Estimation of exposure to polybrominated diphenyl ethers of people surrounding Nanjing Chemical Industry Park via fish consumption

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Abstract. Nanjing Chemical Industry Park (NCIP) is an important industrial base with more than 300 chemical plants. Taking NCIP as a research area, this article conducted a random sampling survey on the aquatic product consumption of residents in the NCIP and its surrounding areas. Then this study preliminarily estimated the exposure level of local residents to polybrominated diphenyl ethers (PBDEs) associated with fish consumption. The mean intake of Σ6 PBDEs via fish consumption was 0.69 ng/kg body weight b.w./day with a range of 0.35-1.63 ng/kg b.w./day. There was no significant difference in total intake of PBDEs at different body weights. Among the six PBDEs congeners, BDE-47 was dominant in the total intake, with an average contribution rate of 77%. The daily exposure to PBDEs decreased with the increase of body weight. During this period, the total intake of PBDES through fish consumption was at a low level. Overall, the estimated daily intake of total PBDEs was far below the LOAEL for the population in this region.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants that have been widely used and are commonly found in various environmental media [1-3]. Since they were first used in the early 1970s, the three main commercial formulations of PBDEs were penta-BDE, octa-BDE and deca-BDE [4]. PBDEs mainly exist in the form of homologues of tri-, tetra-, penta-, and hexabromides [5].

They have environmentally persistent, bioaccumulative and biotoxicity, so they tend to accumulate and biomagnification in organisms through the food chain [6]. Over the past 30 years, the concentration of PBDEs in human blood, milk, and other tissues has doubled every four to six years [7]. Fish consumption is one of the main approaches for human exposure to PBDEs [8]. Some studies have found that the concentration of PBDEs in human samples is positively related to dietary intake of fish and shellfish [9].

In recent years, with the acceleration of industrialization and urbanization process, the urban pollution problem has become worse and worse, especially severe pollution of rivers and lakes caused by discharging a large amount of sewage. Nanjing is a modernized city with rapid development, considered as one of the most active economic development regions in China. Nanjing Chemical Industry Park (NCIP) is located in the north of Nanjing, and situated on the north bank of the Yangtze.
River. NCIP, established in October 2001, is the only chemical industry park which is engaged in development of the petrochemical industry, with the approval by the state in Nanjing, regarded as the second national-level major petrochemical industry base of China. NCIP mainly develops product series like petroleum, natural gas chemical industry, high polymer materials, organic chemical materials, new chemical materials and so on. In the past few decades, environmental incidents have frequently occurred, which has seriously affected the ecological environment, human health and social security.

The global per capita supply of fish rose from 8 kg in 1950 to 16.2 kg (equivalent to live weight) in 2002 [8]. Overall, fish provided at least 20% of the per capita consumption of animal protein for more than 2.6 billion people. Many studies indicated that fish consumption is the main route for persistent halogenated hydrocarbons exposure, which are potential risks to human health. And the maximum residue limit allowed in aquatic products is used to simply evaluate if aquatic products are harmful to the human body. In 2005, our country reset the maximum residue limits for DDTs, HCHs and PCBs in aquatic products. They are respectively 0.5, 0.1 and 2.0 mg kg\(^{-1}\) (wet weight). At present, there is no related residue standard on PBDEs. However, after people eat fish polluted by PBDEs, a certain concentration of PBDEs is accumulated in the body. Therefore, this study aimed to preliminarily estimate human daily intake of PBDEs via fish consumption by local people surrounding NCIP.

2. Determination of model framework

In July, 2009, we carried out the random sampling investigation for residents surrounding the NCIP so as to perform further research for the exposure level of PBDEs via fish consumption by people. In the form of questionnaires, we made a survey in the NCIP and its surrounding areas (Changlu Town, Dachang District, Pudong Village/Xiajia Village, etc.). The investigation content mainly contained fish consumption (including food fish species, intake, frequency, etc.) by people with different ages, weight, genders and occupations. A total of 286 valid questionnaires were collected from the survey. The basic information of respondents was shown in Table 1. Food fish species were described in Table 2.

