

# Brominated flame retardants in food and environmental samples from a production area in China: concentrations and human exposure assessment

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**Abstract** Human exposure to brominated flame retardants (BFRs: decabromodiphenyl ether (BDE209), decabromodiphenyl ethane (DBDPE), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), 1,2,3,4,5-pentabromobenzene (PBBz), and 2,3,5,6-tetrabromo-*p*-xylene (TBX)) in a brominated flame retardant production area (Weifang, Shandong Province, China) was estimated. Thirty food samples, 14 air samples, and 13 indoor dust samples were analyzed. BDE209 and DBDPE were the dominant BFRs in all samples. Higher alternative brominated flame retardant (including DBDPE, HBB, PBEB, PBT, PBBz, and TBX) concentrations were found in vegetables than in fish and meat; thus, plant-original foods might be important alternative BFR sources in the study area. The BDE209 and alternative BFR concentrations in air were  $1.5 \times 10^4$  to  $2.2 \times 10^5$  and 620 to  $3.6 \times 10^4$   $\text{pg/m}^3$ , respectively. Mean total BFR exposures through the diet, inhalation, and indoor dust ingestion were 570, 3000, and 69  $\text{ng/d}$ , respectively (16, 82, and 2 % of total intake, respectively). Inhalation was the dominant BFR source except for DBDPE, for which diet dominated. BDE209 contributed 85 % of the total BFR intake in the study area.

**Keywords** Brominated flame retardants · Dietary intake · Inhalation · Indoor dust ingestion · Exposure assessment

## Introduction

Brominated flame retardants (BFRs) are a large and important group of synthetic chemicals. More than 75 BFRs were reported to have been produced commercially in 2003, and new compounds are still being produced (Alaee et al. 2003). BFRs, such as polybrominated diphenyl ethers (PBDEs) that are used as additive flame retardants (as opposed to flame retardants that are incorporated into the chemical structures of polymers), have attracted a great deal of attention in recent decades (Mikula and Svobodova 2006). Three commercial PBDE mixtures, penta-BDE, octa-BDE, and deca-BDE, have been widely used in textiles, polyurethane foam, thermoplastics, and electronic appliances. The persistent characteristics and the toxicological effects caused by the components of the penta-BDE and octa-BDE commercial mixtures have caused them to be added to the list of chemicals that are scheduled to be eliminated from production and use under the Stockholm Convention on persistent organic pollutants. Stockholm unregulated substitutes, such as decabromodiphenyl ethane (DBDPE), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), 1,2,3,4,5-pentabromobenzene (PBBz), and 2,3,5,6-tetrabromo-*p*-xylene (TBX) have been used in various products as

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replacements for the restricted BFRs (Covaci et al. 2011; Gauthier et al. 2007; Lin et al. 2013). Only a limited amount of information on the environmental behavior of these alternative BFRs is available, and the data that are available suggest that the concentrations of the alternative BFRs are increasing over time and that the alternative BFRs might be persistent, bioaccumulative, and toxic.

DBDPE is a commercially important alternative to the deca-BDE commercial product. DBDPE has been produced and used in China for more than 10 years, and 12000 t of DBDPE was produced in 2006. DBDPE is currently the second-highest-used additive BFR in China, and its production is increasing every year (Zhao et al. 2013). DBDPE has attracted a growing amount of interest in recent years because it has been found to be widespread in the environment (Brommer et al. 2012; De la Torre et al. 2012a, b; Tian et al. 2011; Tue et al. 2013; Wei et al. 2012; Yang et al. 2012). DBDPE has recently been found in biota, and it has been found in home-produced eggs from an electronic waste recycling region in South China, wildlife from San Francisco Bay in the USA, mussels from Asian coastal waters, and even human hair from South China (Isobe et al. 2012; Sun et al. 2012; Zheng et al. 2012).

Polybromobenzenes (including HBB, PBT, PBEB, PBBz, and TBX) belong to a group of organobromine compounds that have one phenyl ring with several bromine atom substituents. It has been reported that 600 t/year of HBB and PBT are produced in Weifang City, China. It has been reported that PBEB is not currently produced in Weifang City. Little information is available on the production of PBBz and TBX in China. The polybromobenzenes have higher vapor pressures than PBDEs and DBDPE have, so they are more likely than the PBDEs and DBDPE to evaporate and enter into the atmosphere. Polybromobenzenes have been detected in many types of environmental media, including sediment, sewage sludge, air, and indoor dust (Gouteux et al. 2008; Saito et al. 2007). More importantly, some polybromobenzenes have been shown to bioaccumulate in wildlife, such as freshwater fish, the eggs of glaucous gulls, and marine mammals (Gorga et al. 2013; Ross et al. 2009; Verreault et al. 2007).

