Chemosphere 110 (2014) 78–84

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Distribution and pollutant load of hexabromocyclododecane (HBCD) in sewage treatment plants and water from Japanese Rivers

Makiko Ichihara [a,*], Atsushi Yamamoto [a], Koh-ichi Takakura [a], Naoya Kakutani [a], Miki Sudo [b]

[a] Osaka City Institute of Public Health and Environmental Sciences, 8-34 Tojo-cho, Tennoji-ku, Osaka 543-0026, Japan
[b] Department of Biological Resources Management, School of Environmental Science, The University of Shiga Prefecture, 2500 Hassaka-cho, Hikone, Shiga 522-8533, Japan

HIGHLIGHTS

- Mean annual HBCDs detected in river water in Japan ranged from 0.19 to 14 ng L^{-1}.
- HBCDs detected in sewage influent ranged from 16 to 400 ng L^{-1}.
- HBCDs detected in sewage effluent ranged from 0.39 to 12 ng L^{-1}.
- Over 90% of HBCDs were removed from wastewater in the sewage treatment plant.
- Approximately 15 kg $year^{-1}$ of HBCDs flows into Osaka Bay from the study area.

ARTICLE INFO

Article history:
Received 15 November 2013
Received in revised form 22 February 2014
Accepted 21 March 2014
Available online 22 April 2014

Handling Editor: Gang Yu

Keywords:
HBCD
Brominated flame retardant
River water
Sewage influent
Sewage effluent
Pollutant load

ABSTRACT

Hexabromocyclododecane diastereoisomers (α-, β-, γ-, δ-, and ε-HBCD) were investigated in river water, sewage influent, and sewage effluent from the Yodo River basin, Japan. The mean annual values of HBCDs ranged from 0.19 to 14 ng L^{-1} in river water. We observed that the concentrations of HBCDs in the brackish water area were low compared with that in the fresh water area. It was implied that, when the flow of the river stagnated in the estuarine area, HBCDs settled with suspended matter because of their hydrophobic character. In the sewage treatment plants, HBCDs ranged from 16 to 400 ng L^{-1} in sewage influent, whereas they ranged from 0.39 to 12 ng L^{-1} in sewage effluent. Over 90% of HBCDs were removed from the wastewater in the sewage treatment plants. By using these results, we estimated the pollutant load of HBCDs that flows into Osaka Bay from the study area. It was estimated that approximately 15 kg of HBCDs flow into Osaka Bay from the study area in a year. This value is five orders of magnitude lower than the 2010 market demand for HBCDs (3019 metric tons) in Japan.

1. Introduction

Hexabromocyclododecane (HBCD) is the principal brominated flame retardant used to inhibit flammability in combustible products. HBCD is applied primarily in extruded and expanded polystyrene foams that are used as thermal insulation in buildings, and secondarily in upholstery textiles in Japan (Managaki et al., 2012). Although recent global annual production estimates for HBCD are not available (Marvin et al., 2011), the world market demand for HBCD was 16700 metric tons in 2001; 57% of the amount was consumed in Europe, followed by Asia (23%) and North America (17%) (Ueno et al., 2006). In Japan, HBCD was used as an alternative for penta- and octa-brominated diphenyl ethers (PBDEs) because of the voluntary limitations on the use of PBDEs in the 1990s. Therefore, until recently, its usage has increased (Managaki et al., 2012) and the 2010 market demand for HBCD in Japan was estimated to be 3019 metric tons (Ministry of Economy, Trade and Industry, Japan, 2012).

At present, HBCD has been detected worldwide in various environmental media and biota, such as air, water, river sediments, wildlife, foodstuffs, house dust, and so on (Remberger et al., 2004; Covaci et al., 2006; Marvin et al., 2006; Minh et al., 2007; Harrad et al., 2009; Takigami et al., 2009; Nakagawa et al., 2010). Recently, the occurrence of HBCDs in the environment has drawn increasing public attention due to their persistency, bioaccumulation, and toxic effects on humans and wildlife (Arnot et al., 2009; Marvin et al., 2011). In 2013, HBCD was designated as Persistent Organic Pollutants (POPs) under the United Nations Environmental Policies (UNEP) Stockholm Convention. In Japan, some industry

* Corresponding author. Tel.: +81 6 6771 3199; fax: +81 6 6772 0676.
E-mail address: mak-ichihara@city.osaka.lg.jp (M. Ichihara).

http://dx.doi.org/10.1016/j.chemosphere.2014.03.074
0045-6535/

organizations such as the Extruded Polystyrene Foam Industry Association and the Japan Textile Federation have already started to voluntarily decrease its usage (Ministry of Economy, Trade and Industry, Japan, 2010). However, HBCD is used in long lifetime products. Furthermore, this compound is an additive flame retardant, and is not covalently bonded to the material. Therefore, HBCD may migrate out of products into the environment during use or after disposal (Managaki et al., 2012). Thus, environmental monitoring data is necessary for adequate risk assessment and management. In particular, it is noted that little is known about HBCDs in fresh water environments worldwide (Harrad et al., 2009).

