



Releasing of hexabromocyclododecanes from expanded polystyrenes in seawater -field and laboratory experiments



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HIGHLIGHTS

- Field and laboratory observations for leaching of HBCDDs from EPS into seawater.
- EPS debris/small fragments as source of hazardous chemicals in marine environment.
- Rapid initial leaching of HBCDDs from EPS fragments is followed by slow desorption.
- Water leaching, UV-light/temperature and fragmentation enhanced the release of HBCDD.

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ABSTRACT

Expanded polystyrene (EPS) is a major component of marine debris globally. Recently, hazardous hexabromocyclododecanes (HBCDDs) were detected in EPS buoys used for aquaculture farming. Subsequently, enrichment of HBCDDs was found in nearby marine sediments and mussels growing on EPS buoys. It was suspected that EPS buoys and their debris might be sources of HBCDDs. To confirm this, the release of HBCDDs from EPS spherules detached from a buoy to seawater was investigated under field (open sea surface and closed outdoor chambers with sun exposure and in the dark) and laboratory (particle-size) conditions. In all exposure groups, initial rapid leaching of HBCDDs was followed by slow desorption over time. Abundant release of HBCDDs was observed from EPS spherules exposed to the open sea surface (natural) and on exposure to sunlight irradiation or in the dark in controlled saline water. Water leaching and UV-light/temperature along with possibly biodegradation were responsible for about 37% and 12% of HBCDDs flux, respectively. Crumbled EPS particles (≤ 1 mm) in samples deployed on the sea surface for 6 months showed a high degree of weathering. This implies that surface erosion and further fragmentation of EPS via environmental weathering could enhance the leaching of HBCDDs from the surface of EPS. Overall, in the marine environment, HBCDDs could be released to a great extent from EPS products and their debris due to the cumulative effects of the movement of large volumes of water (dilution), biodegradation, UV-light/temperature, wave action (shaking), salinity and further fragmentation of EPS spherules.

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1. Introduction

Hexabromocyclododecanes (HBCDDs) are the most widely used brominated flame-retardants (BFRs), with 31,000 tons produced in 2011: 18,000 tons in China and 13,000 tons in Europe and the US (UNEP, 2015). HBCDDs are chief additives to polystyrene (PS) foam

(3–7% by weight) used to make insulation boards and other applications, include upholstery textiles and high-impact polystyrene (Alaee et al., 2003; Heeb et al., 2010). Commercial HBCDDs are usually a mixture of three diastereomers (α 10–13%, β 1–12%, γ 75–89%), where the levels of γ and α are usually the highest in abiotic and biotic environments, respectively (Barotini et al., 2001). The diverse properties (polarity, dipole moment, and solubility in water) of these isomers might be responsible for the differences in their environmental behavior (Janak et al., 2005). Like other persistent organic pollutants (Legret et al., 2005; Oliver et al., 2005), the release of HBCDDs from PS foam products has attracted

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increasing attention (Zhang et al., 2012). Plastics contain large amounts of additive chemicals that leach into the surrounding environment and subsequently bioaccumulate in organisms (Sajiki and Yonekubo, 2003; Osako et al., 2004; Kim et al., 2006; Choi et al., 2009; Zhou et al., 2013; Rani et al., 2014; Jang et al., 2016). HBCDD concentrations of up to 7600 ng/g dry weight (d.w.) have been reported in riverine sediments downstream from industrial effluent outlets or sites where textiles are washed (Sellström et al., 1998; Eljarrat et al., 2004; Yang et al., 2012; Du et al., 2013; Zhang et al., 2013). Production trends in combination with the increasing environmental accumulation of HBCDDs may increase the hazards for marine life. HBCDDs have been categorized as persistent organic pollutants in the Stockholm Convention since 2013 due to their potential toxicity, environmental persistence, bioaccumulative tendencies, and long-range transportability (UN, 2013). However, many materials with added HBCDDs are still in use. In Korea, the use of HBCDDs increased from 530 tonnes in 1993 to 1896 tonnes in 2010 (Korea MOE, 2005, 2012).

Currently, PS foam, including expanded (EPS) and extruded (XPS), is a major component of plastic debris on land and in marine systems globally (Moore et al., 2001; Derraik, 2002; Browne et al., 2007; Zhou et al., 2011). The estimated global demand for PS was around 14.9 million tons in 2010, and its market is projected to grow at a rate of 5.6% from 2010 to 2020 (GBI Research, 2012). Products made from PS are used in different areas, such as food, research, construction, aquaculture, and electronics (IEEP, 2016). The use of HBCDDs in PS-based materials for purposes other than construction is believed to be small (UNEP, 2011). However, the detection of HBCDDs in some packaging materials and EPS buoys revealed they were either treated with HBCDDs or contained recycled PS (Rani et al., 2014). Because of its chemical and physical composition, PS foam can leach or absorb other toxins and contaminants (Al-Odaini et al., 2014; Graca et al., 2014). PS fragments are transported to remote areas by the wind and water currents (Moore et al., 2001). The EPS fragments identified in birds and mussels clearly indicate that marine animals mistake these fragments for food and ingest them (Thompson et al., 2004; Van Franeker et al., 2011; Jang et al., 2016).

