

SPATIAL DISTRIBUTION OF ORGANOHALOGENATED COMPOUNDS IN SEAWATER AND SEDIMENT FROM JINHAE BAY, KOREA

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Introduction

Environmental contamination by organohalogenated compounds (OHCs) is a global concern because these compounds are toxic, persistent, long-range transport, and bioaccumulative. OHCs can cause adverse health effects such as development toxicity, cancer, and endocrine disruption^{1,2}. Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethane (DDTs), chlordanes (CHLs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and pentachlorobenzene (PeCBz) are well-known OHCs detected in various environmental compartments³. Emerging contaminants such as perfluorinated compounds (PFCs) and polybrominated diphenyl ethers (PBDEs) are of global concern because of their widespread distribution in marine ecosystems and their potential toxicity¹. Human activities lead to constant input of OHCs in marine environment⁴. In Korea, approximately 4300 tons of PCBs were used until the 1990s⁵, and approximately 3600 tons of various OCPs were used agricultural purposes until 1980s⁶. Although the use of PCBs and OCPs has been banned or restricted in Korea, these contaminants are still present in coastal environments^{7,8}. PBDEs have not been produced in Korea, but are imported from various countries due to rapid growth of electronic market in Korea. However, there is no regulation on the use of PBDEs in Korea. PFCs have been used as surfactants in many products, but no information are not available on use and production of these compounds in Korea. Jinhae Bay, located on the southeast coast of Korea, is a representative semi-closed bay with a slow rate of water exchange, which results in accumulation of toxic organic contaminants⁹. Jinhae Bay consists of several small bays such as Haengam, Masan, Dangdong, and Gohyeon Bays. In particular, Masan Bay is surrounded by many industrial complexes, comprising of steel manufacturers, machine shops, dye houses, pulp factories, and a sewage treatment plant¹⁰. The objective of this study was to describe the concentrations and chemical profiles of OHCs, to characterize the contamination status and sources of these compounds in Jinhae Bay, Korea.

Materials and methods

The sample collection for surface seawater (n=38) and sediment (n=38) from Jinhae Bay was performed in October, 2011. Seawater and sediment samples were collected using a bucket sampler and a Van-Veen grab sampler, respectively. The collected samples were transported to the laboratory. Detailed descriptions of experimental procedures and instrumental analyses of OHCs for seawater and sediment samples have been described elsewhere^{10,11,12}. In brief, seawater samples (about 10 L) were separated into particulate and liquid phases within two days of collection. The particulate portion was isolated by filtration through glass fiber filters (GFFs; 0.7 μ m, Whatman, Maidstone, England). Particulate samples were dried at room temperature and then weighed, to determine the mass of suspended solids (SS) in water. The liquid phase was extracted using solid phase extraction (SPE) disks (ENVI-18 DISK, 47mm, Supelco, Bellefonte, PA, USA). The GFFs and SPE disks were extracted with mixed solvents of dichloromethane (DCM) and hexane using a Soxhlet apparatus. Similarly, freeze-dried sediment samples were extracted in a Soxhlet apparatus using mixed solvents of DCM and hexane. The extracts of seawater and sediment were cleaned by passage

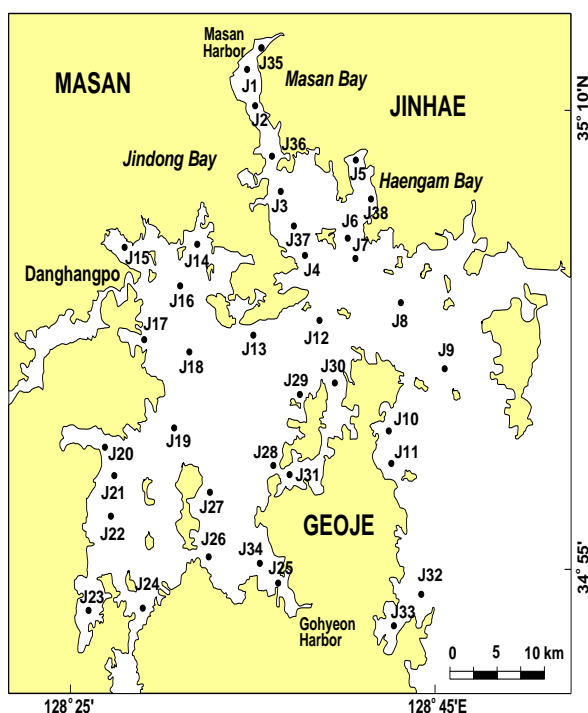


Figure 1. Spatial distribution of OHCs in seawater and sediment from Jinhae Bay, Korea

