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Contamination Status of Organohalogen Compounds in Deep-Sea Fishes in Northwest Pacific Ocean, Off-Tohoku, Japan

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Abstract—Twelve species of deep-sea fishes collected in 2005 from the western North Pacific, off-Tohoku, Japan were analyzed for persistent organochlorine compounds (OCs) and brominated flame retardants (BFRs). PCBs and DDTs were the predominant contaminants, followed by CHLs > HCB ≈ HCHs ≈ HBCDs > PBDEs. Concentrations of DDTs and CHLs were lower than those reported in 1994–95 from the same area. PCBs, however, did not show a decreasing trend, suggesting its recent input from the nearby land areas. BFRs were detected in all the specimens, evidencing that the contamination by these compounds reached even the deep-sea environment. Significant positive correlations between δ^{15}N and concentrations of PCBs, DDTs and PBDEs were observed indicating that these compounds are biomagnified in higher trophic level fish. On the other hand, correlations between δ^{15}N and concentrations of HCHs and HCB were not significant. As PCBs, DDTs and PBDEs have higher logK_{ow} values than those of HCHs and HCB, our findings confirm the fact that lipophilic compounds are bioaccumulated and biomagnified more easily.

Keywords: organochlorines, brominated flame retardants, stable isotopes, deep-sea fishes, off-Tohoku

INTRODUCTION

Persistent organic pollutants (POPs) such as PCBs and DDTs are contaminants entering the marine environment by river inflow, continental runoff and atomospheric deposition. Brominated flame retardants (BFRs) are extensively used in electrical and electronic equipments in recent years. Even though deep-sea environment is the ultimate sink for persistent contaminants (Woodwell *et al.*, 1971), only few reports on contamination in the benthic environment are available at present, due to difficulties in sampling. The present study aimed to elucidate the status of contamination in deep-sea fishes collected from Northwest Pacific Ocean, off-Tohoku, Japan in 2005. We also investigated deep-sea food web using stable carbon and nitrogen isotopes (δ^{15}N and δ^{13}C) as tracers.

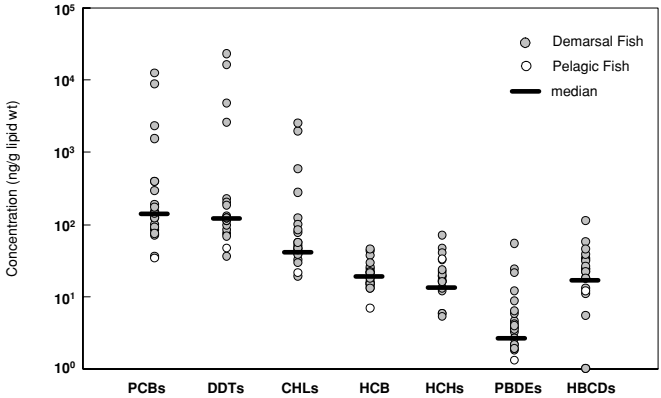

Fig. 1. Organohalogen contamination (ng/g lipid wt.) in demarsal and pelagic fishes collected from Northwest Pacific Ocean, off-Tohoku.

MATERIALS AND METHODS

Samples

Twelve species of deep-sea fishes collected from the western North Pacific, off-Tohoku (36–38°N, 141–142°E) in depths ranging from 400 to 1000 m during October to November 2005 were analyzed in this study. The fish samples were collected using a research bottom trawl during a cruise of R/V *Wakataka-maru* of the Fisheries Research Agency (FRA). The collected samples were placed in polyethylene bags and frozen in a deep-freezer at –25°C until chemical analysis. The whole body of individual specimens was homogenized to prepare a composite sample for chemical analysis. The samples were pooled based on species and location.

Chemical analysis

Analysis of OCs (PCBs, DDTs, CHLs, HCHs and HCB) and BFRs (PBDEs and HBCDs) were carried out following the previous reports (Kajiwara *et al.*, 2003; Ueno *et al.*, 2004). Briefly, samples were Soxhlet extracted, purified by gel permeation chromatography (GPC) and fractionated with an activated florisil column for OCs and an activated silica gel column for BFRs. Identification and quantification of OCs, PBDEs and HBCDs were performed using GC-ECD, GC-MS, LC-MS-MS, respectively. Stable isotopes were measured using GC-IR-MS.

