Polybrominated diphenyl ethers in human milk from Beijing, China

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a family of chemicals which are widely used as flame retardants in electronic appliances, textiles, furnishings and other products. Due to their persistence and bioavailability/biomagification in combination with large consumption and disposal, PBDEs have become ubiquitous in biological and environmental samples worldwide [1]. Risks associated with PBDEs exposure to animals have been founded in laboratory, but the health effects related to PBDE exposure to human has not been identified[2,3]. As emerging environment contaminants, these compounds are a matter of growing concern. Studies on PBDEs levels in breast milk have been conducted to assess the extent human exposure, especially infants, in some countries [2-8]. Human breast milk is an ideal biomarker to monitor the human burden of PBDEs and evaluate the exposure of these chemicals to infant via breast feeding. In this study, Human milk samples were collected to examine the levels of PBDEs in Beijing.

Materials and methods

The selection of voluntary mothers and collection of human milk samples followed the 'Guideline for Developing a National Protocol' of the Fourth WHO-Coordinated Survey of Human milk for Persistent Organic Pollutants in Cooperation with UNEP. Breast milk samples were collected from 40 healthy mothers in 4 different districts of Beijing including Daxing District (DX), Dongcheng District (DC), Chongwen District (CW) and Pinggu District (PG) in 2007. Age and weekly consumption of food of animal origin (WCFAO) were collected by a questionnaire when milk samples were collected (Table 1). Donors were all primipara (first-time) mothers without occupational exposure, and the average age of mothers was 27. All

of the mothers were told the objective of this study and signed the participant information and consent form.

Analysis of PBDEs was performed according to the USEPA Method 1614 Draft using isotope dilution techniques and high resolution gas chromatograph coupling to high resolution mass spectrometry (HRGC/HRMS) with some modification [4]. Briefly, approximately 100mL of human milk sample was freeze-dried and spiked with $^{13}C_{12}$-labled surrogate spiking solution. The samples were Soxhlet-extracted with a mixture of 50% hexane/dichloromethane (1:1). After gravimetric lipid determination, the lipid was removed by shaking with acid-modified silica gel. After purifying and concentrating, extracts were determined by HRGC/HRMS. Prior to injection, the $^{13}C_{12}$-labled injection standards were spiked into each extract.

Result and discussion

Seven selected congeners of PBDEs were detected in all individual samples from Beijing. The concentrations are shown in Table 2. The mean±standard deviation and median ∑PBDEs concentrations were 1.58±1.18 and 1.27 ng g^{-1} lipid respectively, with a range of 0.30-5.79 ng g^{-1} lipid. BDE47, BDE153 and BDE28 were the predominant congeners in breast milk samples and consist of 29%, 26% and 25% of the total of sum PBDEs respectively, with a range of 7.9-50.1%, 8.4-53.4% and 10.5-46.5%. The other four congeners (BDE99, BDE100, BDE154 and BDE183) contributed to 20% of the total of sum PBDEs.

Dongcheng District and Chongwen District are located in urban area, while Pinggu District and Daxing District are in rural area. The concentration of ∑PBDEs in urban samples (1.99 ng g^{-1} lipid) showed higher level than in rural samples' (1.16 ng g^{-1} lipid). Significant statistical difference was found between samples from urban area and rural area (t=-2.32, p=0.025). In order to discover the reasons for the difference, the relationship between WCFAO and PBDE levels were determined. Because the WCFAO of CW5 (40.0 kg/week) showed significant difference from others, this sample was excluded in the determination of correlation between WCFAO and PBDE levels. The WCFAO of mothers from urban area (4.0kg/week) was more

