeersch et al., 2015). Thus, the general population could be exposed to BFRs by various routes, including food consumption, dust ingest and air inhalation. Whereas in some studies dietary exposure estimate, the foods collected at each site were prepared and cooked according to local cuisine to a “table ready” state, and then, all the cooked foods were blended to form the respective group composites with weights proportional to the average daily consumption of each province. The provincial food composites were transferred to our laboratory for measurement. In total, 80 food samples from 20 provinces were tested. Additionally, it should be noted that the sample processing procedures of foodstuffs in the present study were quite different to some other studies. In some other studies, the analyses were performed on fresh unprocessed samples, whereas food samples in our study were cooked. Whether cooking methods can alter the concentration of BFRs in various foodstuffs have been investigated in some studies. For example, Perello et al. (2009) found that traditional cooking processes (fried, grilled, roasted, and boiled) are only of a limited value as a means of reducing PBDE concentrations in various foods. Bendig et al. (2012) reported that when the PBDEs were heated in pure plant oil, no transformation was observed. Bendig et al. (2013) and Vetter et al. (2015) studied evaporation and transformation of PBDEs during cooking processing, the results showed that only small amounts of the semi-volatile PBDEs were evaporated or transformed to other chemical. Based on the above studies, we concluded that BFRs were quite stable during cooking processes, and thus, a comparison between our study and other studies was acceptable.

2. Materials and methods

2.1. Food sample collection

The 5th TDS covered 20 provinces in China to represent the average dietary patterns of different geographical areas in mainland China and approximately 70% of the Chinese population. The 20 provinces were Heilongjian (HLJ), Jinlin (JL), Liaoning (LN), Neimenggu (NM), Hebei (HeB), Beijing (BJ), Henan (HeN), Shanxi (SX), Ningxia (NX), Qinghai (QH), Jiangxi (JX), Fujian (FJ), Shanghai (SH), Hubei (HuB), Sichuan (SC), Guangxi (GX), Zhejiang (ZJ), Jiangsu (JS), Hunan (HuN), Guangdong (GD), respectively. The locations of these provinces are shown in the Supplementary Fig. A1. In each province, one urban site and two rural sites were randomly selected for dietary survey and food collection. At each site, thirty households were randomly selected; a food consumption survey by 24-h dietary recall over 3 days was conducted for each member of the household to record individual food consumption data. After the food survey, foods were collected from local markets, grocery stores and rural households at each site. In each province, all food items were aggregated into various food groups after sample collection, and then, the average food consumption was calculated to present the food consumption pattern of a “standard Chinese man” (Shi et al., 2016). Subsequently, dietary intakes of each analyte were standardized per “standard Chinese man” for easy comparison. On the basis of the information collected from the participants, the “standard Chinese man” was defined as an adult male undertaking light physical work, with the age of 18–45 years and with the body weight of 63 kg.

In this study, because BFRs are normally lipophilic, four animal-origin food groups were chosen for measurement: 1) aquatic foods, 2) meat and meat products, 3) eggs and egg products, and 4) milk and milk products, detail information of the food groups were described in Supplementary. In order to achieve a realistic dietary exposure estimate, the foods collected at each site were prepared and cooked according to local cuisine to a “table ready” state, and then, all the cooked foods were blended to form the respective group composites with weights proportional to the average daily consumption of each province. The provincial food composites were transferred to our laboratory for measurement. In total, 80 food samples from 20 provinces were tested. Additionally, it should be noted that the sample processing procedures of foodstuffs in the present study were quite different to some other studies. In some other studies, the analyses were performed on fresh unprocessed samples, whereas food samples in our study were cooked. Whether cooking methods can alter the concentration of BFRs in various foodstuffs have been investigated in some studies. For example, Perello et al. (2009) found that traditional cooking processes (fried, grilled, roasted, and boiled) are only of a limited value as a means of reducing PBDE concentrations in various foods. Bendig et al. (2012) reported that when the PBDEs were heated in pure plant oil, no transformation was observed. Bendig et al. (2013) and Vetter et al. (2015) studied evaporation and transformation of PBDEs during cooking processing, the results showed that only small amounts of the semi-volatile PBDEs were evaporated or transformed to other chemical. Based on the above studies, we concluded that BFRs were quite stable during cooking processes, and thus, a comparison between our study and other studies was acceptable.

