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Occurrence and trophic magnification of polybrominated diphenyl ethers (PBDEs) and their methoxylated derivatives in freshwater fish from Dianshan Lake, Shanghai, China☆

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ABSTRACT

In this study, polybrominated diphenyl ethers (PBDEs) and methoxylated polybrominated diphenyl ethers (MeO-PBDEs) were analyzed in eleven freshwater fish species from Dianshan Lake, Shanghai, China. The highest concentrations of PBDEs and MeO-PBDEs were found in snakehead, with mean values of 38 ng g^{-1} lw and 4.2 ng g^{-1} lw, respectively. BDE-47 was the predominant congener of PBDEs, followed by BDE-154. Congener pattern variation of PBDEs was observed among different fish species, implying differences in biotransformation potential among fish. Yellow catfish showed highest concentrations of BDE-99, -153 and -183, suggesting that it is more resistant to debromination than any other fish analyzed in the present study. Trophic magnification factors were in the range of 1.35–1.81 for all the PBDE congeners, but not for 2′-MeO-BDE-68. Negative relationship was observed between PBDEs concentration and sample size (length and weight), indicating fish size dilution effect.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been produced since 1970s and widely used as an additive flame retardant in textile, furniture, electronic circuitry and other materials (de Wit, 2002). PBDEs were first found in fish from Viskan River where home to a number of textile industrial companies (Andersson and Blomkvist, 1981). Since then, numerous studies have been carried out on the environmental exposure, (eco)-toxicology, (bio)-transformation and environmental fate of PBDEs (Covaci et al., 2003; Darnerud et al., 2001; Sjodin et al., 2003). Commercially PBDEs have been mainly produced in three technical products as PentaBDE, OctaBDE and DecaBDE (WHO/ICPS, 1994). Among them, OctaBDEs was never manufactured in China (Ni et al., 2013). China stopped PentaBDEs production in 2004, while the domestic production of DecaBDEs increased from 26,000 metric tons (MTs) in 2,000–41,500 MTs in 2005 and decreased to 20,500 MTs in 2011 (Ni et al., 2013). Due to the persistence, bioaccumulation, semi-volatility and adverse effects to human and wildlife, PentaBDE and OctaBDE have been regulated under the Stockholm Convention since 2009 (UNEP, 2015).

Methoxylated polybrominated diphenyl ethers (MeO-PBDEs) were first identified in seals and fish in the Baltic Sea (Haglund et al., 1997) and subsequently detected in various Baltic biota e.g. cyanobacteria, blue mussel (*Mytilus edulis*), herring (*Clupea harengus*) and guillemot (*Uria aalga*) (Malmvärn, 2007). Two of the major MeO-PBDEs, i.e. 6-MeO-BDE-47 and 2′-MeO-BDE-68 have been identified as natural product in True's beaked whale (*Mesoplodon mirus*) (Teuten et al., 2005). Increasing concerns have been attracted to MeO-PBDEs, due to their structural similarity to PBDEs.

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Table 1
Congener based concentrations (ng g^{-1} lw) of polybrominated biphenyl ethers (PBDEs) and methoxylated polybrominated biphenyl ethers (MeO-PBDEs) in freshwater fish collected from Dianshan Lake.

Number	Silver carp (SVC)	Bighead carp (BHC)	Rosy bitterling (RBL)	Stone moroko (STM)	Bigmouth grenadier anchovy (BGA)
	n = 3	n = 4	n(pool) = 5	n(pool) = 5	n(pool) = 5
Lipid content (%)	0.57 (0.51–0.62)	0.76 (0.55–1.3)	4.7 (3.2–6.2)	3.4 (2.6–3.7)	3.5 (2.3–4.4)
BDE-28	1.6[a]/1.3[b] (1.2–2.2)[c]	2.8/3.0 (1.4–3.7)	1.2/1.3 (0.63–1.9)	2.2/2.1 (1.8–2.7)	1.3/1.2 (1.1–1.6)
BDE-47	1.6/1.9 (0.69–2.2)	0.54/0.34 (ND-1.5)	7.3/7.0 (4.5–10)	12/11 (8.2–14)	8.2/8.1 (7.1–9.4)
BDE-99	ND[d]	0.062/ND (ND-0.25)	0.11/0.062 (ND-0.30)	0.11/0.11 (ND-0.20)	0.21/0.22 (ND-0.52)
BDE-100	0.15/ND (ND-0.45)	0.12/0.052 (<LOQ-0.36)	0.069/0.047 (ND-0.21)	0.19/0.20 (0.11–0.32)	1.3/1.8 (ND-2.5)
BDE-153	0.46/0.45 (0.43–0.49)	0.25/0.23 (0.092–0.46)	1.3/1.1 (0.61–1.8)	0.98/0.99 (0.39–1.6)	0.74/0.74 (0.63–0.81)
BDE-154	1.2/0.56 (0.30–2.7)	0.26/0.098 (ND-0.82)	2.6/2.5 (1.2–3.8)	4.9/5.2 (3.3–6.2)	4.8/4.6 (3.9–6.4)
BDE-183	0.10/0.15 (ND-0.16)	0.17/ND (ND-0.67)	0.19/0.11 (ND-0.43)	ND	ND
$\sum_7$PBDEs	5.0/4.3	4.2/3.7	13/12	20/20	17/17
6-MeO-BDE-47	0.53/0.65 (ND-0.94)	2.0/2.5 (ND-3.2)	0.57/0.46 (0.30–1.1)	0.51/0.54 (0.38–0.62)	1.7/1.9 (1.4–2.0)
2′-MeO-BDE-68	0.99/0.29 (ND-2.7)	0.16/ND (ND-0.62)	0.43/0.38 (0.18–0.80)	0.47/0.47 (0.39–0.54)	0.78/0.89 (0.31–0.98)

