PERSISTENT ORGANIC POLLUTANTS (POPS) IN SEDIMENT CORE OF GWANGYANG BAY, SOUTH KOREA

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Abstract

The most compounds of persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs) and dioxins (PCDDs/DFs and dioxin-like PCBs) in sediment samples from Gwangyang Bay in South Korea were investigated to evaluate environmental pollutants during the past 50 years. The estimated levels of ΣOCPs, ΣPCDDs, ΣPCDFs and ΣPCBs in the surface sediments of the outer-bay, St.1 were totally higher than those of the inner-bay, St.2 and 3 in the view point of horizontal variation. Regarding vertical distribution of POPs, the concentration was estimated to be the highest for ΣOCPs (ΣDDTs, followed by ΣCHLs> ΣHCHs> HCB> ΣDrins> mirex), ΣPCDDs> ΣPCDFs> ΣPCBs in almost all layers. Although the sampling location is densely industrial region, the pollution of OCPs was contributed more than 60% to total POPs in the all layers. The DDTs was predominant concentration ranging from 0.097 to 0.202 TOC ng g^{-1} dry wt. and attributed more than 60% to ΣOCPs in all the sediment layers. The maximum burden of OCPs and dioxins in the sediment core was 1.1 kg and 1.3 kg, respectively for 1967-1974 and the total burdens of POPs in the sediment core were estimated to be ca. 13 kg during the past 50 years.

Introduction

The PCDDs, PCDFs, dioxin-like (dl)-PCBs and OCPs, such as hexachlorobenzene (HCB), dichlorodiphenyl trichloroethane and its metabolites (DDTs), heptachlor, chlordane compounds (CHLs), aldrin, dieldrin, endrin, mirex and isomers of hexachlorocyclohexane (HCHs) are persistent, bioaccumualtive and toxic environmental contaminants. In South Korea, although the Stockholm Convention did not enter in force, societal concern about the problem caused by POPs in the environment has become high after the POPs treaty became effective in 2004 and recently ratified. Particularly, Gwangyang Bay, which is located in southern part of South Korea, is one of typical chemical industrial regions and designated recently as special management area by the Minster of Maritime Affairs and Fisheries, South Korea.[1] In addition, in order to extend industrial facilities and port facilities, land is now being reclaimed on the western and central parts of the Bay.[2] On the other hand, in Gwangyang Bay, there are four contiguous cities, Gwangyang, Shuncheon, Yeosu and Hadong-gun, which were famous for typical paddy fields for a long time in South Korea, are having an area of the paddy field more than approximately 26% in each city.[3] The endocrine disrupting chemicals,[4] dioxins,[5] PCBs[2] and OCPs[6] in Gwangyang Bay sediments had been individually reported for horizontal distribution. However, distributions for vertical and historical trends of their pollutions had not been reported in Gwangyang Bay. Our previous studies had been prepared elsewhere for these compounds examined here in the sediment core of in this study area.[7,8] In this study, to evaluate the overall environmental pollution state and to delineate the historical trends of these contaminants, the most of POPs was determined.

Materials and Methods

Sampling Locations

Surface sediment samples were collected at 2 stations, St.1 (N34˚ 52’ 040” and E127˚ 47’ 000”) and St.2 (N34˚ 51’ 210” and E127˚ 39’ 460”), in Gwangyang Bay, South Korea (Fig.1a). The site St.1 is near the steel works and Sumjin River which has the highest inflow, including land-derived suspended sediment, in this Bay. The St.2 is located in front of the Yeochon industrial complex. A sediment core, which was a cylindrical sample with a diameter of 4.5 cm and a length of 40 cm, was obtained at the inner port of Gwangyang Bay, St.3 (N34˚ 53’ 250” and E127˚ 37’ 240”) in 2006. A sediment core was sliced into 5 cm thick disks (n=8) up to bottom. All the sediment samples (n=10) were stored at -20 °C until analysis. In order to estimate the sedimentation rate and age in the sediment core, the 210Pb and 137Cs values were used. Total organic carbon (TOC) and total nitrogen (TN) contents in each sample were analyzed after treated with diluted HCl (2N) to remove carbonate carbon by

using an NC analyzer, Sumigraph NC-900.