2.2. Analysis of foods

2.2.1. Reagents and chemicals

All organic solvents (acetone, n-hexane, etc.) were obtained from Merck (Darmstadt, Germany); anhydrous sodium sulfate (purity 98%) and concentrated sulfuric acid (98%) were obtained from Beijing Chemical Factory (Beijing, China). Analytical standards (α-, β- and γ-HBCD, TBBPA and BDE-209) and isotopic internal standards (labeled 13C12) were obtained from Wellington Laboratories (Andover, MA, USA).
2.2.2. Sample preparation
A slightly modified method described elsewhere was used for sample preparation (Shi et al., 2013b). The details of the sample pretreatment methodology are given in the Supplementary.

2.2.3. Instrumental analysis and quantification
An Agilent 5977A MS linked to a 7890B GC was used for BDE-209 analysis. The MS parameters and GC conditions are given in the Supplementary.

TBBPA and HBCD isomers were separated and quantified using an Agilent 1290 UHPLC coupled to a 6490 triple quadrupole MS. The MS parameters and LC conditions are given in the Supplementary. All the target analytes were quantified using the isotope dilution method to the corresponding 13C12-labeled IS.

2.3. Quality assurance/quality control
Method blank samples were run every 10 samples to check for interference or contamination from solvents or glassware. Levels of analyte in the blank samples were all satisfactory (<5% of the typical analyte concentration in the samples). Hence the blank values were not subtracted from the sample results. Matrix spiking tests were conducted for recovery tests. Various matrices including fish (grass carp), egg, pork and cow milk, were used for recovery tests at two spiked levels (1 and 10 ng/g). Recoveries of the three BFRs ranged from 80% to 120% with RSDs less than 15% (n = 5). All the concentrations of BFRs reported in this study were not corrected according to the results of the recovery tests. Values below the LOD were represented as zero or LOD for data treatment in calculations and statistical analysis. The LODs of each analyte in the four food groups are given in Supplementary Table A2. The laboratory performance was validated by participating in an inter-laboratory comparison study of BFRs organized by the Norwegian Institute of Public Health from 2006 to 2016. Various food items such as fish, beef and cheese were measured for HBCD and PBDEs. Data from our laboratory were usually within acceptable range of the consensus values.

2.4. Risk assessment
The European Food Safety Authority (EFSA) suggested a margin of exposure (MOE) approach for the determination of potential health risks from dietary intake of BFRs. The EFSA Panel on Contaminants in the Food Chain identified effects on thyroid hormones as the critical endpoint for TBBPA (EFSA, 2011c) and neurodevelopment as the critical endpoint for HBCD and BDE-209 (EFSA, 2011a, b). Chronic human intakes, associated with body burdens at 10% change) for TBBPA was 16 mg/kg bw/day (EFSA, 2011c), and for HBCD and BDE-209, were 0.79 and 1.7 mg/kg bw/day, respectively (EFSA, 2011a, b). Mean and max EDIs estimated by TDS were compared with BMDL10 to determine the MOEs. For TBBPA, HBCD and PBDEs, EFSA considers that a MOE above 100, 8 and 2.5, respectively, indicates that a health concern is unlikely, with risk decreasing as the MOE increases.

3. Results and discussion
3.1. BFRs in foods
Levels and comparisons of BFRs in the four food groups in the Chinese TDS 2011 are shown in Table 1 and Supplementary Fig A.2.

