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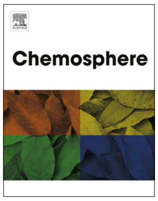

Levels and distribution of hexabromocyclododecane and its lower brominated derivative in Japanese riverine environment

Jung Keun Oh [a],*, Kensuke Kotani [a], Satoshi Managaki [b], Shigeki Masunaga [a]

[a] *Graduate School of Environment and Information Sciences, Yokohama National University, Yokohama 240-8501, Japan*
[b] *Faculty of Environmental Science, Musashino University, Tokyo 135-8181, Japan*

HIGHLIGHTS

- HBCD diastereomeric pattern differed depending on the pollution source.
- The highest level of total HBCDs for surface sediment samples in the world was detected.
- Enantiomer selectivity for HBCDs was found in the sediment samples.
- PBCD derived from HBCD was detected in both water and sediment samples.
- Correlation between the HBCD and PBCD concentration in aquatic samples was confirmed.

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ABSTRACT

Hexabromocyclododecane (HBCD) and its lower brominated derivatives were measured in both surface water and sediment samples from three Japanese rivers; Tsurumi River, Yodo River, and Kuzuryu River. The concentration level of $\sum$HBCD (sum of α-, β-, and γ-HBCD) was in the order of Kuzuryu > Yodo > Tsurumi Rivers, reflective of the different emission sources for each basin. The highest $\sum$HBCD concentration (7800 ng g^{-1} dw) was detected in the sediment sample from the Kuzuryu River that receives effluents from textile industries, which use HBCD in flame retardant finishes. A different diastereomeric pattern of α-, β-, and γ-HBCD of each river was investigated, indicating the level of HBCD in these rivers is directly influenced by emission source. Enantiomer fractions of HBCDs in water and sediment samples were also determined. Racemic mixtures were observed in the water samples, whereas enantiomeric enrichment of (−) γ-HBCD and (+) α-HBCD was observed in the sediment samples. Some lower brominated HBCD derivatives such as pentabromocyclododecenes were detected in both the water and sediment samples, and their concentration ranged from below the detection limit to 15 ng L^{-1} and 20 ng g^{-1} dw, respectively.

1. Introduction

Hexabromocyclododecane (HBCD) is a brominated flame retardant (BFR) used in polystyrene foams, e.g., expanded polystyrene (EPS) and extruded polystyrene (XPS) foam, and in textiles (Marvin et al., 2006). It is manufactured worldwide because of its remarkable flame retardant properties and good blending with polymers. Global use and production of HBCD exceeds 0.16 Mt year^{-1} (BSEF, 2009), and approximately 3.0 kt was used in Japan in 2010 (METI, 2010). It is noted that, in Japan, about 80% of HBCD is used in polystyrene foams, and the rest is mostly used for textiles (METI, 2008). HBCD is an additive BFR that is not covalently bonded to polymers, which means that there is high risk of it being released to the environment during use, disposal, and recycling of materials that contain HBCD (Tomy et al., 2005; POPRC, 2011). Owing to evidence of its persistence, bioaccumulation in environmental compartments, and toxic properties (Tomy et al., 2011; Li et al., 2012; Zhang et al., 2013), HBCD has recently determined to be listed for global elimination after the sixth meeting of the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants (C&EN, 2013).

Generally, it is widely known that HBCD has a high soil–water partition coefficient (log $K_{oc} = 4.66$ for HBCD by applying the QSAR equation (EU RAR, 2008)), high log K_{ow} (5.6, (Covaci et al., 2006)), low water solubility (65.6 μg L^{-1}, sum of solubility of the three major diastereomers), and low vapor pressure (6.27×10^{-5} Pa at 21 °C, (CMABFRIP, 1997)). Theoretically, HBCD has 16

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* Corresponding author. Address: Graduate School of Environment and Information Sciences Yokohama National University 79-7, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan. Tel.: +81 45 339 4346; fax: +81 45 339 4373.
E-mail address: oh-jungkeun-yb@ynu.jp (J.K. Oh).

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stereoisomers, including six diastereomeric pairs of enantiomers and four meso forms (Heeb et al., 2005). The technical HBCD mixture is mainly composed of three enantiomeric pairs of diastereomers (approximately 75–89% γ-isomer, 10–13% α-isomer, and <0.5–12% β-isomer) (Becher, 2005). The three main diastereomers (α-, β-, and γ-HBCD) have different values of polarity, dipole moment, and water solubility, which may cause different stabilities and biological uptake rates in the environment (Hakk et al., 2012). Moreover, the difference in hydrophobicity of the individual diastereomers (log K_{ow} of α-, β-, and γ-HBCD are 5.07, 5.12, and 5.47, respectively) (KEMI, 2005) may lead to different levels of persistence, biological magnification, and toxicity. Peled et al. (1995) observed an interconversion of HBCD diastereomers during heating processes at temperatures above 160 °C.

The degradation and biotransformation products of HBCD have been detected in various environmental matrixes and in biota. The breakable carbon–bromine bond, unlike the carbon–fluorine or carbon–chlorine bond, can be expected to generate significant degradation or biotransformation in biological systems (Tomy et al., 2011). Barontini et al. (2001) reported that 7 isomers of pentabromocyclododecenes (PBCDs) identified as thermal degradation products of HBCDs. Harrad et al. (2009) reported that photolytically mediated loss of HBr from HBCD leads to the formation of PBCD and tetrabromocyclododecadiene (TBCD) isomers in English lakes. Anaerobic degradation products of HBCD, tetrabromocyclododecene (TBCDe) and dibromocyclododecadiene (DBCDi), which are formed by the debromination of vicinal dibromides, have also been reported in sediment microcosms in laboratory studies (Davis et al., 2006; Lo et al., 2012). Moreover, many kinds of metabolites of HBCD have been identified in biotic samples, such as chicken eggs (Hiebl and Vetter, 2007), Pollack (Esslinger et al., 2011), and Wistar rats (Brandsma et al., 2009).

