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Polybrominated diphenyl ethers (PBDES) and hexa-brominated biphenyls (Hexa-BBs) in fresh foods ingested in Taiwan☆

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) and hexa-brominated biphenyls (Hexa-BBs) are bioaccumulative and aggregate in the food chain. Therefore, background monitoring and risk assessment for dietary intake are necessary. In present study, a systematic sampling method was first used to collect the high fat content foodstuff such as poultry, livestock, eggs, fish, other seafood, dairy products, and the infant foods and then foodstuff with high consumption in seven categories of 600 food samples. After integrating four years of background surveys of PBDE levels (2010–2013) and one year of that of Hexa-BBs (2013), the highest estimated daily intake (EDI) of PBDEs for Taiwanese food consumption was found in 0- to 3-year-olds (mean = 9.38 ng kg−1 bw d−1, the 95% upper limit of Monte Carlo Simulation (MCS P95) was 21.52 ng kg−1 bw d−1), and the lowest in 16- to 18-year-old girls (mean = 3.35 ng kg−1 bw d−1, MCS P95 was 6.53 ng kg−1 bw d−1). Moreover, the highest of EDI of Hexa-BBs was found in 0–3 years old (mean = 0.007 ng kg−1 bw d−1, MCS P95 = 0.019 ng kg−1 bw d−1), and lowest in 17–18 years old female (mean = 0.002 ng/kg/day, MCS P95 = 0.005 ng kg−1 bw d−1). This study suggests that the large MOEs (>2.5) for the four important congeners BDE-47, -99, −153, and −209, indicate that the dietary exposures are not probably a significant health concern for Taiwanese.

1. Introduction

The environmental hormones, polybrominated diphenyl ethers (PBDEs) and hexa-brominated biphenyls (Hexa-BBs), which are homologues of polybrominated biphenyls, are persistent; thus, they accumulate in the environment. Tetra-, Hexa-, Hepta-BDEs, and Hexa-BBs are commonly used as brominated flame retardants in the industrial world, and are added to daily necessities, electronic products, and building materials to delay or suppress fires. Hexa-BBs were produced until the 1980s, and the production of PBDEs has been prohibited since 2006. Since July 2006, the European Union (EU) legislation that restricts the use of hazardous substances in electrical and electronic equipment (RoHS) has required that "Member States need to confirm that new commercial electrical and electronic equipment does not contain PBDEs and PBBs (polybrominated biphenyls)". PBDEs and Hexa-BBs bioaccumulate through the food chain, and their long-term intake and accumulation will disrupt an organism's endocrine system, and even cause neurobehavioral deficits and reproductive toxicity. One study (McDonald, 2002) reports that they might cause cancer in laboratory animals. Therefore, it is urgent and necessary to create appropriate analytical methods that will allow new technology to continually monitor domestic commercial foods over the long term to determine whether it is contaminated. The objective of our study was to use our own ongoing total diet survey (TDS) to compare the dietary exposure to PBDEs and Hexa-BBs of Taiwanese with the margin of exposure (MOE) and No Observed Effect Level (NOEL)

Abbreviations: (PBDEs), Polybrominated diphenyl ethers; (Hexa-BBs), hexa-brominated biphenyls; (PBBs), Polybrominated biphenyls; (EDI), estimated daily intake; (MCS), Monte Carlo Simulation; (MOE), margin of exposure; (EFSA), European Food Safety Authority; (TDS), total diet survey; (NAHSIT), Nutrition and Health Survey in Taiwan; (HRGC/HRMS), gas chromatography/high-resolution mass spectrometry; (ADD), average daily dose; (pg g^{-1}), picograms per gram; (IR), intake rate; (bw d)$^{-1}$, body weight per day; (RfD), reference dose; low observed adverse effect level, (LOAEL).

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stipulated by the European Food Safety Authority (EFSA).

2. Materials and methods

2.1. Sampling method

Our systematic sampling method for measuring PBDEs was used to collect 600 samples of a wide variety of foods in 15 categories from 2010 to 2013. In 2013, we added Hexa-BB analysis for 150 high lipid content foods to establish the background information. We planned our samples based on the official food classification (17 groups) and data on food consumption by the general population obtained from the Nutrition and Health Survey in Taiwan (NAHSIT) (Wu et al., 1999; NHRI, 2016).

First, the sampling locations we selected were the townships designated by the Taiwan Council of Agriculture and Fisheries Department as having the highest levels of food production. Second, 600 individual foods were obtained from major food markets in selected towns around Taiwan. The quantity of production of each foodstuff was determined, recorded, and evaluated in every county, village, and town in each area. Third, the foods produced in the greatest quantities in each county were selected for analysis. The foodstuff samples were purchased from traditional markets or supermarkets in selected towns around Taiwan from 2010 to 2014. Finally, we used over 600 individual foods in the four years to prepare samples. All group samples were adequately homogenized, and then frozen at −20 °C until they were analyzed. For example, a pork composite sample weighing 600 g was prepared by homogenizing 10 aliquots of 60 g of homogenized pork, each from separate pork samples of ca. 500–1000 g. We investigated samples of pork (28), beef (28), mutton (28), livestock and poultry viscera (30), chicken (26), duck (26), goose (26), marine fish (34), freshwater fish (58), other seafood (58), milk and dairy products (58), oils (36), eggs (46), vegetables (36), beans (12), grain crops (12), rice (6), mushrooms (12), and infant food (40).

