

Polybrominated diphenyl ethers (PBDEs) in sediment and fish tissues from Lake Chaohu, central eastern China

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Abstract: Polybrominated diphenyl ethers (PBDEs) levels in environmental media have increased over the last 20–25 years in the world. In aquatic environments PBDEs were found to be accumulated along food chain and Endocrine disruptors toxicity. In this study PBDEs were investigated in sediment and fish tissues from Lake Chaohu in central eastern China. There were 10 PBDEs congeners detected out of all 41 PBDEs. BDE-47 was of the highest with 5.17 ng/g in sediment and 58.47 ng/g in fish. PBDEs were evenly distributed across the surface sediment in the whole lake. It implied that the main source of PBDEs may not be an inflow river like Nanfei. Tissue distribution patterns of PBDEs in four fish species were in the order of BDE-47 > BDE-99 > BDE-100 > BDE-66 > BDE-138 > BDE-183 > BDE-154 > BDE-153. Octa- and deca-BDEs were below the detection limit. The concentrations of all PBDE congeners were higher in gills, livers, and kidneys than those in muscles and adipose tissue. Furthermore, PBDEs in different tissues had some different distribution patterns with fish size. Those discrepancies appeared to be correlated with the PBDEs pollution fluxes varying with the change of the year and their metabolism divergences in fish tissues.

Introduction

Polybrominated diphenyl ethers (PBDEs) are widely utilized fire retardants embedded in textiles, plastics, electrical components, paints, foam, rubber, and other casing materials (Petreas et al. 2011). Commercial production began in the 1970s and PBDEs levels in various environmental media have rapidly increased over the last 20–25 years (Tanabe et al. 2008). It is highly concerned due to their toxicity and Endocrine disruptors (Karpeta et al. 2011, Liu et al. 2012). These reports prompted governments all over the world to initiate studies to generate more information regarding their significance in order to take necessary regulatory actions (Kemmllein et al. 2003). For example, penta- and octa-BDEs have been banned from all products in the EU-market from August 2004, as well as in 10 states of the U.S.A. (BSEF 2004), they are still used in China and remain as ubiquitous long-term threats in the environment. Fish consumption has been associated with higher PBDE levels in some human population surveys (Sjödin et al. 2000). Food and water contribute 18% of the total PBDE ingestion (Lorber 2007). Human beings will continue to be exposed to these chemicals despite those increased regulation mentioned before (Frederiksen et al. 2009).

Concentrations and distributions of PBDEs in the environment were well documented in North America (Dallaire

et al. 2009), Europe (Jaraczewska et al. 2006, Roosens et al. 2010), Australia (Besis and Samara 2012) and Asia (Hong et al. 2010). Yet, there is little information about the exposure levels of PBDEs in Chinese lakes (Zhou et al. 2012). It is well known that China has several brominated flame retardants manufacturing plants that mainly produce PBDEs, and they are mostly located in eastern China, near to Lake Chaohu. Therefore, it is important to explore the exposure level of PBDEs in Lake Chaohu to cognize its ecological toxicity risk. The aim of this study was to determine environmental exposure levels of PBDEs and congener-specific deposition profiles in sediment and fish species of Lake Chaohu. It is the fifth largest lake in China which is the most important source of drinking water for five provinces in China. Sediments and fish have played an important role in the distribution and fate of PBDEs and aquatic environments health. Fish pollution investigation can provide information on the transformation and bioaccumulation of PBDE to human being. Correspondingly comprehensive survey of PBDE contamination aimed at Lake Chaohu is urgently needed. Tissues and organs such as adipose tissue, liver, muscle, gill, and kidney of four fish species in Lake Chaohu and forty-one PBDEs congeners were analyzed in this study. The results can provide useful information about the exposure levels of PBDEs and further evaluation for potential ecological risk in Chinese great lakes.

Materials and methods

Samples collection

Sediment and fish samples were collected from Lake Chaohu which is located in Anhui Province, eastern China and within the Yangtze river system. Sediment and fish samples were obtained in July and November 2009. Sample sites recorded by GPS are shown in Fig. 1 where sediment samples were obtained from all four sites, fish samples from No. 3 site.

