Bioaccumulation of polybrominated diphenyl ethers (PBDEs) in sediment aged for 2 years to carps (*Cyprinus carpio*)

S Y Tian[1,2,3], J Y Li[1] and X M Jia[1]

[1]College of Marine and Environmental Sciences, Tianjin University of Science and Technology, Tianjin 300457, China
[2]Tianjin Key Laboratory of Marine Resources and Chemistry, Tianjin 300457, China

E-mail: tiansy@tust.edu.cn

Abstract. In order to understand the risk of polybrominated diphenyl ethers (PBDEs) existing in sediment for years, the accumulation of PBDEs in sediment aged for 2 years to fish was investigated. Simulated aquatic system microcosms were conducted with PBDE contaminated sediment aged for 2 years and carps were cultured in the microcosms for 20 days. PBDE concentrations in carp tissues were analyzed to estimate the bioavailability of aged PBDEs in carps. The main spiked PBDE congeners were detected in sediment even though the contaminated sediment was aged for 2 years. Similarly, the five PBDE (BDE-28, 47, 100, 153 and 154) congeners which probably were bioaccumulated by carp were detected in fish tissues, indicating that PBDEs could be bioaccumulated after aging for 2 years. The PBDEs distribution revealed that the concentrations of polybrominated diphenyl ethers in tissues of *Cyprinus carpio* is in this order of magnitude: gut > liver > gill > fillet. The PBDEs concentrations in fillet were as high as 67.9 ng/g dry wt, in which BDE-47 contributed almost 50% in profile.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a kind of brominated flame retardants thay are widely used in human livings and industry. They have been detected in a variety of environments due to their big production and usage since they came out [1-5]. Because of their persistence, toxicity, bioavailability and long distance transportation. Some PBDE congeners were identified as persistent organic pollutants since 2009.

PBDEs are very hydrophobic, thus are prone to attachment on solid particles. Therefore, sediment becomes the important sink of PBDEs and could impact the transport and fate of PBDEs in environment importantly. PBDEs deposited in sediment are potentially accumulated by aquatic organisms. Several studies have reported the accumulation of PBDEs beimg deposited in sediment by benthic organisms [6-8]. The longer PBDEs are deposited in the sediment, the less of the rapid desorbing part for the sediment-associated PBDEs. Similarly, the proportion of the slowly desorbing part was increased gradually [9]. Consequently, the bioaccumulation of PBDEs deposited in sediment decreases with increase in depositing time. However, little study has been conducted to detect the bioavailable degree of PBDEs deposited in sediment for years through bioaccumulation experiments. The evaluation of the available characteritics of PBDEs to organisms after deposited in sediment for years is helpful for assessment of the PBDEs environmental health risk.

In the present study, simulated pond system microcosms were built up with PBDE contaminated

sediment aged for 2 years and carps were cultured in the microcosms for 20 days. PBDE concentrations in carp tissues were analyzed to evaluate the bioaccumulation of PBDEs in carps. The results would help us to evaluate the risk of sediment-associated PBDEs already existing in environment and nanoparticles.

2. Materials and methods

2.1. Chemicals

The PBDEs standard solution were bought from AccuStandard company (New Haven, CT, USA). Commercial products were purchased from Great Lakes Chemical Corporation (West Lafayette, IN, USA). All solvents used for the analysis were chromatographic and obtained from Concord Science and Technology Co. (Tianjin, China).

2.2. Sediment preparation

The clean sediment was from an ecological preservation area. The procedures to prepare and contaminate the sediment have been reported in details [8]. The spiked sediment was aged for 2 years in the microcosms before the experiment.

2.3. Experimental setup

Microcosms were set up using 6 clean rectangular glass aquaria. There were experimental group and control test. The control test was conducted with unspiked sediment, free of PBDEs. The experimental group was built up with spiked sediment aging for 2 year. The experimental aquaria was built up by depositing the sediment at the bottom, then, water was added to overlay the sediment to obtain a simulated lake system. The microcosms were equilibrated for 1 month before 20 carps (*Cyprinus carpio*) were added. The exposure lasted for 20 days and all fish were sampled for analysis.