Enantiomeric patterns of HBCDs have been identified in some environmental and biota samples (Janak et al., 2005; Guerra et al., 2008; Koeppen et al., 2010; Esslinger et al., 2011; Gao et al., 2011; Li et al., 2012; Vorkamp et al., 2012). Despite the increasing number of studies on HBCD, few have attempted to characterize and identify its degradation products and enantiomeric patterns in environmental compartments. As there is evidence that some degradation products have higher binding affinities for human transthyretin receptor than their parent HBCDs or even thyroxin (Weber et al., 2009), further studies are needed to examine which transformation products are mainly formed in biotic and abiotic environments.

In the previous study (Managaki et al., 2012), it was investigated the distribution of HBCD in sediment from Tsurumi River, Yodo River, and Kuzuryu River. The aim of this study is not only to clarify the behavior of diastereomers of HBCD, but also to identify their lower brominated derivatives in the water and sediment samples collected from these rivers, Japan, with different HBCD emission sources in each basin.

2. Materials and methods

2.1. Standards and reagents

Native, deuterated (d_{18}-), and $^{13}C_{12}$-labeled α-, β-, and γ-HBCD (50 μg mL^{-1}) and native PBCD (50 μg mL^{-1}) in toluene were provided by Wellington Laboratories (Guelph, Canada). LC-MS grade methanol and acetonitrile, and pesticide analysis grade dichloromethane (DCM) and *n*-hexane were purchased from Wako Pure Chemical Industry. (Tokyo, Japan). All the other reagents, such as 44% sulfuric acid-impregnated silica gel, Wakogel S-1, copper (powder), and sodium sulfate (anhydrous) were purchased from Wako Pure Chemical Industry.

2.2. Description of sampling sites

Fig. 1 shows the sampling locations of this study. Tsurumi River, regulated by the Japanese government (Minister of Land, Infrastructure, Transport and Tourism), flows through Tokyo and Kanagawa prefectures, ranked as two of the most highly populated areas in Japan. Its basin is a typical residential area with over 1.8 million people and has the highest population density in Japan. A total of 7 municipal wastewater treatment plants are located in the river basin, and a large amount of effluent from these plants is discharged into the river. In spite of continuous efforts to improve the river water quality, it is still ranked as one of the worst in Japan because of the rapid urbanization in the basin. Yodo River is the only river flowing out of Lake Biwa, the largest lake in Japan. It flows through Shiga, Kyoto, and Osaka prefectures. Approximately 11 million people live in the basin. The river has the most tributaries (965) in Japan. The flow of the river consists mainly of effluents from industries, including EPS and XPS production, and household wastewater. Kuzuryu River flows through Fukui prefecture, and 0.66 million people live in the basin. Many dyeing and textile processing factories (644, 4% of total number in Japan, 2010) are located along the river. Moreover, a large amount of textiles (366 kt, 15% of total volume in Japan, 2010) is produced in this prefecture. Wastewater from textile factories may have released their effluents into the river.

Surface water and sediment samples were collected at 17 sites from the three rivers; Tsurumi River (T-1–T-4, $n = 4$), Yodo River (Y-1–Y-6, $n = 6$) and Kuzuryu River (K-1–K-7, $n = 7$). Samples from Tsurumi River were taken in October, 2011, while samples from Yodo River and Kuzuryu River were collected in December, 2011. 1 L of water was collected at each site using a grab sampler. The water samples were transported to the laboratory and stored at 4 °C in the dark until pre-treatment. Sediments were sampled using an Ekman–Birge sediment sampler at the same sites, simultaneously with the water samples. The sediment samples were put in brown glass bottles and immediately brought to the laboratory for storage at −25 °C prior to analysis.

2.3. Extraction and cleanup

2.3.1. Water

The water samples were analyzed according to the method reported by Suzuki and Hasegawa (2006). Each water sample (1 L) was spiked with 50 ng each of $^{13}C_{12}$-labeled α-, β-, and γ-HBCD (1 mg L^{-1} in acetone, 50 μL) as internal standards. This standard solution was mixed well using test tube mixer, and kept in a refrigerator for 6 h before spiking to the sample. Before this standard was spiked to the sample, it was mixed one more time for 20 s using test tube mixer. After conditioning the solid-phase extraction disk (Empore Disk Styrenedivinylbenzene (SDB-XD, 47 mm) 3 M, USA) with 10 mL each of methanol and purified water, the sample was passed through at a flow rate of 30 mL min^{-1}. After passing the water sample to the SPE disk, 7 mL of acetone was injected to the same SPE disk to escape the loss. Therefore, filtered water sample and 7 mL of acetone were combined and analyzed. After drying in an oven at 45 °C for 1 h, the disk was eluted with 4 mL of acetone followed by 3 mL of DCM. The eluate was evaporated under the flow of N_2 and then reconstituted in 1 mL of methanol including 50 ng of d_{18}-γ-HBCD.

2.3.2. Sediment

Sample information of each sampling point is shown in Table SM-1 in Supplementary Material (SM). All the sediment samples were homogenized, freeze-dried, and sieved through a 2 mm sieve prior to analysis. Subsequently, 2 g of the sample was weighed accurately, placed in a stainless-steel cell, and mixed with

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