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Widespread detection of a brominated flame retardant, hexabromocyclododecane, in expanded polystyrene marine debris and microplastics from South Korea and the Asia-Pacific coastal region☆

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ABSTRACT

The role of marine plastic debris and microplastics as a carrier of hazardous chemicals in the marine environment is an emerging issue. This study investigated expanded polystyrene (EPS, commonly known as styrofoam) debris, which is a common marine debris item worldwide, and its additive chemical, hexabromocyclododecane (HBCD). To obtain a better understanding of chemical dispersion via EPS pollution in the marine environment, intensive monitoring of HBCD levels in EPS debris and microplastics was conducted in South Korea, where EPS is the predominant marine debris originate mainly from fishing and aquaculture buoys. At the same time, EPS debris were collected from 12 other countries in the Asia-Pacific region, and HBCD concentrations were measured. HBCD was detected extensively in EPS buoy debris and EPS microplastics stranded along the Korean coasts, which might be related to the detection of a quantity of HBCD in non-flame-retardant EPS bead (raw material). The wide detection of the flame retardant in sea-floating buoys, and the recycling of high-HBCD-containing EPS waste inside large buoys highlight the need for proper guidelines for the production and use of EPS raw materials, and the recycling of EPS waste. HBCD was also abundantly detected in EPS debris collected from the Asia-Pacific coastal region, indicating that HBCD contamination via EPS debris is a common environmental issue worldwide. Suspected tsunami debris from Alaskan beaches indicated that EPS debris has the potential for long-range transport in the ocean, accompanying the movement of hazardous chemicals. The results of this study indicate that EPS debris can be a source of HBCD in marine environments and marine food web.

1. Introduction

Plastics are versatile materials by virtue of their high durability, light weight, and low price. Expanded polystyrene (EPS, commonly known as styrofoam) is a widely used plastic, with a range of applications from disposable goods to construction materials. The global demand for polystyrene (PS) was around 14.9 million tons in 2010, and its market is expected to grow at a rate of 5.6% from 2010 to 2020 (GBI Research, 2012). As a result of its high production and consumption, EPS has become a major constituent of marine debris throughout the world (Hinojosa and Thiel, 2009; Moore et al., 2001; Smith, 2012; Zhou et al., 2011). After entering the sea, EPS products are easily broken down into fragments and eventually microplastics.

The role of marine plastic debris as a carrier of hazardous chemicals in the marine environment is an emerging concern (Browne et al., 2013; Cole et al., 2011; Koelmans et al., 2014; Rochman et al., 2014). EPS marine debris can contain both sorbed chemicals from the surrounding waters and plastic ingredients,

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such as unreacted raw materials and additives. The hydrophobic and porous surface of EPS is able to sorb contaminants in the water column. Rochman et al. (2013) reported that PS floating on the sea surface had large potential for the adsorption of polycyclic aromatic hydrocarbons (PAHs) compared to polypropylene (PP), polyethylene terephthalate (PET), and polyvinylchloride (PVC). Graca et al. (2014) observed the high accumulation of mercury in EPS debris stranded on beaches. Unreacted raw materials such as the styrene monomer and oligomers can be present inside EPS debris due to incomplete polymerization during manufacturing. The styrene monomer and oligomers are classified as endocrine-disrupting chemicals (Lithner et al., 2011), and can migrate from EPS products into the environment during their use or disposal (Amirshaghaghi et al., 2011); as a result, they are widely detected in coastal waters around the world (Kwon et al., 2015). Hexabromocyclododecane (HBCD) is the main additive chemical applied to PS products, including EPS, and is especially prevalent in construction materials and electronic housings (Alaee et al., 2003). HBCD is one of the most widely used brominated flame retardants (BFRs) with polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBPA) (Hermabessiere et al., 2017). It is added during the manufacturing process to achieve fire safety. The global consumption of HBCD was increased from 16,700 tons to 31,000 in 2001–2011 (Janaäk et al., 2005; POPRC, 2012). HBCD is not covalently bound to the polymer, and can therefore be easily released from plastic products into the environment. Owing to its potential toxicity, environmental persistence, bioaccumulative tendencies, and long-range transportability, HBCD was designated as a global elimination compound in the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2013 with a 5 year exemption for building insulation (UN, 2013). Recently, a number of alternative chemicals are identified and available; however, several years will take to substitute for HBCD (U.S. EPA, 2014; POPRC, 2011; Kavanaugh and Catherine, 2016). The future use and production might be expected to decrease (ECHA, 2009). However, large volumes of EPS containing HBCD are still widely used worldwide.

