

Bioaccumulation of Brominated Flame Retardants (BFRs) in Different Trophic Level Organisms from Jakarta Bay, Indonesia

Agus Sudaryanto^{1,2,3*}, Adi Slamet Riyadi², Iwan Eka Setiawan², Muhammad Ilyas², Tomohiko Isobe¹, Kwang-Hyeon Chang³, Shin Takahashi³ and Shinsuke Tanabe³

¹ Senior Research Fellow Center (SRFC), Ehime University, Bunkyo-cho 2-5, Matsuyama, Japan.

² Technology Center for Marine Survey, Agency for the Assessment and Application of Technology (BPPT), JL. MH. Thamrin 8, Jakarta, Indonesia

³ Center for Marine Environmental Studies (CMES), Ehime University, Bunkyo-cho 2-5, Matsuyama, Japan

Introduction

Bioaccumulation and biomagnification of toxic contaminants in aquatic ecosystems could potentially increase the risk in higher trophic level organisms including human, relative to organisms occupying lower trophic positions. In this regard, some brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDs) which are used in various household products, have been of concern due to their highly toxic, persistent and bioaccumulative nature. Recently, estimation of contaminant biomagnification through a food web has become advanced by using stable isotope ratios of bio-elements (Hoekstra et al., 2003; Muir et al., 2003). For example, stable nitrogen (N) isotopes have been used as a trophic-position indicator and to estimate the biomagnification potential of lipophilic contaminants in diverse ecosystems. The ratio of ¹⁵N to ¹⁴N (in biological tissues relative to air), which are expressed as delta-¹⁵N ($\delta^{15}\text{N}$) in tissue typically increases consistently by 3.4%-3.6% with each trophic transfer, because ¹⁵N is retained from the food resource relative to ¹⁴N. Since concentrations of biomagnifying contaminants also increase with trophic position, there will be a significant relationship between the biomagnifying compounds with increasing $\delta^{15}\text{N}$ values in biota; therefore linear-regression slopes can be used to predict contaminants behavior within food webs. The present study aims at investigating the levels of BFRs and stable isotopes of N and Carbon (C) in various trophic level organisms representing food chain models from Jakarta Bay, to understand the accumulation dynamics of these compounds in tropical aquatic ecosystems.

Materials and Methods

Samples

Sampling was conducted in Jakarta Bay, Indonesia using several catching methods by local fishermen during August 2007. Particulate organic matter (POM) and a total of 88 specimens belonging to 15 species of marine biota were analyzed in this study, including, zooplankton, green mussels, crab, shrimp and various fish species such as smudgepot spinefoot, Java spinefoot, patterned tongue sole, northern sand flathead, sailfin catfish, moses perch, large-toothed flounder, diamond trevally, black-edged conger, and giant seaspine. In the laboratory, the samples were kept frozen in environmental specimen bank (*es-BANK*) of Ehime University at -20 °C until dissection and chemical analyses. Table 1 shows the biota samples used in the present study.

Chemical Analysis

PBDEs (BDE-3, -15, -28, -47, -99, -100, -153, -154, -183, -196, -197, -206, -207 and -209) and HBCDs (α -, β - and γ -HBCD) were analyzed in representative samples following the methods described by

Toyoshima et al. (2009). Briefly, freeze dried samples were ground with anhydrous sodium sulfate. After spiking with labeled PBDEs ($^{13}\text{C}_{12}$ -BDE-3, -15, -28, -47, -99, -153, -154, -183, -197, -207 and -209) and HBCD (α -, β - and γ - $^{13}\text{C}_{12}$ -HBCD) as surrogate standards, the samples were extracted with hexane/acetone (1/1, v/v) using accelerated solvent extractor (ASE 100, Mitsubishi). The extracted sample was then subjected to gel permeation chromatography (GPC) for lipid removal. The GPC extract was further purified and fractionated by silica gel chromatography (1st fraction contains PBDEs and 2nd fraction contains HBCDs). A known amount of internal standard ($^{13}\text{C}_{12}$ -labeled BDE-139 for PBDEs and deuterized HBCD (α -, β - and γ -HBCD-d18) for HBCDs) was added prior to instrumental analysis. Quantification of PBDEs was carried out by gas chromatography with a mass spectrometry detector (GC-MS) in the negative chemical ionization mode, and liquid chromatography with tandem mass spectrometry detector (LC-MS-MS) using electrospray ionization for the isomeric composition of HBCDs.