Surface sediment core samples (0–10 cm) were taken from four sites of Lake Chaohu by a Beeker Sampler with a 30 cm LX 5 cm DI plexiglas cylinder tube. Fish samples including *Cyprinus carpio*, *Culter alburnus*, *Hypophthalmichthys molitrix*, *Aristichthys nobilis* which are the main economy fish species in Chaohu Lake were captured in the center of western Lake Chaohu (Table 1). Adipose tissue, muscles, gills, liver and kidney of fishes were washed first. Sediment and fish samples were preserved in -4°C potable iceboxes in the field. Then they were taken into laboratory to freeze-dry, grind, and sieve for further analysis.

Chemicals and reagents

A PBDE analytical standard solution was purchased from AccuStandard, Inc. (New Haven U.S.A.). It contained 39 PBDE congeners (purity from 95.2% to 100%, concentrations ranging from 98.0–251.3 ng/mL), including 3 mono-BDEs (BDE 1, 2, and 3), 7 di-BDEs (BDE 7, 8, 10, 11, 12, 13 and 15), 8 tri-BDEs (BDE 17, 25, 28, 30, 32, 33, 35 and 37), 6 tetra-BDEs (BDE 47, 49, 66, 71, 75 and 77), 7 penta-BDEs

(BDE 85, 99, 100, 116, 118, 119 and 126), 5 hexa-BDEs (BDE 138, 153, 154, 155 and 166), 3 hepta-BDEs (BDE 181, 183 and 190) at 100–250 ng · mL⁻¹. The other two PBDE standard octa-BDE (BDE 197) and deca-BDE (BDE 209) was solid powder, purity >97.5%, purchased from China Ji'nan Taixing Fine Chemical Co., Ltd. Internal standard ¹³C-BDE99 as the recovery rate indicator and ¹³C-PCB-141 as instrument internal standard were obtained from Cambridge Isotope Laboratory, Andover, USA. Chromatographic grade solvents, methanol, hexane, dichloromethane and sulfuric acid, were purchased from Merck (Darmstadt, Germany). Diatomite was obtained from Beijing Nuoxin Shengyuan Ltd, China. To avoid human exposure, all standards and solvents were manipulated under a hood and using gloves, glasses and clean overalls. Extraction and clean up procedures were also performed under a hood.

Sample extraction and clean-up

5.00 g ground samples of fish and sediment, adding internal standard ¹³C-BDE-99, were mixed with 10.00 g diatomite and extracted with an ASE (Accelerated Solvent Extraction) instrument using 200 ml hexane/dichloromethane (1:1, v/v) 3 times. The extraction solutions of samples were concentrated to 3–5 ml, eluted with 150 ml hexane/dichloromethane (1:1, v/v) in multilayer silica gel columns (inner-diameter 2 cm, length 25 cm) filled from the bottom with 2 g AgNO₃ silica, 1 g of activated silica gel, 3 g of silica/NaOH, 1 g of activated silica gel, 8 g of silica/H₂SO₄ 44% (w/w), 4 g of silica/H₂SO₄ 22% (w/w), and 1 g of activated silica topped with 2 cm of Na₂SO₄. After concentration the eluent was cleaned in a florisil column

