Master's Thesis

DISTRIBUTION OF PCDD/FS, PCBS, AND PCNS IN COASTAL SEDIMENTS COLLECTED FROM MAJOR INDUSTRIAL BAYS IN SOUTH KOREA

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Department of Urban and Environmental Engineering
(Environmental Science and Engineering)

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Abstract

Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs) are persistent organic pollutants (POPs), and they are unintentionally emitted into the environment from incomplete combustion or thermal processes. Since the 1980s, productions and uses of technical mixture of PCBs and PCNs have been very popular such as transformer, insulators, paints, plasticizers, and capacitors. In particular, marine sediments are considered as the final sink of POPs. Those toxic compounds may enter the marine organisms and be accumulated in the human body through the food chain. So far, various researches on PCDD/Fs and PCBs in the sediments have been carried out in Korea; however, there have been only a few studies on PCNs in the sediments. Therefore, the aims of this study were to investigate the levels, patterns, spatial distributions, and to identify the major sources of PCDD/Fs, PCBs, and PCNs in bays located within or near the industrial areas in South Korea.

In this study, the sediment samples were collected in Gwangyang, Jinhae, Busan, and Ulsan bays in March and April 2016. There were 16 sampling sites in the Gwangyang Bay (GY1-16), 20 sites in Jinhae Bay (JH1-20), 18 sites in the Busan Bay (BS1-18), and 15 sites in the Ulsan Bay (US1-15). The target compounds were 17 PCDD/Fs, 18 PCBs (dl-PCBs and indicator PCBs), and 15 PCNs (75 PCNs for 14 sediment samples). The sediment samples were extracted using accelerated solvent extraction system (ASE), and the extracts were purified by multilayer silica gel and alumina columns. PCDD/Fs, PCBs, and PCNs were analyzed using gas chromatography/high resolution mass spectrometry (GC/HRMS).

The concentrations of PCDD/Fs, PCBs, PCNs in sediments ranged from 0.18 pg TEQ/g to 19.80 pg TEQ/g. The highest TEQ concentration was observed near the wastewater treatment plant in Jinhae Bay, which seemed to be due to the effluent discharge. The concentrations in this study were comparable or lower than those of other countries, and the levels of PCDD/Fs and PCBs were lower than those of the previous studies in Korea. The correlation analysis between TOC contents and concentrations of PCDD/Fs (R^2=0.67, $p<0.01$), PCBs (R^2=0.44, $p<0.01$), and PCNs (R^2=0.45, $p<0.01$) indicated positive correlations. Generally, the concentrations in the inner part were higher than those in the outer part, which is due to the industrial complexes. Therefore, the concentrations of PCDD/Fs, PCBs, PCNs might be influenced by various industries.

The concentrations of PCDD/Fs and PCBs have decreased compared with those obtained from the previous studies in Korea. However, this study has been the first comprehensive study for PCNs with high resolution monitoring in industrial bays. On the basis of this study, it could be possible to understand the spatial distributions and major sources of PCDD/Fs, PCBs, and PCNs in industrial bays.

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I. INTRODUCTION

1.1 Introduction of PCDD/Fs, PCBs, and PCNs

1.1.1 Properties of PCDD/Fs, PCBs, and PCNs

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have planar aromatic structures with one to eight chlorine substitution at different positions on benzene rings (Figure 1). There are 75 congeners for PCDDs and 135 congeners for PCDFs. Polychlorinated biphenyls (PCBs) have two benzene rings, and they can be substituted with one to ten chlorine atoms (Figure 1). There are 209 PCB congeners depending on the position and the number of chlorine atoms. In addition, there are coplanar PCBs similar to the PCDD/F structures, and these congeners are called dioxin-like PCBs. Polychlorinated naphthalenes (PCNs) have 75 species, with one and eight chlorine substituents at different positions on naphthalene rings. They have planar structures which are similar to those of PCDD/Fs and PCBs. Similar to the PCBs, there are dioxin-like PCNs. The structure of PCNs is shown in Figure 1.

These three groups of compounds are regulated as persistent organic pollutants (POPs) by the Stockholm Convention because of their properties such as persistence, toxicity, multimedia fate, bioaccumulation, and a long range transport (Oh et al., 2006). Furthermore, PCDD/Fs, PCBs, and PCNs are highly accumulated in the organic fraction of lipids, suspended particles, and sediments (Hong et al., 2005) due to high octanol/water partition coefficient (K_{ow}) values.

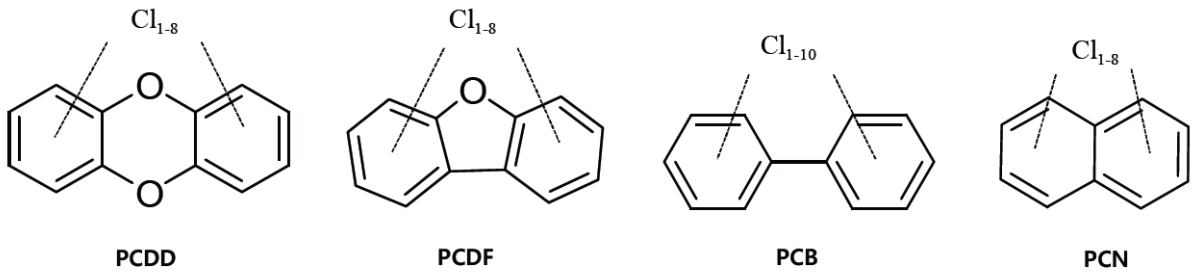


Figure 1. The structures of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs)

Table 1. Physical and chemical properties of PCDD/Fs, PCBs, and PCNs.

Homologue	Molecular formula	Molecular weight (g/mol)	Melting point(℃)	Boiling point (℃)	Log K_{ow}
PCDD/Fs					
Mono-CDD	$C_{12}H_7O_2Cl$	219	89-106	316	4.8-5.0
Di-CDD	$C_{12}H_6O_2Cl_2$	253	151-210	358-374	5.6-5.8
Tri-CDD	$C_{12}H_5O_2Cl_3$	288	129	375	6.0
Tetra-CDD	$C_{12}H_4O_2Cl_4$	322	172-305	419-447	6.6-7.1
Penta-CDD	$C_{12}H_3O_2Cl_5$	356	195	465	7.0
Hexa-CDD	$C_{12}H_2O_2Cl_6$	391	273	488	8.0
Hepta-CDD	$C_{12}HO_2Cl_7$	425	265	507	8.0
Octa-CDD	$C_{12}O_2Cl_8$	460	322	510	8.0
Mono-CDF	$C_{12}H_7OCl$	203	NA	NA	NA
Di-CDF	$C_{12}H_6OCl_2$	237	184	375	5.4
Tri-CDF	$C_{12}H_5OCl_3$	272	NA	NA	NA
Tetra-CDF	$C_{12}H_4OCl_4$	306	227	438	6.1
Penta-CDF	$C_{12}H_3OCl_5$	340	196	465	6.5
Hexa-CDF	$C_{12}H_2OCl_6$	375	226-232	488	7.0
Hepta-CDF	$C_{12}HOCl_7$	409	221-236	507	7.4
Octa-CDF	$C_{12}OCl_8$	444	258	537	8.0
PCBs					
Mono-CB	$C_{12}H_9Cl$	188	25-77.9	285	4.7
Di-CB	$C_{12}H_8Cl_2$	122	24.4-149	312	5.1
Tri-CB	$C_{12}H_7Cl_3$	256	28-87	337	5.5
Tetra-CB	$C_{12}H_6Cl_4$	289.9	47-180	360	5.9
Penta-CB	$C_{12}H_5Cl_5$	323.9	76.5-124	381	6.3
Hexa-CB	$C_{12}H_4Cl_6$	357.8	77-150	400	6.7
Hepta-CB	$C_{12}H_3Cl_7$	391.8	122.4-149	417	7.1
Octa-CB	$C_{12}H_2Cl_8$	425.8	159-162	432	7.5
Nona-CB	$C_{12}HCl_9$	459.7	159-162	445	7.9
Deca-CB	$C_{12}Cl_{10}$	493.7	182.8-206	456	8.3
PCNs					
Mono-CN	$C_{10}H_7Cl$	162.5	2.3-60	259-260	4.3-4.6
Di-CN	$C_{10}H_6Cl_2$	197	37-138	285-298	4.9-5.3
Tri-CN	$C_{10}H_5Cl_3$	231.5	68-133	274	5.5-5.9
Tetra-CN	$C_{10}H_4Cl_4$	266	111-198	NA	5.6-6.5
Penta-CN	$C_{10}H_3Cl_5$	300.4	147-171	313	6.2-6.5
Hexa-CN	$C_{10}H_2Cl_6$	335	194	331	6.7-7.3
Hepta-CN	$C_{10}H_1Cl_7$	369.4	197	348	6.7-7.0
Octa-CN	$C_{10}Cl_8$	404	198	365	7.1

1.1.2 Sources of PCDD/Fs, PCBs, and PCNs

PCDD/Fs, PCBs, and PCNs can be unintentionally produced from combustion and thermal processes from industrial complexes (e.g., incineration, steel manufacturing facilities, non-ferrous industries, and chemical production) (Breivik et al., 2004; Choi et al., 2008a; Fiedler, 1996) (Figure 2). PCDD/Fs were produced as by-products from pesticides such as Pentachlorophenol (PCP) and Chloronitrofen (CNP) (Masunaga et al., 2001). PCBs and PCNs were intentionally produced as technical mixture such as Aroclor, Kanechlor, halowaxes, and Nibren until the 1980s (Breivik et al., 2002; Falandysz, 1998; Kodavanti et al., 2008). Technical mixtures of PCBs were not produced in Korea but were imported (Kim et al., 2007), and used in transformers, paints, plasticizers, capacitors, hydraulic fluids, and polyvinyl acetates (Figure 2). The technical mixtures of PCNs were used in cable electroplating masking compounds, insulation, wood preservatives, and dye carriers (Falandysz, 1998), however, PCN commercial mixtures were not either produced or imported to Korea (Park et al., 2010). On the other hand, small amounts of PCNs can be released as by-products from technical PCBs mixtures (Haglund et al., 1993; Yamashita et al., 2000). Although the production and use of technical mixtures of PCBs and PCNs were banned, they can still be released from the leakage of containing products, disposal of products, and combustion.

Figure 2. Major sources of PCDD/Fs, PCBs, and PCNs.

When they are emitted from the atmosphere caused by combustion or thermal processes from industrial complexes or technical mixtures, most of them are deposited from the air into soil, plants, and surface water (Choi et al., 2008b) (Figure 3). When they enter the aquatic ecosystem, they are deposited in sediments, that are the most important environmental sinks, due to high lipophilicity properties (Moser and McLachlan, 1999; Wang et al., 2009). Monitoring of PCDD/Fs, PCBs, and PCNs in sediments can provide the information on old and recent pollution sources of the marine environment because sediments tend to be accumulated continuously. Besides, sediments are important pathways of absorption of marine organisms, PCDD/Fs, PCBs, and PCNs are finally entering into the human body through the food chain (Choi et al., 2008b). This process requires assessing and managing the quality of sediments in order to protect the aquatic ecosystem.

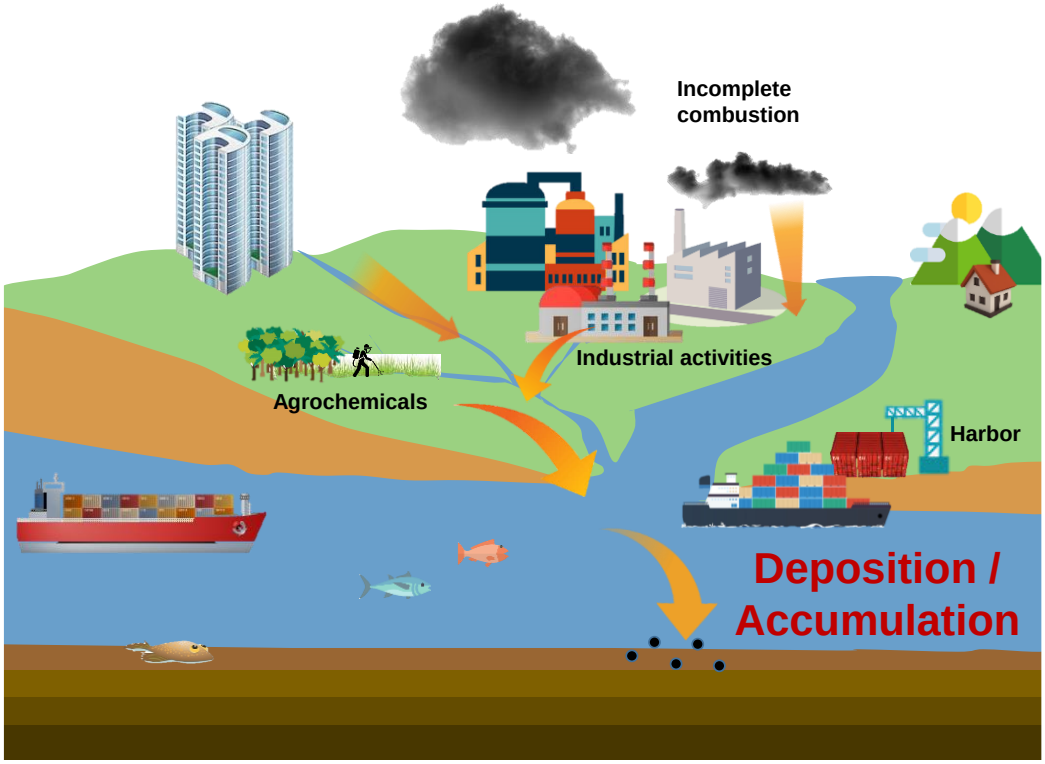


Figure 3. Routes of PCDD/Fs, PCBs, and PCNs into the marine environment.

1.1.3 Toxic equivalency of PCDD/Fs, PCBs, and PCNs

PCDD/Fs, PCBs, and PCNs have acute and chronic toxicity, such as carcinogenicity, immunotoxicity, teratogenicity, and reproductive effects (Fernandes et al., 2010; Safe, 1993). Besides, the toxicity of PCDD/Fs is closely related to their structures, the numbers of chlorine, and the positions of the substituted chlorine atoms. In particular, chlorine substitution at 2,3,7,8-position is highly toxic. Among the PCDD/Fs, 2,3,7,8-TCDD is the most toxic congener. According to the calculation of toxic equivalency (TEQ) by world health organization (WHO) in 1998 and 2005, 2,3,7,8-PCDD/F congeners and coplanar PCB congeners have toxic equivalency factor (TEF) values as shown on Table 2. However, PCNs do not have TEF values suggested by WHO, previous studies suggested relative potency factors (RPFs) (Table 2) (Noma et al., 2004), similar to the TEF values.

Individual TEQ was calculated using the following equation. Regarding to the TEQ concentrations of PCNs, RPF values were used instead of TEF values.

$$TEQ = \sum (C_i \times TEF_i), \quad (1)$$

where C_i: the concentrations of congener *i;*
TEF_i: the TEF value of congener *i.*

Table 2. Toxic equivalency factors (TEFs) of PCDD/Fs and PCBs, and relative potency factors (RPFs) of PCNs.

PCDD/Fs	WHO 1998 TEF	WHO 2005 TEF	PCBs	WHO 1998 TEF	WHO 2005 TEF	PCNs	RPF
2,3,7,8-TCDD	1	1	PCB 77	0.0001	0.0001	PCN 63	0.002
1,2,3,7,8-PCDD	1	1	PCB 81	0.0001	0.0003	PCN 64/68	0.001
1,2,3,4,7,8-HxCDD	0.1	0.1	PCB 126	0.1	0.1	PCN 66/67	0.025
1,2,3,6,7,8-HxCDD	0.1	0.1	PCB 169	0.01	0.03	PCN 69	0.002
1,2,3,7,8,9-HxCDD	0.1	0.1	PCB 105	0.0001	0.00003	PCN 71/72	0.0000035
1,2,3,4,6,7,8-HpCDD	0.01	0.01	PCB 114	0.0005	0.00003	PCN73	0.003
OCDD	0.0001	0.0003	PCB 118	0.0001	0.00003		
2,3,7,8-TCDF	0.1	0.1	PCB 123	0.0001	0.00003		
1,2,3,7,8-PCDF	0.05	0.03	PCB 156	0.0005	0.00003		
2,3,4,7,8-PCDF	0.5	0.3	PCB 157	0.0005	0.00003		
1,2,3,4,7,8-HxCDF	0.1	0.1	PCB 167	0.00001	0.00003		
1,2,3,6,7,8-HxCDF	0.1	0.1	PCB 189	0.0001	0.00003		
1,2,3,7,8,9-HxCDF	0.1	0.1					
2,3,4,6,7,8-HxCDF	0.1	0.1					
1,2,3,4,6,7,8-HpCDF	0.01	0.01					
1,2,3,4,7,8,9-HpCDF	0.01	0.01					
OCDF	0.0001	0.0003					

1.2 Previous studies

PCDD/Fs, PCBs, and PCNs have been reported to be highly hazardous to human health and the environment, and were banned in 1990s. Since 1990s, monitoring and source identification of PCDD/Fs, PCBs, and PCNs have been conducted. For examples, congener profiles and spatial tendency of PCDD/Fs and PCBs (Wang et al., 2016), and PCN diagnostic ratios analyses were applied to identify the sources (Zhang et al., 2015). From the correlation and principle component analysis (PCA), main sources of PCDD/Fs, PCBs, and PCNs were identified as incineration, steel industry, and paint (Oh et al., 2006; Yu et al., 2006).

In Korea, PCDD/Fs and PCBs monitoring and source identification in sediments in Korea have been continuously reported in domestic and international studies. Previous study examined the congener-specific characterization and sources of PCDD/Fs and PCBs in Gwangyang, Jinhae, Busan, Ulsan, and Pohang bays from 2000 to 2002 (Moon et al., 2008). PCA was also applied to identify the sources of PCBs in Kyeonggi, Gwangyang, Busan, Ulsan, and Pohang bays (Hong et al., 2005). Not only instrumental analysis but also bioanalytical measurement of PCDD/Fs, PCBs, and PAHs was conducted in Pohang Bay in 2010 (Hong et al., 2014). Based on these studies, the concentrations of PCDD/Fs and PCBs in sediments gradually decreased, however some areas still showed high concentrations. The monitoring of PCDD/Fs and PCBs in sediments had been studied continuously, however there have been only a few studies on recent sediment samples. In addition, researches about PCNs in sediments have been investigated continuously in other countries, however it is an early research stage in Korea. There have been a few studies on PCNs in sediments, however they were only performed in air and blood samples (Baek et al., 2008; Park et al., 2010).

Therefore, this study was essential to investigate PCDD/Fs, PCBs, and PCNs simultaneously in recent sediment samples collected from the representative southeastern industrial region of Korea.

