



Enrichment of hexabromocyclododecanes in coastal sediments near aquaculture areas and a wastewater treatment plant in a semi-enclosed bay in South Korea



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HIGHLIGHTS

- The spatial distribution of HBCDs revealed the presence of an unknown source.
- A high level of HBCDs was detected in EPS buoys used in aquaculture farms.
- EPS buoys and a WWTP were determined to be important sources of HBCDs.
- An increase in HBCD concentrations over time was observed.

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ABSTRACT

The contamination status and potential sources of hexabromocyclododecanes (HBCDs) in the coastal environment were investigated using sediment samples from a semi-enclosed bay in South Korea. HBCDs displayed a very different distribution profile compared to polybrominated diphenyl ethers (PBDEs) and nonylphenol, indicating different emission sources inside the bay. A strong enrichment of HBCDs was found near aquaculture areas that used expanded polystyrene (EPS) buoys, which were confirmed to be the main source of HBCDs following an analysis of buoys collected from a market and the coast. EPS buoys contained large amounts of HBCDs, with lower levels in the outside layer than inside, implying the leaching of HBCDs from the surface throughout their lifetime. This was reflected in the high levels of HBCDs measured in coastal sediments near aquaculture farms. A wastewater treatment plant was found to be an additional source of HBCDs. A dated core sample revealed an increase in HBCD concentrations over time. The isomeric profiles for most of the surface and core sediment samples were dominated by the γ -diastereoisomer.

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1. Introduction

Hexabromocyclododecanes (HBCDs), a brominated flame retardant (BFR), have been produced since the 1960s and are now one of most widely used aliphatic additive BFRs (Marvin et al., 2006). HBCDs are the main additive (3–7% by weight) in expanded polystyrene (EPS) and extruded polystyrene (XPS), which are commonly used for thermal insulation or in molded foam packing. Other applications of HBCDs include textiles that are used in residential and commercial furniture, upholstery in vehicles, draperies, and wall coverings. HBCDs are also

added to the high-impact polystyrene used in electrical and electronic equipment (Alaee et al., 2011). Technical HBCDs (t-HBCDs) are dominated by three diastereoisomers: α , β , and γ . The relative amounts of these diastereoisomers in the t-HBCDs ultimately depends on the manufacturer, but the γ -diastereoisomer accounts for 75–89% of the total, followed by the α -diastereoisomer (10–13%) and then the β -diastereoisomer (1–12%) (Guerra et al., 2008). The dissimilarities in the structures of α , β , and γ -diastereoisomers lead to differences in their physicochemical properties, such as polarity, dipole moment, and solubility in water (Hakk, 2010). The solubility of α , β , and γ -HBCDs in water is 48.8, 14.7, and 2.1 $\mu\text{g/L}$, respectively (Hakk, 2010; Marvin et al., 2011). The physicochemical properties of HBCDs are similar to those of polybrominated diphenyl ethers (PBDEs) and other persistent organic pollutants (POPs). The $\log K_{ow}$ of HBCDs is 5.6, which places it in the optimum range for bioaccumulation (Law et al.,

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2005; Hakk, 2010). Like PBDEs, HBCDs are a BFR additive that is not covalently bonded to the material; thus, it can easily leach out from the product during its use or disposal, and may then be released into the environment (Alaee et al., 2011). The first detection of HBCDs in the environment was in sediment and fish samples from Swedish rivers in the vicinity of textile plants in 1995 (Sellström et al., 1998). Since then, HBCDs have attracted increasing global attention, and studies have been reported showing that HBCDs are ubiquitous in a wide range of environmental samples, including air (Abdallah et al., 2007), soil (Gao et al., 2011), riverine sediments (Eljarrat and Barcelo, 2004; Oh et al., 2014; Wu et al., 2014), suspended sediments (Marvin et al., 2006), marine sediments (Tanabe, 2008; Ramu et al., 2010), riverine fish (Eljarrat and Barcelo, 2004), marine fish (Xia et al., 2011), and marine mammals (Lam et al., 2009; Bachman et al., 2014).

By virtue of the strict regulations and banning of some PBDE formulations, the use of BFRs has been shifted to non-PBDE halogenated FRs, such as HBCDs, to replace the prohibited commercial PBDEs (Guerra et al., 2009), resulting in a trend of increasing HBCD levels in the environment (Minh et al., 2007; McKinney et al., 2010). Due to its potential toxicity, environmental persistence, bioaccumulative tendencies, and long-range transportability, HBCDs were added to the list of global elimination compounds under the Stockholm Convention on POPs (UN, 2013) in May 2013. However, large volumes of materials that contain HBCDs are still in use. The usage of HBCDs has increased over the years. Korea consumed 530 tonnes of HBCDs in 1993 and by 2010 the annual consumption was 1896 tonnes (Korea MOE (Ministry of Environment), 2005, 2012). Therefore, it is important to monitor the levels of HBCDs in the environment, and to evaluate the effectiveness of regulations/controls on their production and use.

