Contamination by Persistent Organohalogen Compounds in Deep-sea Fishes from off the Pacific Coast of Northern Japan

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Abstract: Twelve species of deep-sea fishes collected in 2005 from off the Pacific coast of northern Japan from depths ranging from 400‒1000 m were analyzed for persistent organochlorine compounds (OCs), including PCBs and organochlorine pesticides and brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane isomers (HBCDs). Among OCs, concentrations of DDTs and PCBs (up to 23000 and 12400 ng/g lipid wt, respectively) were the highest and other OCs were approximately in the order of CHLs > HCHs ≥ HCB. PBDEs and HBCDs were also detected in almost all the deep-sea fishes. The present study is the foremost to report the occurrence of BFRs in deep-sea fishes from the North Pacific region. Although magnitude of contamination by these organohalogen compounds in most of the fish species analyzed was comparable or lower than that reported in shallow-water and deep-sea fishes from Japanese coastal waters, snubnosed eels accumulated some hydrophobic compounds like PCBs, DDTs and PBDEs at extremely high concentrations. Significant positive correlations found between δ^{15}N (‰) and PCBs, DDTs and PBDEs suggest the high biomagnification potential of these contaminants in food web. Nevertheless, large variation in δ^{13}C (‰) values observed between the species indicate multiple sources of carbon in the food web and specific accumulation of hydrophobic organohalogen compounds in benthic dwelling species like snubnosed eel. It is noteworthy that no significant declining trends of PCBs, HCB and HCHs levels were observed in fishes collected in 1995 and 2005, suggesting continuous input of the contaminants into the environment. The results obtained in this study highlight the usefulness of deep-sea fishes as sentinel species to monitor the deep-sea environment.

Key words: organochlorines, brominated flame retardants, stable isotopes, deep-sea fishes, Tohoku region

Introduction

The long-range transport, persistence, and global dynamics of persistent organic pollutants (POPs) are issues of increasing concern in recent years. Organochlorine compounds (OCs), a representative group of classical POPs, are ubiquitous contaminants entering the marine environment in coastal areas, mainly by river inflow and continental runoff and in the open sea by atmospheric deposition. In the global marine environment, the apparent fate of these compounds is to adsorb to the detritus and marine snow and eventually carried to the deep-sea where they biomagnify in the food web (Froescheis *et al.*, 2000). Several models suggested that deep-sea sediments are the final accumulation site for OCs (Woodwell *et al.*, 1971; Tatsukawa and Tanabe, 1984), and fish living in association with sediments are exposed to and accumulate these compounds (Berg *et al.*, 1997). Increasing concern that the deep-sea might act as an ultimate sink for such contaminants and the growing importance of deep-sea commercial fisheries around the world have resulted in numerous

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monitoring studies on the accumulation of OCs in deep-sea organisms (Berg *et al.*, 1997, 1998; Lee *et al.*, 1997; Takahashi *et al.*, 1998, 2000, 2001; Looser *et al.*, 2000; Froescheis *et al.*, 2000; Sole *et al.*, 2001; de Brito *et al.*, 2002a; Mormede and Davies, 2003; Storelli *et al.*, 2004). Although our previous study also found significant levels of OC contaminants in some deep-sea organisms collected from off the Pacific coast of northern Japan, during 1994-1995 (de Brito *et al.*, 2002a), no recent information is available on the contamination status of OCs in the ecosystem of this region.

In addition to OC contamination, aquatic pollution resulting from widespread usage of brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) deserves concern because of the bioaccumulation potential, persistence and endocrine disrupting effects of the contaminants (Watanabe and Sakai, 2003, Tanabe *et al.*, 2008). Therefore, these compounds have been recently reported as emerging global environmental contaminants. Nevertheless, compared to OCs, there is still little information on contamination by BFRs in the Asia-Pacific region, and studies addressing the contamination of deep-sea areas by BFRs are scarce (Ramu *et al.,* 2006).

Concerned over the possible flux of such persistent organohalogen contaminants to the bottom of the oceans, the present study attempted to investigate the contamination and accumulation of OCs, such as polychlorinated biphenyls (PCBs), DDT and its metabolites (DDTs), chlordane-related compounds (CHLs), hexachlorocyclohexane isomers (HCHs) and hexachlorobenzene (HCB), and BFRs such as PBDEs and HBCDs, in deep-sea fishes from off the Pacific coast of northern Japan (Tohoku region). Additionally, the data on OCs in deep-sea fishes reported in our earlier study (de Brito *et al.*, 2002a) were compared with that observed in this study to delineate the temporal trend of OCs contamination during the last decade from 1994/95 to 2005.

Stable isotope analysis is generally used to investigate energy flow through an ecosystem. The $\delta^{15}N$ and $\delta^{13}C$ values in animals reflect their diets. Thus, trophic relationships can successfully be derived using relative abundances of naturally occurring stable isotopes of nitrogen ($^{15}N/^{14}N$, expressed as $\delta^{15}N$ values) (Hobson and Welch, 1992). Furthermore, measurements of $\delta^{15}N$ as a continuous trophic-level variable enable to quantitatively estimate the magnitude of contaminant biomagnification within food webs (Ruus *et al.*, 2002). Hence, to examine the biomagnification of OCs and BFRs through the deep-sea food web, $\delta^{15}N$ and $\delta^{13}C$ analyses were performed on deep-sea fishes from off the Pacific coast of northern Japan.

The present study was conducted as part of a joint research project entitled "Study on Deep-Sea Fauna and Conservation of Deep-Sea Ecosystem" between the Department of Zoology, National Museum of Nature and Science and Center for Marine Environmental Studies, Ehime University.

Materials and Methods

Samples

Twelve species of deep-sea fishes collected from off the Pacific coast of northern Japan (36–38°N, 141–142°E) from depths ranging from 400 to 1000 m during October to November 2005 were analyzed in this study. The fish samples were collected by the R/V *Wakataka-maru* of the Fisheries Research Agency (FRA) using a research bottom trawl. Sampling location and biological information of the samples are shown in Fig. 1 and Table 1, respectively. 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 belonging to the same species collected from the same sampling location were pooled and homogenized to prepare a composite sample for chemical analysis.

Table 1. Sample details of deep-sea fishes from off the Pacific coast of northern Japan. n.m: not measured.

