HISTORICAL TRENDS OF CHLORINATED, BROMINATED AND FLUORINATED CONTAMINANTS IN SEDIMENT CORES FROM JINHAE BAY, KOREA

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Introduction

Jinhae Bay, located on southeastern coast of Korea, is a representative semi-enclosed bay with a slow rate of water exchange. The bay consists of several small bays including Masan, Haengam, Jindong and Gohyeon Bays. Among these, Masan Bay has been designated as 'Special Management Coastal Zone' by Korean government. Previous studies have reported on the distribution of toxic organic contaminants such as polychlorinated dibenzo-*para*-dioxins (PCDDs), polychlorinated dibenzofuran (PCDFs), polychlorinated biphenyls (PCBs), organochlorine pesticide (OCPs), and polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs) in sediments from Masan Bay[1-4]. These studies emphasized that Masan Bay is highly contaminated by toxic organic contaminants because of local discharges from industrial complexes and discharges from a wastewater treatment plant (WWTP) in the bay. There are ports for fishing boats in Haengam Bay and a shipyard complex in Gohyeon Bay. Jindong Bay is characterized by a large numbers of aquaculture farms are located [5].

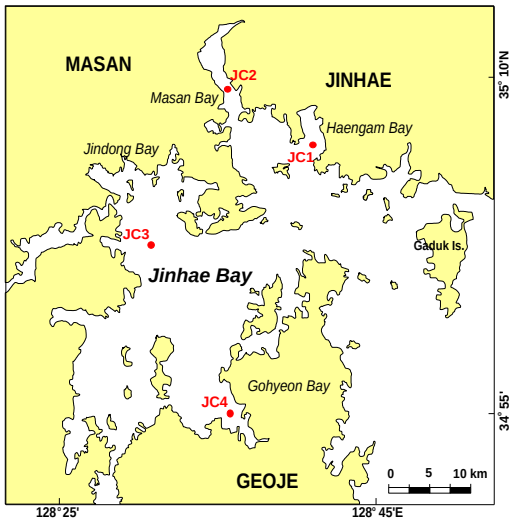

Figure 1. Sampling locations of sediment cores from Jinhae Bay, Korea.

PCBs, DDTs, PBDEs and perfluorinated compounds (PFCs) are widespread environmental contaminants. PCBs and DDTs are included in legacy persistent organic pollutants (POPs) and banned in Korea since 1980s [6]. PBDEs and PFCs are included in emerging POPs with no regulation in Korea. Sediment cores have been used to study pollution histories and trends of toxic organic contaminants in aquatic environments[7,8]. Historical studies are useful to identify and characterize the sources and to establish strategies to control and manage sources of contamination[9]. A few studies have reported on vertical distributions of toxic contaminants including halogenated compounds in Korean coastal environments. In particular, little information is available on historical trends of PFCs in Korean environments. The objectives of this study were to investigate historically contamination trends of PCBs, DDTs, PBDEs and PFCs in 4 sites of Jinhae Bay and estimate the effects of regulation.

Materials and methods

Sample collection

Four sediment cores from Haengam Bay (JC1), Masan Bay (JC2), Jindong Bay (JC3) and Gohyeon Bay (JC4) were collected in October 2011. Core samples were taken with SCUBA diving using acryl tubes (length 150 cm, internal diameter 11.3 cm). Total length of sediment cores collected from each sites was below 80 cm. The samples were transported to the laboratory and were sectioned at 2 cm intervals for 1-30 cm and remained parts were sectioned at 5 cm intervals.

Chemical analysis and instrumental analysis

Detailed experimental procedures and instrumental analysis for target compounds were described in previous studies[1,10]. In brief, the samples were extracted in a Soxhlet apparatus using 200 mL of 25% hexane in dichloromethane for 16 h. Prior to the extraction, surrogate standards, PCBs 103, 198 and 209 were spiked into

the samples. The extracts were concentrated to 10 mL and 4.5 mL was used for analysis PCBs, DDTs and PBDEs. The samples were spiked with internal standards, ^{13}C-labeled PBDEs and ^{13}C-labeled PCBs. The extracts for PCBs, DDTs and PBDEs analysis were cleaned by passing them through a multi-layer silica gel column using successive elutions with 150 mL of 15% DCM in hexane. For analysis PFCs, samples (5 g) were spiked with internal standards, ^{13}C-labeled PFCs and 15 mL of methanol was added to each samples. For extraction, microwave sonication (30 min) was used. The methanol layer was separated by centrifugation, and then transferred to another tube. These procedures were repeated twice. The extracts were adjusted to a volume of 1 mL with methanol, and filtered through a 0.22 μL nylon filter using syringe.