Recently, the enrichment of HBCDDs (49.9 µg/g) in marine sediments has been observed in non-industrial regions, such as near hanging aquaculture areas (Al-Odaini et al., 2014). EPS buoys are widely used floatation devices in aquaculture farming of mollusks (Choi, 2008). High concentrations of HBCDD in EPS buoys (13 ± 22 to 4001 ± 605 µg/g) and mussels growing on them [up to 5160 ng/g lipid weight (l.w.)] suggest that EPS is an important source of HBCDDs in Korean coastal environments (Jang et al., 2016). The HBCDD concentrations in mussels from EPS substrates were comparable to or higher than those reported in industrialized areas of South Korea (140–550 ng/g l.w. in Onsan and Masan Bays) and Japan (32–5200 ng/g l.w.) (Ramu et al., 2007; Ueno et al., 2010). Two million EPS buoys are used annually and there are 7,580,000 spherules in a standard 62-L buoy with a density of 8–15 kg/m³. However, the rate of retrieval of used buoys is around 28% (Korea MOE, 2013). Jang et al. (2014) estimated that about 990,000 styrofoam buoys are lost or disposed of as waste every year and become the dominant type of beach debris (micro-, meso-, and macro-debris) in South Korea (Heo et al., 2013; Lee et al., 2013). In view of the pollution of coastal beaches by polystyrene and plastics, this study investigated the release of HBCDDs and similar plastic additives in natural and field conditions to determine whether these plastics are a vector of those chemicals in marine environments. Previous studies have considered only EPS litter as a contaminant (Derraik, 2002) and there is no field evidence of the potential for HBCDDs to be leached from EPS.

To our knowledge, this is first study of the leaching of HBCDDs

from EPS spherules in seawater under field conditions using controlled outdoor chambers (dark and sunlight exposed) and an open-sea floating cage (natural sea surface). Dark conditions, sun exposure, and open sea-surface experiments were designed to investigate the effects of water leaching, ultraviolet (UV) light/temperature, and the action of sea waves, respectively. However, the effect of biodegradation under each condition could not be avoided. Particle-size effects (with and without shaking) in fresh water were examined in the laboratory to observe the effects of the further fragmentation of EPS spherules. Overall, studies of outdoor chambers and particle size were planned in order to support the releasing of HBCDDs in natural environment. The results increase our understanding of the leaching of HBCDDs from EPS in water.

2. Materials and methods

2.1. Reagents

Native and isotope-labeled (¹³C₁₂) standards of α-hexabromocyclododecane (α-HBCDD) > 98%, β-hexabromocyclododecane (β-HBCDD) > 98%, γ-hexabromocyclododecane (γ-HBCDD) > 98%, and 2,2',3,4,4',6-hexabromo [¹³C₁₂] diphenyl ether (¹³C-BDE-139) were obtained from Wellington Laboratories (Ontario, Canada). All solvents used were of capillary GC/GC-MS grade and procured from Burdick and Jackson (MI, USA). The deionized water used was produced by a MILLI-Q Advantage A10 system (Merck Millipore, Billerica, MA, USA). A stock solution containing a mixture of labeled HBCDD isomers (¹³C-labeled α-HBCDD, β-HBCDD, and γ-HBCDD) at a concentration of 1 µg/mL was used as surrogate and stored in dark under refrigeration.

2.2. Design of leaching experiment

EPS spherules (average size, 3.7 ± 0.8 mm × 3.6 ± 0.6 mm × 3.0 ± 0.56 mm; range, 3.3–4.1 mm) were detached with the help of forceps from new EPS buoys purchased from a local market. To test the effects of size, small EPS fragments (≤1 mm) were obtained by rubbing an EPS buoy with a stainless-steel brush and sieving the particles produced through a 1-mm mesh. Other materials used were Millipore water, black material to produce dark conditions, outdoor glass chambers (50 cm × 100 cm × 50 cm), and a floating open-sea cage used for holding Teflon mesh packets. The selection of the cage and Teflon mesh (1 mm) was based on the need for free contact of the EPS spherules with water without the loss of any spherules. Light intensity (at the sea surface and in the outdoor chamber), salinity, and the water pH were measured with a pyranometer (model No LI-250 A; LI-COR, Lincoln, Nebraska), Master Refractometer (ATAGO, Tokyo, Japan), and pH meter (Thermo Scientific, Waltham, MA, USA), respectively. The detailed design of the leaching experiments is described below and shown in Figs. 1 and 2.

2.2.1. Field experiments (outdoor chambers and sea surface)

EPS spherules were exposed to field conditions for 6 months from August 2013 to January 2014, in Jangmok Bay, Geoje, South Korea. Studies in the field (Fig. 1) were conducted in 1) adjacent closed outdoor chambers placed at the same location for dark and sunlight exposure and 2) a floating cage drifting on the sea surface to examine the effects of open sea surface exposure. One of the chambers was covered with black material to ensure dark conditions and the other was left uncovered to allow sunlight exposure. Thermometers were placed inside each chamber to measure the temperature. The outdoor chambers were continuously supplied with filtered seawater (pore size, 1 µm) with the in/outflow rate set to 600 mL/min. To investigate the leaching profile of HBCDDs in the

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