through a multilayer silica gel column with 150mL of 15% DCM in hexane. The eluants were concentrated to approximately 1mL and were then evaporated to 100 μ L at room temperature for instrumental analysis. For analysis PFCs, 15 mL of methanol was added to each samples (5 g). For extraction, microwave sonication was used for 30 min. The methanol layer was separated by centrifugation, and then transferred. These procedures were repeated twice. The extracts were adjusted to a volume of 1 mL with methanol, and filtered through a 0.22 μ L nylon filter using syringe. HRGC/HRMS (JMS 800D, Jeol) was used for determination of PBDEs, and PCBs and OCPs were determined by GC/MSD (5975C, Agilent) EI mode, using DB-5 MS capillary column. 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)¹³.

Results and discussion

Spatial distribution of OHCs in seawater and sediment

The concentrations of PCBs, OCPs, PBDEs and PFCs in seawater and sediments collected from Jinhae Bay, Korea are summarized in Table 1. The concentrations of PFCs (12 ± 5.6 ng/L) in seawater were the highest among OHCs analyzed, because these contaminants mostly exist in dissolved phase in aquatic environment¹³. The concentrations of PCBs (2.1 ± 0.97 ng/L), DDTs (0.05 ± 0.10 ng/L), CHLs (0.01 ± 0.03 ng/L), HCB (0.02 ± 0.02 ng/L), PeCBz (0.03 ± 0.03 ng/L), HCHs (0.71 ± 1.1 ng/L), PBDEs (0.35 ± 0.33 ng/L) and PFCs (12 ± 5.6) in seawater from Jinhae Bay showed relatively lower levels compared with those found in other studies⁷. In contrast to seawater contamination pattern of OHCs, the concentrations of PCBs (6.4 ± 6.2 ng/g dw) and PBDEs (7.9 ± 6.6 ng/g dw) in sediment samples were the highest chemicals, due to their higher hydrophobic characters¹⁴. Interestingly, the higher concentrations of PBDEs than PCBs in sediments suggest the large consumption of brominated flame retardants (BFRs) in Korean environment. The concentrations of DDTs (0.92 ± 0.88 ng/g dw), CHLs (0.03 ± 0.02 ng/g dw), HCB (0.05 ± 0.06 ng/g dw), PeCBz (0.01 ± 0.01 ng/g dw), HCHs (1.9 ± 2.3 ng/g dw) and PFCs (1.4 ± 0.59 ng/g dw) were in sediment from Jinhae Bay relatively lower levels than other analyzed compounds.

Table 1. Concentration (mean \pm SD) of OHCs measured in seawater and sediment from Jinhae Bay, Korea

	Seawater (ng/L)	Sediment (ng/g dw)
PCBs	2.1 ± 0.97	6.4 ± 6.2
DDTs	0.05 ± 0.10	0.92 ± 0.88
CHLs	0.01 ± 0.03	0.03 ± 0.02
HCB	0.02 ± 0.02	0.05 ± 0.06
PeCBz	0.03 ± 0.03	0.01 ± 0.01
HCHs	0.71 ± 1.1	1.9 ± 2.3
PBDEs	0.35 ± 0.33	7.9 ± 6.6
PFCs	12 ± 5.6	1.4 ± 0.59