3.1.1. Levels of TBBPA
TBBPA was detected above the LOD in approximately 83% of the whole food samples, with mean and median levels of 3.34 and 0.686 ng/g lw (0.327 and 0.063 ng/g ww), respectively. The average level of TBBPA in milk was the highest among the four food groups, followed by egg, aquatic food and meat. The max level of TBBPA was found in milk sample from Shanxi (52 ng/g lw). Few studies have reported on TBBPA in dietary items or biota in the past decade. In general, the concentration and detection frequency of TBBPA in dietary items are relatively low, because the bioaccumulation potential of TBBPA is relatively low, and it was normally used as a reactive flame retardant (Liu et al., 2016). In a market basket study...
in the UK, TBBPA was rarely detected in foods (only detected above the LOD in a few shellfish and fish) (Fernandes et al., 2016). In seafood samples collected from European markets, the mean level of TBBPA was 15 ng/g lw, which was higher than that in the aquatic food in our study (Aznar-Alemany et al., 2016). In a Portugal study, no TBBPA was found in wild seafood sample, whereas in canned samples (tuna and mackerel), TBBPA was detected at levels of 2.12 ng/g ww to 23.9 ng/g ww, which were much higher than our results (Cunha et al., 2017). In fish samples collected from Japan in 2008, TBBPA was detected in 29 out of 45 samples at 0.01–0.11 ng/g ww, which was much lower than the levels of PBDEs (Ashizuka et al., 2008). However, in our study, TBBPA levels in foods were found to be higher than those of BDE-209, additionally, a comparison between this TDS (the 5th TDS) and previous TDS (the 4th TDS) showed that contamination level of TBBPA in food increased from last TDS to this TDS (detail described in section 3.4), therefore we conclude that with the restriction of PBDEs, the production and application of TBBPA increased in China, resulting in a relatively high TBBPA contamination.

3.1.2. Levels of HBCD and isomer profile

Overall, HBCD was detected above the LOD in approximately 95% of the food samples, indicating ubiquitous contamination of HBCD in the environment. Levels of HBCD (sum of α-, β-, and γ-HBCD) in the 80 samples ranged from <LOD to 25.6 ng/g lw, with mean and median levels of 2.98 and 1.66 ng/g lw (0.322 and 0.177 ng/g ww), respectively. Aquatic food group showed the highest contamination level in the four food groups, and aquatic food composite from the Hebei province showed the highest HBCD level of up to 25.6 ng/g lw. However, as shown in Supplementary Fig. A.2, the dominance of HBCD in aquatic food was only found in 7 of the 20 provinces. In 3 provinces, including Henan, Shanghai and Jiangxi, the highest level occurred in egg and egg products and in another 2 provinces (Heilongjiang and Jilin), the highest level of HBCD occurred in meat and meat products. In addition, although the lowest concentrations of HBCD were found in the milk group when using mean levels for comparison, in 8 provinces, the HBCD level in milk was higher than that of the other three food groups.

In commercial HBCD and environmental samples (sludge, soil, air), γ-HBCD is normally the predominant isomer, followed by α-HBCD and β-HBCD. However, in human bodily fluids (breast milk, serum) and animal tissues (muscle, liver, etc.), α-HBCD is usually found to be predominant (Barghi et al., 2016; Fernandes et al., 2016; Shi et al., 2013a). Similarly, in this study, α-HBCD was always the predominant isomer in the four food groups, followed by γ-HBCD and β-HBCD. In the 80 samples, α-HBCD comprises 8%–100% of α-HBCDs with an average of 62%, whereas β-HBCDs ranged from 1% to 61% (average of 9%) and γ-HBCD ranged from 3% to 96% (average of 37%). The predominance of α-HBCD in biota samples is most likely due to the selective metabolism or biotransformation of the three isomers (Du et al., 2012; Erratico et al., 2016). However, although α-HBCD was found to be predominant in most samples, exceptions were observed in 19 samples, in which the contribution of γ-HBCD (from 49% to 96% of the total contribution) was greater than that of α-HBCD, and β-HBCD was always the least prevalent isomer. We inferred that the unusual HBCD pattern in some samples may be due to individual variabilities in metabolizing capacity, in addition, some unknown factors, such as exposure to other sources of HBCD and/or the frequency of HBCD exposure, may also result in the unusual HBCD pattern.

