BIOACCUMULATION OF CHLRINATED, BROMINATED AND FLUORINATED COMPOUNDS IN MARINE FOOD WEB OF KOREA

Kim E.-K[1]*, Lee H.-K[1], Jeong Y[1], Lee S[1], Lee I.-S[2], Kim S[3], MoonH.-B[1]

[1]Marine Environment Analysis Laboratory (MEAL), Department of Environmental Marine Sciences, Hanyang University, Ansan 426-791, Republic of Korea; [2]National Fisheries Research & Development Institute (NFRDI), 408-1, Sirang-ri, Gijang-eup, Gijang-gun, Busan 619-705, Republic of Korea; [3]School of Public Health, Seoul National University, Seoul 110-799, Republic of Korea

Introduction

Organohalogen compounds (OHCs) such as perfluorinated compounds (PFCs), polychlorinated biphenyls (PCBs), polybrominated dipheyl ethers (PBDEs), and dichloro diphenyl trichloroethane (DDTs) have been used as agricultural purpose or industrial materials. Due to their environmental persistence and widespread use in household and commercial product, these compounds can released and are now ubiquitously present in the environment, even in remote areas[2]. Because of their global concerns, PCBs, PBDEs and DDTs have been designated as persistent organic pollutants (POPs) under the Stockholm Convention in 2001 and 2009. Because of higher bioavailability and slow elimination rate, PCBs, PBDEs and DDTs were highly accumulated in biotic compartments, but not well removed from their bodies. Some compounds of these can be biomagnified through food-web.

Jinhae Bay, located on the southern part of Korea, is a semi-closed bay with a slow rate of water. The bay consists of several small bays such as Masan, Haengam, Jindong, Wonmun, and Gohyeon Bays. Approximately 1300 industrial complexes, including petrochemical, heavy metal, electrical and plastic industries, are distributed along the coast of Masan Bay designated as part of the special management coastal zone by Korean government. Jinhae Bay can be subdivided into two zones. One comprises the western part of the bay and is a less polluted area. The other part includes Masan Bay and Haengam Bay with serious environmental problems[6]. Many studies have reported on the substantial contamination in Masan Bay from toxic organic contaminants[7,8,910]. In this study, marine organisms were collected from Jinhae Bay, to investigate the concentrations of OHCs in marine food-web and biomagnifications of these compounds with trophic positions, using stable isotope techniques. To date, no studies were performed on biomagnification of the POPs in Korean coastal waters. This is the first report on the biomagnifications of PFCs, PCBs, PBDEs and DDTs in a marine food-web from Korean coastal waters.

Materials and methods

Sample collection

Marine organism samples were collected from Jinhae Bay during September-December in 2011 (Figure 1). These samples included five aquatic invertebrates, i.e., hard clam (*Meretrix lusoria*), Manila clam (*Ruditapes phillipinarum*), conch (*Turbo cornutus*), mussel (*Mytilus coruscus*), and Japanese mud shrimp (*Upogebia major*), Small octopus (Octopus minor), common octopus (*Octopus vulgaris cuvier*), 17 fish species, i.e., Thread-sail filefish (*Stephanolepis cirrhifer*), dotted gizzard shad (*Konosirus punctatus*), striped beakperch (*Oplegnathus fasciatus*), marbled sole (*Pleuronectes yokohamae*), black rock fish (*Sebastes inermis*), baby sea bass (*Lateolabrax japonicas*), Sea bass, Indian flathead (*Platycephalus indicus*), spotty belly greenling (*Hexagrammos agrammus*), half beak (*Hyporhamphus sajori*), black porgy (*Acanthopagrus schlegelii*), yellowtail (*Seriola quinqueradiata*), horse mackerel (*Trachurus japonicas*), common conger (*Conger myriaster*), and pacific cod (*Gadus macrocephalus*). All samples were homogenized directly and stored in a freezer where they were stored at -20^{o}C until analysis.