The spatial distributions of OHCs in seawater and sediments from Jinhae Bay, Korea are presented in Figure 2. The overall concentrations of OHCs were elevated in seawater and sediments from inner part of the bay than outer parts of the bay, suggesting the existence of sources of these contaminants in industrial complex and/or harbor zones¹⁰. However, PFCs had a homogeneous distribution in seawater and sediment samples, indicating that PFCs have a distinct source. Among the bays surveyed, Masan and Gohyeon Bays showed relatively higher levels of OHCs than those found in other bays, due to higher industrial activities than the other bays. Masan Bay has relatively large industrial complexes such as steel industry, chemical factories and intensive shipping activities. Gohyeon Bay has larger shipyards, situated in the inner bay, with high shipping activities. The concentrations of CHLs in seawater and sediments were close to the limit of quantification (LOQ), indicating a phase-out of this chemical from aquatic environment. Similar to CHLs, PeCBz and HCB showed the low levels compared with other contaminants. There is no considerable recent input of CHLs, PeCB and HCB in study area.

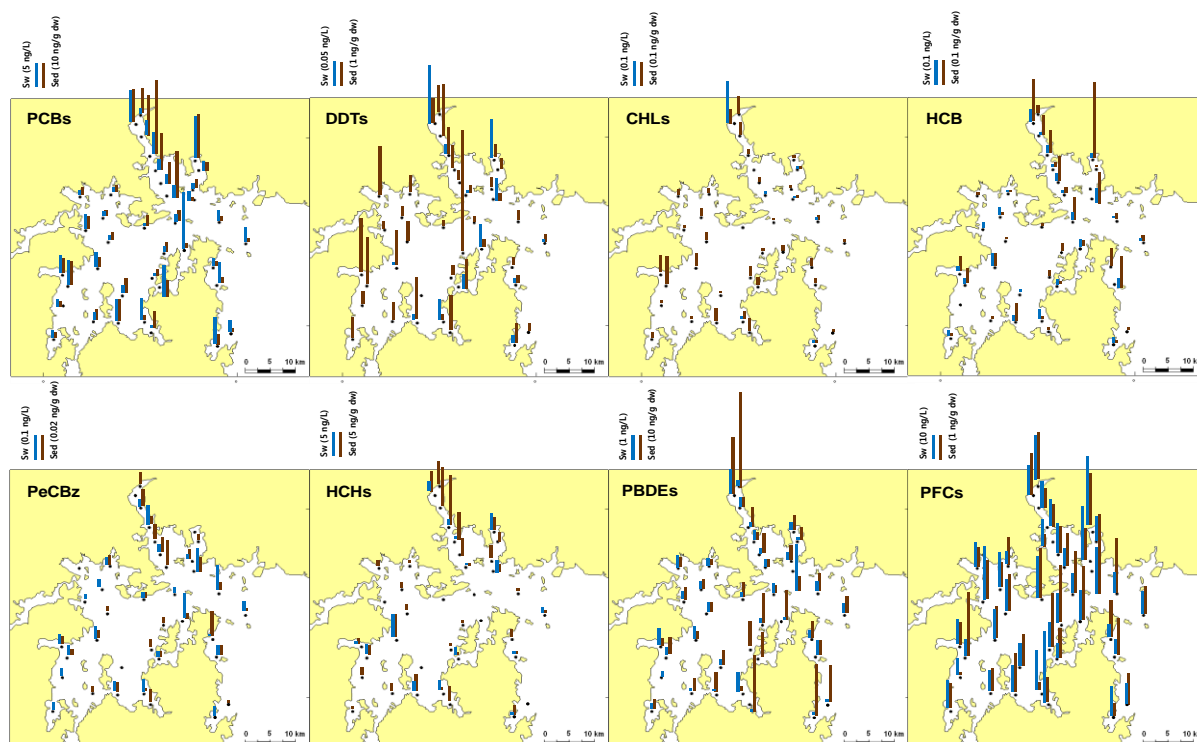


Figure 2. Spatial distribution of OHCs in seawater and sediment from Jinhae Bay, Korea.