| Sample No.	Common name	Scientific name	n	Sampling year	Depth (m)	Mean length (cm)	Mean weight (g)	Habitat
Fish-1	Flathead flounder	*Hippoglossoides dubius*	1	2005	650	37	610	Demersal
Fish-2	Flathead flounder	*Hippoglossoides dubius*	1	2005	650	36	500	Demersal
Fish-3	Longfin codling	*Laemonema longipes*	1	2005	650	47	500	Bathydemersal
Fish-4	Kaup's arrowtooth eel	*Synaphobranchus kaupii*	1	2005	550	67	450	Bathydemersal
Fish-5	Kaup's arrowtooth eel	*Synaphobranchus kaupii*	1	2005	550	61	290	Bathydemersal
Fish-6	Kaup's arrowtooth eel	*Synaphobranchus kaupii*	1	2005	550	69	610	Bathydemersal
Fish-7	Spinyhead sculpin	*Dasycottus setiger*	1	2005	450	26	290	Demersal
Fish-8	Snubnosed eel	*Simenchelys parasitica*	1	2005	900	44	140	Bathydemersal
Fish-9	Snubnosed eel	*Simenchelys parasitica*	1	2005	900	41	100	Bathydemersal
Fish-10	Snubnosed eel	*Simenchelys parasitica*	1	2005	900	36	65	Bathydemersal
Fish-11	Snubnosed eel	*Simenchelys parasitica*	1	2005	900	38	100	Bathydemersal
Fish-12	Sake-bikunin	*Careproctus rastrinus*	2	2005	425	n.m	160	Bathydemersal
Fish-13	Longarm grenadier	*Coelorinchus macrochir*	1	2005	410	59	620	Bathydemersal
Fish-14	Longarm grenadier	*Coelorinchus macrochir*	1	2005	410	59	720	Bathydemersal
Fish-15	Largenose grenadier	*Coryphaenoides nasutus*	5	2005	900	31	71	Bathydemersal
Fish-16	Blackbelly lanternshark	*Etmopterus lucifer*	3	2005	480	50	230	Benthopelagic
Fish-17	Pacific cod	*Gadus macrocephalus*	1	2005	450	39	610	Demersal
Fish-18	Pacific cod	*Gadus macrocephalus*	1	2005	450	38	760	Demersal
Fish-19	Eelpout	*Lycodes hubbsi*	2	2005	750	38	130	Bathydemersal
Fish-20	Brokenline lanternfish	*Lampanyctus jordani*	14	2005	480	13	17	Bathypelagic
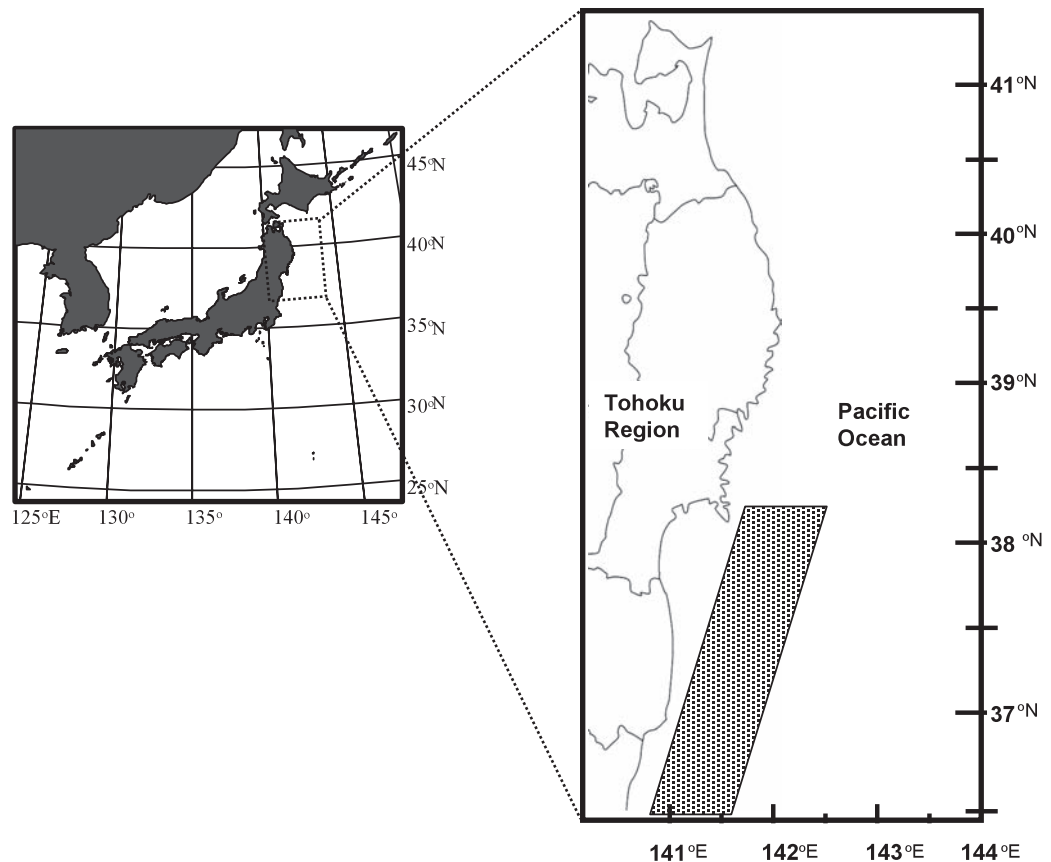
Fig. 1. Map showing the sampling area (shaded portion) off the Pacific coast of northern Japan (Tohoku region).

Chemical analysis

Analysis of PBDEs and HBCDs was performed following the procedures described by Ueno *et al.* (2004, 2006) with slight modifications, while OCs such as DDTs, CHLs, HCHs, HCB, and PCBs were analyzed following the method described by Kajiwara *et al.* (2003).

Briefly, 15–30 g of the homogenized tissue sample was ground with anhydrous sodium sulfate and extracted in a Soxhlet apparatus with a mixture of diethyl ether and hexane for 7–8 h. An aliquot of the extract, after spiking 5 ng of internal standards for PBDEs ($^{13}C_{12}$-labeled BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-153, BDE-154, BDE-183, BDE-197, BDE-207 and BDE-209) and 10 ng of internal standards for HBCDs ($^{13}C_{12}$-labeled α-, β- and γ-HBCD), was added to a gel permeation chromatography column (GPC) for lipid removal. The GPC fraction containing organohalogens was concentrated and passed through 4 g of activated silica gel (Wakogel DX, Wako Pure Chemical Industries Ltd., Japan) column. The first fraction eluted with 5% dichloromethane in hexane for cleanup contained PBDEs, while the second fraction eluted with 25% dichloromethane in hexane contained HBCDs. $^{13}C_{12}$-labled BDE-139 was added to the final first fraction solution prior to GC-MS analysis for PBDEs. Quantification was performed using a GC (Agilent 6890N) equipped with MS (Agilent 5973N) for mono- to hepta-BDEs, and GC coupled with MS (JEOL GCmate II) for octa- to deca-BDEs, using electron ionization with selective ion monitoring (EI-SIM) mode. GC columns used for quantification were DB-1 fused silica capillary (J&W Scientific Inc.) having 30 m x 0.25 mm i.d. x 0.25 μm film thickness for mono- to hepta-BDEs, and 15 m x 0.25 mm i.d. x 0.1 μm film thickness for octa- to deca-BDEs. Fourteen major congeners of PBDEs (BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-206, BDE-207 and BDE-209) were quantified in this study. All the congeners were quantified using the isotope dilution method to the corresponding $^{13}C_{12}$-labeled congener. Recovery of $^{13}C_{12}$-labeled BDE ranged between 60 and 120%.

The fraction containing HBCDs was solvent exchanged into methanol and 10 ng of d_{18}-labeled α-, β- and γ-HBCD was added to the final solution prior to liquid chromatography combined with tandem mass spectrometry (LC-MS-MS) analysis as a performance standard. The diastereomeric analysis of HBCDs was performed on the basis of an analytical method reported by Tomy *et al.* (2004). Samples were analyzed with Quattro Micro API triple-quadrupole mass spectrometer (Waters/Micromass, Tokyo, Japan) equipped with Alliance 2795 LC separation module (Waters, Tokyo, Japan). Separation of HBCD isomers (α-, β- and γ-) was achieved with an Extend-C_{18} column (2.1 mm i.d. x 150 mm, 5 μm particle size). The mobile phase consisted of water/acetonitrile/methanol (20:30:50) at 200 μL/min in initial condition for 2 min and then ramped to acetonitrile/methanol (30:70) in 5 min, and this was then maintained for 6 min. The MS-MS analysis, which was operated in negative mode of electrospray ionization (ESI), was performed in multiple reaction monitoring mode (MRM). Quantification of native HBCDs was achieved from mean value of the response of two MRM transitions (i.e., m/z 640 > 81, m/z 642 > 81) corrected with response of $^{13}C_{12}$-HBCDs (i.e., m/z 652 > 81 MRM transition). HBCD isomers were quantified by isotope dilution using the corresponding $^{13}C_{12}$-labeled isomers. Recoveries of $^{13}C_{12}$-labeled HBCDs during analytical procedure were determined using d_{18}-labeled isomers and the values ranged between 60% and 120%.

For analysis of OCs an aliquot of the extract was subjected to GPC for lipid removal. The GPC fraction containing OCs was concentrated and passed through an activated Florisil column for clean-up and fractionation. Quantification of PCBs and most of the organochlorine pesticides was performed using a GC equipped with a microelectron capture detector (micro-ECD) and an auto-injection system (Agilent 7683 Series Injector). The GC column used for OC analysis was a fused silica capillary (DB-1; 30 m x 0.25 mm i.d. x 0.25 μm film thickness, J&W Scientific Inc.). The concentration of individual OCs was quantified from the peak area of the sample to that of the

corresponding external standard. The PCB standard used for quantification was a mixture of 62 PCB isomers and congeners (BP-MS) obtained from Wellington Laboratories Inc., Ontario, Canada. Concentrations of individually resolved peaks of PCB isomers and congeners were summed to obtain total PCB concentrations.

