PROFILE FOR HEXABROMOCYCLODODECANE AND ITS DEGRADATION PRODUCT IN RIVER SEDIMENT, JAPAN AND KOREA

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Introduction

Hexabromocyclododecane (HBCD), a class of additive brominated flame retardants (BFRs) in polystyrene foams and textile products, has been manufactured worldwide because of its remarkable flame retardancy. However, there is growing concern about whether its consumption should be prohibited in that HBCD has been recently reviewed not only as one of the candidate persistent organic pollutants (POPs) under the Stockholm Convention but also labeled amongst the Type I Monitoring Chemical Substance of the Chemical Substances Control Law, Japan. Monitoring survey of HBCD in biotic and abiotic environment has been done extensively over the past two decades. Furthermore, photolytically mediated loss of HBr from HBCD to form pentabromocyclododecenes (PBCDs) and tetrabromocyclododecadienes (TBCDs) has been reported in abiotic environment [1], which attracted interest in its degradation products.

Notwithstanding the increase in number of monitoring studies of HBCD, few have attempted to characterize and identify its degradation products and enantiomeric patterns in the environmental compartment. Since there are some evidence that degradation products have higher binding affinities to human transthyretin receptor (hTTR) than parent HBCD and even thyroxin[2], it is necessary to examine those surveys extensively. The aim of this study is to offer not only the environmental fate of HBCD, but also identification of its degradation products in sediments which are collected from the rivers in Japan and Korea that have HBCD emission sources in their basin.

Materials and methods

Sampling. Fig. 1 shows the sampling location in this study. Surface sediments were sampled using a grab sampler (Ekman-Birge type bottom sampler) at 27 sites from 3 rivers of Japan (Kuzuryu River (K1~K7), Yodo River (Y1~Y6), and Tsurumi River (T1~T4), n=16) and 2 rivers of Korea (Geum River (G1~G5), and Nakdong River (N1~N6), n=11). Sampling dates were May (Korea), and December (Japan), 2011, respectively. Sediment

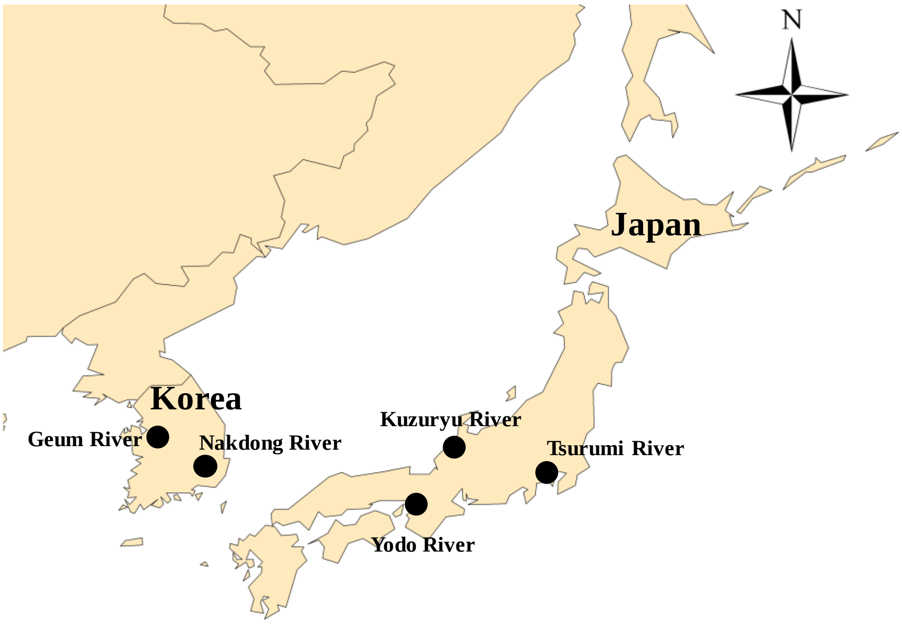

Fig. 1 Sampling locations

samples were immediately brought to the laboratory and were stored at -25 °C prior to analysis.

Sample preprocessing. All sediment samples in brown glass bottles were homogenized, freeze-dried, and sieved by a 2 mm sieve prior to analysis. 2 g for each sediment sample was weighed accurately and prepared in stainless-steel cell with mixed 2 g of Cu powder to remove sulfuric adulteration before conducting extraction. Each sample was spiked with 10 ng of ^{13}C-labeled α-, β-, γ-HBCD as internal standards. Extraction was carried out using Accelerated Solvent Extraction instrument (ASE 200, Dionex) with dichloromethane (DCM) and hexane (80:20, v/v) at 100 ºC, 1500 psi. Approximately 40 ml extracts were collected and subsequently concentrated to 5 ml using nitrogen purge flow. Cleanup procedure was performed using chromatography column packed with 8 g of 44% sulfuric coated silica gel and 0.5 cm hight sodium sulphate. Analytes were eluted with 30 mL of dichloromethane and hexane (50:50, v/v). The fraction was evaporated to dryness under flow of N_2, and redissolved in 1 mL of methanol containing 10 ng of d_{18}-γ-HBCD as recovery standard prior to LC-MS/MS analysis.

