Global monitoring of hexabromocyclododecane (HBCD) and other organochlorines using skipjack tuna

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Introduction

Hexabromocyclododecane (HBCD) is the principal brominated flame retardant (BFR) in polystyrene foams used as thermal insulation in building materials. Although large amounts of HBCD have been used in the Asian region, environmental monitoring for this compound has not been conducted. Moreover, several investigators have monitored HBCD residue levels in localized areas of the world, information on the global distribution and fate of this compound is still largely unknown. In order to assess the extent of HBCD contamination both in the Asian region and globally, we have used skipjack tuna (*Katsuwonus pelamis*) as a bioindicator. The suitability of skipjack tuna for global monitoring of POPs has been established in our previous work[1-4]. The objectives of this study were to study the distribution of HBCD in offshore waters around the Asian region, and to better understand the global transport behavior of this chemical.

Materials and Methods

This study employed the muscle of skipjack tuna (*Katsuwonus pelamis*) archived in the Environmental Specimen Bank (es-*BANK*) at Ehime University. Samples were collected from offshore waters of various regions (Japan, Taiwan, Philippines, Indonesia, Seychelles, Brazil, Japan Sea, East China Sea, South China Sea, Indian Ocean, and North Pacific Ocean) during the years 1997-2001

Muscle samples (20g) were extracted using a Soxhlet apparatus after adding individual surrogate standards ($^{13}C_{12}$-labeled α-HBCD and γ-HBCD). Extracts were subjected to gel permeation chromatography and activated silica gel for clean up. The $^{13}C_{12}$-labeled β-HBCD was added to the fraction contained HBCD as a performance standard. Samples were analyzed on a Sciex API 4000 mass spectrometer (MDS Sciex) equipped with an Agilent 1100 Series LC system (Agilent Technology). MS/MS detection used multiple reaction monitoring (MRM) conditions for the m/z 640.6 ([M-H]$^-$) to Br$^-$ transition. HBCD isomers were quantified by isotope dilution using the corresponding $^{13}C_{12}$-labeled isomers (β-HBCD was quantified using $^{13}C_{12}$-γ-HBCD). MDLs of α-HBCD, β-HBCD and γ-HBCD were 0.001, 0.001 and 0.004 ng/g (wet weight), respectively.
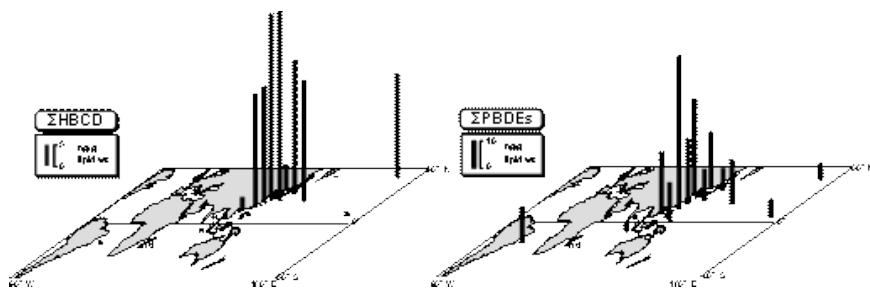
Results and Discussion

Contamination Status

Fig. 1 Geographical distribution of HBCD and PBDEs[3] in the muscle of skipjack tuna

HBCD were detected from all the samples analyzed in this study, with the exception of the off-Seychelles samples (Figure 1). These results indicated a widespread presence of HBCD in the global marine environment. Concentrations of total HBCD ranged from <0.07 to 45 ng/g lipid weight basis. These HBCD concentrations in skipjack tuna were comparable to, or lower than, concentrations in fish collected from inland and coastal waters[5-6]. The lower levels of HBCD contamination in fish in this study can be attributed to the remoteness of the offshore sample collection sites, relative to nearshore areas in closer proximity to urbanized/industrialized areas. Those aspects are similar with PBDEs detected from skipjack tuna[3] (Figure 1).

Geographical Distribution of Dioxins and Related Compounds

The geographical distribution of HBCD concentrations in skipjack tuna is shown in Figure 1. Although the numbers of samples from the southern hemisphere were small (off-Indonesia, off-Seychelles, and off-Brazil), residue levels of HBCDs in skipjack tuna collected from areas of the northern hemisphere were higher than the southern hemisphere. Higher concentrations of PBDEs were also found in skipjack tuna from northern hemisphere[3] (Figure 1).

Among the samples collected from northern hemisphere, higher concentrations of HBCDs were found in mid-latitude areas of the Far East (Figure 1). The highest concentration of HBCD was detected in a sample collected near Japan; relatively high concentrations were also found in the East China Sea and northern North Pacific. Japan, South Korea, Taiwan and coastal China have larger modern industrial/urban societies with higher income per capita, compared with other southern/southeastern Asian developing regions. Greater demand and manufacturing of consumer products including building material and transportation upholstery, in which HBCD is heavily-used, in the higher per capita Asian regions may be a determining factor in the observed regional distribution of HBCD in skipjack tuna.

Table 1. Summary of 1/2 distances and liner regression of (log) concentrations versus distance for organohalogen compounds.

Transportability of HBCD and Other Halogenated POPs

Compounds	n	r2	p	1/2 distance (km)	SE (km)
α-HCH	5	0.83	0.03	-1700	480
a-HBCD	4*	0.45	0.33	8500	6700
g-HBCD	4*	0.73	0.15	1600	680
ΣHBCD	4*	0.86	0.08	5300	1600
BDE99	5	0.87	0.02	1400	320
BDE153	5	0.79	0.05	1200	380
2378-T4CDF	5	0.93	0.01	3200	530
23478-P5CDF	5	0.87	0.02	2100	470
ΣPCDFs	5	0.87	0.02	2000	440
12378-P5CDD	5	0.91	0.01	1300	250
ΣPCDDs	5	0.93	0.01	1200	190
ΣPCBs	5	0.77	0.05	1500	480
p,p'-DDT	5	0.91	0.01	950	170
ΣDDTs	5	0.85	0.03	1100	280

1/2 distance (km) = 1/slope*log(2)
SE (km): standard deviation
N-Pacific-1, off-Japan-1, off-Japan-2, E-China Sea-1 and off-Taiwan were used for calculation
*: N-Pacific-1, off-Japan-1, off-Japan-2 and E-China Sea-1 were used for calculation
ΣHBCD: a + b + g-HBCD
ΣDDTs: p,p'-DDT + p,p'-DDE + p,p'-DDD
ΣPCDDs and ΣPCDFs: sum of 2,3,7,8 substituted congeners
ΣPCBs: sum of major congeners

Our data for skipjack tuna indicate that HBCD occurrence is widespread in the global marine environment (Figure 1). The distribution of this compound was similar to the HCHs, which have one of the highest mobility among POPs. In order to assess the transportable nature of HBCD, empirical half-decline distances (1/2 distance) were calculated, and compared with other halogenated POPs measured in the same skipjack tuna samples[1-4] (Table 1). The 1/2 distance for α-HBCD was 8500 km, which is one of the highest values among organohalogen compounds. This study revealed that HBCD is highly transportable compound compared to other halogenated POPs.

Accnowledgement

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