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GLOBAL POLLUTION MONITORING OF POLYBROMINATED DIPHENYL ETHERS (PBDES) USING SKIPJACK TUNA AS A BIOINDICATOR

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Introduction

Polybrominated diphenyl ethers (PBDEs) are one of the brominated flame retardants (BFRs) widely used in plastics, textiles, and paints and in electronic appliances including computers, televisions, and other electric household equipment. Contamination of PBDEs occurred in environment as evidenced by their detection in a wide range of environmental media and biota (1). Recent study suggested that PBDEs may undergo long range atmospheric transport and deposite in the polar regions such as the Canadian Arctic (2). Although several investigations have monitored the PBDEs pollution in localized areas, no study has reported the global distribution of PBDEs to understand the transport behavior and ultimate fate of these chemicals. In order to elucidate the global distribution of PBDEs, the present study attempted to use skipjack tuna (*Katsuwonus pelamis*) as bioindicator. Skipjack tuna is principally distributed from offshore waters to open seas in tropical and temperate regions almost all over the world oceans such as the Pacific, Atlantic and Indian Oceans. This species is an important commercial fish and its ecology and biology has been well studied. These facts made skipjack tuna as a suitable bioindicator for monitoring PBDEs pollution. The objectives of this study are to elucidate the global distribution of PBDEs in offshore waters and open seas, and to understand the transport behavior of these chemicals using skipjack tuna.

Materials and Method

Skipjack tuna (*Katsuwonus pelamis*) were collected from offshore waters of various Asian countries (off-Japan, Japan Sea, off-Taiwan, East China Sea, South China Sea, off-Philippines, off-Indonesia, Bay of Bengal), off-Seychelles, off-Brazil and open sea (the North Pacific Ocean) during 1996 - 2001. Some of the specimens were obtained from fish market and fisher village after confirming the fishing areas. Skipjack tuna from North Pacific Ocean were caught by fishing during a research cruise . The pooled muscles of five fishes in each location were employed for chemical analysis.

Muscle samples were extracted in a Soxhlet apparatus with a mixture of diethyl ether and hexane. An aliquot of the extract after adding internal standards ($^{13}C_{12}$-labeled BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) was then applied to gel permeation

chromatography (GPC) column for lipid removal. The GPC fraction containing organohalogens was concentrated and passed through an activated silica gel S-1 column for fractionation. Quantification of PBDEs was performed using a GC-MSD (HP6890 and HP5973) having an electron impact with selective ion monitoring mode (EI-SIM). All the congeners were quantified using the isotope dilution method to the corresponding $^{13}C_{12}$-labeled congener.

Results and Discussion

PBDEs concentrations in skipjack tuna from Asian offshore waters, off-Seychelles, off-Brazil and open seas are shown in Table 1. PBDEs were detected in all the specimens analyzed, except in off-Seychelles. PBDEs concentrations ranged from <0.1 to 53 ng/g lipid weight (Table 1). Among PBDEs analyzed in this study, BDE47 was the predominant congener (up to 18 ng/g lipid wt), and the residue pattern of other congeners was in the order of BDE154 > BDE100 > BDE99 (Table 1). Residue levels of PBDEs in skipjack tuna collected from the southern hemisphere such as off-Indonesia, off-Seychelles and off-Brazil were apparently lower than those collected from the northern hemisphere. This observation is likely due to larger usage of these compounds in the northern hemisphere. Concentrations of PBDEs in skipjack tuna from offshore water analyzed in this study were lower than those in fishes collected from inland and coastal areas of Japan, Europe and USA (3).

