

SPATIAL DISTRIBUTION AND BIOACCUMULATION OF POLYBROMINATED DIPHENYL ETHERS (PBDES), HEXABROMOCYCLODODECANES (HBCDS) AND POLYCHLORINATED BIPHENYLS (PCBS) IN AQUATIC ECOSYSTEMS OF SETO INLAND SEA, JAPAN

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Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), which are known as brominated flame retardants (BFRs), have been used to reduce the flammability of a variety of industrial and household products such as housing material, electrical and electronic appliances, personal computers, thermal insulations, textiles, etc. Both PBDEs and HBCDs are primarily used as additive BFRs, which are easily released into the environment during use and disposal of the products. Since some BFRs are persistent and toxic, environmental pollution by and human exposure to these compounds are of public concern¹. Although Penta- and Octa-BDE commercial mixtures have been listed in Stockholm Convention on persistent organic pollutants (POPs) in 2009, Deca-BDE mixture and HBCDs are still in use. Bioaccumulation of PBDEs and HBCDs as well as other persistent organic pollutants such as polychlorinated biphenyls (PCBs) has been reported in quantifiable levels in marine food web²⁻⁵. Open ocean plays an important role as a major sink for those persistent anthropogenic compounds, which are transported via atmospheric or aquatic processes and accumulated in higher trophic level organisms. There are some studies reporting the levels and accumulations of POPs and BFRs in marine biota, but only limited information is available in the Seto Inland Sea, which is a well-known coastal fishing ground. In this study, BFRs and stable isotope ratios ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) in fish from the Seto Inland Sea were measured to understand their contamination status, geographical distribution, biomagnification through food web and human exposure.

Materials and methods

Sample collection

One hundred twenty fish and crustacean samples were collected from various regions of the Seto Inland Sea

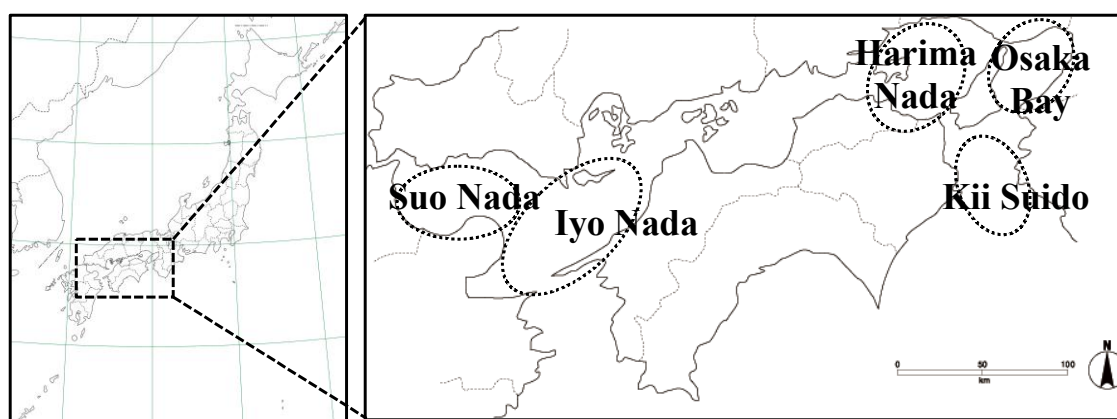


Figure 1. Sampling locations in Seto Inland Sea

including Suo Nada, Iyo Nada, Harima Nada, Kii Suido and Osaka Bay, in September 2008 (Figure 1). Ten species, which were Hairtail (*Trichiurus japonicus*), Red sea bream (*Pagrus major*), Large-scaled grinner (*Saurida macrolepis*), Japanese spanish mackerel (*Scomberomorus niphonius*), Jack mackerel (*Trachurus japonicus*), Cuttlefish (*Sepia Platysepia esculenta*), Velvet shrimp (*Metapenaeopsis barbata*), Anchovy (*Engraulis japonicus*), Whitebait (*Schindleria praematura*), Bobtail squid (*Euprymna morsei*), were collected from each region if it was available. All the samples were transported with ice and stored in the Environmental Specimen Bank (es-BANK) of Ehime University at -25°C until chemical analysis.