than that of rural mothers (2.8kg/week), and statistical difference was shown between areas (t=-2.256, p=0.036). The significant correlation was also found between WCFAO and ∑PBDEs (r=0.346, p=0.031). The prime exposure route is unclear up till now, while the high potential exposure pathway of PBDEs is diary instak for human. Hence, consumption of animal origin food seems to be part of the reason for the geographical difference of PBDE levels. The correlation was founded not only between WCFAO and BDE47 but also between WCFAO and BDE99 (r=0.392, p=0.014, r=0.428, p=0.007, respectively). However, relationships between WCFAO and other PBDE congeners (including BDE28, BDE100, BDE153, BDE154 and BDE183) were not shown (p>0.05), which might be related to different levels of PBDE congeners in different foodstuffs in Beijing. Concentrations and patterns of PBDE congener in fishes, meats and eggs were different in a Norwegian study [9]. PBDEs were also detected in vegetables. Concentrations and patterns of PBDE congeners in a leafy vegetable and root vegetables were different [10]. The further research would be useful to determine the relationship between the human exposure of PBDE congeners and various foodstuffs. Furthermore, there was no correlation between age and PBDE levels (p>0.05), which might be related to the complex human exposure of PBDEs.

In our previous study, 205 individual breast milk samples were collected in Beijing in 2005 and six PBDE congeners (BDE47, BDE99, BDE100, BDE153, BDE154 and BDE183) were selected for determination. There were no statistical differences between concentrations of PBDE congeners in human milk samples from Beijing in 2005 and 2007 (p>0.05). Time-trend study conducted in Japan shows that bans on usage of tetra-BDE can result in decreasing trends of the related congeners in a short period time, but the delayed leakage/disperse may cause increasing trends of some PBDE congeners [5]. Due to their persistence, bioaccumulation and toxic nature, the Europe Union has banned all uses of commercial penta-BDE and octa-BDE in the

Table 1

Main information of volunteer mothers

Pginggu District			Daxing District			Dongcheng District			Chongwen District		
Samples	WCFAO (kg/week)	Age (years)	Samples	WCFAO (kg/week)	Age (years)	Samples	WCFAO (kg/week)	Age (years)	Samples	WCFAO (kg/week)	Age (years)
PG1	1.0	24	DX1	3.0	26	DC1	1.0	22	CW1	2.0	30
PG2	2.7	23	DX2	1.3	21	DC2	2.0	30	CW2	3.0	28
PG3	1.5	23	DX3	3.0	21	DC3	5.5	29	CW3	4.0	25
PG4	2.5	22	DX4	4.0	28	DC4	4.0	23	CW4	2.5	29
PG5	2.8	29	DX5	3.0	29	DC5	6.0	29	CW5	40.0	29
PG6	3.0	28	DX6	3.0	25	DC6	2.5	24	CW6	7.5	27
PG7	3.7	22	DX7	4.0	30	DC7	7.0	30	CW7	2.0	26
PG8	3.5	26	DX8	3.0	27	DC8	6.0	30	CW8	2.3	29
PG9	4.5	20	DX9	1.5	23	DC9	4.0	29	CW9	8.0	31
PG10	2.7	25	DX10	3.0	31	DC10	3.5	30	CW10	3.0	31