[a] Mean.
[b] Median.
[c] Range (min-max).
[d] Not detected.

Kim et al. (2015) suggested that MeO-PBDEs showed a greater biomagnification potential than PBDEs in freshwater food web. In addition, MeO-PBDEs might transform to hydroxylated polybrominated diphenyl ethers (OH-PBDEs) (Wan et al., 2009), a family of chemicals having the potential to disrupt the thyroid hormone system and oxidative phosphorylation (Legradi et al., 2014; Meerts et al., 2000).

Once released into the aquatic environments, PBDEs and MeO-PBDEs can be accumulated into the primary producers and biomagnified through the food chain into the top predator. The trophic magnification of PBDEs and MeO-PBDEs in marine food webs has been well documented in several researches (Kobayashi et al., 2015; Losada et al., 2009; Mizukawa et al., 2013; Shao et al., 2016), whereas fewer studies have been focused on the trophic magnification in freshwater lakes (Yu et al., 2012). Fish play an important role in the aquatic system, covering a wide range of trophic level in the food web. In particular, carnivorous fish occupy a high position in the food web and are commonly consumed by humans (Cheung et al., 2008). With respective to environmental monitoring, fish (e.g. herring) has been selected as a good matrix, serving for early warning of adverse effects due to the exposure of contaminants (Airaksinen et al., 2014). However, the influences of biological parameters (e.g. fish size) on accumulation of PBDEs and MeO-PBDEs have not been well understood.

Dianshan Lake (N 31°04′-31°12′, E 120°54′-121°01′), the biggest freshwater lake in Shanghai, is located in the lower reaches of the Yangtze River Basin with an area of 62 km^2 and an average depth of 2.1 m. Dianshan Lake is one of the important fish sources for the local fish market. It is also one of the drinking water sources for citizens in Shanghai with a population of 24 million. Over the years, although more and more studies on PBDEs have been carried out in the lower reaches of Yangtze River Basin, less study can be found for Dianshan Lake. Pervious study showed that organochlorine pesticides and polychlorinated biphenyls (PCBs) are extensively detected in hen eggs and duck eggs from Dianshan Lake (Xu et al., 2015). However, the brominated compounds such as PBDEs and MeO-PBDEs level in fish, as well as the biomagnication of such anthropogenic and natural contaminants in food web of Dianshan Lake have not been studied.

This study aimed to investigate the occurrence of PBDEs and MeO-PBDEs in fresh water fish from Dianshan Lake, one of the most important fishery and drinking water sources for Shanghai Municipality. Specific objectives included: (1) analyze the concentrations and congener patterns of PBDEs and MeO-PBDEs in eleven fish species from Dianshan Lake; (2) explore the trophic magnification of PBDEs and MeO-PBDEs in the aquatic food web of Dianshan Lake; (3) elucidate the relationship between the concentration of contaminants and fish size.