2.4. Analysis of PBDEs

Organism tissues and the sediment in experimental microcosms were lyophilized and weighed. The concent of PBDEs in fish tissues and sediment was analyzed by the method reported by Zhu *et al* [10]. The measurement was carried out using gas chromatograph (Agilent 7890A) mass spectrometer (Agilent 5975C). GCMS ranned in the mode of negative chemical ionization. The column mode was DB-5 capillary column.

2.5. Quality assurance and quality control

The sample treatment and clean up procedure were carried out in a clean room. The procedural blank was done to ensure the accuracy of the treatment. The qualitative and quantitive of PBDEs contents were conducted by the mixed standards containing known amounts of PBDEs congeners. BDE-77 was used as recovery indicator and the recovery of the ananlysis was between 80% and 120%. The reported data were not corrected by recovery.

3. Results and discussions

3.1. PBDE concentrations variation after aging

Three kinds of PBDEs commercial products were used to contaminate the experimental sediment. They were penta-, octa- and deca-BDE. All the main PBDE congeners in the commercial products could be still detected even though the contaminated sediment were aged for 2 years. The detected PBDE congeners contents decreased after aging for 2 years except for BDE-28 and BDE-47 as shown in figure 1. The main reason for the decreasing concentration may be the transformation of PBDEs. The ratio of BDE-47 to BDE-99 was about 0.65 in the primal spiked sediment. But the ratio of BDE-47 to BDE-99 increased to 1.1 when the contaminated sediment aged for 2 years. Even higher ratios of BDE-47 to BDE-99 were reported in field sediments and biota. For example, it was reported

that the ratio of BDE-47 to BDE-99 were 2.45 ± 0.95 in sediment and even higher ratio of 5.08 ± 2.07 in mussel from Bo Sea [11]. There were two reasons for the difference of the ratios between sediment and organism. On the one hand, BDE-99 is more liabel to be debrominated than BDE-47. On the other hand, BDE-47 is easier accumulated by organism than BDE-99. Furthermore, the concentrations of BDE-183 and BDE-206 in aged sediment were only half of those in primal spiked sediment. And the concentrations decreased more for BDE-207, BDE-208 and BDE-209. It has been verified that BDE-209 would transform to hexa-BDE congeners through nona-BDE congeners. It was reported that meta-position and para-position debromination are preferred pathway for BDE-209, which produced BDE-207 and BDE-208 [12]. The increasing concentration for BDE-47 and BDE-28 could be attributed to the transformation of high brominated congeners to low brominated congeners.

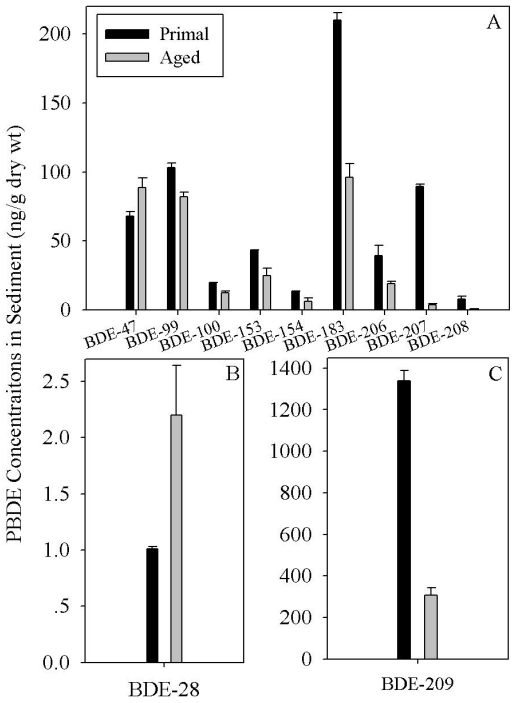

Figure 1. PBDE concentrations in the primal spiked sediment and sediment aged for 2 years. A: the concentrations for BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-206, BDE-207and BDE-208; B: the concentrations for BDE-28; C: the concentrations for BDE-28.

