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Bioaccumulation behavior of polybrominated diphenyl ethers (PBDEs) in the freshwater food chain of Baiyangdian Lake, North China

Guo-cheng Hu [a,c], Jia-yin Dai [a], Zhen-cheng Xu [c], Xiao-jun Luo [b], Hong Cao [a], Jian-she Wang [a], Bi-xian Mai [b,*], Mu-qi Xu [a,*]

[a] Key Laboratory of Animal Ecology and Conservation Biology, Institute of Zoology, Chinese Academy of Sciences, Beijing 100101, PR China
[b] State Key Laboratory of Organic Chemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China
[c] Metropolitan Environment Center, South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou 510655, PR China

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are of great environmental concern due to bioaccumulation in different food chains. Trophodynamics of PBDEs in freshwater food chain is an important criterion for assessing their ecological risk. In the study, PBDEs were analyzed in sixteen aquatic species collected from Baiyangdian Lake, North China. The concentrations of nine PBDE congeners (BDE-28, -47, -66, -99, -100, -85, -153, -154, and -183) in aquatic organisms ranged from 3.4 to 160.2 ng/g lipid weight. BDE-47 was the predominant PBDE congener in most samples except for river snails and swan mussels. BDE-209 was detected in 50% of biota samples, which indicated the bioavailability of BDE209. Correlation between lipid-normalized concentrations of PBDEs and trophic levels determined by stable isotope nitrogen technologies confirmed that PBDEs were biomagnified in the freshwater food chain. The trophic magnification factors (TMFs) ranged from 1.3 to 2.1 for PBDE congeners, greater than one, indicating the biomagnification potential for the PBDE congeners in the freshwater food chain. The relationship between TMFs and Log K_{ow} (octanol–water partition coefficient) indicated that the phenomenon of trophic magnification for lowly brominated congeners was obvious in the freshwater food chain.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used as additive brominated flame retardants (BFRs) in paints, plastics, textiles, electronic appliance, and other materials used for consumer products. Three major commercial PBDE formulations are produced: penta-BDE, octa-BDE, and deca-BDE. There is increasing regulation and phasing-out of production of the commercial penta- and octa-BDE technical mixtures due to their widespread presence in the environment and potential adverse effects to wildlife and human. However, the use and production of deca-BDE mixture (composed of mainly BDE-209) continue in most regions despite that it was discontinued in the European Union and certain states of the United States (Betts, 2008). The deca-BDE constitutes approximately 80% of the world market demand for PBDEs, which in 2001 was reported at 56 100 metric tons (BSEF, 2003). No restrictions on PBDEs exist in Asia. In China, the estimated domestic production of deca-BDE was 20 000 metric tons in 2006 (Xiao, 2006). Toxic effects of PBDEs on animals included thyroid hormone disruption (Meert et al., 2001; Zhou et al., 2001; Richardson et al., 2008), cytochrome P450 enzyme induction (Szabo et al., 2009), developmental neurotoxicity, immunotoxicity (Fowles et al., 1994), reproductive toxicity (Stoker et al., 2004), and, in some cases, carcinogenicity (McDonald, 2002).

The ubiquitous presence and lipophilic properties of these compounds facilitate their accumulation in biota and biomagnification in the food chain, leading to increased concentrations with increasing trophic level. The biomagnification potential of PBDEs in marine food webs has been well documented in several recent studies (Wolkers et al., 2004; Kelly et al., 2008a,b; Wan et al., 2008), few studies have examined the biomagnifications in freshwater food chain in lake. Burreau et al. (2004, 2006) analyzed PBDEs in the food web from Baltic Sea and the northern Atlantic Ocean, and indicated biomagnification potentials for lower brominated congeners in the food webs (Burreau et al., 2004, 2006). The analyses of trophic dynamics of PBDEs from Bohai Bay, North China, indicated the biomagnification of PBDEs in marine food chain, with trophic magnification factors (TMFs) ranging from 2.6 to 7.2 (Wan et al., 2008). TMFs of BDE47 (5.2) and BDE 209 (10.4) have been reported for a freshwater food chain from Lake Winnipeg (Law et al., 2006), which was higher than those of PBDEs from Bohai Bay. Wu et al. evaluated biomagnification of PBDEs and PCBs in a highly contaminated freshwater food chain from South China, which indicated that potential biomagnification for PBDEs was lower than that of PCBs (Wu et al., 2009). However, PBDE congeners exhibited negligible biomagnification in Canadian Arctic marine food web, with TMFs ranging from 0.7 to 1.6 (Kelly et al., 2008a,b). These findings suggested that regional variability in ecosystem characteristics would influence the biomagnification

* Corresponding authors. Xu is to be contacted at Tel.: +86 10 64807169; fax: +86 10 64807099. Mai, Tel.: +86 20 85290146; fax: +86 10 85290706.
E-mail addresses: xumq@ioz.ac.cn (M. Xu), nancymai@gig.ac.cn (B. Mai).

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behavior of PBDEs. TMF values may vary between marine and freshwater food chain (Fisk et al., 2001). In addition, lipid content, depuration rates, size and exposure duration of the organisms, feeding strategy, transformation reaction, food chain length and structure, as well as the contaminant levels, have also been shown to be potential factors influencing bioaccumulation of these contaminants in aquatic organisms. Clearly, more field-based studies are needed to understand the bioaccumulation behavior of PBDEs in freshwater ecosystems.

