Chemosphere 87 (2012) 97–104

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Comparisons of polybrominated diphenyl ethers levels in paired South Korean cord blood, maternal blood, and breast milk samples

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ARTICLE INFO

Article history:
Received 20 February 2011
Received in revised form 24 November 2011
Accepted 28 November 2011
Available online 9 January 2012

Keywords:
Polybrominated diphenyl ethers
Cord blood
Maternal blood
Breast milk
Thyroid hormones

ABSTRACT

Polybrominated diphenyl ethers (PBDEs), commonly used flame retardants, have been reported as potential endocrine disruptor and neurodevelopmental toxicants, thus giving rise to the public health concern. The goal of this study was to investigate the relationship between umbilical cord blood, maternal blood, and breast milk concentrations of PBDEs in South Korean. We assessed PBDE levels in paired samples of umbilical cord blood, maternal blood, and breast milk. The levels of seven PBDE congeners were measured in 21 paired samples collected from the Cheil Woman's Hospital (Seoul, Korea) in 2008. We also measured thyroid hormones levels in maternal and cord blood to assess the association between PBDEs exposure and thyroid hormone levels. However, there was no correlation between serum thyroxin (T4) and total PBDEs concentrations. The total PBDEs concentrations in the umbilical cord blood, maternal blood, and breast milk were 10.7 ± 5.1 ng g^{-1} lipid, 7.7 ± 4.2 ng g^{-1} lipid, and 3.0 ± 1.8 ng g^{-1} lipid, respectively. The ranges of total PBDE concentrations observed were 2.28–30.94 ng g^{-1} lipid in umbilical cord blood, 1.8–17.66 ng g^{-1} lipid in maternal blood, and 1.08–8.66 ng g^{-1} lipid in breast milk. BDE-47 (45–73% of total PBDEs) was observed to be present dominantly in all samples, followed by BDE-153. A strong correlation was found for major BDE-congeners between breast milk and cord blood or maternal blood and cord blood samples. The measurement of PBDEs concentrations in maternal blood or breast milk may help to determine the concentration of PBDEs in infant.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in electronic appliances, paints, textiles, and furnishings. PBDEs are now viewed as ubiquitous environmental pollutants due to their high levels of production and their persistence and bioaccumulation in the environment (de Wit et al., 2010; Covaci et al., 2011). The presence of PBDEs has been extensively investigated in various foods and human tissues (Lorber, 2008; Frederiksen et al., 2009). In Asian countries, including South Korea, large quantities of PBDEs are used; South Koreans rank second to North Americans with regard to PBDE levels. Recently, the manufacture, distribution, and processing of products using penta- and octa-BDE congeners were prohibited in the European Union (EU), Canada, USA, and Asian countries. Deca-BDE is the only PBDE that is still manufactured and used worldwide including South Korea, with the exception of Sweden and Maine, USA (KEI, 2001). However, tetra-, penta-, and hexa-BDE mixtures are still detected in the environment because deca-BDE (BDE-209) can be broken down into the lower brominated congeners (Law et al., 2006; Chen et al., 2007). Deca-BDE is the only PBDE that is still manufactured and used in South Korea and other countries (KEI, 2001).

Recent studies have shown that PBDEs are detected in human maternal blood, breast milk, and adipose tissue samples (Foster et al., 2011; Frederiksen et al., 2010; Petreas et al., 2011). The levels of human exposure to PBDEs from in Asia–Pacific exhibit an

Abbreviations: BDE, brominated diphenyl ether; PBDEs, polybrominated diphenyl ethers; SPE, solid phase extraction; T4, thyroxine; TSH, thyroid stimulating hormone.

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doi:10.1016/j.chemosphere.2011.11.074

increasing trend for the past 30 years (Tanabe et al., 2008; Linderholm et al., 2010); however, the total PBDE levels in Swedish breast milk samples have recently been reported to be decreasing (Fängström et al., 2008). The total PBDEs concentrations in blood and breast milk were higher in America when compared to those of European (Wilford et al., 2005; Roosens et al., 2010). A previous study reported that total PBDEs concentrations in breast milk, including BDE-209, ranged from 26.4 to 586 ng g^{-1} lipid in South Korea (Kang et al., 2010). Another study reported the total PBDEs concentration calculated from the 13 most common congeners (BDE-15, BDE-28/33, BDE-47, BDE-49, BDE-66, BDE-85, BDE-99, BDE-100, BDE-140, BDE-153, BDE-154, and BDE-183) in both incinerator workers and the general population was 16.8 ± 7.5 ng g^{-1} lipid, indicating somewhat higher than those has been observed in other countries (Lee et al., 2007). Individual fetal blood PBDEs concentrations are similar to the corresponding maternal concentrations, implying that measurement of maternal PBDE blood levels would be useful in predicting fetal exposure (Mazdai et al., 2003). Recently, the assessment of fetal exposure to PBDEs has been examined by measuring their concentrations from umbilical cord blood (Herbstman et al., 2007; Antignac et al., 2009). However, there have been no studies of PBDE concentrations in paired samples of maternal, cord blood, and breast milk samples. The aim of this study was to investigate the correlations of PBDE concentrations between cord blood, maternal blood, and breast milk using paired samples. In addition, the relationship between PBDE concentrations and the level of thyroid hormones was examined as well.

