Polybrominated diphenyl ether accumulation: levels in sediment and fish with different aquatic factors and biota-sediment accumulation factors

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Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in many commercial products, such as rubber, electronic equipment, furniture, and building materials. PBDEs are released into the environment when they are manufactured and when products that contain them are used and disposed of [1-3]. The released PBDEs may be accumulated by biota and transported within the biosphere in food webs[4-5]. PBDEs have toxic effects on animals: they are teratogens (can disturb the development of an embryo or fetus) and carcinogens, cause hepatomegaly, result in neurobehavioral deficits, and interfere with thyroid function[6-8]. Many studies have reported the concentrations of PBDEs in sediments and fish from rivers and estuaries, but no attention has been paid to the effects of the accumulation of PBDEs on the water quality index and living patterns of fish. The objectives of this study were (a) to investigate the concentrations of PBDEs in sediments and fish with different living patterns in twelve principal rivers in Taiwan, (b) to evaluate the effects of water quality indices on PBDE accumulation in sediment.

Materials and methods

Twelve principle rivers in Taiwan were selected for sample collection. For each river, three sampling sites near water quality monitoring stations (one upstream and two downstream) were chosen. Samples were collected during the dry (April) and wet (September) seasons in 2004. Seventy-two surface sediment samples were collected and then freeze-dried, ground to fine powder, sieved with 60-screen mesh, and stored at 4 °C until analysis. Nineteen single or pooled fish samples were collected from the downstream of 10 rivers during the wet season, then freeze-dried, homogenized, and stored at −20 °C until analysis. The fish were divided into demersal (bottom dwelling/feeding) and pelagic (not bottom dwelling/feeding) fish based on their feeding habits.

The analytical method for all samples was modified according to Draft USEPA Method 1614.[9] 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.

Water quality indices included dissolvable oxygen (DO), water temperature, pH, 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), suspended solids (SS), ammonia-nitrogen (NH_3–N), and *E. coli* were obtained from the water quality monitoring network of the Taiwan EPA during the same sampling period. The biota-sediment accumulation factors for each PBDE congener were calculated to evaluate the bio-availabilities of PBDEs in different fish species.

Results and discussion:

PBDE levels in sediments and fish

The concentrations of PBDEs in sediment samples collected in the dry season were mostly higher than those in the wet season (Table 1). The reason for this trend may be that the surface sediments with accumulated PBDEs were swept away in the high flow rate of river water during the wet season, thereby resulting in the decline of PBDE concentrations in sediment. The highest PBDE concentrations in sediments from the twelve principal rivers were in the Bajhang River (261 285 pg/g dry weight); sediments from the Beinan River and the Da-an River (170 pg/g dry weight) contained the lowest concentrations of PBDEs. The dominant PBDE congeners in the sediments in this study were BDE-209, -197, -47, -183, and -99, and BDE-209 is the major and ubiquitous congener in the sediments of Taiwanese rivers (Figure 1) because deca-BDE has not yet been banned by the government. The PBDE concentrations of sediments in principal rivers of Taiwan in the present study are comparable to or lower than those in these studies from North America, Europe, and East Asia.

The total concentrations of PBDEs in fish samples ranged from 1280 pg/g d.w. (*Oreochromis niloticus niloticus*) in the Yanshuei River to 33 724 pg/g d.w. (*Varico rhinos barbatulus*) in the Da-an River (Table 1). The dominant PBDE congeners in fish samples were BDE-47, -100, -154, and -209, and the dominant homologues were deca-, tetra-, and penta-BDEs. In general, the PBDE concentrations in fish in the principal rivers of Taiwan are much lower than those in North America and southern China, but comparable with those in Hong Kong and Europe. PBDE levels in the present study were higher in demersal fishes than in pelagic fish, which implies that the exposure scenario of demersal fish is different from that of pelagic fish.

