POLYBROMINATED DIPHEYL ETHER LEVELS IN SEVERAL RETAIL FOODS IN A SOUTH CHINA CITY

Zhang Jianqing*; Jiang Yousheng; Zhou Jian; Fang Daokui; Huang Haiyan; Deng Bo; Liu Bin; Wang Chunlei
(Shenzhen Center for Disease Control and Prevention, Shenzhen, 518020; *CorrespondingAuthor:Zhang Jianqing, E-mail：zhjianqing95@gmail.com)

【**Abstract**】**Objective:** To investigate PBDE levels in several retail foods in a South China city. **Methods:** The total 7 categories of food were collected in the market and PBDE levels were analyzed quantitatively with Soxhlet extraction, acidic silica gel treatment, cleanup through silica gel and alumina column and determination through HRGC/HRMS. **Results:** In each sort of food, the average concentration of PBDE congeners was 227.15 pg/g, 189.50pg/g, 75.40 pg/g, 30.32 pg/g, 13.33 pg/g, 5.21 pg/g, 2.39 pg/g for egg, fish, pork, beef, visceral organs of pig, rice and vegetables respectively and fresh weight was used for report result. The rank of PBDEs total concentration was egg, fish, pork, beef, visceral organs of pig, rice and vegetables. BDE-47 isomer accounted for the greatest proportion of the total amount of the PBDE in all samples, with percentages of 12～65. **Conclusions:** Dietary intake can't be ignored as a route of exposure to PBDEs for the general population and more concern should be given to the pollution of PBDEs in foods.

Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in electric appliances, plastics in computers, foam plastics in furniture and other flammable materials such as carpet and cloth. PBDEs have 209 congeners which were first commercially available in Germany in 1970's. PeBDEs, OcBDEs and DeBDEs are the main congeners used commercially. 82% of the commercially available PBDEs are DeBDEs and approximate 150000 tons brominated flame retardants are produced every year in the world. As mentioned above, flame retardants are widely and massively used. Although the levels of some POPs （polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCs)） in the environment, wildlife, food, water, house dust, human tissues, and fluids these matrices have decreased after their ban, polybrominated diphenyl ethers (PBDEs) have increased in recent years[1,2]. In addition, they are structurally akin to the PCB's and other polyhalogenated compounds, so there may be similar effect on human health as Dioxins. The health hazards of these chemicals have attracted increasing scrutiny in recent years. A bill had been passed to phase out the use of flame retardants in electric appliances by 2006 in European Union, while DeBDEs are still massively used as flame retardants in China. More concern should be given to the pollution of PBDEs in foods.

As one kind of persistent organic pollutants (POPs), PBDEs have characteristics of lipophilicity, difficulty in degradation, structural stability, bioaccumulation and long-range transportation. PBDEs may possess thyroid toxicity, neurodevelopmental toxicity, immune toxicity and other health effects, such as mutagenesis, teratogenesis and carcinogenesis. It is of significance to investigate PBDE levels in foods[3].

In this study, PBDE levels in several retail foods in a South China city were analyzed quantitatively step by step with Soxhlet extraction, acidic silica gel treatment, cleanup through silica gel and alumina column and

determination through isotope dilution HRGC/HRMS.

Materials and Methods

Sample Collection

The sampling strategy used to choose the 7 food categories was based on the main food consumed by the local residents, totally 20 samples, including of rice, egg, marine fish, freshwater fish, pork, beef, visceral organs and vegetables, etc. were analyzed.

Sample Pretreatment and Determination

The edible parts of foods were acquired, which then were grinded, frozen-dry to constant weight and water content was determined. Eight stable C^{13} isotopically labeled analogs of PBDEs were spiked into each sample. Then each sample was extracted with 1:1 hexane/methylene chloride by Soxhlet extraction technique for 18～24h. After extraction, each extract was treated with 30% acidic silica gel, cleaned-up with acidic silica gel and alumina column. After cleanup, the extract was concentrated to near dryness. Prior to injection, C^{13} isotopically labeled internal standards were immediately added to each extract and an aliquot of the extract was injected into the gas chromatograph. The analytes were separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer and quantitative analysis was performed. The PBDEs level was reported by pg/g fresh weight.

Results and Discussion

PBDE Levels in Foods

The main seven PBDE congeners commonly found in the samples were measured, including BDE28, BDE47, BDE99, BDE100, BDE153, BDE154 and BDE183. The concentrations of PBDE congeners in each sort of food were summarized in table 1.