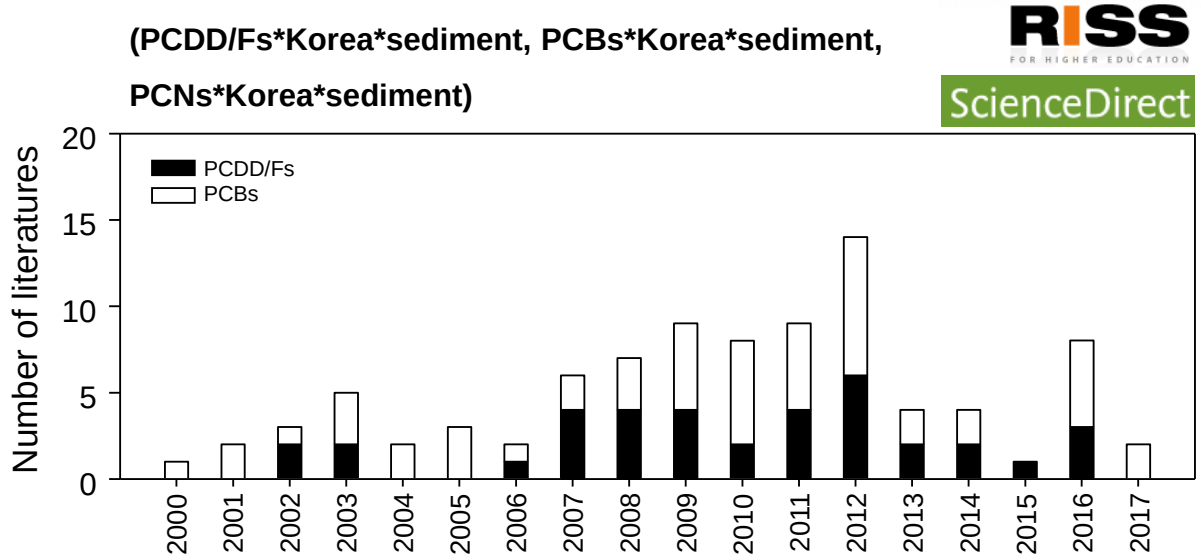


Figure 4. Number of literatures about the concentrations of PCDD/Fs, PCBs, and PCNs in sediments in South Korea.

1.3 Objectives of this study

In order to identify contamination characteristics of PCDD/Fs, PCBs, and PCNs in coastal sediments around industrial complexes, monitoring of sediments was conducted from four bays including Gwangyang, Jinhae, Busan, and Ulsan bays in Korea. The sediment samples were collected using Van Veen grab samplers, to investigate the concentrations of PCDD/Fs, PCBs, and PCNs. Finally, the detail objectives of this study were: (1) to investigate the levels and patterns of PCDD/Fs, PCBs, and PCNs at southeastern region of Korea; (2) to determine spatial distributions of these pollutants; and (3) to identify the potential sources of PCDD/Fs, PCBs, and PCNs in the sampling areas.

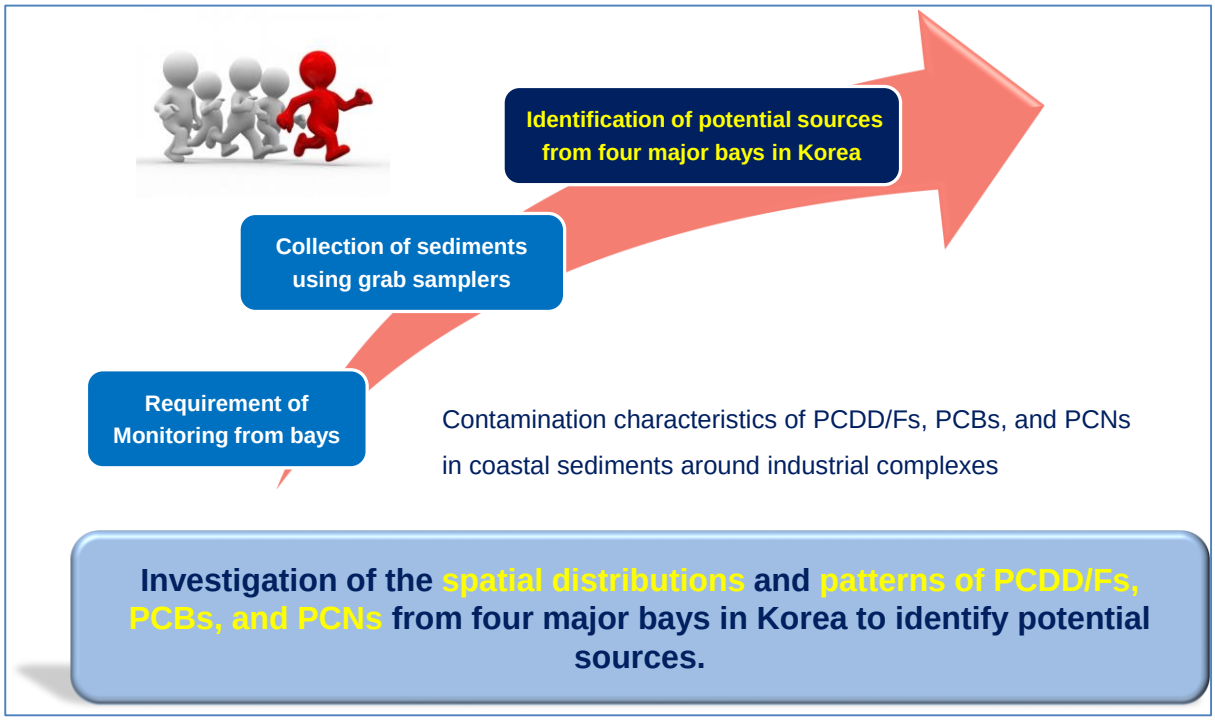


Figure 5. Overall schematic objective of this study.

II. MATERIALS AND METHODS

2.1 Sampling area

There are various industrial complexes in the four industrial complexes (Gwangyang, Jinhae, Busan, Ulsan bays) in the southeastern region of Korea. Moreover, these four bays are the representative industrial bays. In Gwangyang Bay, there are the second largest steel manufacturing facility in Korea, petrochemical industrial complex, harbor, and fertilizer manufacturing. Jinhae Bay is a representative semi-enclosed bay. The most polluted Masan Bay (JH3, JH4, JH5) is included in Jinhae Bay. In particular, JH5 is the site to discharge effluent from wastewater treatment plant. The main industries are the shipbuilding, textile, machine, petrochemical, heavy metal, and fertilizer manufacturing. Busan Bay is the largest harbor in Korea, composed of North, South, and Gamcheon harbors. Container cargoes, nonferrous, midsize shipbuilding, and textile industries are located along the shoreline. Ulsan Bay is one of the major industrial areas in Korea including automobile, nonferrous metal mining, shipbuilding, petrochemical industries, and fertilizer manufacturing.

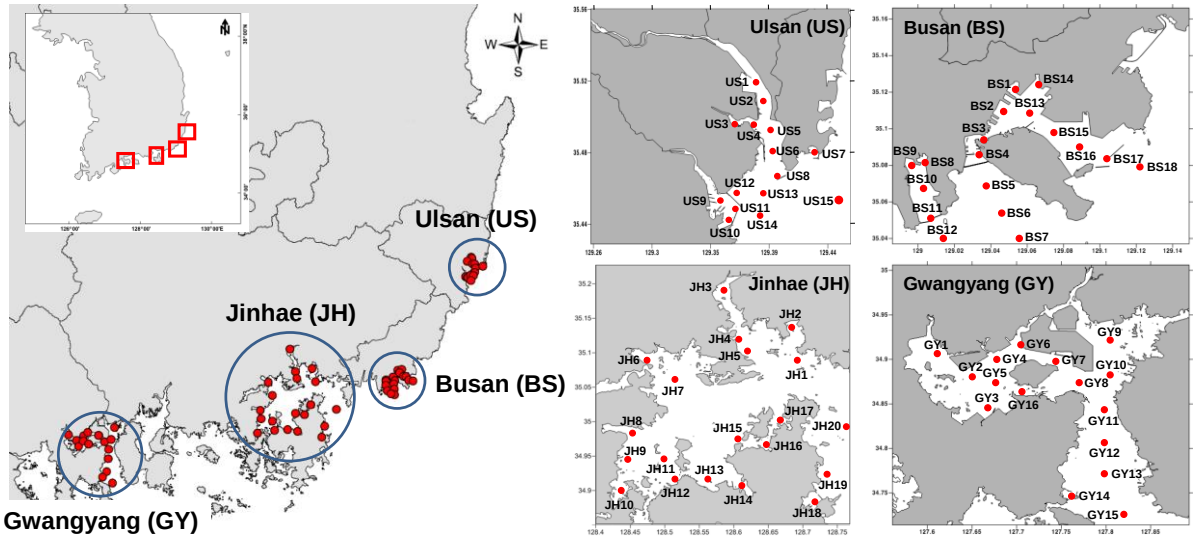


Figure 6. Location of sampling sites in Gwangyang, Jinhae, Busan, and Ulsan bays.

Sediment sampling was conducted in the four bays (Gwangyang, Jinhae, Busan, and Ulsan bays) from March to April 2016. There were 16 sampling sites in Gwangyang Bay (GY1-16), 20 sites in Jinhae Bay (JH1-20), 18 sites in Busan Bay (BS1-18), and 15 sites in Ulsan Bay (US1-15). We collected 69 surface sediment samples (depth: 0-5 cm) from Gwangyang, Jinhae, Busan, and Ulsan Bays using Van Veen grab samplers (Figure 6-7). The sediment samples were wrapped in aluminum foils and stored in glass bottle at -20 ℃. The samples were freeze-dried for about 72 h, and sieved through a 2-mm a stainless-steel sieve.

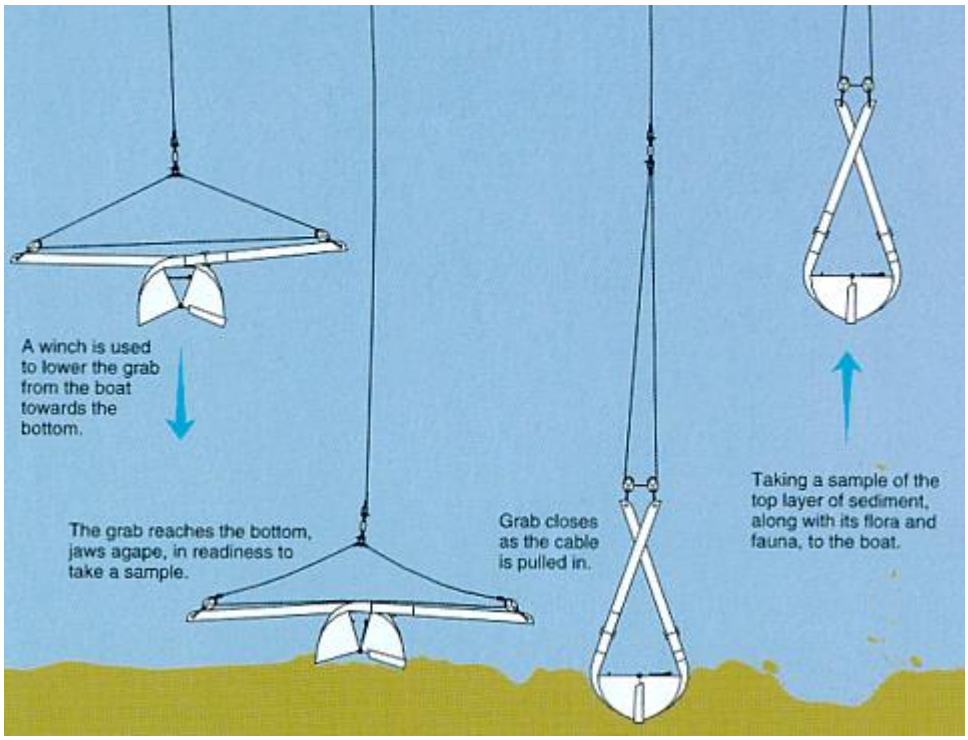


Figure 7. Operation procedure of Van Veen grab sampler (source: http://thecostofthecarat.blogspot.kr/)

2.2 Sample preparation and instrumental analysis

Freeze-dried sediment samples (10 g) were extracted with dichloromethane (DCM) using Accelerated Solvent Extractor (Dionex, Sunnyvale, CA, USA) (detail conditions are shown on Table 3). Before the extraction, $^{13}C_{12}$-labeled surrogate standards (1613-LCS, 1668-LCS, ECN-5490) were spiked into the sediment samples (Figure 8). The extracts were concentrated to 2 mL by TurboVap LV evaporator (Capiler, Hopkinton, MA, USA), and the solvent was exchanged into hexane. The extracts were firstly cleaned up on multi-layer silica gel columns containing anhydrous Na_2SO_4 (0.5 g) (top), 10% $AgNO_3$-silica gel (2 g), activated silica gel (0.5 g), 22% H_2SO_4-silica gel (1.5 g), 44% H_2SO_4-silica gel (1.5 g), activated silica gel (0.5 g), 2% KOH-silica (2 g), activated silica gel (0.5 g), and anhydrous Na_2SO_4 (0.5 g) (bottom). After that, the samples were further cleaned up on activated alumina (10 g) columns. For the multi-layer silica gel column, elution solvent was hexane (130 mL). For the activated alumina column, samples were firstly eluted by 2% DCM in hexane (70 mL) to analyze for PCBs and PCNs, then secondly eluted by 50% DCM in hexane (80 mL) to analyze for PCDD/Fs. Finally, the samples were concentrated to approximately 50 µL and $^{13}C_{12}$-labeled internal standards (1613-ISS, 1668-ISS, ED-910) were added to vials prior to instrumental analysis.

After the pretreatment procedures, 17 PCDD/Fs, 18 PCBs (indicator PCBs and dioxin-like PCBs), and 15 PCNs were analyzed by gas chromatography (GC, Agilent 7890A, USA) coupled with high-resolution mass spectrometry (HRMS, Auto Spec Premier, Waters, USA) (Figure 9) by electron impact (EI). In addition, 14 sediment samples (GY5, GY15, GY16, JH2, JH5, JH11, BS3, BS5, BS13, BS18, US2, US5, US8, and US 13), having different congener profiles, were further analyzed for 75 PCN congeners from mono-CN to octa-CN. The target analytes were separated on a capillary column (DB-5MS, 60 m × 0.25 mm × 0.25 µm film thickness). The instrument analysis conditions of PCDD/Fs, PCBs, and PCNs are shown on Table 4.

Table 3. Conditions of accelerated solvent extractor (ASE)

Conditions	
Pressure	2000 psi
Temperature	140℃
Preheating time	5 min
Heating time	5 min
Static time	5 min
Cycle	3
Purge time	120 sec
Extraction solvent	Dichloromethane (DCM)

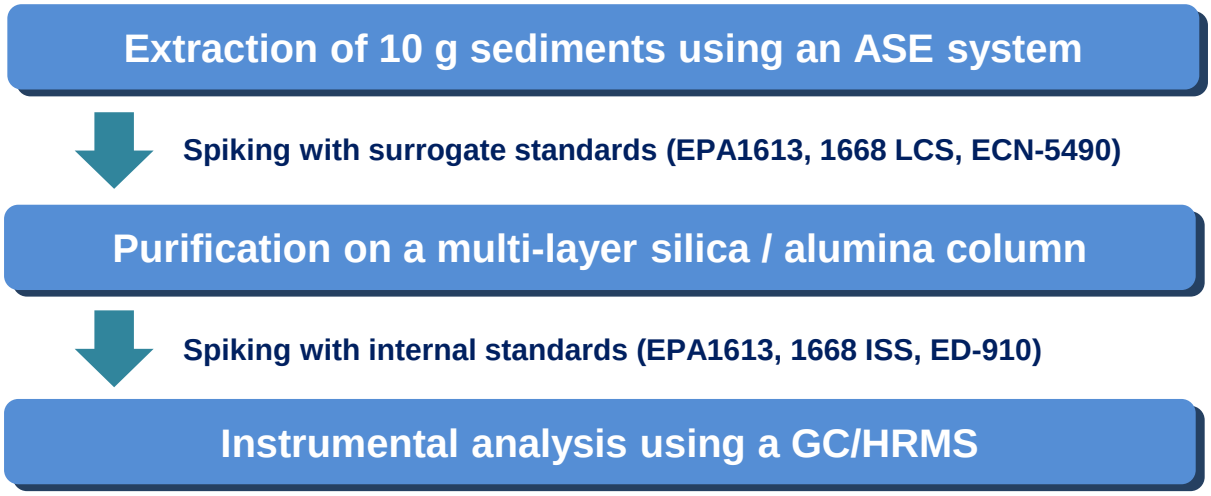


Figure 8. Analysis procedures for PCDD/Fs, PCBs, and PCNs

Table 4. Conditions of GC/HRMS for PCDD/F, PCB, and PCN analysis.

	PCDD/Fs	**PCBs**	**PCNs**
Injection temperature	300℃	300℃	280℃
Injection mode	Spiltless	Spiltless	Spiltless
Carrier gas	Helium (99.9999%), 1.0 mL/min	Helium (99.9999%), 1.1 mL/min	Helium (99.9999%), 1.2 mL/min
Column	DB5-MS (60 m × 0.25 mm × 0.25 μm thickness)	DB5-MS (60 m × 0.25 mm × 0.25 μm thickness)	DB5-MS (60 m × 0.25 mm × 0.25 μm thickness)
Oven	100℃ (1 min) →20℃/min →200℃ → 2.5℃/min → 300℃ →10℃/min →325℃ (1.50 min)	90℃ (1 min) →20℃/min →170℃ → 3.5℃/min → 280℃ →50℃/min →320℃ (3.77 min)	100℃ (3 min) →10℃/min →150℃ → 2℃/min → 260℃ →10℃/min →300℃ (3.00 min)
Mode	EI/SIM	EI/SIM	EI/SIM
Ionization voltage	35 eV	35 eV	35 eV
Resolution	10,000	10,000	10,000

Figure 9. Analytical instrument (GC/HRMS, Autospec Premier,Waters)

2.3 Quality assurance and quality control (QA/QC)

The recoveries of the PCDD/Fs, PCBs, and PCNs ranged from 81.63% to 109.72%, 50.43% to 119.08%, and 57.90% to 106.92%, respectively. Instrumental detection limit (IDL) and limit of quantification (LOQ) were used for accuracy of data. For IDL, CS 1 was analyzed using GC/HRMS for seven times. IDL calculated using standard deviation which were obtained through seven replicates of CS1 (Table 5). LOQ was determined at signal-to-noise ratio (S/N) of 10 (Table 5).

Table 5. The results of instrumental detection limits (IDLs) and limit of quantification (LOQ) for PCDD/Fs, PCBs, and PCNs (unit: pg/g).