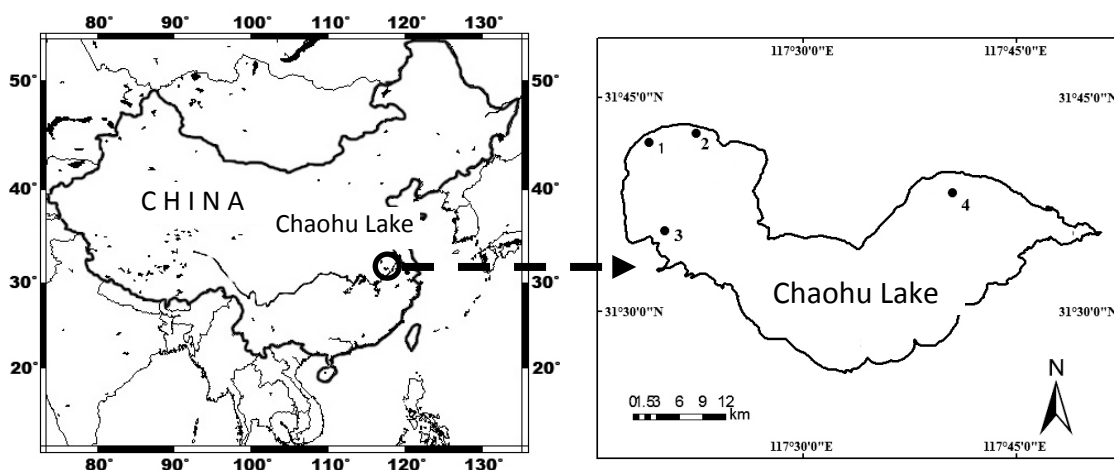


Fig. 1. Map of the sampling sites of Lake Chaohu in China

Table 1. Details of freshwater fishes from Lake Chaohu

Common name	Scientific name	Number of samples	Weight (g)	Length (cm)
Common carp	<i>Cyprinus carpio</i>	5	800±200	26±5
Topmouth culter	<i>Culter alburnus</i>	4	600±400	20±5
Silver carp	<i>Hypophthalmichthys molitrix</i>	5	2125±875	36±6
Big-head carp	<i>Aristichthys nobilis</i>	3	1875±375	33±3

filled from the bottom with 2 g of glass cotton, 5 g of florisil, and topped with 2 cm of Na₂SO₄ 100 ml hexane eluted florisil column. The eluent was collected and concentrated to 20 µl, adding internal standard ¹³C-PCB-141 for GC/MS analysis.

Instrumental analysis

GC/MS analysis of PBDEs was performed following the procedure described by Zhao et al. (2010) with slight modification. PBDEs congeners were detected by GC/MS on Agilent 5973 mass spectrometer (Agilent Technology Company, Wilmington, USA) equipped with a 6890 gas chromatograph. Gas chromatograph with the chromatographic column was DB-5 MS (American Agilent company), 15 m × 25 µm × 0.25 µm. Mass spectrometry with negative chemical ionization mass spectrometry (MS-NCI) in the selected ion mode (SIM), with high pure helium as carrier gas, methane as reactant gas, ion source temperature 150°C, quadropole temperature 150°C. High voltage pulse splitless inlet: inlet temperature was 265°C, interface temperature – 300°C, carrier gas flow rate was 1.5 mL/min, 6 min solvent delay. Temperature program: starting temperature 80°C (1 min), with 10°C/min up to 200°C, with 20°C up to 300°C (15 min). The injection volume was 1 µL. Retention time applied for qualitative and external standard method was used for quantitative analyses. Scanning ion: mono- to hepta-BDE for m/z=79, 81, deca-BDE for m/z=486.7, 488.7, ¹³C-PCB141 for m/z=372,374.

Quality assurance

Instrumental quality control was done by regular injection of solvent blanks and standard solution. Procedural blanks were run in parallel. The concentrations of PBDEs in dosed groups were corrected by subtraction of average procedural blank value and that of the control groups. To evaluate the method performance using ¹³C-BDE 99 as internal standard quantification for extracting and cleaning course, ¹³C-PCB-141 was used as internal standard quantification for instrument analysis. The average recovery rate was 76% and RSD (Relative standard deviation) was less than 15%.

Statistical analysis

Statistical treatment of the obtained results was performed with the SPSS (Statistical Product and Service Solutions) 11.0 for Windows. Spearman rank correlation was used to examine the strength of associations between parameters. Probability values less than 0.05 were considered as statistically significant.

Results and discussion

Spatio-temporal distribution of PBDEs in sediment

PBDEs were detected in Lake Chaohu sediment at all four sample sites in July and November 2009. Of the 41 PBDE congeners analyzed, 10 were present in all sediment samples (Fig. 2), indicating that PBDEs are widespread in the lake. Octa-BDE and deca-BDE were not detected. Mean concentration of ΣPBDEs in sediment in those two months was 33.01 ng/g and 32.76 ng/g respectively. Therefore, it is worthwhile to note that the samples collected between two months did not have significant difference. Mean concentration order of the 10 PBDE congeners based on the two months' average value was: BDE-47 (18.64%), -154 (13.06%), -183 (11.99%), -153 (10.19%), -138 (9.70%), -99 (8.05%), -85