Analytical Procedure

Each compound of OCPs in the sediment samples was analyzed following the method previous work.[9] All samples were identified and quantified by injecting an aliquot into a high-resolution mass selective detector (HRMS) (Micromass Autospec-Ultima) interfaced to a HP6890 series high-resolution gas chromatograph (HRGC). Isomer-specific analysis of individual pesticides in environmental samples based on relative response factor (RRF) quantification by HRGC-HRMS was carried out. HRGC-HRMS system conditions are as follows: a sample injection separated an autosampler onto a 30 m ENV-8MS column (i.d. 250 μm, film thickness 0.25 μm: Kanto Chemical Co., Japan). The HRMS was operated in an electron impact (EI) and SIM mode at resolution more than 10000 (10% valley). The analysis of PCDDs/DFs and coplanar PCBs carried out following previously described elsewhere.[10] Recovery of POPs in spiked environmental samples was 96 ± 11% for HCB, 64 ± 8% for HCHs, 102 ± 21% for CHLs, 76 ± 24% for DDTs, 85 ± 21% for Drins (including endrin and dieldrin except aldrin; less than 30%) and 76 ± 10% for mirex. Similarly, recovery range for PCDDs, PCDFs and coplanar PCBs were 88-117% (average 99 ± 9%, n=10), 95-112% (average 103 ± 6%, n=10) and 89-104% (average 98 ± 6%, n=10), respectively. In addition, the analytical precision of the results for the sediment replicates was acceptable because the deviation of the reproducibility in each individual POP compound ranged from 0 to 9% in environmental samples. The method detection limit (MDL) and method quantification limit (MQL) were calculated by 3 times and 10 times, respectively of the standard deviation of five replicate analysis of OCPs native standard with 1 pg μl^{-1} concentration. Toxic equivalent concentrations of dioxins were calculated based on the toxic equivalency factors (TEFs) for human/mammalians by the World Health Organization (WHO), in 2005.[11]

Statistical Analysis

A more accurate study of identification those source in the sediment core was done using hierarchical cluster analysis (HCA) and principal component analysis (PCA). The PCA of the data were performed using a software package, Excel statistics 2006 for Windows.

Results and Discussion

The sedimentary rate in the sediment core (St.3) was estimated 1.3 year per centimeter by 210Pb. The date of the sediment core was estimated ca. 50 years from the surface to 40 cm depth. In the surface sediments, the total OCPs concentration in the outer-bay, St.1 which is located in front of steel works and Sumjin River was higher than that of inner-bay, St.2 and St.3 (Fig.1b). The composition of POPs in the surface sediment is predominant for OCPs in the inner-bay and for dioxins in the outer-bay (Fig.1c). These facts indicating that the sources of contaminants could be mainly caused from industrial matters in the outer-bay and the agricultural applications in the inner-bay.

Organochlorine pesticides (OCPs)

The distributions of OCPs in Gwangyang Bay, South Korea were elucidated based on the vertical and horizontal investigation. The TOC normalized concentration of OCPs was showed to be high to low, ΣDDTs, ΣCHLs, ΣHCHs, ΣDrins, HCB and mirex in almost all sediment layers. The maximum concentration of ΣOCPs was present during the period of 1974-1981 except for the top layer (2001-2006). In South Korea, the period of most-used pesticides was the decade from the middle 1960s until the middle 1970s, which was occupied over 50% to total used pesticides amounts during the past 35 years.[12] The observed trend of ΣOCPs concentration in the sediment core is significantly coincident with that of the amount of pesticides used in South Korea except for the surface segment. The predominant contaminant was DDTs among the OCPs in the all sediment layers. The temporal trend of DDTs concentration in the sediment core is peaked in the early 1970s except for the top layer and decreasing slowly toward surface but abruptly rising again in the top layer which showed maximum value. The observed ratio of (DDE+DDD)/DDTs, which was below the 0.6, in the top sediment layer sufficiently indicated that it has been caused from the recent input of technical DDTs in Gwangyang Bay. Regarding CHLs, the residues in the sediment core were found that it was caused from the past input based on the ratio of trans-nonachlor to trans-chlordane, which was below the 0.5. The distribution of HCB concentration in the sediment core during the past 50 years indicated that its emission source was caused from the combustion rather

