Marine Pollution Bulletin xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Determination of heterocyclic brominated flame retardants tris-(2, 3-dibromopropyl) isocyanurate and hexabromocyclododecane in sediment from Jiaozhou Bay wetland

Ling Wang [a,*], Quansheng Zhao [a], Yanyan Zhao [a], Yinghua Lou [a], Minggang Zheng [b], Yue Yu [a], Mengyuan Zhang [a]

[a] Environmental Science and Engineering, Qingdao University, Qingdao 266071, China
[b] Research Center for Marine Ecology, The First Institute of Oceanography, State Oceanic Administration of China, Qingdao 266061, China

ARTICLE INFO

Article history:
Received 16 October 2015
Received in revised form 2 August 2016
Accepted 4 August 2016
Available online xxxx

Keywords:
Hexabromocyclododecane (HBCD)
Tris-(2,3-dibromopropyl) isocyanurate (TBC)
Jiaozhou Bay wetland
Sediment

ABSTRACT

The concentration and distribution of tris-(2,3-dibromopropyl) isocyanurate (TBC) and the three isomers of hexabromocyclododecane (HBCDs) were analyzed in the sediment of Jiaozhou Bay wetland in China. The concentrations of TBC and the three isomers of HBCDs (α-HBCD, β-HBCD, γ-HBCD) were in the ranges of 1.20 to 8.76, 1.03 to 5.69, 1.13 to 5.46, and 1.18 to 15.04 $ng \cdot g^{-1}$ dw (dry weight), respectively. γ-HBCD was the predominant congener with an average proportion of 52.42% of ΣHBCDs, average inventory of HBCDs was about 93.53 $ng \cdot cm^{-2}$. Depending on the function of wetland, the concentration of HBCDs tended to decrease as the distance to the Xiaojianxi refuse landfill increased. Compared with previous research studies, the concentration of TBC and HBCDs in the Jiaozhou Bay wetland was at a relatively high level. Therefore, more attention should be paid to TBC and HBCDs on account of their persistent impact on human health and the environment.

Brominated flame retardants (BFRs) have been widely used in plastics, textiles, synthetic fibers, and other materials to decrease flammability (de Wit, 2002; Alaee et al., 2003). However, adverse effects on the environment and human health have been raised due to extensive use. Many BFRs, such as polybrominated diphenylethers (PBDEs) and penta- and octa- BDE mixtures (Costa and Giordano, 2007; Covaci et al., 2006), have been listed as persistent organic pollutants (POPs) in the Stockholm Convention. As novel BFRs, tris-(2,3-dibromopropyl) isocyanurate (TBC) and hexabromocyclododecane (HBCD) have been found in household products, and their usage in daily life is steadily increasing (Ruan et al., 2009; Lam et al., 2009). TBC is a novel heterocyclic BFR with high thermal stability, low viscosity, low tendency towards discoloration, and low corrosivity (Ruan et al., 2009). Its octanol-water partitioning coefficient (log Kow) is 7.37, which means that it can be easily accumulated in sediment and has the potential to be bioaccumulated in wildlife. TBC has been added in polyolefin, polyphenyl alkenes, unsaturated polyester, synthetic rubber, and fibers with a proportion of 5% to 10% (Xiong, 1999). In 2009, TBC was found in the sediment, water, and biota samples for the first time in Hunan Province, China, and the concentration has reached as high as 6000 $ng \cdot g^{-1}$ dw in sediment (Ruan et al., 2009). It has been found in various environmental media, such as in mollusks in the Bohai Sea (Zhu et al., 2012), farm soil in a peri-urban region of Beijing (Wang et al., 2013), and surface soil in an industrialized region of East China (Tang et al., 2014). Data on the worldwide production of TBC over the past decade is not available; however, the annual production of TBC in China is about 500 tonnes. As PBDEs has been banned in the Stockholm Convention, the output of TBC may show a growing tendency with the rapid industrialization of China.

