Biomagnification Pattern of PBDEs and HBCDs in Eastern and Western Boundary Current Ecosystems of the North Pacific Ocean

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Introduction.

Brominated flame retardants (BFRs) are commonly used in a wide variety of consumer products such as printed circuit boards, television and computer housings and other electronic household appliances, automotive parts, thermal insulation foams and furniture upholstery, to reduce their flammability. Concern over environmental contamination by BFRs, particularly by polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), has increased in recent years due to their persistence, bioaccumulative nature, and possible adverse effects on humans and wildlife. Statistical data demonstrated that Asian countries shared about 40 and 23% of the global PBDEs and HBCDs consumption in 2001, respectively (BSEF, 2005), suggesting that this region could be a significant source of contamination by BFRs. Bioaccumulation of PBDEs and HBCDs as well as other persistent organic pollutants such as polychlorinated biphenyls (PCBs) have been reported in significant levels in wildlife. Although the open ocean is considered to play a major role as a final reservoir and sink for environmental contaminants, only limited information is available on contamination status and bioaccumulation pattern of BFRs in the open ocean food web (Fisk *et al.*, 2001; Hop *et al.*, 2002; Muir *et al.*, 2003; Law *et al.*, 2006; Kelly *et al.*, 2008; Wan *et al.*, 2008). Stable isotope methods have increasingly been applied to evaluate food web structure and energy pathways in aquatic ecosystems. δ^{15}N is an indicator of relative trophic level, while δ^{13}C is used to identify sources of carbon to the food web. Stable isotopes can also be used to estimate contamination status and bioaccumulation pattern of a chemical across the entire food web. In the present study, we investigated the bioaccumulation of PBDEs, HBCDs and PCBs through the food webs of the eastern and western boundary current ecosystems of the North Pacific Ocean.

Materials and Methods.

Samples

Fish samples were collected from off Miyagi, Japan (14 species) and off California, the USA (9 species) in 2007. Zooplankton was also sampled using a plankton net from each location. All the samples were frozen on board the ship, transferred in ice and stored at the

Environmental Specimen Bank (*es*-BANK) of Ehime University at -25 ˚C until chemical analysis (Tanabe, 2006).

Chemical analysis

PBDEs, HBCDs, and PCBs were analyzed following the methods described previously (Isobe *et al.*, 2007). Samples were Soxhlet extracted with diethyl ether/hexane (3:1, v/v) solution. An aliquot of extract was spiked with internal standards, purified and fractionated using a gel permeation chromatography and an activated silica gel column. Identification and quantification of, PBDEs and PCBs were achieved using GC-MS, whereas HBCDs were quantified by LC-MS/MS. Concentrations of analytes are normalized by lipid content, which was determined gravimetrically from an aliquot of the extract, and expressed as ng/g lipid weight. $\delta^{13}C$ and $\delta^{15}N$ were determined using GC-C-IRMS. Stable isotope ratios were calculated from ^{13}C /^{12}C or ^{15}N /^{14}N values in the standard material and the sample. Pee Dee belemnite (PDB) limestone carbonate and atmospheric nitrogen (N_2) were used as the standards for carbon and nitrogen isotope ratios, respectively. We assumed that zooplankton (predominantly copepods) represented a trophic level of 2.0, because they are primary consumers feeding on phytoplankton. Trophic levels of fish were estimated using $\delta^{15}N$ based on the relationship previously proposed (Fisk *et al.*, 2001).

Results and Discussion.

Contamination status

All organohalogen compounds targeted in the present study were detected in the entire species analyzed, indicating ubiquitous contamination of fish in the open ocean. Concentrations of PCBs were the highest among the analytes and ranges were almost the same for both ecosystems (9.1 – 710 ng/g lipid for off Miyagi and 14 – 610 for off California). HBCD levels (0.71 – 430 ng/g lipid) were higher than PBDEs (0.21 – 20 ng/g lipid) in fishes from off Miyagi whereas opposite trend was noticed off California (<0.05 – 5.3 ng/g lipid for HBCDs and 0.14 – 92 ng/g lipid for PBDEs). This might reflect the difference in consumption pattern of BFRs in Japan and North America. In fact, the market demand of HBCDs was higher in Japan than in North America (BSEF, 2005).