In the second French TDS performed in 2007–2009, mean HBCD levels in foods ranged from 0.003 to 0.141 ng/g ww, which were lower than our results (mean: 82.9–621 pg/g ww) (Riviere et al., 2014). Compared with a market basket study conducted in Korea, our values from the aquatic food group were lower than those in the fish group in the Korea study, whereas our values in the other three groups were all higher than the values from the corresponding group in the Korea study, indicating that the contamination levels of HBCD in coastal areas of Korea is relatively serious (Barghi et al., 2016). Similar results were obtained in market basket studies conducted in the UK and Spain, where HBCD levels in fish from the UK and Spain were also higher than those in our study, whereas HBCD levels in the other food groups were lower than those in our study (Eljarrat et al., 2014; Fernandes et al., 2016). In seafood samples collected from European markets, the mean level of HBCD was 47.6 ng/g lw, which was much higher than that in aquatic food in our study (Aznar-Alemany et al., 2016). In marine fish from Europe, HBCD range from the lower ng/g level to 689 ng/g (Vandermeeurssch et al., 2015). In a USA study, the mean and median levels of HBCD in 36 food samples were 0.114 and 0.012 ng/g ww, respectively, which were lower than those in our study (Schecter et al., 2012). In summary, our results show that contamination levels in food from China are higher than those in other countries, except in seafood.

3.1.3. Levels of BDE-209

BDE-209 is the predominant component in commercial deca-BDE (at least 95%). After the restriction of penta-BDE and octa-BDE in China, deca-BDE has become the only produced and used commercial PBDE at present. This is the first time we measured BDE-209 in TDS. The levels of BDE-209 ranged from <LOD to 14.9 ng/g lw with mean and median levels of 1.5 and 1 ng/g lw (0.208 and 0.143 ng/g ww), respectively. Combined with the levels of tri-to hepta-BDE (including BDE-28, 47, 99, 100, 153, 154 and 183) in TDS 2011, which were described elsewhere (Bao et al., 2016), we found that in the total PBDE (tri-to deca-BDEs), the mean contributions of BDE-209 were 44%, 66%, 67% and 56% in aquatic food, meat, egg and milk, respectively, indicating that BDE-209 was the predominant congener in the total PBDE in foods. Obviously, the broad and heavy industrial use of commercial deca-BDE should be the source for the high proportion BDE-209 in the current TDS. On the other hand, we noticed that although deca-BDE has become the only produced and used commercial PBDE, tri-to hepta-BDEs could still be found in TDS samples with a contribution of 44%–56%, indicating that the occurrence of penta-BDE and octa-BDE continues in China. Numerous products containing penta-BDE and octa-BDE are still in use in China, which may be a source for penta-BDE and octa-BDE in the environment. Furthermore, the debromination of BDE-209 in the environment and in biota may be another source (Feng et al., 2015). Compared with TBBPA and HBCD, when using mean levels for comparison, the levels of BDE-209 were lower than those of TBBPA and HBCD in all the four food species, indicating that the production and application of deca-BDE in China were below that of TBBPA and HBCD in the meantime of this TDS. This finding is quite different from some recent studies. In a market basket study conducted in the UK in 2013, the levels of PBDEs in foods were evidently higher than those of HBCD (Fernandes et al., 2016). In a seafood survey of European markets conducted in 2014–2015, the levels of PBDEs in seafood were also much higher than those of both HBCD and TBBPA (Aznar-Alemany et al., 2016). With the restriction of PBDEs in China, we predict that the production and application of TBBPA and HBCD in China may continue to increase, thereupon the contamination levels would also continue to increase, and we should pay more attention to the environmental fates and health effects of TBBPA and HBCD.