(7.82%), -66 (7.78%), -100 (7.12%), -28 (5.65%). BDE-47 was the predominant congener with the concentration of 6.13 ng/g. Apart from BDE-47, BDE-154, BDE-183, BDE-153, and BDE-138, the concentrations of other PBDE congeners were less than 3 ng/g. Interestingly, the sum of hexa- and hepta-BDE in sediment from the present study accounted for 44.94% of the total PBDEs. This relative abundance of higher brominated congeners was quite different from previous observations of Yangtze River in China (Shen et al. 2006), where the higher brominated congeners only accounted for mean 15% of the total. The reason is probably due to different production of PBDE congeners using different watersheds. Also there was no significant difference between the sample sites. This revealed that the source of PBDEs may be not inflow rivers, such as the Nanfei and Shiwuli, which are main inflow rivers of Lake Chaohu from northwest and are heavily polluted by municipal sewage. Another source may be air deposition through long distance transportation (Hale et al. 2006). Long distance transportation is considered to be the main pollution source for non-polluted area (Mai et al. 2005, Chen et al. 2013b) in Dongguan area of southeast China. By contrast, the concentration of ΣPBDE in surface sediments of bay area around the Yellow Sea was far lower than those measured in the present study, such as 1.3 ng/g in Laizhou Bay (Jin et al. 2008), and 0.16 ng/g in the Bo Sea (Wang et al. 2009).

PBDE levels in lake, river and marine sediments varied from nanograms per gram of dry weight to micrograms per gram of dry weight, depending on the sampling locations, as reviewed by de Wit (2002) in Europe and North America, Zhou et al. (2012) in Asia, Law et al. (2008) in Europe, and Yogui and Sericano (2009) in USA. Heavily industrialized and populated areas are generally more contaminated where the highest value of ΣPBDEs would reach 14 000 ng/g (Eljarrat et al 2007) than remote areas where the concentration was generally not more than 1000 ng/g (Moon et al. 2012). In addition, the PBDE congeners order found in this study was BDE-47 > BDE-154 > BDE-183 > BDE-153 > BDE-138 > BDE-99, just similar to the traditional distribution pattern (Law et al. 2008, Yogui and Sericano 2009), a large difference from the order for air: BDE-99 > BDE-153 > BDE-166 > BDE-154 > BDE-49 > BDE-47 (Hale et al. 2006). That difference may be related to different degradation mode of PBDEs from air deposit to sediment decomposition.

PBDEs distribution in organs and tissues of fish

Mean ΣPBDEs concentrations of four fish samples ranged from 120.65 to 129.77 ng/g. There were no significant differences between fish species. PBDEs have been shown to be biomagnified in aquatic food chains, including those in remote Arctic (Kelly et al. 2008). Four fishes in this research belong to carnivorous and omnivorous species. No significant discrepancy of PBDEs distribution pattern of inter-species fishes was found. This result is in agreement with a previous research of Weijs (2009). ΣPBDE distribution levels of fishes from Lake Chaohu was similar to that from Yangtze River in China (Xian et al. 2008) and Lake Canal in Belgium (140 ng/g) (Covaci et al. 2005), far lower than Hyco River in Virginia (1,140 ng/kg for carp) (Hale et al. 2001) in USA, and far higher than that in eleven French lakes (0.032±0.056 ng/g wet weight) (Blais et al. 2006), Liobregat River in Spain (43 ng/g) (Labandeira et al. 2007), and Syr Dam Lake in Turkey (44 ng/g)

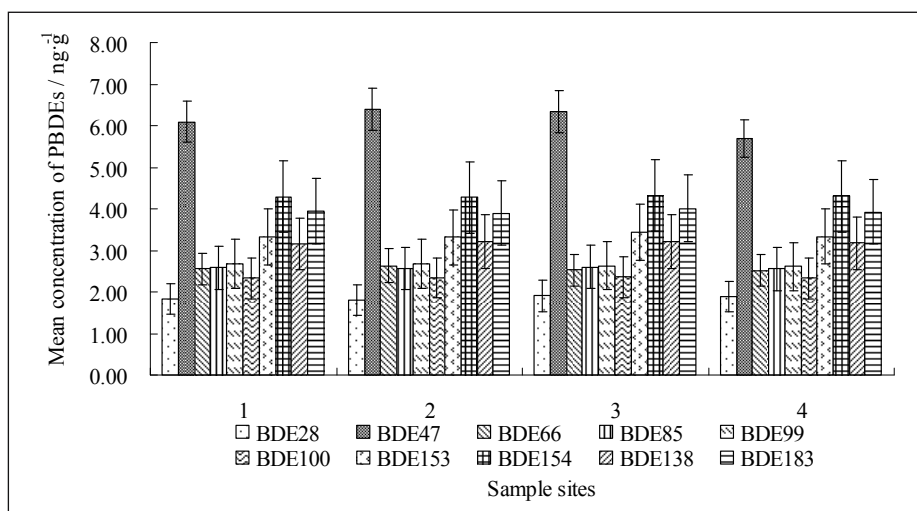


Fig. 2. Mean concentration of ten PBDE congeners of surface sediment in Chaohu Lake