Procedural blanks were analyzed simultaneously with every batch of five samples to check for interferences or contamination from solvents and glassware. Lipid contents were determined by measuring the total nonvolatile solvent extractable material on subsamples taken from the original extracts. The concentrations of organohalogens are expressed on lipid weight basis unless otherwise specified.

Stable isotope analysis

Sub-samples from the homogenized samples were dried for 24 hours at 60°C and ground into powder with a mortar and pestle. The solvent-extractable lipid fraction was removed from the subsample by extraction with a mixture of chloroform: methanol (2:1), and the lipid free residues were centrifuged using micro-tubes and dried at room temperature and later at 60°C for 24 hours. One mg powder subsamples were packed into 4 x 6 mm tin capsules for stable isotope measurements. Stable isotopes were measured using ANCA-SL mass spectrometer (PDZ Europa Ltd.). Isotope ratios of carbon (δ^{13}C) and nitrogen (δ^{15}N) are expressed as the deviation from standards in parts per thousand (‰) according to the following equation:

$$\delta^{13}C, \delta^{15}N = [(R_{sample}/R_{standard})\text{-}1] \text{ X } 1000 \text{ (‰)}$$

where R = ^{13}C/^{12}C or ^{15}N/^{14}N. Pee Dee Belemnite (PDB) limestone carbonate and atmospheric nitrogen (N_2) were used as standards for carbon and nitrogen isotope ratios, respectively.

Results and Discussion

Contamination status of OCs

Concentrations of organohalogen compounds in deep-sea fishes from off the Pacific coast of northern Japan are shown in Table 2. Although concentrations of organohalogen compounds varied among the species, concentrations of PCBs and DDTs were the highest among the OCs analyzed, and other compounds were approximately in the order of CHLs > HCHs ≥ HCB. The predominance of DDTs and PCBs in the fishes analyzed in this study is similar to that in deep-sea organisms 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*., 2002a), the East China Sea (Tanabe *et al.*, 2005) and the Sulu Sea (Ramu *et al.*, 2006). This may be due to the higher bioaccumulative properties and the continuous input of these compounds into the environment.

Concentrations of OCs such as PCBs and DDTs in deep-sea fishes from off the Pacific coast of northern Japan were lower than those in deep-sea fishes from the Atlantic Ocean (Meith-Avcin *et al*., 1973; Harvey *et al*., 1974; Barber and Warlen, 1979; Krämer *et al*., 1984; Looser *et al*., 2000; Froescheis *et al*., 2000), Gulf of Mexico (Baird *et al*., 1975), US coasts (Stegeman *et al*., 1986; Melzian *et al*., 1987) and the Arctic region (Hargrave *et al*., 1992; Berg *et al*., 1997, 1998; Mormede and Davies, 2003) (Table 3). The relatively low contamination by OCs in the present study area might be due to the less usage of these compounds in this region compared to that in the Atlantic countries. In addition to this, decreasing trends of OCs have been noticed globally in recent years in the marine environment even in the deep-sea, as evidenced in the Atlantic Ocean between the 1970s and 1992. The samples analyzed in the present study were collected in 2005 and factors like variations in analytical methods and fish species compared between the studies may

Table 2. Concentrations of organohalogen compounds (ng/g lipid wt), $\delta15N$ and $\delta13C$ in deep-sea fishes from off the Pacific coast of northern Japan. n.a.: not analyzed.

Sample No.	Common name	Scientific name	Fat (%)	PCB	DDTs	CHLs	HCB	HCHs	PBDEs	HBCDs	δ15N	δ13C
Fish-1	Flathead flounder	*Hippoglossoides dubius*	5.7	82	74	39	18	17	3.7	34	13.17	-17.91
Fish-2	Flathead flounder	*Hippoglossoides dubius*	5.4	70	82	32	14	16	3.2	11	11.49	-19.23
Fish-3	Longfin codling	*Laemonema longipes*	7.4	150	120	120	16	16	3.5	22	12.17	-19.39
Fish-4	Kaup's arrowtooth eel	*Synaphobranchus kaupii*	22	120	130	56	15	46	1.8	24	11.53	-22.53
Fish-5	Kaup's arrowtooth eel	*Synaphobranchus kaupii*	20	290	97	100	21	32	2.1	32	11.55	-19.92
Fish-6	Kaup's arrowtooth eel	*Synaphobranchus kaupii*	25	100	36	38	24	22	1.9	18	11.69	-20.12
Fish-7	Spinyhead sculpin	*Dasycottus setiger*	1.4	390	220	77	21	69	4.6	31	13.64	-17.44
Fish-8	Snubnosed eel	*Simenchelys parasitica*	15	8800	16000	1900	43	5.7	24	24	13.99	-21.24
Fish-9	Snubnosed eel	*Simenchelys parasitica*	8.6	2300	4700	580	13	13	21	38	14.33	-19.03
Fish-10	Snubnosed eel	*Simenchelys parasitica*	8.9	12400	23000	2500	25	5.7	53	110	13.86	-19.70
Fish-11	Snubnosed eel	*Simenchelys parasitica*	18	1500	2600	270	22	12	12	57	14.61	-19.50
Fish-12	Sake-bikunin	*Careproctus rastrinus*	1.2	189	200	83	37	19	4.1	45	12.03	-18.42
Fish-13	Longarm grenadier	*Coelorinchus macrochir*	7.5	120	110	51	15	40	2.6	26	12.02	-20.15
Fish-14	Longarm grenadier	*Coelorinchus macrochir*	9.3	90	110	44	29	19	2.1	22	11.51	-19.62
Fish-15	Largenose grenadier	*Coryphaenoides nasutus*	3.8	140	120	19	45	13	1.9	5.4	12.82	-18.17
Fish-16	Blackbelly lanternshark	*Etmopterus lucifer*	13	170	120	47	15	5.2	3.9	18	13.06	-19.10
Fish-17	Pacific cod	*Gadus macrocephalus*	2.5	36	68	29	18	20	5.8	<0.05	13.97	-18.80
Fish-18	Pacific cod	*Gadus macrocephalus*	2.8	73	120	47	21	23	8.5	<0.05	13.26	-18.70
Fish-19	Eelpout	*Lycodes hubbsi*	2.2	390	180	55	13	16	6.2	13	14.77	-16.86
Fish-20	Brokenline laternfish	*Lampanyctus jordani*	11	34	47	21	6.9	33	1.3	12	n.a.	n.a.

Table 3. Comparison of mean concentrations of PCBs and DDTs in deep-sea fishes from various parts of the world. — : not available.

