Occurrence of additive brominated flame retardants in aquatic organisms from Tai Lake and Yangtze River in Eastern China, 2009–2012

Guanyong Su a, David Saunders b, Yijun Yu a,c, Hongxia Yu a,⇑, Xiaowei Zhang a, Hongling Liu a, John P. Giesy a,b,d,e

a State Key Laboratory of Pollution Control and Resource Reuse & School of the Environment, Nanjing University, Nanjing, China
b Toxicology Centre, University of Saskatchewan, 44 Campus Drive, Saskatoon, SK S7N 5B3, Canada
c Changzhou Environmental Monitoring Center, Changzhou 213001, China
d Department of Veterinary Biomedical Sciences, University of Saskatchewan, Saskatoon, SK S7N 5B3, Canada
e State Key Laboratory in Marine Pollution, Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong Special Administrative Region

ABSTRACT

Since the phase-out of PBDEs, reports regarding occurrences of these compounds in the environment have become less frequent. To characterize potential influences of the phase-out of PBDEs' on concentrations in the environment, trends in concentrations as a function of time were investigated for two additive brominated flame retardants, PBDEs and HBCDs. Three aquatic species, including shrimp, common carp, and yellow catfish, were collected from Meiliang Bay of Tai Lake, 2009–2012. The analysis of PBDEs in three aquatic organisms has shown a downward-trend in the first three years but a significant upward-trend in the final year. Concentrations of HBCDs have not shown temporal increases in the investigated environments. Concentrations of both PBDEs and HBCDs in the three studied organisms increased as a function of trophic level, which suggested that these additive flame retardants can be biomagnified through the food web of Tai Lake. In accordance with previous publications, PBDE-47 contributed the greatest proportion of \( \Sigma \)PBDEs and had a detection frequency of 100%. \( \alpha \)-HBCD was the predominate isomer that contributed to \( \Sigma \)HBCDs rather than \( \beta \)- or \( \gamma \)-HBCD. HBCDs' concentrations in samples of Yangtze River were higher than those of Tai Lake.

Keywords:
PBDEs
HBCDs
Trophic level
Temporal investigation

1. Introduction

Due to their low cost and great performance, brominated flame retardants (BFRs) are widely used in various commercial products, such as furniture, textiles, plastics, paints, and electronic appliances, as a means of reducing their flammability (Lau et al., 2006; Zhou and Zeng, 2006). Three BFRs, polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDs) and tetrabromobisphenol A (TBBPA), account for the greatest proportion of production of BFRs. TBBPA is a reactive BFR, which is chemically bound to commercial products and has a limited capacity to leach
into the environment. However, HBCDs and PBDEs are generally used as non-bound additive BFRs, which are simply incorporated into the product and can gradually leach into the environment during production, usage, and disposal of products. Due to their potential to leach to the environment, additive BFRs have been detected in various environmental media such as wildlife (Hale et al., 2001; de Wit, 2002; Pettersson et al., 2004) and humans (Noren and Meironyte, 2000; Akutsu et al., 2003; Johnson-Restrepo et al., 2005; Bi et al., 2007). Because of the ubiquity of these compounds in various environments and potential for toxic effects, PBDEs and their metabolites had been the subject of numerous studies (Su et al., 2012a,b).

Many toxicological investigations have shown that PBDEs can cause various adverse effects to animals, such as nuclear hormone receptor activity (Meerts et al., 2001; He et al., 2008; Kojima et al., 2009; Wan et al., 2010), neurotoxicity (Schreiber et al., 2010), or reproductive effects (Van den Steen et al., 2009). Due to evidence of toxicity and ubiquity in the environment, in May, 2009, the Stockholm Convention committees for Persistent Organic Pollutants (POPs) listed the penta-BDE and octa-BDE formulations as POPs. In October, 2012, the persistent organic pollutants review committee also adopted a recommendation to include HBCDs in the Convention’s Annex A for elimination. Though two technical formulations of PBDEs have been phased-out of production and these chemicals remain at great concentrations in the environment.