The extensive shoreline of Baiyangdian Lake makes it highly sensitive to the changes of the surrounding landscapes and environment (Fig. S1, "S" designated the tables and figures in the Supplementary material). The lake is the largest natural freshwater body in the North China Plain, and is also considered as the Kidney of North China, due to its unmatchable contribution to the surrounding area's groundwater supplies and the ecological environment of Beijing, Tianjin and North China at large. However, heavy pollution and consecutive droughts happened in the past two decades, which reduced water level and affected ecosystem integrity. Increasing inputs of environmental contaminants in Baiyangdian Lake have been documented in many previous studies and have been recognized as an important factor contributing to the decline of diversity of aquatic organisms in the lake (Xu et al., 1998). The bioaccumulation of legacy organochlorine pollutants, such as DDTs, and heavy metals in the food chain of Baiyangdian Lake has been addressed in previous studies (Dou and Zhao, 1998; Chen et al., 2008), however, little attention has been paid to the PBDEs in this highly impacted lake.

This present study was carried out to examine the occurrence of PBDEs in freshwater species at different trophic levels within the Baiyangdian Lake freshwater ecosystem. Both wild and farmed organisms were collected to investigate the influence of breeding habits on the contaminant levels. The potential for PBDEs biomagnification in the wild freshwater food chain was evaluated. We also discussed the metabolic ability of PBDE congeners in different aquatic species and its effects on the PBDE concentrations in organisms.

2. Materials and methods

2.1. Sample collection

The biota samples were collected from Baiyangdian Lake in August 2007. The wild freshwater samples included zooplankton, river snail (*Viviparus*, two composite samples from thirty individuals), swan mussel (*Anodonta*), shrimp (*Macrobrachium nipponense*, three composite samples from forty five individuals), crab (*Eriocheir sinensis*), common carp (*Cyprinus carpio*), crucian carp (*Carassius auratus*), bighead carp (*Aristichthys nobilis*), grass carp (*Ctenopharyngodon idella*), northern snakehead (*Channa argus*), yellow catfish (*Pelteobagrus fluvidraco*), ricefield eel (*Monoperus ablus*), and loach (*Misgurnus anguillicaudatus*). The farmed species included oriental sheatfish (*Parasilurus asotus*), turtles (*Pelodiscus sinensis*), and ducks (*Anatidae*). Details of information on biological parameters were given in the Supplementary material (Table S1). Zooplankton samples were collected using a tow net of 112 µm in surface water of Baiyangdian Lake. Two composite samples were obtained. After collecting, the samples were transported on ice to laboratory and then kept at −20 °C until analysis.

2.2. Sample extraction and analysis

PBDE congeners were analyzed following previously established method with some modifications (Chen et al., 2007; Hu et al., 2008; Luo et al., 2009). The whole bodies of zooplankton, the soft tissues of shrimp, crab, river snail, swan mussel, and the muscles of fish, turtle and ducks were freeze-dried. About 1.0 g of samples was spiked with surrogate standards ($^{13}C_{12}$-BDE-209, CDE-99 and $^{13}C_{12}$-PCB-141) and Soxhlet extracted with 50% acetone in hexane for 48 h. The lipid content was determined gravimetrically from an aliquot of extract. Another aliquot of extract was subjected to gel permeation chromatography (GPC) for lipid removal. The lipid-free eluate was concentrated to 2 mL and purified on a 2-g silica gel solid-phase extraction column (Isolute, International Sorbent Technology, UK). The fraction containing PBDE congeners was concentrated to near dryness and redissolved in 50 µL isooctane. Known internal standards (BDE-118, BDE-128, and $^{13}C_{12}$-PCB-208) were added to all extracts prior to instrumental analysis. The instrumental conditions, and quality assurance/quality control (QA/QC) were provided in Supplementary material.

2.3. Stable isotope analysis

Stable isotopes of nitrogen, expressed as $\delta^{15}N$ were analyzed for biota according to previously described method (Wu et al., 2009). Briefly, samples were freeze-dried and ground to homogeneous powders with a mortar and pestle. Approximately 1 mg of ground samples was weighed for the determination of stable nitrogen isotope using an elemental analyzer-isotope ratio mass spectrometer (CE flash EA1112-Finnigan Delta plus XL; Thermo Fischer Scientific Bremen, Germany). Two replicates of each sample were analyzed, and the relative standard deviation was less than 0.5%. The isotope ratio was standardized against air according to $\delta^{15}N=[R_{sample}/(R_{air}-1)]\times 1\,000‰$, where R is the ratio of $^{15}N/^{14}N$. The $\delta^{15}N$ values were based on an ammonium sulfate standard (IAEA-N-1; International Atomic Energy Agency Analytical Quality Control Services, Wien, Austria). The precision of the analytical method and instrument was ±0.3‰.

2.4. Trophic level calculations

According to previous studies (Fisk et al., 2001; Post, 2002), trophic level (TL) was determined relative to the primary producer (zooplankton), we after which assumed occupied TL 2. For each individual sample of invertebrates and fish TL was determined using the following equations: $TL_{consumer}=[(\delta^{15}N_{consumer}-\delta^{15}N_{primary\ consumer})]/3.4+2$. The trophic magnification factors (TMFs) were based on the entire food chain and were derived from the slope of the plots of natural log concentrations (lipid normalized) versus TL: Ln [Concentrations] $= a + b$ TL. The slope b was used to calculate TMF values using TMF $= e^{b}$. TMFs close to zero imply that contaminants are moving through the food chain without being biomagnified; whereas TMFs > 1 indicates that contaminants are biomagnifying. Negative values indicate that contaminants are not taken up by the organism or that they are metabolized (Fisk et al., 2001).