Stable N and C isotopes were determined using the procedure described by Toyoshima et al. (2009). Briefly, few mg samples were dried for 24 h at 60 °C, ground to a powder and then immersed in chloroform: methanol (2:1) solution for 24 h to remove lipids. The ratios of stable carbon and nitrogen isotopes were analyzed using a gas chromatography-combustion-isotope ratio mass spectrometer (GC-C-IRMS) (PDZ Europa Ltd. ANCA-SL), and presented as per thousand deviations from the standards, calculated as $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ by the following equation:

$$\delta X (\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000,$$

Where X is ^{13}C or ^{15}N , and R is the corresponding ratio $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$. Pee Dee Belemnite (PDB) limestone carbonate and atmospheric nitrogen (N_2) were used as the standards for C and N isotope ratios, respectively.

Food Web Characterization

Trophic level (TL) of a given organism in Jakarta Bay ($\text{TL}_{\text{consumer}}$) was determined relative to primary consumer which is assumed to have trophic level of 2 by using the following equation (Fisk et al., 1998):

$$\text{TL}_{\text{consumer}} = 2 + (\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{primary consumer}}) / 3.8$$

Where 3.8 is the isotopic enrichment factor and $\delta^{15}\text{N}_{\text{primary consumer}}$ is assumed to be the $\delta^{15}\text{N}$ value for *zooplankton* as primary consumer. In the present study, data of $\delta^{15}\text{N}$ planktonic isopod crustacean (*Asellota*) was used for $\delta^{15}\text{N}_{\text{zooplankton}}$.

Trophic magnification factors (TMFs), which are the markers of cumulative bioaccumulation processes across the food web were determined from the log-linear regression between the base-10 logarithm (\log_{10}) of the lipid equivalent concentration in biota (C_B) and trophic level (TL):

$$\text{Log } C_B = (m \times \text{TL}) + b$$

Where m and b are the empirical slope and y-intercept, respectively. TMFs were calculated as the antilog of the slope (m), (i.e., $\text{TMF} = 10^m$).

Results and Discussion

Analysis of stable N and C isotopes illustrates the biota representing trophic levels within Jakarta Bay food web as an increase in $\delta^{15}\text{N}$ values from zooplankton to pelagic fish (Figure 1 and Table 1). In this study, the planktonic isopod crustacean (*Asellota*) which had an average $\delta^{15}\text{N}$ of 6.0‰, were assumed as

the primary consumer with TL = 2.0. The $\delta^{15}\text{N}$ for mussels, shrimps, smudgepot spinefoot, sole and crab (average TLs of 2.6, 2.9, 3.3, 3.7 and 3.7, respectively) indicated that they were the secondary consumers. Some similar feeding habit species such as Java spinefoot showed comparatively higher $\delta^{15}\text{N}$ values than smudgepot spinefoot of the same genus, possibly due to their occasional feeding of organisms of upper trophic levels. Other fish such as catfish, flathead, perch, trevally, little jewfish, conger, etc. occupied trophic levels intermediate between 3.9 and 4.5, suggesting that they were some of the top predators in this web and their diets most likely were a mix of fishes and other species. In the present study, giant seapike which had the highest $\delta^{15}\text{N}$ value (16.7 ‰) was considered as the most top predator in this food web structure with a trophic level of 4.8.

