

Organochlorines and Brominated Flame Retardants in Deep-Sea Ecosystem of Sagami Bay

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Abstract—Organochlorine compounds (OCs), brominated flame retardants (BFRs) and stable isotopes ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) were analyzed in various deep-sea organisms collected from Sagami Bay, Japan in 2004. PCBs and DDTs were the predominant contaminants detected in this study, followed by CHLs > HCB > HBCDs > PBDEs > HCHs. Concentrations of PCBs, DDTs, CHLs, HCB and PBDEs, which have high adsorptive affinities to particles and easily precipitate to sediments, were the highest in demersal fish among the organisms analyzed. Relatively high concentrations of HBCDs were found in species living in surface waters, suggesting recent input of HBCDs in the marine environment. Significant positive correlations between $\delta^{15}\text{N}$ (‰) and concentrations of PCBs, DDTs, CHLs, HCB, PBDEs and HBCDs were found, indicating that these compounds were biomagnified in higher trophic level organisms. On the other hand, concentrations of HCHs decreased with an increase in trophic level implying dilution of this compound through the food web. The trophodynamic magnification factor (TMFs) of the analyzed PCB congeners showed an increasing trend for congeners with low $\log K_{\text{OW}}$ (5–7), while a decreasing trend was observed for congeners with high $\log K_{\text{OW}}$ (7–9). This phenomenon could be due to reduced bioavailability/uptake. This trend was also observed for PBDEs with some exceptions. TMF values calculated for BDE-99, -153, and -209 were lower than those of predicted TMF values. Metabolism or debromination of these congeners in the fish body is a possible reason for this difference. In addition, BDE-209 has extremely low bioavailability due to its large molecular size.

Keywords: PBDEs, HBCDs, PCBs, trophic magnification factors (TMFs), Sagami Bay, deep-sea

INTRODUCTION

Organochlorine compounds (OCs) and brominated flame retardants (BFRs) are ubiquitous chemicals that are used globally in many industries. Several OCs and BFRs have been found in quantifiable levels in wildlife. The deep-sea is considered

to play a potentially major role as a final reservoir and sink for environmental contaminants (Woodwell *et al.*, 1971). Therefore, it is important to examine the behavior of organohalogen compounds in deep-sea ecosystems in order to understanding their transportation and potential effects of human activities on the marine environment. However, few studies have investigated the behavior of organohalogen compounds in deep-sea ecosystems. Sagami Bay is a deep coastal body of water along the Pacific coast of Japan. Because of its proximity to industrial areas, there are concerns on the environmental impact by industry on the Sagami Bay ecosystem. The ecology of the organisms from this region has been well documented in a previous study (Shimode *et al.*, 2006). Therefore, this area is suitable for investigating the environmental behavior and accumulation properties of organohalogen compounds in the deep-sea ecosystem. Stable isotope ratios in aquatic ecosystems have been increasingly used to evaluate food web structure and energy pathways (Fisk *et al.*, 2001; Hop *et al.*, 2002; Muir *et al.*, 2003; Law *et al.*, 2006; Wan *et al.*, 2008; Kelly *et al.*, 2008). $\delta^{15}\text{N}$ is an indicator of trophic level, while $\delta^{13}\text{C}$ is used to identify sources of carbon in the base of the food web (Fry and Sherr, 1984; Hobson and Welch, 1992). Stable isotopes can also be used to estimate the rate of biomagnification of a chemical across the entire food web. Therefore, the present study was conducted to evaluate the organohalogen contamination in Sagami Bay and to clarify the trophic transfer of organohalogen compounds in the biota of the ecosystem.

MATERIALS AND METHODS

Samples

Deep-sea organisms, comprising fishes, crustaceans and zooplankton were collected from Sagami Bay, Japan, in November 2004. Individuals of the same species were pooled and homogenized to prepare composite samples. All samples were stored in the Environmental Specimen Bank (*es*-BANK), Ehime University (Tanabe, 2006) at -20°C until chemical analysis.

Chemical analysis

DDTs, HCHs, CHLs and HCB were analyzed following the method reported by Tanabe (2006) with slight modifications. Analyses of PBDEs and HBCDs were performed following the procedure described by Ueno *et al.* (2004, 2006). Quantification of organochlorine pesticides was performed using a GC equipped with an ECD. PCBs and PBDEs quantification was performed using a GC-MSD. HBCDs quantification was performed using LC-MS-MS.

FOOF WEB CHARACTERIZATION

Stable isotope analysis

The muscle tissues of fish and crustaceans were used for analysis of carbon and nitrogen stable isotopes. All samples were dried for 24 hr at 60°C , ground to

a fine powder and treated with a 2:1 chloroform-methanol solution to remove lipids. Samples were dried and loaded into tin cups. Stable carbon and nitrogen isotopes were measured using an isotope ratio mass spectrometer (IR-MS).