LC-MS/MS analysis. Hewlett-Packard 1100 and triple-quadrupole mass spectrometer (Micromass Quattro Ultima triple-quadrupole MS;Micromass, Milford, MA, USA) were used for the determination of HBCDs, PBCDs, and TBCDs. A ZORBAX Eclipse XDB-C18 column (150 mm, 2.1 mm, 3.5 µm) was used to chromatographic separation of HBCDs and its degradation products. The mobile-phase A (20:50:30 water/methanol/acetonitrile) and B (70:30 methanol/acetonitrile) at a flow rate of 200 uL/min were applied. The MS/MS analysis was performed using negative electrospray ionization (ESI) with multiple reactions monitoring (MRM) mode. α-, β-, γ-HBCD isomers, PBCDs, and TBCDs were determined by MRM transition of m/z 640.7 → 79, m/z 560.8 → 79, m/z 480.4 → 79, respectively. Concentrations of HBCDs in the sediments were calculated using relative response factors (RRFs) for respective target compound. Because of the absence of labeled-standards for quantification of PBCDs and TBCDs, semiquantitative estimating method using the average response factor for α-, β-, γ-HBCDs was applied in this study.

Results and discussion

Total HBCD concentrations (sum of α-, β-, and γ-HBCD) in river sediments are summarized in Fig. 2.

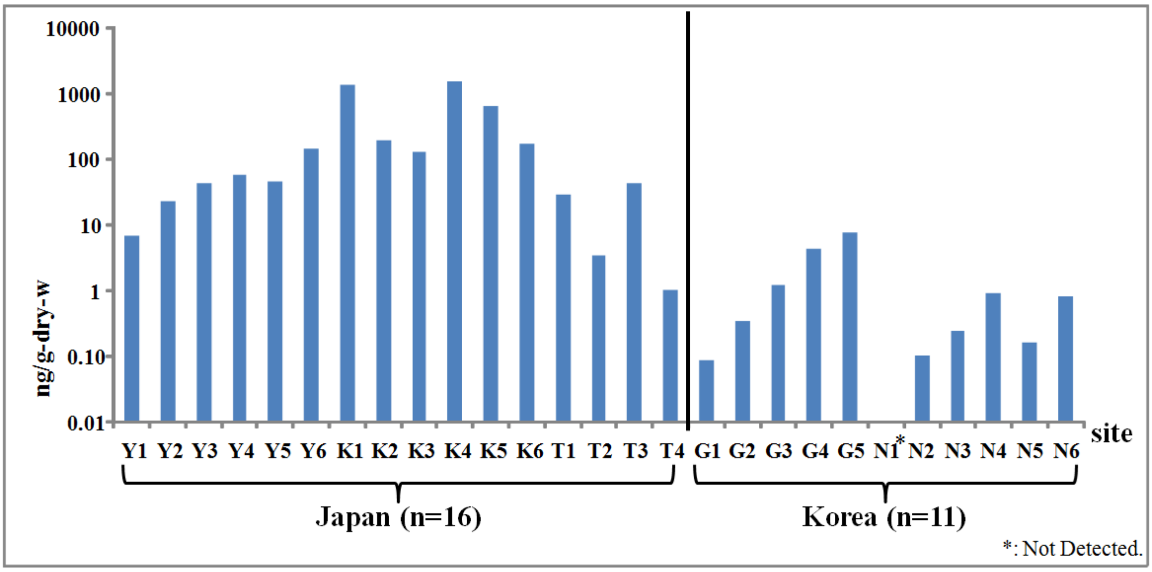

Fig. 2 Spatial distribution of HBCDs from river sediment of Japan and Korea

HBCD level in Japan. HBCDs were detected in all surface sediments collected from the three rivers in Japan, with concentrations ranging from 1.0 to 1500 ng g^{-1} dry weight. The highest concentrations of HBCD were found in the sediment collected from the Kuzuryu River (130 to 1500 ng g^{-1} dry wt.) as a root of emissions from textile wastewater, whereas the lowest concentrations was observed from the Tsurumi River (1.0 to 43 ng g^{-1} dry wt.) with only the domestic/municipal wastewater as the possible source of HBCD. The concentrations of HBCDs from Yodo River flowing near an industrial area producing polystyrene insulation boards which maybe the principal emission source of HBCD were relatively high (6.9 to 150 ng g^{-1} dry wt.). Comparing these results from earlier research[3] which was conducted targeting the same sites, a declining trend was observed in Kuzuryu River and Yodo River indicating a conscious effort by the industry mentioned above to voluntarily lower the amount of their HBCD emission. On the other hand, the concentrations of HBCD in Tsurumi River were relatively low compared with the those reported in the existing study, suggesting HBCD in domestic commodities is little by little, but steadily released through the sewerage. Occurrence of two kinds of degradation products (PBCDs and TBCDs) of HBCD have been known in environmental compartments[4], however only PBCDs were detected (0.40 to 4.5 ng g^{-1} dry wt.) in Yodo (1 sample), and Kuzuryu (6 samples) river sediments, in this study. These levels of PBCDs were higher than those observed for the sediment collected from English Lakes [1].

