AN ASSESSMENT OF DIETARY INTAKE OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN CHINA

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Introduction

Polybrominated diphenyl ethers (PBDEs) were one class of brominated flame retardants (BFRs) used for several decades to protect people from fires, which have been widely used as non-reactive additives in textiles, polyurethane foams, thermoplastics, and electronic appliances, originating from three commercial PBDE mixtures: Penta-, Octa- and Deca-BDE[1, 2]. Due to their persistent characteristics and toxicological effects, components of the Penta- and Octa-BDE commercial mixtures have been recently added to the list of the Stockholm Convention of the Persistent Organic Pollutants (POPs) to be eliminated from production and use[3]. PBDEs are ubiquitous in environmental and biological samples worldwide because of persistence and long-range transport[4]. Because of their lipophilicity, both PBDEs and PCBs can be accumulated through the food chain, which would lead to concerned contamination levels in certain foods, especially fish and fishery products[2]. Therefore, the contamination status of PBDEs in the food and their potential health risk has being a matter of great concern in the world.

Over the past 30 years, China has been rapidly industrializing which has resulted in great release of some organic compounds into the environment[5]. It is urgent to monitor levels of chemical contaminants in various food samples and assess dietary exposure as well as potential health risk. In this study, a national wide survey was conducted to investigate levels of PBDEs and indicator PCBs in various foodstuffs and evaluate the dietary exposure of non-occupational population in China by a total diet study (TDS).At the end, the risk assessment was performed to determine the potential health risk from these pollutants in China

Materials and methods

The present study was conducted as a part of the Chinese TDS performed in 2007, the methodology has been detailed elsewhere[6]. The data of food consumption was obtained by a 3-day household dietary survey that documented all the food consumed by a weighing and recording method. The food consumption survey was conducted in 12 provinces in China, including Heilongjiang, Liaoning, Hebei, Shanxi, Ningxia, Henan, Shanghai, Fujian, Jiangxi, Guangxi, Hubei, and Sichuan. Food samples were collected from local food markets, grocery stores or rural households in each province, and then cooked and prepared according to the local habits. The composite of each food group was made by bending the prepared foods with weights proportional to the average daily consumption in each province. Eight food groups were selected in this study, including aquatic foods, meats, eggs, milk, cereals, legumes and nuts, tubers, and vegetables.

The analysis of PBDEs was described elsewhere[7], with slightly modification. Briefly, approximately 50 g of food sample was freeze-dried and spiked with ^{13}C-labeled internal standards of PBDEs (^{13}C-BDE-28, -47, -99, -100, -153, -154 and -183). The samples were extracted with a mixture of 50% hexane/dichloromethane (1:1) by using an Accelerated Solvent Extractor (ASE300, Dionex, USA) at 120^{o}C and 1500 psi. The bulk lipid was removed by shaking with acid-modified silica-gel after solvent evaporation, and further cleanup was achieved using a Power Prep instrument (Fluid Management Systems, Waltham, MA, USA). The fraction containing the PBDEs was collected. After concentrating this fraction to approximately 50 µL, the ^{13}C-labeled injection standards (^{13}C-BDE-77, and -138) were added prior to instrument analysis. The identification and quantification was performed by high resolution gas chromatography - high resolution mass spectrometry (HRGC/HRMS, MAT95XP, ThermoFinnigan, Germany). A DB-5MS capillary column, 15 m × 0.25 mm i.d. × 0.1 µm, was applied for the analysis of PBDEs.

Estimated dietary intake of PBDEs was calculated by multiplying the concentration of PBDEs in each food composite from each region by the consumption data, respectively. The mean and the 97.5th percentile of the daily exposure levels were used to represent the dietary exposure for average and high consumer, respectively. The concentration of the not detected (ND) congener was set to half of the limit of detection (LOD). The health risk of dietary PBDEs exposure was assessed by calculating the hazard quotient that was equal to the ratio of daily dietary intake per kilogram bodyweight (kg^{-1} bw) to the reference dose (RfD) recommended by US EPA[8]. The draft RfD value was 0.1μg kg^{-1} bw day^{-1} for both BDE-47 and BDE-99, and 0.2 μg kg^{-1} bw day^{-1} for BDE-153[9].