The highest level of PBDE contamination, for BDE-209 and other congeners, was found in the egg group, followed by the aquatic food and the meat group, indicating that the source of BDE-209 and other congeners was similar. In addition, a wide variation in the levels of the three target analytes in this study was observed across
the sampled food groups, and within the same sample type. This behavior has also been observed in many other studies (Bramwell et al., 2016; Fromme et al., 2016). Obviously, human dietary intake of BFRs varies widely according to the various consumable products. A series of factors, including environmental contamination, type of feeding, animal keeping mode (i.e., wild or caged), breeding area, style of cooking and type of food preparation, play roles in the BFRs distribution and data variability (Lü et al., 2014).

Compared to other studies, in fresh foods collected in China, the levels of BDE-209 in animal-original foods were slightly higher than the levels found in our results (Chang et al., 2013). Our results were also higher than TDS conducted in France and the UK. In the second French TDS, mean BDE-209 levels in food ranged from 0.004 to 0.278 ng/g lw (Bramwell et al., 2017). In the UK TDS performed in 2010—2011, mean levels of BDE-209 ranged from 0.015 pg/g ww in aquatic food to 1.18 ng/g ww in eggs, which were lower than levels of our results, except for eggs (Chen et al., 2013). The levels of BDE-209 in animal-original foods were slightly higher than the levels found in our results (Chang et al., 2013). In the UK TDS 2012, the levels of BDE-209 in 20 food groups ranged from 0.020 to 1.95 pg/kg ww (Bramwell et al., 2017). In miscellaneous foodstuffs in Italy, mean levels of BDE-209 ranged from 0.411 to 3.524 ng/g lw, which were similar to our results (Martellini et al., 2016). In seafood samples collected from European markets, the detection frequency of BDE-209 was very low (Aznar-Alemany et al., 2016). No BDE-209 data in food from North America was found to date.

In summary, the levels of the three legacy BFRs, TBBPA, HBCD and BDE-209, in food samples in this study were higher than those in most other studies conducted in general environments worldwide, indicating that China has become one of the most polluted regions affected by BFRs. Bi et al. (2006) inferred that the domestic demand for BFRs has increased by 8% annually with the rapid development of industry in China. Apart from mass production and application, e-waste has also brought serious BFRs pollution to China. Based on the results of the present study, we could come to the conclusion that China is now facing serious environmental problems from BFRs, and the monitoring of BFRs should be continued for a long time.

3.2. Estimated daily intake (EDI) and risk assessment

The total dietary intake of each BFR was calculated by summing the results from multiplying the concentration of each BFR (ng/g ww) in each food group by the amount (g/day) of that food consumed. The consumption data of the “standard Chinese man” for the four animal-origin food groups are shown in Supplementary Table A3. Large differences in food consumption patterns among provinces were found, with a range of 75 g/day in Henan to 405 g/day in Fujian, which was resulted from differences in geographical conditions, culture, food habits and economic levels between regions in China. In the calculations, concentrations under the LOD were assumed to be zero (lower bound EDI) or LOD (upper bound EDI). The lower bound and upper bound dietary intake of BFRs by the “standard Chinese man” for each province is listed in Table 2 and Table A4. For the lower bound EDIs, the median EDIs of the three targeted BFRs were quite similar at 0.936, 0.863 and 0.707 ng/kg bodyweight (bw)/day for TBBPA, HBCD and BDE-209, respectively. A large variety of EDIs was found among provinces, which was thought to result from variations in values of food consumption and contamination levels of the BFRs in the areas. For instance, in some provinces, such as Qinghai, Shanxi and Ningxia, both consumption of animal-origin foods and the contamination levels were low, and thus the EDI of BFRs were accordingly low. Higher dietary intake was mainly observed in regions from coastal areas or developed areas, including Guangdong, Shanghai and Beijing. In these regions, both food consumption and BFR levels are relatively high. However, because of the relatively low contamination levels, the EDI in Fujian was low, even though the animal-origin food consumption in Fujian was the highest (405 g/day). Surprisingly, the EDI$_{HBCD}$ in Jilin was the highest among the 20 provinces (6.94 ng/kg bw/day). Animal-origin food consumption in Jilin was relatively low (190 g/day), whereas the HBCD level in meat and meat products from Jilin was very high, which led to the high EDI in Jilin. Jilin is not an e-waste recycling area or a BFRs production area, it is not even an advanced industrial area. Thus, such a high contamination level of HBCD in foods from Jilin is unexpected. Since what we tested is pooled food composite, we inferred that the high HBCD concentration in meat composite from Jilin might be due to some of the individual samples in the pool, some highly contaminated individual samples might dramatically increase the result of the pool. Additionally, high HBCD concentrations in some individual samples might suggest that these samples were exposed to elevated level of HBCD, although Jilin is not an e-waste recycling area or a BFRs production area, we inferred that the regions where the sample produced or collected is close to some industrial sites where HBCD was heavily used and emitted.