Weifang City is in the eastern coastal part of Shandong Province, which is an important industrial region in North China. The Binhai Economic Development Zone located in Weifang City is the largest BFR-manufacturing center in China because of the

abundant sources of bromine that are found in this region. Therefore, this region is likely to be a hotspot for BFR contamination. High concentrations of BFRs have recently been detected in biota and abiotic samples from this production source region. The residents of this region have been reported to be exposed to elevated PBDE concentrations (Jin et al. 2010). Very little information is currently available on alternative BFR contamination in the environment and human exposure to alternative BFRs in the Binhai Economic Development Zone. The objective of the study was to detect the selected BFR concentrations in food and environmental samples collected from the study area and then to assess the potential human exposure doses posed by the BFRs to the residents of the BFR production area.

## Materials and methods

### Sample collection

The food samples were randomly selected from the local food markets in the Binhai Economic Development Zone (37.120° N, 119.011° E). Eight types of local fish and shellfish (Chinese shrimp, conch, clam, razor clam, crucian carp, pomfret, yellow croaker, and perch), five types of vegetable (bean, potato, carrot, Chinese cabbage, and Suaeda salsa), and three types of meat (chicken, beef, and mutton) were selected after our oral investigation to ensure that all these sampled species were locally caught/grown and were major parts of the diet of the local population. Each food sample was wrapped in aluminum foil and sealed in self-seal bags and then kept frozen at -18 °C until it was analyzed. Seven pairs of gaseous and particulate phase air samples were collected between 1 and 8 July 2013 using a high-volume air sampler (Tisch Environmental, Cleves, OH, USA). Indoor dust samples were collected using a vacuum cleaner from eight residential houses, and the samples were kept frozen at -18 °C until they were analyzed. The sampling sites are shown in Fig. 1.

### Chemicals

The isotope-labeled PBDE standards (<sup>13</sup>C<sub>12</sub>-labeled BDE139 and <sup>13</sup>C<sub>12</sub>-labeled BDE209) were from Cambridge Isotope Laboratories (Cambridge, MA, USA). Dichloromethane, acetone, and hexane were of pesticide analysis grade (J.T. Baker, Phillipsburg, NJ,

USA). Water was purified using a Milli-Q system (Millipore, Billerica, MA, USA). Nitrogen (99.999 %) and helium (99.999 %) were obtained from Chengweixin (Beijing, China). Anhydrous sodium sulfate was of analytical grade and was baked at 450 °C for 5 h before use. Silica gel (100–200 mesh) was from Merck (Darmstadt, Germany) and neutral alumina (60 mesh) was from Alfa Aesar (Ward Hill, MA, USA). The silica gel and alumina were extracted with dichloromethane, activated (at 105 °C for the silica gel and at 130 °C for the alumina) for 12 h, then cooled and deactivated by adding 3 % of the sorbent weight of deionized water.

Extraction and cleanup

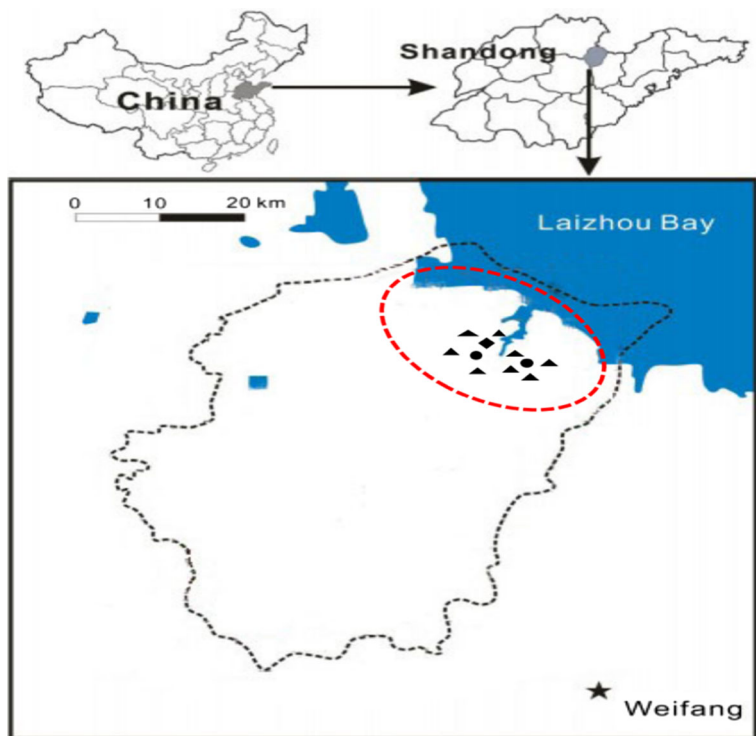
In the laboratory, the aquatic products were cleaned by removing their scales, shells, and bones using a stainless steel knife. The muscle without fishskin was then homogenized using a domestic stainless homogenizer (precleaned by Hexane) (JinTian Technologies, 10000 RPM, CN, USA). The meats samples were thoroughly washed by water and then homogenized. The vegetables were washed thoroughly in water to remove dust and soil, and inedible parts were removed by a stainless steel

