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A national survey of tetrabromobisphenol-A, hexabromocyclododecane and decabrominated diphenyl ether in human milk from China: Occurrence and exposure assessment

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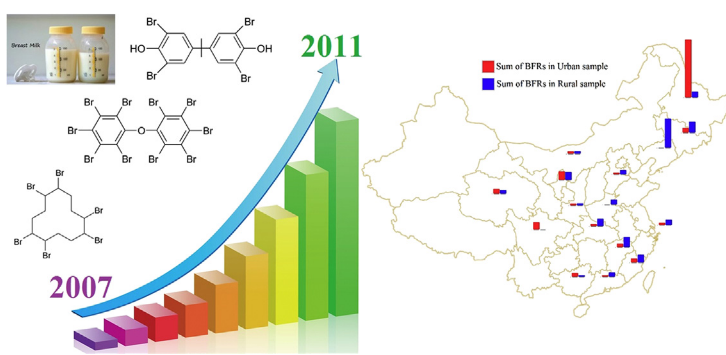
HIGHLIGHTS

- TBBPA, HBCD and BDE-209 were measured in a national survey of human milk.
- The contamination levels of some non-PBDE BFRs were obviously higher than PBDEs.
- Contamination levels of TBBPA and HBCD in human milk increased rapidly from 2007 to 2011.

GRAPHICAL ABSTRACT



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ABSTRACT

A national survey of three currently used brominated flame retardants (BFRs), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) and decabrominated diphenyl ether (BDE-209) in human milk was conducted in 2011. Human milk from 16 provinces of China were collected, pooled and measured. The estimated daily intake (EDI) via human milk ingestion for nursing infant and the related health risks were evaluated. The median levels of TBBPA, HBCD and BDE-209 were 1.21, 6.83 and 0.556 ng/g lipid weight (lw), respectively. Levels of BDE-209 were lower than those of TBBPA, indicating that the production and application of deca-BDE in China has been below that of TBBPA after the restriction of PBDEs. Moreover, contamination levels of TBBPA and HBCD in this survey were higher than those observed in last national survey conducted in 2007, indicating an increase of TBBPA and HBCD in the environment from 2007 to 2011. The mean estimated daily intakes (EDIs) of TBBPA, HBCD and BDE-209 via human milk for 1–6 months old infant were 39.2, 51.7 and 3.65 ng/kg bw/day, respectively. For risk assessment, margin of exposure (MOE) was calculated by comparing the $BMDL_{10}$ (benchmark dose lower confidence limit for a benchmark response of 10%) to the EDI of each BFR. Large MOEs indicates that the estimated dietary exposure to these three BFRs for nursing infant is unlikely to raise significant health concerns. Compared with some currently used novel BFRs which also measured in this survey, higher contamination levels were found in some non-PBDE BFRs, indicating that the consumption pattern of BFRs has shifted from PBDEs to non-PBDE BFRs in China.

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1. Introduction

Brominated flame retardants (BFRs) are widely used in electronics, foams and padding materials, etc., to inhibit or slow the propagation of fire. Because of their long-term and widely used, BFRs have been found to be ubiquitous in various environmental and biota matrices (Fromme et al., 2016; Yu et al., 2016). As "The World's Factory", BFRs are mainly produced and consumed in China, results in ubiquitous pollution (Yu et al., 2016). Furthermore, electrical and electronic waste (e-waste) from developed countries has brought new sources of BFRs to China. According to "The Global E-waste Monitor 2014" reported by United Nations University, huge amounts of e-waste is transported into China for recycling; hence lots of BFRs are inevitably emitted into the environment and present serious threats to the environment and human beings during the crude recycling of e-wastes (UNU, 2015). Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBPA) are the three mainly used BFRs in China in the past decades, they have been used since the 1970s and are called "legacy BFRs" (Covaci et al., 2011; Yu et al., 2016). TBBPA could be used as a reactive or additive BFR. Since the European Union reported that the use of TBBPA in circuit boards and plastics is unlikely to raise health risks, the production and application of TBBPA greatly increased (Liu et al., 2016). However, a recent study reported that long-term exposure to TBBPA may lead to immunomodulatory changes that contribute to carcinogenic processes (Dunnick et al., 2017). PBDEs and HBCD are both additive BFRs and can therefore leach or volatilize from products and enter the environment. There are three types of commercial PBDEs: penta-BDE, octa-BDE and deca-BDE. Penta-BDE and octa-BDE have been phased out since they were listed as persistent organic pollutants (POPs) under the Stockholm Convention in 2009, whereas the deca-BDE, which is mainly composed of BDE-209, is still produced and used in China. Commercial HBCD is composed of three main isomers (α-, β- and γ-HBCD), in which γ-HBCD is predominant, accounting for 75–89% of the total HBCD (α-HBCD, 10–15%; β-HBCD, 1–12%) (Du et al., 2012). Similar to penta-BDE and octa-BDE, HBCD was added into the list of POPs in 2013 because of its persistence, bioaccumulation, and bio-toxicity (UNEP/POPS, 2013). According to an announcement declared by the Ministry of Environmental Protection (MEP) of China, the production, importation and application of HBCD have been banned in China since 2016, however, at the same time the MEP announced that the production and application of HBCD in two types of building materials, extruded polystyrene (XPS) and expanded polystyrene (EPS), is still permitted in China (www.chinasafety.gov.cn). Hence, the production and application of HBCD continues in China. Taken together, environmental monitoring and health risk assessment of these currently used BFRs are not only of scientific interest but also requirement from a management perspective.

