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Polybrominated diphenyl ethers and indicator polychlorinated biphenyls in human milk from China under the Stockholm Convention

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HIGHLIGHTS

- PBDEs and indicator PCBs were measured in a national survey of breast milk.
- There was reduction of BDE-47, 99, 100, 153 in human milk from 2007 to 2011.
- Notable increase was observed for BDE-183 in most regions of China.
- A significant decline in total indicator PCBs with an average reduction of 41%.

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ABSTRACT

Seven congeners of polybrominated diphenyl ethers (PBDEs) (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153,BDE-154 and BDE-183) and six indicator polychlorinated biphenyls (PCBs) (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153 and PCB-180) were measured in 32 regional pooled human milk samples originating from 1760 volunteering primiparous mothers to evaluate the current human body burden of general population and the temporal trend in China. Individual human milk samples were collected following a WHO-designed procedure. This work is one of parts of the evaluation of effectiveness of Stockholm Convention performance. The concentration of $\sum_7$PBDEs ranged from 0.3 ng g^{-1} lipid to 4.0 ng g^{-1} lipid with a mean of 1.5 ng g^{-1} lipid. The concentration of $\sum_6$PCBs ranged from 2.3 ng g^{-1} lipid to 19.0 ng g^{-1} lipid with a mean of 6.6 ng g^{-1} lipid. By comparing with background determination in 2007, there was no significance for $\sum_7$PBDEs. However, BDE-47, BDE-99, and BDE-100 significantly decreased with an average of 45%, 48%, and 46%, respectively, from 2007 to 2011, and an increase of BDE-183 was founded in most regions. For $\sum_6$PCBs, there was a significant decline with an average reduction of 41% from 2007 to 2011. These results indicate the effectiveness of reduction and elimination of POPs in China. Future national human milk biomonitoring is worthy to be done to further evaluate the time trend and effectiveness of the Convention performance.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) are two classes of persistent organic pollutants (POPs). As flame retardants, PBDEs have been widely used as non-reactive additives in electronic and electronical appliances, textiles and furnishings, mainly originating from three commercial penta-, octa-, and deca-BDE mixtures (Lorber, 2008; Wang et al., 2007; Yu et al., 2016). Due to their toxicological effects, commercial penta-BDE and octa-BDE formulations have been phased out on the commercial production and usage in EU and United States since 2004 (Domingo, 2012; Frederiksen et al., 2009; Linares et al., 2015). In 2009, hexa- and heptabromodiphenyl ethers present in commercial octabromodiphenyl ether and tetra- and pentabromodiphenyl ethers present in commercial pentabromodiphenyl ether

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were added to the list of POPs of Stockholm Convention as amendments to the Annexes (Stockholm Convention Clearing House). These amendments were ratified by China and the production, circulation, use and import and export has been all prohibited since April 2014 (MEP of China, 2014). PCBs had been once widely employed as dielectric and coolant fluids, and the produce and use have been banned worldwide since 1970s (Arnich et al., 2009). However, due to their persistence and lipophilicity, these chemical pollutants are ubiquitous in environmental and biological matrix, including human samples (Covaci et al., 2003; Linares et al., 2015).

Owing to the non-invasive and lipid-rich, human milk is recommended by WHO as an ideal matrix to assess body burden of lipophilic chemicals in the mothers (WHO, 2007). In order to evaluate the body burden, human milk monitoring has been carried out in many countries. Concentrations of PBDEs in human milk are known to be significantly higher in North America than other regions (Guo et al., 2016; Marchitti et al., 2017; Siddique et al., 2012). Some previous studies have indicated that levels of PBDEs in human milk reached the peak during the period of late 1990s - early 2000s followed by an appearing downward trend in some countries result from the worldwide efforts on reduction/elimination of POPs, including the implementation of Stockholm Convention (Fängström et al., 2008; Guo et al., 2016; Lignell et al., 2009; Ryan and Rawn, 2014; Toms et al., 2012).

China produces and consumes a large quantity of products containing PBDEs (Yu et al., 2016) and used to be one of the main destinations of electronical wastes, e-waste, from developed countries that resulted in high body burden and negative health effects on workers in e-waste dismantling (Ni and Zeng, 2009). As one of the first signatories to the Stockholm Convention in 2001, China developed China's National Implementation Plan for the Stockholm Convention on Persistent Pollutants (NIP) (Stockholm Convention Clearing House, 2007) and many efforts have been made to reduce and eliminate POPs since then. In accordance with the NIP, the first national human milk monitoring on POPs was conducted in China in 2007 and various POPs such as PBDEs, PCBs, persistent organochlorines were analyzed for the background determination (Zhang et al., 2011; Zhou et al., 2011). The 2nd national human milk monitoring was carried out in 2011 to evaluate effectiveness of the Convention performance in China (Liu et al., 2016; Zhang et al., 2016). In our present work, PBDEs and PCBs in these milk samples were measured, and the major objective was to investigate the current body burden of general population and the temporal trend from 2007 to 2011.

