POLYBROMINATED DIPHENYL EHTERS IN FOOD FROM THE PRODUCTION AREA ALONG THE LAIZHOU BAY, CHINA

Peng Li[1], Hui Wu[1], Qiuxu Li[1], Jun Jin[1,2*], Ying Wang[1]

[1]College of Life and Environmental Sciences, Minzu University of China, 27 Zhongguancun South Street, Beijing, P.R.China; [2]Engineering Research Center of Food Environment and Public Health of Beijing, 27 Zhongguancun South Street, Beijing, P.R.China

Introduction

Many consumer products in modern life contain polybrominated diphenyl ethers (PBDEs) for the purpose of fire protection. PBDEs are used in large quantities as BFR additives in television sets, computers, radios, textiles, and in synthetic building materials and automobiles. The stability and lipophilicity of PBDEs in vivo cause them to bio-magnify up the food chain, increasing in concentration at each successively higher trophic level. It seems that for the general population, one of the main routes of exposure to PBDEs, is through the diet. The intake of fish significantly contributes to human exposure to PBDEs in Japan, Consequently, consumption of foodstuffs such as vegetables, meat, and fish from contaminated sources is a major way of exposure to BFRs. Another study from the US found that elevated consumption of poultry and beef was associated with high serum PBDE levels, vegetarians had approximately 25% lower PBDE concentrations in serum than non-vegetarians[1]. However, the amount of PBDEs can decrease with cooking, here when the food was broiled and the fat dripped away[2].

At present, little is known about levels of PBDEs in foodstuffs in the production area of BFRs in China. To investigate whether human exposure to PBDEs through the diet is significant, the concentrations of PBDEs were determined in aquatic products, meat and vegetables sold in the food markets in the production area of BFRs.

Materials and methods

The food samples were purchase from the local food markets in the Binhai Economic Development Zone (37.120° N, 119.011° E). Eight types of local fish and shellfish (Chinese shrimp, Conch, Clam, Razor clam, Crucian carp, Pomfret, Yellow croaker, and Perch), six types of vegetable (Bean, Potato, Carrot, Spinach, Chinese cabbage and Suaeda salsa) and three types of meat (chicken, beef, and mutton) were selected after our oral investigation to ensure all these sampled species were locally caught/grow and were major parts of the diet of the local population. Each food sample was wrapped in aluminum foil and sealed, then kept frozen at −18 °C until it was analyzed.

In the laboratory, the aquatic products were cleaned by removing their scales, shells and bones using a stainless steel knife. The muscle without fishskin was then homogenized using a domestic homogenizer. The meats samples were thoroughly washed by water and then homogenized. The vegetables were washed thoroughly in water to remove dust and soil, and inedible parts were removed by a stainless steel knife, then homogenized using a domestic homogenizer. The homogenized samples were then mixed with Na_2SO_4 to remove water. Each prepared food samples was spiked with a known amount of internal standards ($^{13}C_{12}$-labeled BDE139 and $^{13}C_{12}$-labeled BDE209), and then Soxhlet extracted with 300 mL of a 1:1 mixture of acetone and

hexane for 24 h. The extract was then cleaned using a column packed with (from bottom to top) 1 g activated silica, 4 g silica treated with 30% w/w of 1 M NaOH, 1 g activated silica, 8 g silica treated with 44% w/w of H_2SO_4, 2 g activated silica, and 4 g granular anhydrous sodium sulfate, and the column was eluted with 100 mL of a 97:3 (v/v) hexane: dichloromethane mixture. The cleaned sample was concentrated to 100 μL using a rotary evaporator and then under a gentle flow of nitrogen.