Table 2

PBDEs concentrations in 40 individual human milk samples from Beijing

Samples	Concentration of PBDEs congeners (ng/g lipid wt)							
	PBDE28	PBDE47	PBDE99	PBDE100	PBDE153	PBDE154	PBDE183	∑PBDEs
PG1	0.56	0.42	0.07	0.08	0.35	0.03	0.06	1.57
PG2	0.47	0.35	0.08	0.06	0.27	0.03	0.07	1.32
PG3	0.10	0.23	0.05	0.05	0.17	0.03	0.04	0.69
PG4	0.20	0.32	0.10	0.06	0.35	0.02	0.04	1.09
PG5	0.24	0.05	0.03	0.02	0.23	0.01	0.04	0.63
PG6	0.15	0.16	0.03	0.03	0.22	0.02	0.07	0.68
PG7	0.19	0.20	0.04	0.04	0.27	0.02	0.07	0.83
PG8	0.10	0.05	0.01	0.01	0.23	0.02	0.04	0.46
PG9	0.32	0.21	0.02	0.03	0.43	0.02	0.07	1.11
PG10	0.15	0.20	0.04	0.04	0.22	0.02	0.04	0.72
DX1	0.28	0.69	0.23	0.27	0.59	0.18	0.12	2.36
DX2	0.21	0.48	0.14	0.16	0.34	0.09	0.09	1.52
DX3	0.12	0.19	0.02	0.03	0.31	0.01	0.04	0.72
DX4	0.21	0.19	0.03	0.08	0.41	0.03	0.07	1.02
DX5	0.16	0.42	0.10	0.09	0.26	0.05	0.05	1.13
DX6	0.27	0.29	0.07	0.07	0.39	0.05	0.08	1.21
DX7	0.10	0.12	0.02	0.03	0.31	0.02	0.11	0.70
DX8	0.16	0.20	0.05	0.04	0.58	0.02	0.10	1.15
DX9	0.12	0.05	0.01	0.01	0.10	0.00	0.02	0.30
DX10	1.50	0.86	0.11	0.11	1.07	0.08	0.32	4.04
DC1	0.25	0.45	0.11	0.12	0.39	0.04	0.12	1.48
DC2	0.50	0.47	0.07	0.07	0.32	0.03	0.07	1.53
DC3	0.82	0.38	0.07	0.08	0.34	0.02	0.05	1.77
DC4	0.38	0.39	0.08	0.07	0.34	0.03	0.14	1.43
DC5	1.06	2.90	0.83	0.37	0.51	0.05	0.07	5.79
DC6	0.31	0.35	0.04	0.07	1.03	0.03	0.10	1.93
DC7	1.06	2.75	0.77	0.36	0.46	0.05	0.07	5.51
DC8	0.14	0.41	0.13	0.09	0.44	0.04	0.08	1.35
DC9	0.07	0.11	0.03	0.02	0.33	0.01	0.13	0.71
DC10	1.03	0.64	0.11	0.09	0.48	0.02	0.03	2.40
CW1	0.41	0.19	0.03	0.04	0.24	0.01	0.07	1.01
CW2	0.76	0.67	0.11	0.12	0.31	0.03	0.07	2.08
CW3	0.21	0.31	0.11	0.13	0.57	0.04	0.10	1.47
CW4	0.32	0.24	0.04	0.05	0.30	0.01	0.05	1.02
CW5	1.21	0.56	0.10	0.17	0.45	0.04	0.12	2.65
CW6	0.58	0.49	0.14	0.12	0.36	0.05	0.09	1.83
CW7	0.51	0.38	0.07	0.22	0.98	0.04	0.09	2.30
CW8	0.44	0.42	0.08	0.10	0.61	0.03	0.08	1.76
CW9	0.11	0.13	0.04	0.02	0.46	0.02	0.04	0.82
CW10	0.17	0.24	0.05	0.04	0.38	0.03	0.06	0.96
mean	0.40	0.45	0.11	0.09	0.41	0.03	0.08	1.58
median	0.26	0.33	0.07	0.07	0.35	0.03	0.07	1.27

market, and the USA ceased the production of these two compounds [1]. The usage of these compounds is legal in China. The demand of brominated flame retardants is increasing annually in China [1]. Hence, further monitoring will be useful to determine changes of PBDE levels in breast milk and elucidate their contamination status.

The concentration of ∑PBDEs in breast milk from Beijing was much lower than those from USA, Brazil, Australia and UK, but the concentration of BDE28 was different. It was higher than other countries' (except USA's) [2,3,5-8]. As we known, BDE47 and BDE153 were main PBDE congeners in human breast milk samples [2-8]. However, BDE28 was also one of predominant PBDE congeners in breast milk samples from Beijing. BDE28 and BDE47 were the major compounds of commercial tetra-BDE which is a peculiar product used in Japan until 1990s [5]. High BDE28 level was determined in Japanese mothers' milk samples collected from Osaka in 1988, which was thought to be partly caused by the usage of commercial tetra-BDE in Japan [5].

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