knife and then homogenized using a domestic homogenizer. The homogenized food samples were chosen using the coning and quartering method, and 30 g food samples were weighted. The homogenized samples were then mixed with Na<sub>2</sub>SO<sub>4</sub> to remove the water. Each prepared food samples or environmental samples was spiked with a known amount of internal standards (<sup>13</sup>C<sub>12</sub>-labeled BDE139, <sup>13</sup>C<sub>12</sub>-labeled HBB, and <sup>13</sup>C<sub>12</sub>-labeled BDE209), and then Soxhlet was extracted with 300 mL of a 1:1 mixture of acetone and hexane for 24 h. The extract was then cleaned using a column packed with (from bottom to top) 1 g activated silica, 4 g silica treated with 30 % w/w of 1 M NaOH, 1 g activated silica, 8 g silica treated with 44 % w/w of H<sub>2</sub>SO<sub>4</sub>, 2 g activated silica, and 4 g granular anhydrous sodium sulfate, and the column was eluted with 100 mL of a 97:3 (v/v) hexane/dichloromethane mixture. The cleaned sample was concentrated to 100 μL using a rotary evaporator and then under a gentle flow of nitrogen.

Instrumental analysis

The samples were analyzed by gas chromatography–mass spectrometry (using an Agilent 6890 gas

**Fig. 1** Sampling sites in the brominated flame retardant production area in Weifang, Shandong Province, North China. (The area within the red dashed line is the main industrial zone, the black triangles show indoor dust sampling sites, the black circles show the food sampling sites, and the black diamond shows the air sampling site)



chromatograph and an Agilent 5975 N mass spectrometer; Agilent Technologies, Santa Clara, CA, USA). The mass spectrometer ion source and quadrupole temperatures were both 150 °C. The carrier gas was helium, and its flow rate was 1.0 mL/min. Aliquots (1 µL) of the samples were injected in splitless mode. HBB, PBBz, PBEB, PBT, and TBX were separated using a DB-5MS column (30 m long, 0.25 mm i.d., 0.1 µm film thickness; J&W Scientific, Agilent Technologies), and the oven temperature program started at 100 °C (held for 2 min) and increased at 4 °C/min to 300 °C. A negative chemical ionization source was used, and the mass spectrometer was operated in selected ion monitoring mode to allow quantitative analysis to be performed. The *m/z* ratios that were monitored were 419.6 and 421.5 for TBX; 471.6 and 473.6 for PBBz; 485.6 and 487.6 for PBT; 499.6 and 501.6 for PBEB; 551.5 and 553.5 for HBB; and 573.6 and 575.6 for <sup>13</sup>C<sub>12</sub>-labeled BDE139. BDE209 and DBDPE were analyzed using a shorter DB-5MS column (15 m long, 0.25 mm i.d., 0.1 µm film thickness; J&W Scientific, Agilent Technologies). The injector temperature was 290 °C, and the oven temperature program started at 100 °C (held for 3 min), increased at 10 °C/min to 290 °C, and then was held for 8 min. The *m/z* ratios that were monitored were 407 and 486 for BDE209; 79, 81, 811, and 813 for DBDPE; and 415 and 494 for <sup>13</sup>C<sub>12</sub>-labeled BDE209.

#### Quality control

A method blank sample was analyzed with every batch of samples. The analyte concentrations in the blank samples were all satisfactory (<5 % of the typical analyte concentration in the samples). HBB, PBBz, PBEB, PBT, and TBX were quantified using <sup>13</sup>C<sub>12</sub>-labeled BDE139 as the internal standard (recoveries were 80–105 % in dust samples and 99–110 % in food samples) and BDE209 and DBDPE were quantified using <sup>13</sup>C<sub>12</sub>-labeled BDE209 as the internal standard (recoveries were 75–127 % in dust samples and 84–102 % in food samples). The recoveries of HBB, PBBz, PBEB, PBT, and TBX in food samples were 73–132, 65–112, 80–101, 77–155, and 55–92 %, respectively. The recoveries of HBB, PBBz, PBEB, PBT, and TBX in dust samples were 85–132, 65–142, 80–122, 90–145, and 83–130 %, respectively. The instrumental limit of detection (LOD) was defined as the concentration that gave a peak with a signal to noise ratio of 5. The instrumental LODs for BDE209 and DBDPE were 5 and 10 pg, respectively.

The instrumental LODs for polybromobenzenes ranged from 0.04 to 0.05 pg.

#### Estimation of human exposure doses

We evaluated human exposure to the BFRs through dietary intake, the ingestion of indoor dust, and the inhalation of air in the BFR production area by calculating estimated exposure doses (EED) for male adults, using methods that have been described by the US Environmental Protection Agency. The equations that were used in the calculations are given below.