Production facilities of HBCDs have been identified as a point source of HBCDs to the aquatic environment based on the very high concentrations (up to 1700 ng/g d.w.) measured in suspended sediment downstream from the production facilities (Morris et al., 2004). Industrial effluents and effluents from municipal sewage treatment plants (STPs) were also identified as emission sources of HBCDs leaching from products (such as EPS packing materials) or from washing of textiles such as curtains; concentrations of up to 7600 ng/g d.w. were measured in riverine sediments downstream from these facilities (Sellström et al., 1998; Eljarrat et al., 2004). The global concentrations of HBCDs in coastal and marine sediments are much lower than those of riverine sediments. In sediments from Tokyo Bay, HBCDs ranged from 0.056 to 2.3 ng/g d.w. released from the municipal and industrialized areas in the Tokyo metropolitan area (Minh et al., 2007). Comparable concentrations were also observed in estuarine and coastal sediments from the Pearl River Delta, China (Feng et al., 2012), Dublin Bay, Ireland (Morris et al., 2004), and the North Sea in The Netherlands (Klamer et al., 2005). The highest concentrations of HBCDs in sediments (59 ng/g d.w.) have been found in samples collected along the coast of South Korea, which suggests that Korea is one of the major consumers of HBCDs in the Asia region (Ramu et al., 2010). The distribution pattern of HBCDs reflects the land-use pattern in that high concentrations are associated with urbanization and industrialization. However, a highly elevated concentration (50 ng/g d.w.) has also been found in some coastal areas located far from suspected emission sources, such as STP effluents, urban areas and industrial zones. The formulations of HBCDs are not produced in Korea; they are imported to be added to various products, such as textiles, EPS, upholstery and plastics (Cischem, 2005). This fact implies the existence of a second source of the HBCDs present in Korean coastal environments in addition to the industrial and urbanization sources.

This study investigated the contamination status and potential sources of HBCDs in the Korean coastal environment using coastal sediments collected from industrial areas, sewage effluent-receiving areas, urbanized areas, a shipbuilding yard, and aquaculture farms. For comparison, the levels of PBDEs (a major BFR used in Korea) and nonylphenol (a wastewater and sewage tracer) were also measured.

We found that HBCDs and PBDEs/nonylphenol had different spatial distributions inside the bay, implying that HBCDs might have a different source. We suspected this source to be EPS buoys, which are used extensively in oyster aquaculture farms. This assumption was verified by quantifying HBCDs in EPS buoys purchased from a market and collected from the coast. In addition, this study also investigated the temporal trend of HBCDs in the bay using archived core samples.

2. Materials and methods

2.1. Sampling

Surface sediment (~2 cm) was collected using a Van-Veen grab sampler and placed in 250-mL pre-cleaned amber glass jars. The samples were immediately frozen and transferred to the laboratory for storage at -20°C until analysis. Nineteen surface sediment samples were collected in March 2010 from Jinhae Bay and Masan Bay, which are located on the southeastern coast of South Korea. In addition, to evaluate whether a wastewater treatment plant (WWTP) could be a point source of HBCDs inside the bay, ten sediment samples were collected from three transects (A–C) originating from its outfall. Sample IDs and the sampling locations are given in Table S1 and Fig. 1. Jinhae Bay is a semi-enclosed embayment located on the southeastern coast of Korea with its mouth opening to the Korean Strait. It is one of the largest bays in Korea and one of the most polluted areas in the country. Masan Bay is located in the north of Jinhae Bay, and is a heavily industrialized location that has experienced rapid urbanization. It receives a large pollution load from rivers and streams via discharges of industrial waste, municipal sewage, and urban runoff. In addition, to determine any temporal trends in HBCD contamination, an archived sediment core was subjected to chemical analysis. The core was taken from Masan Bay in September 2005 (Fig. 1). The PBDE and PCB concentrations in the core were previously published elsewhere (Hong et al., 2010).

EPS buoys (62-L, $n = 3$) were purchased from a local market and stranded buoys ($n = 3$) were collected from the coast of Jinhae Bay in May 2012. The inner parts of the buoys were used for chemical analysis. To observe any changes in the HBCD levels due to environmental weathering, additional stranded buoys ($n = 2$) were collected from the coast, and their inner (fresh) and outer (weathered) parts were analyzed.

2.2. Chemical analysis

The analytical methods used to determine HBCD, PBDE, and nonylphenol levels have been described in detail elsewhere (Li et al., 2008; Hong et al., 2010; Al-Odaini et al., 2013). Briefly, for PBDE analysis, 20 g of wet sediment was dehydrated with anhydrous Na_2SO_4 and then extracted in 200 mL of hexane:dichloromethane (DCM) (1:1, v/v) using a Soxhlet extractor for 16 h after spiking with internal standards (^{13}C -BDE-139 and ^{13}C -BDE-209). Activated copper granules were used to remove elemental sulfur. The extracts were cleaned first using a multilayer column with silica gel and alumina (5% and 1% deactivated, respectively). The eluents were then fractionated using size-exclusion high-pressure liquid chromatography (HPLC, 250 \times 22.5-mm i.d. size-exclusion column packed with Phenogel 100 Å; Phenomenex, Torrance, CA, USA). The eluates were concentrated, and an instrumental recovery standard ($^{13}\text{C}_{12}$ -PCB-189) was spiked into each sample prior to instrumental analysis. Identification and quantification were performed using a gas chromatograph (6890 series: Agilent Technologies, Santa Clara, CA, USA) coupled to a quadrupole mass spectrometer (5975 series: Agilent Technologies) in negative chemical ionization (NCI) mode (using methane as the reagent gas). The separation of BDE congeners was accomplished using a DB-1 column (15 m \times 250- μm i.d. \times 0.25- μm film thickness; J&W Scientific,

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