Table 1 Concentrations of PBDEs in retail foods（pg/g wet weight）

Food category	BDE 28	BDE 47	BDE 99	BDE1 00	BDE 153	BDE 154	BDE 183	∑PBDE（pg/g）
Rice	nd	0.068	0.053	0.154	0.020	nd	nd	0.29
Fragrant rice	0.32	1.45	0.16	0.19	0.18	0.03	0.57	2.90
Mixed rice	2.63	6.03	1.67	0.50	0.36	0.09	1.15	12.43
Carrot	0.13	0.65	0.32	0.13	0.02	0.05	0.14	1.44
Cucumber	0.42	2.00	0.49	0.14	0.089	0.052	0.14	3.33
Beef	0.38	6.08	1.54	0.45	0.26	0.28	0.61	9.60
Mixed beef	2.23	19.34	10.57	1.57	6.96	3.91	6.44	51.03

Pork	0.24	26.69	4.38	1.23	8.98	1.41	14.57	57.51
Mixed pork	7.81	32.96	15.53	3.66	11.43	6.50	15.40	93.29
Liver	2.03	8.05	2.32	0.77	3.06	0.57	3.00	19.80
Mixed kidney	0.62	1.84	1.21	0.09	1.08	0.18	1.84	6.86
Duck egg	0.38	23.03	18.96	6.31	19.88	11.83	24.40	104.80
Egg	1.48	139.19	180.12	43.96	41.50	16.67	9.71	432.63
Salted duck egg	0.61	17.75	19.48	11.53	43.34	19.03	32.27	144.01
Grass carp	5.49	26.64	0.03	2.99	1.03	14.15	0.049	50.38
Tilapia	9.11	65.20	5.35	16.70	10.04	75.74	0.37	182.52
Bullhead	4.66	31.56	2.14	7.77	0.47	24.73	0.015	71.35
Yellow fish	2.24	52.82	64.36	22.36	12.16	11.91	7.51	173.35
Hairtail	6.41	160.34	21.62	96.45	30.79	141.08	10.68	467.37
Pomfret	3.40	66.87	12.18	30.31	13.44	57.65	8.20	192.03
MDL	0.0037	0.0028	0.0076	0.0050	0.0075	0.0079	0.013	

In each sort of food, the average concentration of PBDE congeners was 227.15 pg/g, 189.50pg/g, 75.40 pg/g, 30.32 pg/g, 13.33 pg/g, 5.21 pg/g, 2.39 pg/g for egg, fish, pork, beef, visceral organs, rice and vegetables respectively. It was obvious that the PBDE congeners were detected in every sort of food and the pollution situation was egg>fish>pork>beef>visceral organs>rice>vegetables in the order of concentration. In the present study, the highest concentration of total PBDEs corresponded to egg, followed by fish, it was different from other research. Domingo's research presented that fish processed the highest concentration which was 563.9 ng/kg ww, and the ∑PBDEs of egg was 94.8 ng/kg ww in all categories food. The comparison for ∑PBDEs from other countries was been presented in Fig 5 [4-7]. There were significant difference in pollution accumulation among various sorts of foods, and it even existed in different types of foods within the same categery. The same as fish, for example, the average concentration of PBDE congeners for hairtail and grass carp was 467.37pg/g and 50.38pg/g respectively, it was nearly eight fold high in hairtail fish than grass carp fish . The possible reason lies in sources of foods, degree of pollution within different environment and different bioaccumulation of organism for PBDE congeners.

Characteristics of PBDE Pollution

DBE-47 isomer accounted for the greatest proportion of the total amount of the PBDE in all samples, with percentages of 12～65. In all samples, as fish was similar in characteristics of PBDE pollution, so were pork, beef and visceral organs, so was egg and so were vegetables and rice (Figure 1-4). The main pollutants were

BDE47, BDE154 and BDE100 in fish; The main pollutants were BDE47 accounting for 40%, BDE99, BDE153 and BDE183 accounting for 15%respectively in pork, beef and visceral organs; BDE99, BDE 47and BDE 153 were the main pollutants in egg, accounting for 30%, 26%and 15%respectively; and BDE47, BDE 28 and BDE 99 were the main pollutants in rice and vegetables, accounting for 50%, 17%and 13%respectively. There appeared different characteristics of PBDE pollution in various organisms, due to the diverse bioaccumulation of organism for different PBDE monomers.