The Yangtze River Delta and Tai Lake, located in East China, are major production centers for chemicals, textiles, and electronics, some of which incorporate large amounts of flame retardants such as PBDEs and HBCDs. The annual production and consumption of PBDEs in this area have led to PBDE contamination of sediments (Chen et al., 2006; Shen et al., 2006) and aquatic biota (Xian et al., 2008). With rapid economic development, new industrial and commercial enterprises have been established along both sides of the river into which both polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDs) have been reported to be released (Xian et al., 2008; Gao et al., 2009; Xu et al., 2009). Little information is available regarding temporal trends of concentrations of PBDEs and HBCDs in this region during post PBDE phase-out. In this study, three aquatic organisms which represent different trophic levels in Tai Lake, were collected from 2009 to 2012 to characterize the temporal-trends of PBDEs and HBCDs’ concentrations. Concentration profiles of PBDEs and HBCDs in Tai Lake and Yangtze River were also compared.

2. Materials and methods

2.1. Sampling

All aquatic samples were collected from Tai Lake (Meiliang Bay) and from Yangtze River (Nanjing). (Fig. 1) Samples of three species, including shrimp (Elminius modestus), common carp (Cyprinus carpio) and yellow catfish (Pelteobagrus fulvidraco), were collected four times during 2009–2012. All samples were selected due to their occurrence, natural history and feeding guild. These three species are particularly suitable as sentinel species, as they tend not to migrate. For comparison, samples of three species of aquatic organisms, including the common carp, the yellow catfish and the bigmouth grenadier anchovy (Coilia macragnosthos Bleeker), were collected from the Yangtze River in 2011. Samples were frozen on site, transported to the laboratory, and were stored at –20 °C until instrumental analysis. Details regarding the aquatic organisms are provided in Supporting Information (Table S1).

2.2. Chemicals and reagents

The thirteen PBDE congeners (PBDE-17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190), C\textsubscript{13}-labeled PBDE-139 and C\textsubscript{13}-labeled PCB-178 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The three HBCDs isomers (\(\alpha\)-HBCD, \(\beta\)-HBCD, \(\gamma\)-HBCD) and the C\textsubscript{13}-labeled \(\alpha\)-HBCD were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Solvent reagents for PBDEs and HBCDs analysis were pesticide residue grade and purchased from Tedia and Merck.

2.3. Identification and quantification of PBDEs and HBCDs

After measuring the length and weight of individual fish, the entire fish (at least 3 individuals) was lyophilized and homogenized...
into one pool and stored frozen until prepared for extraction. Three replicates from each pool were analyzed.

Concentrations of individual PBDEs were determined by use of organic solvent extraction, followed by gas chromatography and mass spectrometry (GC/MS/MS). Approximately 2.0 g of dry fish sample, to which surrogate standard-\(^{13}\)C-PBDE-139 was added, was extracted by accelerated solvent extraction (ASE, Dionex ASE-350, Sunnyvale, CA, USA). Extractions were conducted with n-hexane/dichloromethane (DCM) (1:1) as the first extraction solvent at a temperature of 100 °C and pressure of 1500 psi. Two 10 min. cycles were performed for each solvent. The extract was concentrated by rotary evaporation to 10 mL, and 2 mL of extract was taken for gravimetric lipid content determination. The remaining 8 mL of extract was acidified with 10 mL of H\(_2\)SO\(_4\) to remove lipids. PBDEs were back extracted with a total of 30 mL of dichloromethane and hexane (V:V = 1:1) in 3 separate 10 mL extractions.

The organic solvent containing PBDEs was concentrated and passed through a silica gel column for further clean up. The silica gel column was packed with glass-coated, activated silica gel (0.25 g, 44% (w/w) acid silica gel (1.0 g), silica gel (0.25 g), and anhydrous sodium sulfate (0.30 g) from bottom to top in a disposable Pasteur pipette (Su et al., 2010). The fraction containing PBDEs and MeO-PBDEs was eluted with 15 mL of hexane followed by 15 mL of n-hexane/dichloromethane (1:1). The elution was concentrated by rotary evaporation and further concentrated to near dryness under a gentle stream of nitrogen. Then, 9.6 ng of \(^{13}\)C-PCB-178 was added as the internal injection standard and was re-solubilized with 100 μL hexane prior to GC/MS/MS analysis.

