

The characterization of PCDDs, PCDFs and coplanar PCBs during the past 50 years in Gwangyang Bay, South Korea

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Abstract

The PCDD/DFs and coplanar PCBs (co-PCBs) in sediment samples from Gwangyang Bay in South Korea was investigated. The total concentration of dioxins and their toxic equivalent quantity (TEQ; calculated with the WHO 2005 Toxic Equivalency Factors) value in the surface sediment of the outer site (261 pg g⁻¹ TOC, 4.4 pg-TEQ g⁻¹) were 3-fold higher than the inner site (90 pg g⁻¹ TOC, 1.1 pg-TEQ g⁻¹) in the Bay. The dioxin in the sediment samples was found to come from a mixture of the impurities of pentachlorophenol (PCP), chloronitrofen (CNP) and combustion based on the result of hierarchical cluster analysis (HCA). These dioxin sources have been influenced by the characterization associated with this region which was both an agricultural-centered and industrial-centered area. According to principal component analysis (PCA) related to the *K_{ow}* values for the congener-specific composition of co-PCBs in the sediment core, the Kanechlor (KC)-500 and the atmospheric deposition were identified as the possible sources. The maximum burden in the sediment core was 1.3 kg for 1967–1974 and the total burdens of PCDD/DFs and co-PCBs in the sediment core were estimated to be 6.6 kg during the past 50 years. The cumulative burdens of dioxin are still increasing in Gwangyang Bay.

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Keywords: PCDD/DFs; Coplanar PCBs; Sediment core; Burdens; Gwangyang Bay

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (co-PCBs) are endocrine disrupters and persistent in the environment, having long half-lives in air, soil, sediments or biota [1]. Because of their lipophilic nature, they tend to accumulate in higher trophic animals through food chains [2]. Due to the inflow of unpurified sewage and waste water into this semi-enclosed area, which is characteristic along the southern coast in South Korea, and which is also an area of industrial complexes, the sea water flow is not smooth, causing microalgae bloom every year [3]. Gwangyang Bay is located in southern South Korea and has large tidal ranges to 3.4 m. This tidal flat ecosystem is inhabited by several unique benthic organisms, such as

mudskipper fish, crabs, clams, and lugworms [4]. Gwangyang Bay is one of the major industrial areas in South Korea and several industrial complexes are located on the north and south shores of this Bay and has been rapidly industrialized during the past 35 years. 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 [5]. Therefore, the societal concern about the problem caused by dioxins in this area during the past has become high.

Recently, the PCDD/DFs, PCBs and organochlorine pesticides in the Gwangyang Bay sediment had been individually reported for horizontal distribution [5–7]. However, distributions and discussion for the vertical and historical trend of their pollutants have not been reported in Gwangyang Bay. In addition, although there are four contiguous cities, Gwangyang, Shuncheon, Yeosu and Hadong-gun were famous for typical paddy fields for a long time in South Korea, the pollution sources caused from the pesticides has been never reported. These cities have areas of paddy fields of more than approximately

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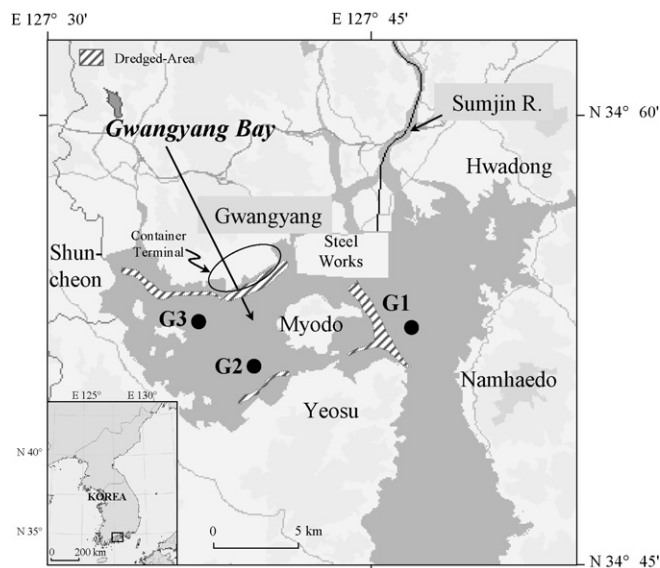


Fig. 1. Sampling locations (G1 and G2: surface sediment. G3: sediment core).

26% in each city [8]. In order to evaluate the environmental pollution situation and to delineate the temporal trends of these contaminants in Gwangyang Bay, South Korea, the concentrations of each kind of the PCDD/DFs and co-PCBs are determined. Furthermore, the inventories and burdens of each kind of compound during the past 50 years are calculated and estimated in this study. Therefore, this study also provides valuable information to understand the behavior of PCDD/DFs and co-PCBs in sediment core from the point of view of environmental historical pollution in Gwangyang Bay, South Korea.

2. Materials and methods

The sampling locations are shown in Fig. 1. Surface sediment samples were collected at 2 stations, G1 (N34°52'040'' and E127°47'000'') and G2 (N34°51'210'' and E127°39'460''), in Gwangyang Bay, South Korea. The site G1 is near the steel works and Sumjin River which has the highest inflow including land-derived suspended sediment in this Bay. The G2 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, G3 (N34°53'250'' and E127°37'240'') on 16 March 2006. The sediment core samples were sliced into 5 cm thick disks up to bottom. All the sediment samples were stored at -20°C until analysis. In order to calculate the sedimentation rate and age in the sediment core, the ^{210}Pb and ^{137}Cs values were used based on the method of our previous study [9]. Total organic carbon (TOC) and total nitrogen (TN) contents in each sample were analyzed after the treatment with diluted HCl (2N) to remove carbonate carbon by using a nitrogen-carbon (NC) analyzer, Sumigraph NC-900. The existence dioxins form in soil and sediments is influenced by differences in characteristics of soil organic mater [10]. Therefore, we used data with TOC normalized concentration in this study. Water content and apparent density in the

sediment core were calculated following previously described methods [11].