Compounds	IDL1	IDL2	IDL3	IDL4	IDL5	IDL6	IDL7	SD	IDL	LOQ
2,3,7,8-TCDD	0.1265	0.0968	0.0956	0.1016	0.0995	0.0944	0.0999	0.0111	0.0348	0.0075
1,2,3,7,8-PCDD	0.5158	0.6063	0.5506	0.4888	0.5313	0.4772	0.4575	0.0504	0.1581	0.0109
1,2,3,4,7,8-HxCDD	0.4579	0.5292	0.5248	0.4951	0.4672	0.4873	0.4899	0.0267	0.0837	0.0110
1,2,3,6,7,8-HxCDD	0.5121	0.5048	0.5153	0.4803	0.5179	0.4898	0.4877	0.0150	0.0472	0.0104
1,2,3,7,8,9-HxCDD	0.5133	0.5257	0.4939	0.5022	0.4888	0.4729	0.4601	0.0226	0.0710	0.0119
1,2,3,4,6,7,8-HpCDD	0.5069	0.4655	0.5681	0.5257	0.4867	0.4173	0.4933	0.0473	0.1484	0.0124
OCDD	1.0947	0.9777	1.1366	1.0337	1.0039	0.9703	0.8197	0.1020	0.3204	0.0053
2,3,7,8-TCDF	0.1130	0.0987	0.0944	0.1110	0.1031	0.1135	0.1223	0.0097	0.0304	0.0033
1,2,3,7,8-PCDF	0.5421	0.5379	0.5300	0.4964	0.4917	0.4821	0.5255	0.0244	0.0765	0.0048
2,3,4,7,8-PCDF	0.5391	0.4804	0.4985	0.4590	0.4785	0.4993	0.4712	0.0262	0.0821	0.0040
1,2,3,4,7,8-HxCDF	0.4875	0.4799	0.5082	0.4830	0.5343	0.4935	0.4616	0.0232	0.0728	0.0057
1,2,3,6,7,8-HxCDF	0.5359	0.5044	0.4831	0.5060	0.5037	0.5141	0.4655	0.0224	0.0703	0.0058
1,2,3,7,8,9-HxCDF	0.4794	0.5041	0.5175	0.5124	0.5109	0.5133	0.5294	0.0154	0.0483	0.0058
2,3,4,6,7,8-HxCDF	0.5186	0.8272	0.5007	0.4953	0.4758	0.4795	0.4729	0.0213	0.0669	0.0064
1,2,3,4,6,7,8-HpCDF	0.5689	0.5447	0.5076	0.4814	0.5238	0.4339	0.4366	0.0518	0.1627	0.0041
1,2,3,4,7,8,9-HpCDF	0.5278	0.4843	0.5402	0.5231	0.4613	0.4648	0.4774	0.0325	0.1022	0.0046
OCDF	1.0208	1.0096	1.0992	1.1012	1.0209	0.8666	0.9233	0.0861	0.2703	0.0092
PCB 28	17.6239	18.5746	18.5415	20.1543	18.1167	18.5000	19.3546	0.8289	2.6027	0.2639
PCB 52	18.2330	19.1777	19.0861	19.9304	19.35733	21.0322	20.3044	0.9152	2.8738	0.0658
PCB 77	0.1620	0.1596	0.1634	0.1519	0.1825	0.1911	0.1785	0.0142	0.0447	0.0217
PCB 81	0.1864	0.1619	0.1722	0.1855	0.1773	0.1618	0.1726	0.0100	0.0313	0.0246

PCB 101	19.5330	19.4002	19.4287	19.6838	19.9984	20.8058	19.6978	0.4905	1.5402	0.0800
PCB 105	0.2237	0.2101	0.2057	0.2138	0.2175	0.2123	0.2108	0.0058	0.0182	0.0597
PCB 114	0.1524	0.1484	0.1670	0.1675	0.1660	0.1569	0.1776	0.0101	0.0318	0.0220
PCB 118	0.1917	0.1893	0.1724	0.1803	0.1795	0.1902	0.1912	0.0075	0.0236	0.0196
PCB 123	0.1718	0.1614	0.1639	0.1440	0.1603	0.1518	0.1421	0.0109	0.0342	0.0223
PCB 126	0.1928	0.1961	0.2034	0.1921	0.2000	0.1991	0.1907	0.0047	0.0148	0.0552
PCB 138	20.7178	19.1439	19.6080	18.2961	19.4802	21.2441	21.1869	1.1193	3.5146	0.1187
PCB 153	20.2062	19.0397	20.1139	20.5253	19.5844	19.8873	20.8659	0.6030	1.8935	0.1070
PCB 156	0.2045	0.1925	0.1973	0.2013	0.1934	0.2067	0.1966	0.0054	0.0171	0.0267
PCB 157	0.1982	0.2071	0.2021	0.2040	0.1926	0.2003	0.2068	0.0051	0.0161	0.0296
PCB 167	0.2086	0.1813	0.2027	0.1985	0.2100	0.2029	0.1989	0.0064	0.0201	0.0275
PCB 169	0.1719	0.1704	0.1766	0.1671	0.1772	0.1813	0.1777	0.0049	0.0155	0.0343
PCB 180	19.9711	19.1773	20.3751	19.6679	19.4984	19.9341	20.4509	0.4593	1.4421	0.0763
PCB 189	0.1884	0.1863	0.1900	0.1846	0.1726	0.1787	0.1720	0.0074	0.0233	0.0310
PCN 52/60	1.0015	0.9931	1.0467	1.0380	1.0124	0.9881	1.0030	0.0224	0.0702	0.0112
PCN 53/55	0.9400	0.9609	0.9719	0.9848	0.9538	0.9064	0.9503	0.0251	0.0788	0.0117
PCN 63	0.890	0.9248	0.9035	0.8549	0.8639	0.8060	0.9015	0.0401	0.1260	0.0143
PCN 64/68	0.9985	0.9530	0.9265	0.8998	0.9094	0.9228	0.9480	0.0332	0.1043	0.0186
PCN 66/67	0.9980	0.9804	0.9745	0.9496	0.9872	0.9244	0.9201	0.0310	0.0972	0.0150
PCN 69	0.8778	0.9394	0.9618	0.9565	0.8951	0.8784	0.9470	0.0371	0.1166	0.0123
PCN 71/72	0.8743	0.8740	0.8757	0.8629	0.8642	0.8631	0.8861	0.0086	0.0269	0.0090
PCN 73	0.9611	0.9471	0.9313	0.9568	0.9537	0.9640	0.9982	0.0204	0.0642	0.0217
PCN 74	0.9673	0.9657	0.9722	0.9407	0.9237	0.9671	0.9616	0.0178	0.0560	0.0223
PCN 75	0.9510	0.9416	0.9481	0.9744	0.9675	0.9300	0.9623	0.0155	0.0486	0.0281

2.4 Total organic carbon analysis

The total organic carbon (TOC) of surface sediments was determined using TOC-5000 analyzer (Shimadzu, Kyoto, Japan) (Figure 10). Both total carbon (TC) and inorganic carbon (IC) contents were determined. The standards of TC and IC used glucose and sodium carbonate, respectively. During the TC analysis, the samples were heated up to 900℃ in the presence of an oxidation catalyst. On the other hand, phosphoric acid was added to the inorganic carbon (IC) analysis, the samples were heated up to 200℃. TOC was calculated by subtracting IC value from TC value.

$$TOC = TC - IC, \quad (2)$$

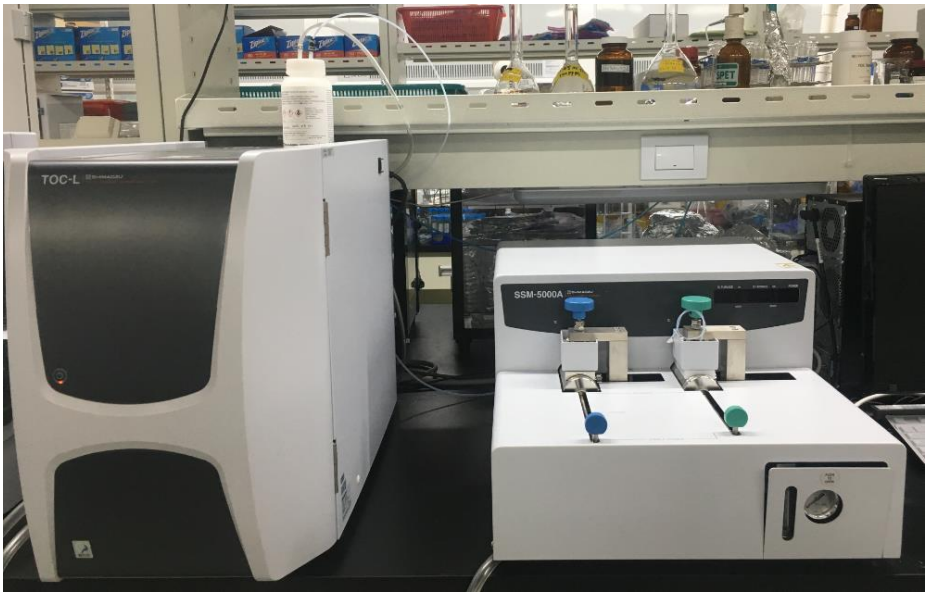


Figure 10. Analytical instrument (TOC-5000 analyzer)

2.5 Statistical analysis

The principal component analysis (PCA) was performed to identify sources according to congener distribution patterns and spearman correlation analysis were used to test the relationship between TOC contents and concentrations of PCDD/Fs, PCBs, and PCNs using IBM SPSS Statistics 20. The statistical analysis were carried out using SigmaPlot software 12.0. In this program, Mann-Whitney rank sum test was applied to analyze the statistical difference.

III. RESULTS AND DISCUSSION

3.1 Distribution of PCDD/Fs in sediments in industrial bays

3.1.1 Concentrations of PCDD/Fs

The concentrations of PCDD/Fs in the four bays (Gwangyang, Jinhae, Busan, and Ulsan bays) is shown in Figure 11 (a), Figure 23 and Table 6. The concentrations of PCDD/Fs in the four bays ranged from 24.38 to 661.85 pg/g dw with a mean value of 197.20 pg/g dw. The mean concentration of PCDD/Fs was the highest in Jinhae Bay (282.74 pg/g dw), followed by Busan (212.73 pg/g dw), Ulsan (188.77 pg/g dw), and Gwangyang (80.71 pg/g dw) bays. There were not statistically significant differences for four bays ($p>0.05$), except for Gwangyang Bay ($p<0.01$). This pattern of PCDD/Fs was also observed in the previous studies (Moon et al., 2008).

The level of PCDD/Fs was the highest at JH5 (661.85 pg/g), located within 5km from a wastewater treatment plant, which seemed to be contaminated by effluent discharge. In particular, Masan Bay (the inside of Jinhae Bay) was highly polluted: the mean concentrations of this area were about 7 times higher than the lowest level in Jinhae Bay. This pattern can be explained by several reasons. Firstly, Masan Bay is a semi-enclosed bay with a very slow flow velocity of sea water. Besides, there are about 1300 industrial complexes (including petrochemical, heavy metal, electrical, and plastic industries) located in Masan Bay. The lowest concentration was recorded in Gwangyang Bay, due to the fast flow of seawater and frequent landfilling and dredging. In Busan Bay, the highest and the lowest concentrations observed at BS13 (538.82 pg/g dw) and BS11 (31.06 pg/g dw), respectively. BS 13 site is located near the harbor with many container cargoes, whereas, BS11 site is located in the outer part of Busan Bay. In Ulsan Bay, the high concentration of PCDD/Fs was measured at US13, which is located near a petrochemical industrial complex.

In comparison to the previous studies in Korea, the concentrations of PCDD/Fs in this research were much lower (Table 7) (Hong et al., 2009; Kannan et al., 2007; Oh et al., 2003; Terauchi et al., 2009). The monitoring results in this study were lower than those of Barcelona, Spain (7564 pg/g dw) (Eljarrat et al., 2005) and East River, China (3,349 pg/g dw) (Ren et al., 2009) and were similar to those of Marmara Sea, Turkey (21.73 pg/g dw) (Okay et al., 2009) and Port of Gdansk, Poland (358.46 pg/g dw) (Lewandowski et al., 2014).

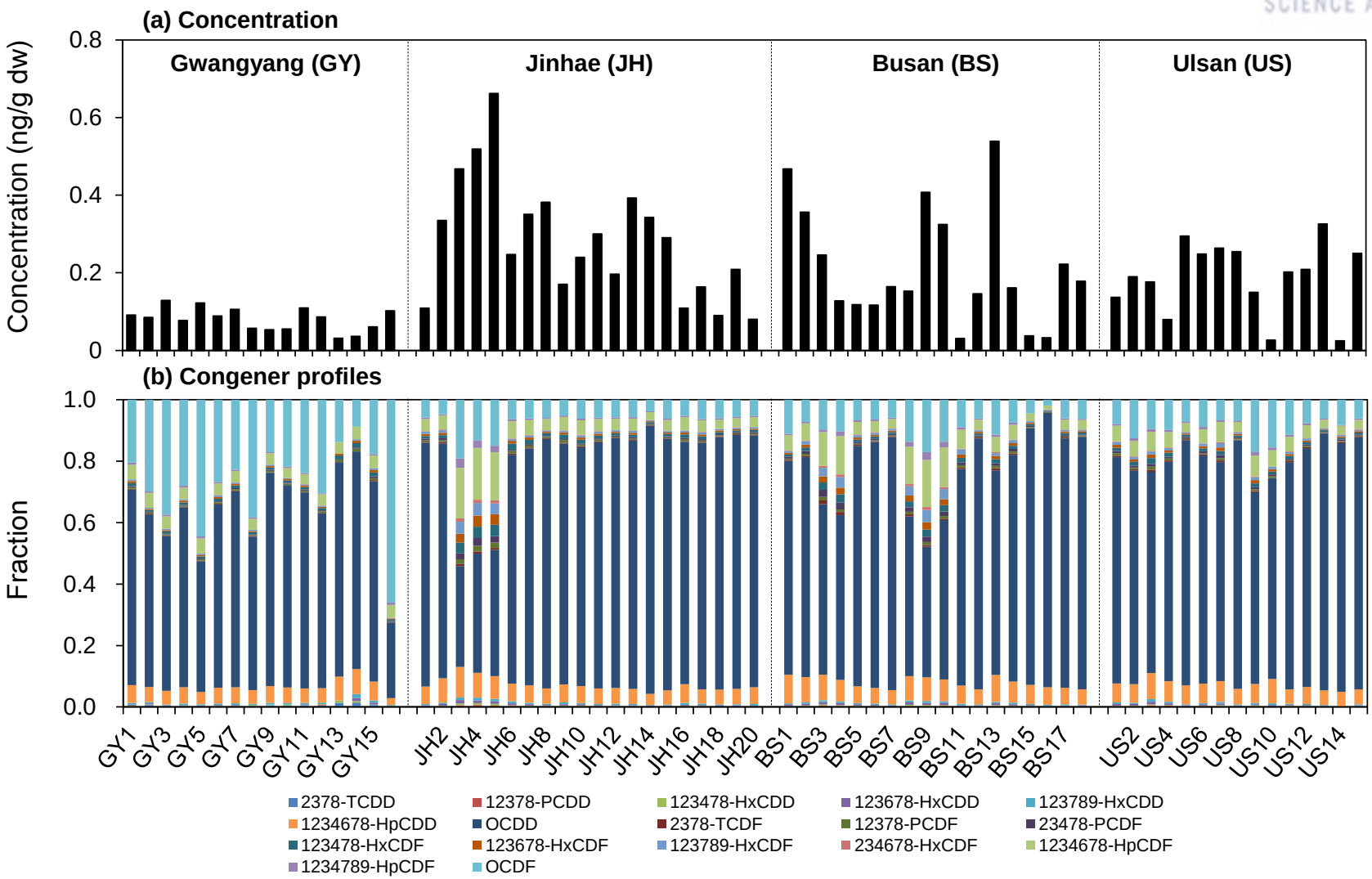


Figure 11. (a) Concentrations and (b) Congener profiles of PCDD/Fs in the four bays.

Table 6. Concentrations of PCDD/Fs in sediment samples obtained from the four bays (unit: pg/g).

Congeners	**Gwangyang**	**Jinhae**	**Busan**	**Ulsan**
2,3,7,8-TCDD	0.24 ± 0.21	0.10 ± 0.17	0.07 ± 0.09	0.05 ± 0.10
1,2,3,7,8-PCDD	0.03 ± 0.07	0.65 ± 0.84	0.43 ± 0.40	0.30 ± 0.23
1,2,3,4,7,8-HxCDD	0.17 ± 0.04	0.81 ± 1.05	0.52 ± 0.44	0.36 ± 0.19
1,2,3,6,7,8-HxCDD	0.20 ± 0.16	1.48 ± 1.57	1.16 ± 1.06	0.72 ± 0.42
1,2,3,7,8,9-HxCDD	0.37 ± 0.15	1.57 ± 1.51	0.97 ± 0.74	0.78 ± 0.42
1,2,3,4,6,7,8-HpCDD	3.95 ± 1.16	17.51 ± 13.43	15.60 ± 13.93	11.07 ± 5.20
OCDD	45.15 ± 15.45	191.83 ± 81.00	140.77 ± 94.27	142.58 ± 75.93
2,3,7,8-TCDF	0.15 ± 0.10	1.08 ± 1.17	1.11 ± 1.09	0.64 ± 0.37
1,2,3,7,8-PCDF	0.35 ± 0.11	2.37 ± 3.22	1.36 ± 1.27	0.90 ± 0.50
2,3,4,7,8-PCDF	0.22 ± 0.09	2.55 ± 4.09	2.19 ± 2.21	1.02 ± 0.63
1,2,3,4,7,8-HxCDF	0.64 ± 0.21	5.03 ± 6.77	2.89 ± 2.76	1.79 ± 0.92
1,2,3,6,7,8-HxCDF	0.39 ± 0.14	3.95 ± 6.49	2.46 ± 2.60	1.22 ± 0.70
1,2,3,7,8,9-HxCDF	0.35 ± 0.17	4.26 ± 7.16	3.50 ± 4.27	1.36 ± 0.84
2,3,4,6,7,8-HxCDF	0.03 ± 0.05	1.14 ± 2.02	0.80 ± 0.95	0.32 ± 0.20
1,2,3,4,6,7,8-HpCDF	3.25 ± 1.36	21.33 ± 29.96	15.47 ± 16.40	8.30 ± 4.08
1,2,3,4,7,8,9-HpCDF	0.39 ± 0.25	3.02 ± 4.73	1.99 ± 2.56	1.13 ± 0.52
OCDF	24.84 ± 17.87	24.02 ± 27.53	21.47 ± 21.09	16.21 ± 7.15
7 PCDDs	50.10 ± 16.70	213.97 ± 89.92	159.51 ± 109.50	155.88 ± 81.21
10 PCDFs	30.62 ± 19.55	68.76 ± 92.45	53.21 ± 53.03	32.89 ± 14.43
17 PCDD/Fs	80.71 ± 29.36	282.74 ± 153.63	212.73 ± 149.39	188.77 ± 91.63
PCDD/Fs (pg TEQ/g)	0.79 ± 0.21	4.53 ± 5.60	3.29 ± 2.95	2.05 ± 1.02

Table 7. Comparison of PCDD/Fs concentrations in sediment samples between this study and other studies.