(Erdgrul et al. 2005). ΣPBDE concentration ranged from 6 to 43 ng/g lipid weight among fish species from Australia marine environment (Hermanussen et al. 2008). Therefore, the PBDEs concentrations were ordered as follows: Europe, Australia ≤Asia < North America. Mean levels in North American people and fish have been found to be up to 10 times higher than in European samples (Huwe et al. 2008), while in South America, e.g. in Brazil, PBDEs concentration was lower than the limit of quantification (Lavandier et al. 2013). The trend is most likely due to the heavier use of PBDEs in North America compared to other areas (Hites 2004).

BDE-47 was taken as an example to (Fig. 3) illustrate that concentrations of all PBDEs congeners analyzed in liver and kidney were significantly higher than those in muscle because of other PBDE congeners showing the same pattern in the present study. It was found that concentrations of PBDEs in adipose tissue were a bit lower than those in liver, kidney, and gill in this study. A similar study conducted by Huwe (2008) on rats exposed to PBDEs showed that the accumulation of these substances in adipose tissue and kidney contributed to almost the same percentage of total PBDEs. A reasonable explanation for the selective accumulation of these lipophilic contaminants

in liver and kidney of these PBDE congeners was likely due to their special tissue which can specifically sorb PBDEs, and unique active hepatic accumulation process in liver (Xian et al. 2008) as well as renal reabsorption in kidney. Furthermore, in recent years, report showed that total PBDE content in the gulls was positively associated with protein but not lipid content when analyzed together with body composition (Verreault et al. 2007). Another interesting thing was that PBDEs concentrations in gill were also higher than those in muscle and adipose tissue at present study. This indicated that PBDEs can straightly enter the fish body through gill respiration (Guo et al. 2007). Another possible reason would be the microcilia of gill absorbing PBDEs. Little similar research has been performed with regard to the distribution in gill, and further study is needed.

Among all the 10 PBDE congeners detected in fish, the sum of tetra-BDE (BDE-47, 66) and penta-BDE (BDE-99, 100) accounted for 70% of total PBDEs. The order of mean PBDE congener concentrations was BDE-47 (46.66%), -99 (8.71%), -100 (7.37%), -66 (7.28%), -138 (6.11%), -183 (5.30%), -154 (5.29%), -153 (5.16%), -85 (4.10%), and -28 (4.02%) (Fig. 4). The distribution pattern of PBDE congeners in this