Dietary exposure was calculated using Eq. 1,

$$EED_D = (C_A M_A + C_M M_M + C_V M_V) / BW, \quad (1)$$

where  $EED_D$  is the estimated exposure dose through the diet ( $\text{pg kg}^{-1} \text{ day}^{-1}$ ),  $C_{A/M/V}$  is the mean concentration of the compound of interest in aquatic products/meat/vegetables ( $\text{pg g}^{-1}$  wet weight), and  $M_{A/M/V}$  is the amount of aquatic products/meat/vegetables consumed ( $\text{g day}^{-1}$ ) by a standard adult male. The  $M_{A/M/V}$  values were taken from a previous Chinese study (Zhang et al. 2013b).  $BW$  is the body weight of a standard adult male in China (70 kg). Because most of Weifang foods come from outside (the locally produced food supply is small), the dietary exposure calculation in the present study is for the worst case scenario.

Exposure through the inhalation of air was calculated using Eq. 2,

$$EED_I = (C_A R_A) / BW, \quad (2)$$

where  $EED_I$  is the estimated exposure dose through inhalation ( $\text{pg kg}^{-1} \text{ day}^{-1}$ ),  $C_A$  is the air concentration of the compound of interest in the study area, and  $R_A$  is the breathing rate for an adult, which was taken from a report by the US Environmental Protection Agency. We assumed that 100 % of the inhaled BFRs were absorbed in this preliminary evaluation of the exposure to BFRs of the inhabitants of the BFR production area.

Exposure through the ingestion of indoor dust was calculated using Eq. 3,

$$EED_A = (C_D I_A) / BW, \quad (3)$$

where  $EED_A$  is the estimated exposure dose through the ingestion of indoor dust ( $\text{pg kg}^{-1} \text{ day}^{-1}$ ),  $C_D$  is the concentration of the compound of interest in indoor dust in the BFR production area, and  $I_A$  is the dust ingestion rate for an male adult.

## Statistical analysis

The data were analyzed using the statistical software package SPSS 18.0 (IBM, Armonk, NY, USA). Unless otherwise stated, all values below the quantification limit were set at half of the quantification limit before the statistical analyses were performed. Correlations were evaluated using the Pearson correlation coefficient.

## Results and discussion

### Concentrations of total BFRs in food and environmental samples

The BFR concentrations that were found in the food, air, and dust samples are summarized in Table 1. The highest total BFR ( $\sum$ BFR) concentration was found in a potato sample (44,000 pg/g wet weight). Relatively high  $\sum$ BFR concentrations were found in the Suaeda salsa, freshwater fish, and beef samples (4400, 3100, and 3000 pg/g wet weight, respectively). In some studies, fish, shellfish, and other foods from aquatic environments have been found to be more contaminated with BFRs than other types of food. We found that Suaeda salsa grown in the study area was also heavily contaminated with BFRs, and the reason for this is that the Suaeda salsa was only grown in the saline–alkali soil where the BFR-manufacturing plants in the study area are concentrated.

### Concentrations of BFRs in food samples

The BFR concentrations that were found in the food samples are shown in Table 1 and Fig. 2. BDE209 was found in all of the food samples. In general, the BDE209 concentrations in the meat samples were comparable with the BDE209 concentrations in the fish and shellfish samples, and the concentrations in those samples were relatively high compared with the concentrations in the vegetable samples. This was mainly because lipid concentrations are higher in fish, shellfish, and meat than in vegetables.

The BDE209 concentrations in the freshwater fish samples were higher (3100 pg/g wet weight) than the BDE209 concentrations in the other fish and shellfish samples (the BDE209 concentrations in the marine fish samples were slightly lower, at 2000 pg/g wet weight). However, in some other studies, higher

BDE209 concentrations have been found in marine fish than in freshwater fish (Cheung et al. 2008; Ni et al. 2012). A possible explanation for the high BDE209 concentrations that were found in the freshwater fish in our study is that the freshwater fish were collected from ponds near the PBDE-manufacturing plants. The mean BDE209 concentration in the fish and shellfish samples was 1800 pg/g wet weight (and the highest concentration was 3100 pg/g wet weight, as mentioned above). Higher mean BDE209 concentrations in fish samples have only previously been found for fish samples collected from two e-waste recycling sites, Guiyu and Qingyuan (in China) (Ma et al. 2009). The BDE209 concentrations found in our study were higher than those that have been found in most fish and shellfish samples from other parts of China, such as Guangdong, Shenzhen, Liaoning, and Fujian Provinces (Zhang et al. 2013a). This shows that fish and shellfish in Weifang are seriously contaminated with BDE209.

The BDE209 concentrations in the meat samples decreased in the order beef>mutton>chicken. This might have been caused by the different types and sources of feed that the animals are given with. The mean BDE209 concentration in the meat samples was 1400 pg/g wet weight, higher than that found in a similar range of meat samples (beef, chicken, and pork) in Taiwan (Chen et al. 2012), for which the mean BDE209 concentration was 550 pg/g wet weight, and in a range of meat samples (ground beef, chicken breast, duck, and other meats) in the USA (Schechter et al. 2010), for which the mean BDE209 concentration was 280 pg/g wet weight.

