

Levels of Brominated Flame Retardants in Sediments and Their Bioaccumulation Potential in Biota from Jakarta Bay and Its Surroundings, Indonesia

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Abstract—The present study determined concentrations of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) in mussels, fish and surface sediments from Jakarta Bay and its surroundings, Indonesia to understand their levels and distribution in sediment and their bioaccumulation in biota. Concentrations of PBDEs and HBCDs in sediments varied widely depending on sampling locations, ranging from 0.15–130 ng/g dry wt. and <0.020–5.9 ng/g dry wt., respectively. Highest concentrations of both brominated flame retardants (BFRs) were found at the sampling locations near harbors, industrial and highly populated areas, implicating industrial and human activities as sources of these compounds to the environment. Calculation of mussel-to-sediment and fish-to-sediment ratios based on concentrations of BFRs in biota as lipid wt. basis and in sediment normalized to organic carbon, showed values >1 showing higher concentrations of certain PBDEs (BDE-28, -47, -99, -100, -153, -154) and α -HBCD in mussels and fishes than those in sediments. These results indicate that these compounds are highly transferrable and bioavailable to biota. However, BDE-209 and γ -HBCD (the dominant compounds in sediments) were not detected or occurred in lower concentrations in biota, indicating their low bioaccumulation potential and/or labile nature.

Keywords: PBDEs, HBCDs, concentration, bioaccumulation, sediment, fish, mussel, Jakarta Bay, Indonesia

INTRODUCTION

Environmental contamination by brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) received public attention during recent years due to their persistency, bioaccumulative nature, and possible adverse effects on wildlife and human as those of classical organochlorines. These compounds are used as additive flame

retardants in a wide variety of commercial and household products such as plastics, textiles, and electronic appliances including computers, televisions, etc. Due to their large usage and disposal and physico-chemical properties, they can be found at all the environmental compartments (Hites, 2004; Covaci *et al.*, 2006).

Sediments, particularly estuarine sediments, are one of the major sinks for these contaminants and have large impact on their distribution, transport, and fate in aquatic environments. Therefore, study of sediments is an important step in mapping possible exposure pathways to various aquatic organisms, since contaminants in the sediments may be bioavailable to sediment dwelling organisms (Covaci *et al.*, 2005). The present study determined concentrations of PBDEs and HBCDs in sediment and biota samples from Jakarta Bay (one of the most polluted areas in Indonesia) to understand their levels and distribution in the bay, and bioaccumulation in mussels and fishes.

MATERIALS AND METHODS

Surface sediments and muscle tissues of green mussel (*Perna viridis*), catfish (*Paraplotosus* sp.), perch (*Lutjanus ruselli*), spinefoot (*Siganus javus*) and jawfish (*Johnius vogleri*) were used in this study. Sediment samples were collected from 16 stations (ST-2 to ST-31, ST-A, ST-B and SK-1), mussels from 3 stations (S-2, S-5 and STK-1) and fish from 1 station (STK-1) in Jakarta Bay (Fig. 1). In addition, 10 river sediments from Jakarta City watersheds (RSJ-01–RSJ-08) and up stream Ciliwung River at Bogor (RSB-03 and RSB-05) and 1 pooled of freshwater mussels (*Elongaria oreantalis*) from Kalimalang Canal (RSJ-08) were also used for comparison and understanding their potential sources. All the samples were collected during the period of July–August 2007. Samples were placed in containers, frozen immediately, transported to Japan and kept at -20°C at the Environmental Specimen Bank (*es*-BANK) of Ehime University until chemical analysis.

Analyses of BFRs were conducted according to the method described by Minh *et al.* (2007) for sediments and Xian *et al.* (2008) for biota samples with some modifications. Briefly, prior to extraction, samples were spiked with $^{13}\text{C}_{12}$ -BDEs ($^{13}\text{C}_{12}$ -BDE-3, -15, -28, -47, -99, -153, -154, -183, -197, -207 and -209) and ^{13}C -HBCD (α -, β - and γ - $^{13}\text{C}_{12}$ -HBCD) as a labeled recovery internal standard (LRIS) for measuring the extraction efficiency and correction of analyte concentrations for losses during extraction and clean-up. After extraction and several purification processes, $^{13}\text{C}_{12}$ -labeled BDE-139 and HBCD- d_{18} (α -, β - and γ -HBCD- d_{18}) were added as a labeled instrument performance and matrix internal standard (LIPMIS) to the final solution prior to analysis using gas chromatography with a mass spectrometry detector (GC-MSD) for PBDEs and liquid chromatography with tandem mass spectrometry (LC-MS/MS) for HBCDs, respectively. All the congeners and isomers were quantified using the isotope dilution method to the corresponding $^{13}\text{C}_{12}$ -labeled congeners.