Chemical profiles of OHCs in seawater and sediment

The relative contributions of PCBs, OCPs, PBDEs and PFCs in seawater and sediments from Jinhae Bay, Korea are summarized in Figure 3. The congener distribution of PCBs in seawater and sediments were different. Among PCB congeners, IUPAC no. CB 110 was the predominant congener in seawater, accounting for 25% of total PCB concentrations. The other dominant congeners were CBs 28, 101 and 118. In sediments, PCB 118 was dominant, followed by CBs 110 and 170. Lower chlorinated congeners in seawater were significantly contributed to the total PCBs than those found in sediments. HCHs were dominant in seawater samples, due to lower K_{ow} values, but the contributions of HCHs and DDTs in sediments were similar to each others. Among of DDTs, *p,p'*-DDT was dominant in seawater, but *p,p'*-DDE was a major compound in sediment, due to degradation potentials in the environment. The major PBDE congeners in seawater and sediments was BDE-209, which accounted for 87% and 85% of total PBDE concentrations, respectively, consistent with those reported for previous studies in Korea¹⁵. Previous study showed that the consumption of deca-BDE technical mixture is the major source of PBDEs in Korean coastal waters^{10,15}. The major compounds of PFCs were PFOA and PFOS and PFOS in seawater and PFUNDA in sediments.

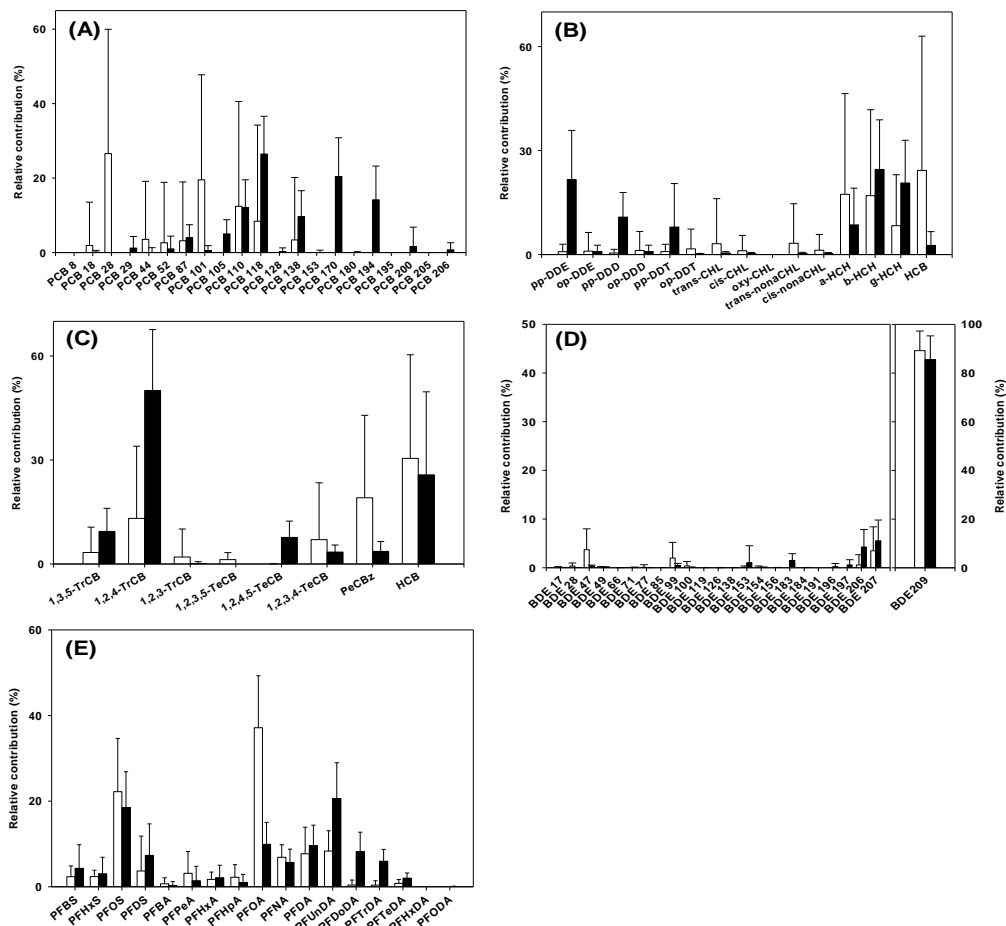


Figure 3. Chemical profiles of OHCs in surface seawater and sediments from Jinhae Bay, Korea. (A) PCBs, (B) OCPs, (C) Chlorobenzenes, (D) PBDEs and (E) PFCs.

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