2. Materials and methods

2.1. Subjects

A total of 21 healthy pregnant women between the ages of 25 and 41 years participated in this study. Study participation was voluntary. Blood samples were donated from mothers following cesarean section at the Cheil Woman's Hospital in Seoul, South Korea. A syringe was used to obtain blood from the umbilical cord vein after delivery. Baseline physical characteristics (e.g., birth weight and sex) of infants were also recorded at the time of birth. Maternal blood samples were collected into a heparin-containing blood collection tube after delivery. Serum was separated from whole blood by centrifugation and then transferred to glass bottles. The serum samples were coded and stored at −20 °C until analysis. Breast milk was collected using a breast milk pump at 7 d after delivery and stored in glass containers at −20 °C until analysis. Basic participant information, including smoking and drinking habits, age, gender, and present and previous occupations, was obtained from self-administered questionnaires at the time of enrollment. The sample collection procedure was approved by the Maternal and Fetal Research Committee (CGH-IRB-2008-13) at the Cheil Woman's Hospital. Informed consent was obtained from all participants.

In this study, a total of 21 paired samples were analyzed for PBDEs concentration. Table 1 summarizes the physical characteristics of the study subjects. The mean infant body weight, height, and head circumference were 2990 ± 752 g (range, 1575–4550 g), 46.9 ± 3.4 cm (range, 31.5–52.7 cm), and 32.7 ± 4.0 cm (range, 30.3–37.5 cm), respectively. No birth defects were documented.

Table 1
Physical characteristics of study subjects.

Subject characteristics (n = 21)	Mean ± SD	Median	Range
Maternal			
Age in years	30.3 ± 3.87	29	25–41
Pre-pregnancy body weight (kg)	51.7 ± 7.98	51	41–72
Post-pregnancy body weight (kg)	68.6 ± 13.9	66	50–96
Height (cm)	161 ± 6.24	160	150–171
Pre-pregnancy BMI (kg m^{-2})	20.9 ± 2.17	20.1	19.4–25.7
Gestation period (weeks)	36.9 ± 2.1	38.5	35.2–41.5
Infants			
Body weight (g)	2990 ± 752	3041	1575–4550
Length (cm)	46.9 ± 3.4	48.7	31.5–52.7
BMI (kg m^{-2})	13.3 ± 2.84	14.5	11.4–14.9
Head circumference (cm)	32.7 ± 3.98	33.8	30.3–37.5

2.2. Reagents and materials

The PBDE standards that contain 2,4,4′-tribromodiphenyl ether (BDE-28), 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99), 2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100), 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153), 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE-154) and 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether (BDE-183) were purchased from Wellington Laboratories (Guelph, ON, Canada). A mixture of ^{13}C-labeled BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-183 was purchased from Wellington Laboratories and used as internal standards (MBDE-MXFS, Wellington Laboratories). ^{13}C-labeled BDE-138 (MBDE-138, Wellington Laboratories) was used as a recovery standard. Acetone, *n*-hexane, dichloromethane (DCM), methanol (MeOH), and nonane (residue pesticide grade) were purchased from J.T. Baker Co. (Phillipsburg, NY, USA). Anhydrous sodium sulfate (Na_2SO_4) was purchased from Wako Co. (Tokyo, Japan). High purity sulfuric acid (98%), formic acid (99%) and silica gel were purchased from Merck (Darmstadt, Germany). All other chemicals were purchased from Fluka Chemical Corp. (Ronkonkoma, NY, USA). Silica gel was heated for at least 19 h at 130 °C and the acidified silica gel (2 g of 44% sulfuric acid impregnated, w/w) was prepared. All glassware was sonicated with detergent, rinsed with de-ionized water, and dried under a hood at room temperature. After dryness of glassware, all glassware was baked overnight at 400 °C. Before use, sonicated glassware was rinsed with acetone and hexane. A Visiprep™ SPE Vacuum manifold (Supelco Inc., Bellefonte, PA, USA) was used for extraction and clean-up procedures.

2.3. Sample extraction and clean-up procedures

PBDE extraction from blood serum was performed according to the modified method of Mazdai et al. (2003). All samples were thawed and homogenized. Internal standards (0.1 ng μL^{-1} mixture of ^{13}C-labeled BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183) were added to a sample vial and the solvent was evaporated with the cap off. The internal standards were re-dissolved in 100 μL acetone, and 2 mL cord blood sample was added. Then, the samples were vortexed and sonicated for 20 min at low intensity. The spiked cord blood samples were equilibrated overnight at 4 °C. Next, 2 mL formic acid and 3 mL de-ionized water were added to the samples, and the samples were equilibrated with ultrasonication for 20 min. Before sample loading, the HLB cartridges were activated with MeOH and water. Samples were loaded at a positive pressure of 2–4 psi. The HLB cartridges were then rinsed with 1 mL distilled water, and the pressure was adjusted to 6–8 psi to remove water from the cartridges. The sorbent bed was dried out thoroughly at <20 psi positive pressure under nitrogen for 10 min and again by centrifugation (4000 rpm) for 20 min. The cartridges were eluted three times with 3 mL DCM using a Visiprep™ SPE Vacuum manifold. The eluant was concentrated to ~1 mL under a gentle nitrogen stream. An empty 6 mL cartridge was filled with 2 g acidified silica, 200 mg activated silica, and 500 mg Na_2SO_4 (bottom to top) and was prewashed with 5 mL DCM. The concentrated eluate was loaded onto the top of the clean-up cartridge