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Levels and Patterns of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Sediments from Korean Coast

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Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) were measured in sediment samples from 19 stations in the coastal areas of Korea from February to July 2000. PCDDs and PCDFs were detected in all sediment samples. The concentrations of these contaminants ranged from 18.2 to 804.0 pg/g dry weight and I-TEQ concentrations varied from 0.1 to 5.5 pg/g dry weight. Examination of homologue groups showed that octachlorinated dibenzo-*p*-dioxin (OCDD) was predominant congener in Korean coast. This pattern was similar to homologue profiles of marine sediments in which the main source of PCDDs/DFs was derived from the atmospheric deposition of particulate matters generated from various industrial activities. Grain size and total organic carbon (TOC) distribution are one of the important factors governing PCDDs/DFs concentration in this study.

Key words: PCDDs, PCDFs, I-TEQ, OCDD, Grain size, TOC

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of tricyclic compounds substituted with one to eight chlorine atoms (Fig. 1). This results in 210 different compounds: 75 PCDDs and 135 PCDFs. Seventeen congeners are more toxic than the others. All of these toxic congeners have chlorine atoms at the 2, 3, 7, and 8 positions. PCDDs and PCDFs are very stable chemicals and have very long residence times in the environment and in organisms, including human. Their hydrophobicity promotes an accumulation in sediments and organisms, resulting in high concentrations in both sediments and organisms. In the substantial number of studies, the effects of PCDDs and PCDFs on various animals are determined. Among toxicological effects reports are teratogenicity, reducing reproduction, liver toxicity, decreased growth rate and behavioral changes (Courtney and Moore, 1971; Zeise et al., 1990; Huff, 1992). PCDDs/DFs are inadvertently produced from various combustion sources and manufacturing processes, such as municipal solid waste incineration (Olie et al., 1977), motor vehicles (Marklund et al., 1987), steel mills (Tsyklind et al., 1989), and chemical production processes (Hutzinger et al., 1985). These contaminants are mainly transported to the aquatic systems through the atmospheric deposition or directly via rivers. Since PCDDs/DFs and other hydrophobic organic microcontaminants tend to be strongly associated with particulate matter, their final sink is thought to be the bottom sediments (Dannenberg et al., 1997). Therefore, sediment is a deposition place

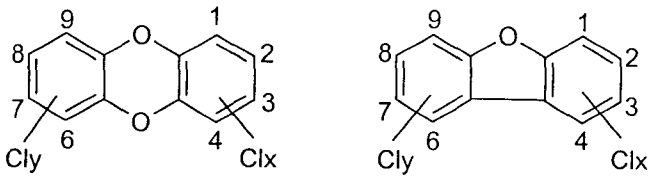

Fig. 1. Molecular structures of PCDDs and PCDFs.

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that provides a valuable record of the recent input of contaminants to the marine environment. The objective of this investigation is the assessment of the contamination levels and patterns of PCDDs/DFs in sediments of the coastal areas of Korea.

Materials and Methods

Surface sediments (depth, 0~5 cm) were sampled at 19 stations in Korean coast during the period of February to July 2000 (Fig. 2). Sediments were collected using a van veen grab sampler and then kept frozen at −70℃ until analysis. They were freeze-dried and sieved through 2 mm mesh. Twenty grams of sediments were extracted in a Soxhlet apparatus with 200 mL of toluene for 20 hours, then the volume was reduced to 1~2 mL in a rotary evaporator. The extract was transferred to *n*-hexane and internal standard (EDF 8999, Cambridge Isotope Laboratories, Inc) was spi-ked. After pre-cleaned up with a multi-layer slilica gel column containing $AgNO_3$-silica gel, H_2SO_4-silica gel and KOH-silica gel, the extract was cleaned up on an activated neutral alumina column with successive eluants of 3% methylene dichloride in *n*-hexane and 50% methylene dichloride in *n*-hexane. The second fraction was concentrated to less than 1 mL, and left at a room temperature for one or two days to evaporate to dryness. The residue was dissolved with 20 μL of *n*-nonane and determined for PCDDs/DFs.