EPS buoys are the most common item of beach debris (size: > 2.5 cm) in South Korea, followed by fishing ropes, glass beverage bottles, plastic bags, and plastic food wrappers (Hong et al., 2014). They accounted for the predominant microplastics (size range: 1–5 mm; 93% of total microplastics) along the Korean coast, which were mainly fragmented from EPS buoys (Heo et al., 2013; Lee et al., 2013). EPS buoys are widely used in the fishing and aquaculture industries in South Korea, especially along the west and south coasts. Small buoys (40–80 L) are abundantly used in long-line hanging culture systems for oyster, mussel, scallop, and sea squirt, while large buoys (>200 L) are used for mooring submerged fish cages and fish nets, and for floating docks and barges. About 2 million EPS buoys are deployed every year, but only 28% of them are retrieved by the government for recycling (Korea MOE, 2012). Jang et al. (2014) estimated that 990,000 EPS buoys were discarded in 2012, resulting in the prevalence of EPS debris and fragments along the Korean coast.

In previous studies, we found that: (1) HBCD was widely incorporated in various PS-based consumer products, including expanded PS (EPS), extruded PS foam, and extruded PS (Rani et al., 2014); (2) HBCD was enriched in marine sediments near aquaculture areas, where a large number of EPS buoys were deployed (Al-Odaini et al., 2015); and (3) mussels inhabiting EPS marine debris accumulated HBCD originating from their substrate (Jang et al., 2016). These observations indicate that EPS debris and its fragments can be a source of HBCD in the marine environment. Therefore, it is necessary to determine the HBCD concentration in marine EPS debris to understand its potential impacts on marine ecosystems. For this reason, intensive sampling of EPS debris, including macro-sized (mainly EPS buoys) and meso-sized (microplastics between 1 and 5 mm) was conducted along the Korean coast. In addition, to identify the reason why HBCD is found in EPS buoys, EPS raw materials were obtained from petrochemical companies and a buoy manufacturing factory. HBCD levels in raw materials and EPS marine debris were compared. To understand the status in other countries, EPS marine debris samples collected from elsewhere in the Asia-Pacific region (12 countries) were also studied. The results of this study reveal that EPS debris and its fragments can be a source and transferring media of HBCD in the marine environment. We believe that the present study should improve our understanding of the environmental exposure of hazardous chemicals through plastic pollution.

2. Materials and methods

2.1. Sample collection

EPS marine debris samples, including buoys and microplastics, were collected from the Korean coast from 2013 to 2015 (Table 1). A total of 121 stranded EPS buoys were collected along the southeastern coast of South Korea, and divided into two groups according to size (Fig. 1a): small buoys (40–80 L, diameter 35 cm × height 45 cm, n = 60) and large buoys (>200 L, diameter 50 cm × height 90 cm, n = 61). Small buoys are commonly used in hanging aquaculture farming, and large buoys are widely used on floating cages, barges and transportation decks. In addition, 14 EPS buoys (or blocks) that contained different shapes or colors of recycled EPS blocks (or panels) inside were also collected (hereafter referred to as recycled buoys), and their inner and outer parts were used separately for chemical analysis (Fig. 1a). To identify the HBCD levels in EPS microplastics that were spread over Korean beaches, EPS microplastics (2–3 mm in diameter, Fig. 1a) were sampled from 12 sandy beaches along the western (n = 4), southern (n = 4), and eastern (n = 4) coasts of South Korea (Fig. S1). Three samples were collected from 3 different locations in each beach, and used for chemical analysis.

EPS products are manufactured in four steps: PS → EPS bead → pre-expanded spherule → end-use product. To identify whether HBCD is included in the EPS raw materials, EPS beads (both non-flame-retardant and flame-retardant types) were obtained from the two largest petrochemical companies in South Korea. In addition, EPS beads, (0.99 ± 0.06 mm in width; Fig. 1b), pre-expanded spherules (3.22 ± 0.21 mm in width; Fig. 1b), and their end products (60 L of EPS buoy) were obtained from a buoy manufacturing factory. For comparison, pre-expanded spherules used in building construction were also obtained from an EPS insulation panel manufacturing factory (Table 1).

EPS marine debris was also collected from 12 other countries in the Asia-Pacific region (Table 1): Bangladesh, Brunei, Canada, Hong Kong, Japan, Peru, Singapore, Sri Lanka, Taiwan, Thailand, USA (California, Hawaii, and Alaska), and Vietnam (Table 1, Fig. 2). Sampling from nine Asian countries and Peru was conducted within the Asia Pacific Economic Cooperation (APEC) Marine Environmental Training and Education Center (AMETEC), Korea Institute of Ocean Science and Technology (KIOST) program between 2013 and 2014 (Fig. S2, Table S1). Participants of AMETEC program collected EPS marine debris from their countries (Table S1). Samples from USA (California, Hawaii) and Canada were collected by KIOST staff (Table S1). Alaskan samples were collected by a US National Oceanic and Atmospheric Administration (NOAA) scientist in 2014. EPS fragments from Alaskan beaches were strongly suspected to be debris from the 2011 tsunami in Japan (Fig. S3). Except for the Alaskan samples, all of the EPS from South Korea and other countries was low-density EPS. Among the nine