2. Materials and methods

2.1. Samples and sampling

Eleven wild fish species were collected from Dianshan Lake located in Shanghai, China, in September, 2014. The fish species included grass carp (*Ctenopharyngodon idella*, GRC, n = 5), bighead carp (*Aristichthys nobilis*, BHC, n = 4), silver carp (*Hypophthalmichthys molitrix*, SVC, n = 3), crucian carp (*Carassius auratus*, CCC, n = 11), common carp (*Cyprinus carpio*, CMC, n = 9), snakehead (*Channa argus*, SNH, n = 16), predatory carp (*Erythroculter ilishaeformis*, PDC, n = 18), yellow catfish (*Pelteobagrus fulvidraco*, YCF, n = 23), rosy bitterling (*Rhodeus sinensis*, RBL, n = 100 in 5 pool), stone moroko (*Pseudorasbora parva*, STM, n = 100 in 5 pool) and bigmouth grenadier anchovy (*Coilia ectenes*, BGA, n = 100 in 5 pool). All of them are common species in the freshwater ecosystem in this region. Whole fish were directly placed on ice and transported to the laboratory where their individual body length (cm) and weight (g) were measured immediately, then frozen and stored at −80 °C before dissection. Rosy bitterling, stone moroko and bigmouth grenadier anchovy, were analyzed as pool sample in whole fish. Muscle tissue from other fish species for analysis was taken from the dorsal portion. Further description of fish species are given in Table S1.

2.2. Chemicals and standards

All solvents used were of pesticide analysis grade. Authentic reference standards of PBDE congeners (BDE-28, 47, 99, 100, 153, 154 and 183) and MeO-PBDEs congeners (6-MeO-BDE-47 and 2′-MeO-BDE-68) were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada) and AccuStandard (New Haven, USA), respectively. BDE-138 and BDE-139 from AccuStandard (New Haven, USA) were used as internal standards. All solvents, acids and salts used were of highest quality commercially available. Silica gel (0.063–0.2 mm) purchased from Merck (Darmstadt, Germany) was activated at 300 °C overnight prior to use.

Grass carp (GRC)	Crucian carp (CCC)	Common carp (CMC)	Yellow catfish (YCF)	Snakehead (SNH)	Predatory carp (PDC)
n = 5	n = 11	n = 9	n = 23	n = 16	n = 18
6.3 (4.0–7.6)	0.95 (0.39–1.5)	0.48 (0.36–0.63)	1.4 (0.83–3.1)	0.74 (0.36–1.6)	0.51 (0.24–0.76)
0.031/0.032 (<LOQ-0.041)	1.0/0.89 (ND-3.9)	0.86/0.72 (ND-1.9)	0.88/0.89 (ND-2.4)	3.9/3.9 (ND-9.9)	0.32/0.23 (ND-1.6)
0.056/0.068 (ND-0.077)	2.8/3.1 (0.21–5.1)	6.5/6.8 (ND-23)	6.1/5.8 (0.15–19)	20/16 (<LOQ-68)	3.4/2.3 (ND-16)
0.021/0.011 (ND-0.049)	ND	ND	2.7/2.3 (ND-7.6)	ND	ND
0.011/0.013 (ND-0.025)	0.67/0.44 (ND-1.4)	0.87/0.29 (ND-3.9)	1.6/1.4 (ND-5.3)	4.3/3.0 (ND-14)	0.47/0.066 (ND-2.9)
0.028/0.032 (ND-0.040)	0.044/ND (ND-0.13)	0.29/0.22 (ND-0.71)	2.4/1.6 (0.15–14)	0.69/0.88 (ND-1.4)	0.53/0.21 (0.63–2.9)
0.098/0.10 (<LOQ-0.11)	1.3/1.3 (0.55–2.0)	2.4/2.4 (0.19–4.5)	3.3/3.2 (0.15–12)	9.4/9.6 (0.17–32)	2.7/2.2 (ND-7.9)
0.014/ND (ND-0.066)	ND	0.36/ND (ND-1.1)	1.0/0.81 (ND-4.8)	ND	ND
0.26/0.26	5.9/5.8	11/10	18/16	38/33	7.5/5.0
ND	0.48/0.43 (ND-1.1)	0.48/0.66 (ND-0.98)	1.8/0.77 (ND-6.6)	4.2/2.9 (1.7–8.6)	0.89/0.67 (0.17–3.6)
ND	0.32/0.16 (ND-1.8)	0.35/ND (ND-1.7)	1.5/1.4 (<LOQ-4.2)	1.8/1.9 (ND-5.3)	0.70/0.61 (ND-2.4)

2.3. Extraction and clean up

Approximately 2 g (dry weight) of sample was homogenized after lyophilization. Prior to Soxhlet extraction, surrogate standard (BDE-139, 2 ng) was spiked. The extraction was performed with 200 mL acetone/hexane (1:1, v/v) for 24 h. After extraction, the lipid content of each sample was determined gravimetrically. Lipids and organic matters were removed using concentrated sulfuric acid (98%), and further clean-up was carried out using a Pasteur pipette packed with activated silica gel (0.1 g) and activated silica (0.9 g) impregnated with concentrated sulfuric acid (2:1 w/w) on top. The columns were conditioned with *n*-hexane (3 mL), the extract was added and the analytes eluted with *n*-hexane:dichloromethane (10 mL, 1:1, v/v). The volume was reduced and solvent was changed to *n*-hexane (final volume 0.2 mL) by a gentle stream of nitrogen gas. Prior to instrumental analysis, BDE-138 (2 ng) were added into the samples as volumetric standard (VS).