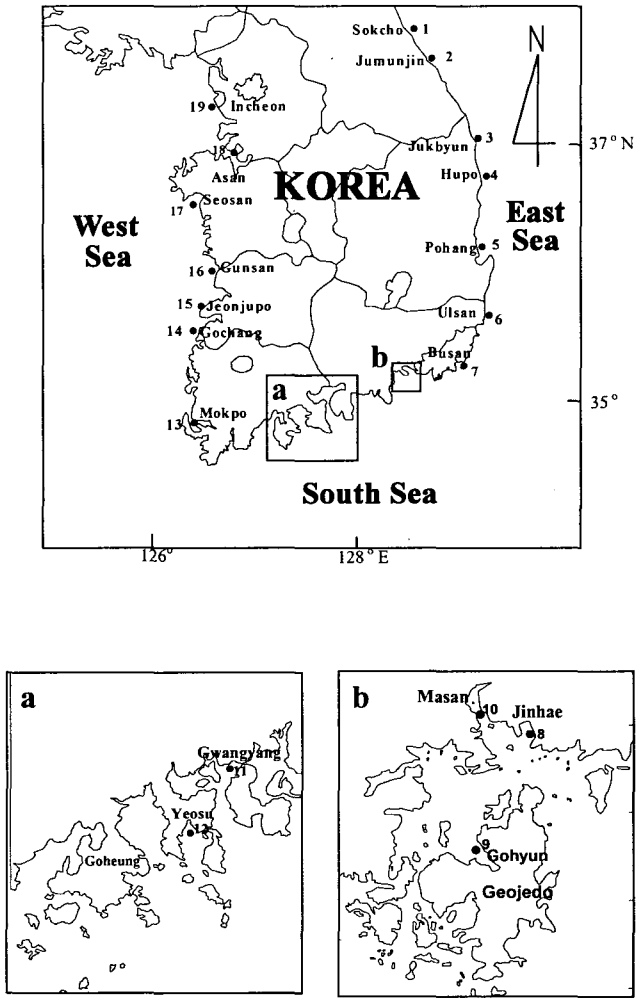

Fig. 2. Map showing sampling stations of sediments collected from Korean coast.

The HRGC/HRMS analyses were carried using an HP6890 Plus gas chromatography coupled to a JMS 700D mass spectrometer at a resolution of 10,000 (10% valley) in selected ion monitoring (SIM) mode, and a 60 m SP 2331 (Supelco 0.25 mm ID, 0.25 μm film thickness) and 60 m DB 5MS (J&W 0.25 mm ID, 0.25 μm film thickness) were used for the separation of compounds. Two molecular ions ($M^{\cdot+}$ and $(M+2)^{\cdot+}$) for each degree of chlorination were monitored in the electron impact (EI) ionization mode at 38 eV. The quantitative determination of PCDDs/DFs was performed by a relative response factor (RRF) method previously obtained five standard solutions injections (EDF 9999, Cambridge Isotope Laboratories, Inc.), as recommended by the US EPA.

Samples were injected splitlessly (2 μL portion of the total 20 μL) at the injector temperature of 260℃. Helium was used as carrier gas, and temperature was programmed as follows: 140℃, 1 min isothermal time, 20℃/min to 200℃, and then 5℃/min to 260℃ for tetra- to hexa-chlorinated compounds; 140℃, 1 min isothermal time, 20℃/min to 220℃, and then 8℃/min to 310℃ for hepta- to octa-chlorinated compounds.

The contents of total organic carbon (TOC) were obtained using a CHN analyzer (Perkin Elmer 2400), after elimination of the calcium carbonate with 1 N HCl. Grain size analyses were carried out by wet sieving, to separate sands, after a pretreatment with H_2O_2.

Results and Discussion

Contaminant levels

PCDDs and PCDFs were detected in all sediments samples. Table 1 shows the results of sediment analysis at each sampling station, giving total concentration and I-TEQ of isomers with four or more chlorines. The total concentration is a measure of the contamination level of a sample, whereas its I-TEQ is a measurement of the toxicity derived from 17 toxic PCDDs/DFs. PCDDs concentrations in surficial sediments ranged from 7 to 563 pg/g dry weight and PCDFs concentrations varied from 8 to 240 pg/g dry weight in Korean coast. I-TEQ levels were 0.1~5.5 pg/g dry weight for investigated stations. Station 8 represented the highest values and Station 2, 3 were the lowest level. Generally, sampling stations from East Sea (Station 1~6) showed low PCDDs/DFs distributions, whereas sampling stations from South Sea (Station 7~12) were the high levels compared to other stations. These results were similar or slightly low values compared to the recent investigated results on PCDDs/DFs in sediments from the southeastern coasts of Korea (Moon et al., 2000).

