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Partitioning of polybrominated biphenyl ethers from mother to fetus and potential health-related implications

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HIGHLIGHTS

- The expectant women living in e-waste recycling area might be highly exposed to PBDEs.
- The placenta could effectively hinder the transfer of PBDEs from mother to fetus.
- Higher-brominated BDEs transfer was hindered more by placenta, but they did not remain in more amounts in it.
- The concentration of BDE congeners among the paired samples could be fitted by equations.
- There was a significant association between BDEs and TT_4 levels in maternal serum.

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ABSTRACT

Presently, knowledge on the partitioning of polybrominated biphenyl ethers (PBDEs) from mother to fetus and the relationship between PBDE exposure and the levels of thyroid hormones (THs) needs to be extended further. In the present study, we investigated the concentrations of PBDEs in paired mother–fetus samples from 72 pregnant women in Wenling, China. The detection of PBDE concentration suggested that the expectant women living in Wenling for over 20 years might be highly exposed to PBDEs, which is largely ascribed to e-waste recycling activities in the local environment. The median concentration ratios between paired cord serum and maternal serum for higher-brominated BDEs were smaller than those for lower-brominated BDEs ($p < 0.05$). This result indicated that the placenta could hinder the transfer of PBDEs from mother to fetus, and the hindrance effect increased with higher-brominated congeners. Median ratios of paired placenta vs. maternal serum concentrations varied in a narrow range (0.15–0.25), with significantly lower value for BDE-209 than that for BDE-28 ($p < 0.01$). The extent of transplacental transfer was larger than that of placental retention for eight BDE congeners ($p < 0.01$). The concentration of BDE congeners among the paired samples could be fitted by equations, implying that their distribution could be predicted for each other ($p < 0.001$). There was a significant association between BDE-153 and TT_4 levels in maternal serum from Wenling local residents ($p < 0.05$), suggesting potential implications for fetal development and their mothers' health in e-waste recycling environment. In addition, it was found that the relationship between BDEs and TH levels was likely affected by the exposure duration of the population to PBDEs.

1. Introduction

Polybrominated biphenyl ethers (PBDEs) are a group of chemicals with 209 congeners and are widely used as flame retardants in commercial products. PBDEs have POPs characteristic, leading to ubiquitous exposure to humans and wildlife (Lyche et al., 2015). Even though stringent worldwide regulations have been adopted since the early 21st century, the PBDE-containing products are still in use for a long time. Therefore, it is expected that the continued release from the currently in-use and gradually

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abandoned PBDE-containing products will cause environmental contamination for a prolonged period in the future.

The transplacental transfer of BDE congeners has been proved consistently, and the extent of PBDE transfer across the placenta had been assessed roughly by the median values of concentration ratios between maternal blood and cord blood in the published literature (Meijer et al., 2008; Frederiksen et al., 2010; Jakobsson et al., 2012; Chen et al., 2013; Li et al., 2013; Zhao et al., 2013; Choi et al., 2014; Vizcaino et al., 2014). However, these ratios obtained in most studies have to be considered with caution because of the lack of transparency, including sample size, timing of sampling, statistical analysis with paired data, and so on, which did not allow proper quantification of the mother to child transfer (Jakobsson et al., 2012). To our knowledge, a mathematical model describing the partitioning relationship of PBDEs from mother to fetus is thus far unavailable.

Animal experiments have proved that PBDEs may be characterized as thyroid hormone (TH) disruptors (Talsness, 2008). In humans, because maternal THs substantially affect fetal neurodevelopment (Haddow et al., 1999), the relationship between prenatal exposure to PBDEs and serum TH levels has raised specific concern. However, previous studies have drawn controversial conclusions. Some studies did not find any association between PBDE exposure and TH levels, whereas other studies found certain correlations—yet the relationship was not definite for specific congener and specific TH (Czerska et al., 2013). Nevertheless, these antecedents, on the one hand, suggested the potential effect of PBDE exposure on the THs levels in humans, and on the other hand, they called for more sound and thorough work to understand the hidden relationship between PBDE exposure and TH levels during women's pregnancy because of the importance of THs in the early development of fetus.

The main purpose of this study was to quantify the partitioning of specific BDE congeners from mother into fetus through paired maternal serum, placental tissue, and cord serum collected simultaneously from the same women and explore the possible effect of PBDE exposure on maternal THs levels. The obtained result was helpful to understand the migration/transformation behaviors of PBDE and health effects of exposure to PBDEs in humans.