Chemical analysis

Analysis of PCBs and BFRs were carried out following our previous report ⁶. Briefly, 30g (wet weight) of muscle sample from fish, shrimps and squids were lyophilized, ground with anhydrous sodium sulfate and extracted using a high speed solvent extractor (SE-100). An aliquot of the extract, after spiking 5 ng of ¹³C₁₂-CBs and 5 ng of ¹³C₁₂-BDEs and 10 ng of ¹³C₁₂-HBCDs, was loaded and extracted through a gel permeation chromatography (GPC) column for lipid removal and then passed through an activated silica gel column for separation. ¹³C₁₂-BDE-126, 205 were spiked as performance internal standards to the fractions containing PBDEs and PCBs prior to quantification using a gas chromatograph-mass spectrometer (Agilent 7890 GC and 5975 MSD). The HBCDs fraction was evaporated and spiked with HBCDs-*d*₁₈ prior to analysis using a liquid chromatograph-tandem mass spectrometer (Waters Acquity UPLC and Quattro Micro API). Lipid content of sample was measured gravimetrically using another aliquot of extract.

Stable isotope ratio measurement

Muscle sample of fish and crustaceans were used for the stable isotope analysis. All the samples were dried for 24 h at 60 °C, powdered and treated with a 2:1 chloroform-methanol solution to remove lipid. Then the samples were dried and loaded into tin cups. Stable carbon and nitrogen isotopes were measured using an isotope ratio mass spectrometer (IR-MS).

Results and discussion

Geographical distribution

All the analytes of the present study, PCBs, PBDEs and HBCDs, were detected in most of the samples analyzed, indicating ubiquitous contamination by these organohalogen compounds in the Seto Inland Sea coastal ecosystem (Figure 2). Among the analytes, PCBs concentrations were the highest in almost all the samples, which could be attributed to the widespread usage in the past and spillage from the stockpiles of PCB containing products. PCBs levels were significantly higher in Osaka Bay, a heavily industrialized and densely populated embayment, than the other areas except for Suo Nada. Since PCBs had been used in the industrial products, levels could be associated with human and industrial activities. Concentrations of PBDEs in Suo Nada were the highest among sampling areas, possibly reflecting the extensive production and usage of PBDEs in the industrial area in the Suo Nada coast ⁷. On the other hand, HBCDs were higher in eastern part of the sea, Harima Nada, Kii Suido and Osaka Bay, than in western part, Suo Nada and Iyo Nada. The same pattern was observed in the previous monitoring survey using mussel as a bioindicator ⁸. This result indicates that fiber and textile industries, which are many in the nearby land area, may be the possible contamination sources of HBCDs ⁹.

Isomer profiles

Among forty-two targeted BDE congeners, BDE-47 was the predominant congener in all the locations, whereas BDE-15 and -28 were detected in fish from Suo Nada. This specific isomer pattern in Suo Nada may indicate the use of specific PBDE technical mixtures in this area ⁷. Among the three HBCD isomers (α -, β - and γ -HBCD), α -HBCD was prevalent in all the species and β and γ -isomers were below detection limits in most of the samples. The prevalence of α -HBCD has already been observed in aquatic biota like fish, shrimp and mussels ¹⁰⁻¹³.

