HISTORICAL TRENDS OF PCDDs, PCDFs, DIOXIN-LIKE PCBs AND NONYLPHENOLS IN DATED SEDIMENT CORES FROM A SEMI-ENCLOSED BAY IN KOREA; TRACKING THE SOURCES

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Introduction

Sediment cores have been used to study pollution histories and trends of toxic organic contaminants in aquatic environments [1,2]. Several studies have examined the vertical profiles and historical records of toxic organic contaminants such as PCDD/Fs, PCBs and PAHs in dated sediment cores from many countries [1,2,3]. Masan Bay, located on the south coast of Korea, is a semi-enclosed bay with a slow rate of water exchange. Approximately 1300 industrial complexes, including petrochemical, heavy metal, electrical, and plastic industries are distributed along the coast of Masan Bay. Previous studies showed that Masan Bay is highly contaminated by toxic organic contaminants because of local discharges from industrial complexes and because of slow water exchange in the bay. There is, however, insufficient information on the pollution history and fluxes of dioxin-like and estrogenic compounds in Masan Bay. Historical trend studies are useful to identify and characterize the sources and to establish strategies to control and manage sources of contamination. The objectives of this study were to describe the vertical distribution and congener profiles of dioxin-like and estrogenic pollutants and to examine the sources of these pollutants in Masan Bay, Korea.

Materials and methods

Two sediment cores, one from the middle of the bay and another one near the outfall of a wastewater treatment plant (WWTP), were collected in May 2005. The WWTP, situated at Duckdong in Masan city, was established in 1994. Most of the wastewater treated in this plant is domestic (1 million inhabitants) effluent (90%), while less than 10% is from industries [4]. Core samples were taken using acryl tubes (length 150 cm, internal diameter 11.3 cm). The cores were immediately sectioned at 2 cm intervals using stainless steel plates. After sampling, all sectioned sediments were transported to the laboratory where they were stored in a freezer at −20ºC until further analysis.

Experimental procedures and instrumental analysis of PCDD/Fs, DLPCBs, and NPs in sediment cores were performed following the methods described elsewhere [5,6]. One sub-core from each location was used for dating the sediment by measuring specific activities of ^{210}Pb and ^{137}Cs [7]. The depositional fluxes for core 1 (middle part of the bay) and core 2 (near the outfall of a WWTP) were determined to be 0.53 g/cm^2/yr and 1.09 g/cm^2/yr, respectively. The calculated sedimentation rates were 0.97 cm/yr and 1.99 cm/yr for cores 1 and 2, respectively. Sedimentation rates at the site of core 2 were twice that at core 1, which can be explained by the presence of WWTP outfall and an advection effect of the bottom current in the bay.

Results and discussion

Temporal Trends

Vertical profiles of TOC, PCDD/Fs, DLPCBs, and NPs in sediment cores from the two locations are presented in Figure 1. The overall contamination by dioxins, DLPCBs and NP was greater in core 2 than in core 1. Specifically, the PCDD/F concentrations in sediment core 2 were an order of magnitude greater than the concentrations in sediment core 1.

In sediment core 1, vertical profiles of DLPCBs and NPs were generally similar, and consistent with TOC profiles. The concentrations of DLPCBs and NPs generally showed an increasing trend from a depth of 20 cm (~ year 1985) to the surface layer (~ year 2005). The concentrations of these contaminants below

20 cm depth were close to the detection limits, and remained constant. The highest concentrations of DLPCBs and NPs were found at the surface or subsurface sediment layers, suggesting ongoing discharges of these contaminants into the bay. The vertical distribution of PCDD/Fs in core 1 showed an increasing trend after 1985, similar to the trends of DLPCBs and NPs. However, the PCDD/F concentrations fluctuated widely in the cores deposited from 1935 to 1965. The varying profiles of PCDD/Fs may reflect the inputs of PCDD/Fs from non-point sources. Prior to 1970, the areas surrounding the Masan Bay had been used for agriculture, primarily for farming, and therefore the area may have received runoff from agricultural activities. Interestingly, DLPCBs and NPs did not exhibit patterns observed for PCDD/Fs, prior to 1970, suggesting that PCBs and NP were not derived from non-point sources such as agricultural run-off.

In sediment core 2, concentrations of PCDD/Fs, DLPCBs and NPs were higher than in core 1 and the vertical profiles of these three contaminant classes were similar, indicating the existence of a point source of these contaminants. The highest concentrations of PCDD/Fs, DLPCBs, and NPs were detected at a depth of 8–10 cm, corresponding to approximately the year 2000. The concentrations of PCDD/Fs, DLPCBs, and NPs increased dramatically from the 1990s to the 2000s, and then decreased after 2000. The vertical distributions of PCDD/Fs, DLPCBs, and NPs in sediment core 2 were characterized by fairly uniform concentrations below a depth of 30 cm (~ year 1990 and older). The vertical profiles of these contaminants in core 2 were coincident with establishment and operation of the WWTP. The WWTP considered in the present study was established in 1994. Although primary treatment was used originally, later in 2001, the plant was upgraded to the activated sludge treatment method. The high concentrations of PCDD/Fs, DLPCBs and NPs are consistent with the establishment of the WWTP in the early 1990s. The decrease in the loads of contaminants after 2000 is associated with the upgrading of the operation to a secondary treatment facility.