Species	Sampling Year	Location	Depth (m)	PCBs (ng/g) wet wt	PCBs (ng/g) lipid wt	DDTs (ng/g) wet wt	DDTs (ng/g) lipid wt	Reference
Snubnosed eel	2005	Northern Japan (off Tohoku)	400-1000	720	6300	1300	12000	This study
Fish (11 spp.)	2005	Northern Japan (off Tohoku)	400-1000	12	150	8.2	100	This study
Chauliodontidae	1970-72	North & South Atlantic	450-900	26	3000	6.2	760	Harvey et al. (1974)
Stenophoridae	1972	North & South Atlantic	130-660	33	2200	8.3	480	Harvey et al. (1974)
Gonostanomiae	1972	North & South Atlantic	510-660	70	15000	14	4300	Harvey et al. (1974)
Blue hake	1972	Atlantic (Cape Hatteras)	2500	—	—	5400	—	Meith-Avcin et al. (1973)
(Antimora rostrata)	1972-74	Atlantic (Cape Hatteras)	2501	—	—	6900	—	Barber and Warlen (1979)
Mesopelagic fish	1973	Gulf of Mexico	0-760	200	13000	19	2000	Baird et al. (1975)
Black Scabbard	—	Atlantic (Madeira Is.)	800-1200	—	5800	—	9200	Krämer et al. (1984)
Rattail	—	Hudson Canyon	3200	2700	—	—	—	Stegeman et al. (1986)
(Coryphaenoides armatus)	—	Carson Canyon	1700-2300	360	—	—	—	Stegeman et al. (1986)
Dover sole	1985	Farallon Is.	500	830	11000	760	11000	Melzian et al. (1987)
(Microstomus pacificus)	1985	off California	1000	980	12000	2300	22000	Melzian et al. (1987)
(Anoplopoma fimbria)	1985	off California	1000	7000	56000	8700	74000	Melzian et al. (1987)
Glacial eelpout	1983	off California	1001	—	2300	—	1500	Melzian et al. (1987)
Cartilagenous fish (2 spp.)	1992	Davis Strait (Greenland)	800-2200	310	430	490	690	Berg et al. (1997)
Bony fish (6 spp.)	1992	Davis Strait (Greenland)	200-2100	300	790	250	670	Berg et al. (1997)
Fish (6 spp.)	1993-94	Suruga Bay, Japan	200-740	160	1000	60	390	Lee et al. (1997)
Cartilagenous fish (1 spp.)	1992	Norway (Nordfjord)	400	1800	2400	4600	6000	Berg et al. (1998)
Bony fish (3 spp.)	1992	Norway (Nordfjord)	400	3900	8700	8800	20000	Berg et al. (1998)
Armed grenadier	1992	North Atlantic	2900	—	2100	—	1090	Looser et al. (2000)
Black halibut	1994-98	North Atlantic	—	—	1000	—	390	Froescheis et al. (2000)
Kingclip	1994-98	South Atlantic	—	—	1400	—	190	Froescheis et al. (2000)
Dover sole	1995	Monterey Bay Canyon	—	—	2200	—	2400	Froescheis et al. (2000)
Longspine thornyhead	1995	Monterey Bay Canyon	—	—	3700	—	2400	Froescheis et al. (2000)
Fish (20 spp.)	1997-98	Tosa Bay, Japan	150-400	39	350	31	290	Takahashi et al. (2001)
Snubnosed eel	1995	Northern Japan (off Tohoku)	1000	1100	6700	2100	13000	de Brito et al. (2002)
Fish (21 spp.)	1995	Northern Japan (off Tohoku)	150-1300	81	400	30	220	de Brito et al. (2002)
Skate	2000	Southern Adriatic Sea	—	—	890	—	—	Storelli et al. (2004)
Ghostshark	2000	Southern Adriatic Sea	—	—	387	—	—	Storelli et al. (2004)
Roundnose grenadier	1999	West of Ireland	1000	450	770	730	1300	Mormede and Davies (2003)
Roundnose grenadier	1999	West of Ireland	2000	800	1900	1000	2400	Mormede and Davies (2003)
Fish (37 spp.)	2001-03	East China Sea	89-512	6.2	230	30	700	Tanabe et al. (2005)
Fish (10 spp.)	2002	Sulu Sea	292-1015	0.59	58	1.8	150	Ramu et al. (2006)

also influence the differences in the OC levels.

To understand the current status of OCs pollution in deep-sea fishes from off the Pacific coast of northern Japan residue levels found in the present study were compared the with studies on deep-sea fishes in adjoining areas carried out by our group (Table 4). Except for snubnosed eels (*Simenchelys parasitica*), which contained some OCs at extremely high concentrations, the concentrations of PCBs, DDTs, CHLs and HCB in deep-sea fishes collected from off the Pacific coast of northern Japan were comparable or lower than the data so far reported in our related studies in the western North Pacific region (Lee *et al.*, 1997; Takahashi *et al.*, 1998, 2000, 2001; de Brito *et al.*, 2002a) and the East China Sea (Tanabe *et al.*, 2005). It was noted that PCBs used in electrical equipment are continuously released into the environment (Hirai *et al.*, 2003). In Japan, CHLs were used largely as a termiticide until 1986. Higher levels of PCBs and CHLs found in fishes from other locations such as Suruga Bay were due to their proximity to urban cities with more intensive human activities. In addition, large scale use of DDT in agricultural practices and the subsequent runoff in the waterways have resulted in their accumulation in the freshwater, estuarine and marine environment of China (Yuan *et al.*, 2001). This might explain the reason for the elevated levels of DDT observed in deep-sea fishes from the East China Sea. On the other hand, concentrations of HCHs in deep-sea fishes from off the Pacific coast of northern Japan were higher than those from other locations along the warm Kuroshio Current. Higher concentrations of HCHs in cold waters along the Oyashio Current than other offshore waters around Japan were also observed in a monitoring study using skipjack tuna (*Katsuwonus pelamis*) (Ueno *et al.*, 2003). Due to high vapor pressure, HCHs are known to rapidly evaporate and be transported from their pollution

Table 4. Comparison of mean and range concentrations of organochlorines (ng/g lipid wt) between fishes from the western North Pacific and East China Sea. Figures in parentheses indicate the range of concentrations. n.d.: not detected (for calculation of mean, n.d. was assumed to be 0). *Data without snubnosed eel.

Location	PCBs	DDTs	CHLs	HCHs	HCB	Reference
Northern Japan (off Tohoku)						
Deep-sea fish*	150	110	54	25	21	This study
	(n.d.–2200)	(14–830)	(3.9–640)	(n.d.–150)	(n.d.–100)	
Tosa Bay						
Shallow-water fish	310	220	46	5.3	5.7	Takahashi *et al.* (2001)
	(n.d.–1100)	(38–1200)	(n.d.–200)	(n.d.–14)	(n.d.–13)	
Deep-sea fish	340	290	44	11	11	Takahashi *et al.* (2001)
	(n.d.–1600)	(7.1–1200)	(5.6–220)	(n.d.–21)	(n.d.–61)	
Suruga Bay						
Shallow-water fish	1600	390	140	4.1	8.8	Lee *et al.* (1997)
	(540–2600)	(80–1700)	(46–320)	(n.d.–8.0)	(3.7–24)	
Deep-sea fish	1000	390	260	25	20	Lee *et al.* (1997)
	(450–1900)	(51–910)	(69–770)	(10–37)	(9.9–50)	
Northern Japan (off Tohoku)						
Deep-sea fish*	420	230	110	30	16	de Brito *et al.* (2002)
	(n.d.–2200)	(14–830)	(3.9–640)	(n.d.–150)	(n.d.–100)	
East China Sea						
Shallow-water fish	150	330	39	11	17	Tanabe *et al.* (2005)
	(20–830)	(110–1200)	(5.9–180)	(2.2–62)	(<n.d.–70)	
Deep-sea fish	230	720	40	11	18	Tanabe *et al.* (2005)
	(36–1400)	(<n.d.–7900)	(3.7–240)	(1.4–41)	(1.7–290)	

sources in the tropics and temperate regions to colder regions via the atmosphere (Iwata *et al.,* 1993; Wania and Mackay 1996; Beyer *et al.,* 2000). The distribution patterns of HCHs found in the biota reflect such highly transportable nature of HCHs and its accumulation in the cold water current of the western North Pacific. Considering the above, the contamination status of OCs in deep-sea fishes analyzed in this study seems to reflect typical magnitude of OCs pollution in open water ecosystems of the western North Pacific.

Contamination status of BFRs

Polybrominated diphenyl ethers which are one of the most commonly used flame retardants were detected in all the deep-sea fishes from off the Pacific coast of northern Japan (Table 2). The present study is the foremost to report the occurrence of PBDEs in deep-sea fishes from the North Pacific region. The concentrations of PBDEs (ranged from 1.3 to 8.5 ng/g with mean 3.6 ng/g lipid wt) in deep-sea fishes (except for snubnosed eels) from this region were lower than the levels reported for marine fish from Japanese coastal waters (Akutsu *et al*., 2001), various species of fish from the Belgian North Sea (Voorspoels *et al.*, 2003) and coastal fishes from Florida (Johnson-Restrepo *et al.*, 2005), but comparable to those found in skipjack tuna from offshore waters of the North Pacific (Ueno *et al.*, 2004) and higher than the levels in deep-sea fishes from Sulu Sea (Ramu *et al.*, 2006). Despite the low levels of PBDEs found in offshore waters, the detection of these compounds in deep-sea fishes confirms that PBDEs, like the classical POPs, are transportable to the deep oceans and, thus, can cause global environmental contamination.

