

EXPANDED POLYSTYRENE (EPS) BUOY AS A POSSIBLE SOURCE OF HEXABROMOCYCLODODECANES (HBCDs) IN THE MARINE ENVIRONMENT

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Introduction

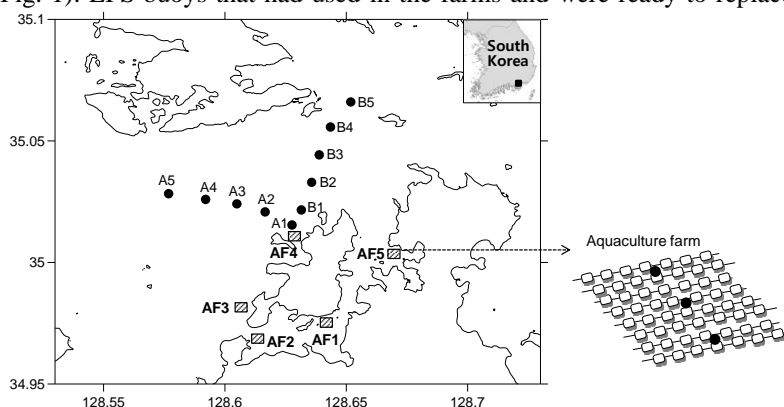
Flame retardant chemicals are added to many consumer products in order to reduce the risk of fire. Hexabromocyclododecane (HBCD) is a brominated flame retardant (BRF) used primarily in extruded and expanded polystyrene for thermal insulation in the building industry, with secondary applications in upholstered furniture, car cushions, packaging material and electrical household equipment¹. The commercial product of HBCD consists mainly of three diastereomers: α -, β -, and γ -HBCD, with the gamma-isomer predominating in the mixture. Similar to polybrominated diphenylethers (PBDEs), HBCDs are additives in BFRs and are not covalently bonded to the material. Therefore, they easily leach from the product during its use or disposal and are released into the environment. HBCD has been detected in various environmental matrixes and in biota. Since they exhibit typical POP properties (i.e., persistence, bioaccumulation, and toxicity), a global ban on HBCDs is currently being considering under the framework of Stockholm Convention on POPs. HBCD is third most used BFRs in South Korea. Its annual production volumes are estimated to be 2,173 ton².

In our previous study, we found the enrichment of HBCD in sediment near oyster farms in a semi-enclosed bay in the southern part of South Korea (the data is not shown here), where are not located near known sources of HBCD such as industrial facilities, sewage treatment plants or densely populated cities. We speculate that the expanded polystyrene (EPS) buoys that are extensively used in aquaculture farms could be the source of HBCD in those areas. Since expanded polystyrenes buoy is abundantly used in aquaculture farms and along the Korean coasts, and the predominant item in beached marine debris, EPS buoy could be the important source of HBCD in the marine environment of South Korea. In order to verify this assumption, we conducted an intensive sampling for aquaculture farm areas that employ EPS buoys. The results are discussed in this presentation.

Materials and methods

Sampling strategy

The multi-media sampling (seawater, sediment, and farmed oyster) was conducted in five aquaculture farms (AFs, AF1-AF5) in December, 2011 (Fig. 1). EPS buoys that had used in the farms and were ready to replace were obtained from farmers. In the center of each aquaculture farm, seawater (surface, middle, and bottom layers), bottom sediment (three different sites at each location), and farmed oyster samples were taken. At each layer of water column, 80 L of seawater was taken, and its dissolved and particulate phases were separated for chemical analysis. To compare the contamination level of HBCDs in between aquaculture farm and surrounding waters, water samples were also taken from surrounding waters along a distance (lines A and B). Wild oyster samples were collected from natural coasts which does not have a known source



of HBCDs such as AFs and urban area.

Chemical analysis

The analysis of hexabromocyclododecane (HBCD) was based on Al-Odaini et al.³ with a minor modification. To measure the representative levels of HBCDs in EPS buoy, EPS spherules from eight different places in a buoy were detached and used for chemical analysis. About 0.03 g of the EPS was dissolved in 4 mL of dichloromethane (DCM). The dissolved EPS was then spiked with 80 μ L of 1 ng/ μ L isotopically labeled internal standard (the mixture of ¹³C- α , β , and γ -HBCD diastereomers), vortexed for 1 min and finally evaporated to dryness under a gentle stream of N₂ gas. The dry extracts were eventually reconstituted with 200 μ L of acetonitrile for instrumental analysis. For checking the recovery of the internal standard, an aliquot of 160 μ L of 1 μ g/mL ¹³C-labeled BDE139 was added to each sample before instrumental analysis.