2. Materials and methods

2.1. Sample collection

The information on sample collection and sampling location had been described in two published studies (Ben et al., 2014; Lv et al., 2015). In brief, Taizhou is one of two largest e-waste recycling regions in China, while Wenling is one of two major cities executing the e-waste recycling activities in the Taizhou region. In total, in 2010–2011, 72 paired samples (including maternal blood, umbilical cord blood, and placenta) were collected from local hospital in Wenling, Taizhou, China. The donors could be classified as R_{20} group ($n = 48$) and R_3 group ($n = 24$). The donors in the R_{20} group ($n = 48$) were living or had recently lived in Wenling villages for more than 20 years, where e-waste recycling activities were undertaken, but did not directly participate in such activities. The donors in the R_3 group ($n = 24$) who had lived in Wenling for less than 3 years had not previously lived in villages where e-waste recycling activities were undertaken. After signing the informed consent, the donor's personal information was obtained through a questionnaire.

2.2. Sample extraction, clean-up, and analysis

The samples (5 mL for maternal serum, 10 mL for cord serum, and 2.0 g dry weight for placenta) were extracted and cleaned up following a previous procedure (Lv et al., 2015). In brief, both BDE-77 and ^{13}C-BDE-209, as the internal standard, were spiked into the serum or placenta sample before the extraction. Then, serum samples were denatured with HCl and isopropanol and ultrasonically extracted by the mixture solution of methyltert-butyl ether (MtBE) and hexane (Hex) with three times repeats. The combined extracts were washed with KCl solution, dried with Na_2SO_4, and then concentrated. Placenta samples were extracted ultrasonically three times with the mixture solution of MtBE, Hex, and dichloromethane with three times repeats, and then dried and concentrated. The concentrated extract for serum or placenta was cleaned up in a multilayer sulfuric acid silica gel column. The final elute of either placenta or serum was concentrated to 20–50 μL, and the known amount of the injection internal standard (BDE-166) was added before the GC/MS analysis.

PBDEs compounds were analyzed by Agilent 6890GC, coupled with 5973MSD. The MS performed in a negative ion chemical ionization and selected ion mode. The separation was performed using a RTX-1614 fused silica capillary column (0.25-mm ID and 0.1-μm film thickness; J&W Scientific, Folsom, CA, USA) with 30-m length for BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183, and 15-m length for BDE-209. The GC oven temperature was programmed as follows: maintaining the initial temperature 100 °C for 2 min; increased to 250 °C at a rate of 25 °C min^{-1}; ramped from 250 °C to 260 °C at a rate of 1.5 °C min^{-1}; and then heated up to high temperature of 310 °C at a rate of 25 °C min^{-1}, which was held for 27 min. The carrier gas used was high purity helium (≥99.9995%) with a flow rate of 1.0 °C min^{-1}, and methane was used as the reaction gas. Samples were injected in the splitless mode, and the injection volume was 1.0 μL. The injector, transfer line, and ion source temperatures were 150 °C, 150 °C, and 320 °C, respectively. The ion fragments monitored were m/z 79 and 81 for the tri-to octa-BDE congeners, m/z 488.7 and 486.7 for BDE-209, and m/z 492.7 and 494.7 for $^{13}C_{12}$-labeled BDE-209.

Lipids in placenta tissue extracts were determined by a gravimetric method, and a colorimetric method based on the sulfo–-phospho–vanillin reaction was used to determine the lipids in the serum samples (Phillips et al, 1989). The levels of THs, including thyroid stimulating hormone (TSH), total triiodothyronine (TT_3), total thyroxine (TT_4), free triiodothyronine (FT_3), and free thyroxine (FT_4), were obtained in the maternal serum samples using a chemiluminescent microparticle immunoassay at a local hospital. The personal information of donors and their infants, and TH levels in the maternal serum from 66 donors had been reported in a previous study (Ben et al., 2014), and are listed in Tables SI-1 and SI-2 of supporting information, respectively.

2.3. Quality control

The recoveries of the surrogate standards that were spiked into the samples before the extraction were 77–109% for BDE-77 and 61–80% for ^{13}C-BDE-209 in the maternal serum, 75–110% and 60–85% in the cord serum, and 72–107% and 68–89% in the placenta, respectively. Bovine serum and fetal bovine serum, and olive oil (0.1 g) were used to represent the method blank of serum and placenta, respectively. Seven replicates of method blank spiked with the mixture of target analytes were processed through the entire extraction procedure and analyzed. The method detection limits (MDLs) were defined as the mean plus three standard deviations of values associated with the analysis. On the basis of the maternal serum (5.0 mL), the cord serum volume (10.0 mL), dry weight of the placenta samples (2.0 g), average lipid concentration (6.4 g L^{-1} for the maternal serum, 2.3 g L^{-1} for the cord serum and 6.24% for the dried placenta), and injection volume (50 μL for the