Fig. 1 shows the mean EDIs of BFRs from the four food groups. Contribution percentages from the four food groups varied between provinces, whereas in the mean EDI, the contribution from meat group is always the greatest, from 43% in BDE-209 to 74% in HBCD, indicating that although contamination levels in meat and meat product were not the highest among the four food groups, the contributions from meat and meat product were still higher than those from the other food groups, because the consumption of meat and meat product was evidently higher than that of other animal-origin foods in China.

Data on TBBPA intake is rare. A duplicate diet study conducted in Japan showed that EDI$_{TBBPA}$ decreased from 0.48 ng/kg bw/day in 2004 to only 0.04 ng/kg bw/day in 2009 (Fujii et al., 2014). Mean

<table>
<thead>
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<th>Province</th>
<th>TBBPA</th>
<th>HBCD</th>
<th>BDE-209</th>
<th>Province</th>
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<td>0.122</td>
<td>Guangdong</td>
<td>5.71</td>
<td>0.876</td>
<td>1.08</td>
</tr>
<tr>
<td>Mean</td>
<td>1.34</td>
<td>1.51</td>
<td>0.96</td>
<td>Median</td>
<td>0.936</td>
<td>0.863</td>
<td>0.707</td>
</tr>
</tbody>
</table>

The values below LOD were treated as zero.
EDIIs via seafood consumption for adults in Europe was 1.3 ng/kg bw/day (Aznar-Alemany et al., 2016). For HBCD, based on the measurement of marine fishes along the Chinese coastline, EDI\textsubscript{HBCD} via fish consumption for the Chinese population were 0.004–1.00 ng/kg bw/day, this value was similar to EDI via aquatic food in the present study (Xia et al., 2011); in another study, the dietary exposure of the population of Tianjin, a large city located in North China, to HBCDs through fish and wheat consumption was assessed, the EDI\textsubscript{HBCD} by the urban residents were 0.16 ng/kg bw/day via fish and 0.57 ng/kg bw/day via wheat consumption, whereas the corresponding data for the rural residents were 1.64 and 0.65 ng/kg bw/day, respectively, these values were higher than our results, showed a relatively high dietary exposure of Tianjin population to HBCD, especially for the urban residents (Zhang et al., 2013b). In the second French TDS, the mean EDI\textsubscript{HBCD} for adults was 0.211 ng/kg bw/day, and delicatessen meats and meats were the main contributors (Riviere et al., 2014). In market basket studies, the average EDIs of HBCD for the Korean, Spanish and Belgian population were 0.816, 2.58 and 0.991 ng/kg bw/day, respectively, and fish and seafood were found to be the major contributors to dietary intake in Korea and Spain, whereas in Belgian meat was the major contributor (Barghi et al., 2016; Eljarrat et al., 2014; Goscinny et al., 2011). Mean EDI\textsubscript{HBCD} via seafood consumption for adults in Europe was 0.49 ng/kg bw/day (Aznar-Alemany et al., 2016). For BDE-209, the mean EDI\textsubscript{BDE-209} for 19–65 year old males in Taiwan was 3.12 ng/kg bw/day, which was two times higher than our results, and freshwater fish and seafood were the major contributors (Chang et al., 2017). In the Hong Kong TDS, the mean EDI\textsubscript{BDE-209} was 0.53 ng/kg bw/day, and fish and seafood were the major contributors (Chen et al., 2013). In the French TDS, the mean EDI\textsubscript{BDE-209} was 0.349 ng/kg bw/day, respectively, and dairy-based desserts and fish were found to be two main contributors (Riviere et al., 2014). In the UK TDS, the mean EDI\textsubscript{BDE-209} was 0.708 ng/kg bw/day, and similar to many other coastal states, fish and seafood were the major contributors (Bramwell et al., 2007). Taken together, because of the relatively high contamination levels, the EDIs in our study were higher than those in most other studies, indicating the heavy BFR body burden of the Chinese population.