Location	Sampling year	Concentration (pg/g dw)	Concentration (pg TEQ/g)	Reference
Gwangyang Bay (Korea)	2016	31.48-128.82	0.52-1.16	This study
Jinhae Bay (Korea)	2016	80.05-661.85	0.62-19.48	This study
Busan Bay (Korea)	2016	31.06-538.82	0.15-9.92	This study
Ulsan Bay (Korea)	2016	24.38-325.81	0.16-4.13	This study
Pohang Bay (Korea)	2010	51-5230	0.72-730	(Hong et al., 2014)
Masan Bay (Korea)	2006	260-4684		(Hong et al., 2009)
Han River (Korea)	2005	23.1-368	0.679-10.5	(Kim et al., 2009)
Gwangyang, Jinhae, Busan, Ulsan, Pohang bays (Korea)	2000-2002		0.44-38.5	(Moon et al., 2008)
Barcelona (Spain)	2002	72-30007	0.1-51.5	(Eljarrat et al., 2005)
Liaohe River (China)	2004	3.19-124.71	0.24-27.49	(Zhang et al., 2010)
East River (China)	2007	1200-5300	2.4-8.1	(Ren et al., 2009)
Marmara Sea (Turkey)	2007	2.04-60.5	0.98-1.01	(Okay et al., 2009)
Maroran Port (Japan)	2008	69-410	0.51-6.2	(Anezaki and Nagahora, 2014)
The Gulf of Gdansk (Poland)	2012-2013		0.30-14.87	(Lewandowski et al., 2014)
HongKong harbor (HongKong)	1996	5000-6900	3-33	(Müller et al., 2002)
Lake Victoria (East Africa)	2011	0.20-56.7	0.07-5.53	(Ssebugere et al., 2013)
Izmit Bay (Turkey)	2012		0.45-255	(Karademir et al., 2013)

3.1.2 Congener profiles of PCDD/Fs

The concentrations of PCDDs accounted for by over 70% at almost every sampling sites. OCDD (71.85%) was the most dominant congener followed by OCDF (13.07%), 1,2,3,4,6,7,8-HpCDD (6.14%), and 1,2,3,4,6,7,8-HpCDF (5.22%) (Figure 11 (b)). By-products of pesticides, such as Pentachlorophenol (PCP) and Chloronitrofen (CNP), contain a large amount of OCDD (Masunaga et al., 2001). Therefore, this profile might be explained by common use of pesticides from 1970 to 1996 in Korea (Moon et al., 2009). Moreover, physical and chemical properties of OCDD (low solubility, photodissociation and high stability) can also lead to high concentrations (Baker and Hites, 2000; Muir et al., 1992). This congener profile pattern is consistent with the previous study (Moon et al., 2008). In general, the fractions of PCDDs increased from the inner bay to outer bay, whereas PCDFs fractions decreased.

At most sites, the ratios of PCDFs to PCDDs were less than 1 except for GY5 and GY16. The ratios of PCDFs to PCDDs were 1.06 and 2.62 at GY5 and GY16, respectively. This might be due to denovo synthesis. During thermal processes, PCDD/Fs are produced from the chlorine precursor at high temperature (above 250℃) by denovo synthesis (Dickson et al., 1992). Therefore, a high temperature is an important factor of PCDD/F productions (Sun et al., 2017). This mechanism was also observed due to the influence of hot flue gas from the steel manufacturing facility in Gwangyang Bay (Ba et al., 2009; Stieglitz et al., 1997).

3.1.3 Source identification of PCDD/Fs

In order to prevent the effect of detection limit, only frequent detected congeners, including 123478-HxCDD, 123678- HxCDD, 123789- HxCDD, 1234678-HpCDD, OCDD, 2378-TCDF, 12378-PCDF, 23478-PCDF, 123478-HxCDF, 123678-HxCDF, 123789-HxCDF, 1234678-HpCDF, 1234789-HpCDF, OCDF, were used as the input data for the PCA. Two components accounted for 67% and 13% of the total variance, respectively (Figure 12).

Principal component (PC) 1 was highly positively related to PCDD/Fs except for OCDD and OCDF, whereas PC2 was significantly characterized by OCDF (one of PCDFs). In the score plot, the sampling sites were divided into several groups. The sediment samples of Gwangyang Bays were characterized by OCDF. The concentrations of PCDFs in the steel manufacturing facility were higher than the concentrations of PCDDs in the previous study (Antunes et al., 2012). Since the steel manufacturing facility is located in Gwangyang Bay, it is evaluated that PCDFs were highly influenced by the flue gas of this industry (Dickson et al., 1992).

OCDD was dominant at all sampling sites among the four bays, except for Gwangyang Bay. The sediment samples at JH3, JH4, and JH5, which are located in the highly polluted Masan Bay, had higher score values of PC1, and were featured by the other congeners except for OCDD and OCDF. In addition, the separated samples at BS3, BS4, BS8, BS9, and BS10 are located in the inner part of the Busan Bay where a harbor with small shipbuilding industries is located, therefore, these sites were characterized by relatively lower chlorinated PCDD/Fs with low molecular weight and K_{ow}.

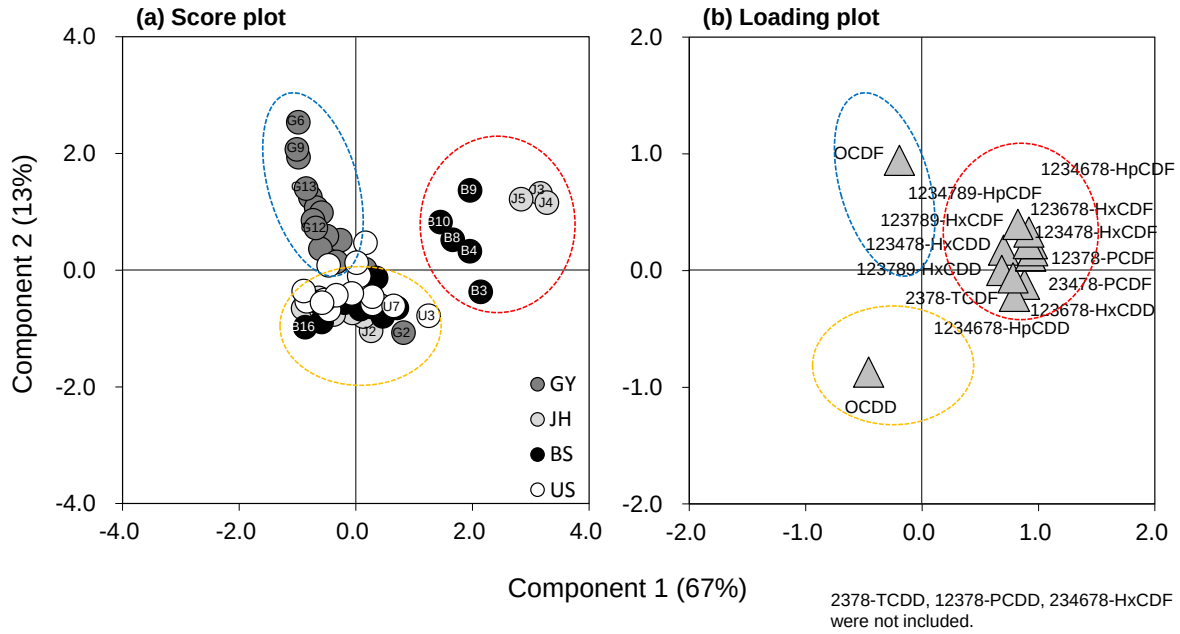


Figure 12. PCA results of PCDD/Fs in the sediment samples from the four bays: (a) score plot and (b) loading plot.

3.1.4 TOC normalization concentration

Total organic carbon (TOC) can be an indicator of pollutants. We investigated the TOC-normalized concentrations to find out the influence of the emission source except for the impact of TOC.

TOC-normalized concentrations of PCDD/Fs ranged from 0.03 to 1.81 ng/g TOC (Figure 13). Several different patterns were observed between concentrations of PCDD/Fs and TOC-normalized concentrations of PCDD/Fs. This indicates that the concentration of PCDD/Fs was highly influenced by organic carbon contents at the several sites. The highest concentrations of TOC-normalized PCDD/Fs were observed at JH11 (1.81 pg/g TOC), followed by JH5 (1.27 ng/g TOC), US5 (0.94 ng/g TOC).

The TOC-normalized concentration of PCDD/Fs at JH11 was significantly high due to the low organic carbon content (0.6%). The TOC content at JH5 (1.9%), located near a wastewater treatment plant, was slightly higher than the mean TOC content (1.6%). Overall the TOC-normalized concentration of PCDD/Fs at this site was higher than those of the other sites. This might be explained by a direct discharge of industrial and domestic wastewater from a wastewater treatment plant and organic carbon content.

In Busan Bay, BS13 is a semi-enclosed site bounded by the ocean current circulation. Furthermore, the ship transportation and anchorage may lead to the generation of large amount of organic carbon contents. Therefore, considerably high concentration of PCDD/Fs was measured at BS13 due to organic carbon content.

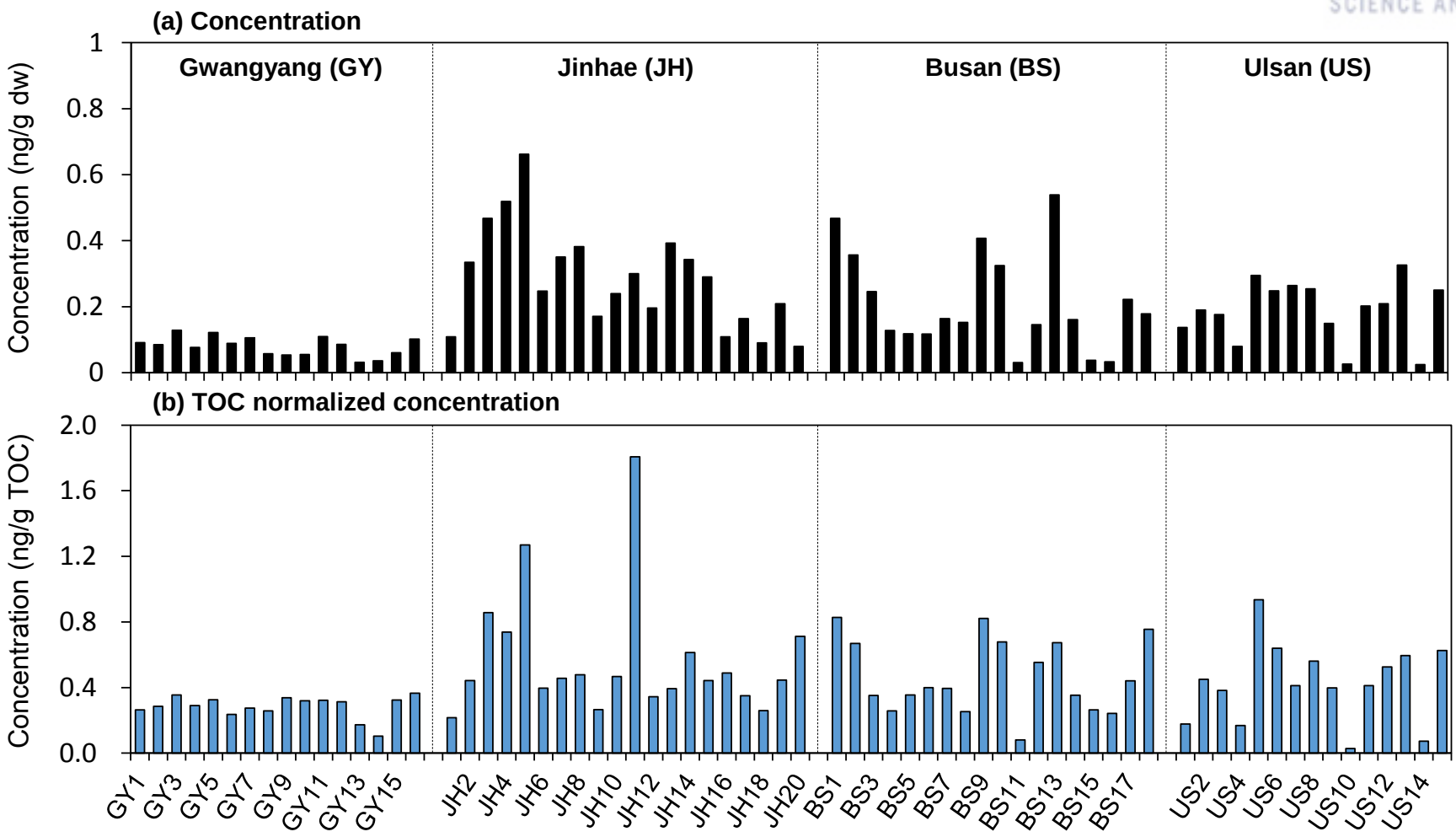


Figure 13. (a) Concentrations and (b) TOC-normalized concentrations of PCDD/Fs in the four bays.

3.2 Distribution of PCBs in sediments in industrial bays

3.2.1 Concentrations of PCBs

The concentrations of PCBs in the four bays varied from 0.03 to 35.33 ng/g dw, with an average of 3.43 ng/g dw (Figure 14 (a), Figure 23 and Table 8). The mean concentrations of indicator PCBs (PCB 28, 52, 101, 118, 138, 153, 180) and dioxin-like PCBs (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) in Ulsan Bay (5.78 and 1.64 ng/g dw) were recorded to be the highest, followed by Busan (5.81 and 0.81 ng/g dw), Jinhae (0.75 and 0.17 ng/g dw), and Gwangyang (0.11 and 0.02 ng/g dw) bays, respectively. There were statistical differences among sampling sites ($p<0.01$) except for Busan and Ulsan bays ($p>0.05$). The patterns of PCB concentration in this study were consistent with previous study (Moon et al., 2008).

The highest concentration of PCBs was found at US5 (35.33 ng/g dw), which is a harbor of Ulsan and located in the vicinity of the automobile and petrochemical industrial complexes. The concentrations of PCBs at BS3 (32.08 ng/g dw), which is the biggest harbor of Busan and located close to small shipbuilding industries, showed the second highest concentration. In Jinhae Bay, the highest concentration was observed at JH2 (5.18 ng/g dw), where harbor is located. In general, the high concentrations of PCBs in the four bays were found in the harbor areas because PCBs containing paints were used as antifoulant in the past (Hong et al., 2005). Therefore, leakage from ship containing PCBs might be emission source. In addition, the concentrations of PCBs in the inner part were higher than those of the outer part except for Gwangyang Bay. This indicates that the industrial complexes might be the major source of PCBs since they are located in the inner part.

In comparison to the previous studies in Korea, our results of PCBs were lower (Table 9) (Choi et al., 2011; Hong et al., 2003; Koh et al., 2005; Terauchi et al., 2009). Compared with previous studies in other countries, the concentrations of PCBs in the four bays were lower than those from Marmara Sea, Turkey (32.10 ng/g dw) (Okay et al., 2009) and Yangtze River, China (9.20 ng/g dw) (Yang et al., 2009). However the concentrations of PCBs were comparable to the previous study in the Danube River, Czech (0.47 ng/g dw) (Kukučka et al., 2015).

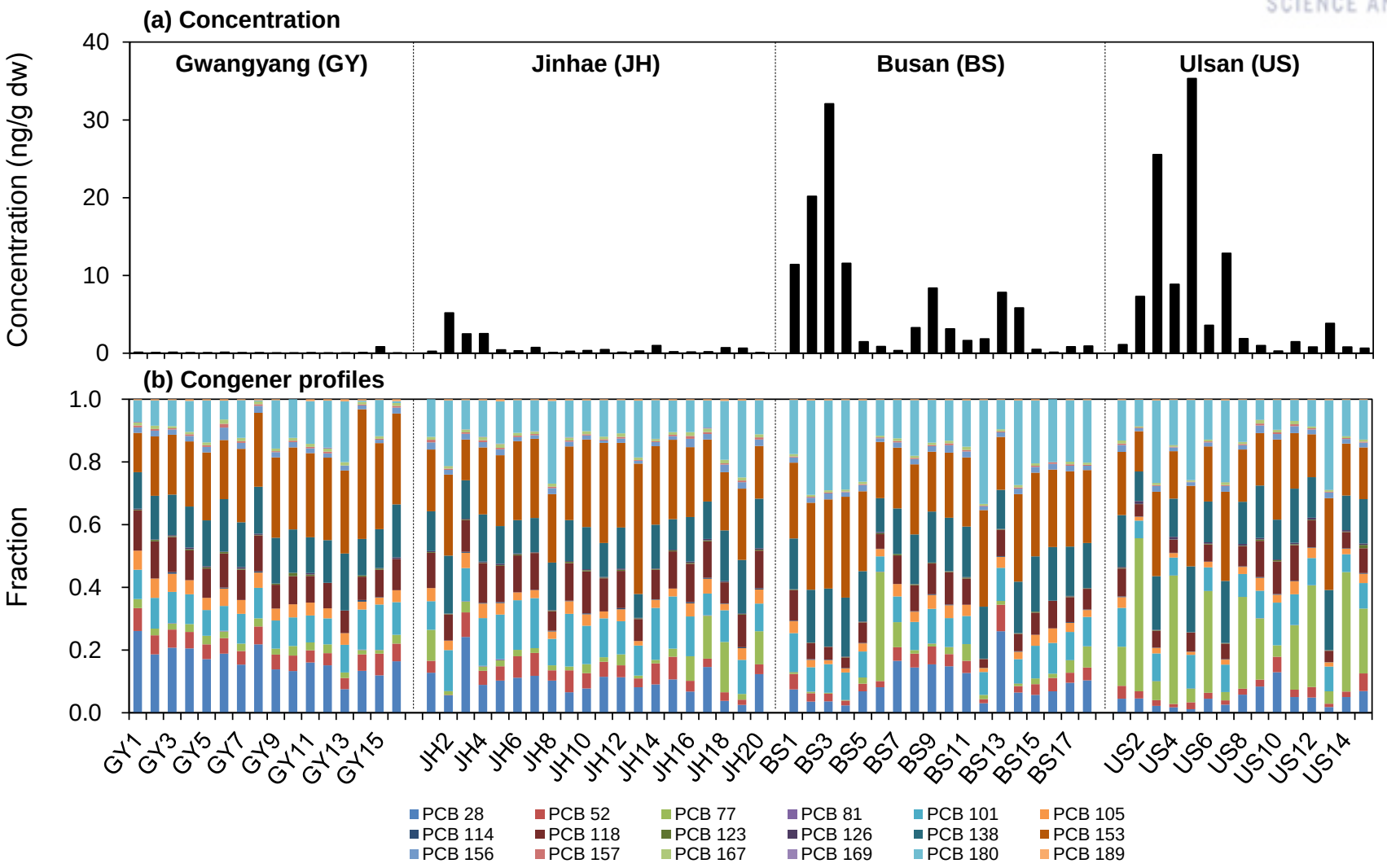


Figure 14. (a) Concentrations and (b) Congener profiles of PCBs in the four bays

Table 8. Concentrations of PCBs in sediment samples obtained from the four bays (unit: pg/g).