In addition to PBDEs, HBCDs were detected in almost all the deep-sea fishes analyzed in this study. To our knowledge, this is the first report on the detection of HBCDs in deep-sea biota. This result again indicates the widespread presence of such 'emerging POPs' even in deep oceans. The concentrations of HBCDs (ranged from 5.4 to 45 ng/g with mean 22 ng/g lipid wt) in deep-sea fishes (except for snubnosed eels) from this region were lower than those in fish collected from the North Sea (Morris *et al.*, 2004) and the Scheldt estuary in the Netherlands (Janak *et al.*, 2005), but comparable to those found in skipjack tuna from offshore waters around Japan (Ueno *et al.*, 2006). On the other hand, concentrations of HBCDs in deep-sea fishes were higher than those of PBDEs (Table 2). Higher concentrations of HBCDs than PBDEs were also observed in skipjack tuna collected from offshore waters around Japan (Ueno *et al.*, 2004, 2006). Increasing levels of HBCDs, which appear to exceed those of PBDEs in recent years, were noted in recent studies on temporal trends of BFRs contamination in marine mammals stranded and collected around Japanese coastal waters (Tanabe *et al*., 2008). In Japan, consumption of HBCDs increased continuously from around 600 tons in 1986 to 2200 tons in 2001, while the use of PentaBDE and OctaBDE was withdrawn from the Japanese market in 1991 and 2000, respectively (Watanabe and Sakai, 2003). Considering the remarkable increase in market demand for HBCDs in Japan, it can be anticipated that contamination by HBCDs in marine ecosystems around Japan may further increase because, unlike PBDEs, HBCDs are currently not regulated.

Species-specific accumulation of organohalogen compounds

It has been well demonstrated that gill-breathing organisms exchange OCs through the gills and equilibrate the levels between ambient water and body lipids (Clayton *et al.,* 1977; Tanabe *et al*., 1984). In this study, concentrations of OCs and BFRs (wet wt basis) in deep-sea fishes (except for snubnosed eels) were significantly correlated with their body lipid content, but considerable variation between the species was observed even in the concentrations of OCs and BFRs on lipid weight basis. Particularly, snubnosed eel accumulated hydrophobic organohalogens (with log K_{ow} *ca.* 6 to 8) such as PCBs, DDTs, CHLs and PBDEs at extremely high concentrations (Table 2). This is quite similar to the results found in our previous study on OCs in snubnosed eel (de Brito

et al., 2002a). This species can be considered as an organism at a high trophic level in the food web due to its strong carnivorous and unique feeding habit; this fish has been found to burrow into the body of large fish such as halibut and shark and feed on their intestine and blood (Caira *et al.*, 1997). Relatively higher concentrations of the hydrophobic OCs and PBDEs were also found in large carnivore and/or bottom dwelling fishes (e.g., blackbelly lanternshark (*Etmopterus lucifer*), eelpout (*Lycodes hubbsi*) and Kaup's arrowtooth eel (*Synaphobranchus kaupii*)) (Table 2). These observations suggest that accumulation of these contaminants is influenced by biomagnification and/or feeding habits of organisms and their long biological half-lives, i.e., higher uptake rate via food and slower equilibrium between ambient water and body lipids. In contrast, less lipophilic compounds (with log K_{ow} less than 6), HCHs, HCB and HBCDs, showed smaller variation in concentrations among species of different trophic levels and feeding habits, owing to their faster rates of attaining equilibrium water concentrations (Ellgehausen *et al.*, 1980; Tanabe *et al.*, 1984; Kelly *et al.*, 2007). In addition to the difference in physico-chemical properties of the compounds, differing rates of uptake and elimination which are dependent on biological factors, like respiration rate, lipid composition and metabolic activities of the organism, may influence the accumulation pattern of organic contaminants in organisms. Importance of these factors should be examined in future studies incorporating experiments and statistical models, including various biological processes for bioaccumulation/biomagnification (Kelly *et al.*, 2007) as well as further field monitoring of various organohalogen compounds in marine ecosystems.

Food web structure and biomagnification of organohalogen compounds

Increase in contaminant concentrations in a marine food web is difficult to assess because the predators diet often consists of prey organisms from different trophic levels and also depend on the availability of prey organisms. Hence, for further discussion of the biomagnification of organohalogen compounds, $\delta^{15}N$ and $\delta^{13}C$ analyses were performed on deep-sea fishes collected in this study to understand their general trophic level and differences in feeding habits. Fig. 2 shows the $\delta^{13}C$ and $\delta^{15}N$ map of deep-sea fishes from off the Pacific coast of northern Japan. The stable isotope ratios of nitrogen $\delta^{15}N$ reflect the trophic level of organisms in a food web (Hobson and Welch, 1992) and, thus, $\delta^{15}N$ analysis is often used to assess trophic transfer of contaminants (Fisk
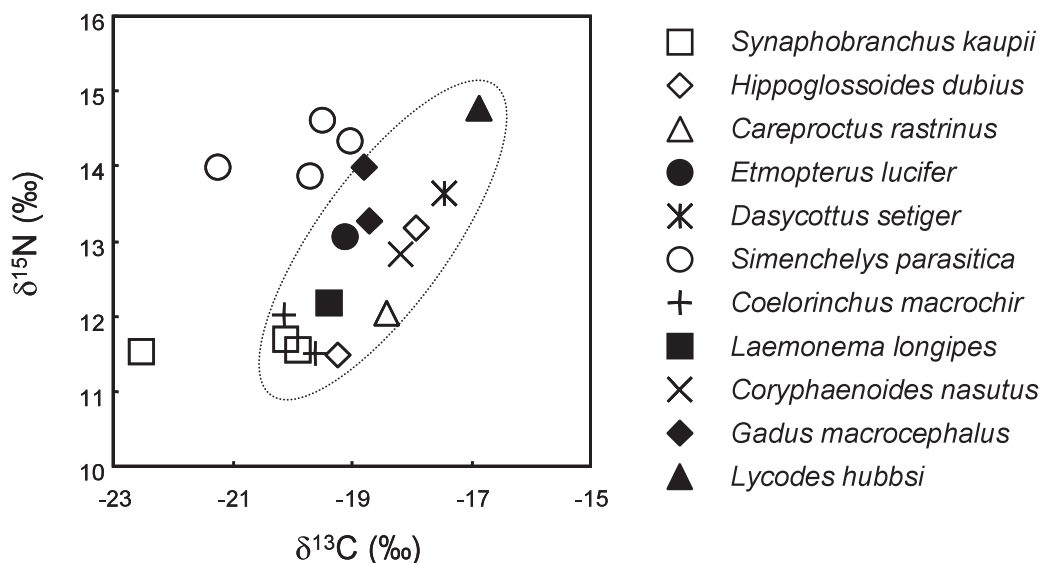

Fig. 2. The food-web of deep-sea fishes on the $\delta^{13}C$-$\delta^{15}N$ map.

et al., 2001; Das *et al.*, 2003; Kelly *et al.*, 2007). It has been assumed that an increase in $\delta^{15}N$ value of *ca.* 3.8 with $\delta^{13}C$ value of *ca.* 1.0 corresponds to one trophic level (Hobson and Welch, 1992; Fisk *et al.*, 2001). Although an eelpout and snubnosed eels showed relatively high $\delta^{15}N$ values, the maximum difference of $\delta^{15}N$ values between the fishes analyzed in this study was only 3.4. This implies that almost all the fishes are included within one trophic level, and snubnosed eels in this region probably do not prey upon higher trophic animals like shark and halibut.

