POLYBROMINATED DIPHENYL ETHERS ACCUMULATION IN FISHES WITH DIFFERENT LIVING PATTERNS IN TAIWAN RIVERS

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Introduction

In 1995, 64 human lives were snatched away by a fire disaster happened in central Taiwan, and then the Fire Act was revised particularly focused on the usage of fireproof building materials. Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in all kinds of commercial products. Increasing evidences showed that PBDEs were released to the environment during the manufacture of these chemicals, use of electronic equipments or disposal of consumer products.[1] However, the investigations of this pollutant situation in Taiwan environment are quite lack. The objectives of study are aimed to investigate the levels of PBDEs in sediments and fishes with different living patterns from twelve principal rivers in Taiwan, and to assess the accumulation of PBDEs via the calculation of biota/sediment accumulation factor (BSAF) between fish and sediment.

Materials and Methods

Sample collection

One middle or upstream sediment samples and two downstream sediment samples were collected from each of twelve principal rivers in Taiwan. The sampling of sediments was implemented during the high and low flow seasons of twelve principal rivers. All the fish samples was collected in the downstream sites of twelve principal rivers during high flow season.

Sediment and fish Samples Cleanups and HRGC/HRMS Analysis of PBDEs

The analytical method for all samples was modified according to Draft USEPA Method 1614.[2] Twenty grams freeze-dried sediment or seven grams freeze-dried edible fish samples were spiked with a suite of ^{13}C-labed-PBDE recovery standards and extracted with Soxhlet extractors. Sample cleanup was accomplished with acidic silica-gel, acidic alumina column. PBDE analysis was conducted using a HRGC-HRMS isotope dilution method using a 15 m DB-5HT column. 22 PBDE congeners selected for quantitative analysis were including tri- to deca-PBDE. However, only 21 PBDE congeners were quantified in fish samples except for BDE-17.

Results and Discussion

PBDE levels in sediments and fishes

The levels of PBDEs in sediments and fish samples from twelve principal rivers are listed in Table 1. The concentrations of PBDEs in sediment collected in low flow season are mostly higher than those in high flow season. This trend maybe due to the surface sediments was swept away in the high flow rate of river water. The highest PBDEs concentration of sediment was found in Bajhang River (261285 pg/g d.w.) and follow by Yanshuei River (120984 pg/g d.w.), Beigang River (89001 pg/g d.w.), and the lowest concentration was found in Beinan River and Da-an River (170 pg/g d.w.). The dominant PBDE congeners in sediments were BDE 209, 197, 47, 183, 99, and dominant homologues were deca-, octa- and tetra-BDE. The different congener profiles of the highest and lowest levels of sediments in Bajhang and Beinan Rivers are shown in Figure 1. Besides the Bajhang and Yanshuei rivers, the PBDEs concentrations of sediments in principal rivers of Taiwan were much lower than those in northern America or Europe[3-5].

The total concentrations of PBDEs in fish samples were ranged from 33724 pg/g d.w. (*Varico rhinos barbatulus*) collected from Da-an River to 1280 pg/g d.w. (*Oreochromis niloticus niloticus*) from Yanshuei

River. The dominant PBDEs congeners in fish samples were BDE-47, BDE-100, BDE-154, BDE-209, and the dominant homologues were deca-, tetra- and penta-BDE. In general, the PBDEs concentrations of fishes in principal rivers of Taiwan were much lower than those in northern America or Europe[5-7]. The higher levels of PBDEs were found in the benthic fishes such as Black porgy (*Acanthopagrus schlegeli*) and Swamp eel (*Monopterus albus*) than the other ichthyoplankton. It meant that the exposure scenario of benthic fish was different with ichthyoplankton.

Biota/sediment accumulation factor (BSAF) between fish and sediment

Table 2 summarizes the biota/sediment accumulation factor of PBDEs between fish and sediment. The data shows that BDE 47, 100, 119, 126, 154 are much easier to transfer and accumulation from sediments to fish tissues. But highly brominated BDEs such as BDE-209 have less accumulation ability than low brominated congeners. The mechanism of this phenomenon is that the low brominated congeners can pass through the membranes and get into the cell. The highly bromine substitution PBDEs with higher molecular masses which pass slowly through the membrane and are 'filtered' out and accumulate in the environment.[8] However, it is interesting that benthic fish have much higher accumulation abilities than ichthyoplankton especially in TeBDE, PeBDE and HxBDE (Figure 2). According to Table 2, BDE 47 and BDE 183 have similar accumulation potential from sediment to fish. But the BSAF of BDE 153 and BDE 154 are much higher than those in Eljarrat et al.[5].

