



Hexabromocyclododecanes in surface sediments and a sediment core from Rivers and Harbor in the northern Chinese city of Tianjin

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HIGHLIGHTS

- ▶ This is the first time to systematically report HBCDs in sediments from China.
- ▶ This is one of the few studies that report HBCDs in a sediment core in the world.
- ▶ The highest concentration of total HBCDs in sediment was found in Southeast Asia.
- ▶ Both diastereomer- and enantiomer-profiles of HBCDs in sediments were reported.

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ABSTRACT

In the present study, hexabromocyclododecanes (HBCDs) were investigated in the sediment from Haihe River (HR), Dagu Dainage Canal (DDC) and Tianjin Harbor (TH) at Bohai Bay using a total of 51 samples of surface sediments and a sediment core collected from May to September in 2010, and its diastereomer- and enantiomer-specific profiles were analyzed. The concentration of total HBCDs were generally high, with mean value and ranges of 31.0 and 1.35–634 ng g⁻¹ dw, respectively. The contamination followed the order of TH > DDC > HR. Higher levels (up to 634 ng g⁻¹ dw) occurred in the lower reach of HR and DDC located in an industrial area of Tianjin. This is the first time to report so high concentration of HBCDs in sediment in Southeast Asia. The γ -diastereomer dominated in most samples (44 out of 51), and this is in agreement with the diastereomer distribution pattern in industrial products, while α -HBCD was the dominant diastereomer in the other seven samples. However, only few samples exhibited γ -diastereomer ratio similar to that (75–89%) in technical products, indicating the inter-transformation and variable degradation of the different isomers. The high ratio of γ -diastereomer could be used as an indicator for fresh contamination input. Enantiomeric factors (EFs) of HBCD isomers in most of the samples were statistically different from technical products ($p < 0.05$), showing a trend of more easily enrichment of the (–)-HBCD-enantiomer compared to the (+)-HBCD-enantiomer. The δ - and ε -diastereomers were frequently detected but at low level. The HBCDs in the sediment core showed several peaks, and the greatest value occurred in 2005, when a plastic manufacture plant using HBCD was set up nearby.

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1. Introduction

Hexabromocyclododecanes (HBCDs), one of additive brominated flame retardants (BFRs), have been extensively applied in plastic materials, textiles and electronics (Remberger et al., 2004; Minh et al., 2007). In 2006, the world market demand for HBCDs was 20000 tons (Zhang et al., 2008), while 3900 metric tons were sold in Asia (Remberger et al., 2004). HBCDs can enter aquatic systems through atmospheric deposition, direct discharges from wastewater treatment plants or land runoff. Recently, HBCDs have

been detected widely in environmental and biota samples (Abdallah and Harrad, 2011; Hu et al., 2011; Meng et al., 2011).

Evidences have been found to support HBCDs' classification as a Persistent, Bioaccumulative and Toxic (PBT) substance and a substance prone to long-range environmental transportation. HBCDs can be metabolized in biotic media due to weakness of carbon-bromine bond, but they exhibit high persistence in abiotic media (Tomy et al., 2010). HBCDs are highly hydrophobic compounds, with $\log K_{ow}$ over 5 being reported or calculated (Davis et al., 2006), and hence HBCDs are easily bioaccumulated with reported $\log BCF = 4$ (Zhao et al., 2010). Toxicology studies reveal that HBCDs have several toxicological endpoints on tested organisms, such as cytotoxicity, neutotoxicity, and genotoxicity (Tomy et al., 2010). Moreover, because of long-range transportation property,

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HBCDs were detected in codfish liver from Norway (Koppen et al., 2010), and in Arctic food web (Tomy et al., 2008). Thus, the use of HBCDs has been increasingly restricted by many countries and organizations. It has been proposed to add HBCDs into the list of persistent organic pollutants (POPs) under the Stockholm Convention, and its risk profile is being evaluated since August, 2010, the US EPA has added HBCDs to the list of Chemicals of Concern (EPA, 2010).

Aquatic sediments act as a sink and reservoir through binding organic pollutants, especially those hydrophobic organic contaminants (HOCs) to the organic moiety in sediments and have great impact on distribution, transport, and fate of HOCs. The bound HOCs in sediment have reduced mobility, bioavailability, and hence less risk; and the degradation rates are also slowed down due to the lowered bioaccessibility. However, aquatic food webs also can be impacted by the contaminants in sediments through uptake of sediment particles by dwelling organisms in sediments (Ilyas et al., 2011). Many studies about sediment contamination by BFRs have been carried out worldwide (Ilyas et al., 2011). The concentration of HBCDs in sediments from Europe (up to 2660 ng g⁻¹, Spain; up to 950 ng g⁻¹, Belgium) were higher than that from America (up to 3.7 ng g⁻¹) and Korea (up to 59 ng g⁻¹) (Table SM-6), which is valuable for the evaluation on risk of HBCDs in different regions.