The mean BDE209 concentration in the vegetable samples (1300 pg/g wet weight) was comparable with the mean BDE209 concentration that was found in vegetable samples collected in Shanghai, China (1200 pg/g wet weight) (Yu et al. 2011). We found higher BDE209 concentrations in the leafy vegetables (Chinese cabbage and Suaeda salsa) than in the fruit and root vegetables (bean, potato, and carrot), as is shown in Fig. 2. Vegetables are usually expected to contain relatively low BFR concentrations because of their high water contents, low lipid contents, and their primary positions in ecosystems. However, we found that the BDE209 concentrations in the leafy vegetables were comparable or even higher than the BDE209 concentrations in the meat, fish, and shellfish. It has been suggested that organic pollutants enter vegetation mainly

**Table 1** Concentrations of brominated flame retardants (BFRs) in food and environmental samples from a BFR production area in China

Groups of samples	No. of samples	BDE209	DBDPE	HBB	PBT	PBEB	PBBz	TBX	$\Sigma$ BFRs
Fish and seafood <sup>a</sup>	14	1800	121	3.2	2.8	n.d.	5.3	2.9	1900
Vegetable <sup>a</sup>	10	1300	120	13	12.0	0.1	6.8	0.1	1400
Meat <sup>a</sup>	6	1400	100	0.8	0.5	0.1	1.0	0.3	1500
Air (particulate phase) <sup>b</sup>	7	$1.4 \times 10^5$	220	360	920	0.5	81	3.7	$1.4 \times 10^5$
Air (gaseous phase) <sup>b</sup>	7	130	16	2400	3100	9.2	1300	13	7000
$\Sigma$ Air <sup>b</sup>	14	$1.4 \times 10^5$	240	2800	4000	9.7	1400	17	$1.5 \times 10^5$
Indoor dust <sup>c</sup>	13	$1.3 \times 10^6$	$2.6 \times 10^4$	8300	360	1.6	300	10	$1.4 \times 10^6$

<sup>a</sup> Values are given in pg/g wet weight and are presented as mean concentrations

<sup>b</sup> Values are given in pg/m<sup>3</sup> and are presented as mean concentrations

<sup>c</sup> Values are given in pg/g dry weight and are presented as mean concentrations

through gas-phase and particle-phase deposition onto the waxy cuticles of leaves or by uptake through the stomata. This would result in BFRs being more likely to remain in and on the leaves of a plant than for them to be translocated to other parts of the plant (Collins et al. 2006; Ohta et al. 2002).

The alternative BFR concentrations in the samples were also measured because there have recently been reports that these compounds can affect human health. DBDPE was found in the samples at concentrations ranging from <LOD to 350 pg/g wet weight, and it was detected at above the LOD in 79 % of all samples. DBDPE has the second highest concentration of all of the analyzed compounds in most of the samples. These results indicate that DBDPE contamination is widespread in the study area, and this is the first time that DBDPE has been detected in vegetables. The DBDPE concentrations in the fish and seafood samples were comparable with DBDPE concentrations that have been found in dolphin samples from Brazil, but much lower than DBDPE concentrations (<LOD to 800 ng/g lipid weight) that have been found in the muscles of water birds collected from an e-waste recycling area in South China (Mo et al. 2012). All of these results show that DBDPE can enter into the food chain, and this is of concern because the production and application of DBDPE is increasing.

