Environment International 96 (2016) 82–90

Contents lists available at ScienceDirect

Environment International

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

Novel brominated flame retardants in food composites and human milk from the Chinese Total Diet Study in 2011: Concentrations and a dietary exposure assessment

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ARTICLE INFO

Article history:
Received 30 June 2016
Received in revised form 4 September 2016
Accepted 5 September 2016
Available online 10 September 2016

Keywords:
Novel brominated flame retardants
Foods
Human milk
Decabromodiphenyl ethane
Dietary exposure assessment
Total diet study

ABSTRACT

On the basis of the fifth Chinese total diet study (TDS) performed in 2011, the dietary exposure of the Chinese population to novel brominated flame retardants (NBFRs) was assessed. Six NBFRs were determined in 80 composite samples from four animal origin food groups and 29 pooled human milk samples. Based on gas chromatography-negative chemical ionization mass spectrometry (GC-NCI/MS) analysis, the levels of the total NBFRs ranged from <LOD to 70.2 ng/g lipid weight (lw) in food composites and from 2.48 to 23.9 ng/g lw in human milk samples. Decabromodiphenyl ethane (DBDPE), with mean levels of 9.03 ng/g lw in food composites and 8.06 ng/g lw in human milk, was the most abundant compound in the total NBFRs. No obvious spatial distribution patterns in China were observed in food samples or human milk. The average estimated daily intake (EDI) of total NBFRs via food consumption for a "standard Chinese man" was 4.77 ng/kg bodyweight (bw)/day, with a range of 0.681 to 18.9 ng/kg bw/day. Meat and meat products were the main dietary source of NBFRs, although levels of NBFRs in aquatic food were found to be the highest among the four food groups. The average EDI of total NBFRs for nursing infants was 38.4 ng/kg bw/day, with a range of 17.4 to 113 ng/kg bw/day, which was approximately eight-fold higher than the EDI for adults, suggesting the heavy body burden of NBFRs on nursing infants. The levels and EDI of DBDPE in the present study were similar to or higher than those of legacy BFRs (i.e., PBDEs and HBCD) in the TDS 2007, indicating that DBDPE, as a main alternative to PBDEs, might have become the primary BFR used in China.

1. Introduction

Brominated flame retardants (BFRs) are a large group of widely used chemicals, which were generally incorporated into the plastic parts of electronic devices and electronic circuits to give them fire-retardant properties. They are also present in foams and padding materials (domestic and industrial), car and aircraft interiors and some textiles. A large quantity of BFRs are produced and consumed in China because the consumption of commodities containing BFRs grew rapidly. The production capacity of BFRs in China are about 100,000 t in 2012 (Zhang and Gu, 2013). Moreover, China, especially southern and southeastern China, "digests" a large quantity of electronic waste (e-waste) from developed countries that formed new sources of BFRs (Yu et al., 2016). Many BFRs with varying chemical properties are produced and used in the Chinese market, including three main groups of "legacy" BFRs (polybrominateddiphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA)) as well as several "novel" BFRs (NBFRs). The term 'novel BFRs (NBFRs)' is defined as relating to BFRs which are new to the market or newly/recently observed in the environment, this term is currently used when referring to BFRs other than PBDEs, HBCD and TBBPA (Bergman et al., 2012; Covaci et al., 2011). There are three types of PBDE commercial products: penta-BDE, octa-BDE and deca-BDE (Abdallah et al., 2009). Penta-BDE and octa-BDE were restricted globally because they have been listed as persistent organic pollutants (POPs) since 2009 by the Stockholm Convention. In 2013, HBCD was also listed as a POP. With the restriction of the legacy BFRs, NBFRs, such as decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE) and so on, are

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http://dx.doi.org/10.1016/j.envint.2016.09.005
0160-4120/

produced and used in increasing amounts (Covaci et al., 2011). For example, DBDPE, the most popular NBFRs in China, has been produced only since 2005 but with production increasing at 80% per year (http://www.polymer.cn/). The production capacity of DBDPE approached 25,000 t in 2012, this volume might have exceeded volume of PBDEs (Zhang and Gu, 2013; Zhang and Lu, 2011). BFRs have been recognized as ubiquitous environmental contaminants and have been found in various environmental matrices due to their wide use (Vorkamp and Riget, 2014; Yu et al., 2016). Consequently, the general population is exposed to these contaminants by numerous routes (food, dust ingestion, inhalation, etc.); however, dietary intake appears to be the main route of exposure for some BFRs, such as PBDEs (Domingo, 2012). Until now, there were relatively few studies reporting the presence of NBFRs in the foodstuffs or human milk from China. Thus, information on human exposure and body burden is extremely limited.