HBCD level in Korea. HBCDs were detected in 10 surface sediments with concentrations ranging from 0.087 to 7.9 ng g^{-1} dry weight from two rivers in Korea. The highest concentrations of HBCD were found in sediments from Sapgyochun estuary (7.9 ng g^{-1} dry wt.) in Nakdong River, situated in an area where automobile factories are concentrated. It is said that Korea is one of the major consumers of HBCD in the Asia[5]. However, this study revealed that the concentration levels of HBCD in sediments from Korea were low compared to the HBCD levels observed from the earlier research conducted in Korea as well as to the HBCD levels reported for the estuarine and riverine sediments in The Netherlands and UK[6], and for Cinca River sediment in Spain[7]. With respect to the remarkably low concentration of HBCD in Korea, it is assumed that the Restoration project of the Four Major Rivers in Korea (2008~2012) have contributed to the decline of HBCD levels in the estuarine and riverine sediments. However, further studies are needed in view of the very limited monitoring data available regarding the environmental distribution of HBCD in Korea. As for the degradation product of HBCD, neither PBCDs nor TBCDs were detected at any sampling locations in Korea.

Setereoisomeric profile of HBCD. Fig. 3 shows the relative composition ratio of three HBCD isomers (α-, β-, γ-HBCD) in all samples of Korea and Japan. γ-HBCD was predominant in all sediment samples indicating that stereoisomeric profile of HBCD in sediment was similar with that of commercial HBCD formulation. However, detailed distribution ratio of the three isomers differed depending on the site when compared with commercial HBCD's ratio (75–89% γ-HBCD, 10–13% α-HBCD, and <0.5–12% β-HBCD, respectively[8]) suggesting a different composition ratio based on the processing activity of HBCD (e.g. polystyrene and textile industry) and its stereoisomeric selectivity in aquatic environment. Further research about HBCD stereoisomeric composition in different source of HBCD is highly recommended.

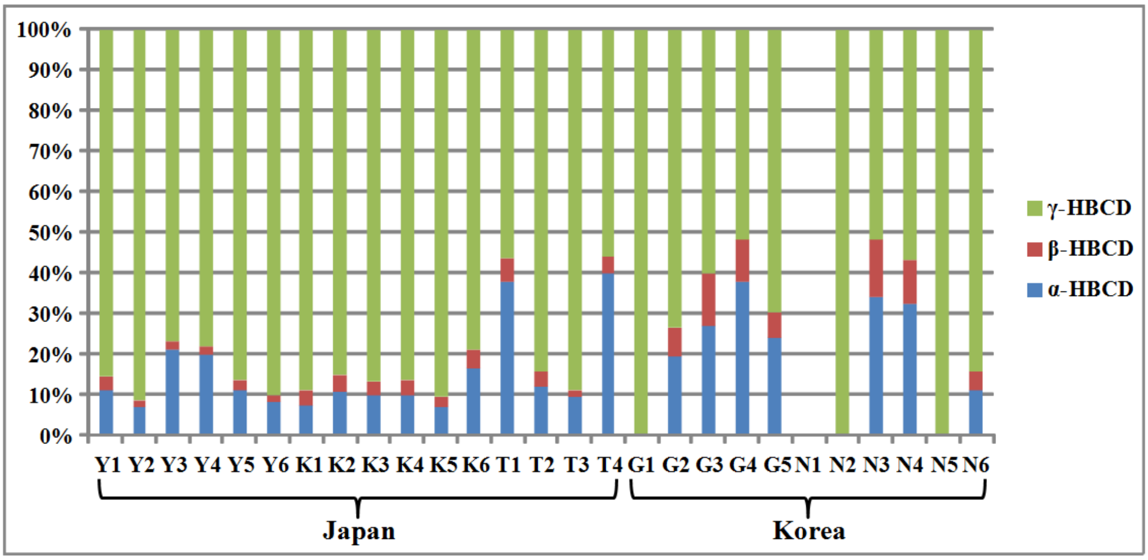

Fig. 3 Isomer distribution ratio of HBCD in this study

Acknowledgements

The sampling in this study was financially supported by Yokohama National University, International Environmental Leaders Program in Sustainable Living with Environmental Risks funded by the Strategic Funds for the Promotion of Science and Technology, Japan. Moreover, this study was supported by the Environment Research and Technology Development Fund of the Ministry of the Environment, Japan (C-1003; “Environmental Risk Minimization Method Based on Lifecycle Risk Assessment and Alternative Assessment for Persistent Organic Pollutants, such as HBCD, in Products”).

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