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Occurrence and bioaccumulation of polybrominated diphenyl ethers in sediments and paddy ecosystems of Liaohe River Basin, northeast China

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ABSTRACT

Concentrations of 16 polybrominated diphenyl ether (PBDE) congeners were measured in river sediments, paddy soils and three species of paddy-field organisms (crab, loach and carp) collected from the Liaohe River Basin, northeastern China. The total contents of PBDEs ($\sum_{16}$PBDEs) in sediments and paddy soils were in the ranges of 273.4–3246.3 pg/g dry weight (dw), and 192.1–1783.8 pg/g dw, respectively. BDE 209 was the dominant congener both in sediments and paddy soils. The concentrations of $\sum_{16}$PBDEs in sediments were significantly higher than those in the adjacent paddy soils, indicating a potential transport of PBDEs from river to paddy ecosystems via river water irrigation. The biota–soil accumulation factor (BSAF) was calculated as the ratio between the lipid-normalized concentration in paddy-field organisms and the total organic carbon-normalized concentration in paddy soil. The average BSAF values of $\sum_{15}$PBDEs followed the sequence of crab (3.6) > loach (3.3) > carp (2.1). BDE 154 had the highest BSAF value, and a parabolic trend between BSAF values of individual PBDE congeners and their logK_{OW} values was observed. In view of the fact that crab had the larger BSAF value and higher lipid content, the ecological risk and health risk for crab cultivation in paddy fields should be of particular concern.

Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used in petroleum, textiles, plastic products, construction materials, transportation equipment and electronic products (Hale et al., 2002; de Wit, 2002). As one type of non-reactive flame retardant additive, PBDEs could be easily released to the environment from their production, application and processing (Voorspoels et al., 2003). Therefore, they have been frequently detected in a variety of environmental matrices (de Wit et al., 2010; Robin et al., 2014). Because of their environmental persistence (de Wit, 2002), long-range atmospheric transport (Goutte et al., 2013), high potential of bioaccumulation (Kelly et al., 2007) and potential adverse effect on the ecosystem and humans (Labunska et al., 2014), commercial penta- and octa-PBDEs were designated as new persistent organic pollutants (POPs) at the fourth meeting of the Conference of the Parties of the Stockholm Convention in May 2009 (UNEP, 2009).

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China is one of the largest producers and consumers of PBDEs in the world, and correspondingly contamination by PBDEs in Chinese environments has received widespread attention (Mai et al., 2005). Since 2000, extensive investigations on the occurrence and distribution of PBDEs in river ecosystems and adjacent seas have been conducted in South and East China (Luo et al., 2007; Wu et al., 2012; Chen et al., 2013). The heaviest PBDE pollution has been found in the Pearl River Delta and several e-waste recycling areas (Xiang et al., 2007; Zou et al., 2007; Wu et al., 2008; Labunska et al., 2014). The average concentrations of PBDEs in sediments from different rivers of the Pearl River Delta were reported to be in the range of 17.1–588 ng/g dry weight (dw) (Chen et al., 2013). Meanwhile, it was found that the mean concentration of PBDEs in the sediments of a river flowing through Guiyu town (Guangdong Province), a typical e-waste recycling area, had surprisingly reached up to 9400 ng/g dw (Luo et al., 2007).

The Liaohe River, which includes the Daliao, Taizi and Hun rivers, is one of the most heavily polluted rivers in China. The tributaries Taizi and Hun rivers flow into the Daliao River at their confluence, before finally entering the Bohai Sea. Since the 1950s, the Liaohe River Basin has been the largest industrial region in northeastern China, with metallurgy, machinery, petrochemical, and building material industries. Meanwhile, there are more than one million acres of irrigated paddy fields in this plain, and the commercial cultivation of river mitten-handed crab and loach in these paddy fields has a long history. Before 2000, most industrial wastewater was directly discharged into the rivers without effective treatment. Previous studies have indicated the ubiquitous occurrence of PBDEs in the sediments of the Daliao River mouth and its adjacent sea, as well as significant bioaccumulation of PBDEs in the marine food web (Zhao et al., 2011a, 2011b; Ma et al., 2013). However, information on the pollution status of PBDEs in the entire Liaohe River Basin is still unavailable, limiting the evaluation of their ecological risks.