The WHO Global Environmental Monitoring System/Food Contamination Monitoring and Assessment Programme (GEMS/Food) has for many years supported the use of the TDS as one of the most cost-effective methods for monitoring dietary intake of chemicals or nutrients (WHO, 2011). In China, the total diet study (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 Chinese 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; WHO, 2011). In our previous studies, dietary intakes of PBDEs, HBCD and TBBPA of the Chinese population were estimated from the Chinese TDS in 2007, showing a widespread presence of BFRs in foods and human milk in various regions of China (Shi et al., 2009; Zhang et al., 2013; Zhang et al., 2011). The aim of the present study was to examine the levels of six commonly used NBFRs, 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), BTBPE and DBDPE, in two categories of samples: pooled human milk samples collected in 2011 from 16 provinces of China and food samples from the 5th Chinese total diet study, including four food groups with different animal origins. The dietary intakes of the NBFRs via human milk and food consumption were subsequently estimated for nursing infants and adults in China.

2. Materials and methods

2.1. Food sample collection

The 5th Chinese total diet study was carried out in 2011. The Chinese TDS is a continuous national study monitoring the levels of various chemical pollutants and nutrients in foods and estimating the dietary intake of these chemicals and nutrients by the general population in China. The overall study design and experimental methods were similar to those carried out in 2007 (Shi et al., 2009). The food composite approach was used to study the total diet in 20 provinces representing the average dietary patterns of different geographical areas in mainland China and covering approximately 70% of the Chinese population. In the previous TDS carried out in 2007, 12 provinces were included, i.e., Heilongjian, Liaoning, Hebei, Henan, Shanxi, Ningxia, Jiangxi, Fujian, Hubei, Sichuan, Guangxi and Shanghai. In the 2011 TDS, 8 more provinces were included (Jilin, Qinghai, Neimenggu, Zhejiang, Jiangsu, Hunan, Guangdong and Beijing). Their locations are shown in the Supplementary Fig. A.1. In each province, three sampling sites, including one urban site and two rural sites, were randomly selected. Thirty households were randomly sampled from each site to conduct the food consumption survey by 24-h dietary recall over 3 days for each member of the household, enabling recording of individual food consumption data. In each province, all of the food items were aggregated into various food groups, and then, the average food consumption was calculated to present the pattern of food consumption of a "standard Chinese man". Dietary intakes of the NBFRs were then standardized per "standard Chinese man" for easy comparison. The "standard Chinese man" was defined as an adult male 18–45 years of age having 63 kg of body weight and undertaking light physical work. The body weight of 63 kg was the average body weight of all of the male participants with an age over 18 and undertaking light physical work.

In this study, because BFRs are normally lipophilic, the following four food groups with different animal origins were subjected to analysis for NBFRs: 1) eggs and egg products; 2) aquatic foods; 3) milk and milk products; and 4) meat and meat products. Food samples were collected from local markets, grocery stores, and rural households. To achieve more realistic dietary exposure estimates, the foods were prepared and cooked to a "table ready" state according to local cuisine and then blended to form the respective group composites with weights proportional to the average daily consumption of each province. These provincial composites were shipped to the China National Center for Food Safety Risk Assessment and frozen at −20 °C until analysis. In total, 80 food samples from 20 provinces were tested.

2.2. Human milk collection

In 2011, human milk samples were collected from healthy donors living in the same provinces of China as in the TDS except for Beijing, Hunan, Jiangsu and Liaoning. In each province, there are 50 urban donors and 50–60 rural donors according to the living area. The samples were collected within 3–8 weeks after childbirth. Each milk donor had resided in her place of residence for more than five years. The occupation, age, diet, and smoking habits of the mother as well as the birth weight and sex of each infant were recorded in a questionnaire when the samples were collected. The questionnaires revealed no evidence of abnormally high occupational exposure among these mothers. All of the mothers were primiparous and none of them were smokers; all donors were told the objective of this study and signed the participant information and consent form. An individual human milk sample was collected either using a pump or by hand directly expressing the milk into the pre-washed polypropylene jar, which was provided to the mothers by the study team. The sample was frozen immediately and kept at −20 °C. These samples were divided into 32 pooled samples based on the mother's residence. For each province, the urban individual human milk samples were pooled into one composite sample, and rural samples were pooled into another composite sample. When the collection of a pool was completed, the milk was thawed, homogenized by shaking, and 10 mL from each individual was pooled giving a composite milk sample from each region. Pooled samples were stored at −20 °C until analysis. In this study, 29 pooled samples were employed for NBFR analysis, with the rural sample of Sichuan as well as the urban samples of Henan and Liaoning being insufficient, and thus, they were excluded.

2.3. Reagents and chemicals

All HPLC-grade quality solvents used in the extraction and analysis procedures were purchased from Merck (Darmstadt, Germany); reagent grade sulfuric acid and anhydrous sodium sulfate were purchased from Beijing Chemical Factory (China). The individual PBDE standards solution BDE-77 and BDE-128 were obtained from AccuStandard Inc. (New Haven, CT, USA). The individual NBFRs standards, DPTE, PBT, PBEB, HBB, BTBPE and DBDPE, were also obtained from AccuStandard Inc. Standard solution of $^{13}C_{12}$-labelled BDE-209 was obtained from Wellington Laboratories (Guelph, Ontario, Canada).

2.4. Sample preparation and analysis

A slightly modified method described elsewhere was used for sample preparation and analysis (Shi et al., 2013b). Briefly, approximately 20–25 mL of pooled breast milk or 5–30 g of composite food sample