All the sediment samples were extracted, fractionated and analyzed following the methods recommended by Kim et al. [12] with modification. Briefly, approximately 10 g of sediment samples were homogenized after air-drying at room temperature and extracted with 300 ml of toluene for 16 h by Soxhlet. The extract was concentrated to 10 ml and a 5 ml (approximately 5 g) aliquot was transferred to hexane. Nineteen $^{13}\text{C}_{12}$ -labeled PCDDs, PCDFs and 12 co-PCBs (Wellington Laboratories Inc., Canada) were spiked as clean-up spikes. The concentrated extracts were eluted with a multilayer silica gel column consisting of Na_2SO_4 (1 g, Kanto Chemical Co., Japan), 2% KOH (3 g, Wako, Japan), 44% H_2SO_4 (10 g, Wako, Japan), 10% AgNO_3 (3 g, Wako, Japan) with silica gel (1 g, Merck, Germany) in each layer. The activated carbon impregnated silica gel column (0.9 g, 8 mm i.d.) was connected with the packed multilayer column. The mono- and di-*ortho* PCBs were separated by eluting with hexane (220 ml, 5 ml min^{-1}) and CH_2Cl_2 /hexane (60 ml of 25%, 2.5 ml min^{-1}) as first fraction. Then the PCDDs, PCDFs and non-*ortho* substituted PCBs in second fraction were eluted using the activated carbon column back-flushed with 100 ml of toluene (2.5 ml min^{-1}). As syringe spikes, $^{13}\text{C}_{12}$ -labeled PCBs IUPAC 70, 111 and 138 were added to first fraction. Similarly, 1,2,3,4,6-PentaCDF and 1,2,3,4,6,8,9-HeptaCDF with above labeled PCB congeners were added to second fractions. The eluates were concentrated to 0.1 ml under a gentle stream of nitrogen gas. All solvents for the analysis of persistent pesticides, PCBs, and dioxins were analytical grade and purchased from Kanto Chemical Co., Japan. All samples were identified and quantified by injecting an aliquot into a high-resolution gas chromatography coupled with a high-resolution mass spectrometric detector (HRGC-HRMS) (Micromass Autospec-Ultima) with a selective ion monitoring (SIM) mode. The SIM mode was constituted by tracing M^+ and $(\text{M}+2)^+$ ions of each compound. For the quantification of target and surrogate standards, the two most abundant ions in the chlorine cluster of the molecular ion were monitored and the HRMS was operated using the same conditions as previously described by Guruge et al. [13]. The method of identification and quantification for the dioxin compounds in sediment samples was previously described elsewhere [12]. The limits of detection (LOD) in all samples ranged from 0.1 pg g^{-1} to 1.0 pg g^{-1} dry weight which was calculated to 3-fold value of the blank value for each dioxin compound. Recovery range for $^{13}\text{C}_{12}$ -labeled PCDDs, PCDFs and co-PCBs in sediment samples were 88–117% (average $99 \pm 9\%$, $n = 10$), 95–112% (average $103 \pm 6\%$, $n = 10$) and 89–104% (average $98 \pm 6\%$, $n = 10$), respectively. Toxic equivalent concentrations were calculated based on the toxic equivalency factors (TEFs) for humans and mammals by the World Health Organization [14]. A procedural blank was run for a set of three samples to check for cross contamination.

The identification of PCDD/DFs and co-PCBs source in the sediment core was done using statistic tools, 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.

Table 1
Concentration of PCDD/DFs and co-PCBs (pg g⁻¹ TOC) in the surface sediments (G1 and G2) and the sediment core (G3) from Gwangyang Bay, South Korea