Congeners	Gwangyang	Jinhae	Busan	Ulsan
PCB 28	19.86 ± 22.87	83.82 ± 142.98	462.62 ± 554.71	164.89 ± 161.82
PCB 52	7.01 ± 13.98	31.52 ± 47.30	214.07 ± 263.53	132.87 ± 209.06
PCB 77	2.33 ± 2.05	22.93 ± 30.65	64.93 ± 66.71	929.18 ± 1200.35
PCB 81	0.06 ± 0.12	0.62 ± 1.33	2.04 ± 2.97	0.62 ± 0.61
PCB 101	14.65 ± 28.54	108.64 ± 163.83	578.84 ± 768.21	623.61 ± 1048.45
PCB 105	4.66 ± 4.27	29.25 ± 44.89	151.72 ± 167.01	106.76 ± 133.48
PCB 114	0.19 ± 0.32	1.58 ± 2.33	9.50 ± 11.50	5.61 ± 6.40
PCB 118	12.16 ± 16.92	83.86 ± 115.05	375.81 ± 421.83	389.44 ± 593.13
PCB 123	0.43 ± 0.73	1.60 ± 1.74	9.75 ± 9.64	9.04 ± 10.19
PCB 126	0.27 ± 0.26	1.76 ± 1.99	4.59 ± 5.43	17.49 ± 21.90
PCB 138	16.84 ± 23.51	124.48 ± 218.81	1058.96 ± 1521.17	1232.73 ± 2074.73
PCB 153	31.42 ± 53.20	190.01 ± 298.38	1626.09 ± 2391.70	1671.75 ± 2754.57
PCB 156	2.05 ± 2.21	13.56 ± 20.33	107.05 ± 151.92	101.45 ± 144.65
PCB 157	0.57 ± 0.61	3.72 ± 5.16	20.40 ± 25.96	17.16 ± 21.85
PCB 167	1.11 ± 1.50	7.53 ± 10.48	42.16 ± 54.65	44.88 ± 61.78
PCB 169	0.07 ± 0.18	0.53 ± 0.88	0.02 ± 0.08	0.96 ± 0.79
PCB 180	12.14 ± 22.66	125.46 ± 238.63	1491.84 ± 2446.69	1560.13 ± 2744.93
PCB 189	0.42 ± 0.43	2.93 ± 4.27	20.27 ± 32.44	18.92 ± 28.12
Indicator PCBs	114.09 ± 179.85	747.80 ± 1134.60	5808.23 ± 7954.55	5775.42 ± 9532.61
dl-PCBs	24.32 ± 29.04	169.87 ± 224.20	808.24 ± 864.12	1641.51± 1800.87
18 PCBs	126.26 ± 191.62	833.80 ± 1239.84	6240.66 ± 8389.15	7027.49 ± 10334.09
dl-PCBs (pg TEQ/g)	0.03 ± 0.03	0.20 ± 0.23	0.49 ± 0.57	1.89 ± 2.34

Table 9. Comparison of PCBs concentrations in sediment samples between this study and other studies.

Location	Sampling year	Congener	Concentration (pg/g dw)	Concentration (pg TEQ/g)	Reference
Gwangyang Bay (Korea)	2016	18[a)]	33.17-833.55	0.00-0.13	This study
Jinhae Bay (Korea)	2016	18[a)]	101.60-5181.83	0.02-0.82	This study
Busan Bay (Korea)	2016	18[a)]	137.63-32077.05	0.00-2.37	This study
Ulsan Bay (Korea)	2016	18[a)]	283.85-35331.66	0.08-7.30	This study
Kyeonggi Bay (Korea)	2000	22[b)]	550-16020		(Hong et al., 2005)
Gwangyang Bay (Korea)	2000	22[b)]	220-2910		(Hong et al., 2005)
Busan Bay (Korea)	2000	22[b)]	5710-198600		(Hong et al., 2005)
Ulsan Bay (Korea)	2000	22[b)]	2060-22310		(Hong et al., 2005)
Youngil Bay (Korea)	2000	22[b)]	560-72820		(Hong et al., 2005)
Jinhae Bay (Korea)	2007	22[b)]	640-18000		(Shim et al., 2010)
Barcelona (Spain)	2002	12[c)]	1644.82-11601.96	0.08-2.72	(Eljarrat et al., 2005)
Yangtze River (China)	2005	39[d)]	1200-45100		(Yang et al., 2009)
Narragansett Bay (USA)	1997-1998	22[b)]	20800-1760000		(Hartmann et al., 2004)
Naples harbor (Italy)	2004	38[e)]	10000-899000		(Sprovieri et al., 2007)
Liaohe River (China)	2004	22[b)]	1853-1075606	0.015-0.65	(Zhang et al., 2010)
CauBay River (Vietnam)	2013	12[c)]	14254-17369	5.3-11.9	(Toan, 2014)
East River (China)	2007	12[c)]	48-270	0.042-0.45	(Ren et al., 2009)
Donube (Czech)	2007-2008	12[c)]	34-13700	0.16-1.6	(Kukučka et al., 2015)
Marmara Sea (Turkey)	2007	18[a)]	17.9-539746	0.00-15	(Okay et al., 2009)

[a)]PCB-28,52,77,81,101,105,114,118,123,126,138,153,156,157,167,169,189,180, [b)]PCB-8,18,28,29,44,52,66,87,101,105,110,118,128,138,153,170,180,187,195,200,206,209

[c)]PCB-77,81,105,114,118,123,126,156,157,167,169,189

[d)]PCB-17,18,28,31,33,44,49,52,70,74,82,87,95,99,101,105,110,118,128,132,138,149,151,153,158,170,171,177,180,183,187,191,194,195,205,206,208,209

[e)]PCB-28,,29,44,49,52,60,66,70,74,77,81,82,87,95,99,101,105,110,114,118,126,128,138,146,149,151,153,156,158,166,169,170,177,179,180,183,187,189

3.2.2 Congener profiles of PCBs

Congener pattern of PCBs is presented in Figure 14 (b). Indicator PCBs accounted for 45-92% (mean value: 78%) of the 18 PCBs in the four bays. Among indicator PCBs, CB-153 (0.85 ng/g d.w.) was the most abundant congener, followed by CB-180 (0.77 ng/g d.w.), CB-138 (0.58 ng/g d.w.), and CB-28 (0.19 ng/g d.w.). These congener patterns were similar to those of the previous studies (Motelay-Massei et al., 2004; Vives et al., 2007).

CB-118 (42%) of dl-PCBs was the most abundant because it was contained in commercial products such as Aroclors. The most toxic congener, CB-126, contributed 1.22% (6.20 ng/g d.w.) in the four bays. The concentration distributions of dl-PCBs were similar in Jinhae, Busan, and Gwangyang bays, however, CB-77 was the most dominant in Ulsan Bay. These results in Ulsan Bay were consistent with those of a previous study (Moon et al., 2008). There was a little of CB-77 contained in technical PCBs such as Aroclors 1016, 1242, 1248, and 1254 (Frame et al., 1996). In addition, CB-118 and CB-77 were related to volatilization from technical mixtures of PCBs (Masunaga et al., 2001). Therefore, it is evaluated that Ulsan Bay might use the technical products or there might be sources of CB-77.

On the other hand, the proportions of CB-81, CB-126, CB-169, and CB-189, related to thermal processes (Nieuwoudt et al., 2009), were very low in the four bays. This indicates that combustion sources near the four bays might not affect the profiles of PCBs in the sediments.

3.2.3 Source identification of PCBs

The first principal component and second principal component accounted for 32% and 15%, respectively (Figure 15). The PC1 was highly positively correlated with relatively lower chlorinate congeners such as CB-28, CB-52, CB-105, and CB-118. The PC2 was positively influenced by dioxin-like PCBs, and negatively influenced by indicator PCBs.

The sediment sampling sites BS1, BS2, BS10, US4, US6, and US14 were clustered with Aroclor 1260 and Aroclor 1262, widely used in transformers, hydraulic fluids, dedusting agents, and polyvinyl chlorides (Bedard and May, 1995). Besides, these sites were significantly characterized by higher chlorinated biphenyls of indicator-PCBs. Hence, PCBs contamination at these sites might originate from the commercial mixtures.

Meanwhile, the sediment samples collected from Gwangyang and Ulsan bays had higher PC2 scores than those of the other bays, and these samples were correlated with dioxin-like PCBs. These sites seemed to be more related to combustion than the technical PCBs (Aroclor) because the nonferrous metal complex is located in these sites of Ulsan Bay.

On the other hand, sediment samples in Busan and Jinhae bays had lower value of PC2 in the score plot and were characterized by indicator-PCBs such as CB-101, CB-118, and CB-52. Harbors and shipbuilding industries are located in these bays. It implies that shipping activity and shipbuilding industry might be the potential sources of PCBs in the bays.

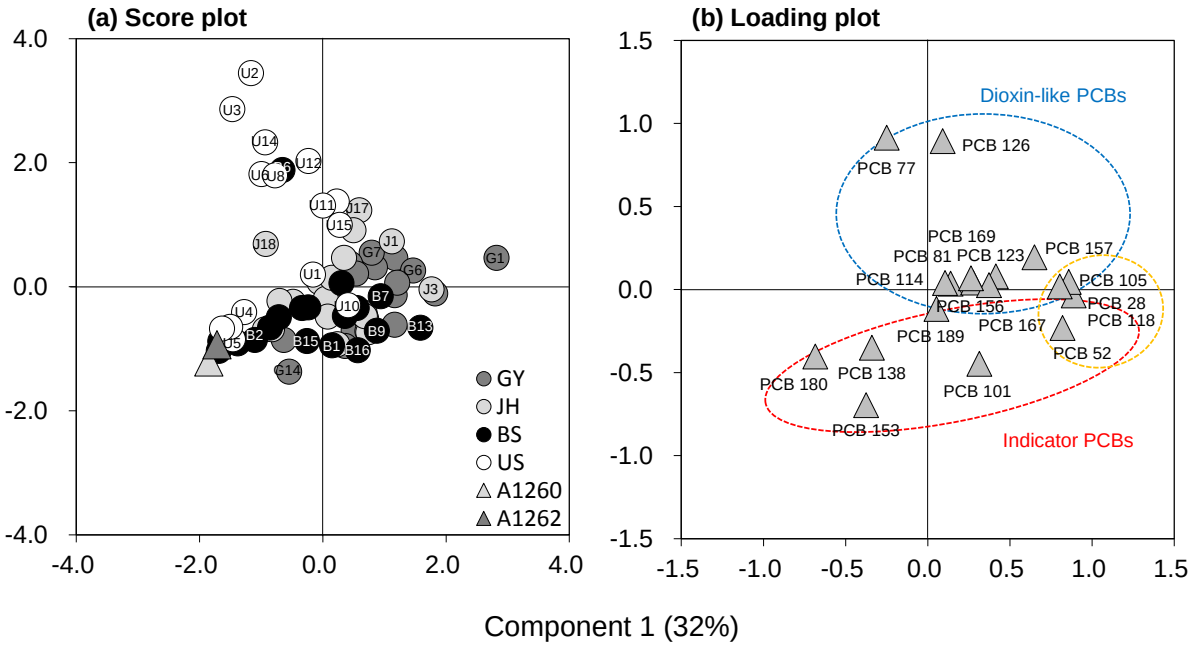


Figure 15. PCA results of PCBs in the sediment samples from the four bays: (a) score plot and (b) loading plot. A1260: Aroclor 1260; A1262: Aroclor 1262

3.2.4 TOC normalization concentration

TOC normalized concentrations of PCBs were in the range of 0.13–112.17 ng/g TOC (Figure 16). Similar to the concentration of PCBs, the highest TOC-normalized concentration of PCBs was found at US5 (1.2%). This site is located in harbor with automobile and petrochemical industries, leading to a direct inflow of PCBs.

In Busan Bay, the TOC-normalized concentration of PCBs at BS3 (45.82 ng/g TOC) decreased due to high organic carbon contents (2.6%). BS3 is semi-enclosed site and bounded by ocean current circulation. In addition, ship transportation and anchorages are common activities at BS3. Therefore, this sediment sample in this site might be affected by organic carbon contents rather than the local sources.

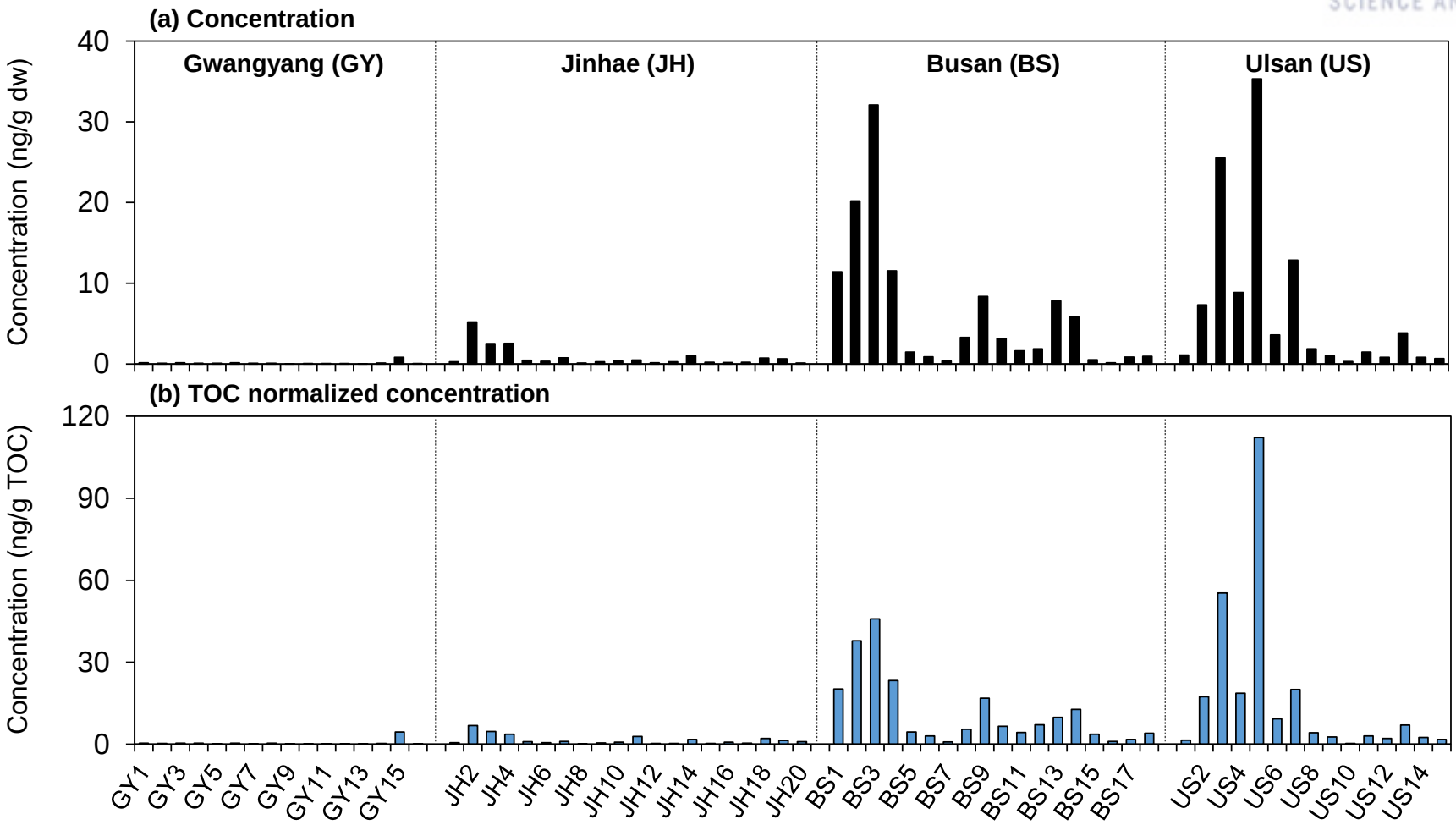


Figure 16. (a) Concentrations and (b) TOC-normalized concentrations of PCBs in the four bays.

3.3 Distribution of PCNs in sediments in industrial bays

3.3.1 Concentrations of PCNs

The concentrations of PCNs in four bays were in the range of 0.90–2628.15 pg/g dw, with a mean concentration of 84.54 pg/g dw (Figure 17 (a), Figure 23 and Table 10). The highest mean concentration of PCNs in the four bays was observed in the Busan Bay (275.55 pg/g dw), the largest harbor in Korea. Industrial complexes (including shipbuilding, textile, and nonferrous industries) located in Busan Bay might explain for this pattern. On the other hand, the concentrations of PCNs in the other bays were relatively lower.

In details, the highest concentration of PCNs was observed at BS5 (2628.15 pg/g dw), which was 2,000 times higher than the lowest concentration at GY13 (0.90 pg/g dw). BS5 is the site where the shipping activities frequently occur. The potential sources of PCNs might be shipment and shipbuilding due to leakage of paints containing PCNs or scrapping of old ships (Zhang et al., 2015). The concentrations of PCNs were low at all sites except for Busan Bay, suggesting that there might be specific sources of PCNs in Busan Bay.

There have been a few researches about PCNs in sediments in Korea, however, in comparison to other studies in different countries, the average concentrations of PCNs in the Canada (28900 pg/g dw) (Helm et al., 2008) and the Czech (1080 pg/g dw) (Kukučka et al., 2015) were higher than those of this study, whereas the average PCN concentration in the Pakistan (89.3 pg/g dw) (Mahmood et al., 2014) was lower (Table 11). However, the numbers of target congeners and sampling periods and locations are different among studies, it is difficult to make an accurate comparison.