Results and discussion

Dietary intake of PBDEs for average and high consumer based on body weight results by age/sex groups are listed in Table 1. The dietary exposure to PBDEs for average consumer and high consumer varied from 0.7 to 1.5 ng kg^{-1} bw day^{-1}, and from 2.0 to 4.2 ng kg^{-1} bw day^{-1}, respectively. Some studies have shown a decreasing trend of dietary intake of PBDEs per kilogram bodyweight with age[10]. In the present study, there was a significantly negative correlation between dietary intake of PBDEs and the age because of higher food consumption per kilogram of body weight for young individuals. Moreover, although no sexual difference of dietary PBDEs exposure per kilogram bodyweight was found, the amount of dietary intake of PBDEs per day for the male was significantly higher than that for the female possibly because of higher food consumption for the male.

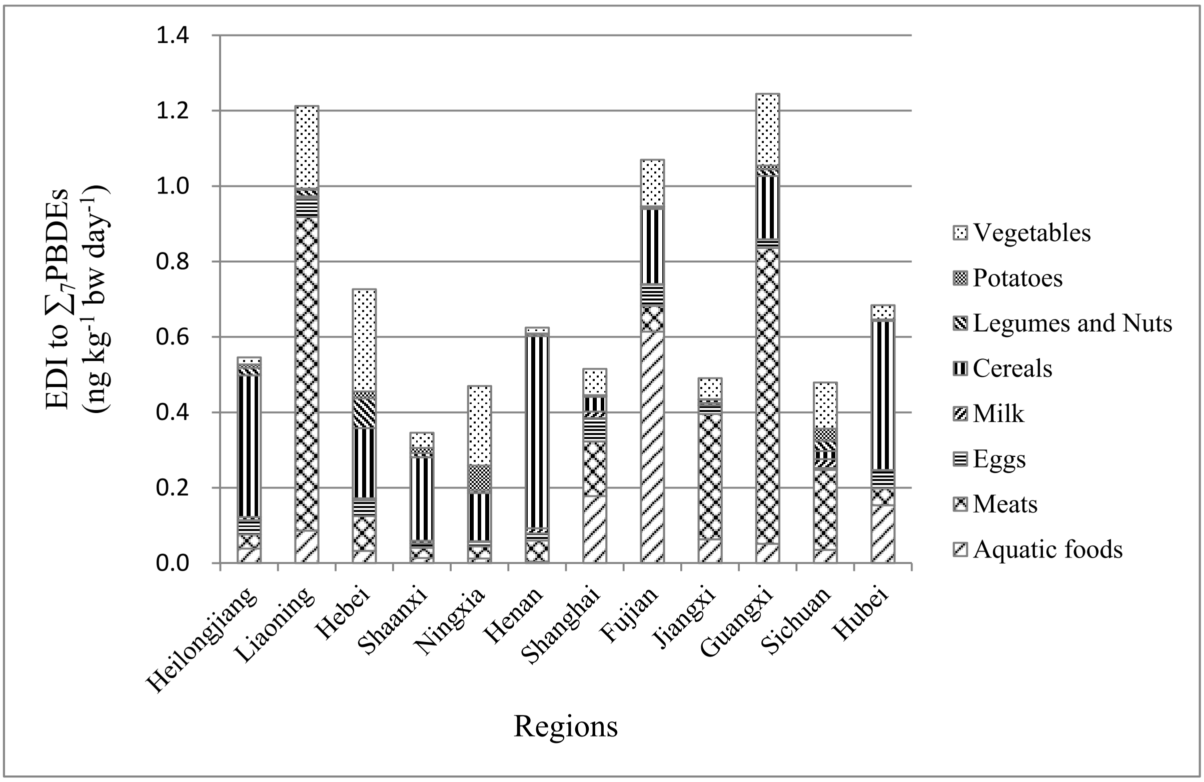
Table 1 Estimated dietary exposure to PBDEs for various age/sex groups in China (ng kg^{-1} bw day^{-1}, ND=1/2)

Age groups (year)		Gender	$\sum_7$PBDEs	
			mean	97.5^{th} percentile
Children	3 – 6	male	1.5	4.0
		female	1.5	4.5
	7 – 12	male	1.3	3.9
		female	1.3	4.2
	13 – 17	male	0.9	2.6
		female	0.9	2.8
Adults	18-44	male	0.8	2.7
		female	0.8	2.3
	45-59	male	0.7	2.3
		female	0.7	2.0
	≥60	male	0.7	2.3
		female	0.7	2.0