Principal component analysis

The relationships between the BSAF of benthic fish and ichthyoplankton were analyzed by PCA. The result was shown in Figure 3. The first principal component (PC1) accounted for 59.1% of the variance, and PC2 accounted for 19.8% of the variance. PC1 is affected by BDE 71, BDE 100, BDE138, and PC2 is affected by BDE196, BDE209. Figure 3 shows that there is a cluster in Ichthyoplankton group. From this viewpoint, one may say that Ichthyoplankton have the same accumulation situation. Benthic fish, on the other hand, scatter over the figure. It seems likely that benthic fish have different diet habits which result in different congener pattern. More data are needed to clarify it.

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Table 1. Levels of total PBDEs in sediment and fish samples from twelve principal rivers in Taiwan.

Rivers	Sediment		Fish	
	dry season (pg/g d.w.)*	wet season (pg/g d.w.)*	Benthic fish (pg/g d.w.)	Ichthyoplankton (pg/g d.w.)
HoulungRiver	5744 (3503－8221)	2770 (2163－3842)	-	3871[a], 2453[a]
Beinan River	825 (582－1098)	831 (170－1428)	-	-
Da-an River	16994 (2351－29775)	592 (170－880)	33724[b]	3328[c]
Wu River	12716 (10240－14957)	3083 (840－6742)	12892[d]	-
Beigang River	34946 (1428－89001)	16100 (2258－25672)	-	1962[e], 2719[f]
Bajhang River	90105 (3442－261285)	70135 (1535－206377)	-	6725[g], 6447[g]
Jishuei River	3956 (3041－5609)	3946 (800－9025)	5363[h]	3020[i]
Yanshuei River	43193 (933－104538)	46293 (592－120984#)	10586[j]	1280[g]
Linbien River	4433 (2129－6036)	940 (747－1103)	-	2758[g], 1640[g]
Hualien River	1410 (244－2101)	536 (477－639)	-	3890[k], 2663[c]
Donggang River	14943 (7514－27506)	15361 (5126－23929)	-	2323#, [g], 6640[g]
Siouguluan River	609 (110#－1067)	1922 (518－4696)	-	-

* Mean (range)
# matrix effect interfere with quantitative analysis of PBDE congeners
[a] Common carp, [b] Taiwan shoveljaw carp, [c] Pale chub, [d] Black porgy, [e] Indo-Pacific tarpon, [f] Tenpounder, [g] Nile tilapia, [h] Pleco, [i] Greenback mullet, [j] Swamp eel, [k] Longarm mullet

Table 2. Biota/sediment accumulation factors of 21 PBDE congeners in two fishes with different living patterns.

Fish habitual behavior / PBDEs congeners	Benthic fish BSAF[a] (N=4)	Ichthyoplankton BSAF[a] (N=13)	BSAF investigate from previous study[b]
BDE-28	7.0 (0.1－17.5)	5.7 (1.4－16.2)	-
BDE-47	20.4 (0.9－58.9)	13.8 (2.6－35.8)	40 (29－49)
BDE-49	9.8 (0.5－25.2)	7.6 (1.6－26.0)	-
BDE-66	5.7 (0.2－12.0)	1.7 (0.8－3.3)	-
BDE-71	3.0 (0.1－11.3)	0.6 (0.1－1.8)	-
BDE-77	13.2 (1.1－35.2)	1.7 (0.2－3.9)	-
BDE-85	12.4 (0.0－48.8)	0.6 (0.0－1.6)	-
BDE-99	27.5 (0.4－102.4)	1.7 (0.2－4.9)	-
BDE-100	60.1 (1.7－179.7)	14.8 (4.0－36.8)	-
BDE-119	33.0 (6.9－48.3)	18.4 (2.5－61.3)	-
BDE-126	63.6 (21.8－112.1)	58.8 (11.2－178.8)	-
BDE-138	11.3 (0.1－43.9)	0.6 (0.0－1.9)	-
BDE-153	21.4 (3.6－60.0)	2.3 (0.3－6.4)	88 (75－104)
BDE-154	25.2 (8.4－62.8)	10.8 (2.6－22.9)	201 (177－216)
BDE-156	7.2 (0.2－25.7)	4.7 (0.1－30.8)	-
BDE-183	6.9 (0.1－21.9)	0.3 (0.0－0.9)	12 (9－17)
BDE-184	7.4 (0.7－19.6)	1.3 (0.2－4.1)	-
BDE-191	3.2 (0.4－6.4)	1.8 (0.1－12.9)	-
BDE-196	3.0 (0.2－8.3)	2.4 (0.1－17.4)	-
BDE-197	3.3 (0.1－8.5)	1.5 (0.1－8.0)	-
BDE-209	1.6 (0.0－5.2)	0.6 (0.0－2.8)	-