Site	G1	G2	G3							
Total organic carbon (TOC, %)	1.89	1.94	1.84	1.84	2.03	2.16	2.05	2.1	2.06	2.11
Water content (%)	35.3	46.8	41.5	35.8	36.9	39.6	38.5	38.7	39	42.1
Depth (cm)	Surface (<ca. 5 cm)		0–5	5–10	10–15	15–20	20–25	25–30	30–35	35–40
Corresponding year	NM	NM	2006–2001	2001–1993	1993–1987	1987–1981	1981–1974	1974–1967	1967–1961	1961–1954
PCDDs										
1368-TetraCDD	3.63	1.8	3.68	3.03	3.98	4.46	4.08	5.21	4.14	4.34
1379-TetraCDD	1.6	0.76	1.83	1.01	1.49	2.02	1.85	2.35	1.8	2.14
2378-TetraCDD	0.18	0	0.01	0.11	0.13	0.02	0.04	0.23	0.08	0.04
12378-PentaCDD	0.18	0.13	0.09	0.11	0.12	0.31	0.08	0.11	0.18	0.21
123478-HexaCDD	0.4	0.07	0.21	0.1	0.03	0.14	0.27	0.25	0.05	0.21
123678-HexaCDD	0.41	0.16	0.2	0.34	0.26	0.25	0.36	0.26	0.11	0.24
123789-HexaCDD	1.31	0.44	0.58	0.65	0.33	0.55	0.66	0.81	0.27	0.56
1234678-HeptaCDD	5	2.16	2.23	3.05	2.86	2.42	2.72	4.44	3.19	3.5
OctaCDD	59.56	18.81	29.09	17.61	20.04	22.53	21.69	30.93	25.25	24.55
PCDFs										
1278-TetraCDF	0.26	0.13	0.2	0.22	0.3	0.22	0.27	0.35	0.21	0.19
2378-TetraCDF	0.62	0.12	0.34	0.18	0.11	0.18	0.12	0.09	0.19	0.19
12378-PentaCDF	0.38	0.07	0.22	0.13	0.21	0.33	0.23	0.26	0.28	0.22
23478-PentaCDF	0.75	0.05	2.23	0.23	0.15	0.15	0.13	0.3	0.26	0.15
123478-HexaCDF	0.73	0.17	0.21	0.19	0.3	0.31	0.45	0.44	0.29	0.41
123678-HexaCDF	0.79	0.22	0.46	0.53	0.42	0.2	0.21	0.24	0.28	0.49
123789-HexaCDF	1.48	0.55	0.32	0.09	0.17	0.24	0.16	0.46	0.13	0.23
234678-HexaCDF	4.43	0.47	12.28	2.33	0.23	0.23	0.38	0.37	0.2	0.38
1234678-HeptaCDF	38.64	11.39	6.49	4.15	2.45	3.46	3.29	3.71	2.95	3.36
1234789-HeptaCDF	0	0	0.7	0.52	0	0.25	0.34	0.27	0.16	0.55
OctaCDF	88.15	25.82	15.85	9.46	6.29	5.28	8.91	5.95	5.89	5.28
Total										
TetraCDDs	7.51	4.47	7.78	6.65	7.87	8.38	8.18	10.28	8.3	8.88
PentaCDDs	4.17	1.86	4.39	3.33	3.51	3.08	2.95	3.61	3.16	3.26
HexaCDDs	6.73	3.64	6.26	5.75	4	4.56	5.32	6.64	4.44	3.89
HeptaCDDs	15.71	5.81	9.18	10.91	8.48	7.32	10.22	12.1	10.69	9.94
OctaCDD	59.56	18.81	29.09	17.61	20.04	22.53	21.69	30.93	25.25	24.55
ΣPCDDs	93.68	34.59	56.7	44.24	43.91	45.87	48.36	63.56	51.85	50.51
TetraCDFs	6.9	3.27	4.58	3.93	4.03	3.82	3.69	5.15	3.95	3.82
PentaCDFs	5.88	2.29	6.39	3.03	2.73	2.99	2.57	3.62	3.6	3.44
HexaCDFs	12.49	4.62	15.65	4.96	3.34	2.74	3.73	4.41	3.28	4.78
HeptaCDFs	40.74	12.12	7.8	5.65	3.4	5.46	4.72	5.26	4.01	5.12
OctaCDF	88.15	25.82	15.85	9.46	6.29	5.28	8.91	5.95	5.89	5.28
ΣPCDFs	154.17	48.12	50.28	27.02	19.8	20.3	23.62	24.4	20.73	22.44
Σ(PCDDs + PCDFs)	247.85	82.71	106.99	71.26	63.71	66.16	71.98	87.95	72.58	72.95
Ratio of PCDDs/PCDFs	0.6	0.7	1.1	1.6	2.2	2.3	2	2.6	2.5	2.3
Co-PCBs										
33'44'-TetraCB (#77)	2.01	1.18	1.42	0.91	1	0.95	1.04	1.4	1.67	0.99
344'5-TetraCB (#81)	0.12	0.13	0.2	0.13	0.12	0.16	0.09	0.08	0.06	0.05
33'44'5-PentaCB (#126)	0.44	0.24	0.1	0.13	0.33	0.11	0.15	0.17	0.11	0.14
33'44'55'-HexaCB (#169)	0.05	0.25	0.1	0.14	0.16	0.1	0.12	0.16	0.06	0.11

Table 1 (Continued)

Site	G1	G2	G3	2.03	2.16	2.05	2.1	2.06	2.11
Total organic carbon (TOC, %)	1.89	1.94	1.84	1.84	2.16	2.05	2.1	2.06	2.11
Water content (%)	35.3	46.8	41.5	35.8	39.6	38.5	38.7	39	42.1
Depth (cm)	Surface (<ca. 5 cm)		0–5	5–10	15–20	20–25	25–30	30–35	35–40
Corresponding year	NM	NM	2006–2001	2001–1993	1987–1981	1981–1974	1974–1967	1967–1961	1961–1954
23'344'-PentaCB (#105)	2.05	1.02	2.22	1.87	2.27	2.47	2.8	2.07	1.99
23'44'5'-PentaCB (#114)	0.26	0.12	0.3	0.16	0.18	0.18	0.36	0.23	0.18
23'44'5'-PentaCB (#118)	5	2.59	5.26	4.68	5.01	5.52	6.39	5.99	4.72
2'344'5'-PentaCB (#123)	0.76	0.5	0.74	0.63	0.61	0.92	0.89	0.89	0.67
23'3445'-HexaCB (#156)	0.81	0.35	0.71	0.48	0.65	0.62	0.81	0.73	0.71
23'3445'-HexaCB (#157)	0.23	0.08	0.24	0.27	0.11	0.19	0.22	0.22	0.11
23'44'55'-HexaCB (#167)	1.33	0.54	1.14	1.08	1.18	1.41	1.47	1.39	1.19
23'34455'-HeptaCB (#189)	0.29	0.12	0.31	0.07	0.13	0.11	0.22	0.16	0.2
22'33'44'5'-HeptaCB (#170)	3.94	1.56	2.76	1.52	2.65	3.27	2.65	2.37	2.63
22'34455'-HeptaCB (#180)	7	2.76	4.99	3.13	5.38	5.9	6.46	5.45	4.66
ΣNon-ortho PCBs	2.62	1.81	1.82	1.31	1.31	1.4	1.81	1.89	1.3
ΣMono-ortho PCBs	10.72	5.33	10.91	9.25	10.13	11.41	13.17	11.69	9.77
ΣDi-ortho PCBs	10.94	4.32	7.75	8.85	8.03	9.18	9.11	7.82	7.29
ΣCoplanarPCBs	24.29	11.46	20.49	15.21	19.48	21.99	24.09	21.4	18.36
Σ(PCDDs + PCDFs + Co-PCBs)	272.14	94.18	127.47	86.47	85.65	93.96	112.04	93.98	91.31