Homogenized oyster, sediment, particulate-phase of water samples fortified with the isotopically labeled internal standard were dehydrated with anhydrous Na₂SO₄ and then extracted in DCM:hexane (4:1) using soxhlet for 16 h. The extracts were then purified by being passed through a silica gel column (5% deactivated). The loaded column was eluted with 7 mL of hexane:DCM (1:1, v/v), 15 mL of hexane, 20 mL of hexane:diethyl ether (3:1, v/v) and finally 20 mL of hexane:diethyl ether (1:1, v/v). Oyster extracts were further purified by size-exclusion chromatography (250 \times 22.5 mm I.D.; packed with Phenogel 100 Å, Phenomenex) for lipid removal using DCM as the mobile phase. Then, the extract was concentrated, solvent-exchanged to IPA/toluene (9:1) for instrumental analysis. Dissolved water samples were liquid-liquid extracted using dichloromethane, and the rest of the steps are similar to particulate-phase samples. The final extracts were analyzed on an ABI/Sciex API 3200 mass spectrometer (MDS Sciex, Toronto, ON, Canada) equipped with an Agilent 1200 Series HPLC system (Agilent Technology, USA). Separation of HBCD isomers was achieved on a Zorbax Eclipse C18 analytical column (4.6 \times 150 mm, particle size 3 μ m). Details of the HPLC-APCI-MS/MS analysis can be found elsewhere³. Total HBCD concentrations (HBCDs) were presented by summing the α , β , and γ -HBCD diastereomers in the text.

Results and discussion

EPS buoy

All of the buoy samples analyzed in this study were found to contain HBCDs. The concentrations of HBCDs in EPS buoys used in the aquaculture farms were in the range of 28-249 μ g/g with the median concentration of 91 μ g/g (Fig. 2). The HBCD contents among EPS buoys showed a large variation, even within one buoy. The strong signal of HBCDs in aquaculture buoy demonstrates the lack of proper control for the use of HBCDs in manufacturing polystyrene products. The composition profile of HBCD diastereoisomers (α : β : γ = 19%:11%:70%) in EPS buoys was very close to that of commercial HBCD mixtures (α : β : γ = 10-13%:1-12%:75-89%) (Fig. 3).

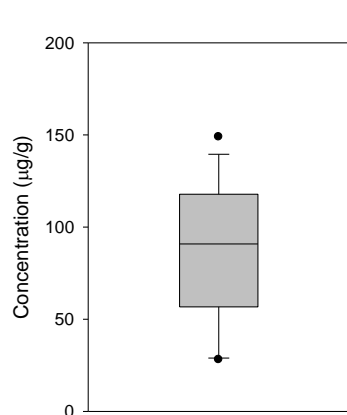


Figure 2. The concentration of HBCDs in EPS buoys.

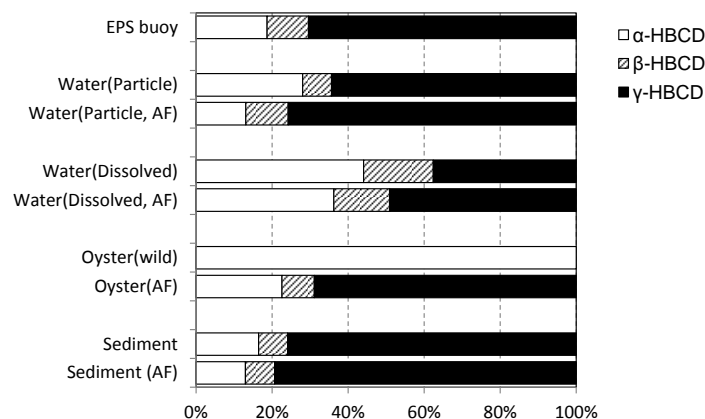


Figure 3. Stereoisomer composition of HBCDs in EPS buoy, seawater, oyster, and sediment collected from aquaculture farms and natural coast

EPS buoy can gradually fragment into millions of spherules with a diameter 1-5 mm that float on the water's surface or become stranded on the shoreline. At our previous studies, EPS was the most dominant macro

(>2.5cm) and micro (1mm<size<5mm) debris on the beaches of South Korea, accounting for 30% and 99% to total number of debris, respectively. The fragmentation of EPS buoys increases the surface-to-volume ratio and thus enhances the leaching rate of HBCDs into the surrounding environment. Abandoned buoys and their fragments can transport HBCD to areas away from aquaculture farms throughout the coastal environment.

Water column

HBCDs were widely detected in both dissolved and particle phases of seawater collected from aquaculture farms. The overall concentration of HBCDs in the water column ranged from 0.08 to 1.62 ng/L, with the median concentration of 0.24 ng/L (Fig. 4). Dissolved and particle phases contributed 54% and 46% to total HBCDs, respectively. Among three layers, relatively high HBCD concentration was measured in the surface compared to middle and bottom layers. And the isomeric signature of HBCDs in surface layer (α/γ ratio=0.38) was closer to commercial HBCDs (0.13) than middle and bottom layer samples (0.59 and 0.49, respectively), implying the direct effect of floating EPS buoys to surface water column. The concentration of HBCDs in seawater from aquaculture farms was higher than those from surrounding waters (Fig. 5), indicating the leaching of HBCDs from the floating EPS buoy to water column. The incensement of HBCD concentrations at B4 and B5 might be due to the effect of other aquaculture farms nearby the stations.

