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Polybrominated biphenyl ethers in breast milk and infant formula from Shanghai, China: Temporal trends, daily intake, and risk assessment

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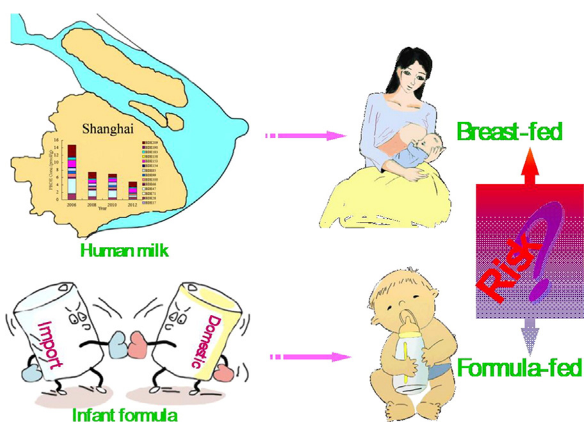
HIGHLIGHTS

- PBDEs in milk decreased from 2006 to 2012 which decreases by half every 4 years.
- No significant differences in PBDE conc. among the different brand infant formulas.
- No correlations between the total PBDE conc. and age, parity and BMI of mothers.
- Breast-fed infants are exposed to much more PBDEs during nursing than formula-fed ones.
- PBDE exposure has no obvious adverse effects on breast- and formula-fed infants.

GRAPHICAL ABSTRACT



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ABSTRACT

To investigate the temporal trend of polybrominated diphenyl ethers (PBDEs) in breast milk and assess the risks to breast- and formula-fed infants, breast milk and infant formula samples were collected from Shanghai, China. The PBDE concentrations decreased from 14.8 to 4.85 pmol/g lipid weight during 2006–2012, with a rate of decrease by half approximately every four years. Although there were no significant correlations between the total PBDEs in breast milk and age, parity, and pre-pregnant BMI of mothers, there were significant differences between primiparous and multiparous mothers for tri- to hepta-BDEs. PBDEs in breast milk were much higher than those in infant formula (equivalent to 91.9 vs. 5.25 pg/mL). Among the different brand infant formulas, there were no significant differences in their PBDE concentrations. The estimated daily intake of PBDEs by breast- and formula-fed infants suggested that breast-fed infants are exposed to much more PBDEs than formula-fed ones (12.9 vs. 0.72 ng/kg-bw/day). However, the hazard quotient values were much smaller than one, indicating that the ingested PBDEs did not exert obvious adverse effects on both breast- and formula-fed infants considering non-carcinogenic effect endpoint. This is the first report on temporal trend of PBDEs in breast milk from China.

Abbreviations: BMI, body mass index; BW, body weight; EDI, estimated daily intake; GC, gas chromatograph; HQ, hazard quotient; IRIS, Integrated Risk Information System; LOD, limits of detection; MS, mass spectrometer; PBDEs, polybrominated diphenyl ethers; QA, quality assurance; QC, quality control; RfD, reference dose; SIM, selective ion monitoring.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are one class of commonly used brominated flame retardants. They are generally added to polymers which are widely used in various consumer products, especially in electronic appliances (La Guardia et al., 2006). As a kind of additive flame retardants, they are not chemically bound to the materials, and may release from their products into the environment during the entire life span. Because of their high lipophilicity and stability in the environment, PBDEs are persistent with potential for bioaccumulation in organisms and biomagnification through food chains (Wu et al., 2009; Yu et al., 2012a). Finally, they can enter human bodies by various sources and routes, such as food and air by oral ingestion and inhalation, respectively (Domingo, 2012; Harrad et al., 2010). It is possible that PBDEs might cause neurodevelopmental deficits, immunotoxicity, adverse effects on the reproductive system, and endocrine disruption (Chao et al., 2011; Kim et al., 2013; Main et al., 2007; Martin et al., 2007; Zota et al., 2011). Thus, there is a growing public concern over the PBDE exposure. Technical Penta- and Octa-BDE products have been listed as priority-controlled contaminants by Stockholm Convention on persistent organic pollutants (UNEP/POPS/COP.4/17, 2009).

Breast milk is the natural and ideal food for infants, and contains the optimal composition of nutrients to meet the nutritional needs of the newborn. In addition, breast-feeding has practical advantages for mothers. However, many mothers have no sufficient breast milk, or no milk at all. As an alternative, infant formula, a manufactured food designed and marketed for feeding infants, is usually used. Therefore, monitoring of PBDEs in breast milk and infant formula provides a good marker for the PBDE exposure from the environment and the food chain, especially for mothers and their nursing infants (Chao et al., 2007; Devanathan et al., 2012; Dunn et al., 2010; Thomsen et al., 2010a).

