LEVELS AND PATTERNS OF PBDES IN CHILDREN FROM DALIAN, CHINA

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Abstract
The levels and patterns of PBDEs in children's plasma from Dalian, China were studied for the first time. Seventeen PBDE congeners (BDE-30, 28, 35, 37, 75, 47, 66, 100, 99, 116, 155, 154, 153, 183, 181, 190 and 209) in 29 plasma samples were measured. Median of PBDE concentrations was 31.61 ng g^{-1} lipids. BDE-153 was the predominated congener, followed by BDE-99, 47, and 183. Higher abundant of BDE-183 may suggest more Octa-BDEs used in China. No significant differences were observed between males and females or among different age groups. The levels of PBDEs in children's plasma in the present study were much higher than those in no-occupational exposure people from GuangZhou, South China and those in human milk of general adults from other cities of China, but were at the moderate levels of those in children around the world. These results suggest that children in Dalian were at high risk of exposure to PBDEs.

Introduction
Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants (BFRs) widely used in a variety of consumables, such as electrical and electronic products, textiles, foams and fabrics[1]. Their extensive use[2] , relatively high potential for bioconcentration and biomagnification[3] have resulted in their ubiquity in the environment[4], biota[5] and people[6]. Moreover, PBDEs are found toxic to the animals, and have potential adverse effects on human health[7]. In this general context, the effects of PBDEs on specific vulnerable population groups appear as a critical issue.

PBDEs make their way into the human body primarily through food intake[8], and ingestion of dust [9]through inhalation (particularly for children). Now PBDEs were being called "indoor POPs"[10]. It is necessary to assess the risk of exposure to PBDEs, especially for children.

Human samples like plasma, serum, and breast milk are nondestructive matrices adequate for monitoring human exposure to PBDEs[11]. Most data on human PBDEs exposure are from Europe and North America [6,12]. A few reports are from Asian. PBDE levels in humans from China, especially for general populations, are clearly more limited. In addition, data on exposure levels in children are extremely scarce, and none in China up to now, to our best knowledge. Studies showed higher concentrations in children than in adults [13,14].

In the current study children's plasma were collected from Dalian, to assess PBDEs exposure in children. The main objective was to provide the primary information on concentrations and congener specific profiles of PBDEs in children from Dalian.

Materials and Methods
Sampling
We collected 29 blood samples (15 males, 14 females) randomly in Dalian Children's Hospital in June, 2008, from donors aged ranging form 0 to 11 years.

Chemicals
"BDE-CM" (contained BDE-28, 47, 99, 100, 153, 154, 183 and 209) and individual standards: BDE-30, 35, 37, 66, 75, 116, 155, 181, and 190, internal standards: BDE-166 and surrogate standard: PCB-204 were all purchased from Accustandard (USA). *n*-hexane, acetone, dichloromethane, isopropanol, ethanol and methyl tetra-butyl ether (MTBE) were of pesticide grade (Tedia, USA); potassium hydroxide and tetrabutylammonium hydrogen sulfate (TBA) were of analytical grade, obtained from Tianjin Bodi and Shanghai Guoyao Chemical companies, China, respectively.

Extraction and Clean-Up

Extraction and gravimetric lipid weight determination were performed by following the procedure described by Hovander et al [15]. Briefly, surrogate standard (PCB-204) was added to the plasma in a test tube, vortexed and then left to equilibrate overnight. Hydrochloric acid and 2-propanol were added to denaturize the proteins and release the lipids and the organohalogen compounds. The analytes were extracted by hexane and methyl tert-butyl ether (V/V, 1:1). The organic phase was washed with a solution of potassium chloride (1%), followed by evaporation to dryness for gravimetric determination of extracted lipid content. The analytes and lipids were redissolved in hexane. Potassium hydroxide was added to remove acidic impurities. The neutral extract underwent further sulphur clean-up[16]. The samples were then blowed to near dryness under a gentle stream of nitrogen. The internal standard was added prior to GC/MS analysis.

Instrument Analysis

PBDEs were analyzed by Agilent GC6890-MS5975N, and operated in the negative chemical ionization mode with selected-ion monitoring (SIM). DB-XLB column (15 m × 0.25 mm, 0.1 μm film thickness; J & W Scientific, Folsom, CA, USA) was used. The injector temperature was 280 °C. Auto injection of the 1 μL sample was conducted at the splitless mode. Methane was used as reaction gas and helium as the carrier gas at a flow rate of 1.2 mL/min. The ion source and interface temperatures were set at 150 °C and 300 °C, respectively. The temperature of the GC oven was programmed as follows: 90 °C (2 min), 15 °C /min to 320 °C (7 min). The compounds were monitored at m/z 79 and 81 for the 2-7 brominated BDEs and m/z 79, 81, 487 and 489 for BDE-209, m/z 428, 430 for PCB-204.

Quality Assurance/Quality Control

Prior to use, all glassware was washed with detergent, rinsed with warm tap water, and triple-rinsed with distilled water. After oven drying, all glassware was rinsed with ACS-grade acetone and hexane and baked at 450 °C for 4 hours. A procedural blank was run in parallel with every ten samples to check for laboratory contamination and concentrations of most target compounds were below detection limit (except for BDE-28, 153, 183 and 209). The average amount of PBDEs in blanks was subtracted from the amount in the samples. Sample recovery was evaluated using surrogate standard PCB-204, and the average recovery was 109 ± 12.7%. Recoveries were also evaluated by spiking blanks with the standards (all the 17 PBDEs), and were found to be 87.1 ± 4.0% ~ 106.9 ± 5.7%.