Therefore, in this study, we have investigated the occurrence and spatial distribution of HBCD in water from the Yodo River Basin, Japan. We have also investigated the occurrence of HBCD in sewage treatment plants (STPs) in the study area. Our specific objectives were to reveal the abundance of HBCDs in Japanese rivers, and estimate the pollutant load of HBCD in water from an urban area. The annual discharge amounts of HBCD into the water environment were calculated using required monitoring data and flow rate. We analyzed water samples by LC-MS/MS for the relative distribution of α-, β-, γ-, δ-, and ε-HBCD. To our knowledge, this study represents the first report on HBCD levels in river water in Japan.

2. Materials and methods

2.1. Sampling

The study area and sampling sites are shown in Fig. 1. The Yodo River Basin is located in western Japan. Its watershed includes the metropolitan areas of Osaka, Kyoto, and Shiga Prefectures with an associated combined population of roughly sixteen million people. Forests, paddy fields, and city areas spread in the upper reach of the Yodo River Basin. In contrast, the watershed of the lower reach is highly urbanized and industrialized. Approximately 100% of the population is served by sewer systems, with 12 STPs in the study area (Construction Bureau of Osaka City, Japan, 2013), and we investigated the sewage influent and effluent in these STPs. The water quality of the study areas is affected by urban and industrial activities along the upper reach of the river. Therefore, the study area has various problems associated with water contamination by chemicals such as polychlorinated dibenzodioxins and perfluorooctanoic acid (Sakiyama et al., 2005; Takagi et al., 2008).

Water flow in the study area is dominated by tidal action. Therefore, water was sampled at ebb tide, when water flow is in the downstream direction, every couple of months during July 2012–May 2013. The amounts of rainfall within 2 days before sampling were over 20 mm in September 2012 and November 2012. Except on these days, water flow was ordinary water discharge. The concentrations of α-, β-, γ-, δ-, and ε-HBCD, suspended solids (SS), and chloride ions of the samples were measured. Sewage influent and sewage effluent from 12 STPs (STP1–12) were sampled in December 2012. These samples were taken as 24-h flow proportional samples.

2.2. Chemicals

Native (α and β) HBCD were purchased from Accu Standard, Inc. (New Haven, CT, USA). Native (γ) HBCD and ^{13}C-labeled (α, β, and γ) HBCD were purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA). Native (δ and ε) HBCD and deuterated (d_{18}-γ) HBCD were purchased from Wellington Laboratories Inc. (Ontario, Canada). Dichloromethane, n-hexane, and methanol were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Acetone was purchased from Kanto Chemical Co. Inc. (Tokyo, Japan).

2.3. Sample preparation

The sample volumes of the river water, sewage influent, and sewage effluent used in the experiments were 5 L, 500 mL, and 5 L, respectively. A water sample was spiked prior to extraction with 25 ng each of ^{13}C-labeled (α, β, and γ) HBCD as a clean-up spike. Sewage influent was spiked with 100 ng each of these. The spiked sample was simultaneously passed through a solid extraction disk (Empore Disk C18; 3 M, USA) and a glass fiber filter (1 μm pore size, GA100; Advantec Co. Ltd., Japan) of 90 mm diameter at a flow rate of approximately 150 mL min^{-1}. The disk and filter were washed with 20 mL of methanol and 200 mL of reverse osmosis (RO) water prior to extraction. After extraction, the glass sample bottle and glass funnel were washed with 60% methanol and the wash solution was also passed through the disk and filter.

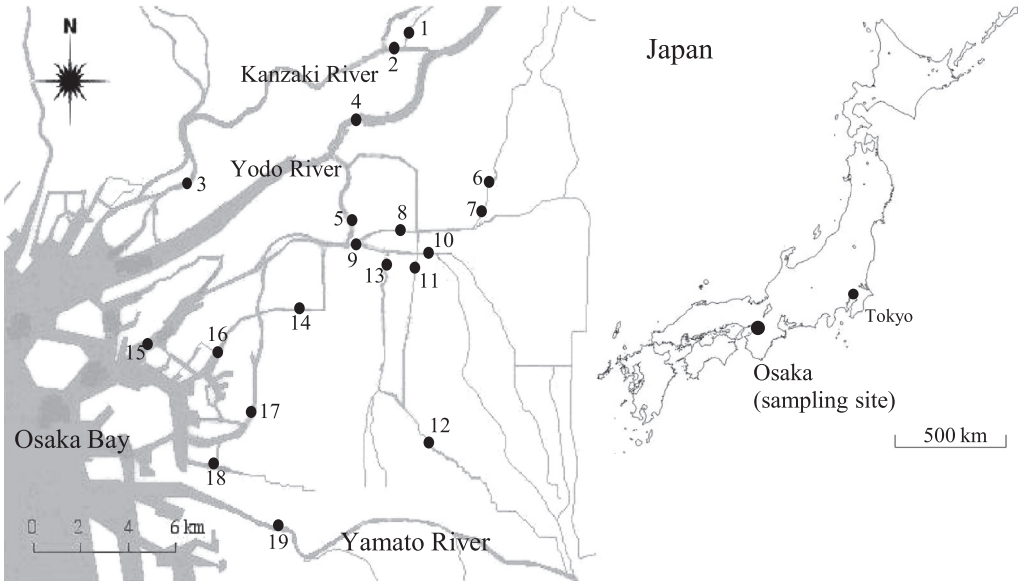

Fig. 1. Locations of sampling sites.