2.4. Instrumental analysis

PBDEs and MeO-PBDEs were analyzed by Agilent 7890A gas chromatography coupled to a 5975C mass spectrometry (GC-MS) using chemical ionization (CI) and selective ion monitoring (SIM) mode, scanning bromine ions (*m/z* 79 and 81). Automated 1 μL injection was conducted on a DB-5MS column (15 m × 0.25 mm i.d. × 0.10 μm film thickness; Agilent J&W), with methane as reagent gas. The injector was operated at temperature of 280 °C. Helium was used as carrier gas at a set constant flow of 1.4 mL/min. The oven program was 80 °C for 2 min, 15°C/min to 300 °C, 2°C/min to 310 °C and hold for 5 min. The ion source and transfer line temperature were set at 200 °C and 290 °C, respectively.

2.5. Stable nitrogen and carbon isotope analysis and TMF calculation

Samples were lyophilized and finely powdered. Approximately 1 mg dry weight of the ground samples were weighed in tin capsules and analyzed using a Flash HT element analyzer interfaced with a Thermo Scientific MAT 253 isotope ratio mass spectrometer. Stable isotope ratios of samples were assessed against the reference standards urea for $\delta^{15}N$ (0.4‰) and $\delta^{13}C$ (30.9‰). The isotope ratios (δ‰) were calculated using the following Formula (1):

$$\delta^{15}N \text{ and } \delta^{13}C = \left[\left(R_{sample}/R_{standard}\right) - 1\right]*1000 \quad (1)$$

where R is $^{15}N/^{14}N$ for $\delta^{15}N$ and $^{13}C/^{12}C$ for $\delta^{13}C$. The precision for this technique is about 0.5‰ (±standard deviation (S.D.)) for $\delta^{15}N$ and 0.2‰ (±S.D.) for $\delta^{13}C$.

Trophic level (TL) was calculated for each individual sample by applying Eq. (2) (Post, 2002):

$$TL_{consumer} = \left[\left(\delta^{15}N_{consumer} - \delta^{15}N_{zooplankton}\right)\right]/3.4 + 2 \quad (2)$$

where 3.4 is the isotopic trophic enrichment factor according to Fisk et al. (2001).

TMFs were calculated according to Tomy et al. (2004) and the references therein using following equations:

$$\text{Log concentration(lipid} - \text{normalized)} = A + B*TL \quad (3)$$

The slope B was used to calculate TMF values using Eq. (4):

$$TMF = 10^{B} \quad (4)$$

TMFs > 1 indicates that contaminants are biomagnifying through the food chain, whereas negative values imply that contaminants are not taken up by the organism or that they are metabolized (Fisk et al., 2001).

2.6. Quality assurance and quality control

One procedural solvent blank was analyzed in parallel with each batch of five samples to assess any potential contamination during laboratory work. Limit of detection (LOD) was set to three times the background noise (S/N = 3). Limit of quantification (LOQ) was set to 10 times the background noise (S/N = 10). The detailed LOQ of each PBDEs in each fish species is presented in Table S2. The range of recoveries (mean ± S.D.) of BDE-139 was 63–115% (95% ± 5.1%).

2.7. Statistics

Statistical analysis was performed on SPSS (PASW Statistics 18). Spearman rank correlation test was used to assess the correlation between concentrations of analytes and fish size. The significant level was set at 5% ($\alpha = 5\%$).