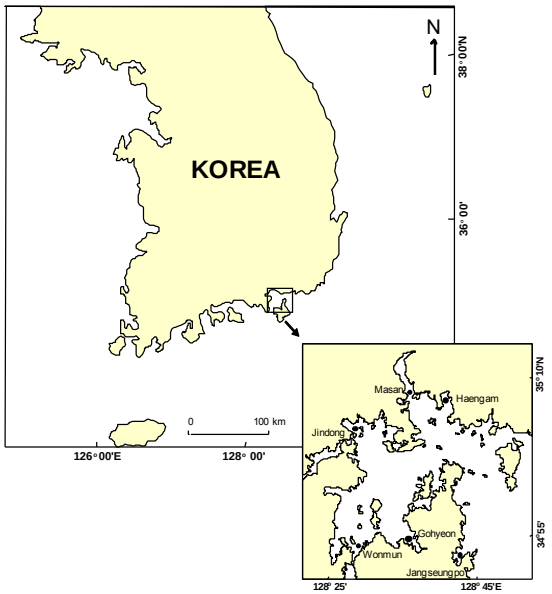

Figure 1. Map showing the sampling location (Jinhae Bay), Korea.

Sample extraction and clean up

Edible tissue (~15 g) and liver (~5 g) homogenized with anhydrous Na_2SO_4 were extracted with mixed solvents of dichloromethane (DCM) and using a Soxhlet apparatus. Prior to extraction, PCB congeners103, 198, and 209 were spiked into samples, as internal standards. The extract was concentrated to 11mL and an aliquot (1mL) was taken for gravimetric determination of lipid content. In order to remove lipids, the remaining parts were cleaned up by gel permeation chromatography (GPC) using Bio-beads S-X3. An aliquot (6mL) was used for analysis of PBDEs, PCBs and DDTs and was spiked with ^{13}C-labeled PBDEs and PCBs for the determination these compounds, respectively. The aliquot was purified by passing it through a multi-layer silica gel column using 150 mL of 15% DCM in hexane.

Biota samples (~1 g) were treated by the ion-pairing liquid extraction method for analysis of PFCs. The samples were homogenized in 2 mL ofMilli-Q water. A 2 mL aliquot of this homogenate was spiked with 5 ng of ^{13}C-labled perfluorinated carboxylic acids (PFCAs) and perfluoroalkylsilanes (PFASs) as internal standards. One millilitre of 0.5 M tetrabutylammonium hydrogen sulfate solution, 2 mL of sodium carbonate buffer (0.25 M, pH 10), and 5 mL of methyl-tert-butyl ether (MTBE) were added to the sample. After shaking for 30 min, the organic layer was separated by centrifugation, and the extraction was repeated with a further 5 mL of MTBE. The extracts were combined and evaporated to dry under a gentle flow of nitrogen, before being reconstituted in 1 mL of methanol, and vortexed. The extract was filtered through a 0.2 µm nylon filter into an autosampler vial with a polypropylene cap.

Chemical analysis

Identification and quantification of PBDEs were carried out using a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC/HRMS; JMS 800D; JEOL, Tokyo, Japan). The HRMS was operated in selected ion monitoring (SIM) mode. Twenty-four PBDE congeners were separately determined, ranging from tri- to hepta-BDEs and from octa- to deca-BDEs, using a DB5-MS capillary column (15 m length, 0.25 mm inner diameter, 0.1 lm film thickness; J&W Scientific, Palo Alto, CA, USA). PCBs and DDTs were quantified by an Agilent 7890 GC coupled with a 5975C series mass selective detector using an electron impact (EI) ion source. A DB5-MS capillary column (30m length, 0.25mm inner diameter, 0.25µm film thickness; J &WScientific, Palo Alto, CA, USA) was used for analysis of 21 PCB congeners and 6 DDT compounds. PFCs were quantified using Agilent 1100 series high-performance liquid chromatography (HPLC) coupled with an Applied Bio-systems API 2000 electrospray triple quadruple mass spectrometer (ESI-MS/MS). A 150 mm x 2.0 mm (3 µm) Imtackt CD C_{18} column was used for analysis of PFCs.