According to Table 2, due to more river network systems in the Yangtze River Basin, there are over 10 species of food fish and the consumption is different. Crucian carps with the maximum consumption cover 28.15%; the consumption of grass carps ranks second, occupying 27.80%; the sum of them is 55.95%; bighead carps with the minimum consumption hold 0.51%.

| Table 1. Basic information of respondents. |
|--------------------------------------------|
| Sexuality | Male | 51% | Female | 49% | 11-20 | 3% |
| Age | 0-10 | 7% | 11-20 | 13% | 21-30 | 3% |
| | 21-40 | 41% | Weight (kg) | 41-50 | 18% |
| | 41-60 | 31% | 51-60 | 33% |
| | >61 | 7% | 61-70 | 27% |
| Occupation | self-employed | 34% | worker | 26% |
| | farmer | 11% | Eat fish | 96% |
| | sales clerk | 9% | 71-80 | 10% |
| | driver | 8% | 81-90 | 2% |
| | others | 7% | Don't eat fish | 4% |
| | student | 5% | | |
Table 2. Food fish species.

| Food Fish Species | Grass Carp | Crucian Carp | Chub | Bream | Hairtail | Ricefield Eel | Yellow Catfish | Black Carp | Catfish | Whitefish | Bighead Carp | Others |
|-------------------|------------|--------------|------|-------|----------|--------------|----------------|------------|---------|-----------|--------------|--------|
| Proportion (%)    | 27.80      | 28.15        | 15.98| 7.80  | 8.94     | 2.99         | 1.57           | 1.97       | 2.05    | 1.06      | 0.51         | 1.10   |

3. Estimated daily intake of PBDEs via fish consumption

3.1. Estimation of the total intake amount of PBDEs

As there are many species of fish food, due to the existence of factors like family diet and personal habits, it is impossible that every species of fish has detailed and sufficient data. Therefore, we select crucian carps with the maximum consumption in the investigation area to make a survey, and carry out the research for the daily exposure level of PBDEs via crucian carp consumption by people with different weights. Gao Zishen et al [10] investigated the content of 12 kinds of PBDEs in crucian carps in the Yangtze River Basin of Eastern China. Among them, 6 kinds of PBDEs were not detected and the others were detected. This article takes the related information as the model estimation data.

Recommended by the Food and Agriculture Organization of the United Nations and the World Health Organization, the acceptable daily intake (ADIs) is used to estimate the exposure level of persistent halogenated hydrocarbons in the human body (estimated daily intake, EDI). The computational formula for the EDI of PBDEs via the crucian carp consumption by residents is as follows:

$$EDI_{\Sigma PBDEs} = C_{\Sigma PBDEs} \times IR \times f$$

In the formula, $C_{\Sigma PBDEs}$ is the total content of 6 kinds of PBDEs in the fat of crucian carps consumed (ng g$^{-1}$ fat$^{-1}$); f is the fat content of food fish (with regard to crucian carps, f is 1.23%) [10]; IR is the average daily crucian carp intake by residents (g d$^{-1}$); it is assumed that, for all people, the absorption rate of PBDEs is 100% [8].

According to the data obtained from the investigation, the intake of PBDEs via crucian carp consumption by residents with different weights is shown in Figure 1.

**Figure 1.** Estimated daily intake of PBDEs via fish consumption with different weights. The numbers on the bar shows the values of total PBDEs intake.

According to the information shown in the Figure, infants with a weight of 0-10 kg are not investigated. With regard to other people, there is corresponding information on the exposure level of PBDEs. People with a weight of 11-20 kg and 20-30 kg are mainly children. The daily intake of PBDEs via crucian carp consumption is 24.42-26.25 ng d$^{-1}$, higher compared with other weight ranges, which may be related to the diet habit. Among people with the weight of 31-90 kg, the daily intake of PBDEs rises with the increase of body weight. The daily intake of PBDEs via fish consumption by
people with the weight of 81-90 kg is the highest, reaching 30.13 ng d⁻¹. This may be due to the fact that people with heavier weight have a relatively larger total daily diet and correspondingly more fish.