2. Materials and methods

2.1. Sampling

The methodology of sampling human milk in the latest national human milk biomonitoring has been detailed elsewhere (Zhang et al., 2016). Briefly, 16 provinces were randomly sampled from 31 provinces of mainland China based on a multistage random cluster sampling method. The population of the selected provinces accounts for about 55% of the total population of China. In each province, one urban site and two rural sites were randomly selected for sampling. 50 donors were selected in each urban area, and 30 donors in each rural area. Finally, a total of 1760 human milk samples were obtained in 2011, and then shipped to China National Center for Food Safety Risk Assessment. These samples were divided into 32 pools based on mother's residence. All samples were stored at −20 °C until analyzed.

In order to get comparable data, the 'Guideline for Developing a National Protocol' of the Fourth WHO-Coordinated Survey of Human milk for Persistent Organic Pollutants in Cooperation with UNEP was followed for the selection of volunteering mothers and collection of human milk samples in this study (WHO, 2007). The criteria for selection of donors were following: 1) mothers should be primiparae; 2) both the mother and the child should be apparently healthy, including normal pregnancy; 3) mothers should be breastfeeding one child only; 4) mothers should have resided in the area for at least the previous 10 years; 5) mothers should not reside in local areas where emissions of POPs are known or suspected to result in elevated levels of POPs in the local population; 6) mothers should be available for sample collection within 3–8 weeks of delivery. Moreover, the upper limit of mothers' age was set to 35 years of age to get a sufficient number. All participants were told the objective of this study and signed the participant information and consent form.

2.2. Standard solutions and chemical reagents

Calibration standard solutions (P48-M-CVS for PCBs determination and BDE-CVS-F for PBDEs), ^{13}C-labeled surrogate standards (P48-M-ES for PCBs and MBDE-MXFS for PBDEs) and injection standards (P48-RS for PCBs and MBDE-MXFR for PBDEs) were all purchased from Wellington Laboratories (Guelph, Canada). All solvents were ultra resi-analyzed grade (J.T. Baker, Center Valley, PA, USA). Silica gel was purchased from Merck KGaA (Darmstadt, Germany).

2.3. Analytical methods

The analysis of PBDEs and PCBs in human milk were described elsewhere (Zhang et al., 2011), with slight modification. Briefly, 50 mL milk sample was lyophilized. Then, the freeze-dried samples were extracted by using accelerating solvent extractor (ASE350, ThermoScientific, Sunnyvale, CA, USA) after spiking ^{13}C-labeled surrogate standards (P48-M-ES and MBDE-MXFS). The mixture of n-hexane and dichloromethane (1:1, v/v) was applied as solvent. Lipid determination was done gravimetrically after solvent evaporation. The bulk lipid was removed by shaking with acid-modified silica-gel. The Power Prep instrument (Fluid Management Systems, Waltham, MA, USA) with multiple commercial columns was applied for further cleanup. The fraction containing PBDEs and PCBs was collected and concentrated to less than 40 μl. ^{13}C-labeled injection standards were added into the final extract prior to instrumental analysis.

In this study, PBDEs (BDE-28, 47, 99, 100, 153, 154, and 183) and PCBs (PCB-28, 52, 101, 138, 153, and 180, so-called indicator PCBs) were analyzed by gas chromatograph – high resolution mass spectrometry (GC-HRMS) using a Thermo Scientific™ Trace 1300L gas chromatograph (Milan, Italy) coupled to a DFS™ magnetic sector high resolution mass spectrometer (Thermo Scientific, Bremen, Germany) operating in EI mode at 45 eV and an emission current of 0.76 mA. The mass resolution was set at >10,000 for the measurement. A DB-5 HT capillary column (15 m × 0.25 mm i.d. × 0.10 μm) and a DB-5 MS capillary column (60 m × 0.25 mm i.d. × 0.25 μm) were equipped to determine PBDEs and PCBs, respectively.

2.4. QA/QC

One test of procedural blank was carried out for every eight samples. The concentration of each detectable congener of PBDEs and PCBs in the blank must be lower than 1/3 of that in human milk samples. If not, the samples of the same batch should be reanalyzed. The recoveries of internal standards were all in the