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

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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