NM: not measured.

3. Results and discussion

3.1. Characteristic PCDD/DFs

Total organic carbon (TOC) showed a variation from 1.84% to 2.16% in the sediment samples. The detected congeners of tetra- to octachlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and coplanar PCBs (co-PCBs) as normalized by TOC concentration in the surface sediments and the sediment core are summarized in Table 1. The sum of TOC normalized concentrations of PCDD/DFs in the surface sediments of G1 (248 pg g⁻¹ TOC) was approximately 3-fold higher than that of G2 (83 pg g⁻¹ TOC). The G1 site is located between the mouth of the Sumjin River and the entrance to the open sea. The Sumjin River has the highest flow (23 m³ s⁻¹) in this Bay. When it was compared to the actual concentration in sediment (without TOC normalization) previously reported for other sites, the concentrations of ΣPCDD/DFs in surface sediments of Gwangyang Bay were 4–10-folds lower than those of Sendai Bay, Japan [15] and Queensland, Australia [16]. Although this area is one of the most industrialized regions in South Korea, the contaminant levels of PCDD/DFs measured in this study are lower than that of the other sites, Ulsan Bay, Busan coast, Pohang coast and Jinhe Bay in South Korea [6].

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 or closer (Table 1). The most predominant homologue in surface sediments was OctaCDF among PCDD/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 [17]. The composition profile of PCDD/DFs in pine needles, which was influenced by a combustion source, is generally characterized by relatively high concentrations of PCDFs [18,19]. Therefore, the influences of combustion as the sources of pollution in the surface sediment of Gwangyang Bay could be implied.

The container terminal is located in the northern part, which is nearby the sampling location and the area around here has been dredged for shipping. The sedimentation rate in sediment core (G3) was estimated to be 1.3 cm per year by the ²¹⁰Pb. The dynamic distribution of PCDD/DFs and co-PCBs (TOC normalized) in the subsurface core reached the maximum value in 1967–1974 and thereafter the concentration decreased until the early 1990s (Table 1). The concentration ranged from 74 pg g⁻¹ to 120 pg g⁻¹ TOC. When the concentration is compared to other sites, the level in Gwangyang Bay, South Korea is very low [16,20,21]. Profiles of the concentration and composition of PCDDs and PCDFs congeners in all sediment layers were predominated by higher chlorinated PCDDs, in particular OctaCDD and HeptaCDDs, followed by TetraCDDs (Table 1 and Fig. 2) which contributed more than an average 31%, 13% and 11% to the total PCDD/DFs concentration, respectively. In the 1970s and 1980s, the most abundant OctaCDD in the sediment core could be assumed to have been attributed to the impurity of the herbicide, pentachlorophenol

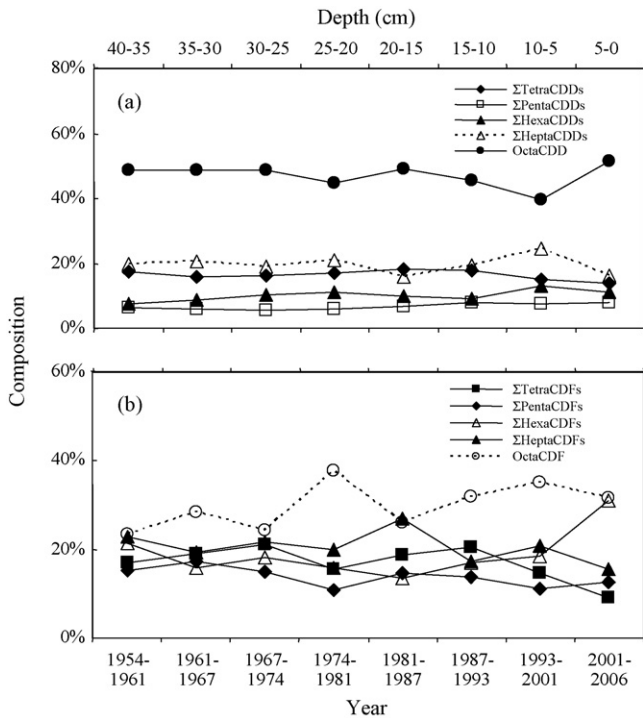


Fig. 2. Composition profiles of PCDDs (a) and PCDFs (b) homologues group in the sediment core (G3) from Gwangyang Bay.