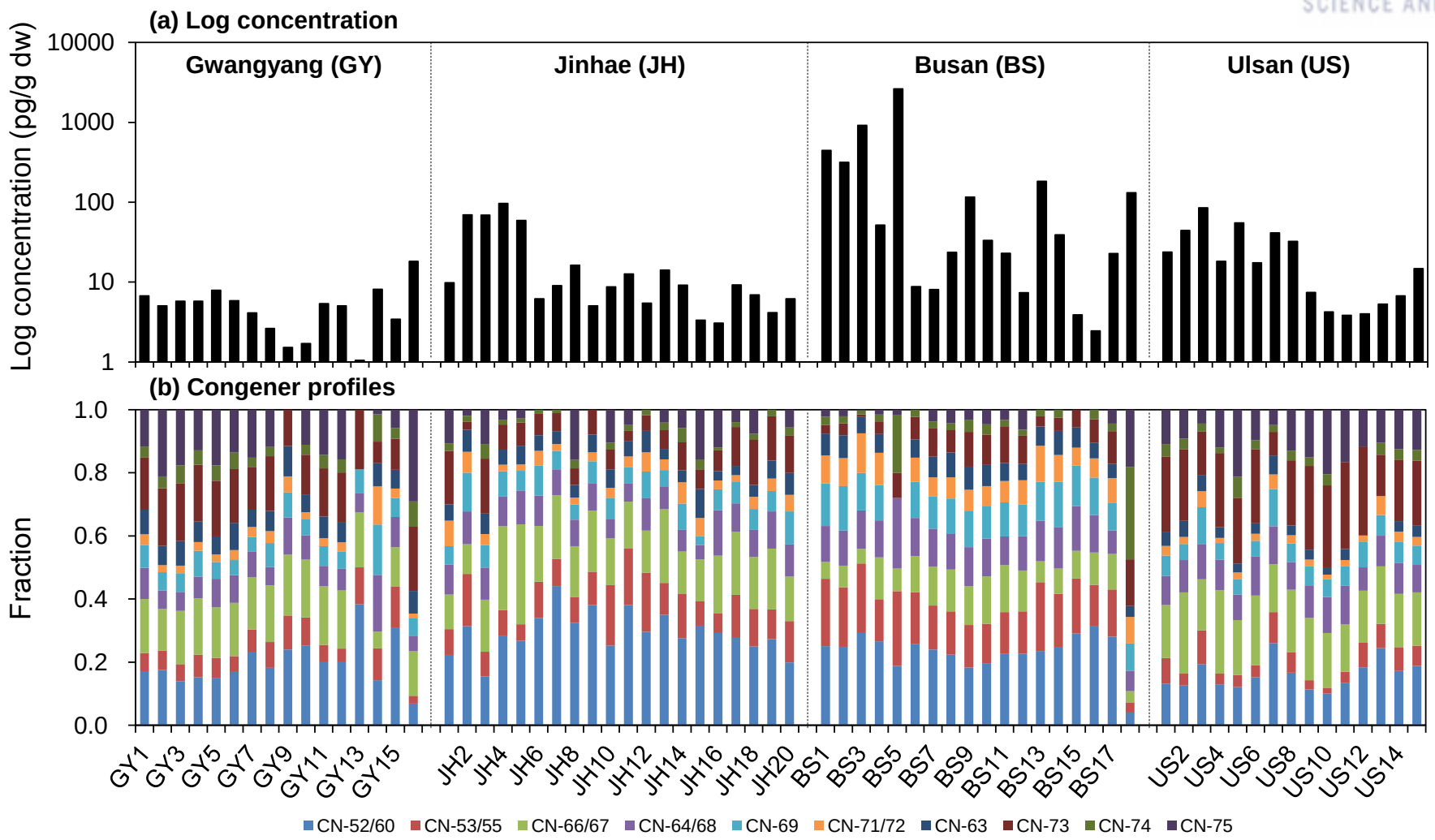


Figure 17. (a) Log concentrations and (b) Congener profiles of PCNs in the four bays.

Table 10. Concentrations of PCNs in sediment samples obtained from the four bays (unit: pg/g).

Congeners	Gwangyang	Jinhae	Busan	Ulsan
PCN 52/60	0.88 ± 0.30	5.78 ± 7.42	59.88 ± 127.04	4.05 ± 4.47
PCN 53/55	0.34 ± 0.17	2.17 ± 2.90	59.43 ± 149.14	1.64 ± 2.32
PCN 63	0.83 ± 0.57	4.19 ± 6.74	18.59 ± 43.75	4.54 ± 4.21
PCN 64/68	0.44 ± 0.36	2.02 ± 2.82	47.60 ± 137.57	2.46 ± 2.52
PCN 66/67	0.37 ± 0.34	1.65 ± 2.51	15.92 ± 28.57	1.86 ± 2.56
PCN 69	0.19 ± 0.22	0.77 ± 1.10	13.30 ± 27.65	0.80 ± 1.09
PCN 71/72	0.37 ± 0.30	1.17 ± 1.66	7.76 ± 13.09	1.00 ± 1.22
PCN 73	0.90 ± 0.83	1.81 ± 2.98	16.40 ± 48.43	4.48 ± 3.84
PCN 74	0.29 ± 0.36	0.48 ± 0.75	31.18 ± 112.30	0.81 ± 0.98
PCN 75	0.88 ± 1.24	1.10 ± 1.73	5.50 ± 11.74	2.57 ± 2.83
15 PCNs	5.49 ± 4.02	21.15 ± 27.82	275.55 ± 630.19	24.20 ± 23.50
PCNs (pg TEQ/g)	0.64 ± 0.21	0.02 ± 0.03	0.19 ± 0.40	0.03 ± 0.03

Table 11. Comparison of PCNs concentrations in sediment samples between this study and other studies.

Location	Sampling year	Congener	Concentration (pg/g dw)	Concentration (pg TEQ/g)	Reference
Gwangyang Bay (Korea)	2016	15[a)]	0.90-18.15	0.00-0.02	This study
Jinhae Bay (Korea)	2016	15[a)]	2.96-96.51	0.00-0.12	This study
Busan Bay (Korea)	2016	15[a)]	2.33-2628.15	0.00-1.69	This study
Ulsan Bay (Korea)	2016	15[a)]	3.84-84.86	0.01-0.11	This study
East River (China)	2009	63[b)]	600-4600000		(Zhang et al., 2015)
Baltic sea (Sweden)	1991-1992	38[c)]	270-2800	0.19-0.23	(Lundgren et al., 2003)
Barcelona (Spain)	2003	63[b)]	170-6560		(Castells et al., 2008)
River Chenab (Pakistan)	2013	39[d)]	8940-489000	0.1-57.1	(Mahmood et al., 2014)
Baltic sea (Sweden)	1989	38[c)]	140-760		(Järnberg et al., 1999)
Lake Kitaura (Japan)	2000	63[b)]	2-1300		(Horii et al., 2004)
Daliao River (China)	2007	39[d)]	33.1-284.4	0.008-0.28	(Zhao et al., 2011)
Lake Ontario (Canada)	2002	39[d)]	21000-38000		(Helm et al., 2008)

[a)]PCN-52/60, 53/55, 63, 66/67, 69, 71/72, 73, 74, 78, [b)]Tri-Octa-CNs, [c)]Tetra-hepta-CNs, [d)]Tetra-Octa-CNs

3.3.2 Congener profiles of PCNs

The congener patterns of PCNs in the four bays were also investigated (Figure 17 (b)). The most dominant congener was CN-52/60 (4-44%, mean: 23%), followed by CN-66/67 (4-32%, mean: 16%) and CN-73 (1-13%, mean: 13%). CN52/60 and CN-66/67 have been used as combustion indicators in many previous studies (Helm and Bidleman, 2003). Therefore, combustion at almost every sampling sites seemed to be an important source of PCNs. In particular, CN-73 accounted for more than 21% (mean value) of the total PCN concentrations in Ulsan Bay. In addition, CN-73 was known as a by-product of many technical PCBs mixtures (Yamashita et al., 2000). Therefore, concentrations of PCNs may increase at the sites where the technical PCB mixtures were used. CN71/72 accounted for 5% of the total PCN concentrations in the four bays, Since CN71/72 were known to be contained in commercial mixtures of PCNs such as Halowaxes (Meijer et al., 2001), the effect of halowaxes in the four bays seemed to be relatively small.

Compared to the other sites, we found the different profile at BS18, located in the outermost part of Busan Bay. Since there were no direct sources at this site, higher chlorinated naphthalenes, which has longer half time than lower chlorinated naphthalenes, were abundant.

3.3.3 Source identification of PCNs

PC1 and PC2 explained 35% and 21% of the total variance, respectively (Figure 18). Ulsan, Gwangyang bays and the sites of Jinhae Bay seemed to be clustered by technical mixtures of PCBs (Aroclor and Kanechlor), characterized by CN-64/68, CN-63, CN-66/67 and CN-69. This indicates that the PCNs might be produced as by-products of the PCBs technical mixtures.

Busan Bay was classified as the same group in the sites of Jinhae bay, and PC1 and PC2 values are low in these bays. There are various industrial complexes such as shipbuilding, automobile, and petrochemical industries. Therefore, these bays might be influenced by relatively lower chlorinated congeners.

In the score plot, US6, US10, US14, and BS13 which had low PC1 value and high PC2 value, were correlated with PCN technical mixtures "Halowax 1051". These sites were featured by higher chlorinated naphthalenes.

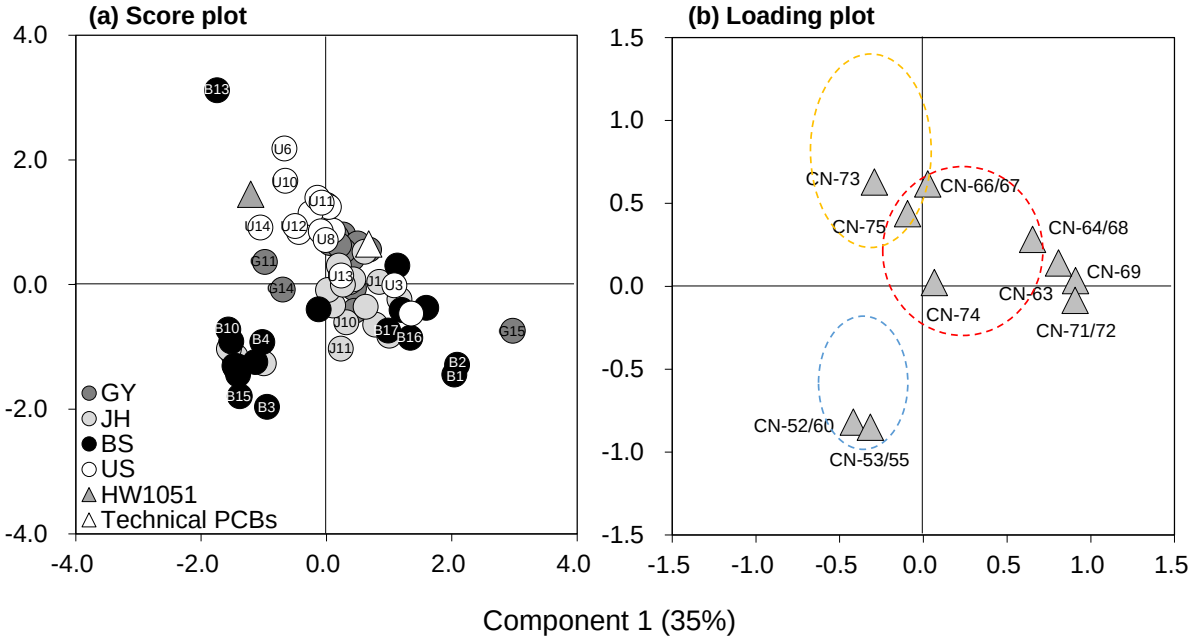


Figure 18. PCA results of PCNs in the sediment samples from the four bays: (a) score plot and (b) loading plot. HW1051: Halowax 1051; Technical PCBs: Aroclor and Kanechlor

Diagnostic ratio analysis was conducted to determine the potential sources of PCNs in the sediment samples of the four bays (Figure 19). The potential sources of PCNs can be evaluated using the ratio analysis between individual PCN congeners (Noma et al., 2004; Wang et al., 2012a; Yamashita et al., 2000). CN-66/67 are released by combustion and thermal processes from industrial complexes and CN-71/72 are mainly contained in Halowax 1014 (Helm and Bidleman, 2003; Meijer et al., 2001). The mean diagnostic concentration ratios of CN66/67 to CN71/72 in the four bays were 4.43 (Gwangyang Bay), 5.44 (Jinhae Bay), 1.40 (Busan Bay), and 5.71 (Ulsan Bay). It indicates that the main source of PCNs in Busan Bay might be technical PCBs mixtures.

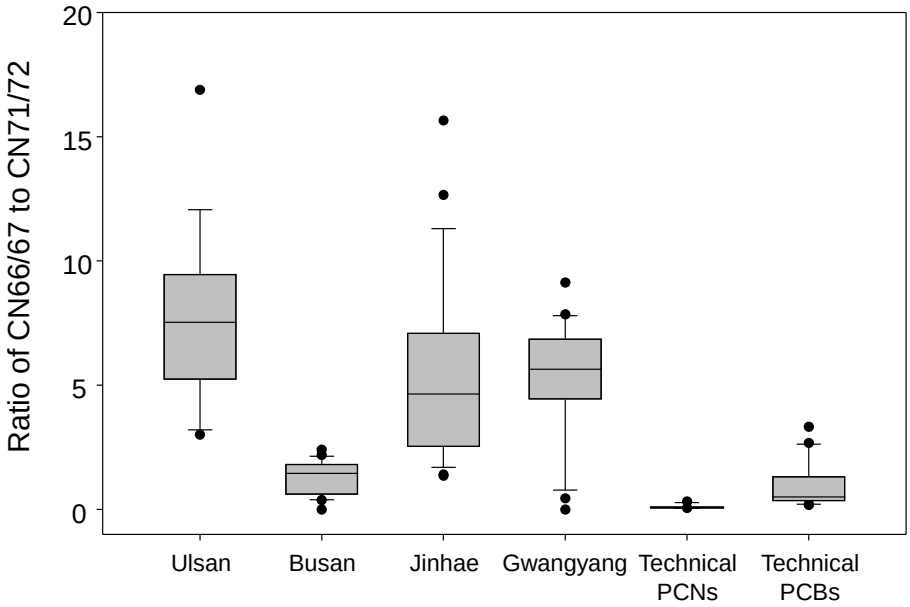


Figure 19. Diagnostic ratios of PCN congeners in the four bays and technical mixtures

3.3.4 TOC normalization concentration

TOC normalized concentrations of PCNs varied from 0.00 to 7.90 ng/g TOC in the four bays (Figure 20 (b)). The highest TOC-normalized concentration was observed at BS5 (7.9 ng/g TOC), located near the North Harbor of Busan Bay. BS5 (with TOC value of 1.2%) is semi-enclosed site and bounded by ocean current circulation. In addition, BS5 is located in small shipbuilding industrial complexes. Therefore, it implies that there might be stationary PCNs sources rather than organic carbon contents.

However, the distribution of TOC-normalized PCNs concentrations was similar to those of PCNs. It indicates that the levels of PCNs might be influenced more by the sources than organic carbon contents.

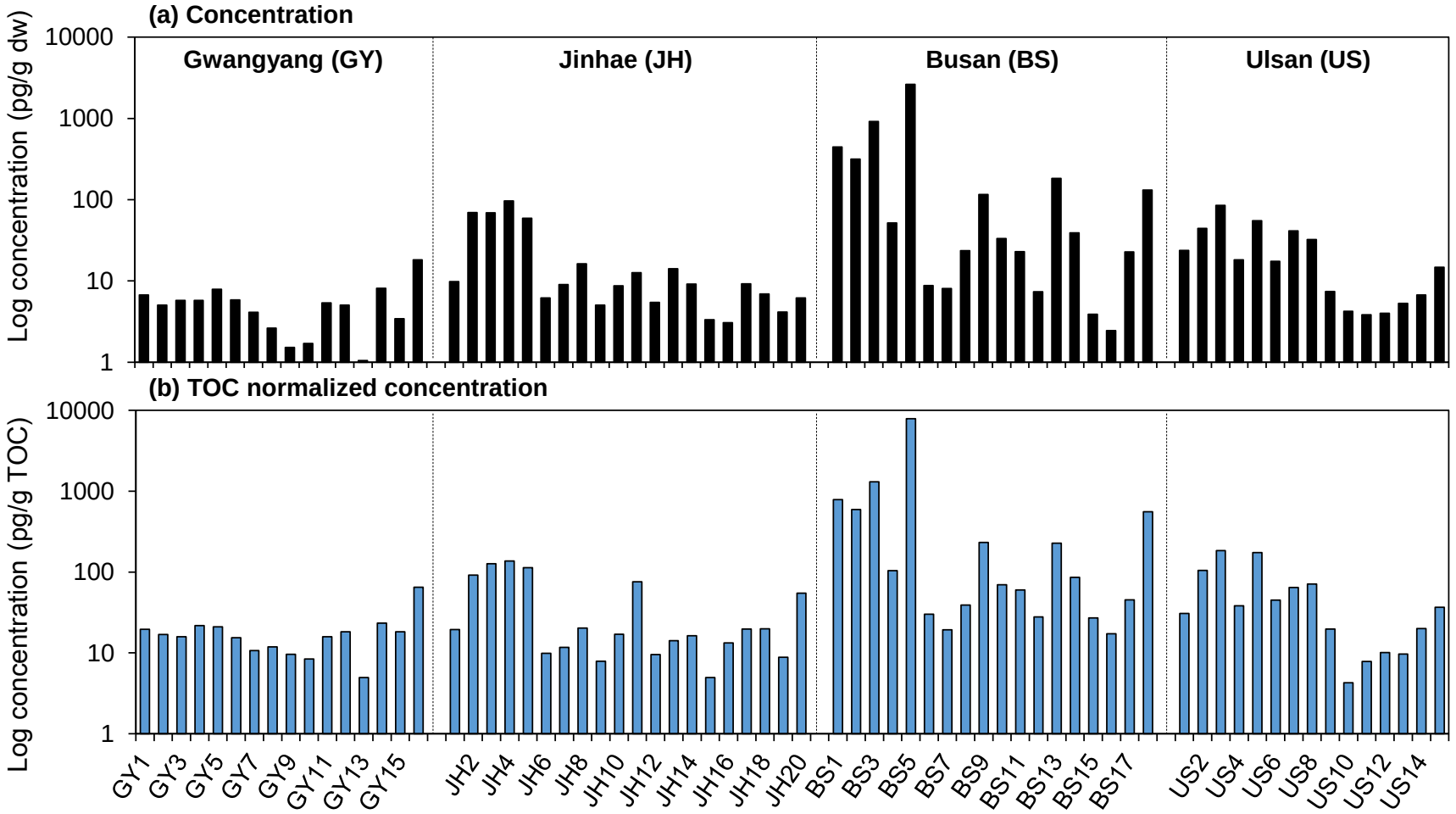


Figure 20. (a) Concentrations and (b) TOC-normalized concentrations of PCNs in the four bays.

3.3.5 Full congener analysis

For additional analysis of 14 sediment samples (3 Gwangyang, 3 Jinhae, 4 Busan, 4 Ulsan), the highest concentration was observed at BS5 (9.76 ng/g dw), followed by BS3 (9.60 ng/g dw), BS13 (3.86 ng/g dw) (Figure 21 (a)). The mean concentrations of PCNs in Busan Bay were much higher than those of the other bays. This implies that there might be potential sources of PCNs in Busan Bay. The concentration distribution of PCNs full congener was almost similar to those of 15 PCNs, except for BS3. The concentration of PCNs full congener at BS3 was higher than that of 15 PCN congeners because the high concentration of lower chlorinated congeners were observed.

For congener profiles (Figure 21 (b)), tetra-CNs and penta-CNs were predominant species, accounting for 29% and 22% of the total PCNs concentrations in the four bays sediment, repectively. In particular, CN-24 was dominant in tri-CNs (about 50%), and this congener was associated with wood and coal burning (Lee et al., 2005; Wang et al., 2012a; Xu et al., 2015). It is evaluated that the four bays might be affected by wood and coal burning.