RESULTS AND DISCUSSION

Contamination status

OCs and BFRs were detected in all the specimens, evidencing that the

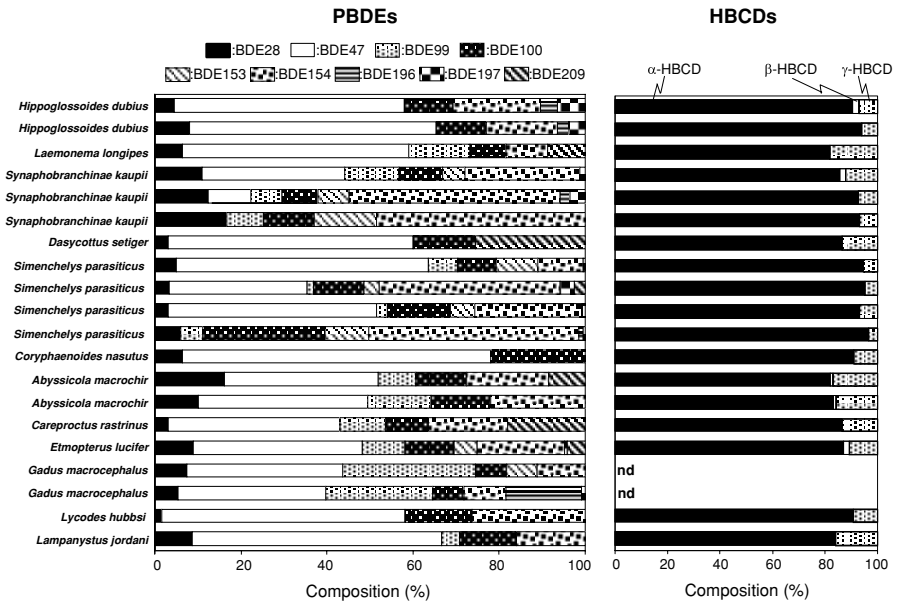

Fig. 2. Composition of BFRs in deep-sea fishes collected from Northwest Pacific Ocean, off-Tohoku.

contamination by these compounds reached the deep-sea environment. PCBs and DDTs were the predominant contaminants, followed by CHLs > HCB ≈ HCHs ≈ HBCDs > PBDEs (Fig. 1). Concentrations of organochlorine compounds were in the same range or slightly lower than those reported earlier from the East China Sea, Tosa Bay, Suruga Bay and Sagami Bay (Lee *et al*., 1997; Takahashi *et al*., 2001; Tanabe *et al*., 2005). Concentrations of HCHs in deep-sea fishes from the western North Pacific, off-Tohoku, Japan were higher from locations along the warm Kuroshio Current. Due to its high vapor pressure, HCHs are known to be rapidly evaporated and transported from their pollution sources in the tropics and temperate regions to colder regions via the atmosphere. The distribution patterns of HCHs found in the biota reflect such highly transportable nature and their accumulation in the fishes along the cold water current of the western North Pacific. PBDEs and HBCDs were also detected in almost all the deep-sea fish samples. The present study is the foremost to report the occurrence of PBDEs in deep-sea fishes from the North Pacific region. The congener profiles of PBDEs varied between species. In most fish samples the congeners from tri- to hexa-BDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-154) were predominant (Fig. 2). The higher contribution of BDE-47 to total BDE burdens could be attributable to the higher bioaccumulation potential of this congener and/or possible debromination of BDE-99 or other higher BDE congeners to BDE-47 in fish tissues. Higher accumulation of BDE-209 in Benthic fish such as spinyhead

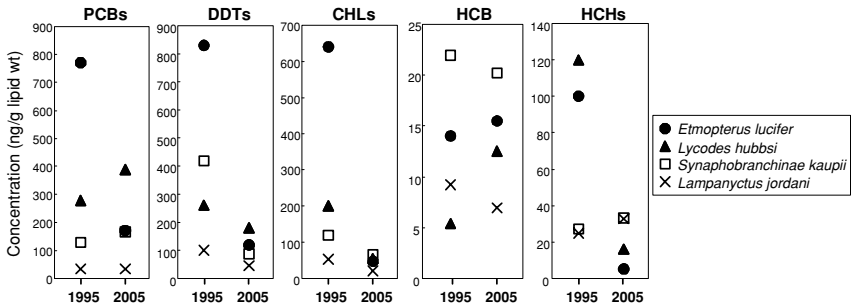

Fig. 3. Temporal trends of OCs in the deep-sea fishes.