(PCP). The PCP consumption in South Korea was most abundant in the early 1970s [22] (Fig. 3). Homologue profiles of PCP samples revealed that the most abundant impurity of dioxin was OctaCDD [23]. The characteristic isomer among each PCDD/DFs homologue in the estimated past 50 years of Gwangyang Bay is shown as follows: 1,3,6,8- and 1,3,7,9-TetraCDD; 2,4,6,8/1,2,3,8/1,4,6,7/1,2,3,6-TetraCDF;

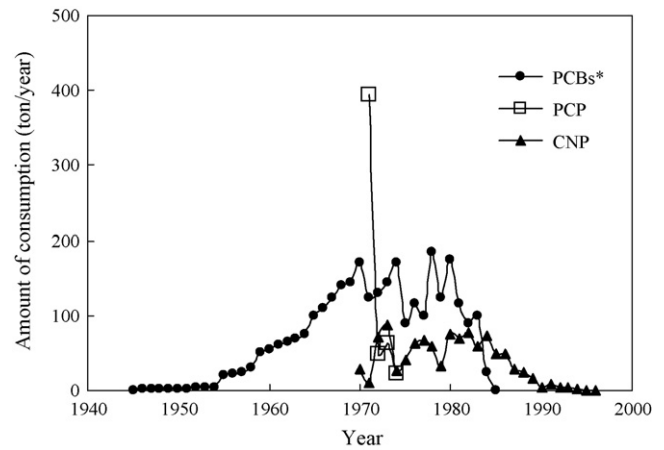


Fig. 3. The annual consumption amount of polychlorinated biphenyl (PCB), pentachlorophenol (PCP) and chloronitrofen (CNP) in South Korea. The data of PCP and CNP amount were cited from the Agrochemicals Year Book [22], South Korea. (*) The amount of PCBs was estimated by considering characterizations in South Korea through their emissions, economic level and the time of prohibited use in the world [31]. The minimum value of PCBs amount, which was estimated by Shin et al., [31] is available in this study.

1,2,4,6,8/1,2,4,7,9-, 1,2,3,6,8- and 1,2,3,7,9-PentaCDD; 1,2,4,6,8-, 1,2,3,6,8/1,3,4,7,8- and 2,3,4,6,8-PentaCDF; 1,2,3,4,6,8/1,2,4,6,7,9/1,2,4,6,8,9- and 1,2,3,6,7,9/1,2,3,6,8,9-HexaCDD; 1,2,3,4,6,8-, 1,2,4,6,7,8-, 1,2,3,4,7,8/1,2,3,4,7,9- and 2,3,4,6,7,8-HexaCDF; 1,2,3,4,6,7,8-HeptaCDF; OctaCDD; OctaCDF. In general, these predominant isomers were well known as the pollution sources, such as impurities of PCP, chloronitrofen (CNP) and combustion. This assumption also could be supported by the fact that the principal component analysis (PCA) of the congener-specific data of dioxins with respect to the herbicides PCP and CNP in Japan has been frequently

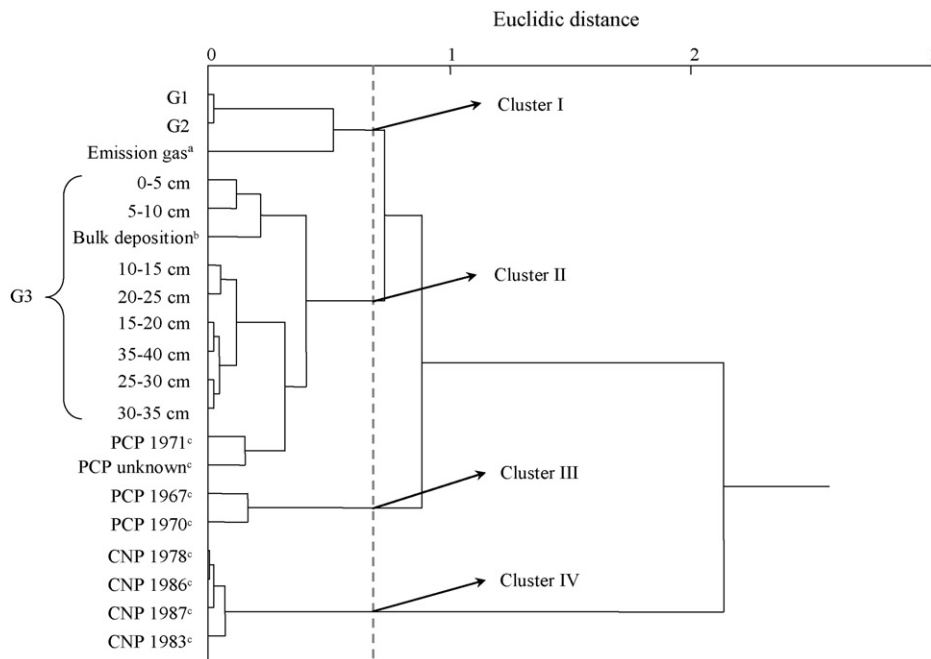


Fig. 4. Dendrogram of hierarchical cluster analysis for PCDD/DFs in Gwangyang Bay with emission gas, bulk deposition, annual technical PCP and CNP. (a) The data is quoted from Hiura et al. [28]; (b) the data are referred from Sakai et al. [29]; (c) the data are referred from Masunaga et al. [24].