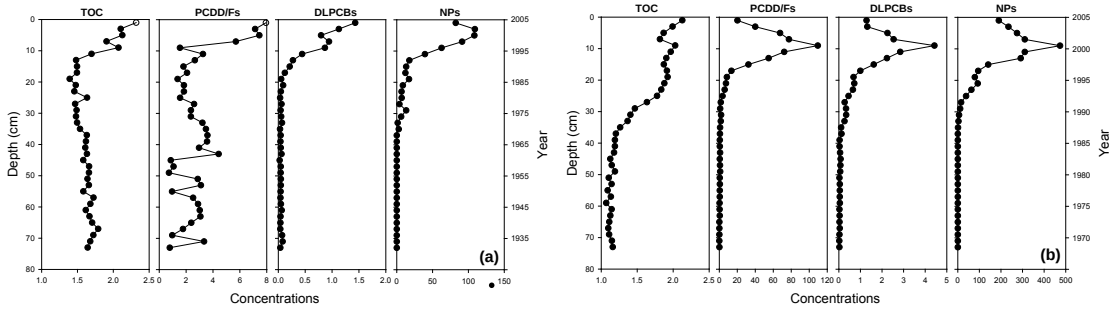

Figure 1. Vertical distributions of TOC, PCDD/Fs, DLPCBs and NPs in sediment core 1 (a) and core 2 (b) from Masan Bay, Korea. Concentration units for each of the compounds were as follows: % TOC; pg TEQ/g dry weight for PCDD/Fs and DLPCBs; and ng/g dry weight for NPs.

Chemical Profiles and Sources

In order to characterize contamination sources of PCDD/Fs in each section of the sediment cores, two-dimensional ordination was performed by non-parametric multidimensional scaling (MDS) using PRIMER for Windows (PRIMER Version 5.2.9, Plymouth, UK). This multivariate statistical technique has been used to determine the spatial variability and potential sources in sediments [6]. Two clusters were identified on the variable plots for both sediment cores, based on the homologue patterns of PCDD/Fs.

In sediment core 1, the first group composed of core segments with recent sedimentation years of 1999 to 2005. This group was characterized by a high contribution of OCDD (Figure 2). All of the PCDF congeners, except OCDF, showed similar contribution. This pattern is similar to the patterns reported for atmospheric deposition samples in Korea [8] and in sediments from Tokyo Bay, Japan, where the deposition of combustion emissions is the major source [1]. The second cluster of sediment core 1 included the core segments with sedimentation years of 1931 to 1997. The sediment layers from this cluster were characterized by high contributions of tetra-CDDs (TCDDs) and OCDD, which collectively accounted for 41 ± 17% of total PCDD/F concentrations. The PCDF homologue profiles were similar to those found for the other cluster in core 1. As mentioned above, the sedimentation years, 1931–1997, seems to be affected by inputs from agricultural pesticides such as CNP and PCP. In Korea, CNP was used as an herbicide until the 1980s [9]. TCDDs and penta-CDDs are relatively abundant in CNP in comparison with PCP [10]. 1,3,6,8- and 1,3,7,9-TCDDs, which are indicative of sources originating from CNP [10], showed an

increasing trend with increasing depth from the 1990s, while the vertical distributions of the other congeners such as 1,2,7,8-TCDF; 1,2,3,4,6,8,9-HpCDF, and OCDD were different from those of congeners derived from CNP. Therefore, the second cluster of core 1 is indicative source of PCDD/Fs arising from CNP and combustion.

In sediment core 2, the first cluster of sediment core 2 was characterized by a higher contribution of PCDFs than the contribution of PCDDs to the total PCDD/F concentrations (Figure 2). Hexa-CDF homologue dominated in total PCDF concentrations, and progressively decreased with increasing chlorination. OCDD dominated in the PCDD concentrations, and the abundance of other congeners decreased with low levels of chlorination. This is similar to the homologue profiles of PCDD/Fs generated from a typical municipal waste incinerator [11]. The WWTP considered in the present study receives wastewaters from various industrial complexes located in the cities of Masan and Changwon. Therefore, industrial wastewaters contribute to high contamination of PCDD/Fs in Masan Bay sediment through the WWTP. The second cluster of sediment core 2 consisted of core segments with sedimentation years 1968 to 1997. This group was characterized by a high contribution of OCDD (53 ± 11%) to the total PCDD/F concentrations, which is similar to the typical homologue profiles of PCDD/Fs in marine sediments [1,11].