Food web structure

A food web based on pelagic plankton and an increase in $\delta^{15}N$ values was observed from zooplankton to pelagic fish. Based on $\delta^{13}C$ and $\delta^{15}N$ values, we assumed that most of the species analyzed in the present study belonged to roughly their respective food webs. Overall the food web off northern California was considerably more truncated to that off Miyagi. That is, many species off California were relatively low on the food web compared to those from off Miyagi. This trend may be due to the fact that the California Current is an eastern boundary current upwelling ecosystem, exhibiting very high levels of primary and secondary production. This production is subsequently directly consumed by many fish, including top predators, leading to a relatively more truncated food web (Brodeur and Pearcy, 1992).

Bioaccumulation of organohalogen contaminants

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

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

Significant positive correlations between TL and concentrations of PCBs, PBDEs and HBCDs were observed in fish samples from off Miyagi, indicating these compounds were biomagnified in higher trophic level organisms (Figure 1). Trophic transfer of organic pollutants was evaluated using the slope of the linear regression between trophic level and concentration of each compound. The slopes of PCB congeners showed an increasing trend

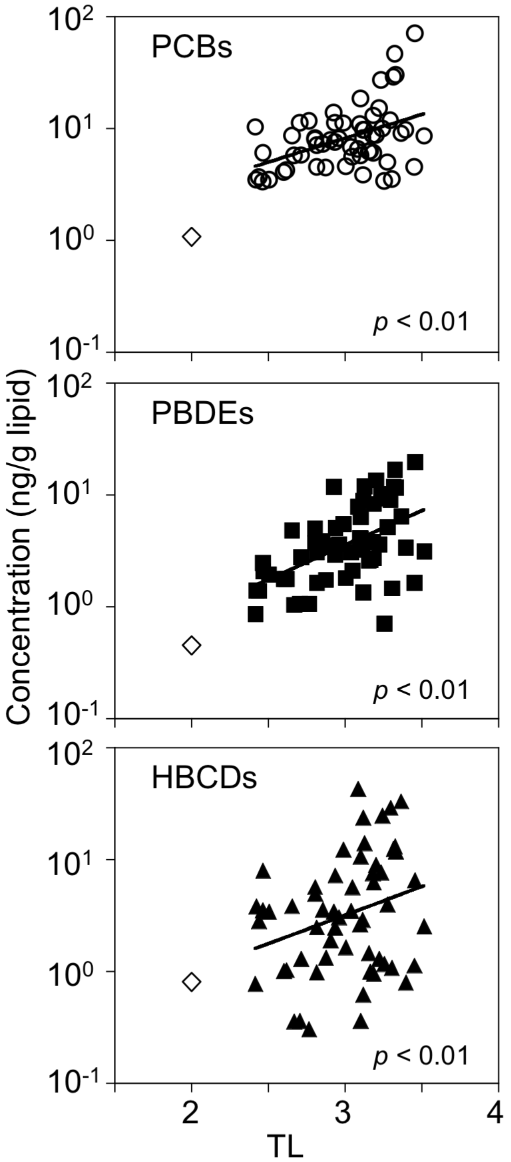

Figure 1. Relationship between organohalogen concentration and trophic level (TL) in fish from off Miyagi