There are possible 16 stereoisomers of HBCDs (Fig. SM-1 in Supplemented Material (SM)). Six stereoisomers of HBCDs ((-) α , (+) α , (-) β , (+) β , (-) γ , (+) γ) account for nearly 100% of HBCDs in environmental matrix (Heeb et al., 2007), and hence they are the target HBCDs of environmental concern. The HBCDs exhibit diastereomeric and enantiomeric selectivity in organisms (Esslinger et al., 2011) and environmental matrix (Davis et al., 2005; Li et al., 2011; Meng et al., 2011). The HBCD diastereoisomers and enantiomers exhibit quite different toxicity e.g. to Hep G2 cell (Hu et al., 2009). Information on diastereomer- and enantiomer-specific profiles of HBCD in environmental media is indispensable for understanding their fate and evaluating their risk. But only few studies are available on the diastereomer- and enantiomer-profiles of HBCDs in surface sediments (Marvin et al., 2006; Ramu et al., 2010). In our knowledge, up to the date, no systematic study on HBCDs in surface sediment has been conducted in China.

Tianjin City is the third largest city in China. It is located in the northeast of China, facing Bohai Sea on the eastern side. Tianjin is a commercial and industrial city, and its economic development is currently the fastest in China. To better delineate the content level and fate of HBCDs in the environment of Tianjin City, we investigated the concentrations, diastereomer- and enantiomer-profiles of HBCDs in surface sediments from Haihe River (HR), Dagou Drainage Canal (DDC) and Tianjin Harbor (TH) at Bohai Bay. The HR is a primary river through Tianjin and protected as reserved drinking water resource, and DDC is a main sewage drainage canal, which receives effluents from municipal wastewater treatment plants (WWTPs) as well as untreated waste waters from industries along the line. One sediment core was obtained at the sea entrance of the HR to evaluate the change of HBCDs with time.

2. Material and methods

2.1. Reagents and standards

All solvents used in extraction and analysis procedures were of HPLC grade. The native α -, β -, and γ -HBCD were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The d₁₈ labeled α -, β -, and γ -HBCD were purchased from Wellington Laboratories (Guelph, ON, Canada). Individual stock standard solutions

containing these compounds (1.0 mg L⁻¹) were prepared in methanol and stored at 4 °C.

2.2. Sampling campaign

Fourteen sites along HR (H₁–H₁₄), sixteen sites along DDC (D₁–D₁₆) and 21 sites along TH (T₁–T₂₁) were sampled in April, May, and September 2010, respectively. The site locations are shown in Fig. 1, and their geographic information is given in Table SM-1. Surface sediment samples (0–10 cm) were collected with a stainless steel grab sampler and placed in polypropylene bags. Besides, a sediment core sample (70 cm depth) was collected at T₂ and sorted into 2-cm intervals. The sediment samples were transported to laboratory at 0 °C, and then dried in a freeze-drier. The HR, DDC and TH are not wide, and hence only one sampling was conducted along the midline at each site. Three travel blanks were checked for sampling events. The travel blank was 100 g wet sediment from YuQiao reservoir, Tianjin, which had been confirmed without HBCD contamination through beforehand analysis. The travel blank were shipped to the field and exposed to the same conditions as the real sample. All dried samples were stored at -20 °C before extraction.

2.3. Sample extraction and cleanup

The extraction of HBCDs from sediment followed the literature (Li et al., 2011) with little modification. In brief, sediment samples were freeze-dried, and extracted with 1:1 acetone–hexane in a Soxhlet extraction device. Then, the extracts were cleaned up with concentrated H₂SO₄ and silica column. Finally, the elute was concentrated to almost dryness and reconstituted in methanol prior to analysis. The detail of extraction and cleanup could be referred in SM.

2.4. Instrumentation and analysis

Quantitative determination of HBCD diastereoisomers and enantiomers were performed on Agilent 1200 series liquid chromatography and an Agilent 6410B triple quadrupole mass spectrometer with an electrospray interface working in negative ionization mode. The separation of diastereoisomers and enantiomers were accomplished using C₁₈ column (150 mm × 4.6 mm i.d., 5 μ m particle size, CNW, Germany) and β -PM chiral LC column (200 mm × 4 mm i.d., 5 μ m particle size) containing permethylated β -cyclodextrin on silica (Macherey–Nagel, GmbH&Co, Duren, Germany), respectively. The mobile phase for diastereomer separation was methanol and water at a ratio of 9:1 (V:V) at a constant flow rate of 0.5 mL min⁻¹, acetonitrile and water at a ratio of 8:2 (V:V) containing 10 mmol L⁻¹ ammonium acetate was used for enantiomer separation. Good separation of the six enantiomers was achieved (Fig. SM-2). The optimized multiple reaction monitoring (MRM) mode was used for mass monitoring (Table SM-2). Other details for analysis could be referred in SM.

2.5. Quality assurance and quality control

The average recoveries of internal standards by spiking 5 ng (1 mg L⁻¹, 5 μ L) of d₁₈ labeled HBCDs into approximately 5 g sediment samples ranged between 82.7% and 99.7% (Table SM-3). Duplicate samples were analyzed separately; and their relative standard deviations were less than 11%. The enantiomeric factors (EFs) was corrected based on the internal standards for the three HBCD diastereoisomers following those of Peck et al. (2008), which ranged from 0.495 to 0.505 for standard solutions. EFs in the environmental samples that significantly differ from the range of technical products (Table SM-4) (*t* test, *p* < 0.05) were considered as

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