3. Results and discussion

3.1. Concentration and congener profile of contaminants

The concentrations of PBDEs are presented in Table 1 and visualized in Figs. S1 and S2. The highest mean concentration of $\sum_7$PBDEs was observed in snakehead (38 ng g^{-1} lw) whereas the lowest concentration was observed in grass carp (0.26 ng g^{-1} lw). Mean concentrations of PBDEs were in the following descending order: snakehead > stone moroko ≈ yellow catfish ≈ bigmouth

grenadier anchovy > rosy bitterling ≈ common carp > predatory carp ≈ crucian carp ≈ silver carp ≈ bighead carp > grass carp. In order to compare the $\sum_7$PBDEs level with other studies in terms of the same species, the results are summarized and given in Table S3. In general, the contaminant levels in fishes from Dianshan Lake were in moderate to low range compared with other studies. The $\sum_7$PBDEs level in silver carp (1.6 ng g^{-1} lw), bighead carp (4.2 ng g^{-1} lw), grass carp (0.26 ng g^{-1} lw), crucian carp (1.3 ng g^{-1} lw) and snakehead (38 ng g^{-1} lw) in the present study were much lower than those in southern China, including silver carp (1600 ng g^{-1} lw) (Luo et al., 2007b), bighead carp (6300 ng g^{-1} lw) (Luo et al., 2007a), grass carp (19–31 ng g^{-1} lw) (Cheung et al., 2008), crucian carp (1900 ng g^{-1} lw) (Luo et al., 2007b) and snakehead (19–960 ng g^{-1} lw) (Cheung et al., 2008). The $\sum_7$PBDEs levels in silver carp (5.0 ng g^{-1} lw), grass carp (0.26 ng g^{-1} lw), crucian carp (5.8 ng g^{-1} lw) and common carp (11 ng g^{-1} lw) were one magnitude lower or comparable to those from Taihu lake, including silver carp (13 ng g^{-1} lw), grass carp (3.8 ng g^{-1} lw), crucian carp (12 ng g^{-1} lw) and common carp (14 ng g^{-1} lw) (Yu et al., 2012). Further, PBDEs contamination in common carp was much less serious than the same species in Gila river (3600 ng g^{-1} lw) in USA, where the samples were collected before the commercial PBDEs products ceased (Echols et al., 2013).

The congener profile of PBDEs in eleven fish species is shown in Fig. 1. BDE-47 was the predominant congener, accounting for 43% (with a range of 13–58%) of $\sum_7$PBDEs, followed by BDE-154 (24%), BDE-28 (14%) and BDE-100 (6%). BDE-99 only contributed to 2.5% of $\sum_7$PBDEs with a detection frequency of 36% (37/104). The average ratio between BDE-99/BDE-100 in the fish was 0.58, which is much lower than those in technical PentaBDE mixture (3.7–5.7) (La Guardia et al., 2006). Zeng et al. (2012) feeded common carp with commercial PentaBDE mixture in food and found the most abundant congener BDE-99 degraded to BDE-47. However, BDE-100 was resistant to debromination. This indicates the structure selection of reductive debromination. In addition, Stapleton et al. (2004) found that BDE-99 undergoes debromination to form BDE-47 in common carp by removal of a *meta*-bromine atom. In the present study, BDE-99 was not detected in common carp, predatory carp, crucian carp and snakehead, however, the compositions of BDE-47 were relatively high (i.e. 48% in common carp, 45% in predatory carp, 57% in crucian carp and 53% in snakehead), indicating strong metabolism of BDE-99 occurred in these species. Nevertheless, yellow catfish showed highest concentration (2.7 ng g^{-1} lw) and congener profile

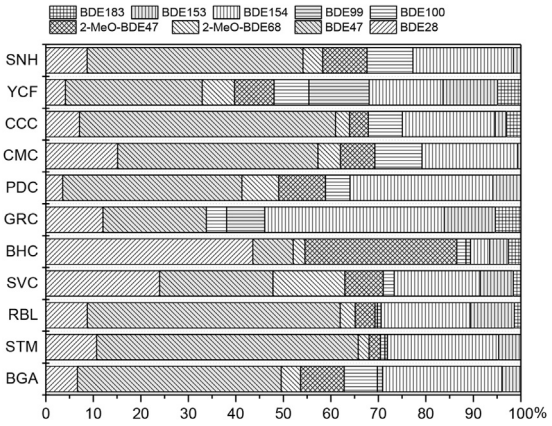

Fig. 1. Congener profile of PBDEs and MeO-PBDEs in 11 freshwater fishes from Dianshan Lake, including Bigmouth grenadier anchovy (BGA); Stone moroko (STM); Rosy bitterling (RBL); Silver carp (SVC); Bighead carp (BHC); Grass carp (GRC); Predatory carp (PDC); Common carp (CMC); Crucian carp (CCC); Yellow catfish (YCF) and Snakehead (SNH).

contribution (13%) of BDE-99, indicating species specific in debromination of BDE-99.

