SPATIAL DISTRIBUTION OF HBCD IN JAPANESE RIVER SEDIMENT AND ITS SOURCE

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Abstract

We investigated the distribution of HBCD in the Japanese river sediment and compared them with the estimated concentration. High concentrations of HBCD were detected in the Japanese river, which receives the textile wastewater at concentrations of 134-2061 ng/g. This contrasts with the results from the Japanese urban river, where HBCD concentrations (0.8-4.8 ng/g) were comparable to those in the urban river from other countries. The median of the observed HBCD concentrations were close to those estimated from the fate model. These results demonstrate the importance of considering the source contribution of HBCD to aquatic environment.

Introduction

The increasing number of reports have shown the environmental distribution of hexabromocyclododecanes (HBCDs) in Europe[1,2], the U.S.A[3] and Asia[4, 5]. HBCD has been detected in various environmental compartments such as riverine sediment, sewage sludge from municipal sewage treamtment plant and house dust [6]. Potential emission sources of HBCD include production, manufacture (industrial use), product use (private use of consumer product) and disposal. The highest concentrations in suspended particulate matters (up to 1700 ng/g dry weight) were measured downstream of HBCD production sites and of industrial users of HBCDs, whereas low concentrations (<10 ng/g dry weight) were found at sites without known sources of HBCDs[6]. These result imply that HBCDs in the environment has originated from a number of different pathways.

In Japan, the market demand in 2005 was estimated to be 2,600 tones for HBCD [7]. It is reported that Asian countries account for 20% of the global HBCDs consumption in 2001 and the domestic demand has been increasing every year. The annual domestic production of HBCD is presently assumed to be less than 1000 ton, whereas the amount of import HB CD is two or three times higher. In the industrial activity, the use of HBCD was divided into polystyrene as insulation board and textile and thus some portion of HBCD contained in materials was transferred to the use phase. Among application pattern in HBCD, polystyrene as insulation board make up by far the most important component of HBCD consumption (80% in the present year). The application areas, textiles/furniture (20% each) is less important. This means that there are potential inputs of HBCD through life cycle (i.e., from production to disposal) waste. In Japan, monitoring studies for HBCD have been performed, mainly in surface sediment from urban coastal zone (i.e., Tokyo Bay) with concentrations between 0.056 and 2.3 ng/g dry wt[4]. So far, however, wide-scale monitoring of HBCD not only in close proximity of the sources but also urban rivers has not been reported. Furthermore, concentrations of HBCD detected in the environment vary among areas and countries depending on the consumption and use of HBCD. For a reliable assessment, it would be necessary to perform a more detailed study aiming at the identification of its sources and quantification of emissions.

In this study, we investigated the distribution of HBCD in sediment from several rivers. The investigation aimed at recognizing different input sources, i.e., industrial wastewaters and municipal wastewaters. Based on the measured concentrations and the estimated source profile, a simple model calculation has been conducted. The objective of this work was to determine the source contribution of HBCD to aquatic environment. The obtained results should provide a basis for assessing their potential environmental risk.

Materials and Methods

Site/description. The sampling locations were selected to cover the locations near industrial activities (i.e, HBCD production, polystylene and textile factories) and the locations for non industrial activities of HBCD. The samples were collected up- and down-stream from possible point sources. River sediment samples were collected at four locations in the Tsurumi River, which runs through the Tokyo metropolitan area, Japan in October 2008. The Tsurumi River catchment has a drainage basin of 235 km^2 and a population of 1.8 million, but no industrial activities for HBCD around sampling locations. The river is heavily influenced by sewage treatment plants: secondary effluent accounts for more than half of the river water in period of normal flow. In addition, six samples were taken from the Yodo River in November and December 2008. The river has a population of 11 million in the 8240 km^2 drainage basin. As impacted sites from textile factory, sediment samples were collected at eight locations in the Kuzuryu River and one in branch for the Kuzuryu River, which has 0.66 million with 2936 km^2 drainage basin in the catchment in November and December 2008. It flows through Fukui prefecture, Japan. There are HBCD-processing factories (i.e., compound factory) and textile factories along the river.