The samples were analyzed by gas chromatography-mass spectrometry (using an Agilent 6890 gas chromatograph and an Agilent 5975N mass spectrometer; Agilent Technologies, Santa Clara, CA, USA). The mass spectrometer ion source and quadrupole temperatures were both 150 °C. The carrier gas was helium, and its flow rate was 1.0 mL/min. Aliquots (1 μL) of the samples were injected in splitless mode. PBDEs were separated using a DB-5MS column (30 m long, 0.25 mm i.d., 0.1 μm film thickness; J&W Scientific, Agilent Technologies) and the oven temperature program started at 100 °C (held for 2 min), and increased at 4 °C /min to 300 °C. BDE-209 was anlyzed using a shorter DB-5MS column (15 m × 0.25 mm i.d., 0.1 μm film thickness; J&W Scientific, Agilent Technologies). The injector temperature was 290 °C and the oven temperature program was: 100 °C for 3 min, increased to 300 °C at 4 °C /min, then held for 22 min. A negative chemical ionization source was used and the mass spectrometer was operated in selected ion monitoring mode to allow quantitative analysis to be performed.

A method blank sample was analyzed with every batch of samples. The analyte concentrations in the blank samples were all satisfactory (<5% of the typical analyte concentration in the samples). BDE-28, -47, -99, 153, -154, -183, -190 were quantified using $^{13}C_{12}$-labeled BDE139 as the internal standard, and BDE209 were quantified using $^{13}C_{12}$-labeled BDE209 as the internal standard. The instrumental limit of detection (LOD) was defined as the concentration that gave a peak with a signal to noise ratio of 5. The instrumental LODs for BDE209 were 5 pg. The instrumental LODs for PBDEs ranged from 0.15 pg to 5 pg.

Results and Discussion

The concentrations of PBDEs in aquatic products, meat, and vegetables purchased from food market in the production area of BFRs are presented in Table 1. PBDEs concentrations in aquatic products were ranged between 47.15 and 3.65×10^3 pg/g w.w (wet weight). The concentrations of PBDEs were the lowest in shrimps (47.15 pg/g), and it increased in marine fishes (1.73×10^3 pg/g), followed by shellfish (3.10×10^3 pg/g), and were the highest in freshwater fishes (3.65×10^3 pg/g). When the concentrations of PBDE in marine fishes and freshwater fishes were compared, PBDE concentrations in freshwater fishes were higher than in marine fishes. The differences in the total concentrations of PBDEs and the occurrence of certain PBDE congeners among different species are influenced by metabolic differences, age of the fish, lipid content. It is quite likely that other environmental factors such as diet and aquatic exposure also contribute to the differences in aquatic products body burdens. When compared with similar studies conducted in other countries or regions, the PBDEs concentrations in fish were high in the production area of BFRs. Darnerud et al.[3] reported the sum of five PBDEs in market fish collected from four major Swedish cities with a mean concentration of 634 pg/g wet weight. Domingo et al.[4] determined the PBDEs contents in 14 edible marine species widely consumed by the population of Catalonia (Spain), and the mean total (tetra- to octa-BDE) PBDEs was 564 pg/g wet weight. The results from the present study were relatively higher compared to these previous results, but lower than the

results from other surveys of PBDEs levels in fish samples of Guiyu[5]（7.86×10^5 pg/g wet weight） and Qingyuan[6] (5.45×10^5 pg/g wet weight), China.

The concentrations of PBDE in chicken, mutton and beef were 2.90×10^2, 1.26×10^3 and 2.99×10^3 pg/g fresh wet weight, respectively. Studies have reported the occurrence of PBDEs in meat. Souichi Ohta et al.[7] reported that the PBDE concentrations in chicken and beef were 16.2 and 6.25 pg/g fresh weight, respectively. Compared with the result, the PBDEs concentrations in meat from present study was much higher. PBDE concentrations in vegetables were ranged from 21.66 to 4.44×10^4 pg/g. It was determined that PBDE concentrations were the lowest in carrot (21.66 pg/g), and followed by beans (2.11×10^2 pg/g), spinach (8.95×10^2 pg/g), chinese cabage(1.12×10^3 pg/g), suaeda salsa (4.02×10^3 pg/g), and were the highest in potato (4.44×10^4 pg/g). The concentration was higher than a study which reported that the concentrations of PBDE in spinach, potato and carrot were 134.0, 47.6 and 38.4 pg/g fresh weight in Japan, respectively [8]. Although both carrot and potato are root vegetables, their PBDE concentrations are very different from each other. The concentrations of PBDE in root vegetables were much higher than in leafy vegetables. It has been suggested that organic pollutants enter vegetation mainly through gas-phase and particle-phase deposition onto the waxy cuticles of leaves or by uptake through the stomata [8]. This would result in BFRs being more likely to remain in and on the leaves of a plant than for them to be translocated to other parts of the plant.