Results and discussion

The concentrations of PFCs, PCBs, DDTs and PBDEs were found in edible and liver tissues from Jinhae Bay, Korea (Table 1). The lipid content in the liver (43 ± 24 %) in fish samples was approximately 8 times higher than lipids in edible tissues (5.8 ± 3.1%). The overall lipid-normalized concentrations of PFCs, PCBs, DDTs and PBDEs in liver tissues were approximately two to three times higher than those measured in edible tissues of fish, suggesting preferentially accumulation of these compounds in liver than in muscle for marine organisms. The total concentration of PFCs in the edible tissues ranged from 118 to 1082 (mean: 367) ng/g lw. The total PFCs concentration in fish liver ranged from 95 to 2279 (mean: 597) ng/g lw. PFOS was dominant among the 17 PFCs. The concentrations of PFOS in edible tissue and liver were 144 ± 148 ng/g lw and 396 ± 417 ng/g lw, respectively. Other studies reported that PFOSs was the most widely detected compound in organisms at various trophic levels[4]. The concentrations of PCBs, DDTs, and PBDEs in edible tissue ranged from nd to 68.2 (mean: 15.0) ng/g lw, from 0.15 to 71.0 (mean: 13.5) ng/g lw and from 1.07 to 56.4 (mean: 8.89) ng/g lw, respectively. The concentrations of PCBs, DDTs, and PBDEs in liver ranged from nd to 321 (mean: 44.7) ng/g lw, from 1.75 to 460 (mean: 44.0) ng/g lw and from 0.94 to 135 (mean: 29.4) ng/g lw, respectively. Among PCB congeners, PCB 153 showed the highest concentration, ranging from nd to 62.4 (mean : 5.96) ng/g lw in edible tissue and from nd to 85.3 (13.0) ng/g lw in liver.

Table 1. Biological parameters and the concentrations of organohalogen compounds (ng/g lw) in marine organisms collected from Jinhae Bay, Korea