Further, the ratios between BDE-153/BDE-154 in fish were in the range of 0.03–0.98, with a mean value of 0.33, which is reversed in the technical PentaBDE mixture (1.2–8.1) (La Guardia et al., 2006). Mizukawa et al. (2013) exposed five BDE congeners (BDE-47, -99, -100, -153 and -154) to ureogenic goby (*Mugilogobius abei*) and marbled sole (*Pseudopleuronectes yokohamae*), and found BDE-99 and BDE-153 had higher metabolic debromination potential than BDE-100 and BDE-154. This could be explained by the fact that BDE-99 and BDE-153 have one more bromine atom substituted in *meta*-position than BDE-100 and BDE-154, respectively, and the debromination primarily takes place in the *meta*-position. Another explanation could be that BDE-154 can be formed by debromination of BDE-183 (Zeng et al., 2012).

Species specific PBDE congener profiles were observed among the fish. For instance, snakehead showed highest concentration of BDE-28, -47, -100 and -154 whereas yellow catfish showed highest concentration of BDE-99, -153 and -183 (Fig. S2). Considering the structure similarity discussed above, it is plausible that yellow catfish is more resistant to debromination than any other fish analyzed in the present study. Unfortunately, no PBDEs metabolism study has been conducted on yellow catfish so far.

Table 1 and Fig. S2 present the concentration of two MeO-PBDEs congeners (6-MeO-BDE-47 and 2′-MeO-BDE-68). Mean concentration of 6-MeO-BDE-47 ranged from ND (in grass carp) to 4.2 ng g^{-1} lw (in snakehead) whereas 2′-MeO-BDE-68 varied from ND (in grass carp) to 1.8 ng g^{-1} lw (in snakehead). This is in accordance with the level in mandarin fish from its upstream lake, Tai Lake (Qiu et al., 2012) and in anchovy (*Coilia* sp.) from the Yangtze River Delta region (Su et al., 2010). However, such level were one magnitude lower than those reported in ocean fish (Baron et al., 2013; Covaci et al., 2008; Dahlgren et al., 2016; Losada et al., 2009). The major source of MeO-PBDEs is naturally synthesized in sea water in the presence of bromine, bromoperoxidase and hydrogen peroxide (Malmvärn, 2007). However, limit data on MeO-PBDEs in freshwater has been reported and the sources of MeO-PBDEs is uncertain. In our previous study on fish in Tai Lake, it is purposed that MeO-PBDEs was probably produced due to the algae bloom (Qiu et al., 2012), which occurs annually. Su and co-workers suggested that the source of MeO-PBDEs in anchovy is due to the migration of fish to sea water (Su et al., 2010). It could also result from the water flow exchange, i.e. saltwater intrusion.

No correlation was observed between BDE-47 and 6-MeO-BDE-47. The mean ratio between 6-MeO-BDE-47 and BDE-47 in the present study was 0.49. Fish showed much less oxidative metabolites of PBDEs (e.g. OH-PBDEs) than debromination products (Roberts et al., 2011). Zeng et al. (2012) found the ratio of OH-PBDEs to their PBDEs precursor was only 0.5–0.7% in common carp's serum. Accordingly, it is plausible that the presence of MeO-PBDEs in fish from Dianshan Lake was produced in natural process rather than metabolism of PBDEs (i.e. hydroxylation followed by *O*-methylation). However, further studies needs to be conducted to get solid conclusion on this.

3.2. Trophic magnification

The stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope ratio was shown in Fig. S3. The variance of $\delta^{13}C$ was relatively large in some of benthic fish species, such as snakehead, common carp and crucian carp. It is indicated that the sources of carbon were not sole in sediments, which would hinder the research on trophic magnification. In particular, $\delta^{13}C$ value of snakehead is isolated from other species, indicating a different food source (Fig. S3). Therefore, snakehead was excluded when trophic magnification was assessed.

Table 2
Trophic magnification factor (TMF) calculated as the regression coefficient of the trophic level versus the logarithm of the concentration (ng g^{-1} lw) in fish. Log K_{ow} of PBDEs and MeO-PBDEs were measured by Yu et al. (2008).

	Log K_{ow}	All individuals except snakehead (n = 89)				
		n	*p*	R	Slope	TMF
BDE-28	5.94	66	0.000**	0.500	0.201	1.59
BDE-47	6.81	71	0.000**	0.419	0.199	1.58
BDE-99	7.32	31	0.017*	0.414	0.257	1.81
BDE-100	7.24	59	0.067	0.240	0.129	1.35
BDE-153	7.90	64	0.002**	0.380	0.179	1.51
BDE-154	7.82	76	0.004**	0.327	0.150	1.41
BDE-183	8.27	29	0.010**	0.470	0.238	1.73
6-MeO-BDE-47	6.44	65	0.103	0.204	0.104	1.27
2′-MeO-BDE-68	6.16	60	0.040*	−0.265	−0.136	0.73

*Significant level at 5%; **Significant level at 1%.