Concentrations of individual HBCDs were determined by use of organic solvent extraction, followed by gas chromatography and mass spectrometry (HPLC/MS/MS). Approximately 2.0 g of dry sample, to which surrogate standard \(^{13}\)C-\(^{15}\)N-HBCD (Wellington Laboratories, Canada) was added, was Soxhlet extracted with a mixture of acetone and hexane (V:V = 1:1) for 15 h. The extract was concentrated by rotary evaporation and lipid content was determined gravimetrically. The extract was dissolved in hexane and acidified with 20 mL of H\(_2\)SO\(_4\) to remove lipids. HBCDs was back extracted with a total of 150 mL of hexane in 3 separate 50 mL extractions. The organic solvent containing HBCDs was concentrated to 1 mL approximately and passed through a silica gel column for further clean up. The silica gel column was packed with glass-coated, anhydrous sodium sulfate (1 g), silica gel (2 g), 33% (w/w) acid silica gel (1.0 g), 16.5% silica gel (8 g) and anhydrous sodium sulfate (1 g) from bottom to top in a disposable Pasteur pipette. The fraction containing HBCDs was eluted with 100 mL of a mixture of hexane and dichloromethane (1:1). The eluate was concentrated by rotary evaporation and further concentrated to near dryness under a gentle stream of nitrogen and was re-solubilized with 100 μL methanol prior to HPLC/MS/MS analysis.

### 2.4. Instrumental Analysis

Concentrations of 13 PBDEs were determined by use of a Thermo Scientific TSQ Quantum GC (USA), coupled with an Agilent DB-XLB column (15 m × 0.25 mm × 0.25 μm, USA). The mass spectrometric detector was operated in electron impact ionization (EI) mode. Samples and standards were analyzed in selected reaction mode (SRM). Quantification and qualification were processed by SRM modes. The precursor ion and product ions selected in SRM mode for each chemical were based on the mass spectrum of the standard solution. Detailed information about precursor ion, product ions, ratios, and collision energy are given in Supporting Information (Table S2).

Concentrations of HBCDs were determined by use of an Agilent 1200 series HPLC system (Agilent, USA), coupled with an API 3000 triple quadrupole MS/MS system (PE Sciex, Concord, ON, Canada). Both the LC and mass spectrometer were controlled by AB Sciex Analyst 1.4.1 software (Applied Bioscience, Foster City, CA, USA). An Agilent Eclipse XDB-C18 column was used for chromatographic separation. Separations were conducted at room temperature. The volume injected onto the column was 20 μL. Methanol was selected as the mobile phase at a flow rate of 0.25 mL min\(^{-1}\). HBCDs were detected using a turbo ion spray ion source operated in the negative ion, multiple-reaction monitoring (MRM) mode. The ion source and instrumental parameters were optimized prior to analysis by infusing HBCDs isomers at a concentration of 1 mg L\(^{-1}\) into the mass spectrometer. Parameter specific settings were as follows: DP (−30 V), FP (−130 V), EP (−7 V), Focusing lens (9) and Prefilter (20). Transitions selected for HBCDs and \(^{13}\)C-\(^{15}\)N-HBCD are \(m/z\) 640.8–78.9 and 653.0–78.9 (collision energy −50 ev), respectively.

### 2.5. Quality assurance/quality control

QA/QC was conducted by performing laboratory blanks, GC/MS detection limit (based on 35/N) and standard spiked recoveries. One procedural blank was run with every batch of 6–10 samples to assess potential sample contamination. Concentrations of target analytes in laboratory blanks were less than 5% of the sample minimum concentration, which demonstrated that samples were free from contamination. The limit of detection (LOD) was defined as the concentration that resulted in a signal-to-noise ratio of 3. LOD based on 2.0 g of dry sample and instrument sensitivity, varied from congener to congener, from 5.3 to 21.3 pg g\(^{-1}\) dry wt. Concentrations less than the LOD were assumed to be non-detects in calculating summary statistics. Prior to sample analysis, matrix spikes (n = 4) had been evaluated for each target compound. Recoveries of matrix spike tests ranged from 71.2 to 128.2% for each congener of PBDEs and HBCDs. To ensure accuracy of analytical procedures, \(^{13}\)C-labeled PBDE-139 and \(^{13}\)C-labeled \(^{15}\)N-HBCD were used as internal standards for PBDEs and HBCDs, respectively. And the concentration of PBDEs and HBCDs was adjusted according to the recoveries of the \(^{13}\)C-labeled congeners internal standard.