HBCDs are mainly composed of three diastereoisomers: α-HBCD, β-HBCD, and γ-HBCD (Heeb et al., 2005), and it has been reported that γ-HBCD can be transformed to α-HBCD when the temperature is above 160 °C (Barotini et al., 2001). As the third most widely used BFR (Covaci et al., 2006; Lam et al., 2009; Law et al., 2003) following PBDEs and tetrabromobisphenol-A (TBBPA), HBCDs have been widely applied as an additive BFR in building materials, upholstery textiles, as well as electrical household equipment in recent years (Alaee et al., 2003; Marvin et al., 2011). China is one of the main manufacturing countries of HBCDs. In 2007, the product capacity of HBCDs reached 7500 metric tonnes (Luo et al., 2010) in China. As an additive BFR, HBCDs can be easily released into the environment during production, use, disposal, and recycling processes (Li et al., 2013). HBCDs had been found to be ubiquitous in biota, from zooplankton to polar bears and humans (Johnson-Restrepo et al., 2008; Meng et al., 2012; Tomy et al., 2008). Studies focused on HBCDs in sediments were mainly conducted in Scandinavian countries (Remberger et al., 2004; Thomsen et al., 2007), United States (Hoh and Hites, 2005), and major river drainage basins in China (Li et al., 2013). Also, HBCDs had been shown to disrupt the functioning of thyroid hormone systems in wildlife, along with causing oxidative damage to lipids, proteins, and DNA in animals (Marvin et al., 2011). Moreover, HBCDs were listed as a persistent organic pollutant at the 6th meeting of the Stockholm Convention on Persistent Organic

* Corresponding author at: Environmental Science and Engineering, Qingdao University, Qingdao 266071, China.
E-mail address: 195134679@qq.com (L. Wang).

http://dx.doi.org/10.1016/j.marpolbul.2016.08.013
0025-326X/

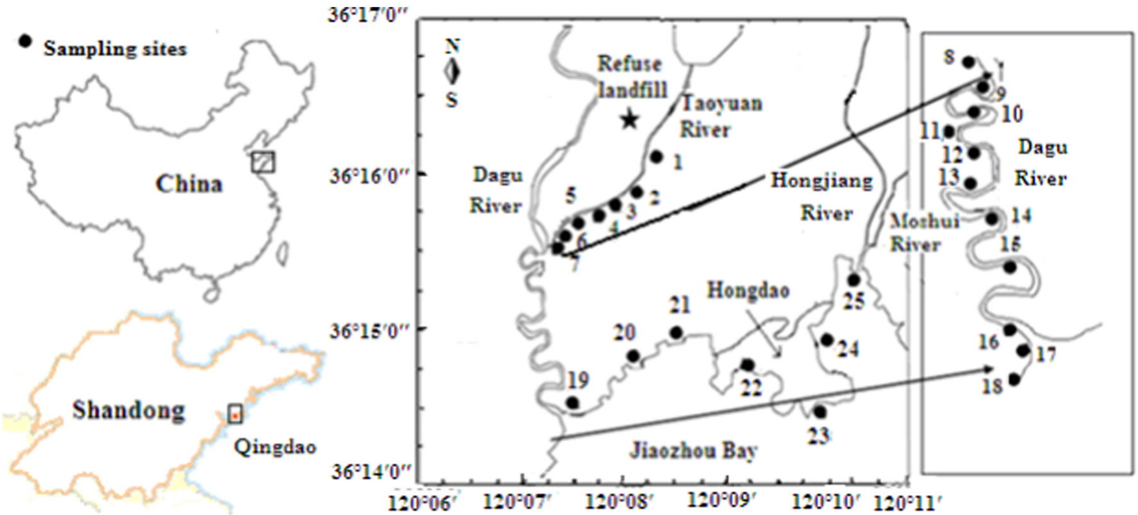

Fig. 1. Distribution of sampling location sites in Jiaozhou Bay wetland.

Pollutants (UNEP, 2013), which makes the occurrence of these pollutants to be a global concern.

Sediment is one of the important sinks and reservoirs of this kind of pollutant. The investigation of contamination in sediment can reveal the historical input processes of pollutants and provide important information for general contamination status in wetland regions (Li et al., 2013). Wetlands are natural filters that help slow down the flow of water. When the water with poison and impurities (pesticides, domestic sewage, and industrial emissions) flows through the wetlands, the slow flow rate is conducive to the precipitation and removal of toxic substances and impurities. Therefore, the wetland can be used as a natural treatment field for the purification and reduction of pollutants. However, systematical studies are still unavailable on TBC and HBCDs in sediments from any isolated wetland.