The MOEs were calculated following the EFSA approach. All three BFRs demonstrated large MOEs for dietary exposure. For TBBPA, the MOEs for mean and max EDIs were 1.2 × 10^6 and 2.8 × 10^6, respectively, although the threshold MOE of 100 is insufficient to account for uncertainties and variability due to deficiencies in the toxicological database for TBBPA (EFSA, 2011c), such high MOEs estimated in our study indicated that exposure to TBBPA via food consumption does not raise significant health concerns for adults. HBCD is also unlikely to pose a health risk, as the MOEs for the mean and max EDIs were 5.2 × 10^5 and 1.1 × 10^5, respectively, which is also several orders of magnitude higher than the threshold of 8 set by the EFSA (EFSA, 2011a). BDE-209 also demonstrated a large MOE, with 1.8 × 10^6 and 3.1 × 10^5 for the mean and max EDIs, respectively, which was several orders of magnitude higher than the threshold of 2.5 (EFSA, 2011b). In summary, based on the BFR levels measured in the present study, it is unlikely that the current dietary exposure of the general population to TBBPA, HBCD and BDE-209 would pose a health risk.

3.3. Temporal trends of TBBPA and HBCD in the TDS

This is the second time we measured TBBPA and HBCD in the TDS, the first time being in the last TDS (the 4th Chinese TDS) conducted in 2007. In TDS 2007 TBBPA and HBCD were tested in the same four food groups; however, TDS 2007 was performed in only 12 provinces (HLJ, HeB, LN, SX, HeN, NX, FJ, SH, JX, SC, HuB and GX) (Shi et al., 2009). A comparison between the present TDS and TDS 2007 is illustrated in Fig. 2. Average contamination levels of TBBPA and HBCD in the four food groups in TDS 2011 were found to be 3 to 30 times higher than those observed in TDS 2007, indicating a sharp increase in TBBPA and HBCD in the environment. Accordingly, an increase in the intensity of human exposure was also observed. Average EDI\textsubscript{TBBPA} values for the “standard Chinese man” increased from 0.232 ng/kg bw/day in TDS 2007 to 1.34 ng/kg bw/day in TDS 2011, whereas EDI\textsubscript{HBCD} values increased from 0.258 ng/kg bw/day in TDS 2007 to 1.51 ng/kg bw/day in TDS 2011, respectively. In detail, when the EDIs of TBBPA and HBCD via food consumption in the same 12 provinces from TDS 2007 and 2011 were compared (Fig. 3), an increase in the EDIs of both TBBPA and HBCD were also observed from 2007 to 2011. For HBCD, rising EDIs were observed in most

![Fig. 1. EDI of BFRs via various food groups.](image-url)