Trophic level calculations

Stable isotope values were expressed as

$$\delta^{15}X = \left\{ \left(R_{\text{sample}} / R_{\text{standard}} \right) - 1 \right\} \times 1000 \quad (1)$$

where X is ^{13}C or ^{15}N and R is the corresponding ratio of $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$. Pee Dee belemnite (PDB) limestone carbonate and atmospheric nitrogen (N_2) were used as the standards for carbon and nitrogen isotope ratios, respectively. We assume that zooplankton (almost all copepods) represent trophic level 2.0, because they are the primary herbivores feeding on phytoplankton. For the samples from other trophic levels, we used the relationship by Fisk *et al.* (2001):

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

where $\text{TL}_{\text{consumer}}$ is the trophic level.

Bioaccumulation parameters

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

$$\log C_B = a \times \text{TL} + b \quad (3)$$

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

RESULTS AND DISCUSSION

Accumulation patterns of organohalogen compounds

PCBs and DDTs were the predominant contaminants detected in this study, followed by CHLs > HCB > HBCDs > PBDEs > HCHs (Fig. 1). The predominance of DDTs and PCBs in deep-sea organisms from the Sagami Bay is similar to deep-sea fishes from Suruga Bay, Japan (Lee *et al.*, 1997); Tosa Bay, Japan (Takahashi *et al.*, 2001); Western North Pacific, off-Tohoku, Japan (de Brito *et al.*, 2002), the East China Sea (ECS) (Tanabe *et al.*, 2005) and the Sulu Sea (Ramu *et al.*, 2006). This may be due to the higher bioaccumulative properties of these compounds and continuous release of these compounds into the aquatic environment. Concentrations of PCBs, DDTs, CHLs, HCB and PBDEs were the highest in demersal fish among the organisms analyzed, probably because these compounds

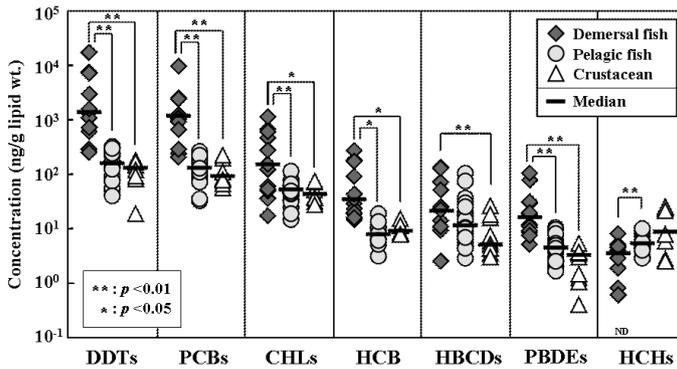


Fig. 1. Concentrations of organohalogen compounds in demersal fish, pelagic fish and crustaceans.

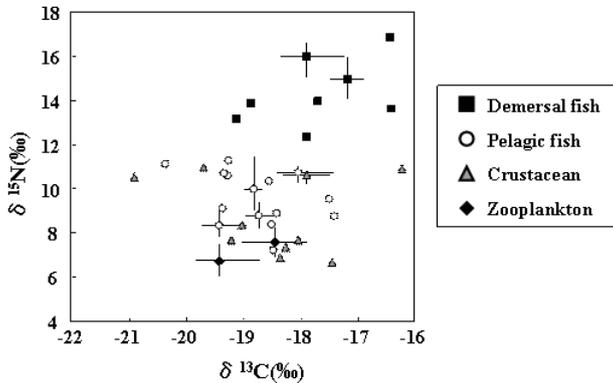


Fig. 2. Food web of deep-sea organisms based on $\delta^{13}\text{C}$ – $\delta^{15}\text{N}$ map.

have high adsorptive affinities to particles and easily precipitate to sediments and accumulate in demersal fish which are typically high trophic level species in the deep sea ecosystem. Relatively high concentrations of HBCDs were found in species living in surface waters (i.e. mackerel and anchovy), suggesting recent input of HBCDs to the marine environment.