reported by Masunaga et al. [24–27]. Furthermore, since the *D:F* ratio in PCP profiles ranges from 1 to 10 [16], their pattern of PCDD/DFs in Gwangyang Bay had been reflecting PCP as one of the sources. The characteristic congeners caused from impurities of CNP include some homologues, the TetraCDD, PentaCDD and TetraCDF [20]. Thus, the sediment core which has a relatively high composition of these congeners from the 1970s and 1980s could be explained by the presence of CNP pollution in Gwangyang Bay. The CNP consumption was also prevalent during the 1970s and 1980s in South Korea (Fig. 3). In addition, the predominant isomer, 2,3,4,6,7,8-HexaCDF, which is well known as a dominated isomer in combustion pattern [20,25,26] in the upper layers (0–10 cm), is caused from the combustion source origin. Therefore, according to these interpretations, interesting results show that Gwangyang Bay was exposed to a mixture of pollution sources, PCP, CNP and combustion source. This assumption could be supported by hierarchical cluster analysis (HCA) result which could be clustered by similarity of their characterization of PCP, CNP and atmospheric sources (Fig. 4). The cluster dendrogram shows the results from dioxins' composition data in sediment samples of Gwangyang Bay with related data of emission gas [28], atmospheric bulk deposition [29] and technical products of PCP and CNP [24] (Fig. 4). The dioxins data in sediment samples of Gwangyang Bay could be classified into four major groups based on the HCA. The surface sediments, G1 and G2 are clearly divided into the emission gas for the first group (Cluster I). The relative surface sediments ranging from top to 10 cm depth in the sediment core also could be divided into the bulk deposition. The rest layers (10–40 cm depth) are most closed to technical PCP products (Cluster II). Some PCP products are grouped as a Cluster III. The Cluster III, which is a group of technical PCP products, is taking to the Clusters I and II. Those three clusters were weakly reflected by Cluster IV which was consistence of technical CNP products. These results suggest that the major source of dioxin in the surface sediments and subsurface sediments is from atmospheric deposition and PCP applications, respectively.

3.2. Source identification of coplanar PCBs in the sediment core

The concentration of co-PCBs in the surface sediments of G1 was approximately 2-fold higher than that of G2, similar to the trend of PCDD/DFs (Table 1). When compared with the concentration in surface sediments of PCBs, which was previously determined by Hong et al. [5] in this Bay (0.22–2.9 ng g⁻¹ dry weight) and other industrialized regions in South Korea (10.3–148 ng g⁻¹ dry weight) [30], the level was the lowest. The estimated PCBs production by Shin et al. [31] in South Korea started in the late 1950s and reached a peak in the 1970s, but PCB was only banned for use in electronic products in 1979 (Fig. 3). The observed temporal trend of co-PCBs concentration in a sediment core (G3) in this Bay coincided with the estimated amount from use and production of PCBs in South Korea.

The composition of PCB IUPAC 118 presented the most dominant congener in all detectable samples and then followed by

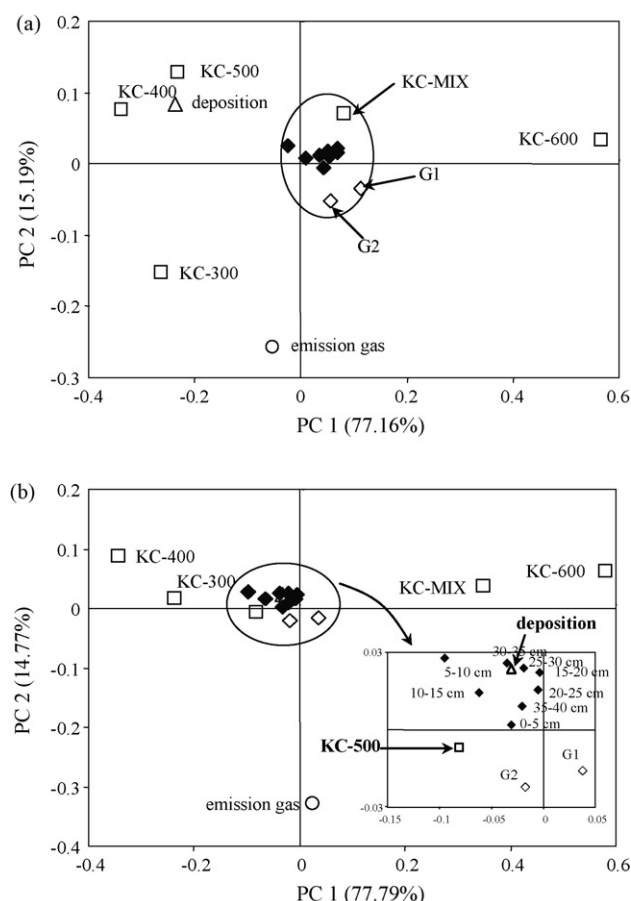


Fig. 5. Principal component analysis (PCA) score plot (a) of the co-PCBs congener pattern in samples from Gwangyang Bay, PCB products and emission sources. The identification of co-PCBs in the sediment core is calculated based on the K_{ow} value of each congener (b). The filled lozenges (◆) denote samples of the sediment core (G3) and open lozenges denote the surface sediment, G1 and G2. The abbreviation, KC, is the Kanechlor. The data used regarding emission gas and atmospheric deposition data referred to previously reported data [29].