[a] Mean (range)
[b] Eljarrat et al., 2005

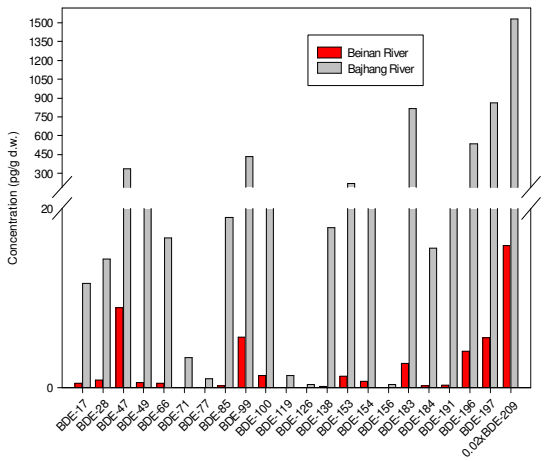

Figure 1. 22 congeners profile of PBDE in sediments with the highest and lowest PBDE levels.

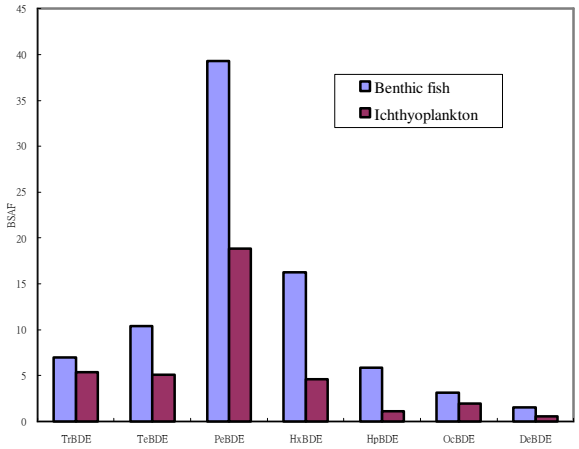

Figure 2. The BSAF value of PBDE homologues between two fishes with different living patterns.

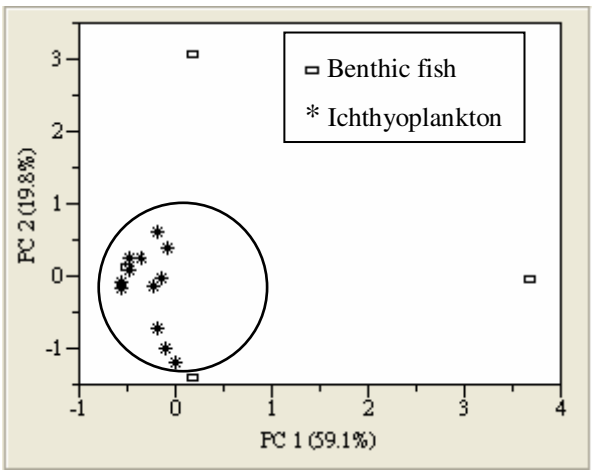

Figure 3. The score plot of PCA for the BSAF values from 21 PBDE congeners in Benthic fish and Ichthyoplankton