Table 1 PBDEs concentrations in the muscle of skipjack tuna collected from offshore waters of Asia, off-Seychelles, off-Brazil and open seas

Location	Lipid %	Concentration (ng/g lipid wt)											
		BDE3	BDE15	BDE28	BDE47	BDE100	BDE99	BDE154	BDE153	BDE138	BDE183	BDE209	Total PBDEs
N-Pacific-1	4.3	<0.05	0.030	0.48	3.1	0.56	0.43	0.92	0.24	<0.05	<0.05	<5.0	5.8
N-Pacific-2	1.1	<0.05	0.051	0.77	7.9	2.1	3.0	5.7	1.7	<0.05	0.13	<5.0	21
N-Pacific-3	4.4	<0.05	0.027	0.14	2.9	1.0	0.18	2.0	0.16	<0.05	<0.05	<5.0	6.4
off-Japan-1	5.8	<0.05	0.017	0.35	3.6	0.62	1.7	0.98	0.39	<0.05	<0.05	<5.0	7.7
off-Japan-2	5.2	<0.05	0.028	0.67	5.3	1.2	1.1	2.2	0.62	<0.05	<0.05	<5.0	11
Japan Sea	4.0	<0.05	<0.05	0.53	8.0	2.9	2.0	5.1	1.5	<0.05	0.11	<5.0	20
E-China Sea-1	3.4	<0.05	<0.05	0.72	15	4.4	4.7	5.9	2.3	<0.05	0.085	<5.0	34
E-China Sea-2	1.4	<0.05	<0.05	0.53	9.0	3.4	2.4	5.6	1.7	<0.05	<0.05	<5.0	23
off-Taiwan-1	0.7	<0.05	0.17	0.82	18	9.2	4.7	16	4.2	<0.05	<0.05	<5.0	53
S-China Sea	1.3	<0.05	0.058	0.91	8.2	1.6	2.1	2.0	0.66	<0.05	0.21	<5.0	16
off-Philippines	0.6	<0.05	<0.05	0.36	5.9	1.5	2.1	2.4	0.90	<0.05	0.35	<5.0	14
Bay of Bengal	1.2	<0.05	<0.05	0.12	0.88	0.21	<0.05	0.32	0.25	<0.05	0.069	<5.0	1.8
off-Indonesia	0.7	<0.05	<0.05	<0.05	1.1	0.41	<0.05	1.1	0.43	<0.05	<0.05	<5.0	3.1
off-Seychelles	0.9	<0.05	<0.05	<0.05	<0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<5.0	n.d.
off-Brazil	3.2	<0.05	<0.05	0.34	7.1	1.8	1.9	1.2	0.45	<0.05	<0.05	<5.0	13

n.a. : no data available
n.d.: less than detection limit
N-Pacific : the North Pacific
E-China Sea: the East China Sea
S-China Sea : the South China Sea

Geographical distribution of PBDEs concentrations in skipjack tuna was shown in Fig. 1. The highest concentration of PBDEs was detected in skipjack tuna collected from offshore waters of Taiwan (53 ng/g lipid weight) and relatively higher concentrations of these compounds were observed in the East China Sea (location E-China Sea-1 and E-China Sea-2) (Table 1 and Fig. 1). It is known that many industries manufacturer (computers, televisions, and other electric household equipment) are located in coastal areas of Asian developing countries, where huge amounts of plastics are produced and used (4). These results indicate that sources of PBDE in Asia-Pacific region might exist in developing countries around the East China Sea.

PBDE concentrations in skipjack tuna collected off-Japan were comparable to those in tuna collected from the North Pacific Ocean (location N-Pacific-1 and N-Pacific-3) (Table 1 and Fig. 1). Similar distribution pattern was also observed in PCBs concentrations in skipjack tuna (5). It has been assumed previously that PBDEs are less transportable like as DDTs and PCDDs due to their lower vapor pressure and higher particle affinity. In contrast, our result suggests that PBDEs might have relatively higher transportability similar to PCBs.

Compositions of PBDEs in skipjack tuna collected from Asia-Pacific region were shown in Fig. 2. Among PBDEs, BDE47 was the most predominant congener (Table 1 and Fig. 2). It is interesting to note that di-, tri- and tetra-BDEs in the samples from N-Pacific-1 accounted for relatively higher proportions (Fig. 2). In contrast, proportions of hexa- and hepta-BDEs were higher in southern regions such as off-Taiwan and off-Indonesia (Fig. 2). These results suggest that lower brominated congeners (BDE15, 28 and 47) might be preferentially transported through air from the sources and deposited in the northern colder regions.