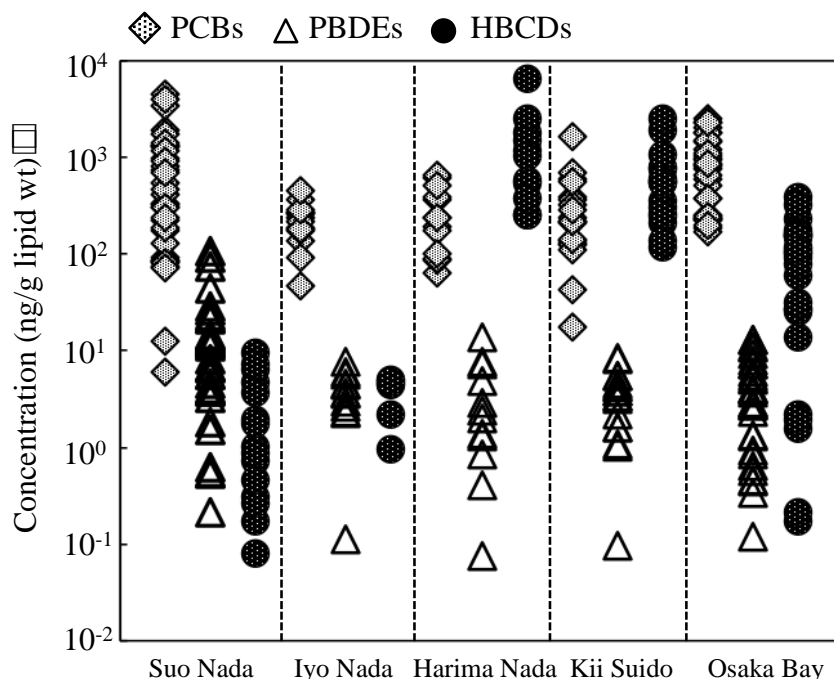


Figure 2. Concentrations of PCBs, PBDEs and HBCDs in fish from several locations of Seto Inland Sea

Biomagnification through the food web

Trophic level (TL) was calculated from $\delta^{15}\text{N}$ (‰) values using the following equation:

$$\text{TL} = 2 + (\delta^{15}\text{N consumer} - \delta^{15}\text{N zooplankton}) / 3.4$$

Significant positive correlations between TL and lipid normalized concentrations of PCBs, PBDEs and HBCDs were found in almost all locations, indicating that these compounds are biomagnified in higher trophic level organisms. PBDEs in Iyo Nada and HBCDs in Suo Nada, however, did not show clear correlations. This result indicates that both PBDEs and HBCDs are in use at present but less persistent compared to PCBs. Relationships between trophodynamic magnification factors (TMFs) calculated from the slope of the linear regression line and concentrations of each isomer were examined. In Suo Nada and Osaka Bay, TMF values of the analyzed PCB congeners increased with increasing $\log K_{\text{OW}}$ (5-7), and then decreased with increasing $\log K_{\text{OW}}$ (7-9). This phenomenon is consistent with the previous report, which concluded that the PCB congeners with $\log K_{\text{OW}}$ greater than 7 showed less TMFs because of their reduced bioavailabilities². BDE-28 showed higher TMF values than PCB congeners which have similar $\log K_{\text{OW}}$, implying debromination of BDE-47 to BDE-28.

Hazard assessment

Estimated daily intake (EDI) of PCBs, PBDEs and HBCDs through fish consumption was calculated from the concentrations of analytes, average body weight of Japanese (60 kg)¹⁴ and Japanese fish consumption (about 100 g/day)¹⁵, and compared with threshold reference values reported by USEPA¹⁶ (0.1, 0.1, 0.2 and 1 $\mu\text{g}/\text{kg}$ bw-day for BDE47, BDE99, BDE153 and PCBs, respectively) and ATSDR¹⁷ (0.2 $\mu\text{g}/\text{kg}$ bw-day for HBCDs), for hazard quotients (HQ) calculated using the following equation.

$$\text{HQ} = \text{concentration} \times \text{intake} / \text{body weight} \times \text{reference dose}$$

All HQ values for PBDEs and HBCDs were 2-3 orders of magnitude lower than 1, indicating minimal health risk. On the other hand, HQ values for PCBs were close to 1 implying that PCBs exposure may be of concern for population consuming a large amount of fish. Therefore, continuous monitoring and proper regulation should be implemented on the production, use and disposal of these chemicals to reduce human exposure and toxic implications.

Acknowledgements

This research was partly supported by Grant-in-Aid for Scientific Research (S: 20221003), for challenging Exploratory Research (24651010) and for Young Scientists (B: 23710077) from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) and Japan Society for the Promotion of Science (JSPS) and the Environment Research and Technology Development Fund (ZRFc-1201) of the Ministry of the Environment. This research was also supported by MEXT program "Promotion of Environmental Improvement for Independence of Young Researchers" under the Special Coordination Funds for Promoting Science and Technology.

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