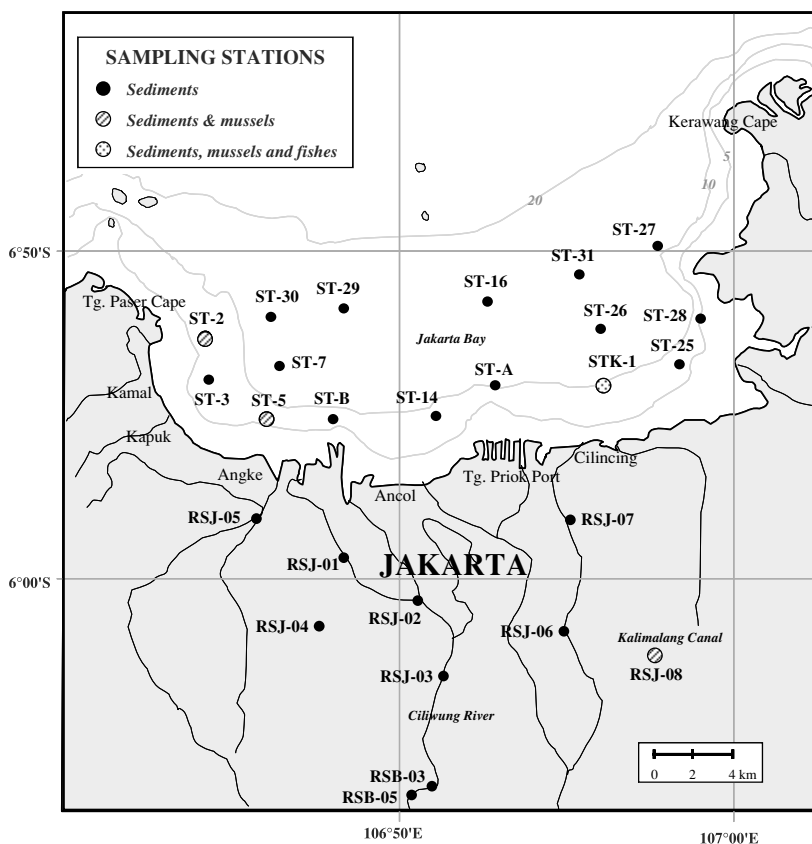


Fig. 1. Map showing sampling locations of sediments and biota.

RESULTS AND DISCUSSION

Occurrence of BFRs

BFRs were detected in sediment and biota samples (Fig. 2), being Σ PBDEs were found higher than Σ HBCDs, probably due to their difference in amount of usage between these two BFRs. Concentrations of total PBDEs and HBCDs in sediments were ranging from 0.15–130 ng/g dry wt. and <0.020–5.9 ng/g dry wt., respectively, whereas in biota from 6.0–42 ng/g lipid wt. and 0.42–30 ng/g lipid wt., respectively. Figure 3 shows distribution of BFRs in sediments from the study area. Highest concentrations of both BFRs were found at the stations in coastal area near harbor (ST-A, ST-5 and STK-1), industrial and highly populated areas (ST-3, ST-5, ST-25, ST-A, STK-1). In particular, high concentrations of BFRs were found in river sediments collected from Jakarta City watersheds (RSJ-01, RSJ-04, RSJ-05 and RSJ-07). Furthermore, BFRs concentration in freshwater