### 2.6. Nitrogen isotope measurements

The stable nitrogen isotope ratio in muscle tissue from freshwater fish samples was measured by use of the procedure described by Sun et al. (1999). Measurements of stable nitrogen isotopes were used to identify the relative trophic levels of organisms in the environment. The isotopic ratio was standardized to air according to Eq. (1).

\[
\delta^{15}\text{N}_{\text{air}} = \frac{\left[\text{^{15}\text{N}}/\text{^{14}\text{N}}\right]_{\text{sample}} - \left[\text{^{15}\text{N}}/\text{^{14}\text{N}}\right]_{\text{air}}}{\left[\text{^{15}\text{N}}/\text{^{14}\text{N}}\right]_{\text{air}}} \times 1000 \tag{1}
\]

### 2.7. Statistical analysis

Statistical analysis was performed with the OriginPro 8. Spearman rank correlation was used to examine the relationships of \(\Sigma\)PBDEs and \(\Sigma\)HBCDs’ concentrations. A Mann–Whitney U non-parametric test was used to compare concentration differences of target compounds between/among groups (year to year, species to species). It was considered statistically significant when \(p < 0.05\).

### 3. Results

#### 3.1. Nitrogen isotope analysis

Organisms at higher trophic levels generally accumulate greater amounts of \(^{15}\)N. The \(\delta^{15}\text{N}_{\text{air}} = 3 ± 1\%_c\) was used to discriminate the different trophic levels. To characterize the relative trophic posi-
Concentrations of PBDEs in aquatic organisms from the Tai Lake, China. Inter-species comparison of the three organisms showed concentrations of lipid and 28.1 ng g⁻¹ lipid for the common carp (13.93 ng g⁻¹ lipid). For all samples from Tai Lake, concentrations of PBDEs ranged from 1.13 to 97.59 ng g⁻¹ lipid with mean and median values of 23.09 ng g⁻¹ lipid and 16.48 ng g⁻¹ lipid. The greatest concentration of PBDEs was detected in the yellow catfish sampled in 2009 (mean: 97.59 ng g⁻¹ lipid). Thirty more brominated PBDEs including PBDE-138, PBDE-183 and PBDE-190, were detected in any sample from both locations. Detection frequencies of the 10 detected PBDEs were as follows: PBDE-17 (83%), PBDE-28 (92%), PBDE-71 (75%), PBDE-47 (100%), PBDE-66 (8%), PBDE-85 (8%), PBDE-154 (92%) and PBDE-153 (58%). For all samples from Tai Lake, concentrations of PBDEs ranged from 1.13 to 97.59 ng g⁻¹ lipid with mean and median values of 23.09 ng g⁻¹ lipid and 16.48 ng g⁻¹ lipid. The greatest concentration of PBDEs was detected in the yellow catfish sampled in 2012 (mean: 97.59 ng g⁻¹ lipid). Concentrations of PBDEs in yellow catfish ranged from 29.35 to 97.59 ng g⁻¹ lipid with a mean value of 41.79 ng g⁻¹ lipid, which was greater than that in the common carp (13.93 ng g⁻¹ lipid) and shrimp (11.27 ng g⁻¹ lipid).