2.2. Food consumption data

Food intake rate and bodyweight were obtained from the database of the NAHSIT survey. In this survey, a multi-staged, stratified, clustered sampling scheme was conducted and recruited 9962 participants. The data of this survey will provide information on the dietary intake and the health (e.g., body weight) of Taiwan's population. We can generalize our findings not only to the entire population of Taiwan, but also to various age and gender groups, and to Taiwanese who are members of different cultural groups and who live in most of Taiwan's geographical regions.

In this survey, 24-h dietary recall and a simple food frequency questionnaire were used to assess the dietary intake of the participants. More than 15 years ago, food models and operational details for 24-h recall were designed, validated, and documented for Chinese in Taiwan (Chang et al., 2001; Lee, 1999), which should reduce the uncertainties in this study.

2.3. PBDE and Hexa-BB analysis

A high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) method combined with a ^{13}C isotope labeled internal standard was used to determine 24 PBDEs (tri- through deca-BDEs) and 5 Hexa-BBs in different foodstuffs, as previously described (Chen et al., 2013). We consulted the analytical procedures from USEPA Method 1614 A and NIEA M802.00 B and made proper modifications.

We purchased various commercially available standards from Wellington Laboratories (Guelph, Canada): 24 individual PBDE standards (BDE-17, -28, −47, −49, −66, −71, −77, −85, −99, −100, −119, −126, −138, −153, −154, −156, −183, −184, −191, −196, −197, −206, −207, −209), 5 individual Hexa-BB standards (PBB-153, 154, 155, 156, 169), ten internal standards (^{13}C-labeled BDE-28, -47, −99, −100, −153, −154, −183, −207, −209, ^{13}C-labeled PBB-153), and one recovery standard (^{13}C-labeled BDE-138). Toluene (>99%), n-hexane (>98%), acetone (>99.5%), dichloromethane (>99%), sulfuric acid (>90%), and sodium sulfate were purchased from Merck (Darmstadt, Germany). Silica gel and alumina oxide were purchased from Supelco (Bellefonte, PA). Different weights of freeze-dried foodstuffs (e.g., 7 g for meat and fish, 15–20 g for eggs, 2–5 g for milk) were spiked with a suite of ^{13}C-labeled-PBDE internal standards and extracted with Soxhlet extractors. In general, foodstuffs were extracted using n-hexane/acetone (1:1) for 6 h, and then the extracts were concentrated using a rotary vacuum evaporator (EYELA; Tokyo Rikakikai Co. Ltd., Tokyo, Japan). Two milliliters of the extract from each food sample was used to determine the lipid content. Cleanup procedures for the extracts involved using sulfuric acid, acidic silica-gel, and an acidic alumina column. A final volume of 10 μL of ^{13}C-labeled BDE-138 was added as the recovery standard. HRGC/HRMS (GC6890/VG-AutoSpec; Agilent Technologies, Santa Clara, CA) with a 15-m DB-5HT column (0.25 mm i.d. × 0.1 μm film thickness) (J&W Scientific, Folsom, CA) was used to determine the concentration of PBDEs.

2.4. Quality assurance and quality control

The quality assurance and quality control criteria followed the Draft USEPA Method 1614 (EPA, 2007). For quality control (QC), a laboratory blank and a QC pooled sample were analyzed in each batch of approximately 12 samples. The observed isotope ratios of two monitored ions per congener were within 15% of the theoretical isotopic ratio. Quantification was done using the ^{13}C isotope dilution and internal standard method. The limit of detection (LOD) was estimated by determining minimal concentrations of calibration standards resulting in chromatographic peaks with a signal-to-noise ratio ≥ 2.5. Signal-to-noise ratios were calculated using MassLynx 4.1 software. The LOD for all congeners (except BDE-209) ranged from 0.23 to 0.58 ng/mL and 1.1 ng mL^{-1} for BDE-209. For samples with analytical concentrations less than the LOD, half of the LOD was used for the calculations. The initial precision and recovery samples ranged between 66% and 161%. Total labeled PBDE compound recovery from samples in this study ranged from 25% to 150%, including BDE-209. All final results were adjusted based on the recoveries.

2.5. Estimated daily intake of PBDEs and Hexa-BBs

We calculated each PBDE (24 congeners) and Hexa-BB (5 congeners) concentration separately and then added all the concentrations for the total intake of PBDEs. The individual exposure expressed as the average daily dose (ADD) can be calculated using the following equation:

$$ADD = \frac{C \times IR \times AF}{BW} \quad (1)$$

In Eq. (1), C is the measured concentration of PBDEs and Hexa-BBs in the corresponding food item from our laboratory. Here, we use an upper-bound exposure estimate, which is estimated by assigning the LOD to all samples with ND results; IR is the intake rate (g/day) of foodstuffs by a gender- and age-specified population database derived from the Nutrition and Health Surveys in Taiwan (NAHSIT) conducted in 2001–2002 and 2005–2008 (Tu et al., 2007, 2011); AF is the absorption factor (assuming 100%); and BW is the

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