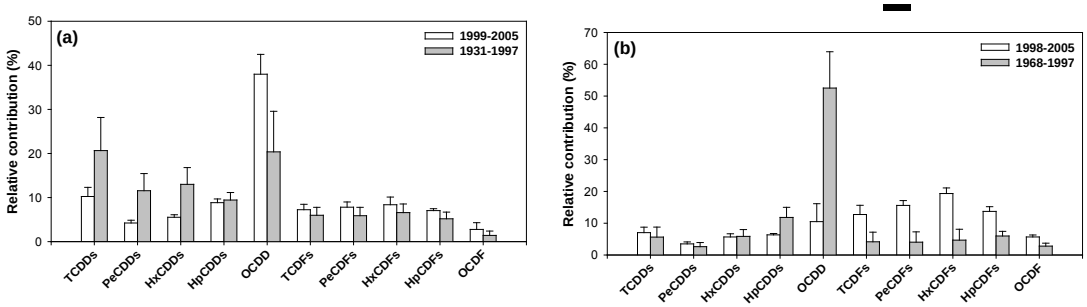

Figure 2. Comparison of average homologue profiles of PCDD/Fs in core 1 (a) and core 2 (b) for each group clustered by non-parametric MDS ordination.

Inventories and Fluxes

Overall, the inventories and fluxes of these contaminants were 3–10 times higher in core 2 than in core 1, due to the high sedimentation rate and inputs from the WWTP after 1997 (Table 1). Average inventories of total PCDD/Fs were 1,343 pg/cm^2 in core 1 and 4,567 pg/cm^2 in core 2. The total TEQ inventories for cores 1 and 2 were 16.1 and 80 pg/cm^2, respectively. Our values were lower than the TEQ inventories reported for the Venice Lagoon (34–5311 pg/cm^2) [12] but higher than the inventories reported a Canadian arctic lake (0.014 pg/cm^2) [13]. The NP inventories in our study for core 1 (177 ng/cm^2) and core 2 (774 ng/cm^2), were 10-fold lower than the inventories reported for the Pearl River Delta and South China Sea [3]. Input fluxes of total PCDD/Fs, total TEQs and NPs in sediment core 1 were 134 pg/cm^2/yr, 1.6 pg TEQ/cm^2/yr and 18 ng/cm^2/yr, respectively. In sediment core 2, input fluxes of total PCDD/Fs, total TEQs and NPs were 939 pg/cm^2/yr, 17 pg TEQ/cm^2/yr and 159 ng/cm^2/yr, respectively. NP fluxes in our study were an order of magnitude lower than fluxes of NPs in Tokyo Bay, Japan [1].

Table 1. Inventories and fluxes of PCDD/Fs, DLPCBs and NPs in sediment cores from Masan Bay, Korea

	Total PCDD/Fs	TEQ-PCDD/Fs	TEQ-DLPCBs	NPs
	Inventories (pg/cm^2 for PCDD/Fs and DLPCBs and ng/cm^2 for NPs)			
Core 1	1,343 ± 813	15 ± 9	1.1 ± 1.9	177 ± 205
Core 2	4,567 ± 6,838	76 ± 144	3.5 ± 5.4	774 ± 743
	Fluxes (pg/cm^2/yr for PCDD/Fs and DLPCBs and ng/cm^2/yr for NPs)			
Core 1	134 ± 81	1.5 ± 0.9	0.1 ± 0.2	18 ± 20
Core 2	939 ± 1,406	16 ± 30	0.7 ± 1.1	159 ± 153

To investigate the contribution of WWTP to environmental release of PCDD/Fs, DLPCBs, and NPs, we estimated inventories and fluxes in sediment core 2 before and after the establishment of the WWTP in 1994 (Table 2). The inventories and fluxes of PCDD/Fs, DLPCBs and NPs have rapidly increased since operation of the WWTP. In particular, TEQ inventories and fluxes of PCDD/Fs were approximately 40

times higher after the establishment of WWTP. Consequently, WWTP discharge into Masan Bay is an important source of sediment contamination, as evidenced by historical records of toxic organic contaminants such as PCDD/Fs. Therefore, guidelines for discharges from the WWTP to coastal bays in Korea should be established in order to protect the health of the coastal marine environment.

Table 2. Comparison of inventories and fluxes of PCDD/Fs, DLPCBs and NPs before and after the establishment of WWTP in 1994

	Total PCDD/Fs	TEQ-PCDD/Fs	TEQ-DLPCBs	NPs
	Inventories (pg/cm^2 for PCDD/Fs and DLPCBs and ng/cm^2 for NPs)			
Before 1994	1,181 ± 1,084	6.4 ± 9.3	0.8 ± 1.0	153 ± 176
After 1994	13,709 ± 7,507	263 ± 172	11 ± 5.8	1,272 ± 632
	Fluxes (pg/cm^2/yr for PCDD/Fs and DLPCBs and ng/cm^2/yr for NPs)			
Before 1994	243 ± 223	1.3 ± 1.9	0.16 ± 0.21	31 ± 36
After 1994	2,819 ± 1,544	54 ± 35	2.2 ± 1.2	262 ± 130

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