Table 1 The concentrations of PBDE in foodstuffs (pg/g wet weight)

	aquatic products	meat	vegetables
BDE28	$5.45\text{-}4.01\times10^2$	0.66-46.90	0.83-21.10
BDE47	$14.6\text{-}3.24\times10^2$	6.89-29.0	3.72-51.80
BDE100	6.87-27.90	2.80-27.60	0.47-31.90
BDE99	0.68-2.41	0.38-5.96	0.61-60.50
BDE154	n.d.	n.d.	n.d.
BDE153	7.09-47.80	9.86-54.70	3.05-44.30
BDE183	1.62-22.20	4.60-17.80	1.10-12.10
BDE209	$9.13\text{-}3.05\times10^3$	$2.62\times10^2\text{-}2.89\times10^3$	$9.56\text{-}4.44\times10^4$
$\sum_8$PBDE	$47.2\text{-}3.65\times10^3$	$2.90\times10^2\text{-}2.99\times10^3$	$21.7\text{-}4.44\times10^4$

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The reasons that we observed relatively higher PBDEs levels in foodstuffs from the production area than those in other countries or regions may be due to the production and usage patterns of PBDEs-containing commercial products. As a major congener (98%) in commercial deca-BDE products, the detection ratio of BDE-209 was 100% of the total foodstuff samples, and BDE-209 was the predominant congener observed in almost all samples analyzed, which was more than 75% of the total PBDEs (shown in Fig.1). Interestingly, the percentages of BDE-47 and BDE-99 were the highest in shrimps and beans, respectively. BDE-209 was the predominant congener in meat samples, different from Alaska (USA) where BDE-47 was the predominant congener[9]. The percentages of BDE-28, -47,-100 and -99 were relatively higher in shrimps, in marine fishes and in beans, in carrot, and in spinach. The differences between species caused this discrepancy probably. On the other hand, low brominated PBDE, such as BDE-28,-47,-100 and -99 were likely to come from the degradation of high

brominated PBDE, such as BDE-209.

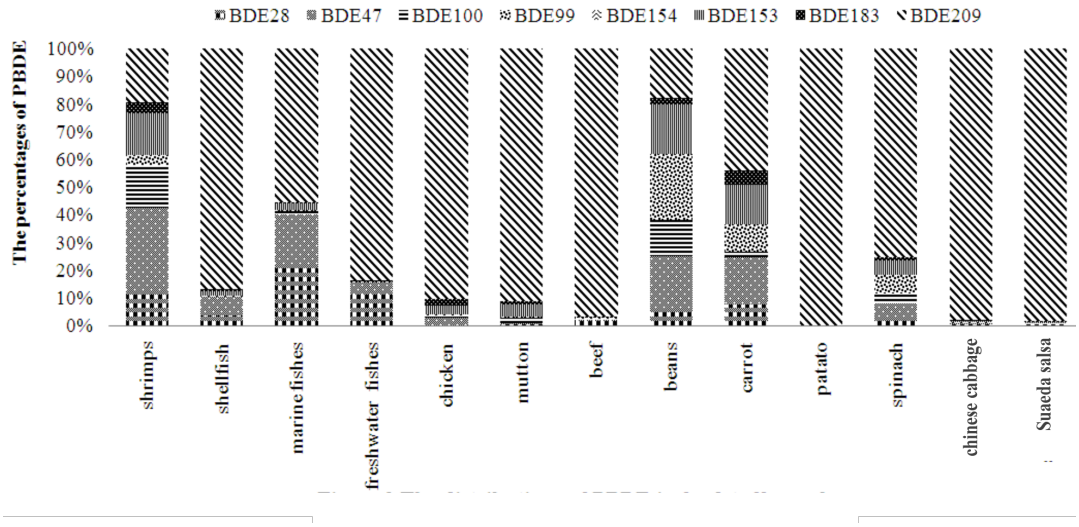

Fig 1 The distributions of PBDEs in food stuff samples

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