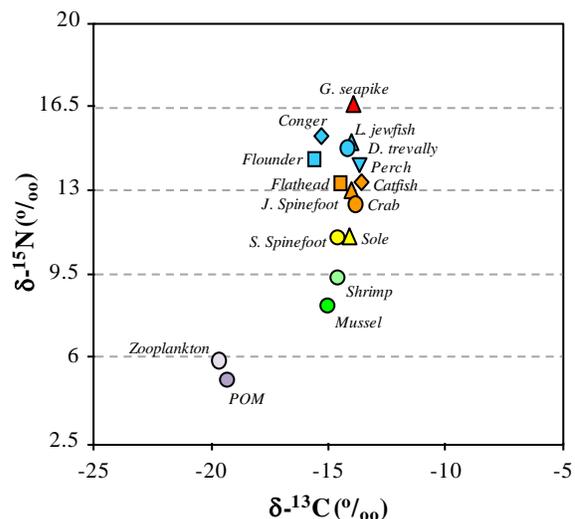


Figure 1. Food web structure of coastal organisms at Jakarta Bay based on $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ map.

PBDEs and HBCDs were detected in the samples of the present study with varying concentrations, ranging from 1.6–57 ng/g lipid wt. and nd–4.1 ng/g lipid wt., respectively (Table 1). The large variation in concentrations, particularly for PBDEs seems to be related to different trophic levels of fish species. For instance, as shown in Figure 2, significant increase in the lipid-normalized concentrations of total PBDEs with increasing trophic level was found, and this indicates biomagnification of PBDEs in the aquatic food

Table 1. Concentrations of BFRs, stable nitrogen and carbon isotope values (mean \pm standard deviation) and derived trophic level (TL) of Jakarta Bay marine biota.

Sample Biota	n	Fat (%)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	TL	PBDEs (ng/g lw)	HBCDs (ng/g lw)
POM	3	na	-19.3 \pm 0.83	5.1 \pm 1.0	1.8 \pm 0.27	na	na
Zooplankton	1*	na	-19.7	6.0	2.0	na	na
Green mussel	3*	1.9 \pm 0.37	-15.0 \pm 0.15	8.2 \pm 0.77	2.6 \pm 0.20	11 \pm 1.4	4.1 \pm 1.4
Shrimp	3*	0.59	-14.6 \pm 0.17	9.4 \pm 2.0	2.9 \pm 0.56	1.6	nd
Crab	3*	0.79	-13.9 \pm 0.13	12.6 \pm 0.36	3.7 \pm 0.09	20	nd
Smudgepot spinefoot	5	2.8 \pm 1.3	-14.6 \pm 0.30	11.1 \pm 0.46	3.3 \pm 0.12	10 \pm 1.7	0.22 \pm 0.28
Java spinefoot	5	3.0 \pm 0.61	-14.0 \pm 0.31	13.1 \pm 0.48	3.9 \pm 0.13	13 \pm 1.2	2.8 \pm 3.5
Sailfin catfish	3	1.7 \pm 1.2	-13.6 \pm 0.23	13.4 \pm 0.38	4.0 \pm 0.10	9.1 \pm 2.7	1.7 \pm 2.1
Little jewfish	7	1.1 \pm 0.36	-13.9 \pm 0.55	15.0 \pm 0.48	4.4 \pm 0.13	16 \pm 4.4	0.76 \pm 0.74
Northern sand flathead	3	0.53 \pm 0.25	-14.4 \pm 0.28	13.4 \pm 0.58	3.9 \pm 0.15	15 \pm 9.3	0.07 \pm 0.07
Large-toothed flounder	2	0.79 \pm 0.36	-15.6 \pm 0.53	14.4 \pm 1.1	4.2 \pm 0.28	23 \pm 10	nd
Moses Perch	8	0.88 \pm 0.38	-13.9 \pm 0.46	14.5 \pm 1.1	4.2 \pm 0.29	12 \pm 0.35	0.87 \pm 1.2
Patterned tongue sole	1*	0.82	-14.1	11.2	3.7	22	0.05
Diamond trevally	1*	0.66	-14.2	14.8	4.3	8.2	nd
Black-edged conger	1*	1.37	-15.2	15.3	4.4	12	nd
Giant seapike	1*	0.32	-13.9	16.7	4.8	57	0.14