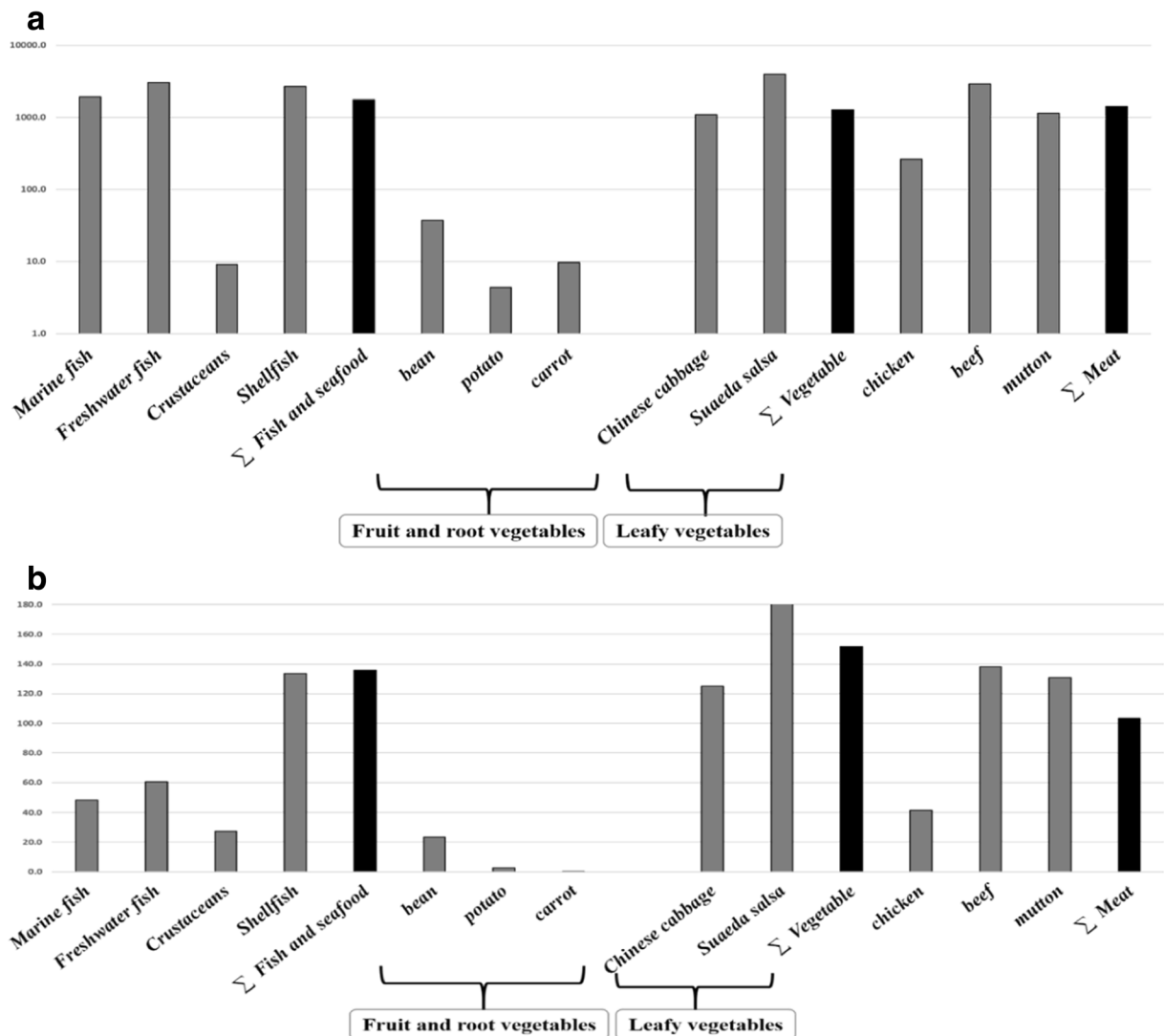
All of the polybromobenzenes were detected in the food samples, although PBEB was only detected in the Chinese cabbage, chicken, and beef samples. As far as we know, this is the first time that HBB, PBT, and PBBz have been detected in vegetables. The

polybromobenzene concentrations were lower than the BDE209 and DBDPE concentrations. The polybromobenzenes have previously been found in sediment, air, and dust samples from China (Fromme et al. 2014). The extent to which the polybromobenzenes are distributed in the environment and the extent to which they are biologically enriched are still unknown, so the behaviors of polybromobenzenes in the environment require further study.

#### Concentrations of BFRs in environmental samples

The BFRs were detected in the air (particulate plus gaseous phase) and indoor dust samples. The mean BDE209 concentrations in the air and indoor dust samples from the BFR production area were  $1.4 \times 10^5$  pg/m<sup>3</sup> and  $1.3 \times 10^6$  pg/g, respectively, and these concentrations were relatively high compared with concentrations that have been found in air and dust in other parts of the world.

The DBDPE concentrations in the particulate phase samples and the gaseous phase samples were 40–220 and 4.6–35 pg/m<sup>3</sup>, respectively. The particulate phase DBDPE concentration contributed 85–96 % of the total DBDPE concentration in the air samples. The total DBDPE concentrations in the air samples were only lower than concentrations that have been found in air samples from the highly industrial and urban Pearl River Delta region (400–3600 pg/m<sup>3</sup>) and were higher than DBDPE concentrations that have been found in air samples from the North American Great Lakes ( $3.2 \pm 0.5$  pg/m<sup>3</sup>), Ohio



**Fig. 2** Concentrations (pg/g wet weight) of **a** BDE209 and **b** BFRs (without BDE209) in different foodstuffs from the study area

in USA (7–35 pg/m<sup>3</sup>), and Taihu Lake in China (23–90 pg/m<sup>3</sup>) (Ma et al. 2013; Qiu et al. 2010; Shi et al. 2009).

The polybromobenzenes were significantly higher in the gaseous phase than in the particulate phase, and this was mainly because the polybromobenzenes have higher vapor pressures than BDE209 and DBDPE have, meaning that they partition more into the gaseous phase than do BDE209 and DBDPE. The mean whole air (particulate phase plus gaseous phase) HBB, PBT, and PBBz concentrations were 2800, 4000, and 1400 pg/m<sup>3</sup>, respectively. The PBEB concentrations (7–16 pg/m<sup>3</sup>) and TBX concentrations (3.1–73 pg/m<sup>3</sup>) in the air samples were much lower than the concentrations of the

other polybromobenzenes analyzed in the present study. The HBB and PBBz concentrations in the air samples were higher than those that have been found in studies in the North American Great Lakes basin, the Taihu Lake basin, and at the Egbert sampling site (ON, Canada). HBB concentrations are generally higher in China than in other countries, which is consistent with the fact that China is one of the major manufactures of HBB in the world.