TMFs for each PBDE and MeO-PBDE congeners together with their Log K_{ow} were listed in Table 2. All of the PBDE congeners showed trophic magnification potential (TMF > 1) in Dianshan Lake. TMFs of seven PBDE congeners ranged from 1.35 to 1.81. This was in line with the TMF value in food web in Bohai Bay ($\sum_{13}$PBDEs = 2.29) (Shao et al., 2016) and Taihu Lake (1.5–2.9) (Yu et al., 2012). The mean TMF of BDE-47 was 1.58 close to that in Canadian Arctic marine food web (1.6) (Kelly et al., 2008) but lower than that in Sydney harbor (4.1) (Losada et al., 2009). Such differences could be due to a number of factors (e.g. size of food chain, species difference, contamination level). Ma et al. (2013) found the TMF would increase accompanied by the enlargement in the food chain. Hop et al. (2002) found TMF of halogenated compounds in poikilotherms were lower than those in homeotherms, probably due to the lower energy requirement of poikilotherms. Mizukawa et al. (2013) found that PCBs were more biomagnified than PBDEs in both *in vitro* and field study. They concluded that selective debromination at the *meta* position of PBDEs, in particular in high trophic level fish species, was an important factor, while other factors must be responsible for the lower biomagnification of PBDEs in natural ecosystems.

MeO-PBDEs showed less or none trophic magnification potential than PBDEs. This was in contrast with previous studies (Kelly et al., 2008; Kim et al., 2015). MeO-PBDEs have a relative long half live than its PBDE precursor under transformation conditions (4-MeO-BDE-17 t1/2 = 79 000s, BDE-17 t1/2 = 57 000s) (Moreira Bastos et al., 2008). Recently, Dahlgren et al. (2016) studied bioaccumulation and biomagnification of OH-PBDEs and MeO-PBDEs in Baltic Sea food chain. They found MeO-PBDEs concentration increased accordingly up to perch and then dropped dramatically. The opposite trend was observed for OH-PBDEs, indicating the conversion between MeO-PBDEs and OH-PBDEs. In addition, other factors e.g. bio-dilution through the food web (Zhang et al., 2012) and seasonal variation (Lofstrand et al., 2011) could influence the accumulation of MeO-PBDEs in aquatic biota and further impact the TMFs.

3.3. Influence of fish size on biomagnification

Fish size has been commonly used to assess the accumulation effects of contaminants. In the present study, five species (predatory carp, snakehead, crucian carp, common carp and yellow catfish) due to the high length variation and large number of samples (over 10), were used to discuss relationships between fish size and PBDEs concentrations. Correlations between sample size and concentrations of PBDEs were significantly negative ($p < 0.05$) in predatory carp, snakehead and crucian carp, indicating “fish size dilution” (Fig. 2). A negative correlation has been reported in fishes from Taihu Lake, China (Yu et al., 2012) and French estuaries, France

