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Legacy and emerging brominated flame retardants in China: A review on food and human milk contamination, human dietary exposure and risk assessment

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HIGHLIGHTS

- EDI of BFRs via food consumption is unlikely to raise significant health concerns.
- Decline of contamination levels of tri-to hepta-BDE has been observed.
- Levels of TBBPA and HBCD in food and human milk increased rapidly from 2007 to 2011.
- High levels of BFRs were found in foods collected in e-waste recycling areas.
- Research on emerging BFRs should be enhanced, especially in highly polluted area.

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ABSTRACT

Brominated flame retardants (BFRs) are a large group of widely used chemicals, which have been produced and used since 1970s. As a consequence of substantial and long-term usage, BFRs have been found to be ubiquitous in humans, wildlife, and abiotic matrices around the world. Although several reports have reviewed BFRs contamination in general, none have focused specifically on foods and human milk, and the corresponding dietary exposure. Foods (including human milk) have long been recognized as a major pathway of BFRs intake for non-occupationally exposed persons. This review summarizes most available BFRs data in foods and human milk from China in recent years, and emphasizes several specific aspects, i.e., contamination levels of legacy and emerging BFRs, dietary exposure assessment and related health concerns, comparison between various BFRs, and temporal changes in BFRs contamination.

1. Introduction

Brominated flame retardants (BFRs) are a large group of chemicals generally used in the plastic parts of electronic devices and/or electronic circuits for fire retardant, they are also used in textiles, foams and padding materials, car and aircraft interiors, etc. As "The World's Factory", BFRs are mainly produced and consumed in China. The production capacity of BFRs in China is about 100,000 t in 2012 (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 was transported into China for recycling; hence lots of BFRs are inevitably released into the environment and present serious threats to the environment and human beings during the crude recycling of e-wastes (UNU, 2015; (Yu et al., 2016). Large groups of BFRs with varying chemical properties are produced and used in China, including three "legacy" BFRs (polybrominateddiphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA)) and a series of "emerging" BFRs (EBFRs). The term 'EBFRs' is defined as relating to BFRs which are new to the market or newly/recently observed in the environment, the term 'EBFR' is currently used when referring to BFRs other than PBDEs, HBCD and TBBPA (Covaci et al., 2011). PBDEs are additive BFRs and can therefore leach or volatilize from products and enter the environment. There are three types of PBDE commercial products: penta-BDE, octa-BDE and deca-BDE. Penta-BDE and octa-BDE were phased out globally after they were listed as persistent

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organic pollutants (POPs) in 2009 by the Stockholm Convention, whereas the production and use of deca-BDE continues. In 2017, deca-BDE was also added into the list of POPs by the Stockholm Convention, however, when the deca-BDE will be phased out in China is unknown. HBCD is also used as an additive BFR, it was added into the list of POPs in 2013 and has been phased out in many fields since 2016. However, the use of HBCD in special building materials, such as extruded polystyrene (XPS) and expanded polystyrene (EPS), is still permitted in China. Hence, the production and application of HBCD also continues in China. TBBPA could be used as a reactive or additive BFR. Since the European Union reported in 2006 that the use of TBBPA in circuit boards and plastics is unlikely to raise health risks, the production and application of TBBPA greatly increased (EU, 2006). However, a recent study suggested that long-term exposure to TBBPA may lead to immunomodulatory changes that contribute to carcinogenic processes (Dunnick et al., 2017). With the regulation of the legacy BFRs, EBFRs grew up sharply in Asia (Covaci et al., 2011). For example, decabromodiphenyl ethane (DBDPE), a replacement of deca-BDE, has been produced only since 2005 but with production increasing at 80% per year, and has become the most popular EBFRs in China (http://www.polymer.cn/). The production capacity of DBDPE approached 25,000 t in 2012, this value might have exceeded that of PBDEs (Zhang and Lu, 2011; Zhang and Gu, 2013). Due to long-term and widely used, BFRs have been found ubiquitous in various environmental matrices (Vorkamp and Riget, 2014; Yu et al., 2016). Consequently, the population is exposed to BFRs by numerous routes (food, dust ingestion, inhalation, etc.); however, the exact contribution of these several pathways varies substantially on a compound-specific basis and between individuals and within national populations (Covaci et al., 2011; Domingo, 2012). For non-occupational populations, in most countries except for the UK and USA, the contribution of house dust ingestion was less important than diet intake up to date (Besis and Samara, 2012). For example, in two studies from Korea and China, diet intake was both found to be the major contributor of total PBDEs intake (Kim et al., 2016; Wang et al., 2018). Because dietary intake appears to be the main route of exposure for BFRs in China, the main purpose of this review is to summarize recent experimental data on legacy and emerging BFRs in foods (including human milk) from China, human dietary exposure (adult and infant) and related health risk.