2.5. Data analysis

For samples with contaminants concentration below LOD, zero was used for the calculations. All data were wet weight and lipid weight normalized. $\sum_{(9)}$PBDEs are defined as the sum of these 9 BDE congener (BDE-28, -47, -66, -100, -99, -85, -154, -153, and -183). PBDEs concentrations for all biota samples were naturally logarithmically transformed to ensure a normal distribution of the data. The normality test of the data was analyzed using a Kolmogorov–Smirnov test. The differences of PBDEs among aquatic species were analyzed using Kruskal–Wallis H nonparametric test. Linear regression was performed to evaluate relationships between Ln (PBDE concentrations) and TL. All statistical analyses were conducted with SPSS software (Version 16.0 for Windows, SPSS Inc., Chicago, IL). The level of significance was set at $\alpha = 0.05$ throughout the present study.

3. Results and discussion

3.1. Concentrations of PBDEs

The concentrations of PBDEs congeners in aquatic organisms from Baiyangdian Lake are summarized in Table 1. Nine PBDE congeners were detected in most samples (94%) analyzed, indicating ubiquitous contamination in aquatic organisms from

Table 1
Concentrations of PBDE congeners (pg/g wet weight) in aquatic organisms from Baiyangdian Lake, North China in August 2007.

	$\delta^{15}N$	BDE28	BDE47	BDE66	BDE100	BDE99	BDE85	BDE154	BDE153	BDE183	∑ PBDEs
ZPK[a] ($n=2$)	5.9	1.1	5.4	0.2	0.2	0.9	ND	0.4	1.4	4.7	14.3
RSN ($n=2$)	9.8 ± 0.4[b]	8.5	27.9	211.8	6.0	33.4	25.6	10.0	14.2	15.5	352.9
SWM ($n=5$)	10.2 ± 0.2	2.0–4.1[c] (3.1)	6.5–9.2 (7.5)	0.9–18.0 (12.3)	1.5–2.4 (1.8)	3.9–5.1 (4.4)	1.3–5.8 (4.2)	1.8–3.1 (2.6)	2.5–5.4 (3.9)	0.3–11.6 (5.4)	25.4–58.9 (45.2)
SRM[c] ($n=3$)	5.8 ± 0.3	9.2–23.9 (15.6)	57.6–129.7 (86.4)	4.0–5.5 (4.7)	4.0–9.2 (6.7)	7.1–16.8 (12.8)	4.2–9.9 (7.5)	4.7–8.4 (6.1)	3.9–11.2 (7.9)	12.8–23.7 (16.7)	115.8–218.5 (164.4)
CRB ($n=3$)	12.5 ± 0.8	9.0–11.7 (10.0)	26.1–35.6 (29.8)	6.7–16.1 (5.1)	4.5–6.5 (5.2)	17.1–28.1 (21.0)	7.1–17.3 (11.2)	7.2–9.8 (8.6)	10.7–18.8 (13.6)	15.6–29.3 (22.6)	106.4–173.3 (36.0)
CCA ($n=5$)	5.7 ± 0.3	8.0–18.1 (12.7)	24.9–53.9 (39.0)	1.6–4.1 (3.1)	2.8–5.3 (4.0)	2.9–9.5 (6.8)	1.4–4.1 (3.4)	7.0–13.1 (9.9)	3.9–14.5 (9.7)	0.1–0.3 (0.2)	53.8–116.9 (88.8)
CRC ($n=6$)	6.4 ± 0.5	7.4–15.8 (11.3)	22.7–43.2 (32.5)	5.0–11.7 (8.0)	4.1–7.5 (5.4)	5.5–19.5 (12.4)	5.2–18.3 (11.7)	5.5–14.3 (8.9)	4.9–11.5 (8.2)	3.9–12.6 (8.0)	73.8–141.9 (106.4)
BCA ($n=4$)	9.8 ± 0.6	7.3–11.1 (9.2)	18.1–24.9 (21.7)	1.7–3.6 (2.7)	4.9–7.6 (6.1)	1.4–2.7 (2.1)	8.1–10.4 (9.2)	14.5–31.3 (20.2)	5.6–14.1 (9.8)	4.4–15.0 (8.9)	77.4–117.2 (90.0)
GCA ($n=5$)	6.5 ± 0.2	25.0–48.5 (35.8)	133.0–260.4 (186.3)	1.7–3.1 (2.4)	0.5–3.5 (3.4)	3.6–10.2 (6.1)	8.0–10.8 (9.4)	0.2–2.1 (1.3)	0.4–2.6 (1.2)	0.3–4.4 (1.7)	177.8–337.1 (245.0)
NSH ($n=14$)	15.7 ± 1.3	4.8–81.6 (33.2)	6.8–353.1 (129.4)	2.6–98.1 (41.9)	2.6–88.1 (30.2)	2.1–63.9 (17.9)	6.4–21.7 (13.1)	5.8–109.2 (40.3)	5.1–68.2 (20.4)	0.2–48.4 (14.8)	60.3–728.6 (341.2)
YCF ($n=4$)	12.8 ± 1.1	25.6–42.7 (30.6)	189.6–290.7 (243.3)	26.4–44.8 (33.6)	49.2–77.1 (64.3)	97.4–127.7 (116.1)	4.8–17.8 (9.7)	196.4–460.9 (321.1)	61.7–127.1 (93.8)	0.5–1.8 (1.3)	714.9–1154.6 (913.8)
RFE ($n=8$)	12.0 ± 1.4	16.9–101.0 (36.8)	161.9–619.6 (272.4)	23.1–128.9 (55.8)	51.4–216.0 (97.5)	110.1–910.9 (242.3)	10.9–45.3 (23.1)	83.8–406.8 (243.6)	8.7–290.0 (113.6)	1.7–53.4 (19.1)	480.6–2672.1 (1104.1)
LCH ($n=2$)	12.0 ± 1.1	29.8	89.2	5.7	18.1	11.0	11.0	54.9	17.8	17.0	254.5
OSF ($n=5$)	9.5 ± 0.8	8.9–15.3 (12.0)	19.7–58.6 (39.4)	3.1–7.7 (5.9)	4.9–11.5 (8.1)	8.3–35.0 (25.6)	12.3–19.6 (14.1)	13.5–18.7 (15.6)	9.0–16.3 (13.6)	12.5–27.1 (20.0)	95.8–198.8 (154.1)
TUR ($n=4$)	12.8 ± 0.4	1.0–5.1 (2.9)	5.7–25.9 (15.9)	0.9–3.9 (2.4)	2.2–4.1 (3.0)	2.5–16.2 (9.3)	1.1–3.2 (2.3)	2.8–6.9 (4.0)	4.1–12.4 (6.9)	0.1–0.3 (0.2)	20.7–78.0 (47.0)
DUC ($n=5$)	5.2 ± 0.3	1.7–6.0 (2.8)	8.1–30.2 (14.5)	1.5–3.8 (2.1)	2.4–6.2 (4.1)	6.2–23.8 (11.9)	1.8–4.4 (2.4)	4.2–11.3 (7.1)	8.4–19.1 (11.1)	0.3–0.7 (0.5)	34.6–105.4 (56.6)