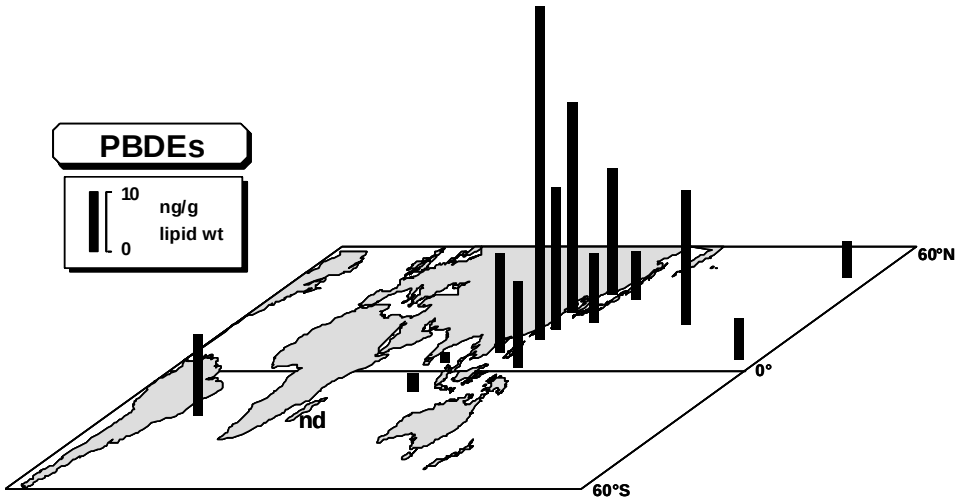

Fig. 1 Geographical distribution of PBDEs concentrations in skipjack tuna collected from offshore waters of various Asian countries, off-Seychelles, off-Brazil and open seas

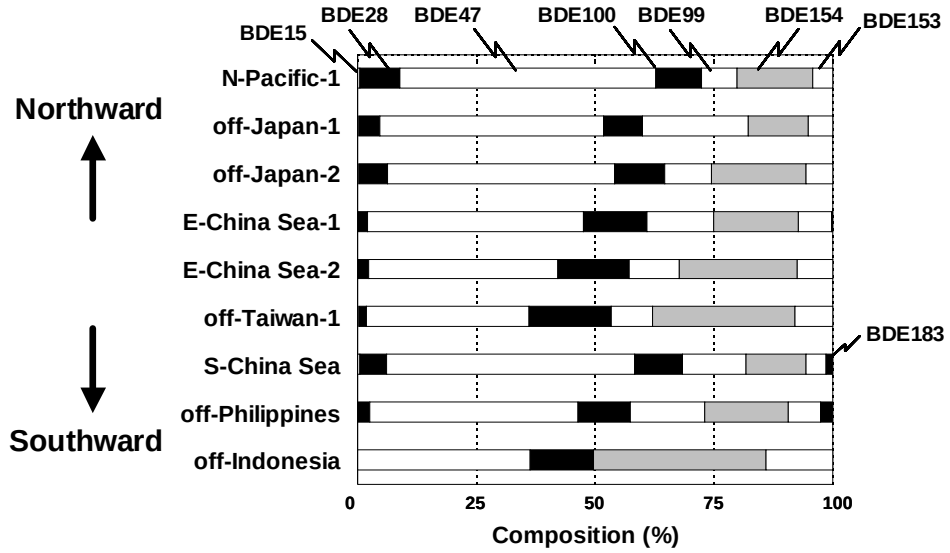

Fig. 2 PBDEs compositions in skipjack tuna collected from Asia-Pacific region

Our findings indicate that PBDEs are globally transported and cause global pollution. Therefore PBDE should be designated as a new member to the list of POPs and regulatory measures on the production and usage on global term should be implemented. Although several developed nations have banned or restricted the production and usage of these compounds, results of this study indicate that some developing countries in Asia-Pacific region are supposedly the "hot spots" of these chemicals. Further investigations of PBDEs pollution is required in the developing countries in Asia-Pacific region.

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