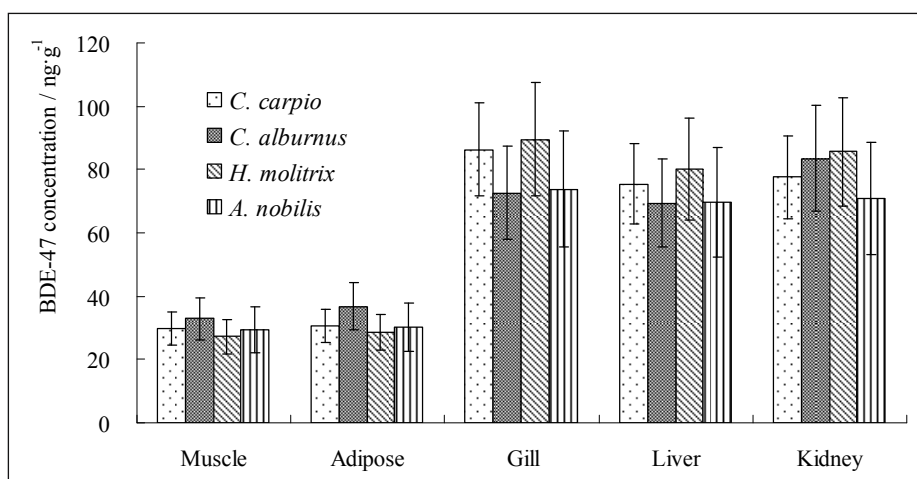


Fig. 3. Concentrations of BDE-47 in five tissues of four fishes in Chaohu Lake

study was typical, and is similar to the pattern of most aquatic animals investigated from other lakes of the world (Binelli et al. 2008), except for Taiwan rivers where the order was BDE-47 > 154, 153 > 99 (Peng et al. 2007). These results are due to the greater use of octa-BDE rather than penta-BDE in Tai Wan than in China mainland and other countries. Not surprisingly, BDE-47 was the predominant congener found in the tissues. Its concentrations in gill, liver and kidney tissues ranged from 69.31 to 89.41 ng/g which was 2.5-fold higher (Fig. 3) than that in muscle and adipose tissues ranging from 27.11 to 36.83 ng/g. Those were higher than those in fishes from Yangtze river (Xian et al. 2008). Furthermore, BDE-47 concentration was also one order magnitude higher than that in the sediment of Lake Chaohu. The dominance of BDE-47 in fishes of the present study was consistent with the general pattern found in biota samples (Chen et al. 2013a). The reason for higher BDE-47 concentration may be due to its high assimilation efficiencies and due to the production of BDE 47 in fish tissues being a result of debromination of higher-brominated compounds (Stapleton et al. 2004a). The accumulation extent of another important congener BDE-99 in fish was in the second place just following BDE-47. Its distribution pattern and level were consistent with eel from Italy lagoon (Mariottini et al. 2008). But in some other previous reports, the BDE-99 contributed < 1% of total PBDEs (Xian et al. 2008; Xia et al., 2011).

The concentration of BDE-47 was 5.4 folds higher than that of BDE-99. This ratio was about 5 in European eel from Orbetello lagoon in Italy (Mariottini et al. 2008), close to that research. Marked differences in the ratios of BDE47 to BDE99 were observed among the examined biological species of the St. Lawrence Estuary food web. BDE47/99 ratios in some fish species such as rainbow smelts, American eels, American plaice and smooth flounders were much higher 22–75 than in other organisms, such as zooplankton 1 and shrimp 8.5 (Law et al. 2003). It seemed that the distribution pattern of BDE-47 and -99 was similar between freshwater and marine fishes, while BDE47/99 ratio may be influenced by trophic level. In most wildlife and human samples, the ratio of BDE-47 to BDE-99 is much higher than the ratio of these two congeners in Penta-BDE formulations. The average ratio in biotic sample is generally 3–6, and in commercial products is

≤ 1 (Huwe et al. 2007). One reason for the greater accumulation of BDE-47 relative to BDE-99 in biota tissues is the higher metabolism rate for BDE-99 (Huwe et al. 2008). At least 9.5 of the BDE 99 mass in the gut was debrominated to BDE-47 and assimilated in carp tissues (Stapleton et al. 2004b). The ratio of BEE-47 to other PBDEs was close to BDE-99 and remains constant among tissues indicating that BDE-47 is one of the most readily accumulated PBDEs.

Octa-BDE (BDE-197) and BDE-209 were not detected in this work. As a highly bioavailable congener, BDE-197 has not been included in most reports of PBDEs in biota, but is an apparent byproduct of anaerobic and photolytic (Stapleton et al. 2008) degradation of BDE-209. It was considered to be low bioavailability, only less than 0.5% to be absorbed into biota (Hardy et al. 2002). Therefore, BDE-209 was hard to detect unless there was a certain extent of accumulation level in biota tissues (He et al. 2012). A BDE-209 exposure experiment showed that no net accumulation of BDE 209 in carp tissues was observed (Stapleton et al. 2004c). However, seven apparent debrominated products of BDE 209 accumulated in whole fish and liver tissues over the exposure period. That is to say, debromination occurred in fish tissues may be another reason for no BDE-209 detection. No matter how, these results implied that no significant BDE-209 pollution existed surrounding Lake Chaohu, indicating that the commercial octa- and deca-BDE formulations were not massively manufactured in that area. This situation was quite different from Zhujiang area in Southern China where electronic industry was highly developed. Detection rate of BDE-209 was 45.2% of total fish samples (Guo et al. 2007).

It is obvious that individual PBDEs have different pharmacokinetic properties and should not necessarily be considered as a sum of the total in this context. One reason for different distribution patterns may be the involvement of transport proteins necessitated by different molecular weight of PBDE congeners (Huwe et al. 2008, Chen et al. 2013a). Further investigations are needed to determine what role carrier proteins may play in the uptake, distribution, metabolism, and excretion of PBDEs in aquatic animal systems.