ZPK, zooplankton; RSN, river snail; SWM, swan mussel; SRM, shrimp; CRB, crab; CCA, common carp; CRC, crucian carp; BCA, bighead carp; GCA, grass carp; NSH, northern snakehead; YCF, yellow catfish; RFE, ricefield eel; LCH, loach; OSF, oriental sheatfish; TUR, turtle; DUC, duck. ND, not detected.
[a] ng/g dry weight.
[b] Average ± standard deviation.
[c] (min − max) mean.

Baiyangdian Lake. Relatively higher concentration of $\sum_{(9)}$PBDEs (14.3 ng/g dry weight) was detected in zooplankton. The total concentrations of PBDE congeners in biota samples (excluding zooplankton) ranged from 20.7 (turtle) to 2672.1 pg/g wet weight (ww) (ricefield eel). Mean concentrations were in the following ranking order: swan mussel < turtle < duck < common carp < bighead carp < crucian carp < crab < oriental sheatfish < shrimp < grass carp < loach < northern snakehead < river snail < yellow catfish < ricefield eel (Fig. 1). Both river snail and swan mussel belong to mollusk. The river snail is a genus of large, freshwater snails with operculum, aquatic gastropod mollusks. The animal prefers to live in quiet water, either in slow-moving streams or in ponds, lake margins and irrigation ditches, where there is some vegetation and a mud substrate. Mud particles in water possibly affiliated contaminants. The swan mussel is a large species of freshwater mussel, an aquatic bivalve mollusk in the family Unionidae, that is found side by side in clear shallow water. The animal can filter organic particles and breathe by passing large quantities of water through its body via siphon. The special habitats between river snail and swan mussel possibly result from the different levels of PBDEs in the present study. The detritivorous fish include common carp, crucian carp, and bighead carp. Grass carp belong to typically herbivorous fish and often feed on phytoplankton, zooplankton, and bacteria in addition to synthetic feeds. The concentrations of PBDEs in grass carp were significantly higher than that of detritivorous fish ($p < 0.05$), which related to the biological characteristics. The size of grass carp was larger than that of common carp, crucian carp, and bighead carp (Table S1). The larger individuals may accumulate contaminants for longer period. The carnivorous fish include yellow catfish, northern snakehead, ricefield eel, loach and oriental sheatfish in the present study. Significant difference of $\sum_{(9)}$PBDEs concentrations was observed among the carnivorous fish ($p < 0.05$). The concentrations of $\sum_{(9)}$PBDEs in yellow catfish and ricefield eel were significantly higher than those of other organisms ($p < 0.05$). It was noteworthy that relatively lower concentration in oriental sheatfish was observed among the carnivorous fish. The results possibly suggested different accumulations of PBDEs between farmed and wild freshwater fish. Farmed oriental sheatfish mainly feed on synthetic feeds. Thought the transfer of TL, the wild carnivorous fish possibly accumulate more organic pollutants. The concentrations of $\sum_{(9)}$PBDEs in semi-captive ducks were significantly lower than those of wild fish species ($p < 0.05$), although the ducks belong to mammals, occupying higher ecological position in the freshwater ecosystems. In the present study, significant accumulation of PBDEs at the higher TLs of the food chain in Baiyangdian Lake is evident. The carnivorous fish in general occupy higher TLs of the food chain in an aquatic ecosystem, which may accumulate PBDEs when consuming other organisms contaminated with PBDEs.