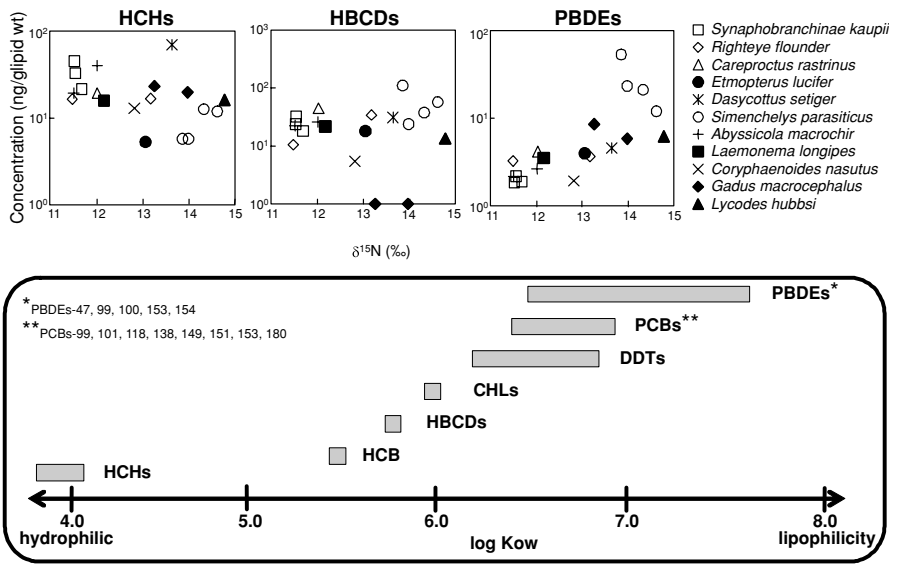

Fig. 4. Relationship between δ^{15}N (‰) and concentrations of OCs and BFRs.

sculpin (*Dasycottus setiger*) and largenose grenadier (*Coryphaenoides nasutus*) can be explained by their sediment dwelling habits as BDE-209 is mainly associated with sediment particles. Among HBCD isomers (α-, β- and γ-HBCD), α-HBCD was prevalent in all the species, while β-isomer was below detection limits in most of the samples (Fig. 2). The prevalence of α-HBCD has already been observed in aquatic biota like fish, shrimp and mussels (Morris *et al*., 2004; Tomy *et al*., 2004; Ueno *et al*., 2006; Ramu *et al*., 2007).

To elucidate the temporal trends of OCs contamination during the last decade, the results of the present study were compared with the data reported on

deep-sea fishes in our earlier study in which sampling locations overlapped with the present study (Takahashi *et al*., 2000; de Brito *et al*., 2002). Concentrations of DDTs and CHLs were lower than the levels reported in 1994–'95 from the present study area (Fig. 3). However, PCBs did not show a decreasing trend, suggesting its recent and continuous input from the nearby land areas.

Biomagnification of organohalogen compounds

Significantly positive correlations were observed between $\delta^{15}N$ (‰) and lipid normalized concentrations of PCBs, DDTs and PBDEs ($p < 0.05$), showing their high biomagnification potential in marine food webs (Fig. 4). No such relationship was found for HCB, HCHs and HBCDs. Rapid elimination of these compounds through gills to surrounding water may prevent biomagnification of these compounds. As PCBs, DDTs and PBDEs have higher $\log K_{ow}$ values than those of HCHs and HCB (IUCLID, 1996; Kelly and Gobas, 2000; Echols *et al*., 2004), our findings confirm the fact that lipophilic compounds are bioaccumulated and biomagnified more easily.

Interestingly, *simenchelys parasiticus* collected from the deepest water in this study area showed lower concentrations of HCHs than other fishes with significantly higher concentrations of other hydrophobic OCs and PBDEs. In our earlier studies on deep-sea fishes from the western North Pacific, off-Tohoku, Japan (Takahashi *et al*., 2000; de Brito *et al*., 2002), higher concentrations of PCBs, DDTs and CHLs were found in non-migratory fishes from deeper waters. On the contrary, HCHs and HCB accumulated to higher levels in shallow/migratory fishes. Therefore, results of this study also suggest that OCs and BFRs are widely distributed in the marine ecosystem, particularly; hydrophobic OCs and PBDEs are accumulated in the demersal fauna.

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