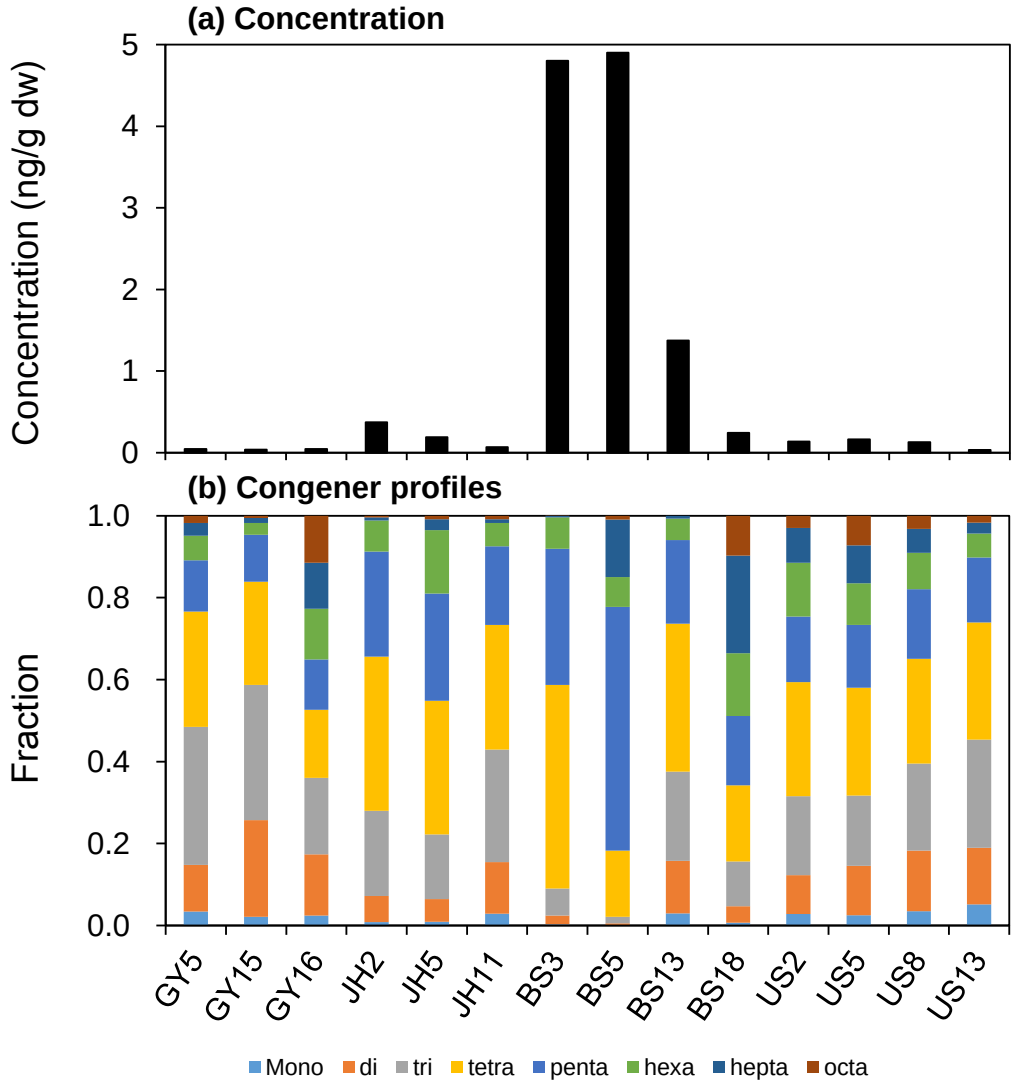


Figure 21. (a) Concentrations and (b) Congener profiles for the 14 sediment samples.

Ratio analysis was performed using the combustion indicators (CN 17/25, CN 36/45, CN 39, CN 35, CN 52/60, CN 50, CN 51, CN 54 and CN 66/67) reported in previous studies (Noma et al., 2004; Wang et al., 2012b; Yamashita et al., 2000). The ratio of the concentrations of combustion indicator PCNs to PCN concentrations (tri-octa) was used to evaluate the major sources of PCNs. If the concentration ratio is more than 0.5, the source of PCNs is related to combustion. On the contrary, when the concentration ratio is lower than 0.11, technical mixtures of PCNs, halowaxes, are the major sources. When the ratio is between 0.11 and 0.5, it is affected by both combustion and halowax mixtures.

The ratio of combustion indicator PCN concentrations to total PCN concentrations for the 14 samples ranged from 0.10 to 0.39, and the mean value was 0.20 (Figure 22). Most of the samples were influenced by mixed combustion sources and halowax mixtures except for BS18. The ratio was 0.1 at BS18, located in the outer bay compared with other sites, indicating that technical mixtures of PCNs might be the major sources of PCNs.

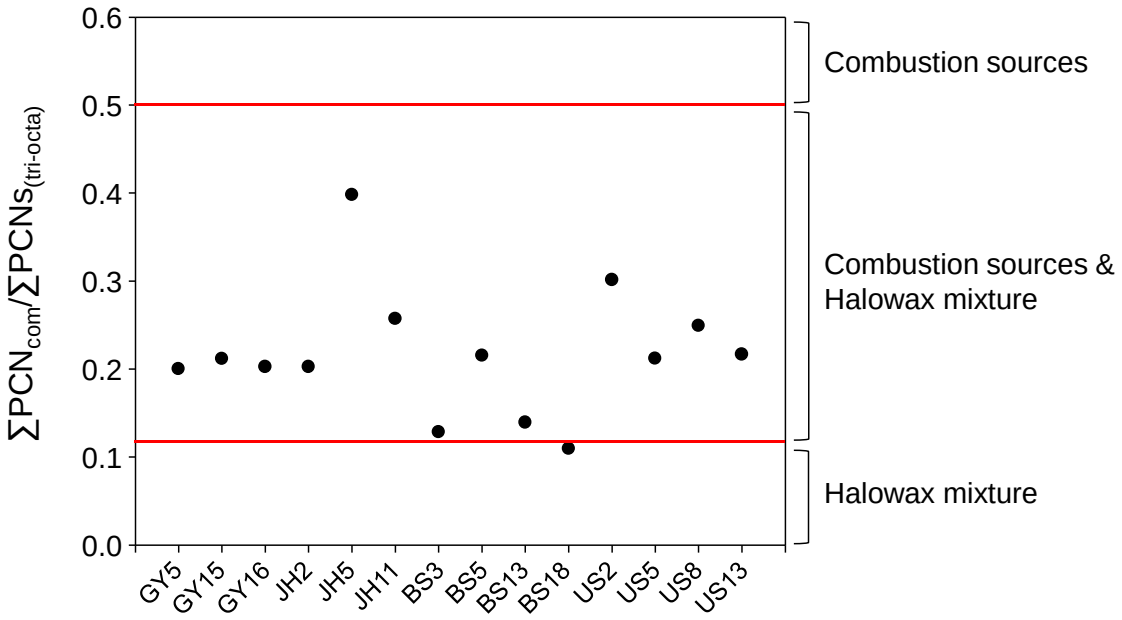


Figure 22. Ratios of $\sum PCN_{com}/\sum PCN$ in the 14 sediment samples.

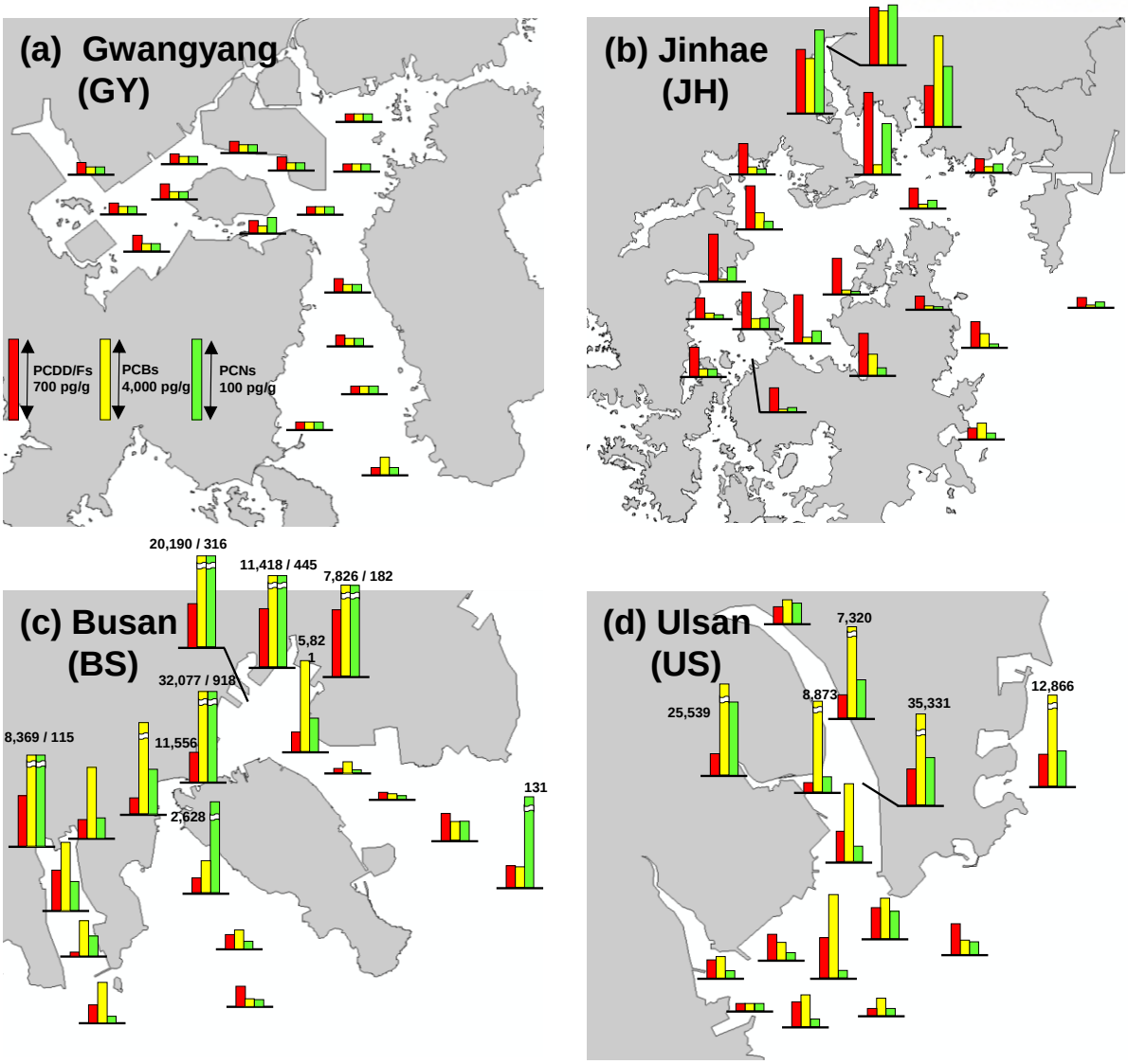


Figure 23. Spatial distribution of PCDD/Fs, PCBs, and PCNs concentrations (pg/g dw) sediments from (a) Gwangyang Bay, (b) Jinhae Bay, (c) Busan Bay, and (d) Ulsan Bay.

3.4 TEQ concentration

TEQ concentrations were calculated using WHO 2005 TEF values. The TEQ concentration of PCDD/Fs, dioxin-like PCBs, and dioxin-like PCNs in the sediments from the four bays are shown in Figure 24. The highest mean TEQ concentration was observed in Jinhae Bay (4.75 pg TEQ/g dw) because of the high concentration of PCDD/Fs. Masan Bay, the inner part of Jinhae Bay, showed high concentrations because this bay is an enclosed bay. In particular, JH5 (19.80 pg TEQ/g dw) in Masan Bay showed the highest TEQ concentration due to its location near the wastewater treatment plant for various industrial complexes. Busan (3.97 pg TEQ/g dw) and Ulsan (3.97 pg TEQ/g dw) bays showed similar mean concentrations, whereas Gwangyang Bay (0.83 pg TEQ/g dw) was found in relatively low concentration. The concentration of Jinhae Bay except for Masan Bay was 2.31 pg TEQ /g, which was lower than those of Busan and Ulsan bays.

In Gwangyang and Jinhae Bays, PCDD/Fs were dominant in the TEQ concentrations (Figure 25). However, PCN concentrations at BS5 constituted over half of TEQ concentrations, and PCBs were comprised of about 40% of TEQ concentrations in the Ulsan Bay. These patterns seem to be influenced by the unique characteristics of each industrial complex in the bays.

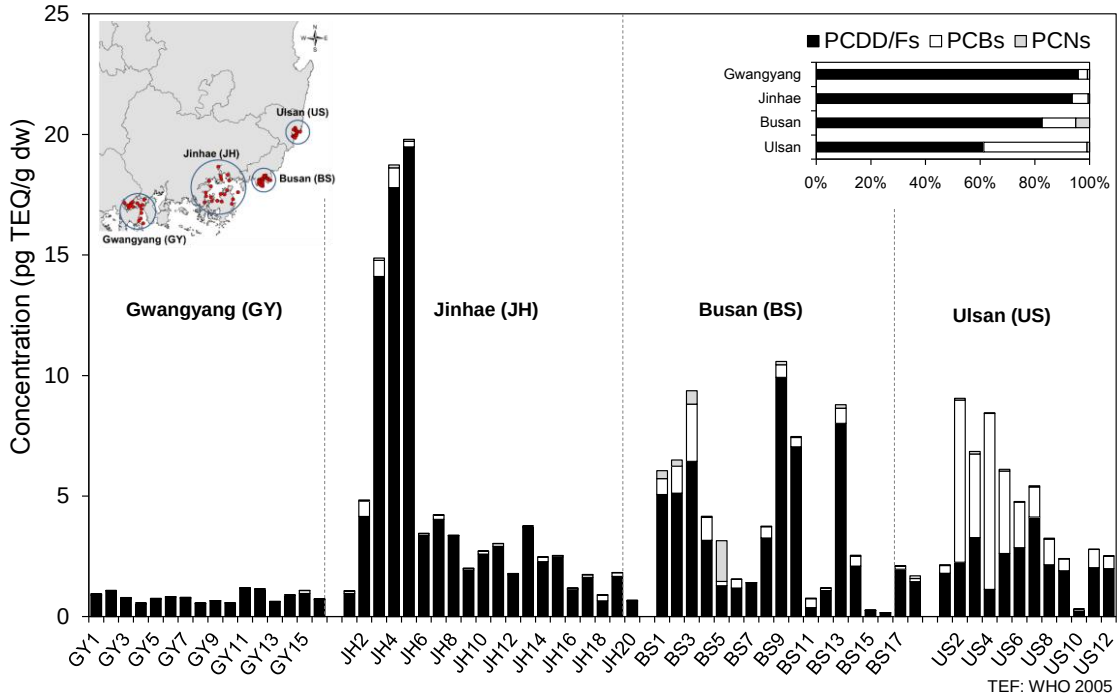


Figure 24. TEQ concentrations of PCDD/Fs, PCBs, and PCNs in the four bays

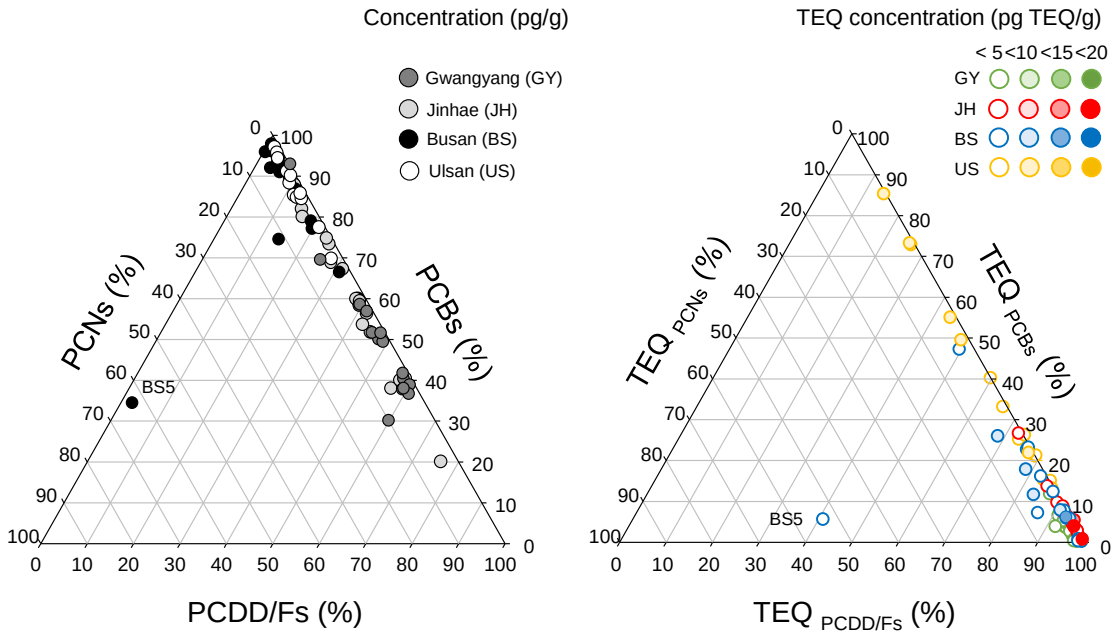


Figure 25. Ternary plot of concentration of PCDD/Fs, PCBs, and PCNs in the sediments of the four bays (a) Concentrations (pg/g), (b) TEQ concentrations (pg TEQ/g)

Interim sediment quality guidelines (ISQGs) of Canadian Sediment Quality Guidelines (CSQGs) was 0.85 pg TEQ/g, and Probable effect level (PELs) of CSQGs was 2.50 pg TEQ/g (CCME, 2002). In this study, the TEQ concentrations of PCDD/Fs were higher than ISQGs of CSQGs. Besides, the TEQ concentration of PCDD/Fs at JH5 (21.58 pg TEQ/g) was also higher than PEL of CSQGs. However, this site is located near the wastewater treatment plant, which seems to be contaminated by effluent discharge. Therefore, the negative impact of PCDD/Fs on organism might be not considerable in almost all sampling sites except for JH5.

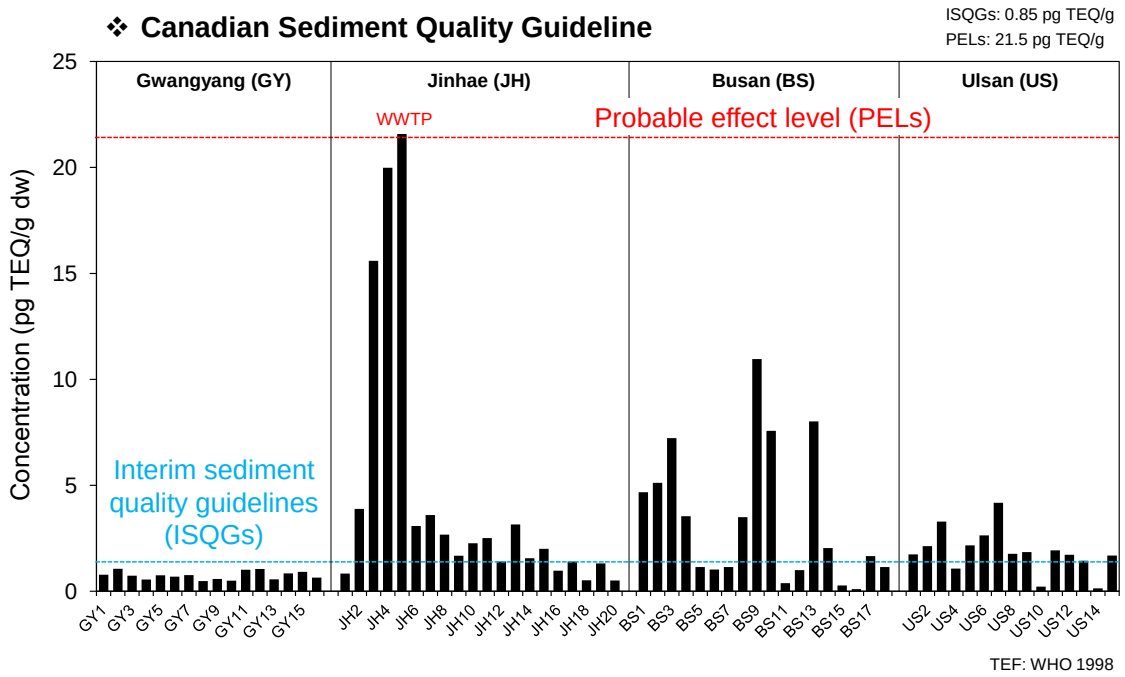


Figure 26. TEQ concentrations of PCDD/Fs in the four bays

3.5 Correlation analysis with TOC

The correlation analysis between PCDD/F, PCB, and PCN concentrations in surface sediments and TOC were examined using Spearman correlation analysis (Table 12-15). TOC ranged from 0.41% to 3.67%. TOC contents were significantly positively correlated with the concentrations of PCDD/Fs (R^2=0.323), PCBs (R^2=0.029), PCNs (R^2=0.062) in surface sediment of the four bays.