To compare the PBDEs levels with other studies, the concentrations were expressed on a lipid weight (lw) basis. The $\sum_{(9)}$PBDEs levels (maximum, 160.2 ng/g lw) in Baiyangdian Lake were similar to those reported for aquatic biota samples collected from Gaobeidian Lake and Bohai Bay, North China (Wang et al., 2007a,b; Wan et al., 2008). Wang et al. (2007a,b) analyzed $\sum_{(13)}$PBDEs contamination in aquatic biota from Gaobeidian Lake in Beijing with levels ranging from 13.6 to 355 ng/g lw (Wang et al., 2007a,b). Lower concentrations were found in aquatic biota samples, including zooplankton, shellfish, and fish species, collected from Bohai Bay with levels ranging from 10.5 to 198 ng/g lw (Wan et al., 2008). In contrast, higher levels were found in

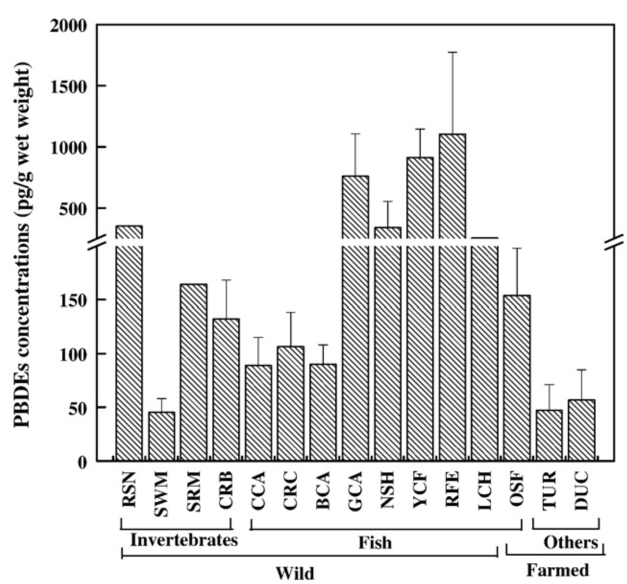

Fig. 1. The total concentrations of PBDEs in aquatic organisms collected from Baiyangdian Lake, North China in August 2007. RSN = river snail, SWM = swan mussel, SRM = shrimp, CRB = crab, CCA = common carp, CRC = crucian carp, BCA = bighead carp, GCA = grass carp, NSH = northern snakehead, YCF = yellow catfish, RFE = ricefield eel, LCH = loach, OSF = oriental sheatfish, TUR = turtle, and DUC = duck.

aquatic biota from Yangtz River (Xian et al., 2008) and E-wastes recycling site in South China (Wu et al., 2008). Wu et al. (2008) studied the PBDE contamination in a reservoir surrounded by E-waste recycling workshops, with concentrations ranging from 67.5 to 490 ng/g wet weight. The spatial variability of PBDEs may reflect the higher population density and industrialization in the coastal cities from Yangtze River and Pearl River. It is also likely that the high PBDEs levels are related to the rapid economic development during the past two decades in East China and South China.

Comparisons of levels from different studies can be done by using individual congeners. Using $\sum$PBDEs can have a few drawbacks since the congeners included might vary. BDE-47 was the most dominant in a majority of biological samples in a few studies (Law et al., 2006; Xiang et al., 2007; Wu et al., 2008; Xian et al., 2008). In the present study, BDE-47 was the most abundant in 90% of all biota samples. The concentration of BDE-47 in biota samples ranged from 0.18 to 40.3 ng/g lw. The relatively high BDE-47 concentrations were observed in yellow catfish (30.6 ng/g lw) and ricefield eel (12.1 ng/g lw) from Baiyangdian Lake. However, recent studies also showed that higher concentrations of BDE-47 were reported in Pearl River estuary, South China (42–150 ng/g lw) (Xiang et al., 2007; Wu et al., 2008), Yangtze River (8.3–160 ng/g lw) (Xian et al., 2008), Lake Winnipeg, Canada (1.8–83.8 ng/g lw) (Law et al., 2006), and Belgian North Sea (3–108 ng/g lw) (Voorspoels et al., 2003), which were probably related to intense industrial activities and point sources of pollution. Another study showed that the concentration of BDE-47 in catfish collected from Vietnam Can Tho was lower than that of the present study, which was ranging from 0.4 to 0.7 ng/g lw (Minh et al., 2006). BDE-209, with large molecular weight, could be detected in 50% of biota samples from Baiyangdian Lake.

3.2. Distribution of PBDEs congeners in various aquatic species

The distributions of PBDEs congeners in biota samples from Baiyangdian Lake were showed in Fig. 2. Of all the congeners, BDE-47 was the most predominant compound in most biota samples, excluding river snails and swan mussels, a contribution of 36.4% to the total concentrations. The dominance of BDE-47 in aquatic species of the present study was consistent with the general pattern found in aquatic organism (Hites, 2004; Labandeira et al., 2007; Guo et al., 2008; Wu et al., 2008). BDE-47 is probably produced by debromination of higher brominated congeners (Stapleton et al., 2004a,b). Gandhi et al. (2006) showed that biotransformation pathway was the debromination of BDE-100 to BDE-47 and the debromination of BDE-153 to BDE-99 and then to BDE-47 (Gandhi et al., 2006). For zooplankton samples, BDE-47 was the most abundant congener, accounting for 37.3% of the total PBDEs, followed by BDE-183, with 34.5% contribution to the total PBDEs, which differed from the profiles of zooplankton in Bohai Bay (predominant congener: BDE-99) (Wan et al., 2008). It was interesting that river snail and swan mussels exhibit different distribution of PBDE congeners, comparing with profiles of other aquatic species (Fig. 2). BDE-66 was the most predominant congener in river snails and swan mussels, accounting for 60.2% and 30.6% of the total PBDEs, respectively. Wang et al. (2008) also found that BDE-66 was the second-most-dominant congener in *Mytilus edulis*. BDE-66 could be intermediate product of metabolic debromination of Penta-BDEs (e.g., BDE-99) to Tri-BDEs, such as BDE-28 (Wang et al., 2008). Shrimp and crab belonging to shellfish exhibit similar distribution of PBDE congeners to fish. Excluding BDE-47, BDE-183 was another major congener for shrimp and crab, which accounted for 10.7% and 17.0%, respectively. The lower metabolic capacity for shrimp and crab may be responsible for the observation.