Analysis and Method Validation. After spiking $^{13}C_{12}$-γ -HBCD, two hundred milligrams of freezed dried sediment were extracted by Accelerated Solvent Extraction (ASE) on a Dionex 200 instrument with dichloromethane. Column cleanup and fractionation was performed packed with 100% activated silica gel. The samples were eluted with 80 mL n-hexane/ dichloromethane 95:5 and 100 mL of n-hexane/dichloromethane 75:25 (HBCD faction). HBCD with d_{18}-γ -HBCD were separated by liquid chromatography/tandem mass spectrometry (Micromass Quattro Ultima triple quadrupole MS; Micromass, Manchester, UK) for the determination. Analytical precision was examined through four replicate analyses of two hundred milligrams of the Tsurumi River. The relative standard deviations of HBCD were less than 10%. The recoveries of spiked standards ranged between 68% and 93%. The limit of quantification was 0.1 ng/g.

Model calculation. To examine the region-to-region differences the ChemCAN model (version 6.00), which describes the fate of a chemical in a region, assuming steady-state, or Level III, conditions in the environment, was selected as the model platform in this study. For physico-chemical property of HBCD, same values were added to target area (i.e., three Japanese rivers). Information of region parameter such as surface area, was selected from the data from each river catchment. Emission rates for HBCD to aquatic environment in three rivers were extrapolated from the estimation data based on substance flow analysis. In this study, we have not considered about the input from non point source. Input of municipal wastewater were considered for the Tsurumi River and the Yodo River catchment. For the Kuzuryu river, the input from textile wastewater were added.

Results and Discussion

Distribution of HBCD in Japanese river sediment. HBCD concentrations in river sediments were summarized in Table.1. Significant concentrations of total HBCD, i.e., sum of α-,β- and γ-HBCD, were detected at all river sediments collected from three rivers, with concentrations ranging from 0.8 to 2061 ng/g. The freshwater sediment monitoring demonstrated that HBCD are widely distributed in the riverine environments in Japan. The concentration of HBCD in the Tsurumi river, which are representative as urban river was comparable to those in the urban river from U.S.A[3] and Sweden[2]. The Tsurumi river is highly influenced by sewage effluent, which comprises more than 50% of the river water, and has no industrial activities of HBCD in its catchment. To confirm the occurrence of HBCD in municipal wastewater treatment plant in Japan, we analyzed HBCD in wastewater treatment plant, which receives no industrial effluents along the Tsurumi river. The analyses were performed on flow- proportional composite samples.We detected HBCD with concentrations of 48 ng/g in raw influent, and 6 ng/g in secondary effluent, which showed significantly lower concentrations than those of raw influent. Our analyses suggest that the effective removal processes during treatment have been occurred because higher HBCD concentrations were found at activated sludge with concentrations of 168 ng/g. Thus, the less input of (small but a significant amount of) HBCD in the effluent might be contributor to urban river environment with no HBCD related industry.

The highest concentrations of HBCD were found in sediments from the Kuzuryu river, whereas the concentrations in the Tsurumi river were 2 order of magnitude lower than those in the Kuzuryu river. No decreasing trend was observed from upstream to downstream (i.e., coastal zone). The highest concentrations in SPMs (up to 1700 ng/g dry weight) were measured downstream of HBCD production sites (Rivers Skerne and Tees, U.K.; Western Scheldt and Scheldt basin, Belgium) and of industrial users of HBCDs (River Viskan, Sweden,Ref; River Cinca, Spain)[8]. Our results in Kuzuryu river were good consistent with those concentrations range. Because a population in the Tsurumi river (1.1 million) and the Yodo river (11 million) is higher than those of Kuzuryu river (0.6 million), suggesting less input of municipal sewage, the concentrations difference can be explained by different inputs of HBCD. In the Kuzuryu river, more than ten textile industry, which treats HBCD as brominated flame retardants is mainly located along the river. The major waste water effluents

Table.1 concentrations of total HBCD in Japanese river sediment

River	Number of sample	Total HBCD (ng/g)
R. Tsurumi	4	0.9-4.8
R. Yodo	6	7.6-81
R. Kuzuryu	8	134-2061

from these industries are treated by local sewage treatment plants, whose effluents go to the river Kuzuryu. On the hand, sewage-derived contaminants, including natural hormones and phenolic endocrine-disrupting chemicals have been detected at trace amounts, which have less concentration than those of Japanese urban rivers. These data suggest that the main contributor to the Kuzyuru river are the effluent from textile industry.