On the other hand, large variation in $\delta^{13}C$ values was observed among the deep-sea fishes (Fig. 2). The stable isotope ratios of $\delta^{13}C$ are varied due to different carbon sources. For example, organisms dependent on primary production from phytoplankton in offshore surface waters can be expected to have higher $\delta^{13}C$ values than those living in coastal regions affected by fresh water inputs (Michener and Schell, 1994). Fry and Wainright (1991) demonstrated that diatoms can be a source of ^{13}C-rich carbon in many marine food webs. In Fig. 2, snubnosed eels and one Kaup's arrowtooth eel appear to be outliers. A significant positive correlation was found between $\delta^{15}N$ and $\delta^{13}C$ in deep-sea fishes when the data of snubnosed eels and one Kaup's arrowtooth eel were excluded ($p < 0.01$, Speaman's rank order correlation test). However, a wide range of $\delta^{13}C$ values (more than *ca.* 1.0) between fishes was observed even after the exclusion of outliers, implying the existence of multiple carbon sources in the food web of this region. Although there are still unclear factors, lower $\delta^{13}C$ values observed in some fishes, particularly snubnosed eels, may indicate that they are related to the food web which depends on carbon sources in sediments rather than fresh atmospheric carbon (enriched ^{13}C) assimilated by phytoplankton in surface waters. To make clear such variation of carbon isotope in the food web it is necessary to collect surface sediments and particulate organic matter (POM) in the benthic and epibenthic ecosystems of deep-seas.

Significant positive correlations were found 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. 3). No such relationship was found for HCB, HCHs and HBCDs (Fig. 3). The rapid elimination of these compounds through gills to surrounding water and by excretion via other means may prevent biomagnification of these compounds. Similar results on HCB and HCHs were observed in marine food webs (Ruus *et al.*, 2002; Kelly *et al.*, 2007). Relatively high water solubility of α-HBCD isomer (48.8 µg/l, Hunziker *et al.*, 2004), which is a major contributor to total HBCD concentration as shown in the later section, may also result in lower biomagnification of HBCDs than other hydrophobic organohalogen compounds such as PCBs, DDTs and PBDEs. On the other hand, biomagnification of $\alpha-$ and γ-HBCD isomers was reported in a Lake Ontario food web (Tomy *et al.*, 2004). Less biomagnification observed for some organohalogen compounds in this study may be due to smaller difference in trophic levels of fishes as noted above. In fact, there were no significant correlations between $\delta^{15}N$ values and the concentrations of almost all the compounds analyzed when the data of snubnosed eels was excluded ($p > 0.05$ for all OCs and HBCDs, only a significant relationship for PBDEs with $p < 0.05$, Spearman's rank order correlation test). In addition, such accumulation profiles of organohalogen compounds in deep-sea fishes may reflect not only their trophic transfer but also different sources of the substances in the food web and/or species-specific distribution of fishes. As noted above, fishes showing lower $\delta^{13}C$ values such as snubnosed eels may be affected by substances originated from sediments. Interestingly, snubnosed eels showed lower concentrations of HCHs than other fishes with significantly higher concentrations of other hydrophobic OCs and PBDEs (Table 2 and Fig. 3). In our earlier studies on deep-sea fishes from the western North Pacific, off-Tohoku, Japan (Takahashi *et al.*, 2000; de Brito et al., 2002a) higher concentrations of PCBs, DDTs and CHLs were found in nonmigratory fishes from deeper waters and, on the contrary, HCHs and HCB were accumulated at higher concentrations in shallow/migratory fishes. These observations may reflect the vertical distribution of these contaminants in the water column of this region (until at least *ca.* 1000 m depth).
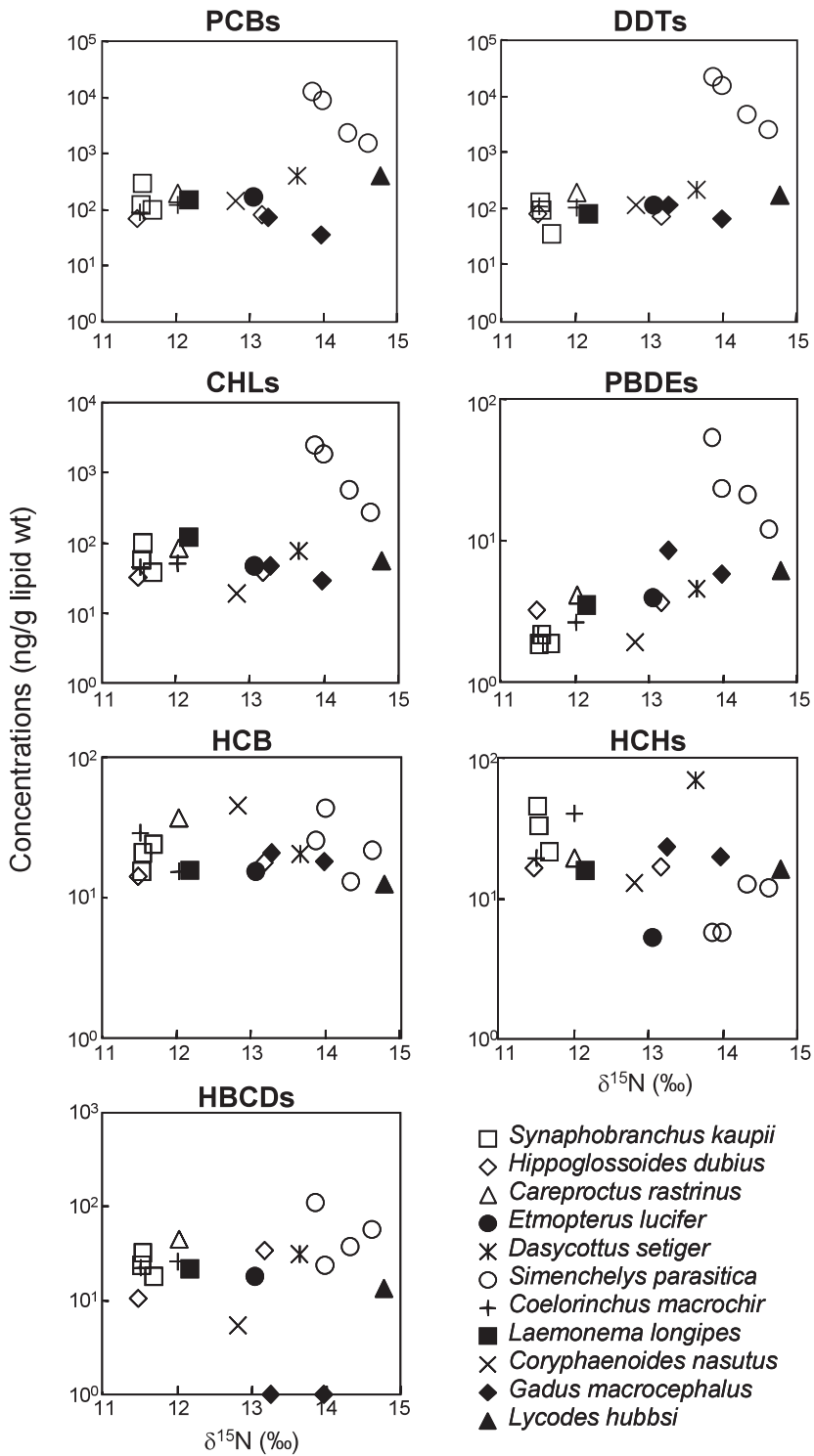
Fig. 3. Relationship between δ¹⁵N (‰) and organohalogen compounds (ng/g lipid wt) in deep-sea fishes from off the Pacific coast of northern Japan.

Tanabe and Tatsukawa (1983) showed that the concentrations of HCHs significantly decreased with depth in the open water column of the Pacific Ocean. Hargrave *et al.* (1992) reported that benthic amphipods from the Arctic continental shelf accumulated between ten to sixty times the concentrations of PCBs, DDTs and CHLs but only two to five times those of HCHs and HCB found in pelagic plankton, and suggested that OCs with lower water solubility and higher affinity for absorption to particles will be transported to deeper waters and incorporated into the benthic food web more readily than higher water soluble compounds. Snubnosed eel, a bathydemersal fish species, was collected from the deepest waters (900 m) in this study area. Therefore, results of this study are also suggestive of the distribution of OCs and BFRs in the ecosystem and the accumulation of hydrophobic OCs and PBDEs in the demersal fauna.