Correlation between PBDEs in sediment and water quality index

The correlation between PBDE levels in sediment and water quality index was positive for NH_3-N and BOD_5, but inverse for pH, DO, and SS (Table 2). The levels of BDE-99, -100, -153, -154, -183, -184, -197, and -209 in sediment were positively associated with BOD_5 (Spearman rho = 0.281-0.325, $p < 0.05$). All of the PBDE congeners positively correlated with NH_3-N (Spearman rho = 0.342-0.566, $p < 0.05$). Only BDE-154 was significantly associated with COD (Spearman rho = 0.272, $p < 0.05$); however, pH and DO were negatively associated with all PBDE congeners (Spearman rho = –0.33 ~ –0.565, $p < 0.05$). SS was negatively correlated with BDE-47, -99, -100, -153, -154, -183, and -184 (Spearman rho = –0.321~ –0.5, $p < 0.05$). All of the PBDE congeners were significantly correlated with pH, DO, and NH_3-N, but only some were correlated with SS, BOD_5, and COD. It is interesting that hexa- and hepta-BDEs are highly correlated with pH, DO, BOD_5, SS, and NH_3-N. It appears that NH_3-N, pH, and DO significantly affect the partition behaviors of all PBDE congeners in sediment and can be used to predict PBDE contamination levels in sediment.

Biota-sediment accumulation factor (BSAF)

Demersal and pelagic fish much more easily accumulate low-brominated BDEs (e.g., BDE-47, -100, -119, -126, and -154) than highly brominated BDEs (e.g., BDE-209) from sediment. After comparing our BSAF results with those of Eljarrat et al.[10], we found that BDE-47 and BDE-183 had similar accumulation potential from sediment to fish. However, the BSAFs of BDE-153 and BDE-154 in the present study were much lower than those in Eljarrat's study. Furthermore, there is a parabolic relationship of BSAF values from low- to high-brominated BDEs, especially in demersal fish. The average BSAF values for TriBDE and TeBDE in demersal fish were less than 20.4. However, for PeBDE and HxBDE, they were much higher (maximum value: 63.6), and the BSAF value for BDE-209 was 1.6. This trend was similar to the results reported by Debruyn et al.[11], which focused on the BSAF pattern of different PBDE congeners in marine mussels.

3.4 Principal component analysis

In order to determine the major components of PBDEs between demersal fish and pelagic fish, we used principal component analysis (PCA). The first principal component (PC1) accounted for 59.1% of the variance, and PC2 accounted for 19.8% (Figure 2). PC1 was affected by BDE-71, -100, and -138, and PC2 was affected by BDE-196 and -209. Figure 3 shows that there is a cluster in the pelagic fish group. We conclude that in pelagic fish, the BSAFs for different PBDE congeners are similar. In contrast, in demersal fish, the principal components are scattered over the figure. It seems that demersal fish have different dietary habits, which result in different BSAFs for different PBDE congeners. We hypothesize that when demersal species ingest food hidden in sediments or among stones, they develop a higher body burden of PBDEs by swallowing sediment. When they eat only moss or zooplankton, they develop a lower body burden of PBDEs.

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

Rivers	Sediment (pg/g d.w.)[*]		Fish(pg/g d.w.)	
	Low-flow season	High-flow season	Species	ΣPBDE
Houlung River	5744 (3503-8221)	2770 (2163-3842)	*Cyprinus carpio carpio*[b]	2453; 3871
Beinan River	825 (582-1098)	831 (170-1428)	-	-
Da-an River	16 994 (2351-29 775)	592 (170-880)	*Varicorhinus barbatulus*[a] *Zacco platypus*[b]	33 724 3328
Wu River	12 716 (10 240-14 957)	3083 (840-6742)	*Acanthopagrus schlegeli*[a]	12 892
Beigang River	34 946 (1428-89 001)	16 100 (2258-25 672)	*Megalops cyprinoides*[b] *Elpos machnata*[b]	1962 2719
Bajhang River	90 105 (3442-261 285)	70 135 (1535-206 377)	*Oreochromis niloticus niloticus*[b]	6447; 6725
Jishuei River	3956 (3041-5609)	3946 (800-9025)	*Peterygoplichthys sp.*[a] *Liza subviridis*[b]	5363 3020
Yanshuei River	43 193 (933-104 538)	46 293 (592-120 984[#])	*Monopterus albus*[a] *Oreochromis niloticus niloticus*[b]	10 586 1280
Linbien River	4433 (2129-6036)	940 (747-1103)	*Oreochromis niloticus niloticus*[b]	1640; 2758
Hualien River	1410 (244-2101)	536 (477-639)	*Valamugil cunnesius*[b] *Zacco platypus*[b]	3890 2663
Donggang River	14 943 (7514-27 506)	15 361 (5126-23 929)	*Oreochromis niloticus niloticus*[b]	2323[#]; 6640
Siouguluan River	609 (110[#]-1067)	1922 (518-4696)	-	-