In addition, we investigated the relationships between PCDD/F, PCB, and PCN concentrations and TOC for each bay (Figure 27-28). The PCDD/F, PCB, and PCN concentrations in Gwangyang, Jinhae, and Busan bays showed positive correlation with TOC. However, no significant correlation was found between levels of PCDD/Fs, PCBs, and PCNs and TOC in Ulsan Bay. This pattern can be explained by that the sediment samples of Ulsan Bay included 6 river sediments (US1-US6), which are relatively coarse-grained sediment compared with marine sediments.

TOC showed negative correlations with the concentrations of PCDD/Fs (R^2=-0.94, $p<0.01$), PCBs (R^2=-0.49, $p<0.01$), and PCNs (R^2=-0.14, $p<0.01$) in river sediments of Ulsan Bay. On the other hand, the correlations between TOC and the concentrations of PCDD/Fs (R^2=0.42, $p<0.05$), PCBs (R^2=0.27, $p<0.05$), and PCNs (R^2=-0.02, $p<0.05$) in marine sediments of Ulsan Bay were higher than those in river sediments. Thus, the size of the particles is evaluated to affect the correlation between TOC and concentrations of these compounds.

Table 12. Spearman correlation analysis between the PCDD/F concentrations and TOC.

	TOC	2378-TCDD	12378-PCDD	123478-HxCDD	123678-HxCDD	123789-HxCDD	1234678-HpCDD	OCDD	2378-TCDF	12378-PCDF	23478-PCDF	123478-HxCDF	123678-HxCDF	123789-HxCDF	234678-HxCDF	1234678-HpCDF	1234789-HpCDF	OCDF
TOC	1																	
2378-TCDD	0.069	1																
12378-PCDD	0.672**	0.152	1															
123478-HxCDD	0.660**	0.280*	0.922**	1														
123678-HxCDD	0.721**	0.166	0.960**	0.936**	1													
123789-HxCDD	0.715**	0.223	0.919**	0.920**	0.966**	1												
1234678-HpCDD	0.690**	0.165	0.934**	0.939**	0.966**	0.965**	1											
OCDD	0.636**	0.047	0.798**	0.808**	0.848**	0.868**	0.925**	1										
2378-TCDF	0.686**	0.168	0.944**	0.926**	0.969**	0.931**	0.949**	0.819**	1									
12378-PCDF	0.727**	0.218	0.951**	0.951**	0.979**	0.967**	0.956**	0.825**	0.969**	1								
23478-PCDF	0.666**	0.129	0.924**	0.912**	0.953**	0.910**	0.931**	0.798**	0.975**	0.947**	1							
123478-HxCDF	0.719**	0.202	0.954**	0.953**	0.979**	0.958**	0.959**	0.837**	0.964**	0.986**	0.946**	1						
123678-HxCDF	0.709**	0.167	0.950**	0.944**	0.977**	0.945**	0.949**	0.816**	0.973**	0.981**	0.975**	0.984**	1					
123789-HxCDF	0.693**	0.142	0.930**	0.930**	0.957**	0.915**	0.935**	0.802**	0.972**	0.955**	0.981**	0.961**	0.983**	1				
234678-HxCDF	0.697**	0.145	0.916**	0.925**	0.946**	0.897**	0.923**	0.791**	0.963**	0.943**	0.964**	0.955**	0.969**	0.976**	1			
1234678-HpCDF	0.701**	0.193	0.937**	0.947**	0.956**	0.935**	0.953**	0.828**	0.953**	0.963**	0.950**	0.975**	0.983**	0.973**	0.954**	1		
1234789-HpCDF	0.677**	0.161	0.914**	0.916**	0.929**	0.904**	0.923**	0.790**	0.931**	0.932**	0.940**	0.951**	0.964**	0.962**	0.940**	.984**	1	
OCDF	0.298*	0.382**	0.522**	0.523**	0.477**	0.516**	0.537**	0.399**	0.503**	0.524**	0.484**	0.531**	0.535**	0.520**	0.491**	.618**	.636**	1

**Correlation is significant at the 0.01 level (2-tailed) and *Correlation is significant at the 0.05 level (1-tailed)

Table 13. Spearman correlation analysis between the PCB concentrations and TOC.

	TOC	PCB 28	PCB 52	PCB 77	PCB 81	PCB 101	PCB 105	PCB 114	PCB 118	PCB 123	PCB 126	PCB 138	PCB 153	PCB 156	PCB 157	PCB 167	PCB 169	PCB 180	PCB 189
TOC	1																		
PCB 28	0.438**	1																	
PCB 52	0.442**	0.940**	1																
PCB 77	0.289*	0.780**	0.768**	1															
PCB 81	0.290*	0.754**	0.669**	0.559**	1														
PCB 101	0.474**	0.936**	0.951**	0.804**	0.712**	1													
PCB 105	0.428**	0.948**	0.931**	0.842**	0.754**	0.973**	1												
PCB 114	0.435**	0.836**	0.830**	0.748**	0.797**	0.891**	0.898**	1											
PCB 118	0.473**	0.950**	0.947**	0.831**	0.740**	0.989**	0.986**	0.897**	1										
PCB 123	0.433**	0.928**	0.931**	0.821**	0.709**	0.957**	0.959**	0.875**	0.965**	1									
PCB 126	0.441**	0.862**	0.854**	0.891**	0.719**	0.903**	0.907**	0.868**	0.926**	0.882**	1								
PCB 138	0.419**	0.929**	0.932**	0.844**	0.716**	0.987**	0.982**	0.901**	0.980**	0.960**	0.902**	1							
PCB 153	0.442**	0.933**	0.930**	0.794**	0.709**	0.985**	0.957**	0.881**	0.969**	0.957**	0.883**	0.982**	1						
PCB 156	0.429**	0.926**	0.919**	0.859**	0.727**	0.973**	0.984**	0.901**	0.975**	0.952**	0.906**	0.993**	0.968**	1					
PCB 157	0.448**	0.939**	0.926**	0.851**	0.738**	0.979**	0.988**	0.899**	0.985**	0.952**	0.923**	0.989**	0.968**	0.992**	1				
PCB 167	0.475**	0.937**	0.929**	0.838**	0.735**	0.983**	0.976**	0.902**	0.985**	0.963**	0.920**	0.984**	0.975**	0.983**	0.988**	1			
PCB 169	0.336**	0.379**	0.380**	0.503**	0.342**	0.427**	0.403**	0.413**	0.443**	0.382**	0.525**	0.390**	0.380**	0.385**	0.397**	0.424**	1		
PCB 180	0.413**	0.896**	0.904**	0.809**	0.663**	0.966**	0.949**	0.862**	0.947**	0.935**	0.870**	0.977**	0.973**	0.966**	0.962**	0.962**	0.355**	1	
PCB 189	0.449**	0.913**	0.912**	0.787**	0.722**	0.970**	0.946**	0.895**	0.957**	0.942**	0.885**	0.967**	0.972**	0.958**	0.958**	0.976**	0.395**	0.959**	1

**Correlation is significant at the 0.01 level (2-tailed)

Table 14. Spearman correlation analysis between the PCN concentrations and TOC.

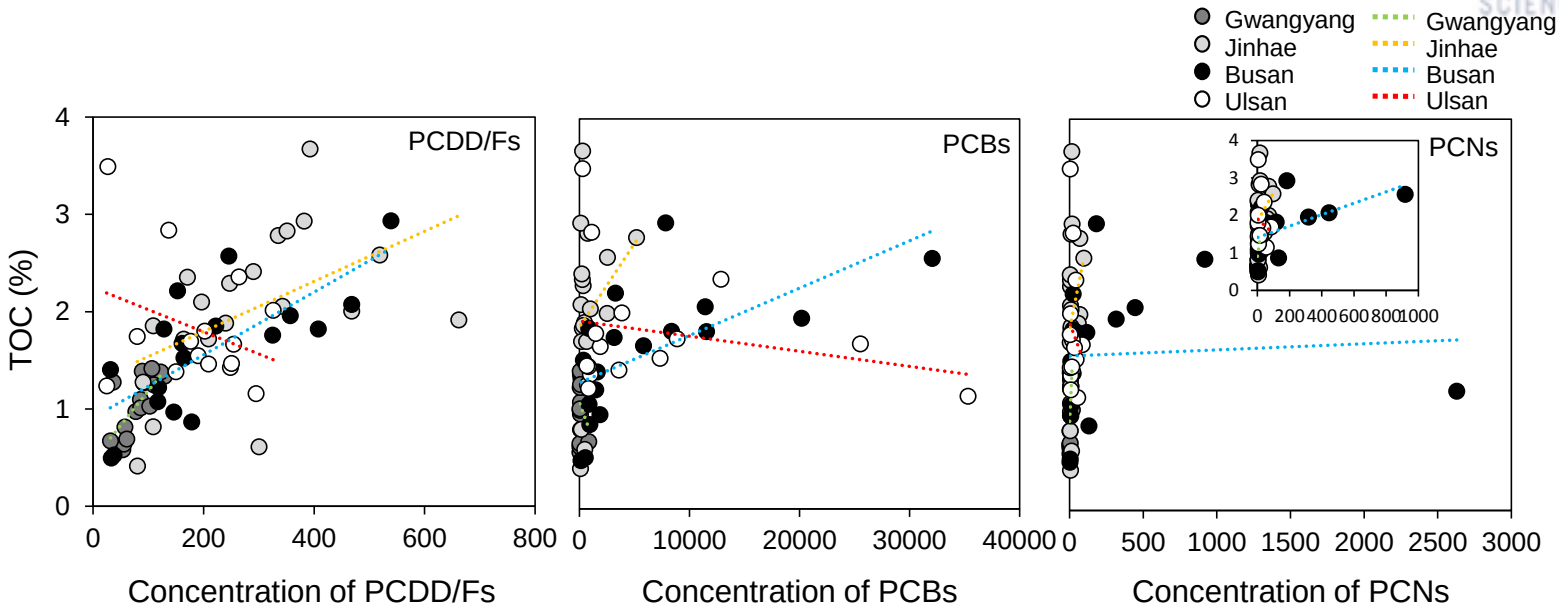
	TOC	CN-52/60	CN-53/55	CN-66/67	CN-64/68	CN-69	CN-71/72	CN-63	CN-73	CN-74	CN-75
TOC	1										
CN-52/60	0.519**	1									
CN-53/55	0.429**	0.960**	1								
CN-66/67	0.487**	0.920**	0.849**	1							
CN-64/68	0.438**	0.933**	0.907**	0.920**	1						
CN-69	0.427**	0.850**	0.862**	0.810**	0.883**	1					
CN-71/72	0.453**	0.851**	0.865**	0.757**	0.856**	0.958**	1				
CN-63	0.407**	0.813**	0.803**	0.807**	0.835**	0.935**	0.914**	1			
CN-73	0.331**	0.719**	0.666**	0.875**	0.833**	0.706**	0.630**	0.700**	1		
CN-74	0.320**	0.815**	0.789**	0.881**	0.878**	0.791**	0.770**	0.834**	0.871**	1	
CN-75	0.215	0.533**	0.461**	0.724**	0.618**	0.488**	0.429**	0.565**	0.838**	0.773**	1

**Correlation is significant at the 0.01 level (2-tailed)

Table 15. Spearman correlation analysis between the PCDD/F, PCB, and PCN concentrations and TOC.

	TOC	PCDD/Fs	PCDD/Fs (TEQ)	dl-PCBs	Indicator-PCBs	PCBs	dl-PCBs (TEQ)	PCNs	PCNs (TEQ)
TOC	1								
PCDD/Fs	0.666**	1							
PCDD/Fs (TEQ)	0.694**	0.928**	1						
dl-PCBs	0.397**	0.498**	0.603**	1					
Indicator-PCBs	0.449**	0.542**	0.652**	0.964**	1				
PCBs	0.436**	0.526**	0.639**	0.977**	0.996**	1			
dl-PCBs (TEQ)	0.447**	0.524**	0.631**	0.957**	0.905**	0.921**	1		
PCNs	0.452**	0.584**	0.667**	0.697**	0.724**	0.723**	0.685**	1	
PCNs (TEQ)	0.419**	0.542**	0.627**	0.712**	0.709**	0.715**	0.710**	0.984**	1

**Correlation is significant at the 0.01 level (2-tailed)



Gwangyang

	TOC	PCDD/Fs	PCBs	PCNs
TOC	1			
PCDD/Fs	0.71**	1		
PCBs	0.48*	0.26	1	
PCNs	0.66**	0.52*	0.45*	1

Jinhae

	TOC	PCDD/Fs	PCBs	PCNs
TOC	1			
PCDD/Fs	0.64*	1		
PCBs	0.20	0.51*	1	
PCNs	0.34	0.70**	0.50*	1

Busan

	TOC	PCDD/Fs	PCBs	PCNs
TOC	1			
PCDD/Fs	0.73**	1		
PCBs	0.74**	0.58*	1	
PCNs	0.59**	0.59*	0.73**	1

Ulsan

	TOC	PCDD/Fs	PCBs	PCNs
TOC	1			
PCDD/Fs	-0.09	1		
PCBs	-0.01	0.43	1	
PCNs	-0.11	0.20	0.73**	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

Figure 27. Correlation analysis between TOC and the concentrations of PCDD/Fs, PCBs, and PCNs for each bay.

Inner bay of Ulsan

	TOC	PCDD/Fs	PCBs	PCNs
TOC	1			
PCDD/Fs	-0.94**	1		
PCBs	-0.49	0.31**	1	
PCNs	-0.14	0.20*	0.66	1

Outer bay of Ulsan

	TOC	PCDD/Fs	PCBs	PCNs
TOC	1			
PCDD/Fs	0.42	1		
PCBs	0.27	0.73*	1	
PCNs	-0.02	0.40	0.33	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

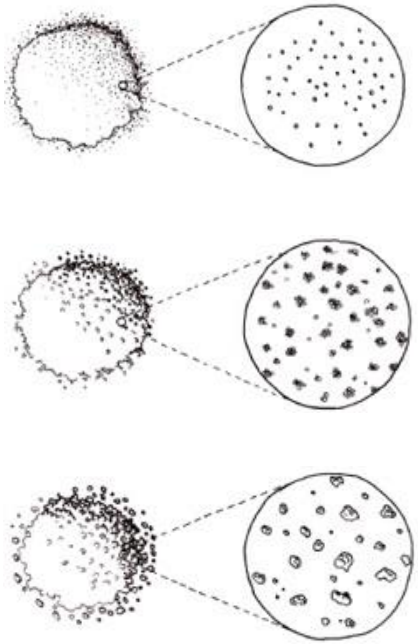


Figure 28. Correlation analysis between TOC and the concentrations of PCDD/Fs, PCBs, and PCNs for the inner and outer parts of Ulsan Bay.

IV. Conclusions

In this study, the concentration distributions and potential sources of PCDD/Fs, PCBs, and PCNs in the sediments samples of the representative industrial bay (Gwangyang, Jinhae, Busan, and Ulsan bays) in Korea were investigated. The target compounds were 17 PCDD/Fs, 18 PCBs, and 15 PCNs (75 PCNs for 14 sediment samples). The main results can be summarized as follows.

1. The concentrations of PCDD/Fs in the sediment samples ranged from 0.02 to 0.66 ng/g dw , the highest concentration was observed in Jinhae Bay (0.28 ng/g dw), followed by Busan Bay, Ulsan Bay, and Gwangyang Bay. In almost all sediment samples, OCDD with low solubility and low photodegradation was the most abundant congener due to wet and dry deposition and the use of agricultural pesticides (PCP and CNP) in the past. On the other hand, PCDFs, produced during the thermal process, showed high concentrations at the sites of Gwanyang Bay in the vicinity of steel manufacturing facility.

2. The concentrations of PCBs in the sediment samples varied from 0.03 to 35.33 ng/g dw, the concentrations in Ulsan Bay (7.03 ng/g dw) were the highest among the four bays. The high PCB concentrations were found in the harbor, shipbuilding, and automobile industrial areas. PCB-153, PCB-180, and PCB-138 were dominant in the four bays. This pattern of PCB concentrations at several sites in Ulsan and Busan bays might be related to technical PCBs such as Aroclor 1260 and Aroclor 1262, commonly used in transformer, hydraulic fluids, synthetic resins, dedusting agent, and polyvinyl chloride.

3. The mean concentrations of PCNs had the highest value in the Busan Bay (0.28 ng/g dw) among the southeastern bays. The concentrations of PCNs were significantly high at BS5 (2.63 ng/g dw), having a harbor and a small shipbuilding industry. CN-52/60 was associated with combustion, and accounted for 23% of the 15 PCN concentrations in most sites of the four bays. In general, Halowax 1051, a technical mixture of PCNs, showed similar profiles in Ulsan Bay.

4. TEQ concentrations were in the range of 0.16-19.80 pg TEQ/g dw, with a mean value of 3.47 pg TEQ/g dw. The TEQ concentrations were lower than those of previous studies collected from coastal sediments in South Korea, and were comparable to those of the other country sediments.

5. TOC content was positively correlated with the concentrations of PCDD/Fs, PCBs, and PCNs in the four bays, apart from Ulsan Bay. The concentrations of PCDD/Fs, PCBs, and PCNs in

Ulsan Bay had relatively low correlation with TOC due to the coarse particles from river sediments.

6. The concentrations of PCDD/Fs, PCBs, and PCNs in the inner part were higher than those in the outer part because industrial complexes (petrochemical, nonferrous metal mining, shipbuilding, and steel manufacturing) are located in the inner bays. It seems that the major sources of PCDD/Fs, PCBs, and PCNs might be from industrial processes.

This has been, so far, the first research about the concentration distributions of PCDD/Fs, PCBs, and PCNs simultaneously in the representative industrial bays (Gwangyang, Jinhae, Busan, and Ulsan bays) in South Korea. This study can be useful as basic data for establishment of environmental management system for dioxin like compounds in marine environment in southeastern industrial bays of Korea in the future.

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