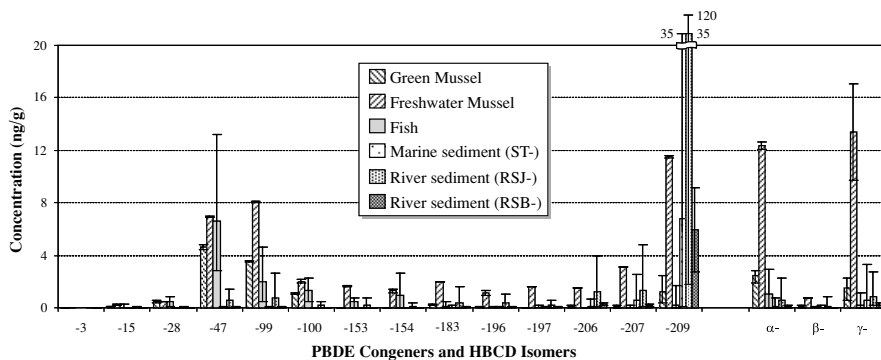


Fig. 2. Levels and profiles of BFRs in sediments (ng/g dry wt.) and biota (ng/g lipid wt.) from Jakarta Bay and its watersheds.

mussels collected from a canal closer to inhabitant of Jakarta City were also higher than that in mussel collected from Jakarta Bay (Fig. 2). These results implicate that industrial and human activities are important sources of these compounds to these aquatic environments and responsible for their higher concentrations in surrounding areas. Significant positive correlation was found between concentration of BFRs and total organic carbon in sediments ($r = 0.79$, $p < 0.05$ for PBDEs, and $r = 0.42$, $p < 0.05$ for HBCDs), suggesting that organic matter plays an important role in transport and trapping of BFRs in the aquatic environment.

Of the PBDEs analyzed, BDE-209 was almost the only congener detected in sediments (more than 73% of Σ PBDEs) (Fig. 2), indicating that the presence of PBDEs in Jakarta Bay environment is mainly caused by Deca-BDE (consist mainly BDE-209) rather than Penta- and Octa-BDE commercial mixtures, which is consistent with the high consumption of Deca-BDE in Asia (Hites, 2004). For HBCDs, γ -isomer was the predominant compound (Fig. 2), corresponding to its commercial formulation (Covaci *et al.*, 2006).

PBDE congener and HBCD isomer profiles in mussels and fishes were significantly different with those in sediments (Fig. 2), which were predominated by lower congeners (mainly BDE-47, -99, and -100) and α -HBCD, respectively. These profiles were generally consistent with the patterns in biota samples (Hites, 2004; Covaci *et al.*, 2006). BDE-209 and γ -HBCD are easily degraded in the environment, leading to the occurrence of lower congeners and more stable compounds, which are then readily to bioaccumulate in biota. The detectable levels of BDE-209 in mussels but not in fish may be due to their filter feeding behavior, which could be associated with the sediments.