3.2. Concentrations of PBDEs

In the present study, 10 of 13 targeted PBDEs were detected in the aquatic organisms from Tai Lake. (Table 1) Three more brominated PBDEs including, PBDE-138, PBDE-183 and PBDE-190, were not detected in these aquatic organisms. Frequencies of detection of the 10 detected PBDEs were as follows: PBDE-17 (83%), PBDE-28 (92%), PBDE-71 (75%), PBDE-47 (100%), PBDE-66 (8%), PBDE-85 (8%), PBDE-154 (92%) and PBDE-153 (58%). For all samples from Tai Lake, concentrations of PBDEs ranged from 1.13 to 97.59 ng g⁻¹ lipid with mean and median values of 23.09 ng g⁻¹ lipid and 16.48 ng g⁻¹ lipid. The greatest concentration of PBDEs was detected in the yellow catfish sampled in 2009 (mean: 97.59 ng g⁻¹ lipid). Three more brominated PBDEs including, PBDE-138, PBDE-183 and PBDE-190, were detected in any sample from both locations. Detection frequencies of the 10 detected PBDEs were as follows: PBDE-17 (83%), PBDE-28 (92%), PBDE-71 (75%), PBDE-47 (100%), PBDE-66 (8%), PBDE-85 (8%), PBDE-154 (92%) and PBDE-153 (58%). For all samples from Tai Lake, concentrations of PBDEs ranged from 1.13 to 97.59 ng g⁻¹ lipid with mean and median values of 23.09 ng g⁻¹ lipid and 16.48 ng g⁻¹ lipid. The greatest concentration of PBDEs was detected in the yellow catfish sampled in 2009 (mean: 97.59 ng g⁻¹ lipid). Thirty more brominated PBDEs including, PBDE-138, PBDE-183 and PBDE-190, were detected in any sample from both locations. Detection frequencies of the 10 detected PBDEs were as follows: PBDE-17 (83%), PBDE-28 (92%), PBDE-71 (75%), PBDE-47 (100%), PBDE-66 (8%), PBDE-85 (8%), PBDE-154 (92%) and PBDE-153 (58%). For all samples from Tai Lake, concentrations of PBDEs ranged from 1.13 to 97.59 ng g⁻¹ lipid with mean and median values of 23.09 ng g⁻¹ lipid and 16.48 ng g⁻¹ lipid. The greatest concentration of PBDEs was detected in the yellow catfish sampled in 2009 (mean: 97.59 ng g⁻¹ lipid). The decrease in concentrations of the PBDE-47 congener. Similar decreasing trends in blood of newborns has been observed from 1997 to 2011 in New York state (Ma et al., 2013). In May, 2009, the commercial penta-BDE and octa-BDE formulations were listed as POPs and banned worldwide. The ban of two technical formulations of PBDEs might have a strong impact on the environmental concentrations of PBDEs and their potential substitute compounds (Covaci et al., 2006), such as HBCDs. Here, the analysis of PBDEs in three aquatic organisms collected from Tai Lake and the Yangtze River from 2009 to 2012, has shown a downward-trend in the first three years but a significant upward-trend in the final year (Fig. 2). Specifically, concentrations of PBDEs in aquatic organisms have been compared with those reported in previous publications at Tai Lake and the Yangtze River sampling sites (Gao et al., 2009). Due to the disposal of waste containing PBDEs and the persistence of these compounds, it can be inferred that they would continue to exist at high concentrations in the environment surrounding Tai Lake and the Yangtze River. Only slight temporal variations in concentrations of HBCDs have been observed from 2009 to 2012, which indicates that concentrations of HBCDs in the environment have not been influenced by the phase-out of PBDEs (Fig. 3).

4. Discussion

In a time-trend study from Sweden from the early 1970s to 1997, concentrations of PBDEs in human milk significantly increased (Meirionty et al., 1999), while decreases have been observed for samples since 1996 (Lind et al., 2003). The decrease of concentrations of PBDEs was mainly due to the reduction in concentrations of the PBDE-47 congener. Similar decreasing temporal trends in blood of newborns has been observed from 1997 to 2011 in New York state (Ma et al., 2013). In May, 2009, the commercial penta-BDE and octa-BDE formulations were listed as POPs and banned worldwide. The ban of two technical formulations of PBDEs might have a strong impact on the environmental concentrations of PBDEs and their potential substitute compounds (Covaci et al., 2006), such as HBCDs. Here, the analysis of PBDEs in three aquatic organisms collected from Tai Lake and the Yangtze River from 2009 to 2012, has shown a downward-trend in the first three years but a significant upward-trend in the final year (Fig. 2). Specifically, concentrations of PBDEs in aquatic organisms have been compared with those reported in previous publications at Tai Lake and the Yangtze River sampling sites (Gao et al., 2009). Due to the disposal of waste containing PBDEs and the persistence of these compounds, it can be inferred that they would continue to exist at high concentrations in the environment surrounding Tai Lake and the Yangtze River. Only slight temporal variations in concentrations of HBCDs have been observed from 2009 to 2012, which indicates that concentrations of HBCDs in the environment have not been influenced by the phase-out of PBDEs (Fig. 3).

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Biomagnification of PBDEs and HBCDs has been reported at significant levels through various freshwater food webs (Wu et al., 2009), which indicates that concentrations of these chemicals will increase with increasing trophic level. A similar trend was observed here. Based on the δ^{15}N content analysis in this investigation, the three aquatic organisms occupy different trophic levels in their respective food webs. Evidence of bioaccumulation of PBDEs and HBCDs in a freshwater food web in Tai Lake have been observed: shrimp (PBDEs: 11.27 ng g^{-1}; HBCDs: 71.6 ng g^{-1}; δ^{15}N: 17.18‰) < common carp (PBDEs: 13.93 ng g^{-1}; HBCDs: 19.85 ng g^{-1}; δ^{15}N: 20.16‰) < and the yellow catfish (PBDEs: 41.79 ng g^{-1}; HBCDs: 71.6 ng g^{-1}; δ^{15}N: 21.97‰).