Results and Discussion

PBDE Levels in Children's Plasma

Generally, the concentrations of ΣPBDEs from this study (Table 1) were much higher than those in adult serum from Guangzhou (4.4 ng g^{-1}lipid) [17], breast milk from Beijing (1.17 ng g^{-1}lipid) [18], Tianjin (2.8 ng g^{-1}lipid) [19] and Taiwan (3.93 ng g^{-1}lipid) [20]. However, the PBDE levels in this study were lower than those in the adults from Guiyu (91 ng g^{-1}lipid), an electronic waste dismantling region, Guangdong, South China [21], representing occupational exposure, but higher than those in the adults from Haojiang (11 ng g^{-1}lipid), a nearby region where the fishing industry dominates in Guangdong [21], when expressed as the ΣPBDEs of tri- to hexa-BDEs (BDE-28, 47, 85, 99, 100, 153, 154 and 183).

Table 1 Concentrations of PBDEs (ng g^{-1} lipid) in children's plasma from Dalian (n = 29)

Analyte	Range	Analyte	Range
BDE-30	0.00 ~ 7.13	BDE-155	0.00 ~ 8.39
BDE-28	0.00 ~ 21.89	BDE-154	0.00 ~ 14.76
BDE-75	0.00 ~ 21.67	BDE-153	0.00 ~ 27.14
BDE-47	0.00 ~ 19.44	BDE-183	0.00 ~ 16.73
BDE-66	0.00 ~ 12.82	BDE-181	0.00 ~ 6.88
BDE-100	0.00 ~ 11.90	BDE-190	0.00 ~ 9.44
BDE-99	0.00 ~ 18.06	ΣPBDEs	0.00 ~ 188.37

When compared with children from around the world (Table 2), PBDE concentrations in the present study were much higher than those in newborns and 4 years old children from Menorca Island [8], and 7 years old children from Faroe Island [22], and comparable with those in Mexico children [23] and newborns from Indiana, USA [24], but lower than those in 0 ~ 4 years old children from Australia[14] and much lower than those in the two children from California, USA [25].

Several studies focusing on the different age groups were published (see Table 2), which shows that young people have higher PBDEs level than adults. Thomsen and co-workers [26] assessed the temporal trends and influence of age and gender on levels of selected PBDEs in human serum from Norway. It was found that the PBDE concentrations in the serum from the different age groups were relatively similar, except for the age group 0 ~ 4 years, which had 1.6 ~ 3.5 times higher serum concentrations, but lower than those in this study. Fischer et al. [25] compared PBDE concentrations in blood drawn from a family of four, and found that PBDE levels were much higher in the infant (18-month-old son: 450 ng g^{-1}lipid) and young child (5-year-old daughter: 245.5 ng g^{-1}lipid) than those in their parents (35-year-old father: 67.5 ng g^{-1}lipid; 36-year-old mother: 124 ng g^{-1}lipid).

Table 2 Concentrations of ΣPBDEs in children's blood from different countries/regions (ng g^{-1} lipid)

Countries /regions	n	Age(years)	Mean/median of ΣPBDEs (Σ_{Low}BDEs[a])	Congeners in ΣPBDEs	Reference
Dalian, China	29	0 ~ 11	40.08/31.61 (33.44/31.61)	BDE-30, 28, 75, 47, 66, 99, 100, 153, 154, 155, 183, 181, 190	This study
Menorca Island	92 244	newborn 4	6.2/ 4.3/	BDE-17, 28, 47, 99, 100, 153, 154, 183	8
Mecico	173	6 ~ 13	29.45/	BDE-47, 99, 100, 153, 154	23
Faroe Islands	42	7	/5.72	BDE-47, 99, 100, 153, 154, 209	22
Indiana USA	12	newborn	/39	BDE-47, 99, 100, 153, 154	24
California, USA	4	35 (F[b]) 36 (M[b]) 5 (D[b]) 18 months (S[b])	67.5/ 124 / 245.5 / 450 /	BDE-47, 99, 100, 153, 154	25
Australia	85 pools	0 ~ 4 5 ~ 15 16 ~ 30 31 ~ 45 46 ~ 60 > 60	73/75 28/29 19/18 17.5/17 15/13.5 13.5/11.5	BDE-15, 17, 28, 47, 66, 71, 85, 99, 100, 119, 126, 138, 153, 154, 183, 209	14

[a] Sum of BDE-28, 47, 85, 99, 100, 153, 154 and 183; [b] F – father, M – mother, D – daughter, S – son

PBDE Congener Profiles

Generally, BDE-153, 99 and 47 were the most abundant PBDE congeners in this study, attributing 25.2 %, 21.9 % and 19.4 % respectively to ΣPBDEs, followed by BDE-183, 100, 66, and 154. BDE-47, 100, 99, 154, 53 and 183, which are the most frequently reported congeners in previous studies, together accounting for about 83 % of ΣPBDEs. This preliminary report indicates the need for further research in more child-related samples, such as dairy products, breast milk, toys and urine, to assess the exposure route and sources of PBDEs for children in China and their health effects.

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