The distribution of different PBDE congener in tissues of four fishes displayed different pattern with the varieties of

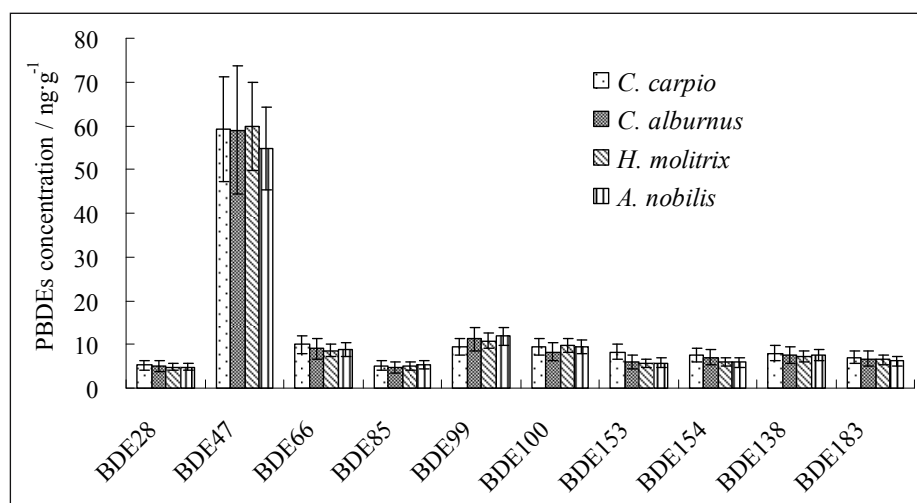


Fig. 4. Mean concentration of ten PBDE congeners of four fishes in Chaohu Lake

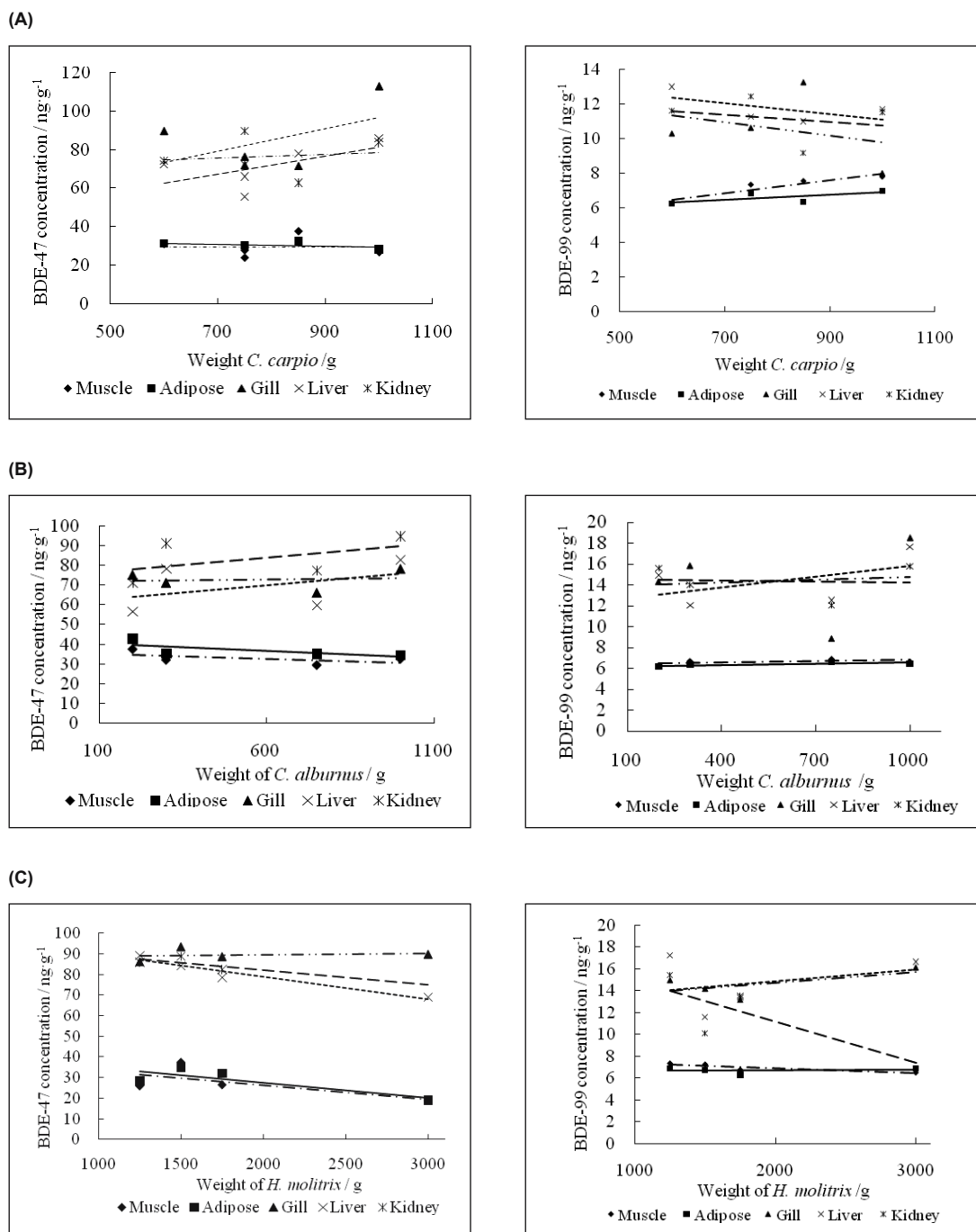


Fig. 5. BDE-47, -99 concentrations in five organs of three fishes with different sizes. Five tissues included muscle, adipose, gill, liver and kidney. (A) Fish size of *Cyprinus carpio* between 600–1000 g. (B) Fish size of *Culter alburnus* between 200–1000 g. (C) Fish size of *Hypophthalmichthys molitrix*

fish size. For example, BDE-47 concentration was constant in adipose tissue, muscle, and kidney, but was slightly positively correlated with fish size increasing in liver and gill of *Cyprinus carpio* (Fig. 5A). Interestingly, BDE-99 concentration was constant in adipose tissue, increased in muscle, and slightly decreased in liver, kidney, and gills. For *Culter alburnus*, BDE-47 concentrations were close to constant in adipose tissue, muscle, and gill, and slightly increased in liver and kidney (Fig. 5B). BDE-99 concentration was slightly increased in liver, and remained stable in other organs with fish size increasing. For *Hypophthalmichthys molitrix*, BDE-47 concentration slightly decreased in adipose tissue, muscle, liver and kidney

and remained stable the gills (Fig. 5C). BDE-99 was constant in muscle and adipose tissue, slightly increased in liver and gills, and significantly decreased in the kidneys with fish size growth. Vives et al (2004) found that the concentrations of most PBDEs in liver were correlated with fish age, this cannot apply to muscles. There is also evidence that the age of fish (Weijjs et al. 2009), ringed seal (Ikonomou et al. 2002) and sparrow hawk (Law et al. 2003) all influence biotransformation and concentration levels of PBDEs. These results almost certainly reflect the increase in the production and industrial usage of PBDEs worldwide. However, Waszak et al. (2012) found that there is no clear positive correlation between the PBDE

