

ORGANOHALOGEN COMPOUNDS IN DEEP SEA ORGANISMS FROM EAST CHINA SEA: LEVELS, PROFILES, AND FATE

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Abstract

Deep-sea organisms collected from East China Sea (ECS) from depths of 91 to 500 m during 2001-2003 were analyzed for organohalogen compounds. Among the compounds analyzed, concentrations of DDTs (up to 2500 ng/g lipid wt.) were the highest and those of other compounds were approximately in the following order: PCBs > CHLs > HCB > HBCDs > PBDEs = HCHs. The congener profiles of PBDEs were generally dominated by tetra- to hexa-BDEs, while BDE-209 was major congener in some sediment dwelling organisms. The isomer composition of HBCDs revealed predominance of α -HBCD and γ -HBCD in higher and lower trophic organisms, respectively. Strong negative relationships were observed for log normalized concentrations and $\delta^{13}\text{C}$ for all the organohalogen compounds indicating that the main input of these compounds to ECS is by continental input and riverine discharges. Significantly higher concentrations of DDTs, CHLs, HCHs, HCB and PBDEs were found in fishes from deep waters than shallow waters, which suggest a long term downward vertical transport of organohalogen contaminants via the organic carbon flow and their recycling in the biophase of the deep-sea.

Introduction

The long-range transport, persistence, and global distribution of organohalogen compounds are issues of increasing concern in recent years. Organohalogen contaminants enter 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 be carried to the deep sea where they biomagnify in the food web.¹ Although there are several studies on levels of organochlorine (OC) contaminants in deep-sea organisms from different regions of the world, aquatic pollution resulting from widespread usage of brominated flame retardants (BFRs) deserves concern because of their bioaccumulation potential, persistence and endocrine disrupting effects. Studies addressing contamination of deep-sea areas by BFRs are relatively scarce. With the deep sea acting as an ultimate sink for such contaminants and the growing importance of deep-sea commercial fisheries around the world, it is imperative that more studies need to be done to understand the ultimate fate of BFRs.

The objective of the present study was to examine the extent of contamination and bioaccumulation of polychlorinated biphenyls (PCBs), organochlorine insecticides, BFRs such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) in deep-sea organisms from East China Sea (ECS). Furthermore, food chain magnification of organohalogen compounds was examined using stable isotopes of nitrogen and carbon as continuous measures of trophic position.

Materials and Methods

Samples

Deep-sea organisms belonging to forty four species, representing fishes ($n=30$), crustaceans ($n=9$), cephalopods ($n=3$), mollusk ($n=1$) and echinoderms ($n=1$), collected along the ECS continental shelf from depths ranging from 91 to 500 m during 2001 to 2003 were analyzed in the present study. The collected samples were placed in polyethylene bags and frozen at -20°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 which was employed for chemical analysis.

Chemical analysis

Briefly, 20-30g of the samples was Soxhlet extracted with a mixture of diethyl ether and hexane. An aliquot of the extract, after spiking 5 ng of internal standards for PBDEs ($^{13}\text{C}_{12}$ -BDE-3, -15, -28, -47, -99, -100, -153, -

154, -183, -197, -207 and -209) and 10 ng of internal standards for HBCDs ($^{13}\text{C}_{12}$ -labeled α -, β - and γ -HBCD), was loaded to a gel permeation chromatography (GPC) column for lipid removal. The GPC fraction containing organohalogenes was concentrated and subjected to an activated silica gel column (Wakogel DX) for further clean-up and fractionation. For analysis of OCs, another aliquot of the Soxhlet extract was purified and fractionated using a GPC and an activated florisil column. Identification and quantification of PBDEs was done using gas chromatography combined with mass spectrometry (GC-MS), while HBCD isomers were identified and quantified using liquid chromatography combined with tandem mass spectrometry (LC-MS-MS) in a multiple reaction monitoring (MRM) mode, and identification and quantification of OCs was done using GC-ECD. Detailed analytical procedure for analysis of PBDEs, HBCDs and OCs was described previously.²

For analysis of stable isotopes, the samples were dried for 24h at 60°C, powdered and treated with a 2:1 chloroform-methanol solution to remove lipid. The dried samples were loaded into tin cups. Stable carbon and nitrogen isotopes were measured using an isotope ratio mass spectrometer (IR-MS).