Biotransformation of BDE-99 to BDE-47 in common carps has been demonstrated in condition of feeding on dietary spiking with BDE-99 (Stapleton et al., 2004a,b). Common carp, crucian carp, grass carp, and bighead carp are from the same family. Similar profiles of PBDEs are exhibited among these species except for grass carp, with BDE-47 contribution to the total PBDEs ranged from 24.5% to 43.4%. It was apparent that in addition to accumulating BDE-47, the species tended to preferentially accumulate BDE-28, BDE-99, BDE-153, and BDE-154. A similar observation was found in freshwater fish from Yangtze River (Xian et al., 2008). It was noted that relatively high proportion of BDE-47 in grass carp, which accounted for 75.7% of the total PBDEs concentrations, indicates that the species from Baiyangdian Lake might be exposed to commercial BDE mixture for a long time. Although northern snakehead, yellow catfish, ricefield eel, and loach are from different families, the distribution of PBDE congeners in these carnivorous fish was remarkably similar (Fig. 2). The contributions of BDE-47 to total PBDEs were in the range from 23.7% to 35.6% in the species, followed by BDE-154 ranging from 10.7% to 33.8%, and BDE-99 ranging from 4.4% to 16.1%. Elevated proportions of lower congeners suggested the occurrence of debromination of highly brominated congeners in aquatic organisms and confirm the prevalence of biotransformation of these compounds in freshwater organisms.

Congener ratio between BDE-99 and BDE-100 has been found to be distinguishably different among different environmental samples. The ratio between BDE-99 and BDE-100 in abiotic matrixes (air and sediment) was 80:20, which was similar to those in industrial product Bromkal 70-5DE (84:16), but 30:70 in fish and marine mammals (Christensen et al., 2002; Voorspoels et al., 2003). In the present study, the ratio of BDE-99/-100 in aquatic organisms ranged from 26:74 (bighead carp) to 85:15 (zooplankton). For zooplankton, mollusks (river snail and swan mussel) and shellfish (shrimp and crab), the ratios were close to 80:20 or 70:30. These findings were consistent with those of previously reported by other authors (Voorspoels et al., 2003; Wang et al., 2008). Voorspoels et al. (2003) reported that the ratios of BDE-99/-100 in various organisms in the Belgian North Sea range from 30:70 to 80:20. It was interesting to see that the ratios in zooplankton and river snail were 84:16, as in the technical penta

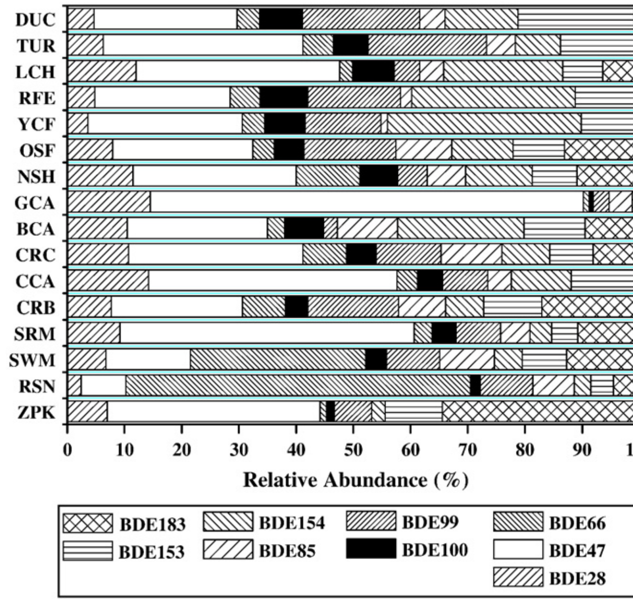

Fig. 2. Compositional profiles of PBDEs in aquatic organism collected from Baiyangdian Lake, North China. ZPK = zooplankton, RSN = river snail, SWM = swan mussel, SRM = shrimp, CRB = crab, CCA = common carp, CRC = crucian carp, BCA = bighead carp, GCA = grass carp, NSH = northern snakehead, OSF = oriental sheatfish, YCF = yellow catfish, RFE = ricefield eel, LCH = loach, TUR = turtle, and DUC = duck.

mixture. The finding indicated that there may be a source of penta-BDE formulations. The significant difference in ratios may reflect the different metabolism abilities of the organisms as well as possibly higher biodegradability of BDE-99 compared with BDE-100.

The different fish species with similar feeding habitats indicated that strong positive relationships between PBDEs concentrations and the ratios of BDE-99/-100 were observed ($p<0.05$). For example, the ratios of BDE-99/-100 in carnivorous fish increased significantly with increasing PBDE concentrations ($p<0.05$). Similar results were also found among detritivorous and herbivorous fish, and invertebrates. The ratios of BDE-99/-100 may reflect the different metabolism abilities of various aquatic organisms. Therefore, metabolism ability, the feeding habitats, and biological parameters may play an important role in controlling the accumulation of PBDEs in aquatic organisms.

3.3. Trophic magnification factors

Previous studies indicate that PBDEs can biomagnify in aquatic organisms through the food chain, with higher contaminant concentrations in an organism with higher TL than that of its prey (Law et al., 2006; Kelly et al., 2008a,b; Wan et al., 2008). The trophic status of Baiyangdian Lake freshwater food chain has been elucidated firstly using stable isotopes of nitrogen. Oriental sheatfish, turtle and duck were omitted because these organisms were collected from markets and raised in captive conditions indicating different diets from wild species. Based on the stable isotope values, the rank orders of TLs were as follows: zooplankton, shrimp < herbivorous and detritivorous fish < crab and carnivorous fish, especially northern snakehead, yellow catfish.