Bioaccumulation of BFRs

Deposited sediments often act as a local sink for contaminants, which may

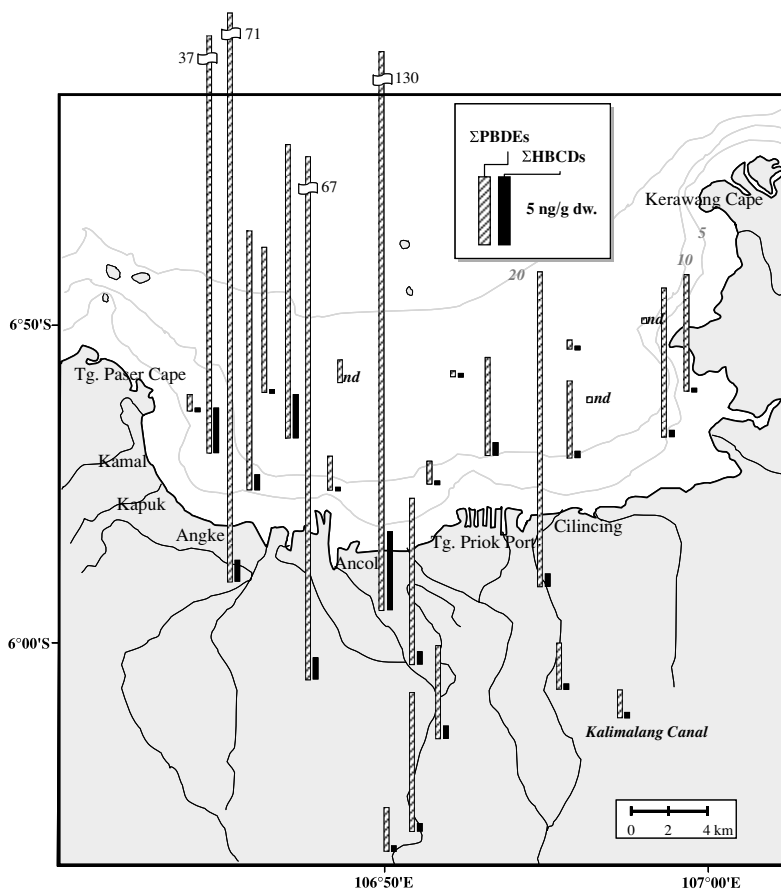


Fig. 3. Distribution of BFRs in sediments from Jakarta Bay and its watersheds.

increase the contaminant exposure for sediment-associated biota that indiscriminately ingest sediment particles while foraging. In this regard, the biota-sediment accumulation factor (BSAF) has been widely used as a measure of net bioaccumulation of chemicals by aquatic organisms (Xiang *et al.*, 2007). Table 1 shows values of BSAF for individual PBDE congeners and HBCD isomers in each biota species taken from station ST-2, ST-5, STK-1 (green mussel), STK-1 (fish) and station RSJ-08 (freshwater mussel). The BSAFs of individual BDE congeners and HBCD isomers for mussels and fishes showed values more than 1 for certain PBDEs (BDE-28, -47, -99, -100, -153, -154) and α -HBCD (Table 1). These results indicate that these compounds are highly transferrable and bioavailable to biota. However, BDE-209 and γ -HBCD (the dominant compounds in sediments) were not detected or occurred in lower concentrations in biota, indicating their low bioaccumulation potential and/or

Table 1. Biota sediment accumulation factors (BSAFs) of BFRs from Jakarta Bay and its surrounding*.

Species	Station	PBDE Congeners												HBCD isomers		
		-15	-28	-47	-99	-100	-153	-154	-183	-196	-197	-206	-207	-209	α -	β -
<i>Perna viridis</i>	ST-2	0.082	>1.0	5.5	>1.0	>1.0	na	>1	0.048	<1	0.023	0.002	0.003	>1	>1.0	0.56
<i>Perna viridis</i>	STK1	0.27	>1.0	8.5	>1.0	na	na	0.10	>1.0	na	<1.0	<1.0	0.002	0.42	>1.0	0.031
<i>Perna viridis</i>	ST-5	0.20	1.1	1.0	0.86	1.4	na	0.052	0.014	0.0085	0.021	0.002	0.005	0.39	0.047	0.068
<i>Elongaria oreantalis</i>	RSJ-08	>1.0	>1.0	2.1	>1.0	>1.0	>1.0	0.60	0.68	0.73	0.12	0.29	0.037	2.6	>1.0	0.33
<i>Paraplatusus sp.</i>	STK1	<1.0	>1.0	6.6	>1.0	>1.0	>1.0	0.15	>1.0	>1.0	<1.0	0.005	<1.0	0.50	>1.0	0.034
<i>Luftjanus raselli</i>	STK1	<1.0	>1.0	13	>1.0	>1.0	>1.0	<1.0	na	na	<1.0	<1.0	<1.0	0.33	na	0.015
<i>Siganus javus</i>	STK1	0.16	>1.0	7.5	>1.0	>1.0	>1.0	0.31	>1.0	>1.0	<1.0	<1.0	0.009	0.10	na	<1.0
<i>Johnius vogleri</i>	STK1	0.71	>1.0	19	>1.0	>1.0	>1.0	<1.0	>1.0	na	<1.0	<1.0	<1.0	0.26	na	<1.0

*BSAFs is ratio between concentration in biota (ng/g lipid wt.) and sediment (ng/g TOC), na = not available (BFRs was not detected in both biota and sediment), BSAFs value >1.0 means BFRs was detected in biota but not in sediment and opposite for >1.0.

labile nature. Generally, BSAF increases from BDE 28 to BDE 100 and subsequently decline from BDE 100 to BDE 209. The decline of BSAFs was partly attributed to steric hindrance that limits large, very hydrophobic organic compounds from penetrating the cellular membranes and to a high affinity of these compounds for carbonaceous geosorbents, such as black carbon, coal, and kerogen in sediments (Xiang *et al.*, 2007).

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