Results and Discussion

Status of organohalogen contamination

Among the organohalogen compounds analyzed, concentrations of DDTs were the highest and those of other compounds were approximately in the order: PCBs > CHLs > HCB > HBCDs > PBDEs = HCHs (Table 1). The predominance of DDTs and PCBs was also observed in deep-sea organisms from other locations.³⁻⁵ This may be due to the higher usage amounts and continuous release of these contaminants into the environment, as well as their bioaccumulative properties. The total concentrations of PBDEs in the present study ranged from 0.31 to 57 ng/g lipid wt., while that of HBCDs ranged from 0.15 to 210 ng/g lipid wt. Reports on PBDEs and HBCDs in marine ecosystems and food chains, particularly for the deep-sea environment, are relatively scarce. The levels of PBDEs and HBCDs in all the deep-sea organisms from the current study were low when compared to those in animals from other areas,^{6,7} probably due to longer distances from the contaminant sources. However, the detection of these BFRs in deep-sea organisms indicates that these compounds have reached even the remote locations, similar to classical OCs. The sources of BFRs in the present study area could be from the various manufacturing operations as well as e-waste recycling activities along the Chinese coast,⁸ while that of OCs could be the result of the past excessive usage or the ongoing illegal usage of these compounds and the subsequent transport of OCs from soil to the sedimentary system along the coasts of China.⁹ Moreover, analysis of stable carbon isotope ratios (see discussion below) also indicate input of these compounds from continental runoff and riverine discharges. It is also assumed that the contamination status of organohalogenes in ECS is affected by the various hydrological processes such as the Kuroshio Current, Changjiang run-off and the East Asia monsoon winds which effect the water circulation in ECS.

Table 1. Range and mean concentrations of organohalogen compounds (ng/g lipid wt.) in deep-sea organisms from East China Sea.

Species	<i>n</i>	Fat (%)	PCBs	DDTs	CHLs	HCHs	HCB	PBDEs	HBCDs
Fishes	30	2.5 (0.48-10)	290 (36-1400)	560 (<3-2200)	51 (8.4-240)	11 (2.2-41)	23 (<1.5-290)	10 (0.31-40)	4.0 (0.25-20)
Cephalopods	3	2.1 (0.69-4.5)	120 (29-190)	220 (76-410)	39 (8.4-91)	5.7 (3.7-7.3)	8.5 (3.2-14)	11 (0.65-26)	71 (0.18-210)
Crustaceans	9	3.1 (0.47-12)	230 (25-850)	610 (21-2500)	40 (7.5-140)	14 (4.5-28)	7.5 (0.55-17)	16 (1.1-57)	16 (0.15-73)
Mollusk	1	0.23	220	300	23	33	17	4.7	3.1
Echinoderm	1	0.041	590	72	1.9	3.4	<8.8	28	11

*Figures in parentheses indicate the range; *n*: number of species

Composition of brominated flame retardants

Of the fourteen PBDE congeners analyzed, a total of ten congeners from tri- to deca-BDE were identified in deep-sea organisms from ECS. The congener profiles of PBDEs varied between the species and in most cases the congeners from tetra- to hexa-BDEs were predominant (Fig. 1). The higher brominated congeners from octa- to deca-BDE were detected in very few samples, suggesting the relatively low bioaccumulation potential as well as the low bioavailability of these congeners. It is noteworthy that BDE-209 was the dominant congener in case of an echinoderm (*Holothuroidae* sp.) and in flatfish (*Chascanopsetta lugubris*), and this can be explained by their sediment dwelling habit as BDE-209 is mainly associated with sediments. However, the presence of BDE-209 in deep-sea organisms from ECS indicates that this congener probably is capable of long-range transport and dispersal. 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. Similar to BDE-209, higher proportion of γ -HBCD was observed in sediment dwelling organisms (Fig. 1).

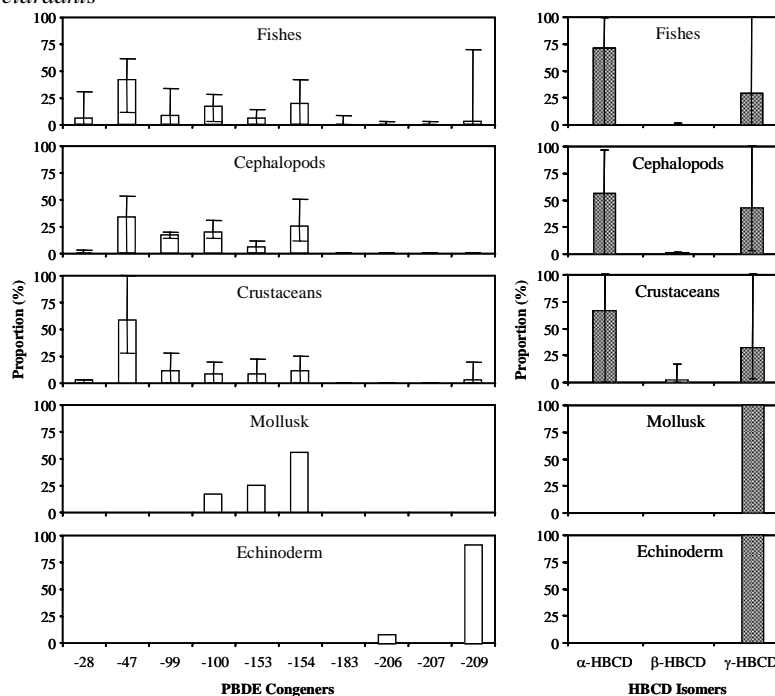


Fig. 1. Compositions of PBDEs and HBCDs in deep-sea organisms from East China Sea.