Trophic magnification factors (TMFs) have been used to assess the food chain magnification for entire freshwater ecosystem and are based on the relationship between the lipid-normalized concentrations of $\sum_{(9)}$PBDEs (natural log-transformed) and the TLs (Fig. 3). Generally speaking, the occurrence of biomagnifications is defined by a TMF statistically greater than 1. In the present study, the TMF values for PBDE congeners were significantly higher than 1, which indicated that PBDEs congeners can biomagnify in Baiyangdian Lake freshwater food chain. The statistical results of the regression analysis are listed in Table 2. Lipid-normalized concentrations of $\sum_{(9)}$PBDE concentrations increased with increasing TLs ($p>0.05$). The calculated TMFs for $\sum_{(9)}$PBDEs in Baiyangdian Lake (1.5) were approximately twofold smaller than those observed in the Lake Winnipeg (3.7) and Bohai Bay (3.5) food chain (Law et al., 2006; Wan et al., 2008). In the present study, TMFs of individual congeners (BDE-28, -47, -66, -99, -100, -153, -154, and -183) and $\sum_{(9)}$PBDEs were reported, ranging from 1.3 (BDE-47) to 2.1 (BDE-154), and significant positive relationships were obtained for most PBDE congeners except BDE-47 (TMF, 1.3, $p=0.09$), as shown in Fig. 3. Although BDE-47 was the most predominant congener, TMFs of BDE-47 (1.1, $p>0.05$) were lower than those of Lake Winnipeg (5.2) (Law et al., 2006), Bohai Bay (7.2) (Wan et al., 2008) and Canadian Arctic (1.6) food chain (Kelly et al., 2008a,b), which may be due to the different ecological factors, such as the food chain length, species, and locations. The trophic positions in Bohai Bay and Canadian Arctic food chain included birds and aquatic mammals, and the length of food chain was longer than that of Baiyangdian