d.w., dry weight; [*]mean (range). [a]Demersal fish; [b]pelagic fish;
[#]Matrix effect interfered with the quantitative analysis of some PBDE congeners.

Table 2 Spearman correlation coefficients between levels of PBDE congeners in sediment and water quality indexes (N =72).

PBDE congeners \ Water quality index	WT	pH	DO	BOD_5	COD	SS	NH_3-N
BDE-28	0.034	–0.335*	–0.330*	0.225	0.215	–0.248	0.375**
BDE-47	0.089	–0.389**	–0.367**	0.271	0.261	–0.321*	0.424**
BDE-99	0.103	–0.422**	–0.386**	0.281*	0.256	–0.357**	0.445**
BDE-100	0.114	–0.427**	–0.375**	0.283*	0.264	–0.376**	0.443**
BDE-153	0.162	–0.516**	–0.479**	0.316*	0.262	–0.454**	0.535**
BDE-154	0.243	–0.541**	–0.489**	0.325*	0.272*	–0.500**	0.566**
BDE-183	0.203	–0.565**	–0.485**	0.300*	0.244	–0.469**	0.494**
BDE-184	0.151	–0.541**	–0.497**	0.314*	0.255	–0.396**	0.472**
BDE-196	0.114	–0.482**	–0.430**	0.264	0.202	–0.224	0.342*
BDE-197	0.176	–0.535**	–0.465**	0.281*	0.215	–0.265	0.384**
BDE-209	0.036	–0.413**	–0.424**	0.283*	0.219	–0.238	0.354**

*< 0.05, **< 0.01

Table 3. Biota-sediment accumulation factors of 21 PBDE congeners in fish with different living patterns.

PBDE congeners \ Fish habitual behavior	Demersal fish BSAF[a] (N = 4)	Pelagic fish BSAF[a] (N = 13)	BSAF investigated 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

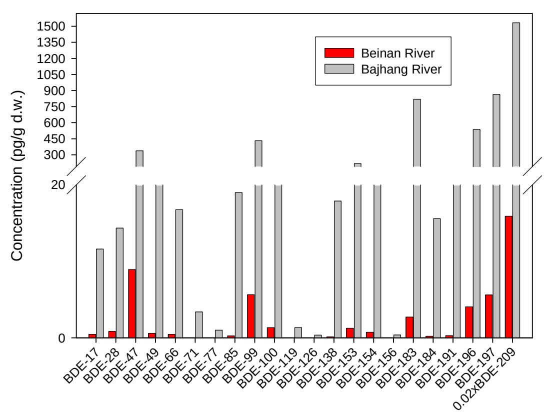

Figure 1. Concentration profile of PBDEs in sediments for the Beinan and Bajhang Rivers.

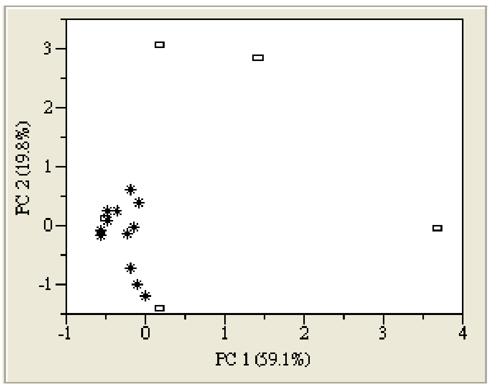

Figure 2. The score plot of PCA for the BSAF values from 21 PBDE congeners in demersal fish and pelagic fish.