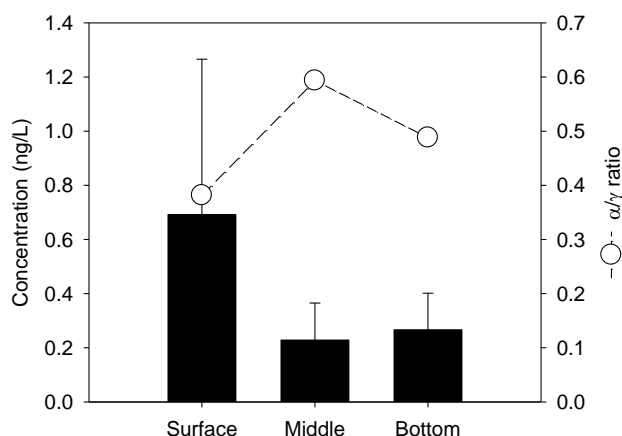


Figure 4. Vertical HBCD distribution and its stereoisomer profile in the water column of aquaculture farm.

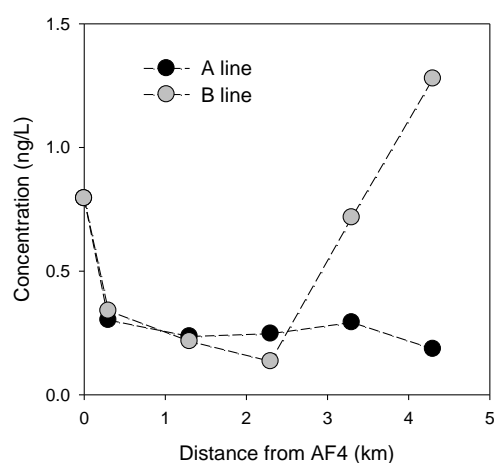


Figure 5. Distribution of HBCDs in seawater according to the distance from aquaculture farm

Oyster and Sediment

To obtain preliminary information about the impact of EPS buoys on farmed oysters, the concentration levels and profiles of HBCDs were measured in oyster samples collected from aquaculture farms and natural coasts. Two times higher concentration of HBCDs was measured in farmed oyster than in wild oyster (Fig. 6). The level of HBCDs in farmed oyster is higher than those from the coastal areas of Korea, Japan, China, Malaysia, Vietnam, Indonesia, France, and Norway^{4,5,6}.

In all of the farmed oysters, all HBCD diastereoisomers were detected, whereas only α -HBCD was detected in wild oyster samples. Although γ -HBCD is dominant in the technical mixture, α -HBCD is shown to prevail in the majority of aquatic biota including invertebrates, fish, and marine mammals¹. The prevalence of α -HBCD in aquatic biota is due to its higher assimilation efficiency and slower degradation. It was suggested that γ -HBCD is metabolized more quickly than α -HBCD, resulting in enrichment of the α -HBCD isomer. Therefore, the abundance of γ -HBCD in farmed oyster is unusual observation in the environment, which is the evidence of its direct exposure to high level of γ -HBCD included in EPS buoys.

HBCDs were also widely detected in bottom sediment of aquaculture farms. The HBCD concentrations in the sediment from aquaculture farms were in the range of 18.7-56.5 ng/g dw. The HBCD level is higher than those reported from the Korean coasts⁷, the Pearl River in China⁸, Japan⁹, North Sea¹⁰, and USA¹¹, while it is lower

than the levels detected near industrial regions in Tianjin, China¹². Similar to EPS buoy and seawater, γ -HBCD was dominant in the bottom sediment at both aquaculture farms and natural coasts.

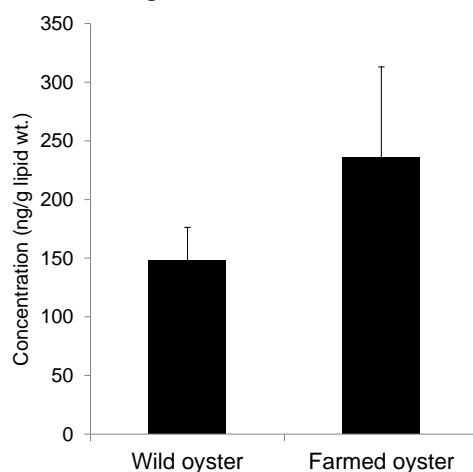


Figure 6. The concentration of HBCDs in wild and farmed oysters.

Acknowledgements

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