Concentrations of ∑PBDEs in aquatic organisms from the Tai Lake were generally less than those in biota from other countries (Darnerud, 2003; Kiviranta et al., 2004; Schecter et al., 2004, 2006), but equal to those concentrations found in other locations in China (Meng et al., 2007; Gao et al., 2009). Fish from Tai Lake had concentrations of PBDEs which ranged from 0.87 to 195.17 ng g^{-1} lipid, which were lesser than concentrations in fish from the USA (1100 pg PBDE g^{-1} ww) (Schecter et al., 2004, 2006), Spain (330 pg ∑PBDE g^{-1} ww) (Bocio et al., 2003), Sweden (630 pg ∑PBDE g^{-1} ww) (Darnerud et al., 2006), Finland (850 pg ∑PBDE g^{-1} ww) (Kiviranta et al., 2004) and Japan (910 pg ∑PBDE g^{-1}) (Ohta et al., 2002). Mean concentrations of ∑PBDEs in fish were similar to those detected in fish from Guangdong, South China (160 pg ∑PBDE g^{-1} ww) (Meng et al., 2007; Gao et al., 2009). Similarly, concentrations of PBDEs in shrimp from Tai Lake were lesser than those from other countries, such as the Netherlands (1765–2962 ng g^{-1} lipid) (Verslycke et al., 2005), Belgium (ND-8.3 ng g^{-1} ww) (Voorspoels et al., 2003) and Canada (48 pg g^{-1} ww) (Tittlemier et al., 2004). Concentrations of PBDEs in shrimp were similar to those from other locations in China (Gao et al., 2009). Concentrations of ∑HBCDs in fish from the Yangtze River ranged from 169.6 to 316.5 ng g^{-1} lipid, which were significantly greater than those (ND-92.1 ng g^{-1} lipid) from Tai Lake. Previous investigations have also shown that concentrations of ∑HBCDs in the Yangtze River were similar or greater than those from other countries, but were generally lower than concentrations detected at contaminated sites or downstream of point sources (Covaci et al., 2006). The high concentrations of HBCDs detected in the Yangtze River are in accordance with several previous publications (Xian et al., 2008; Li et al., 2013), however, the ultimate source of HBCDs is still unknown. In this investigation, concentrations of PBDEs and HBCDs were positively correlated, indicating a similar property between these two chemicals (Pearson corrections; r^2 = 0.57; p = 0.05).

Similar to previous publications, PBDE-47 contributed the greatest proportion to ∑PBDEs and had a detection frequency up to 91.4%.
to 100%. In this analysis, PBDE-17, PBDE-28, PBDE-71 and PBDE-154 were also predominant congeners contributing to $\Sigma$PBDEs, which is consistent with results of previous investigations. PBDE-138, PBDE-183 and PBDE-190, were not detected in any aquatic organism, which might indicate that PBDEs congeners with greater degrees of bromination were not readily accumulated by aquatic organisms. The deficit of heavier PBDE congeners in this analysis might be related to the source profile or their limited aqueous solubilities. In this research, the $\alpha$-HBCD isomer was detected at the greatest concentrations and frequencies in aquatic organisms, which corresponds with previous publications (Isobe et al., 2007; Xian et al., 2008). However, the stereochemical analysis of commercial HBCD mixtures has shown that the content of $\alpha$-HBCD, $\beta$-HBCD and $\gamma$-HBCD was 10–13%, 1–12% and 75–89%, respectively (Heeb et al., 2005). Though the $\gamma$-HBCD isomer comprises the greatest proportion of the HBCDs commercial mixture, the isomer is known to undergo rapid hepatic biotransformations to other diasteroomers and metabolites, and fecal/urinary elimination (Halk et al., 2012). In contrast, the $\alpha$-HBCD isomer is more biologically persistent, resistant to metabolism, to have a longer biological half-life of up to 21 d and bioaccumulates in lipid-rich tissues (Szano et al., 2011).