A high-resolution gas chromatographer (GC)/high-resolution mass spectrometer (JMS 800D, Jeol, Tokyo, Japan) was used for identification and quantification of PBDEs based on the relative response factors of individual congeners. PCBs and OCPs were determined using a gas chromatographer (Agilent 7980 N) coupled to a mass spectrometer. The GC/MSD was operated in the electron impact (70 eV) and selected ion monitoring modes for most intensive ions of the molecular ion cluster of individual compounds. Quantification of each compound was performed by external standard method. The PFCs were analyzed by high-performance liquid chromatography (HPLC, Agilent 1100) coupled with an Applied Bio-systems API 2000 electrospray triple quadruple mass spectrometer (ESI-MS-MS).

Sedimentation rate and age dating

Sedimentation rates from four sediment cores were measured by the ^{210}Pb and ^{226}Ra dating techniques using a well-type HPGe gamma detector at Korea Basic Science Institute (KBSI). ^{210}Pb and ^{226}Ra activities were determined following the method proposed by Kim and Burnett[11]. The calculated sedimentation rates were 0.98 cm/yr for JC1, 1.95 cm/yr for JC2, 1.25 cm/yr for JC3 and 0.76 cm/yr for JC4.

Results and discussion

Concentration of PCBs, DDTs, PBDEs and PFCs

Concentrations of PCBs, DDTs, PBDEs and PFCs in sediment core from Jinhae Bay in Korea are summarized in Table 1. Among the sampling sites, the concentrations of all the chemicals from Masan Bay were the highest, suggesting that industrial complex are major contamiatnion source of these compounds in Jinhae Bay.

Vertical distribution of PCBs and DDTs

Vertical profiles of PCBs, DDTs, PBDEs and PFCs in sediment cores from 4 locations are presented in Figure 2. Among the sampling sites, the concentrations of a sediment core from JC2 (Masan Bay) were the highest in all compounds. In sediment core from JC1 (Haengam Bay), the vertical profiles of legacy POPs (PCBs and DDTs) and emerging POPs (PFCs and PBDEs) were clearly different, suggesting both chemical groups have different contamination history. The highest concentration of PCBs (2.73 ng/g dw) in JC1 was found for a sediment around 1980s based on the age dating results. The vertical profiles of PCBs reflect a largest consumption of products containing PCBs in Korea during 1980s[12]. In JC2, there was a peak in 1990s, unlike JC1 sediment core. In order to improve sediment contamiation and/or to make shipping route in Masan Bay, extensive dredging was performed during 1990-1994[13]. Resuspension of PCBs seems to be associated with these activities. In comparision with vertical profiles of PCBs from JC1 and JC2, other sites (JC3 and JC4) showed the highest level of PCBs in surface sediments, suggesting the ongoing souce of PCBs in these sites. Although the concentrations of DDTs were close to limit of quantification (LOQ), the overall concentrations of DDTs were similar to PCBs.

Table 1. Concentrations (ng/g dw) of PCBs, DDTs, PBDEs, and PFCs in Jinhae Bay, Korea (mean ± SD)

	Haengam Bay	Masan Bay	Jindong Bay	Gohyeon Bay
PCBs	1.00 ± 0.84	2.58 ± 1.80	0.09 ± 0.15	0.20 ± 0.32
DDTs	0.19 ± 0.16	1.01 ± 0.76	0.24 ± 0.16	0.70 ± 0.41
PBDEs	1.19 ± 1.53	4.74 ± 2.88	1.02 ± 1.43	2.03 ± 3.30
PFCs	0.89 ± 0.94	1.82 ± 1.05	1.03 ± 0.91	0.58 ± 0.25