#### Correlation analysis of the BFR concentrations

We expected that the concentrations of most of the alternative BFRs would correlate with each other

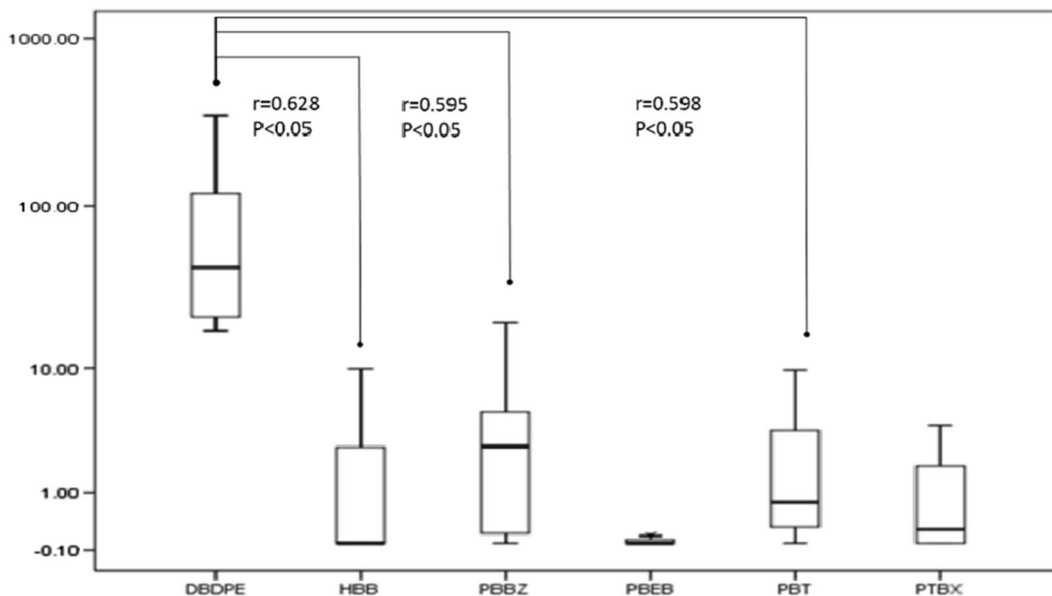
because of their structural similarities, so we explored the correlations between the alternative BFR concentrations using Pearson correlation coefficients (Fig. 3). We found that the DBDPE concentration correlated with the HBB ( $r=0.628$ ,  $P<0.05$ ), PBBz ( $r=0.598$ ,  $P<0.05$ ), and PBT ( $r=0.595$ ,  $P<0.05$ ) concentrations in the food samples. This might add evidence for PBT and PBBz being products of the in vivo cleavage of the two-carbon alkyl chain in DBDPE. We also found that the HBB concentrations correlated significantly with the PBT ( $r=0.988$ ,  $P<0.01$ ) and PBBz ( $r=0.748$ ,  $P<0.01$ ) concentrations in the food samples. This may have been because PBBz is a less-brominated homolog of HBB. Overall, these data confirm that the concentrations of some of the alternative BFRs in food samples correlated with each other. Furthermore, we did not find the correlation in alternative BFRs in dust and air samples. Further work is required to improve our understanding of the sources and degradation pathways of the alternative BFRs.

#### Assessment of male adult exposure to BFRs

The estimated exposure doses are shown in Table 2. The mean  $\Sigma$ BFR exposure through dietary intake, the

inhalation of air, and the ingestion of indoor dust was found to be 3600 ng/day for an adult, and BDE209 accounted for almost 90 % of that. The exposure to BDE209 through the inhalation of air was 2800 ng/day for an adult, which was higher than the values that have been found for Sweden (620 ng/day) (Tornkvist et al. 2011), Finland (1200 ng/day) (Kiviranta et al. 2004), the Slovak Republic (420–1100 ng/day) (Chovancova et al. 2011), and Belgium (400–540 ng/day) (Voorspoels et al. 2007). To the best of our knowledge, the preliminary estimated exposure of male adults to BDE209 through the inhalation of air for the inhabitants of the BFR production area that we studied is the highest in the world.