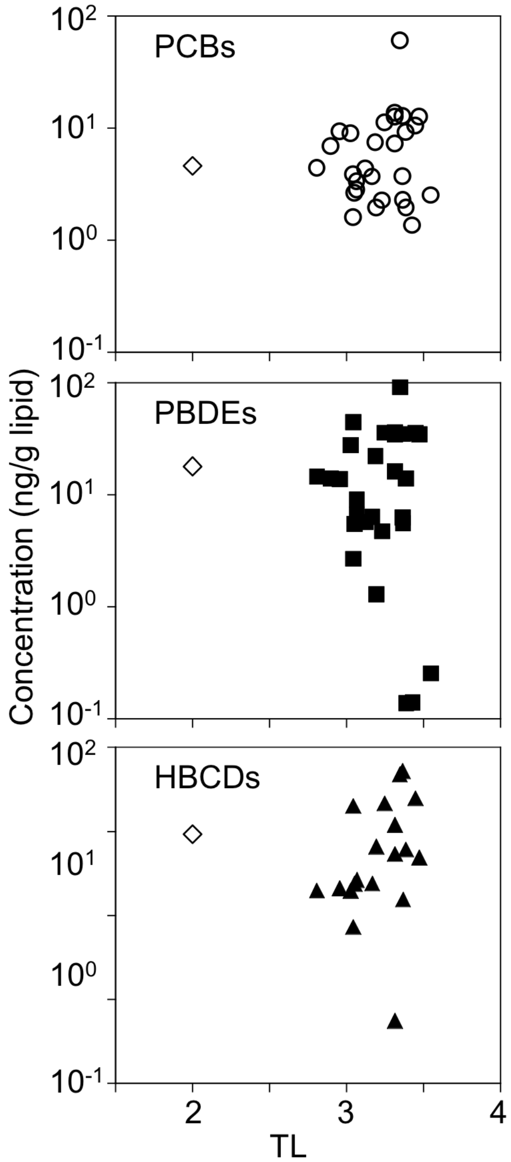

Figure 2. Relationship between organohalogen concentration and trophic level (TL) in fish from off California

for congeners with low log K_{OW} (5-7), whereas a decreasing trend was observed for congeners with high log K_{OW} (7-9). This phenomenon may be due to reduced bioavailability/uptake of higher chlorinated congeners. A similar trend was observed for PBDEs with some exceptions. The slopes of BDE-99, -153, and -209 were lower than those of predicted values. A possible reason for this difference may be metabolism or debromination of these congeners within the fish. In addition, BDE-209 has extremely low bioavailability due to its large molecular size and consequent low bioavailability. On the other hand, no relationship between TL and concentrations of analytes were observed in samples from off California (Figure 2). This lack of a trend in bioaccumulation is likely due to the more truncated food web and trophic levels of the California Current food web. Instead of $\delta^{15}N$, $\delta^{13}C$ showed a more positive correlation with concentrations of contaminants off California, implying littoral fish are more exposed to these hydrophobic chemicals than those residing more offshore.

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References.

Brodeur RD and Pearcy WG, 1992. Marine Ecology Progress Series 84, 101-119.

BSEF, 2005. http://www.bsef.com/.

Fisk AT, Hobson KA and Norstrom RJ, 2001. Environ Sci Technol 35, 732-738.

Hop H, Borga K, Gabrielsen GW, Kleivane L and Skaare JU, 2002. Environ Sci Technol 36, 2589-2597.

Isobe T, Ramu K, Kajiwara N, Takahashi S, Lam PK, Jefferson TA, Zhou K and Tanabe S, 2007. Mar Pollut Bull 54, 1139-1145.

Kelly BC, Ikonomou MG, Blair JD and Gobas FA, 2008. Sci Total Environ 401, 60-72.

Law K, Halldorson T, Danell R, Stern G, Gewurtz S, Alaee M, Marvin C, Whittle M and Tomy G, 2006. Environ Toxicol Chem 25, 2177-2186.

Muir D, Savinova T, Savinov V, Alexeeva L, Potelov V and Svetochev V, 2003. Sci Total Environ 306, 111-131.

Tanabe S, 2006. J Environ Monit 8, 782-790.

Wan Y, Hu J, Zhang K and An L, 2008. Environ Sci Technol 42, 1078-1083.