	Species	n	weight (g)	Lipid (%)		$\delta^{15}N$		PCBs		DDTs		PBDEs		PFCs	
				E.T	L	E.T	L	E.T	L	E.T	L	E.T	L	E.T	L
Fish	Thread-sail filefish	5	117.2	3.7	70.8	12.51	11.59	11.10 ± 1.35	14.30 ± 1.35	10.21 ± 2.04	2.64 ± 0.86	0.81 ± 0.06	0.75 ± 0.07	122.70 ± 8.45	94.62 ± 16.08
	horse mackerel	6	152.2	6.0		12.52		nd		2.93 ± 0.46		4.23 ± 0.76		222.80 ± 20.30	
	common conger	12	107.0	13.9	16.1	13.22	14.23	nd	7.82 ± 1.18	19.19 ± 5.52	9.22 ± 2.58	2.51 ± 0.26	8.12 ± 0.25	1082.36 ± 104.30	652.00 ± 61.77
	dotted gizzard shad	10	66.6	15.1		14.40		2.79 ± 0.61		23.23 ± 3.63		3.88 ± 0.49		329.54 ± 26.55	
	striped beakperch	4	205.0	7.6	28.3	14.74	14.45	2.60 ± 0.57	nd	11.38 ± 2.62	1.75 ± 0.61	5.40 ± 0.76	1.68 ± 0.18	219.52 ± 20.46	402.84 ± 50.26
	half beak	21	50.1	3.3	85.9	15.45	15.17	15.41 ± 1.60	3.96 ± 0.86	9.65 ± 2.89	2.04 ± 0.67	4.36 ± 0.40	3.38 ± 0.24	227.79 ± 16.84	305.20 ± 48.88
	yellowtail	5	523.8	4.9	12.1	15.47	16.04	18.50 ± 1.93	17.3 ± 2.86	12.44 ± 3.14	5.76 ± 1.59	5.40 ± 0.56	8.12 ± 0.54	750.23 ± 85.88	2279.30 ± 353.71
	black porgy	4	389.7	5.2	19.4	15.57	14.72	nd	10.09 ± 1.22	3.31 ± 0.45	10.44 ± 2.80	5.45 ± 0.85	3.97 ± 0.32	231.33 ± 33.78	646.22 ± 104.30
	marbled sole	8	116.3	3.7	48.1	15.67	14.46	4.63 ± 1.01	17.22 ± 1.60	4.63 ± 0.74	8.05 ± 2.98	4.88 ± 0.86	1.57 ± 0.13	353.78 ± 49.95	135.55 ± 17.93
	spotty belly greenling	5	149.8	5.1	57.1	16.77	16.35	nd	19.81 ± 1.68	4.74 ± 0.50	17.61 ± 5.81	3.38 ± 0.49	7.30 ± 0.46	535.84 ± 94.95	345.87 ± 63.59
	Indian flathead	3	145.6	3.6	34.9	16.38	-	nd	24.58 ± 2.27	4.58 ± 1.44	21.24 ± 7.34	2.19 ± 0.18	7.09 ± 0.69	152.66 ± 19.93	957.32 ± 194.55
	sea bass	1	619.6	3.7	74.6	16.09	-	30.08 ± 2.70	18.37 ± 1.63	71.01 ± 15.24	18.43 ± 5.73	22.90 ± 2.12	7.16 ± 0.63	117.90 ± 14.80	169.56 ± 31.08
	baby sea bass	10	95.1	5.5	24.9	16.32	-	9.21 ± 1.43	5.17 ± 0.78	12.56 ± 2.50	8.35 ± 2.66	4.18 ± 0.43	11.09 ± 0.84	379.48 ± 67.32	1069.23 ± 209.75
	black rock fish	11	165.7	5.2	46.3	16.39	15.88	7.84 ± 1.18	21.80 ± 2.06	10.93 ± 2.38	6.13 ± 2.13	2.66 ± 0.33	3.28 ± 0.30	138.92 ± 15.63	121.41 ± 12.11
	pacific cod	5	5400.0	3.1	36.8	14.09	13.32	41.74 ± 3.34	321.30 ± 20.10	40.78 ± 9.88	459.82 ± 122.73	11.42 ± 1.17	134.58 ± 13.61	237.7 ± 19.07	587.40 ± 80.64
Invertebrate	hard clam	13	104.7	4.6		10.03		5.82 ± 1.27		4.05 ± 1.52		1.05 ± 0.07		165.59 ± 10.42	
	Manila clam	10	13.9	5.7		12.77		nd		5.85 ± 1.00		1.25 ± 0.15		128.58 ± 11.04	
	conch	10	58.8	6.0		13.00		21.96 ± 2.35		0.15 ± 0.06		7.77 ± 0.61		366.08 ± 37.58	
	mussel	10	22.3	5.9		10.68		nd		31.11 ± 9.42		1.66 ± 0.19		727.52 ± 96.66	
	Japanese mud shrimp	10	458.8	3.5		16.66		35.46 ± 2.92		6.29 ± 1.60		3.76 ± 0.55		861.06 ± 122.65	
	Small octopus	10	50.9	3.8		12.26		13.07 ± 1.20		4.84 ± 1.28		1.72 ± 0.14		436.92 ± 48.80	
	common octopus	2	284.7	3.5		13.17		9.37 ± 1.43		2.73 ± 0.73		4.13 ± 0.35		292.61 ± 27.83	

The concentrations of major compounds for each chemical groups with trophic levels are presented in Figure 2. The concentrations of PCB 153, *p,p'*-DDE, BDE-47 and PFOS relatively increased with increasing trophic levels, but no significant relationships were not found for both factors. In particular, benthic organisms such as bivalves and gastropds showed the relatively higher concentrations of target compounds, but their trophic positions were not so high compared with pelagic fishes. Thus, to clarify biomagnification of these compounds in marine food-web, the kinds of food-web should be separated (e.g. pelagic or benthic). In addition, the food-web structure should be considered using stable carbon isotope for determing their food sources.