3.2. PBDEs concentrations in tissues of Cyprinus carpio

After exposure in the microcosms for 20 days, several PBDE congeners were detected in fillet, liver, gill and gut tissues of *Cyprinus carpio*. The variation of PBDEs in the fish tissues are shown in figure 2. Five PBDE (BDE-28, 47, 100, 153 and 154) congeners were detected in the fish tissues. The PBDEs distribution shows that the concentrations in different tissues is in this order of magnitude: gut > liver > gill > fillet. Several studies have found that PBDEs are prone to be accumulated in liver tissues [13, 14]. The PBDEs concentrations in fillet were even up to 67.9 ng/g dry wt, indicating that PBDEs could be bioaccumulated after aging for 2 years.

As showed in figure 3, the first congener in all the tissues was BDE-47, which accounted for 50% to 70% of the total amount of the detected congerners. BDE-154 was the second congener in the five congeners. This result was in agreement with other studies. BDE-47 always accounts for the largest propotion in organism tissues whether in field research or in lab experiment. In the commercial PBDE

products of Penta and Octa, BDE-99 and BDE-183 is the important congeners, respectively. And the contents of the both congeners were relatively high in spiked sediment, However, they were not detected in any of the fish tissues. This finding was also aggress with other reports [13]. The reason for the phenomenon that BDE-99 and 183 were not detected in fish tissues was because for the biotransformantion in biota tissues. Roberts *et al* [15] reported that some congeners, such as BDE-153 and BDE-183, are liable to be transformed into some lower brominated congeners by common carp through *in vitro* experiment, while other congeners, such as BDE-47 and BDE-154 were resistant to debrominating metabolism.

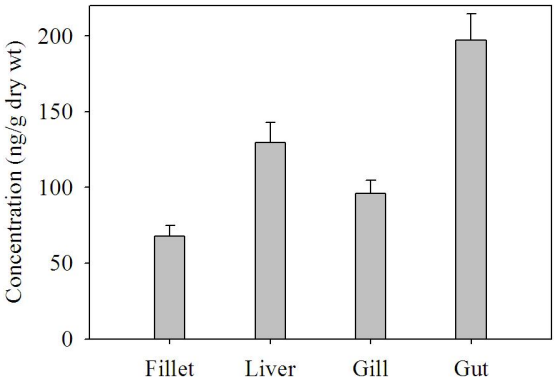

Figure 2. PBDE concentrations (ng/g dry wt) in *Cyprinus carpio* tissues.

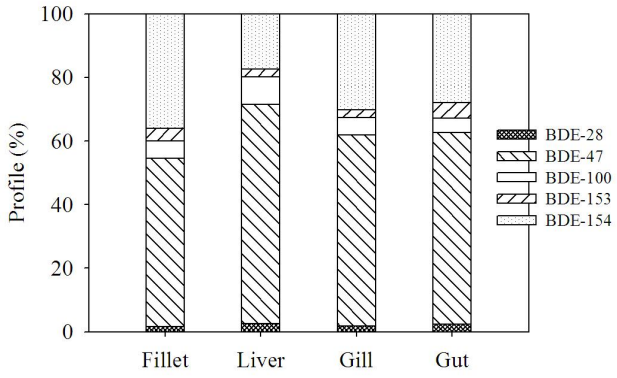

Figure 3. PBDE congener profiles in *Cyprinus carpio* tissues.

4. Conclusions

The sediment-associated PBDEs could be bioaccumulated by fish even aged for 2 years in a pond simulated microcosm.

Acknowledgments

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