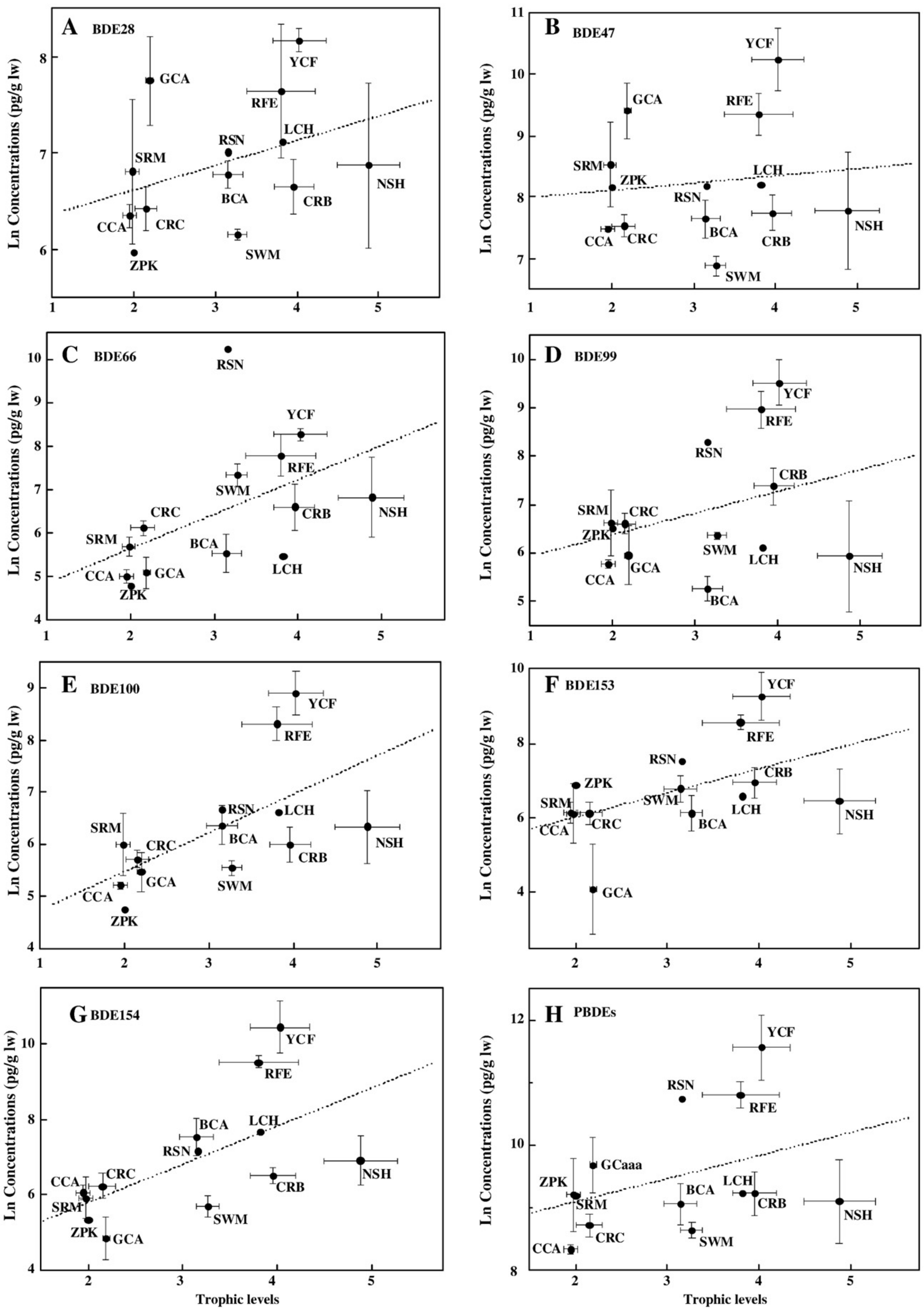

Fig. 3. Relationship of major PBDE congeners (pg/g lw) in the Baiyangdian Lake food chain and TLs calculated from $\delta^{15}N$ values. Vertical and horizontal bars represent standard errors for mean values in each species. ZPK = zooplankton, SRM = shrimp, CRB = crab, RSN = river snail, SWM = swan mussel, CCA = common carp, CRC = crucian carp, GCA = grass carp, BCA = bighead carp, NSH = northern snakehead, YCF = yellow catfish, LCH = loach, and RFE = ricefield eel. The oriental sheatfish, turtle, and duck samples were purposely omitted from the plot.

Table 2
Slope and *p*-value of slope of regression analysis between logarithm of concentration and TLs, and TMFs for PBDE congeners in Baiyangdian Lake food chain, North China.

	Slope	R^2	TMF	*p*
BDE28	0.35	0.11	1.41	0.01*
BDE47	0.27	0.06	1.31	0.09
BDE66	0.73	0.37	2.07	0.00*
BDE100	0.60	0.29	1.82	0.00*
BDE99	0.33	0.08	1.39	0.05
BDE85	0.44	0.16	1.55	0.00*
BDE154	0.73	0.35	2.08	0.00*
BDE153	0.50	0.20	1.65	0.00*
BDE183	0.50	0.14	1.64	0.03*
$\sum$ PBDE	0.41	0.15	1.51	0.01*

* Represent statistically significant difference.

Lake food chain. Previous studies also demonstrated that TMFs of persistent halogenated compounds (PHCs) estimated based on a food chain including only poikilotherms (invertebrates and fish) are usually lower than those estimated based on a food chain including both poikilotherms and homeotherms (seabirds and mammals) (Fisk et al., 2001; Hop et al., 2002; Wan et al., 2008). The relationship between observed TMFs and Log octanol–water partition coefficient (Log K_{ow}) for PBDEs was shown in Fig. 4. TMFs of PBDE congeners were relatively high, increasing from 1.3 to 2.1 between Log K_{ow} of 7 and 8, dropping slightly after Log K_{ow} exceeds 8. Fig. 4 also reveals that TMFs of PBDE congeners are above 1 and indicates biomagnification in the food chain.

The relationships between the biomagnifications of PBDEs and TLs in freshwater food chain remain far from being fully understood. The length of the food chains, feeding strategy and lipid contents are potential factors influencing the bioaccumulation of contaminants in freshwater ecosystems. In large scale food chain, such as zooplankton–mollusks and shellfish–fish–seabirds food chains, bioaccumulations of contaminants are always observed. The scale of TLs was narrow for Baiyangdian Lake food chain without containing waterbirds in the present study. In addition, the values of δ^{15}N in aquatic organisms varied depending on the food supplies in the habitat and season, both of which affect their physiology. These may weaken the simple correlation and complicate the investigation on the relationships between TLs and contaminant accumulation in aquatic organisms.

4. Conclusions

To our knowledge, this is the first study to report concentrations and profiles of PBDE congeners in biota from Baiyangdian Lake, North China. The various concentrations and profiles of PBDEs in aquatic organisms from Baiyangdian Lake indicated different metabolisms of contaminants. BDE-209 can be detected in biota samples, indicating its biovailability. BDE-47 was the most predominant in aquatic organism. The variations of ratios of BDE-99/-100 reflected the different metabolic abilities for organism. TMF values provided obviously evidence of biomagnification of individual PBDEs in freshwater food chain. Significant positive relationships could be found between concentrations of most PBDE congeners and trophic levels ($p<0.05$). The correlation between the TMF values and Log K_{ow} suggested that chemical properties of contaminants have profound effects on the trophic transfer for contaminants in freshwater food chain.

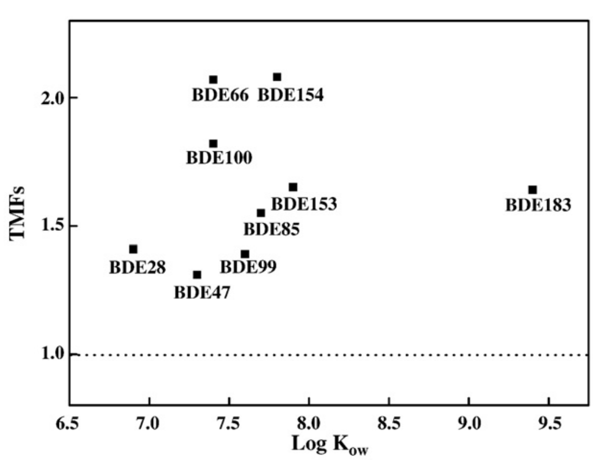

Fig. 4. Relationship between TMF values for PBDE congeners in Baiyangdian Lake freshwater food chain and Log K_{ow}.

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Appendix A. Supplementary material

Supplementary information included text, figures, and tables, which addressed (1) chemicals used in the analysis; (2) instrumental condition; (3) details quality assurance and quality control (QA/QC) for analysis; (4) maps of sampling collection; and (5) basic information of organisms from Baiyangdian Lake. This material is available free of charge via the Internet (doi:10.1016/j.envint.2010.01.002).

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