Composition of OCs

The residue patterns of OCs in organisms are influenced by the patterns in food, habitat and metabolism of the fishes and reflect environmental inputs of these compounds. Among DDT compounds, *p, p*'-DDE and *p, p*'-DDT were the predominant constituents in almost all the deep-sea fishes (Fig. 4). Relatively high proportions (> 40%) of *p, p*'-DDT were found in some deep-sea fishes compared to those reported in Suruga (Lee *et al.*, 1997) and Tosa Bay, Japan (Takahashi *et al.*, 2001). The present study area lies in the Kuroshio-Oyashio transitional zone which is a confluence of various currents resulting in the formation of diverse water masses. Takahashi *et al.* (2000) analyzed myctophid fishes from the western North Pacific, Japan and reported high proportion of *p, p*'-DDT (>50%) in non- or less-migratory fishes living in mesopelagic waters. Similarly high proportions of *p, p*'-DDT (> 40%) were also found in Japanese common squid (*Todarodes pacificus*) from off Sanriku, Japan even though this location seems to be far away from the sources of DDT (Ueno *et al.*, 2003). It has been suggested that the North Pacific Intermediate Water (NPIW), which is found at depths of 300–800 m in the North Pacific subtropical gyre, originates from the
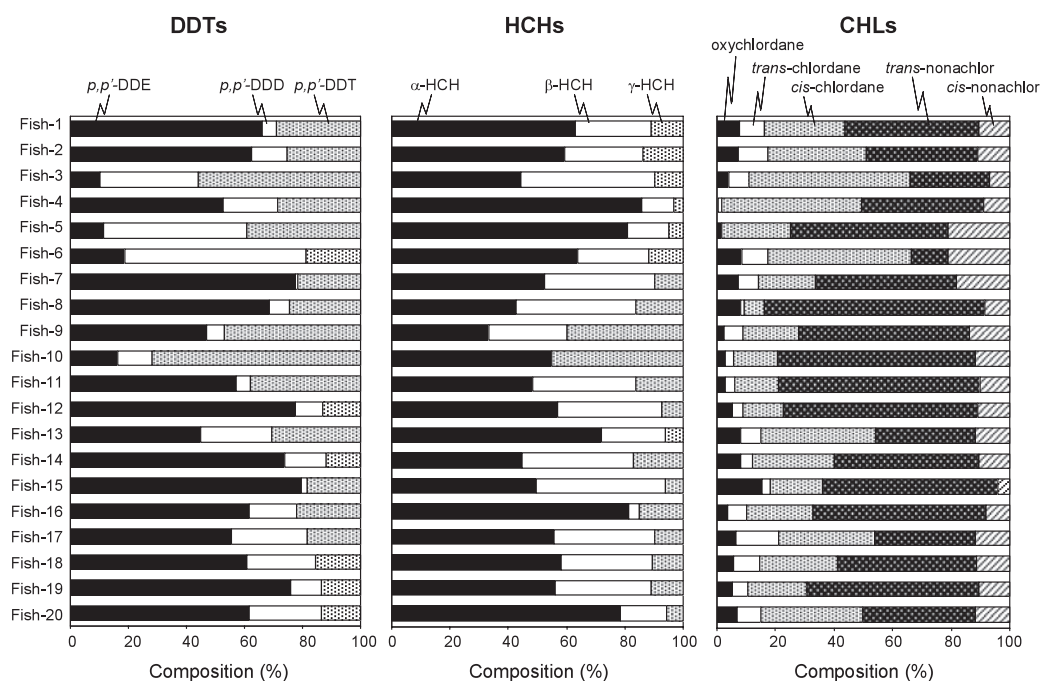

Fig. 4. Composition of DDTs, HCHs and CHLs in deep-sea fishes from off the Pacific coast of northern Japan.

watermass in the Okhotsk Sea, and new NPIW is formed along the Kuroshio-Oyashio interfrontal zone (Yasuda, 1997). Elevated background levels of DDTs in the Okhotsk Sea have been reported in several studies (Iwata *et al.*, 1995, 2000). In this context, the intermediate water in the study area can be expected to have relatively fresh input of DDTs, which originate from more contaminated Okhotsk Sea. However, information on the distribution of OCs and geophysical and geochemical studies, which can support this hypothesis, is very limited.

Among HCHs isomers, α-HCH was the predominant isomer in all the deep-sea fishes of the present study (Fig. 4). It has been reported that the ratio of α-HCH to total HCH concentrations in seawater and fish has a tendency to increase with the increasing latitude (Iwata *et al.*, 1993; Ueno *et al.*, 2003). α-HCH is preferentially transported to northern colder regions due to higher vapor pressure among various HCH isomers. Higher proportion of α-HCH was found in fishes from northern part of Japan, such as off-Tohoku and Japan Sea (Takahashi *et al.*, 2000; de Brito *et al.*, 2002). In case of CHLs, the most predominant CHL-related compound was *trans*-nonachlor, which is a stable form of the CHL-related compounds, followed by *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor and oxychlordane (Fig. 4). Similar pattern was noted for walleye Pollock (*Theragra chalcogramma*) from the North Pacific and the Bering Sea (de Brito *et al.*, 2002b).

Congener/isomer profiles of BFRs

Of the fourteen PBDE congeners analyzed, a total of nine congeners from tri- to deca-BDE were identified in deep-sea fishes of the present study (Fig. 5). The congener profiles of PBDEs varied between the species and, in most fish samples, the congeners from tri- to hexa-BDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-154) were predominant. The PBDE congener profiles varied between the species and the different profiles in the fish species could be related to specific uptake, metabolism, storage and excretion mechanisms. The higher contribution of BDE-47 to total BDE burdens could be attributable to a higher bioaccumulation potential of this congener and possible debromination of BDE-99 or other BDE congeners in biota tissues. In the present study, BDE-183 was not detected in any of the fish samples. Debromination of BDE-183 to lower congeners may be the reason, as experimental studies in fish have shown debromination of BDE-183 to BDE-154 (Stapleton *et al.*, 2004). The higher brominated congeners from octa- to deca-BDE were detected in few samples, suggesting the relatively low bioaccumulation potential as well as the low bioavailability of these congeners. Accumulation of BDE-209 in some fishes such as spinyhead sculpin (*Dasycottus setiger*) and largenose grenadier (*Coryphaenoides nasutus*) can be explained by their sediment dwelling habit as BDE-209 is mainly associated with sediments.

Among the HBCD isomers, α- and γ-HBCD were detected in all the samples, while β-isomer was below detection limits in most of the samples. The prevalence of α-HBCD has been observed in other aquatic biota samples like fish, shrimp and mussels (Morris *et al.*, 2004; Tomy *et al.*, 2004; Janak *et al.*, 2005; Ueno *et al.*, 2006; Ramu *et al.*, 2007). The dominance of α-HBCD over the other two isomers could be due to the isomer specific metabolism as well as the potential of α-HBCD for long range atmospheric transport. Zegers *et al.* (2005) reported that β- and γ-HBCD were significantly metabolized when compared to α-HBCD, in the microsomal preparations of seal liver. Ueno *et al.* (2006) observed that, like that of α-HCH, the percentage contribution of α-HBCD also increased with increasing latitude and a high proportion of α-HBCD was found in skipjack tuna from the northern cold-water region of North Pacific, Japan. These results may indicate that α-HBCD could have the highest transportable potential among the HBCD isomers in the environment.