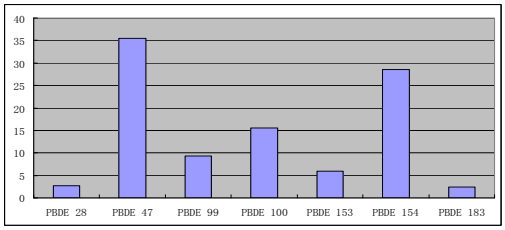

Fig 1 Characteristics of PBDE pollution in fish

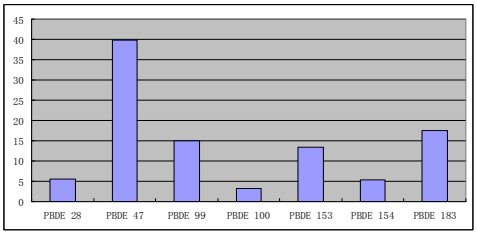

Fig 2 Characteristics of PBDE pollution in pork and visceral organs

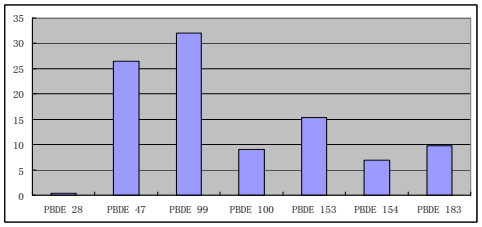

Fig 3 Characteristics of PBDE pollution in egg

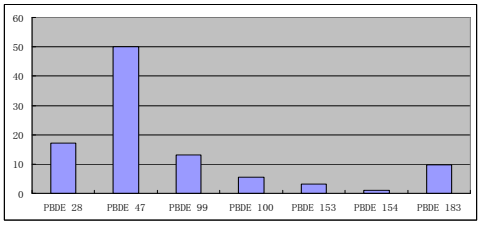

Fig 4 Characteristics of PBDE pollution in rice and vegetables

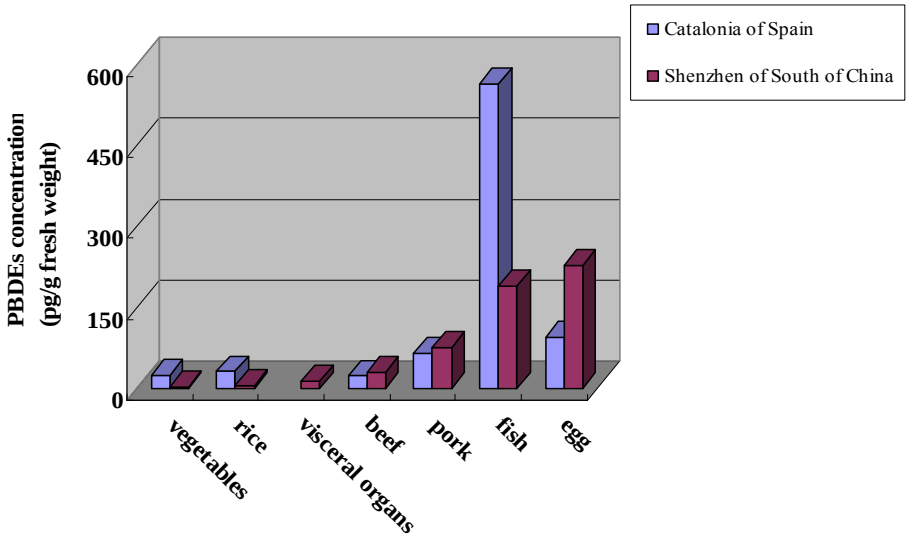

Fig.5 Comparison ∑PBDEs concentration in different categories food from Spain and Shenzhen of South of China

Conclusions

The methods for determination of PBDE in foods were established in our laboratory, through which the background levels of PBDE in foods were investigated. Further investigation is being or to be performed. According to the results, the PBDE congeners were detected in each sort of food. In conclusion, dietary intake can't be ignored in route of exposure to PBDEs for the general population and more concern should be given to the pollution of PBDEs in foods. Further research is needed to establish the background levels of different categories food in order that exposure from food and other sources for the general population could be approached in the future.

Acknowledgement

This project was supported by Medical Scientific Research Foundation of Guangdong Province, China and municipal Science & Technology Bureau of Shenzhen, Guangdong, China.

References

[1] Doucet J, Tague B, Arnold DL Cooke GM, Hayward S, Goodyer CG. *Environ Health Perspect.* 2009; 117(4):605-10.

[2] Toms LM, Hearn L, Kennedy K, Harden F, Bartkow M, Temme C, Mueller JF. *Environ Int.* 2009;35(6):864-9.

[3] Schecter A, Shah N, Colacino JA, Brummitt SI, Ramakrishnan V, Robert Harris T, Päpke O. *Chemosphere.* 2009; 75(5):623-8.

[4] Schecter A., Harris TR., Shah N., Musumba A., Papke O.. *Mol. Nutr. Food Res.* 2008; 52:266 – 272

[5] Domingo JL., Martı′-Cid R., Castell V., Llobet JM. *Toxicology.* 2008; 248:25–32

[6] Covaci A., Bervoets L., Hoff P., Voorspoels S, Voets J, Van Campenhout K, Blust R, Schepens P. *J Environ Monit*, 2005; 7(2): 132-6.

[7] Schecter A., Papke O, Tung K.C., Joseph J, Harris TR, Dahlgren J. *J Occup Environ Med,* 2005; 47(3): 199-211.