Note: n= number of individual, *pooled samples, PBDEs= total PBDEs from mono- to deca-BDE, HBCDs= total HBCDs, na= not available, nd= below detection limit.

web, with higher trophic organisms having relatively higher concentrations. In this study, the TMF values for PBDEs ranged from 0.69 to 3.0 and HBCDs ranged from 0.30-0.57 (data not shown). Among the compounds analyzed, only BDE-47 (1.9), BDE-100 (1.8) and Σ PBDEs (1.7) having TMF values significantly greater than one ($p < 0.05$), showed evidence of biomagnification in Jakarta Bay food web. Other BDEs and HBCDs including BDEs-15, -183, -196, -197, -206, -207 and -209, and α -, β - and γ -HBCD were observed to have trophic dilution ($TMFs < 1$) with BDE-15, -206 and -209 showing significant TMF/trophic dilution value ($p < 0.05$). There are not many studies on biomagnification of BFRs in coastal food web, particularly for HBCDs. The TMF of PBDEs in Jakarta Bay was generally lower than those from Lake Winnipeg (1.5–5.2; Law et al., 2006) and Bohai Bay food webs (1.6–7.2; Wan et al., 2008), similar with freshwater food web from China (0.26–4.47; Wu et al., 2008), but were higher than the values from Canadian Arctic food web (0.8–1.6; Kelly et al., 2008). The variation of TMFs among the studies may be due to different PBDE levels in the organisms, different environmental conditions (e.g., water temperature) and different food web compositions between these food webs (Wu et al., 2008).

Acknowledgements

This study was partly supported by Grants-in-Aid for Scientific Research (S) (No. 20221003) and (B) (No. 18310046), Young Scientist (B) (No. 19780239) and the “Global COE Program” from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT), and Japan Society for the Promotion of Science (JSPS).

References

- Fisk AT, Norstrom RJ, Cymbalisty CD, Muir DCG. 1998. Environ Toxicol Chem 17: 951.
- Hoekstra TM, O'Hara, Fisk AT, Borga K, Solomon KR, Muir DCG, 2003. Environ Pollut 124: 509.
- Kelly BC, Ikononou MG, Blair JD, Gobas FAPC. 2008. Sci Total Environ 401: 60.
- Law K, Halldorson T, Danell R, Stern G, Gewurtz S, Alae M, Marvin C, Whittle M, Tomy G. 2006. Environ Toxicol Chem 25: 2177.
- Toyoshima S, Isobe T, Ramu K, Miyasaka H, Omori K, Takahashi S, Nishida S, Tanabe S. 2009. In: Interdisciplinary Studies on Environmental Chemistry-Environmental Research in Asia, p. 83.
- Wan JY, Hu K, Zhang Y, An L. 2008. Environ Sci Technol 42: 1078.
- Wu JP, Luo XJ, Zhang Y, Luo Y, Chen SJ, Mai BX, Yang ZY. 2008. Environ Int 34: 1109.
- Muir D, Savinova T, Savinov V, Alexeeva L, Potelov V, Svetochev V. 2003. Sci Total Environ 306: 111.

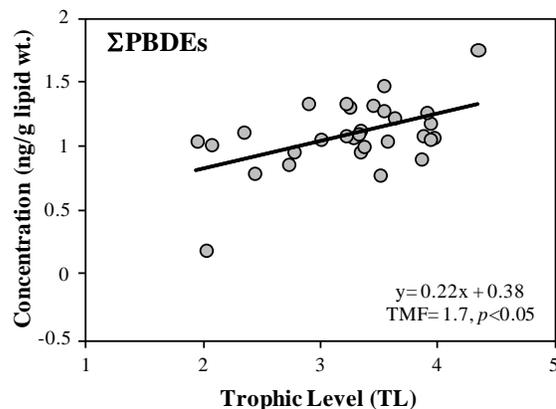


Figure 2. Relationship between PBDEs concentrations and trophic levels of biota from Jakarta Bay.