Temporal trends of OCs

To elucidate the temporal trend of OCs contamination during the last decade, the results of the
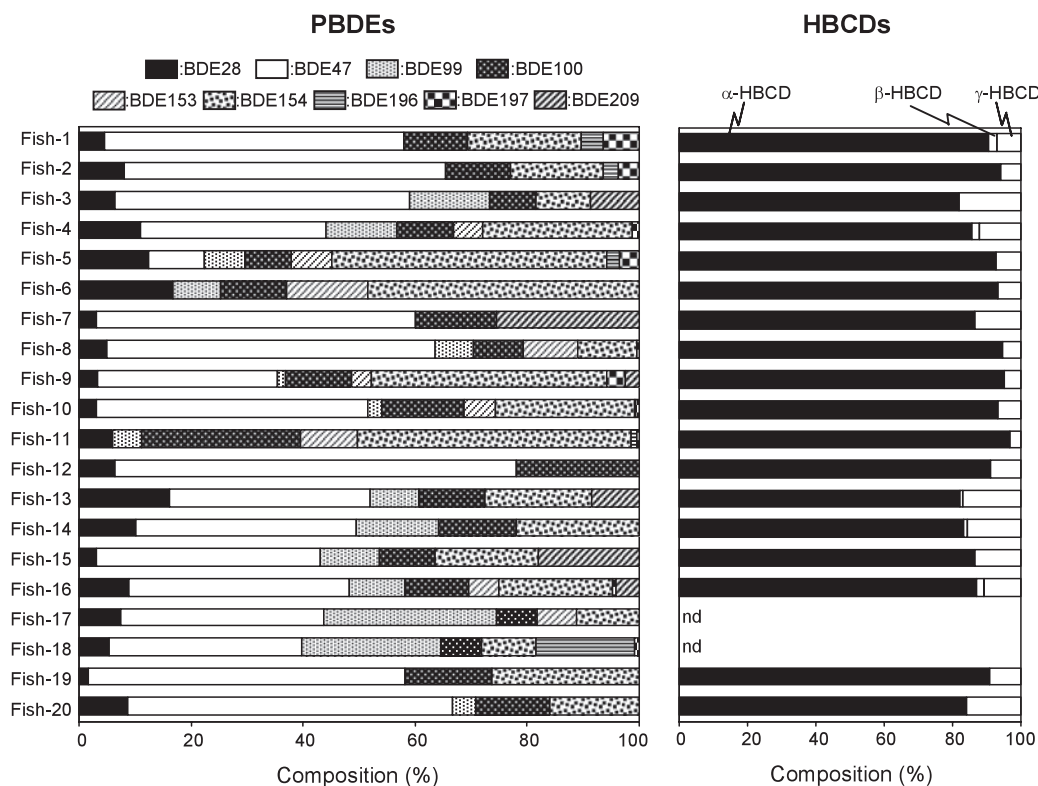
Fig. 5. Congener/isomer profiles of BFRs (PBDEs and HBCDs) in deep-sea fishes from off the Pacific coast of northern Japan.

present study were compared with the data reported for deep-sea fishes in our earlier study (de Brito *et al.*, 2002), in which the area of survey, off the Pacific coast of northern Japan, almost overlapped the sampling locations of the present study. In Fig. 6, the concentrations of OCs (ng/g lipid wt) and ratios of parent to stable compounds of DDTs and CHLs were compared between the same species of fishes collected in 1995 and 2005 (the data for snubnosed eels were excluded from the comparison because of the species-specific accumulation of OCs and large variation of data between the individual specimens). Decreasing trends in the concentrations of DDTs and CHLs from 1995 to 2005 were observed in almost all the fish species analyzed. It is also noteworthy that ratios of parent compounds, *p, p*'-DDT and *trans*-chlordane, to stable compounds, *p, p*'-DDE and *trans*-nonachlor, respectively, which are an indication of recent input of technical DDTs and CHLs into the environment, decreased during this period. These results suggest declining environmental loads of DDTs and CHLs in this region during the last decade. On the other hand, no significant trend was observed for the concentrations of PCBs, HCB and HCHs between 1995 and 2005. Tanabe *et al.* (1994) reported residue levels of PCBs and DDTs in archived fat tissues of northern fur seals (*Callorhinus ursinus*) collected from northern North Pacific; 1) DDT levels declined continuously even in the 1980s and 1990s, and those levels at the end of the 1990s reached about one thirtieth of the maximum values found in the early 1970s; Nevertheless, 2) PCB levels in the 1980s and the 1990s showed a steady-state condition of about half the maximum value found in the 1970s; and 3) HCH and CHL levels were stable and no apparent decline was noticed since 1971. In addition, Kajiwara *et al.* (2004) confirmed no apparent decline of HCB levels during 1971 to the 1990s by analyzing the same archived samples of northern fur seals. Except for CHLs, the results of the present study agree well with the data reported for OCs in northern fur seals.
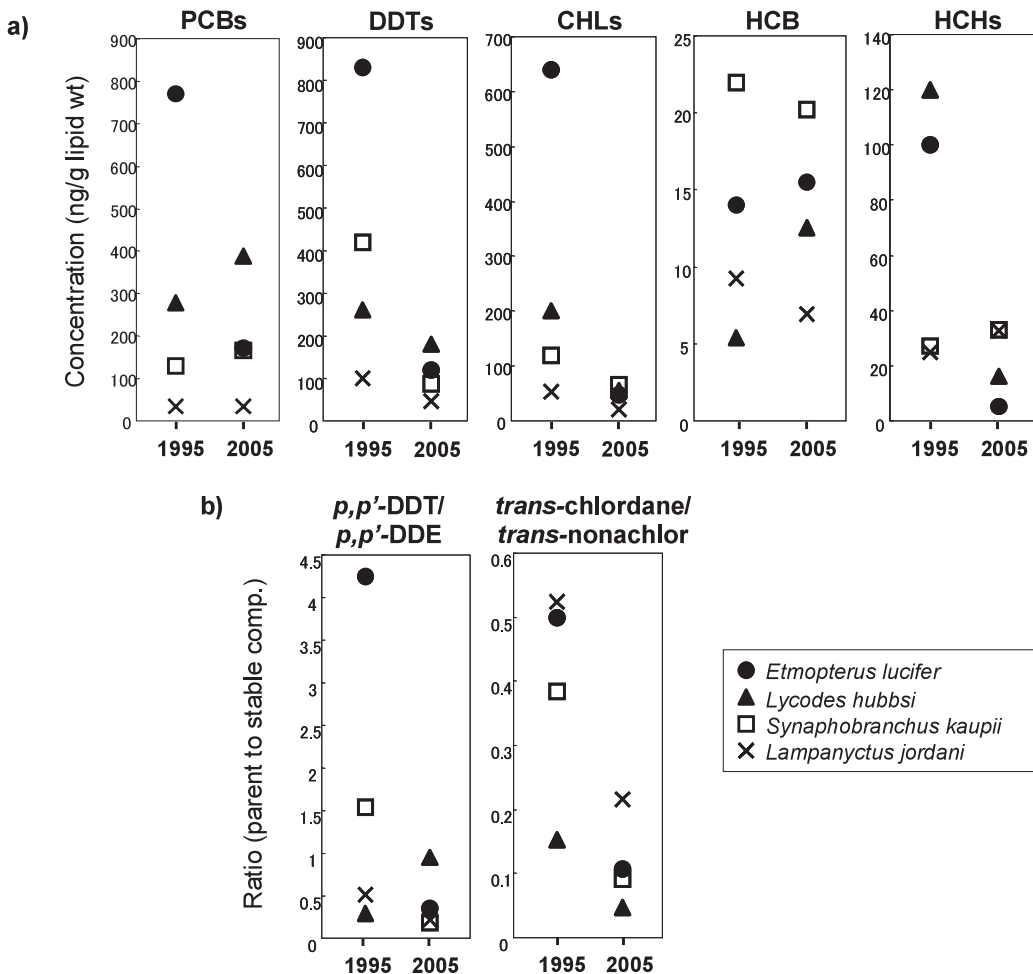
a)

b)

Fig. 6. Comparison of the concentrations of OCs (ng/g lipid wt) (a) and ratios of parent to stable compounds (b) in deep-sea fishes from off the Pacific coast of northern Japan sampled in 1995 and 2005.

Chlordane was used largely as a termitcide in Japan until 1986, even after the prohibition of its use as pesticide, and thus, it can be hypothesized that environmental levels of CHLs have not declined significantly during the 1980s/90s. On the other hand, continuous release of PCBs and HCB from various sources (e.g., PCB containing wastes such as stored transformers and obsolete electrical and electric products, secondary formation of dioxin-like PCBs and HCB in combustion processes, generation of HCB as by-product in manufacturing processes etc.) has been suggested in Japan (Sakai *et al*., 2001; Hirai *et al*., 2003). No declining trend of HCH levels may be attributable to their long range atmospheric transport and cold condensation in the colder regions (Iwata *et al.,* 1993; Wania and Mackay 1996; Beyer *et al.,* 2000). In addition to the present study, further monitoring studies are required to delineate contamination status by organohalogen compounds including emerging POPs such as PBDEs and HBCDs and their temporal trends in deep-sea fauna because of their significant increasing levels during the last decades in marine mammals and sediment cores from Japanese waters (Tanabe *et al.,* 2008).

Acknowledgments

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