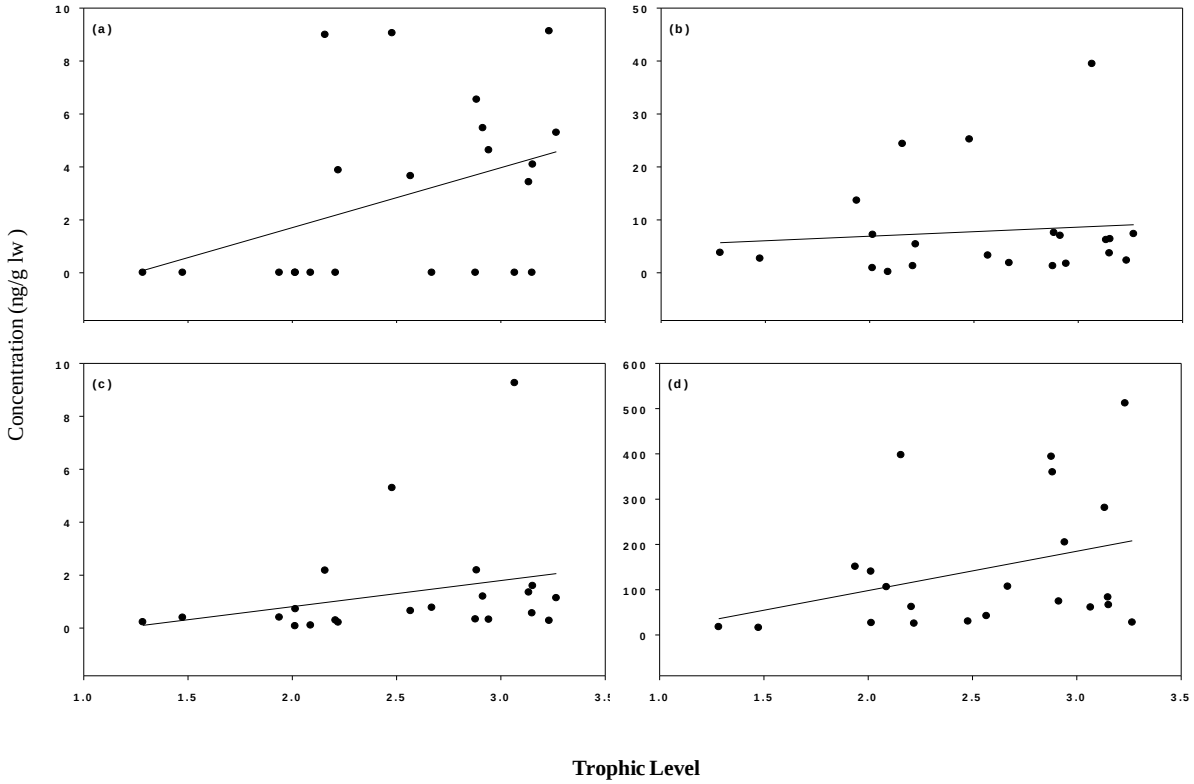

Figure 2. The concentration of organohalogen compounds in different organisms from Jinhae Bay. (a) PCB 153 (b) *p,p'*-DDE (C) BDE-47 (d) PFOS.

Acknowledgements
This study was funded by a grant from the National Fisheries Reseach and Development Institute (NFRDI) and the Ministry of Land, Transport and Maritime Affairs (MLTM), Korea.

References:

1. Burreau S, Zebuhr Y, Broman D, Ishaq R. (2004) *Chemosphere.*55: 1043-52
2. De Wit, C.A., Alaee, M., Muir, DCG. (2006) *Chemosphere.* 62: 209-33
3. Fisk AT, Hobson KA, Norstrom RJ (2001) *Environ Sci Technol.* 35: 732-8
4. Kannan K, Tao L, Sinclair E, Pastva SD, Jude D.J, Giesy J.P. (2005) *Arch Environ Contam Toxicol.* 48: 559-66
5. Kuo TM, Sepulveda MS, Hua I, Ochoa-Acuna HG, Sutton TM. (2010) *Ecotoxicology*. 19: 623-34
6. Moon HB, Kannan K, Choi M, Choi H.G. (2007) *Mar Pollut Bull.* 54: 1402-12
7. Moon HB, Yoon SP, Jung RH and Choi M. (2008) *Chemosphere.* 73: 880-9
8. Khim JS, Kannan K, Villenuve DL, Koh CH and Giesy JP. (1999) : *Environ Sci Technol.* 33: 4199-205
9. Hong S, Won EJ, Ju HJ, Kim MS and Shin KH. (2010*) Mar Pollut Bull.* 46: 303-13
10. Yim UH, Hong SH, Shim WJ and Chang M. (2005) *Mar Pollut Bull.* 50: 319-26