The exposure level of PBDEs via crucian carp consumption by residents in the Yangtze River Basin is 21.68-30.13 ng d⁻¹ and the average value is 25.22 ng d⁻¹. The foreign similar researches indicate that the average value of Sweden is 23 ng d⁻¹ [11], the average value of Catalonian (Spain) is 20.8 ng d⁻¹ [12], the average value of Finland is 23 ng d⁻¹ [13], the value of America is 4.5-15.7 ng d⁻¹ [14], the average values of Netherlands are respectively 29.6 ng d⁻¹ and 15.9 ng d⁻¹ [15] in 2001-2002 and 2003-2004, and the average value of Canada is 1.3 ng d⁻¹ [16]. Compared to foreign researches, our country is at the same level as Sweden, Catalonian (Spain), Finland, Netherlands (2001-2002), but higher than Netherlands (2002-2003) and Canada.

3.2. Estimation intake of PBDE congeners

According to the literature [10], the level of 6 PBDE congeners detected in crucian carps in the Yangtze River Basin is combined with crucian carp consumption by NCIP population to calculate the daily intake of PBDEs via crucian carp consumption by people with different weight. The distribution pattern of PBDEs is shown in Table 3. The distribution pattern of BDE congeners is shown in Table 2.

Table 3. Daily exposure levels of PBDEs with different weight.

| Weight Range (kg) | 11-20 | 21-30 | 31-40 | 41-50 | 51-60 | 61-70 | 71-80 | 81-90 |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Exposure Level   | 1.63  | 1.05  | 0.62  | 0.51  | 0.44  | 0.39  | 0.36  | 0.35  |

Figure 2. Congener-specific contributions of total PBDEs (including 6 PBDE congeners) intake with different weight.

In order to assess the potential harm of PBDEs to the human body, Darmerud et al [17] selected the most sensitive end point of toxicity based on the murine thyroid effect, and recommended the lowest observed adverse effect level (LOAEL) as the evaluation index, and its value was 1 mg/kg b.w./d. It can be seen from Figure 2 that the exposure level of PBDEs via crucian carp consumption by people in the Yangtze River Basin (0.35-1.63 ng/kg b.w./d) is much lower than the index. Meng Xiangzhou et al [8] pointed out that the intake of PBDEs via fish consumption and breathing by Chinese residents (except infants) is 103-319 pg/kg b.w./d. The exposure level of PBDEs via crucian carp consumption by people in the Yangtze River Basin was greater than that in Meng Xiangzhou’s study. However, it is at the same level compared with foreign researches on exposure level of PBDEs via food consumption,
like America (0.9-1.2 ng/kg b.w./d), Spain (1.2-1.4 ng/kg b.w./d), Sweden (0.53-0.63 ng/kg b.w./d) and Netherlands (1.7 ng/kg b.w./d). In addition, the daily exposure level of PBDEs per unit body weight decreased with the increase of body weight. The daily exposure level of people with a weight of 11-20 kg was the highest, reaching 1.63 ng/kg b.w./d. The daily exposure level of people with weight of 81-90 kg was the lowest, reached 0.35 ng/kg b.w./d. The reason may be that the family diet in China mainly takes the family as the unit, and the diet of the same family is the same. There is a difference in intake, but not obvious (except for special preferences). Therefore, the heavier the body weight was, the less the load of PBDEs per unit body weight would be.

Moreover, according to Figure 2, among PBDE congeners, BDE 47 was the most important compound, which was the same as the research by Meng Xiangzhou et al. The daily exposure level of BDE 47 covered 77% of the total amount of PBDEs. In the proper order, the others were BDE 154 (7.5%), BDE 153 (4.8%), BDE 99 (4.6%), BDE 100 (3.2%) and BDE 71 (2.9%).

4. Conclusions
According to the exposure estimation, the highest exposure level of PBDEs only via crucian carp consumption by residents in the Yangtze River Basin was 1.63 ng/kg b.w./d, lower than the LOAEL 1 mg/kg b.w./d recommended by Darnerud et al, similar to the exposure levels via food consumption or other ways that have been studied abroad. At present, PBDEs are still widely present in various environmental media. Therefore, to understand the daily intake of PBDEs through fish consumption has certain significance for quantitative studying on the effects of pollutants on human health.

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