![Fig. 2. Comparison of mean levels of TBBPA and HBCD between TDS 2007 and 2011.](image-url)
provinces, except in Shanghai and Hubei; however, the high EDI_BCD value in Shanghai in TDS 2007 was exceptional because of the extremely high BCD levels in aquatic foods. For TBBPA, the EDIs in some provinces, such as Shanxi, Jiangxi, Sichuan and Guangxi, jumped sharply by 20–80 times from 2007 to 2011, whereas in other provinces, only a small increase or small decrease were observed. In summary, higher levels and EDIs of TBBPA and HBCD in TDS 2011 suggested a rapid increase in demand for these two BFRs between 2007 and 2011. In China, the legislative focus is still firmly on PBDEs, while TBBPA has received little attention until now; especially after the restriction of PBDEs and the EU official approval of the use of TBBPA as a safe flame retardant, the production and application of TBBPA obviously increased (Liu et al., 2016). Thus, we predict that TBBPA contamination levels in China will continue to increase in the future. HBCD was listed as a POP in 2013; the TDS in the present study was conducted in 2011, and thus HBCD was still in use when we performed the study. Therefore, we conclude that the production and application of HBCD also continued to increase between 2007 and 2011, resulting in higher levels of HBCD in TDS 2011. In addition, although HBCD has been phased out in many fields in China since 2016, the use of HBCD in building materials is still permitted. That is, the production and application of HBCD continues in China, and the contamination levels of HBCD may also continue to increase in the future.

3.4. A comparison to novel BFRs

In the present TDS, six currently used novel BFRs (NBFRs), including pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and decabromodiphenyl ethane (DBDPE), were also measured in the same food groups (Shi et al., 2016). A comparison between the legacy BFRs and the novel BFRs is shown in Fig. 4. Obviously, when the EDIs for the “standard Chinese man” were used for comparison, EDI_DBDE via food consumption was not only far higher than those of the other NBFRs, but was also 3 to 5 times higher than those of the three legacy BFRs, indicating that the production and application of DBDPE has outperformed most other BFRs, resulting in relatively high contamination levels in various matrices. DBDPE was introduced into the market as a replacement for PBDEs since the end of last century, and it was produced and used in increasing amounts (Covaci et al., 2011). In China, DBDPE has been produced only since 2005 but with production increasing 80% per year (http://www.polymer.cn/). Currently, DBDPE is the most popular NBFR in the Chinese market with a production capacity of 25,000 t in 2012; this volume may outperform that of other BFRs to make DBDPE the most produced and used BFR at present (Zhang and Gu, 2013; Zhang and Lu, 2011). In summary, the comparison between DBDPE and the three legacy BFRs indicated an obvious shift in the consumption pattern between PBDE and non-PBDE BFRs in China.

4. Conclusion

A national survey of three currently used BFRs, TBBPA, HBCD and BDE-209, was described and discussed in this report. Based on the determination of animal-origin foods collected from various
areas of China, dietary exposures of Chinese population to BFRs were calculated for risk assessment. The level and EDI of BDE-209 were found to be lower than those of TBBPA and HBCD, as well as DBDPE, suggesting an obvious shift in the consumption pattern between PBDE and non-PBDE BFRs in China. In addition, the levels and EDIs of TBBPA and HBCD in the present TDS were several times higher than those in TDS 2007, indicating a rapid increase in contamination levels of these two BFRs from 2007 to 2011. In conclusion, with the restriction of PBDEs, the production and application of TBBPA and HBCD has increased rapidly, and levels, spatial trends and temporal trends for TBBPA and HBCD all confirm their relatively high current use in the flame retardant market. Since as of now there is no restriction on TBBPA and the use of HBCD in building materials is still permitted in China, we predict that the contamination levels of TBBPA and HBCD in China may continue to increase in the future. On the other hand, the levels and EDIs of the three BFRs were higher than most other studies worldwide, suggesting that China is now facing serious environmental problems from BFRs because of the mass production and application of BFRs, along with the improper recycling of e-wastes. Therefore, although the results of risk assessment in this TDS indicate that the current estimated dietary exposures of these three BFRs are unlikely to raise significant health concern, exposure and risk assessment for BFRs should be continued, especially for those with high and rising contamination levels, including TBBPA, HBCD and DBDPE.

Conflict of interest statements

The authors have no conflict of interest to declare.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.06.093.

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