concentrations and size or length suggesting that the fluxes of PBDEs are still not constant (Vives et al. 2004). This research showed that it should be treated differently to each congener, especially those typical ones that have higher pollution levels in environmental matrix when the relationship between distribution pattern in tissues and fish size was analyzed. Those discrepancies appeared to be correlated with the PBDEs pollution fluxes varying with the change of the year, varying lipid content, lipid composition, congener-specific physico-chemical properties and their metabolism divergences in fish tissues (Waszak et al. 2012).

Conclusions

41 PBDE congeners were analyzed in sediment and fish from Lake Chaohu in China. Ten of them were detected. BDE-47 concentration was found to be the highest one with 5.17 ng/g in

sediment and 58.47 ng/g in fish. Compared with other regions in the world, the levels of PBDEs in Lake Chaohu appeared to be in moderate position. PBDEs in surface sediment were evenly distributed across the lake. This implied that the source of PBDEs might be air deposition, rather than being water-borne. Tissue distribution patterns of PBDEs in four fish species are similar, BDE-47 > BDE-99 > BDE-100 > BDE-66 > BDE-138 > BDE-183 > BDE-154 > BDE-153. BDE-47/99 ratio was found to be 5.4, which was a traditional value compared with other data detected elsewhere. The concentrations of all PBDE congeners detected in this study were higher in fish gills, livers, and kidneys than those in muscles and adipose tissues. Furthermore, it was found that PBDE congeners in different tissues and organs of the three fish species had some different distribution patterns with fish size growth. Those discrepancies may be correlated with the PBDEs pollution fluxes varying with time and their metabolism divergence in fish tissues.

Acknowledgements

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