In this present study, average estimated dietary intake of PBDEs for adult Chinese population was 0.76 ng kg^{-1} bw day^{-1}. Many studies have been conducted in some countries or regions to systematically estimate dietary PBDEs exposure for residents. However, because of different methodology applied in various studies as well as different sampling year, the interpretation of these results should be cautious. The average dietary intake of PBDEs for adult Chinese was lower than that in Norway[11], Spain[12], Germany[13], and comparable or slightly higher than that in Finland[14], Sweden[15], Belgium[16], the Netherlands[17], and Japan[18]. Moreover, PBDEs levels were detected in various un-cooked foods in most of these studies, which might lead to slight overestimation of dietary exposure[16, 19]. However, a further study in Spain has shown that cooking does not all lead to the reduction of PBDEs levels in foods[20]. Thus, it is necessary to take into influence of cooking process on contamination levels in foods for the actual estimation of dietary exposure.

The average estimated daily intake (EDI) of PBDEs for adults from various regions results by various food groups was depicted in Figure 1. Among various regions in China, the minimum dietary intake of PBDEs was 0.35 ng kg^{-1} bw day^{-1} found in Shanxi, and the maximum was 1.24 ng kg^{-1} bw day^{-1} foud in Guangxi. The highest percentage contributor to average dietary intake in China corresponded to meats (32%), followed by cereals (27%), vegetables (16%), and aquatic foods (15%). Depending on national or regional food habits and culture, the relative contribution of different food items to total dietary PBDEs intake might vary considerably. In European countries, fish is usually the main contributor to the dietary PBDEs exposure, but also other food groups like dairy products and meats has been shown high contribution to the dietary intake[11-16]. In Japan, fish is the predominant contributor to the dietary PBDEs because of consumption of large quantities of fish[18]. In United States, the highest contributor to dietary PBDEs intake corresponded to meats rather than fish because of the tendency to eat less fish in North America[21,10]. In China, large variations in contribution of various food groups to dietary PBDEs intake were also found among regions in the present study, which might result from considerably geographical variations in food consumption as well as PBDEs contamination levels. The meat would make more contribution than aquatic foods in most regions, possibly because of more consumption of meats than aquatic foods, except Shanghai and Fujian where aquatic foods made the highest contribution because of relative high consumption of these foods. For milk, the contribution to dietary PBDEs intake could be negligible due to relative small consumption of milk in China as well as very low PBDEs contamination levels. Moreover, impressively high contribution to total dietary PBDEs intake was made by plant origin foods, which would be resulted from considerable consumption of these foods in China, although very low levels of PBDEs were detected. Thus, plant origin foods such as cereals and vegetables should not automatically be omitted from the calculation of dietary exposure.

Figure 1.Estimated daily intake (EDI) of $\sum_7$PBDEs for adults from various regions in China



In our previous study, the human body burden of PBDEs for general population was estimated by determination of PBDEs in human breast milk samples in China[7]. There was a weak but significant correlation between levels of total PBDEs in breast milk and dietary PBDEs exposure per kilogram bodyweight ($r=0.69$, $p<0.05$), indicating that dietary intake should be a major route of PBDEs exposure in China. The weak correlation might be caused by other exposure routes occurred in China.

The estimated hazard quotients for PBDEs were all far less than 1, even on the basis of the 97.5^{th} percentile dietary exposure, suggesting a very low non-cancer risk associated with dietary PBDE exposure in China. However, much more stringent reference threshold ranged from 0.23 to 0.30 ng kg^{-1} bw day^{-1} was established in a Dutch study based on the reproductive toxicity[17]. Comparison with this data, the dietary exposure to BDE-99 for average consumer of children touched it. It is notable that the toxicological values presented in this study present a source of uncertainty because of possible cumulative effects between congeners as well as various chemicals, and missing RfD values for other PBDEs congeners. Nevertheless, further studies and strict legislations must be done to try our best for the reduction of levels of POPs in foods and dietary exposure, and the protection of the health.

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