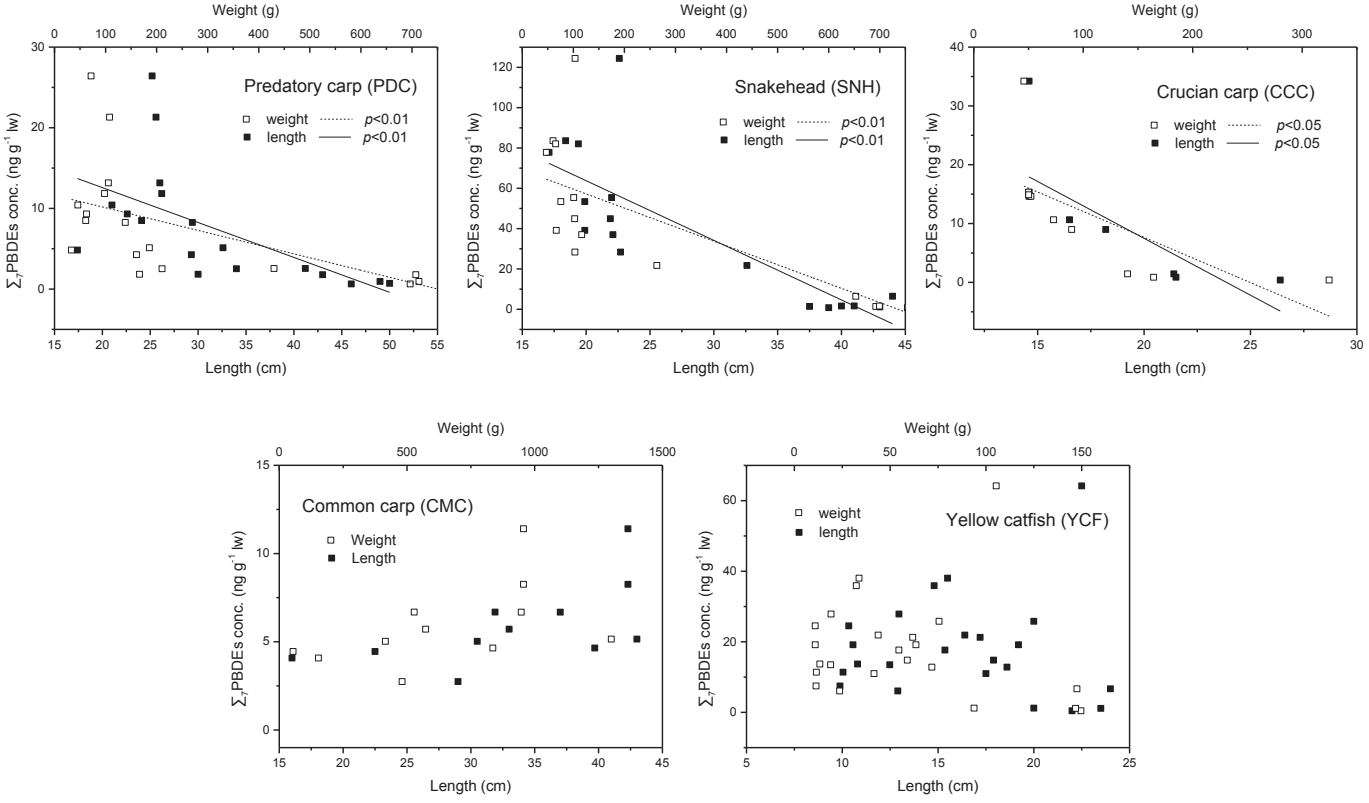

Fig. 2. Relationship (Spearman rank correlation test) between PBDEs (ng g^{-1} lw) and fish size (length (cm) and weight (g)) in selected fish species from Dianshan Lake.

(Bragigand et al., 2006). However, this was inconsistent with other study (Olsson et al., 2000), which found concentration of organochlorine substances positively correlated with size increase in perch (*Perca fluvatilis*). These results imply a number of factors influence the accumulation of contaminants in different ways. On one hand, organisms accumulate more contaminants with the increase of exposure time. Larger fish also indicate their prey status in higher trophic level in food web and accumulate more contaminants. In addition, increased body size can lead to less efficient contaminants clearance over the gills due to a reduced gill area to body volume ratio or increased distance between HOC storage tissues and sites of elimination (Burreau, 2001; LeBlanc, 1995; Yu et al., 2012). On the other hand, compared with those top predatory in food web (e.g. sharks, predator birds), the steady-state of contaminants can be reached more rapidly in fish, as a consequence, the growth of size would not increase the concentration (Gewurtz et al., 2011). Another explanation could be the correlation between sample size and PBDE concentration in Fig. 2 was assessed by concentration on lipid weight base. It is commonly found that larger fish possess more lipid content, and thus concentration reported on lipid weight would be diluted by such high lipid content (Yu et al., 2012). Nonetheless, it is noteworthy that fish dilution effect does not indicate the decrease of trophic magnification. Fish in low trophic level could show stronger dilution effect than those in high trophic level, and as a result, trophic magnification still occurs.

4. Conclusion

The concentration and congener profile of PBDEs and MeO-PBDEs in fresh water fish were reported in Dianshan Lake, one of the main fishery and drinking water resources for Shanghai Municipality. Snakehead showed highest concentration of PBDEs and MeO-PBDEs. The contamination level of those natural and anthropogenic brominated substances were in the moderate to low range compared with other studies. Trophic magnification was observed in freshwater fishes for all target PBDE congeners, but the trophic magnification for MeO-PBDEs was negligible. Concentrations of PBDEs decreased with length or weight in predatory carp, snakehead and crucian carp, indicating fish size dilution effect in these species. Future study can pay more attention to the relationship between physical biological parameters and organohalogen contaminants level. Moreover, other aquatic organisms such as algae, bivalve, and water bird can be included to enlarge the aquatic food web. It is noteworthy to point out that yellow catfish showed a unique PBDEs pattern (with high composition of BDE-99, -153 and -183) compared with other species. More efforts on the metabolism and biotransformation mechanism in yellow catfish is valuable.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.09.043.

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