5. Conclusions

Since the phase-out of PBDEs in 2009, two additive brominated flame retardants (PBDEs and HBCDs) were determined in three aquatic species (shrimp, common carp, and yellow catfish). Concentrations of PBDEs were decreasing during the first three years, but then increased during the last year. This investigation has shown that both PBDEs and HBCDs were bioaccumulated in a freshwater food web in Tai Lake. Aquatic species from Yangtze River were contaminated by HBCDs more heavily than those from Tai Lake. Despite the phase-out of penta-BDEs, PBDE-47 still contributed the greatest proportion to $\Sigma$PBDEs. Isomer specific determination of hexabromocyclododecanes (HBCDs) in small cetaceans from the China Sea South–Level and temporal variation. Mar. Pollut. Bull. 54, 1139–1145.


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Guanyong Su¹; David Saunders²; Yijun Yu¹,³; Hongxia Yu¹*; Xiaowei Zhang¹; Hongling Liu¹; John P. Giesy¹,²,⁴,⁵

¹State Key Laboratory of Pollution Control and Resource Reuse & School of the Environment, Nanjing University, Nanjing, China
²Toxicology Centre, University of Saskatchewan, 44 Campus Drive, Saskatoon, SK, Canada, S7N 5B3
³Changzhou Environmental Monitoring Center, Changzhou, 213001, China
⁴Department of Veterinary Biomedical Sciences, University of Saskatchewan, Saskatoon, SK, Canada S7N 5B3
⁵State Key Laboratory in Marine Pollution, Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong SAR, China

Authors for correspondence:
School of the Environment
Nanjing University
Nanjing, 210089, China
Tel: 86-25-83593649
Fax: 86-25-83707304
E-mail: yuhx@nju.edu.cn (Hongxia Yu)
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<th>Common name</th>
<th>Latin name</th>
<th>Number</th>
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<td>13-19 cm</td>
<td>81.9-115.4 g</td>
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<td>3</td>
<td>14-18 cm</td>
<td>23.3-84.1 g</td>
</tr>
<tr>
<td></td>
<td>2012.07</td>
<td>the yellow catfish</td>
<td><em>Pelteobagrus fulvidraco</em></td>
<td>9</td>
<td>7-22 cm</td>
<td>22.2-131.4 g</td>
</tr>
<tr>
<td>Yangtze River (2011)</td>
<td>2011.07</td>
<td>the common carp</td>
<td><em>Cyprinus carpio</em></td>
<td>3</td>
<td>26-33 cm</td>
<td>420.7-885.3 g</td>
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<tr>
<td></td>
<td></td>
<td>the yellow catfish</td>
<td><em>Pelteobagrus fulvidraco</em></td>
<td>32</td>
<td>10.0-14.0</td>
<td>11.7-32.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>the bigmouth grenadier anchovy</td>
<td><em>Coilia macrognathos</em></td>
<td>9</td>
<td>20.0-26.0</td>
<td>30.0-65.8 g</td>
</tr>
</tbody>
</table>

a. For each species, at least 3 individuals were pooled together and run for the instrumental analysis in three replicates.
b. Due to the shrimps’ small size, the number of shrimp was not counted by us.
<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Ion pairs for Quantification and Qualification</th>
<th>Abundance Ratio</th>
<th>Collision Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDE-17</td>
<td>245.88, 138.85</td>
<td>100/30</td>
<td>20</td>
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<tr>
<td>PBDE-28</td>
<td>245.88, 138.86</td>
<td>100/12</td>
<td>20</td>
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<tr>
<td>PBDE-71</td>
<td>216.79, 218.94</td>
<td>92/100</td>
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<td>PBDE-47</td>
<td>216.79, 218.95</td>
<td>61/100</td>
<td>30</td>
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<td>PBDE-66</td>
<td>216.79, 218.96</td>
<td>100/93</td>
<td>30</td>
</tr>
<tr>
<td>PBDE-100</td>
<td>296.60, 405.63</td>
<td>100/44</td>
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<td>PBDE-99</td>
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<td>PBDE-85</td>
<td>296.60, 405.65</td>
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<td>PBDE-154</td>
<td>483.64, 402.57</td>
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<td>483.64, 402.59</td>
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<td>PBDE-183</td>
<td>563.73, 485.15</td>
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<tr>
<td>PBDE-190</td>
<td>563.73, 485.15</td>
<td>5/100</td>
<td>30</td>
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