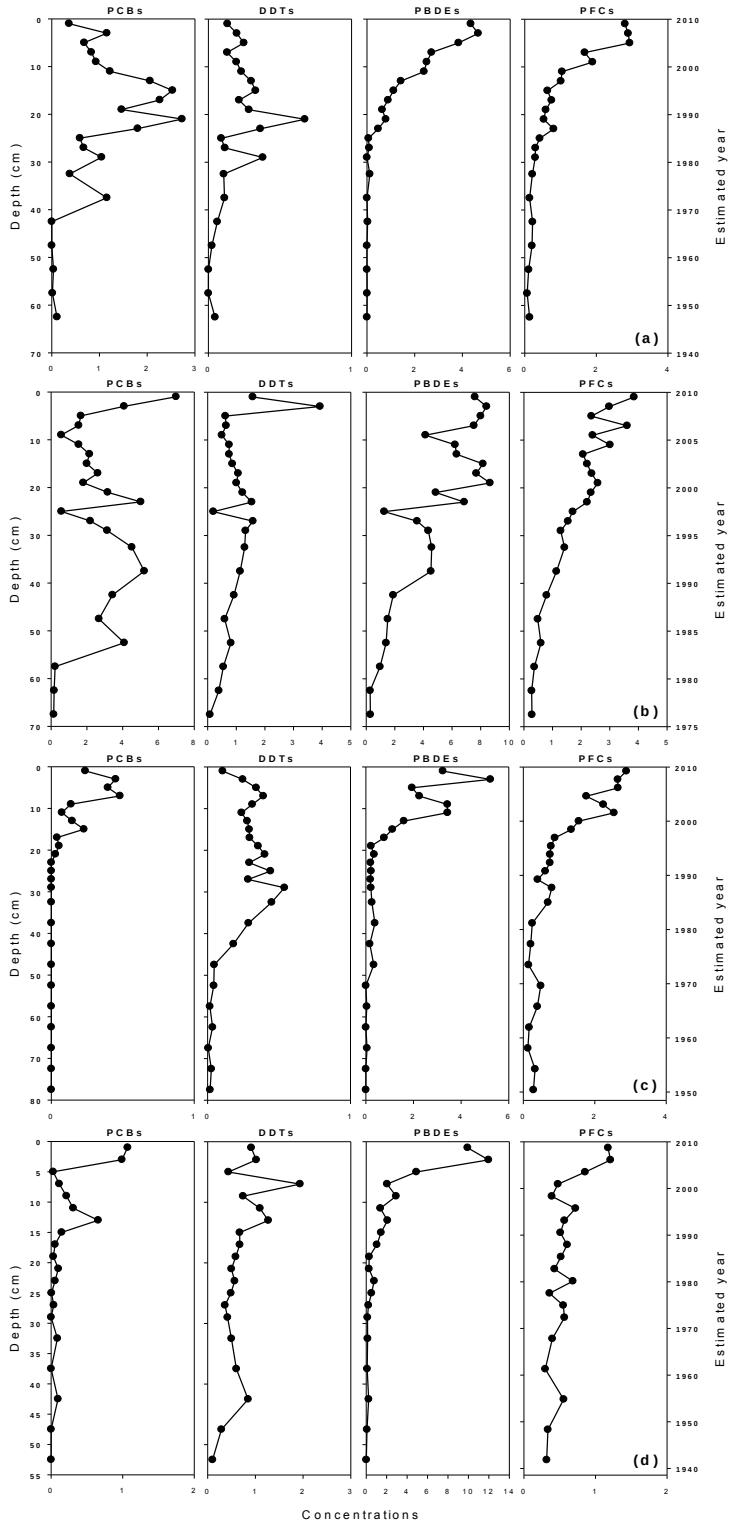

Figure 2. Vertical distributions of PCBs, DDTs, PBDEs and PFCs in sediment cores from Jinhea Bay (ng/g dw). (a) Haengam Bay, (b) Masan Bay, (c) Jindong Bay, (d) Gohyeon Bay.

Vertical distribution of PBDEs and PFCs

In comparision with PCBs and DDTs, the concentration of PFCs and PBDEs were generally increased in all sites with increasing years, indicating these chemical groups are contaminated by on-going sources. JC4 showed the highest level of PBDEs (0.01-11.97 ng/g dw), compared with other sites. In all sampling sites, the concentrations of PBDEs increased from 1990s, because of large consumpotion of brominated flame retardants (BFRs) around the world as well as Korea since 1990s. In particular, the vertical profiles of PBDEs in the sediment core from JC2 (Masan Bay) showed wide range of concentrations with large fluctuation during estimated year, suggesting the existence of multiple souces of PBDEs in Masan Bay. Similar to PBDEs, the highest concentrations of PFCs were found for the sediment from JC2 (0.27-3.84 ng/g dw), associated with the discharge of a WWTP[14]. Most of the sediment samples collected from 4 sites showed that the concentrations of PFCs increased from 1980s, suggests that the PFC contamination would be associated with around the 1980s. This result is consistent with the global production of PFCs, which incresaed from1975 to 1989 and then constant during the 1990s[16].

Acknowledgements

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