Food web structure

A food chain based on pelagic plankton and an increase in $\delta^{15}\text{N}$ values was observed from zooplankton to pelagic fish and from crustaceans to demersal fish (Fig. 2). Pelagic fishes analyzed in this study were dominated by the family *Mictophidae* and *Gonostomatidae*. Most demersal fish analyzed in this study feed

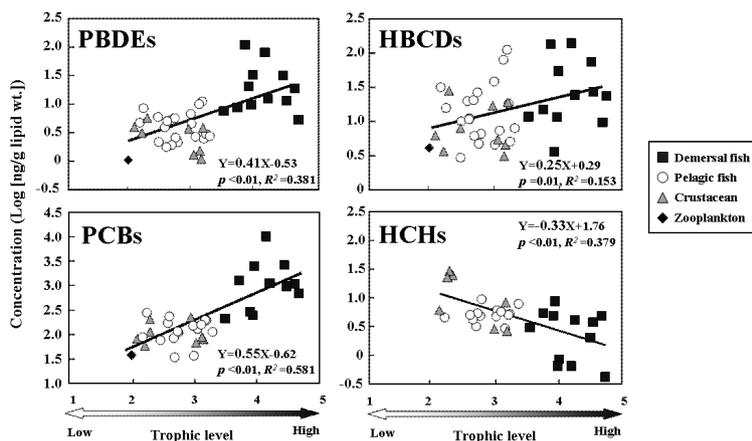


Fig. 3. Relationships between $\delta^{15}\text{N}$ and concentrations of PBDEs, HBCDs, PCBs and HCHs in demersalfish, pelagicfish and crustaceans.

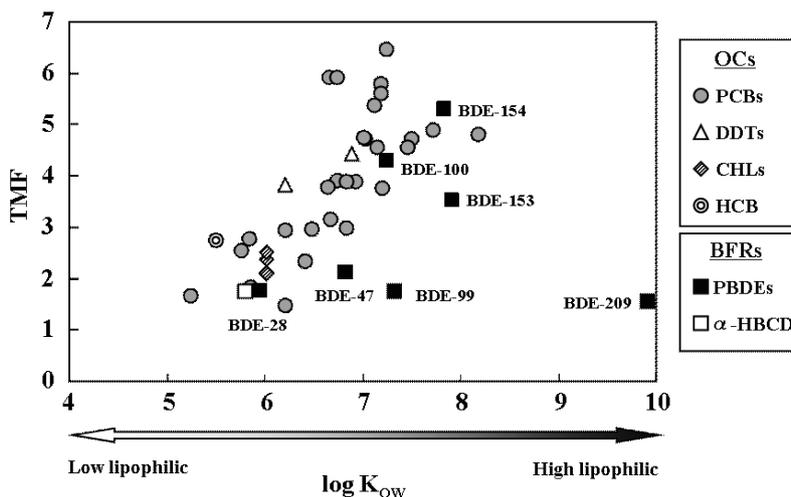


Fig. 4. Relationships between $\log K_{ow}$ and TMFs of OC and BFR congeners.

chiefly on these pelagic species and mesopelagic crustaceans. Therefore, most of the species analyzed in this study were considered to belong to the same food web.

Trophic transfer of organohalogen compounds

Significant positive correlations between $\delta^{15}\text{N}$ (‰) and concentrations of PCBs, DDTs, CHLs, HCB, PBDEs and HBCDs were found, indicating these

compounds were biomagnified in the higher trophic level organisms (Fig. 3). PCBs and PBDEs in deep-sea organisms showed a strong positive relationship between concentrations and trophic levels, implying high biomagnification potential. On the other hand, compounds of HCHs decreased with increasing trophic level, implying dilution of this compound through food web; HBCDs showed no apparent trend. These results suggest that trophic transfer of organohalogen compounds depends on their lipophilicity.

Concentrations of PBDEs, PCBs, DDTs, CHLs and HBCDs, which have high adsorptive affinities to particles were the highest in demersal fish living in mud (e.g. eels). Concentrations of HCHs and HCB which have low adsorptive affinities to particles were low in these species. These species were exposed to high adsorptive compounds through sediment particles.

Trophic magnification of organohalogen compounds

The Trophic magnification factors (TMFs) of the analyzed PCB congeners showed an increasing trend for congeners with low log K_{OW} (5–7), while a decreasing trend was observed for congeners with high log K_{OW} (7–9) (Fig. 4). This phenomenon could be due to reduced bioavailability/uptake. This trend was also observed for PBDEs with some exceptions. TMF values calculated for BDE-99, -153, and -209 were lower than those of predicted values (Fig. 4). Metabolism or debromination of these congeners in the fish is a possible reason for this difference. Debromination of highly brominated congeners can also confound their biomagnification behavior in fish. Significant debromination has been found in the common carp by independent dietary exposure experiments, converting BDE-99 to BDE-47 and BDE-183 to BDE-154 (Stapleton *et al.*, 2004a). In this study, we found that the fractions of BDE-99 in deep-sea organisms were lower than other BDE congeners, which is consistent with the findings of Stapleton *et al.* (2004a). The TMF value of BDE-154 was higher than other BDE congeners. BDE-154 was reported to be a metabolite of BDE-209 in fish (Tomy *et al.*, 2004; Stapleton *et al.*, 2004b). Our results also suggest that the biotransformation of BDE-209 may contribute, in part, to the enhanced TMF value of BDE-154. In addition, BDE-209 has extremely low bioavailability due to its large molecular size.

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