The primary objectives of the present study were to investigate the residual levels, spatial distribution and congener profiles of PBDEs in sediments and paddy soils of the Liaohe River Base, and to examine their accumulation in aquatic organisms (crab, loach and carp) of paddy ecosystems. The site-specific bio-soil accumulation factor (BSAF) was also determined to evaluate the bioaccumulation of aquatic organisms in the paddy ecosystem. The obtained results will be of particular value for assessing the ecological risk and human health risk of PBDEs in this typical traditional industrial base.

1. Material and methods

1.1. Sampling sites and sample collection

Twenty-two sediment samples and 14 paddy soil samples were collected from the Liaohe River Basin in June 2010. To investigate the mutual influence between the sediments and soils, the soil samples collected were located close to the corresponding sediment samples (site-specific). The distribution and detailed location information for the sampling sites are shown in Appendix A Fig. S1. Surface sediments of 0–10 cm were sampled using a grab sampler, and paddy soils of the plow layer (0–20 cm) were sampled using a stainless steel scoop. Five subsamples were taken from each site, and then mixed together to form one composite sample for each sampling site. Three species of aquatic organisms including 6 crab (*Eriocheir sinensis*, ES) samples, 3 loach (*Paramisgurnus dabryanus*, PD) samples, and 5 carp (*Carassius aumtus*, CA) samples, were collected from the paddy fields by a simple net bag. All collected samples were put into pre-cleaned self-sealing aluminum/polyethylene bags with zip closures, and transported on ice to the laboratory and freeze-dried immediately. The soft parts of biological samples were dissected after checking the weight. The crab samples included meat, embryo, and muscle tissues (in chelae and walking legs). The loach and carp samples consisted of flesh (musculature) and internal organs. The lyophilized samples were ground, homogenized, and stored in pre-cleaned brown glass bottles at −20°C for further analysis.

1.2. Chemical reagents and PBDE analysis

A standard mixture containing 15 PBDE congeners (IUPAC No. BDEs 10, 15, 28, 47, 49, 66, 71, 85, 99, 100, 118, 119, 153, 154 and 183) and a single standard (BDE-209) were purchased from AccuStandards (New Haven, CT, USA). Nine kinds of ^{13}C-labeled surrogate standards (BDEs 3, 15, 28, 47, 99, 138, 153, 154 and 183) and one kind of ^{13}C-labeled internal standard (68A–IS, ^{13}C-PCB-138) were purchased from Wellington Laboratories Inc. (Ontario, Canada). Hexane, dichloromethane, acetone and nonane were pesticide grade and purchased from Fisher Scientific (J.T. Baker, USA). Sodium sulfate and silica gel (100–200 mesh size) were analytical grade and purchased from Beijing Chemical Reagent Company (Beijing, China) and Merck Co. (Germany), respectively.

About 15 g of sediment/soil and 5 g of organism sample were extracted by a mixture of dichloromethane (DCM) and hexane (V:V = 1:1) using Accelerated Solvent Extraction (ASE350, Dionex, USA). About 5.0 g of activated copper powder was used to remove elemental sulfur in the sediment extract, and 30.0 g of acid silica gel was added to remove lipids in the organism extract. Then the concentrated extracts were further cleaned with multilayer silica columns (10 mm I.D.) and filled from bottom up with activated silica gel (1 g), basic silica gel (4 g), activated silica gel (1 g), acidic silica gel (8 g), activated silica gel (1 g), and $AgNO_3$ silica gel (2 g). A short DB-5HT capillary (15 m × 0.25 mm × 0.10 μm film thickness; J&W Scientific, USA) was used for the separation of mono- to octal-BDE congeners with a programmed temperature. The target compounds were determined by a Trace GC Ultra gas chromatograph (Thermo, USA) coupled with a Trace DSQ II mass spectrometer (Thermo, USA) in electron capture negative ionization (ECNI) mode. Samples were injected in splitless mode, and all data were obtained in the selected ion monitoring (SIM) mode using $^{13}C_{12}$ isotope dilution analysis for qualitative and quantitative analysis.

1.3. QA/QC

Strict quality controls were implemented to ensure the correct identification and accurate quantification of the