than agricultural impurities. On the other hand, the observed results indicated that the total OCPs contaminant of inner-bay site was slightly higher than that of outer-bay site. Although the inner-bay site is densely located in industrial chemical complex, the DDTs concentration in top sediment layer was observed the highest level (0.27 ng g^{-1} dry wt.). The HCHs were the largest amount of used pesticide during the past of South Korea, the residue concentration of HCHs was lower than those of DDTs and CHLs in the sediment samples. In this study, it is noticed that HCB and mirex have been unregistered pesticides, both were detected in the range of ppt level in the all sediment samples using HRGC-HRMS. The increasing concentration of HCB and mirex to the top sediment layer could be thought that it might be reflecting from the neighboring countries because Japan was widely used HCB during the past and China is still producing HCB and mirex. It was sufficiently supported by HCA and PCA results.

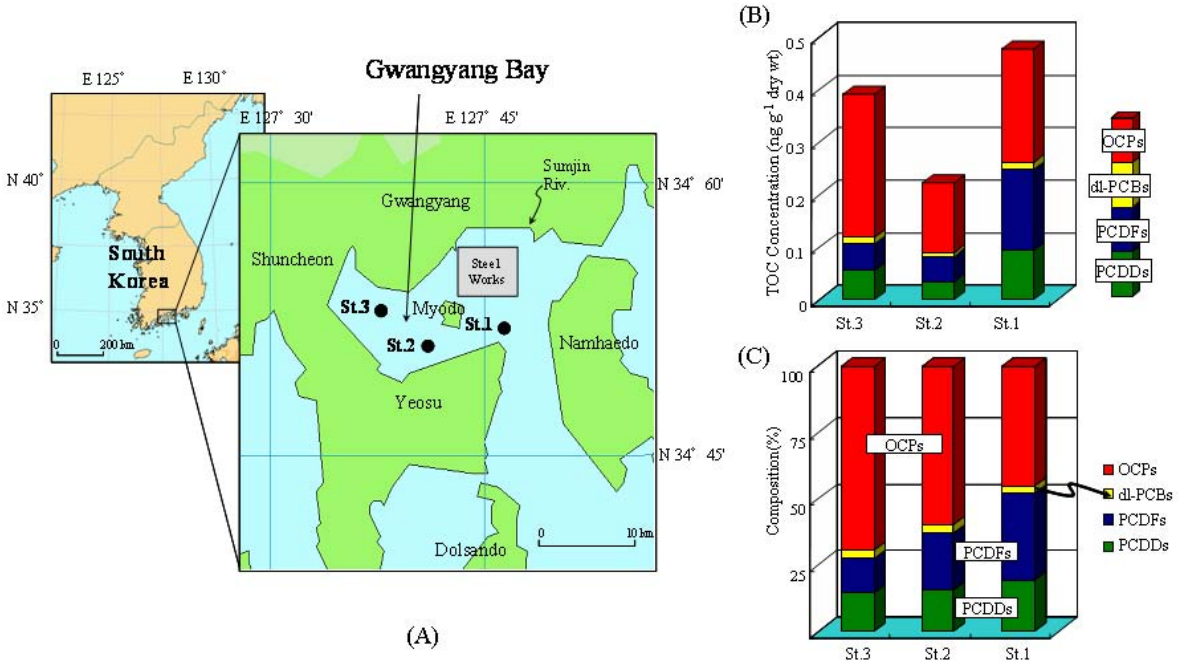

Fig. 1. Sampling locations (A), the surface sediment are collected at St.1 and St.2 site and the sediment core is collected at St.3 site, TOC concentrations (B) and composition (C) of total POPs in the surface sediments

Dioxins (PCDDs/DFs and dioxin-like PCB)