PCB IUPAC 180, 170, 105, 167 and 77. The contributions of PCB IUPAC 118, 180, 170, 105, 167 and 77 to the Σ co-PCBs concentration in the sediment core (G3) accounted for about 27%, 25%, 12%, 11%, 6.2% and 6.0%, respectively. These isomers were the major components of the PCB products such as some kinds of Kanechlor (KC) or Aroclor (Ar) [32]. These commercial PCBs were widely used to industrial and agricultural applications in South Korea and Japan [31,32]. The compositional pattern for PCB congeners in pine needles in Tokyo, Japan [19] was similar to our result in the sediment core. It could be assumed that the PCB concentration in Gwangyang Bay might have originated from an atmospheric source from its deposition after being used in the environment. Moreover, in order to identify possible sources, the PCA was applied to the composition of samples normalized to concentration of Σ co-PCBs (Fig. 5). The value of the five commercial PCBs products, KC-300, 400, 500, 600 and mixture [32] was coplotted with the emission gas and atmospheric depositions [29] to the sediment samples. There are two major PCs (principal component) with proportions of approximately 77% for PC1 and 15% for PC2. Therefore, most of the data variation in this PCA could be explained by PC1. The

characteristic congeners in PC1 were PCB IUPAC 180, 170, 123 and 189 for positive congeners and PCB IUPAC 118 and 105 for negative congeners. This means that the plot follows the compositional difference of low and high chlorinated compounds within samples. Both PCB IUPAC 180 and 170 were obviously included in hexa- to octa-chlorinated PCBs, such as KC-600 product (including 42% for hexaCBs, 39% for heptaCBs and 7% for octaCBs) of PCBs and the PCB IUPAC 118 and 105 were included in KC-300 (5% for pentaCBs), 400 (28% for pentaCBs) and 500 (52% for pentaCBs) [32]. Based on these comparisons, PC1 was interpreted to be an industrial PCB product. In the case of PC2, the characteristic congeners appeared the PCB IUPAC 118, 105 and 167 for positive and 81, 126, 169 and 189 for negative. According to the emission and deposition patterns of PCBs [29], the deposition of PCB congeners 81, 126, 169 and 189 was found in amounts similar to those released via the waste-incinerated emissions but deposited congeners, 105, 114 and 118 greatly exceeded that. It is found that PC2 significantly corresponds to the combustion process as the main factor. Therefore, the PCA results indicated that all of the sediment samples are similar in composition to the KC mixture (KC-MIX) without the PCBs K_{ow} calculation (Fig. 5a). However, it should be considered that high chlorinated PCBs with relatively high K_{ow} values are more stable than low chlorinated PCBs in sediment by adsorbing to suspended particles [6,33]. Moreover, the K_{ow} value of PCB congeners was significantly related to biota-sediment accumulation factors (BSAFs) and the high chlorinate PCB congeners were likely to retain in sediments [34,35]. Therefore, the calculated data of PCBs K_{ow} in the sediment samples, KC products and emission gas was used in this study (Fig. 5b). The source of PCBs congeners, which was estimated by each PCBs K_{ow} value [36], was identified to be the KC-500 among the KC-products and the atmospheric deposition in Gwangyang Bay, South Korea (Fig. 5b). Based on these results, source information of PCBs can be obtained and observed about the source identification of PCBs in the sediment core.

3.3. TEQs, inventories and burdens

The 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TetraCDD) toxic equivalent quantity (TEQ- pg g^{-1}) was estimated by WHO 2005 TEFs (toxic equivalency factors) [14] for dioxin and co-PCBs (Table 2). The G1, which is located near the mouth of the Sumjin River, was found to be 4.42 pg-TEQ g^{-1} in the surface

sediment. The concentration of total toxic dioxins in G2 was approximately 4-fold ($1.12 \text{ pg-TEQ g}^{-1}$) lower than those of G1. This strongly implied that the pollution source of dioxins might be emitted from nearby G1 in the northern part of Gwangyang Bay. The contribution of PCDFs in the surface sediments was obviously higher than that of PCDDs and PCBs. The PCDD/DFs contributed more than 95% of the ΣTEQ (PCDD/DFs and PCBs) in all detectable sediment core layers. The obtained TEQs value was lower than that of the other sites among the industrial regions in South Korea [6].

Inventories, which represent the total integrated amount of the contaminants, can be used as a tool to understand a suitable insight for further behavior of the compounds per unit area [37,38]. The inventories of dioxins (PCDD/DFs and co-PCBs) (I_{DXNs}) in the sediment core of Gwangyang Bay were estimated using the applied equation which was previously reported [38,39].

$$I_{\text{DXNs}} = \sum_{i=1}^n (1 - W_i) C_i D_i T_i$$

where W_i is the water content in i sediment layer. C_i , D_i and T_i are the concentration (pg g^{-1}), the apparent density (g cm^{-3}) and the thickness (cm) of the i sediment layer, respectively.

The results of the inventories are summarized in Table 3. In the surface sediments, the total inventory of G1 was 3–4-fold higher than other sites in Gwangyang Bay, probably due to the migration of sediment to this site from the Sumjin River. Using the inventory values, the load of the dioxins in sediment core of Gwangyang Bay was estimated on the basis of surface areas at various depths. Since Gwangyang Bay is one region among the representative developed industrial areas in South Korea during the past 30 years, there has been changing of the costal line by reclamation for industrialization. The burdens of dioxins were calculated using a water surface area of 99.75 km^2 for 0–5 cm depth, 131.37 km^2 for 5–25 cm depth and 200 km^2 for rest of the layers, respectively [8]. The burdens of total dioxins (PCDD/DFs and co-PCBs) in the sediment core were 6.6 kg in which was included 3.9 kg for PCDDs, 1.8 kg for PCDFs and 0.92 kg for co-PCBs. The dioxin burdens in the sediment core are expressed in weight (Fig. 6). The PCDD/DFs derived burdens contributed 86% of the total burden during the past 50 years, indicating that PCDD/DFs may have been extensively contaminated since the middle 1950s. The maximum value of the total dioxins burden