Relationship between stable isotopes and organohalogen concentrations

Stable carbon and nitrogen isotope ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) have been proven to be a useful tool in delineating carbon flows and trophic relationships in a variety of continental and marine ecosystems. To examine the biomagnification of organohalogen contaminants in deep-sea organisms from ECS, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ analyses were performed to understand the general trophic level at which the organisms were feeding. The $\delta^{15}\text{N}$ values in the present study ranged widely from 7.18 to 14.17 ‰. It is indicative of a mixing food web of both planktonic as well as benthic type. No clear relationships were observed between $\delta^{15}\text{N}$ (‰) and concentrations for all the contaminants. It has been well demonstrated that gill-breathing organisms exchange OCs through the gills and equilibrate the levels between ambient water and body lipids.¹⁰ The lack of relationship between $\delta^{15}\text{N}$ and organohalogen compounds in the present study is because of the fact that most of the samples analyzed were gill-breathers. Another plausible explanation could be because of the large location difference in pollution

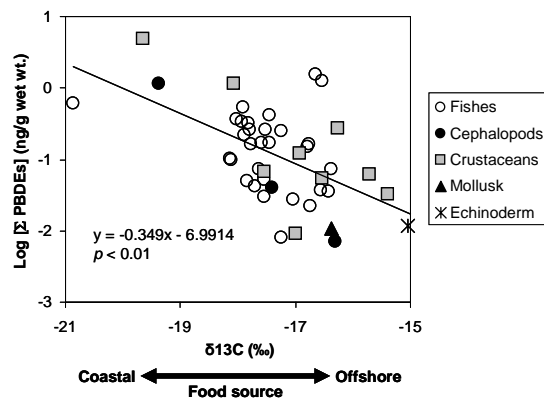


Fig. 2. Relationship between total PBDE concentrations and $\delta^{13}\text{C}$ in deep-sea organisms from East China Sea.

status of these compounds in ECS as noted below. The carbon isotopic composition has been widely used to study the origin of organic matter in marine environments. Generally, the terrigenous organic matter is more depleted in $\delta^{13}\text{C}$, while the marine organic matter is usually more enriched in $\delta^{13}\text{C}$.¹¹ Thus, the carbon isotopic composition is used as a tracer to distinguish marine from terrigenous organics. In the present study, the $\delta^{13}\text{C}$ values ranged from -20.87 to -15.04 (‰). Mean $\delta^{13}\text{C}$ value of suspended particulate matter in the Changjiang Estuary was previously reported to be -22.6‰.¹² The ECS receives enormous amounts of fresh water, suspended matter and nutrients and it was also suggested that the ECS shelf is an important source of particulate matter to the deep-sea.¹³ Therefore, the samples with low $\delta^{13}\text{C}$ (-20.87 ‰) in the present study could be representative of the terrigenous materials discharged to ECS. In the present study, strong negative relationships were observed for log normalized concentrations and $\delta^{13}\text{C}$ for all the organohalogen compounds (Fig. 2, data shown for PBDEs). Thus, the negative relationships indicate that the main input of these compounds to ECS is by continental input and riverine discharges.

Vertical distribution of contaminants

In the present study to understand the vertical distribution of contaminants, fishes were grouped into two categories, shallow water (< 200 m) and deep water (> 200 m), based on their sampling depths. Significantly higher concentrations of DDTs, CHLs, HCHs, HCB and PBDEs were found in deep water fishes than fishes from shallow waters. Higher molecular weight compounds (e.g., DDTs, CHLs, PBDEs) have high affinity to particulate matter and thus get transported to deep waters. While, evaporation of volatile OCs (e.g., HCHs and HCB) from surface waters to atmosphere can be suggested in ECS due to high temperature in subtropical regions. Such a nature of these compounds would result in elevated accumulation in deep-sea fishes. Similar trend of higher concentrations of PCBs, DDTs and CHLs in fishes from deeper waters were noticed in the Western North Pacific and off-Tohoku, Japan.^{4,5}

The results of this study highlight the usefulness of deep-sea organisms to monitor the deep-sea environment. The results demonstrated that deep sea is the ultimate sink for anthropogenic contaminants. In view of the importance of deep-sea environment as the final recipient for persistent pollutants, further studies are required to characterize exposure of deep-sea fauna to coastal contaminants and the consequences to the marine ecosystem.

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