HBCD diastereomeric pattern. Figure 1 shows the relative compositions of HBCD at each Japanese river. The HBCD diastereomeric pattern in most sediment samples. The stereoisomeric profile of HBCDs in most sediment samples was found to be similar to that of commercial HBCD formulations, with γ-HBCD being the most abundant stereoisomer. However in some locations, the contribution of β-HBCD was higher than in the technical mixture. At present, it is not clear whether this difference in the composition of the HBCD stereoisomers between some sediments and technical HBCDs is caused by thermal isomerization during the processing of HBCDs or by stereoisomer-specific processes in the environment.

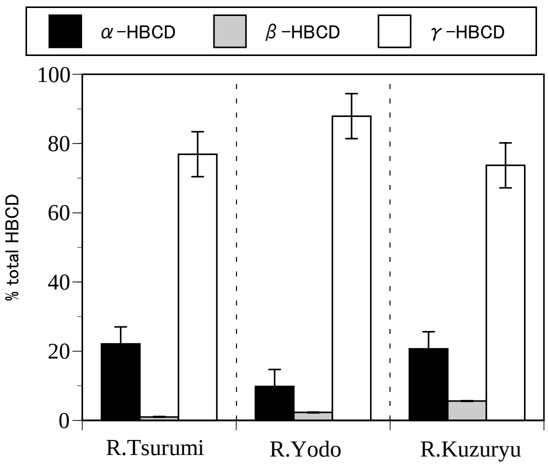

Figure 1 Stereoisomer distributions of total HBCD in river sediment

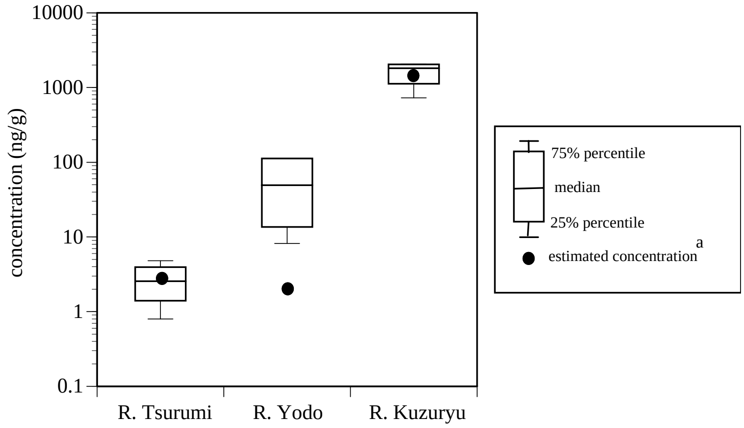

Figure 2 HBCD concentrations in river sediment. [a] estimated HBCD concentration by ChemCAN as described in the text.

Comparison of predicted and measured HBCD concentrations in river sediment. To verify the source of HBCD, we estimated the HBCD concentration in each river based on the input from each source. The input from textile wastewater and municipal wastewater have been included in the Kuzuryu river. For the Tsurumi river and the Yodo river, only the input from municipal wastewater have been incorporated. Figure 2 illustrates the measured concentrations in the river sediment and additionally, shows the predicted environmental concentrations in the sediment estimated by using chemCAN. For the Kuzuryu river and the Tsurumi river, a very good agreement was obtained between the measured median concentrations and calculated concentrations. Our comparison means that widespread inputs of textile wastewater to the Kuzuryu River would be a main contributor. On the other hand, the estimated concentrations from Yodo river are less than 25th percentile of the measured concentrations. The difference might be inferred by the additional input such as the wastewater from polystyrene and/or textile factory. So far, there have been only limited data on the environmental distribution of HBCD based on the source profile of regional scale. It is necessary to further study the comparison between measured concentrations and estimated concentrations.

Acknowledgments

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