Table 2
TEQ concentration (pg g^{-1} TOC) of PCDD/DFs and co-PCBs in the surface sediments (G1 and G2) and the sediment core (G3) from Gwangyang Bay, South Korea

Site	G1 G2		G3						
	Surface (ca. 5 cm)		0–5	5–10	10–15	15–20	20–25	25–30	30–35
Corresponding year	NM	NM	2006–2001	2001–1993	1993–1987	1987–1981	1981–1974	1974–1967	1967–1961
TEQ (PCDDs)	1.19	0.41	0.42	0.66	0.69	0.97	0.56	1.09	0.68
TEQ (PCDFs)	3.02	0.58	4.72	0.93	0.47	0.53	0.51	0.76	0.59
TEQ (PCDDs + PCDFs)	4.21	0.99	5.14	1.59	1.16	1.5	1.07	1.85	1.27
TEQ (Co-PCBs)	0.09	0.05	0.02	0.03	0.07	0.03	0.04	0.04	0.03
TEQ (PCDDs + PCDFs) + TEQ (Co-PCBs)	4.3	1.04	5.16	1.62	1.24	1.53	1.11	1.89	1.3

NM: not measured.

Table 3
Density (g cm^{-3}) and inventories (ng cm^{-2}) of PCDD/DFs and co-PCBs in the sediment core from Gwangyang Bay (G3), South Korea

Depth (cm)	Corresponding year	Density (g cm^{-3})	Inventories (ng cm^{-2})													
			TetraCD Ds	PentaCD Ds	HexaCD Ds	HeptaCD Ds	OctaCD D	Σ PCDDs	TetraCD Fs	PentaCD Fs	HexaCD Fs	HeptaCD Fs	OctaCD F	Σ PCDFs	Σ Co-PCBs	Σ PCDDs + PCDFs + Co-PCBs
0–5	2006–2001	0.92	0.04	0.02	0.03	0.05	0.14	0.28	0.02	0.03	0.08	0.04	0.08	0.25	0.06	0.59
5–10	2001–1993	1.07	0.04	0.02	0.04	0.07	0.11	0.28	0.02	0.02	0.03	0.04	0.06	0.17	0.07	0.52
10–15	1993–1987	1.04	0.05	0.02	0.03	0.06	0.13	0.29	0.03	0.02	0.02	0.02	0.04	0.13	0.07	0.49
15–20	1987–1981	0.97	0.05	0.02	0.03	0.05	0.14	0.29	0.02	0.02	0.02	0.03	0.03	0.13	0.07	0.49
20–25	1981–1974	1	0.05	0.02	0.03	0.06	0.14	0.3	0.02	0.02	0.02	0.03	0.06	0.15	0.08	0.53
25–30	1974–1967	0.99	0.07	0.02	0.04	0.08	0.2	0.4	0.03	0.02	0.03	0.03	0.04	0.16	0.1	0.66
30–35	1967–1961	0.98	0.05	0.02	0.03	0.07	0.16	0.32	0.02	0.02	0.02	0.02	0.04	0.13	0.08	0.53
35–10	1961–1954	0.91	0.05	0.02	0.02	0.05	0.16	0.3	0.02	0.02	0.03	0.03	0.12	0.06	0.48	
Total	1954–2006	–	0.4	0.16	0.25	0.48	1.18	2.47	0.2	0.17	0.25	0.25	1.23	0.59	4.29	

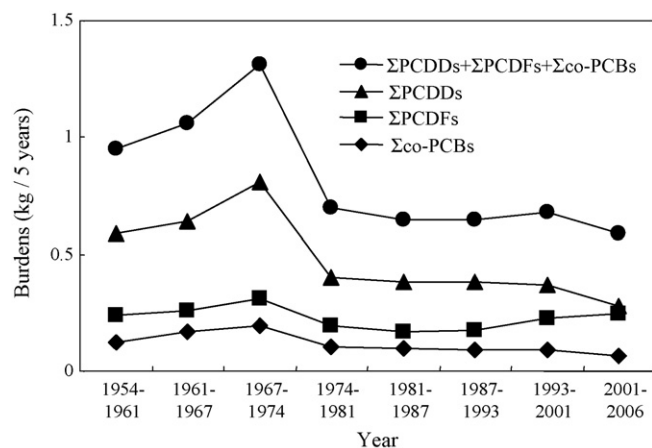


Fig. 6. The burdens of PCDD/DFs and co-PCBs in sediment core (G3) during the past 50 years in Gwangyang Bay, South Korea.

was 1.3 kg in 1967–1974 and decreasing toward present (Fig. 6). The inventories and burdens of PCBs in the sediment core of Gwangyang Bay were at least three order of magnitude lower than the Lower St. Lawrence Estuary, Canada [39]. Increasing trends of dioxins cumulative burdens are still observed and could foretell an accumulation in the sediment. In addition, half-life times for 2,3,7,8-substituted PCDD/DFs and some PCBs in sediment were calculated in the range of 274 years for PCDDs, 80 years for PCDFs and 38 years for some PCBs [40].

4. Conclusions

The observed results in the sediment core during the past 50 years in Gwangyang Bay, South Korea show evidence of PCDD/DFs and co-PCBs sources. 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 congener-specific composition of co-PCBs in the sediment core was applied to principal component analysis (PCA) significantly related to the K_{ow} values. The source of co-PCBs was identified as the KC-500 and the deposition in Gwangyang Bay by the PCA. The increasing total concentration of PCDD/DFs and co-PCBs toward the surface sediment did not agree when it was compared to evaluation of the burdens. The PCDD/DFs derived burdens contributed 86% of the total 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 sites in South Korea.

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