The dynamic distribution of PCDDs/DFs and dioxin-like (dl)-PCBs TOC concentration in the subsurface core reached the maximum value in 1967-1974 and thereafter the concentration decreased until the early 1990s. The concentration ranged from 74 to 120 pg g^{-1} dry wt. When the concentration is compared to other sites, the level in Gwangyang Bay, South Korea is very low.[13,14,15] The pollution source was found to be a mixture of PCP, CNP and combustion based on the variation of congener pattern. It is obviously seen that the surface sediments and subsurface sediment layers (10-40 cm depth) were influenced from atmospheric sources and PCP, respectively. The concentration in surface sediments was revealed to be the highest for ΣPCDDs, follwed by ΣPCDFs and Σdl-PCBs. The ΣPCDFs concentration in the surface sediments was higher than ΣPCDDs and the ratio of ΣPCDDs to ΣPCDFs (D:F ratio) showed less than 1. The most predominant homologue in surface sediment was OctaCDF among PCDDs/DFs congeners. In combustion processes with a chlorine and inorganic carbon source, chlorine constituents are evenly distributed between the two aromatic rings, and furans dominate the profile. For example, the D:F ratios are shown less than 1.[16] The composition profile of PCDDs/DFs in pine needles, which was influenced by a combustion source, is generally characterized by relatively high concentrations of PCDFs.[17] Therefore, the influences of combustion as the sources of pollution in the surface sediment of Gwangyang Bay could be implied. The congener specific composition of dl-PCBs in the sediment core was applied to principal

component analysis (PCA) deeply related to the *Kow* values. The source of dl-PCBs was identified as the KC-500 and the deposition in Gwangyang Bay by the PCA.

Burdens of POPs

The increasing total concentration of OCPs, PCDDs/DFs and dl-PCBs toward the top sediment did not agreed when it was compared to evaluation of the burdens. The results of the burdens calculated are shown in Fig.2. The maximum of the burden for ΣPOPs during 1965-1972 was 2.4 kg which is including 1.1 kg for OCPs (Fig.2a) and 1.3 kg for dioxins (Fig.2b). The PCDDs/DFs derived burdens contributed 86% of the total dioxins' burden during the past 50 years. The highest burden of dioxins in the sediment core which corresponds with the early of 1970s was reflected of the use of PCP, CNP and PCBs at that time in South Korea. Although this study area is the most developed industrial region, the concentration of dioxins in sediment samples of Gwangyang Bay has sufficiently low levels compared with other site in South Korea.

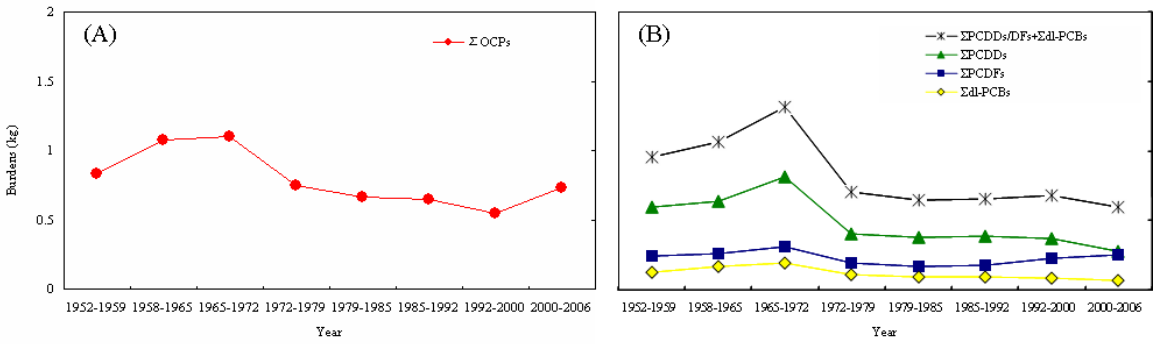

Fig. 2. The vertical distribution of burden for the OCPs (A) and the dioxins (B) during the past 50 years in the sediment core of Gwngyang Bay, South Korea

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