2. BFRs in foods and human milk

2.1. TBBPA

2.1.1. TBBPA in foods and dietary exposure

There is a lack of information concerning the concentrations of TBBPA in foods or human milk in China. In general, as a phenolic substance, the concentration and detection frequency of TBBPA in foods or human body fluid are relatively low because of the relatively low bioaccumulation potential (half-life of 2 days), moreover, TBBPA is normally used as a reactive BFR and therefore the leaching/release into the environment is limited (Jakobsson et al., 2002). Total diet study (TDS) is often used to evaluated chemicals and nutrients in foods in China. TDS has been performed since 1990 with goals of providing contamination and nutrition data for food prepared and consumed by the population as well as dietary intake data to help the authorities make public health decisions, and TDS has become an important tool for monitoring dietary exposure to chemicals and nutrients and their relationship to public health in China (Chen and Gao, 1993) (Shi et al., 2009). conducted a preliminary study on TBBPA levels in food composites and pooled human milk on the basis of the 4th Chinese TDS and Nation Human Milk Survey (NHMS) conducted in 2007. In TDS 2007 the food composite approach was used to study the total diet in 12 provinces representing the average dietary patterns of different geographical areas in mainland China and covering approximately 50% of the Chinese population. The 12 provinces are Heilongjiang, Liaoning, Hebei, Henan, Shanxi, Ningxia, Jiangxi, Fujian, Hubei, Sichuan, Guangxi and Shanghai, respectively. All food items collected in each province were aggregated into 12 groups, including aquatic foods, meats, eggs, milk, cereals, legumes and nuts, tubers, vegetables, fruits, sugar, alcoholic drink and water (including beverage). Because BFRs are normally lipophilic, four food groups with different animal origins were subjected for TBBPA analysis: 1) eggs and egg products, including chicken and duck eggs, and salted and limed duck eggs; 2) aquatic foods, including fish, shrimp, and oysters; 3) milk and milk products, including cow milk, cow milk powder, yogurt, and sheep milk; 4) meat and meat products, including pork, mutton, beef, chicken, duck, rabbit, pork liver, and swine blood. The results of TDS 2007 revealed that TBBPA could be found in 70% of the whole food items: mean level of 0.738 ng/g lw in aquatic food; 0.263 ng/g lw in meat/meat products; 0.211 ng/g lw in milk/milk products; 0.194 ng/g lw in egg/egg products, respectively. Based on food survey, estimated dietary TBBPA intake of a "standard Chinese man" (a Chinese male with body weight of 63 kg) was 256 pg/kg bw/day, in addition, although the contamination level of aquatic food was the highest in the four food groups, the contribution from aquatic food (30%) was less than that from meat/meat products (52%), because consumption of meat was higher than that of aquatic food in Chinese population. In the subsequent study, the 5th Chinese TDS conducted in 2011, TBBPA was measured in the same four animal food composites from 20 provinces across China (8 more provinces including Jilin, Qinghai, Neimenggu, Zhejiang, Jiangsu, Hunan, Guangdong and Beijing were added into TDS, 2011). In TDS 2011 TBBPA was detected in approximately 83% of the whole food items: mean level of 3.05 ng/g lw in aquatic food; 1.78 ng/g lw in meat/meat products; 5.76 ng/g lw in milk/milk products; 3.12 ng/g lw in egg/egg products, respectively. A comparison between TDS 2011 and TDS 2007 showed that average contamination levels of TBBPA in the same four food groups in TDS 2011 were found to be 3 to 30 times higher than those observed in TDS 2007, indicating a sharp increase of TBBPA in the environment. Accordingly, an increase in the intensity of human exposure was also observed. Average EDI_{TBBPA} value for the "standard Chinese man" increased from 0.256 ng/kg bw/day in TDS 2007 to 1.34 ng/kg bw/day in TDS 2011 (Shi et al., 2017a). However, when the EDIs of TBBPA via food consumption in the same 12 provinces between TDS 2007 and 2011 were compared, we found that the EDIs in some provinces, such as Shanxi, Jiangxi, Sichuan and Guangxi, jumped sharply by 20–80 times from 2007 to 2011, whereas in other provinces, only a small increase or small decrease were observed. In summary, the two Chinese TDSs suggested a rapid increase in demand for TBBPA between 2007 and 2011. In China, the legislative focus is still firmly on PBDEs, while TBBPA has received little attention until now; especially after the restriction of PBDEs and the EU official approval of the use of TBBPA as a safe flame retardant, the production and application of TBBPA obviously increased (Liu et al., 2016). Thus, we predict that TBBPA contamination levels in China will continue to increase in the future. However, although EDI_{TBBPA} in China is increasing, the values of EDI from TDS 2011 were still much lower than the tolerable daily intake (TDI) of 1 mg/kg bw/day suggested by the U.K. Independent Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT), which indicated that current exposure to TBBPA via food consumption in China is unlikely to raise significant health concerns for adults. On the other hand, margin of exposure (MOE) approach which recommended by European Food Safety Authority (EFSA) is used for evaluating