Compared to blood and urine, human milk has a far higher lipid content, hence it is utilized as a very suitable matrix for evaluating human internal exposure to lipophilic organic pollutants. Furthermore, human milk monitoring can also be utilized as a perfect non-invasive approach to assess the external exposure of nursing infant to environmental pollutants. In China, national survey of human milk is conducted as part of the Chinese Total Diet Study (TDS) in the past decades. The Chinese TDS is a continuous national study, which has been conducted five times since 1990, and it has become an important tool for monitoring dietary exposure of the Chinese population to chemicals and nutrients (Li et al., 2011). In the 4th Chinese TDS carried out in 2007, the national survey of human milk covered 12 provinces of China, and the occurrence of TBBPA, HBCD and PBDEs (not including BDE-209) was measured for the first time, showing the widespread presence of BFRs in Chinese human milk (Shi et al., 2009; Zhang et al., 2011). The 5th Chinese TDS was performed in 2011, and on this occasion, the national survey of human milk expanded from 12 provinces to 16 provinces. In this survey, a series of BFRs, including legacy BFRs (TBBPA, HBCD and BDE-209), and some "novel" BFRs were measured. The results of the novel BFRs have been published (Shi et al., 2016). The objective of the present study is to measure the contamination levels of TBBPA, HBCD and BDE-209 in the national human milk survey. Based on occurrence measurement, the dietary intakes of the three BFRs via human milk ingestion for nursing infants were subsequently calculated for risk assessment. In addition, since this is the second time we measured TBBPA and HBCD in national human milk survey, a comparison between TBBPA and HBCD in 2007 and 2011 is presented. In order to assess the current consumption pattern of BFRs in China, a comparison between the legacy and novel BFRs is also presented.

2. Materials and methods

2.1. Human milk collection

As part of the 5th Chinese TDS, the national human milk survey in this study was conducted in 2011. Individual human milk samples were collected from healthy volunteer donors living in 16 provinces of China. These provinces are Heilongjiang (HLJ), Jilin (JL), Neimenggu (NM), Hebei (HeB), Henan (HeN), Shanxi (SX), Ningxia (NX), Qinghai (QH), Jiangxi (JX), Fujian (FJ), Shanghai (SH), Hubei (HuB), Sichuan (SC), Guangxi (GX), Zhejiang (ZJ), Guangdong (GD), respectively. These 16 provinces cover approximately 48% of the land area of China and 56% of the Chinese population. The locations of these provinces are shown in Fig. 1. In each province, 50–60 rural donors and 50 urban donors were recruited according to their living area; each had resided in her place of residence for at least 5 years. A questionnaire was employed to collect information on the donors, and the data from the questionnaires revealed no evidence of abnormally high occupational exposure to BFRs among these donors. All donors were primiparous and non-smokers. After being told the purpose of the study and signing the consent form and questionnaire, human milk was collected within 3–8 weeks after delivery. An individual sample was collected either using a pump or by hand directly expressing the milk into a polypropylene jar, which was pre-washed and provided to the donors. The samples were stored at −18 °C, after all the human milk sample in a province were collected, all the samples were put into ice box, packed with drikold and shipped to our lab immediately. Subsequently, for each province, 10 mL of milk from each urban individual human milk sample was pooled to form one composite sample (urban sample), and each rural sample was pooled to form another composite sample (rural sample). All the pooled samples were stored at −40 °C until analysis. That is, a total of 32 pooled human milk samples from 16 provinces were subjected to analysis. However, only 29 pooled samples were tested in the present study because in earlier study these pooled samples have been

Fig. 1. Sampling provinces in the Chinese national human milk survey.