In this study, sediment samples were collected from Jiaozhou Bay wetland in Qingdao, Shandong Province, China. As the largest estuary bay wetland in the Shandong Peninsula, Jiaozhou Bay wetland is the most industrialized and urbanized region with a large number of industries. In addition, there is a significant amount of household refuse in ditches around the region. For example, since 2003, the Xiaojianxi refuse landfill has had about 1710 tonnes of processed garbage added every day. Therefore, the Xiaojianxi refuse landfill may be the main source of pollution in the local area. It provides an ideal model to investigate the contamination and spatial distribution of TBC and HBCDs in sediments from wetlands. Moreover, the inventory of total HBCDs in sediment from Jiaozhou Bay wetland was also estimated in the study.

Fig. 1 is a map of the sampling sites, which were mainly located in two rivers, Taoyuan River (Sites 1 to 7) and Dagu River (Sites 8 to 18), and an intertidal zone (Sites 19 to 25). Taoyuan River and Dagu River come together in the downstream of Site 7. In this study, all samples were collected from the Xiaojianxi refuse landfill to Jiaozhou Bay intertidal, which is located in Qingdao, Shandong Province, China. Samples were collected by spade (preconditioned with hexane and deionized water) at a depth of about 10 cm. Three parallel samples were collected at each site. After collection, the samples were immediately wrapped in several layers of aluminum foil in sealed plastic bags to avoid being irradiated by light. Then, the samples were placed in an icebox before being transported to the laboratory and stored in −20 °C until analysis.

The frozen samples were first dried in a vacuum freeze dryer for at least 48 h. Then, the samples were ground into a powder, sieved through 100 mesh stainless steel, and homogenized. 1 g of dried sample was mixed with 15 g anhydrous sodium and spiked with surrogate standards native 10 ng of [$^{13}C_{12}$]-γ-HBCD. The mixed homogenized sediment samples were extracted by Soxhlet using 160 mL hexane/DCM (1:1; v/v) for 24 h. The extract was then concentrated to about 1 mL using a rotary evaporator. The concentrated mixtures were loaded on the column packed with 5 g activated silica gel and 1 g anhydrous sodium sulfate from bottom to top. After loading, the extract was eluted with 38 mL *n*-hexane followed by 60 mL DCM. The final elutuate was then concentrated to 2 mL and evaporated to incipient dryness under N_2 stream, and reconstituted with 200 μL of methanol/water (8:2). Finally, 10 ng of [$^{2}H_{18}$]-γ-HBCD was added as injection internal standard for LC-MS/MS analysis. Instrument analysis was performed on a Waters ACQUITY UPLC-TQD system (Waters, Milford, MA) using a Halo C_{18} reversed-phase chromatographic column (2.1 mm × 50 mm, 1.7 μm, Waters, USA).

The following are the results of the experiment. The concentration of TBC in the 25 sediment sites is summarized in Fig. 2, and the concentration of α-HBCD, β-HBCD, and γ-HBCD in the 25 sediment sites are summarized in Fig. 3.

As shown in Fig. 2, the concentration of TBC in the sediment was in the range of 1.20 to 8.76 ng·g^{-1} dw, and the mean concentration was 3.60 ng·g^{-1} dw. It is predicted that the physical-chemical properties of TBC are similar to HBCD (Lam et al., 2009). However, the data of TBC in the environment is limited (Ruan et al., 2009; Feng et al., 2010). In a similar study conducted on TBC in farm soil in a peri-urban region in 2010 (Wang et al., 2013), the concentration ranged from

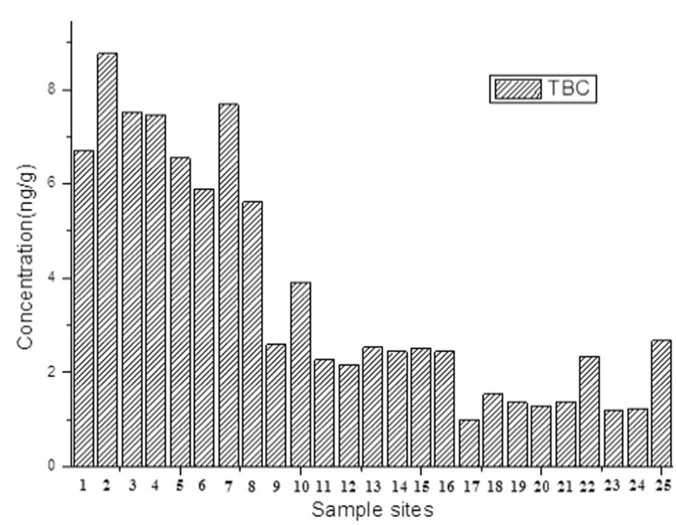

Fig. 2. Concentration of TBC in sediment from Jiaozhou Bay wetland.