Studies have shown that PBDE concentrations in breast milk in North America are at least 10- and can be 100-times higher than those in Europe and Asia because of production of PBDEs at large amounts and their wide usage in North America (Eslami et al., 2006; Fängström et al., 2008; Schecter et al., 2003; Zhang et al., 2011). Time-trend studies indicated that the PBDE levels in breast milk increased rapidly from 1970s, but appeared to have stabilized or decreased since late 1990s or early 2000s (Lind et al., 2003; Meironyté et al., 1999; Thomsen et al., 2007). This may be attributed to the restriction and ban on the production and usage of low brominated BDEs (technical Penta- and Octa-BDE products) in Europe and some countries, such as USA and Japan. Since March 26, 2014, the production, usage, and trade of tetra- to hepta-BDEs have been prohibited in China.

It has been estimated that human milk is the main exposure source of PBDEs for breast-fed infants (Carrizo et al., 2007). PBDEs in breast milk can pose adverse effects on nursing infants, who are far more sensitive than adults (Chao et al., 2011; Main et al., 2007). Hence, continuous surveillance on PBDE levels in breast milk is necessary to accurately evaluate the environmental impact of PBDEs on human health in China (Zhang et al., 2011). However, there has been no investigation on the temporal trends in PBDE levels in breast milk in China.

Therefore, it is critical to conduct surveys and build a continuous monitoring program for PBDEs to assess the impact on human health. Thus, the aim of the present study was to investigate contamination of PBDEs in breast milk and infant formula, and the temporal trends in the PBDE levels during the period of 2006–2012, as well as the associated risk to breast- and formula-fed infants via PBDE exposure. We also examined if PBDE concentrations in breast milk are associated with age, parity, and pre-pregnant body mass index (BMI) of mothers. To our best knowledge, this is the first report on the temporal trends of PBDEs in breast milk in China.

2. Materials and methods

2.1. Sample collection

To determine the temporal trends of PBDE concentrations, we collected breast milk samples in 2006 (n = 16), 2008 (n = 13), 2010 (n = 21), and 2012 (n = 30). A total of 80 breast milk samples were collected in an infant health hospital in Huangpu (combined to the district of Pudong in 2011), Shanghai. The donors, who came from different districts of the city, were all local residents who have lived in Shanghai for at least 5 years. Before sample collection, all mothers were told about the objective of this study and all of them agreed to participate in the study. Their ages, parities, and pre-pregnant heights and weights were recorded. Breast milk samples were collected from these donors within 5 days after delivery. For each donor, more than 20 mL of milk was collected by manual expression or pumping. The collected samples were stored in brown glass flasks at −20 °C until analysis.

To compare the daily intake of PBDEs for breast-fed infants with formula-fed ones and the associated health risks, infant formula samples were collected from Shanghai markets. The samples covered infant formulas (from cow milk) from nine brands for 1–6 or 1–12 month infants, including Beingmate (n = 5), Dumex (n = 4), Wyeth S-26 (n = 5), Frisolac (n = 5), Meiji (n = 4), Enfapro (n = 5), Nestle (n = 5), YiLi (n = 5), and Similac (n = 5), which account for at least 80% of the total consumption amounts in Shanghai markets. A total of 43 samples were collected in 2012 (the production time ranged from 2011 to 2012). The samples were purchased and stored at −20 °C until analysis.

2.2. Analytical methods

The methods used for sample extraction and cleanup were similar to those reported in our previous study (Zhou et al., 2012). In brief, breast milk samples were thawed and then homogenized through sonication. After spiking with the surrogate standards of ^{13}C-PCB141 and ^{13}C-BDE209, potassium oxalate solution (8%, w/w), ethanol, and diethyl ether were added before extraction. Generally, breast milk samples (8–10 mL) were extracted three times with *n*-hexane. The organic phases were combined and dried. The amounts of lipids were determined gravimetrically. Then, the lipids were redissolved in *n*-hexane, and the obtained solutions were passed through a Bio-beads S-X3 (Bio-Rad Laboratories, Hercules, CA, USA) packed glass column to remove lipids. The mixed solvent of dichloromethane and *n*-hexane (v/v = 1:1) was used as the mobile phase. The fractions containing PBDEs were collected, concentrated, and then passed through a silica-alumina column for further cleanup. The eluents containing PBDEs were collected and concentrated to 50 μL after the internal standard of ^{13}C-PCB208 was added. They were stored at −20 °C until analysis.

For infant formula samples, after adding surrogate standard of ^{13}C-PCB141 and ^{13}C-BDE209 to accurately weighed samples (3 g), the samples were added into 20 mL of acetonitrile. Then, anhydrous sodium sulfate (4 g) was added and the mixtures were vortexed violently for 1 min and centrifuged at 4200 rpm for 5 min. The supernatants were collected and the residues were extracted again. The organic phases were combined and dried. The residues were redissolved in 1 mL of *n*-hexane, and cleaned up with the same procedure as that used for breast milk.

2.3. Instrumental analysis

The PBDE concentrations were determined using a Hewlett-Packard (HP) 6890N gas chromatograph (GC) coupled to a 5975 mass spectrometer (MS). Negative chemical ionization mode was used. Splitless injection of a 1-μL sample was performed. The temperatures of injector and ion source were set at 280 and 250 °C, respectively. Quantification of