It is currently understood that the general population is exposed to BFRs mainly through a combination of dietary exposure, the ingestion of indoor dust, and the inhalation of air. However, the contributions of each exposure route to the BFRs are different. The contributions of air inhalation, dietary intake, and the ingestion of indoor dust to the total exposure of the inhabitants of the study area to each compound are shown in Fig. 4. The contributions of air inhalation, dietary intake, and the ingestion of indoor dust to the  $\Sigma$ BFR intake were 82, 16, and 2 %, respectively. This indicates that the inhalation of air plays a very significant role in the exposure of



**Fig. 3** Correlations between the alternative brominated flame retardants concentrations in the food samples. (DBDPE decabromodiphenyl ethane, HBB hexabromobenzene, PBBz

1,2,3,4,5-pentabromobenzene, PBEB pentabromoethylbenzene, PBT pentabromotoluene, PTBX 2,3,5,6-tetrabromo-*p*-xylene)



**Table 2** Estimated daily exposures for male adults to brominated flame retardants (BFRs) in the BFR production area in China that was studied

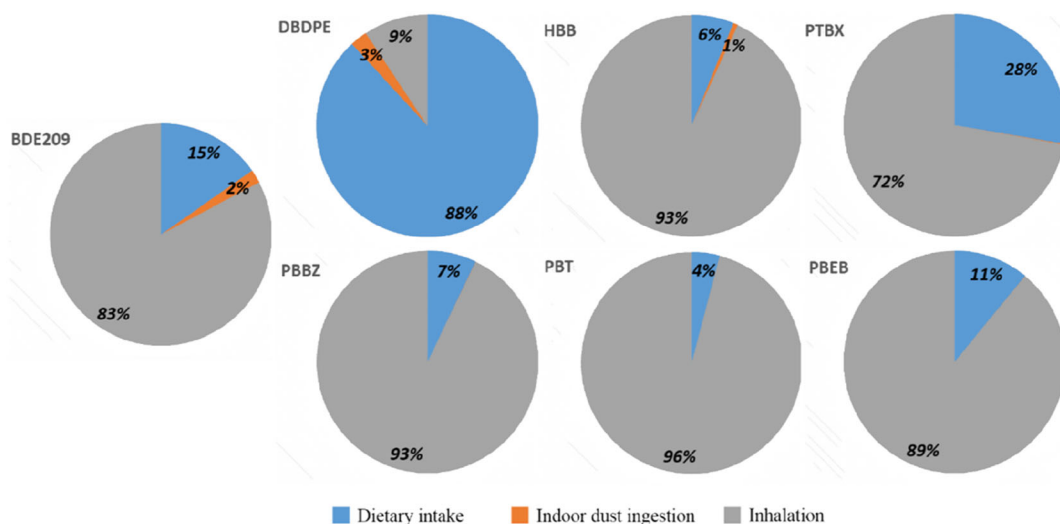
	Dietary intake (pg kg <sup>-1</sup> body weight day <sup>-1</sup> )	Inhalation of air (pg kg <sup>-1</sup> body weight day <sup>-1</sup> )	Ingestion of indoor dust (pg kg <sup>-1</sup> body weight day <sup>-1</sup> )	ΣExposure dose
BDE209	7400	40,000	960	48,000
DBDPE	640	68	18	730
HBB	53.0	800	5.9	860
PBT	49	1100	0.3	1200
PBEB	0.3	2.8	0.1	3.2
PBBz	30	390	0.2	420
TBX	1.8	4.7	0.1	6.7
Σ BFRs	8200	42,000	980	52,000

(*BDE209* decabromodiphenyl ether, *DBDPE* decabromodiphenyl ethane, *HBB* hexabromobenzene, *PBT* pentabromotoluene, *PBEB* pentabromoethylbenzene, *PBBz* 1,2,3,4,5-pentabromobenzene, *TBX* 2,3,5,6-tetrabromo-*p*-xylene)

the general population in the BFR production area that was studied to BFRs except for DBDPE. In contrast, 80 % of the exposure of the general population of USA to BFRs was estimated to come from dietary intake (Vonderheide et al. 2008). The predominant DBDPE exposure pathway for the inhabitants of the study area was found to be dietary intake, which is very different from the dominant exposure route for the other BFRs that were analyzed. It is interesting that the dominant exposure pathways for DBDPE and BDE209 are different even though their structures and usage patterns are very similar.

**Conclusions**

Out of all of the BFRs that were analyzed, BDE209 was the dominant BFR, followed by DBDPE. With the restriction of the production and application of BDE209 all around the world, its main alternative product DBDPE is becoming another important contaminant in the production source area. The contributions of dietary intake, the inhalation of air, and the ingestion of indoor dust to the total intake of the BFRs (except for DBDPE) were 16, 82, and 2 %, respectively. This indicates that inhalation is the predominant pathway for male adult exposure to BFRs except for DBDPE in the



**Fig. 4** Relative contributions of the three exposure pathways

study area. The dominant exposure pathway in the study was different from the dominant exposure pathway at e-waste recycling sites and in other areas where BFRs are not produced. The estimated exposure of male adults to BDE209 through the inhalation is the highest in the world. Thus, effective measures should immediately be taken to decrease human exposure to BDE209 in the Binhai Economic Development Zone in Weifang City. Further researches are urgently needed into the exposure of the inhabitants of the study area to alternative BFRs and the health impacts caused by that exposure.

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