The PCDDs/DFs levels in sediments measured in this study with those in other countries were summarized in Table 2. Dannenberg et al. (1997) reported PCDDs/DFs concentrations in sediments from Western Baltic Sea and Oder River were higher about 2~3 times than those measured in this study. However, the other reports were about an order of 10~4,000 magnitude greater than the Korean coast for total and I-TEQ concentrations. In Japan, a large-scale program, which was initiated to cope with an elevated public concern in recent years, was designed to investigate dioxin levels (PCDDs, PCDFs and Co-PCBs) contained in air, water, soil, sediment and aquatic organisms. Of these, PCDDs/DFs in marine sediments was observed based on categories of classified potential sources. PCDDs/DFs levels in marine sediments were a range of 0.00037 to 230 pg-TEQ/g dry weight in the vicinity of incinerator, 0.0014~200 pg-TEQ/g dry weight in large cities, and 0.0013~160 pg-TEQ/g dry weight for small/medium cities. The PCDDs/DFs levels in the marine sediments from background sites represented 0.0~4.9 pg-TEQ/g dry weight (Takei et al., 2000). According these results, it seems that PCDDs/DFs levels in marine sediments of Korean coast belong to background levels. Similarly, Rose et al. (1994) suggested a simple categorization of PCDDs/DFs contamination in sediments from UK river system. This characterization as follows; <200 pg/g in background, 200~1,000 pg/g in slightly polluted area, 1,000~2,000 pg/g in polluted area, 2,000~10,000 pg/g in heavily polluted area, and >10,000 pg/g in very heavily polluted area. In terms of above categorization, a contamination by PCDDs/DFs of Korean coast could be regarded as background or slightly polluted area and do not appear serious. However, periodic monitoring of persistent organic pollutants (POPs) including toxic dioxins should be necessary

Table 1. Total and I-TEQ concentration of PCDDs/DFs (pg/g dry weight) in sediments collected from each sampling station of Korean coast

	Stations																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
TCDDs	2.07	0.18	0.54	3.95	5.24	3.54	3.06	23.45	29.57	1.02	12.20	4.83	9.29	2.11	3.73	24.52	6.95	4.57	3.93
PeCDDs	2.25	0.30	1.08	4.10	4.63	2.74	4.16	26.62	19.12	1.49	5.79	4.74	4.04	2.11	5.80	6.32	8.40	6.67	4.47
HxCDDs	5.03	0.90	2.20	7.20	11.10	5.86	10.30	47.10	38.00	3.30	17.15	13.65	10.10	4.60	20.90	7.80	18.06	12.20	10.90
HpCDDs	15.28	1.13	9.50	16.52	16.00	35.18	27.60	168.18	165.10	8.50	19.75	11.05	19.90	3.50	22.70	9.75	24.56	11.20	22.10
OCDD	35.25	4.60	15.24	35.60	66.40	108.54	64.50	298.15	241.40	31.60	66.70	28.20	34.80	14.20	43.20	46.20	32.40	34.00	42.30
TCDFs	4.40	0.16	0.36	3.24	8.37	6.14	4.29	25.87	27.08	0.48	7.85	6.07	4.54	1.80	5.18	13.90	12.73	8.16	6.42
PeCDFs	4.43	2.24	1.91	8.34	9.02	4.47	6.04	34.89	28.95	2.93	7.32	6.86	5.86	2.62	11.75	9.52	13.31	10.32	12.36
HxCDFs	7.25	4.63	1.83	6.50	9.90	5.38	7.62	45.65	30.20	2.50	15.55	16.00	6.90	3.60	9.90	20.10	18.98	11.50	16.15
HpCDFs	6.38	3.55	2.65	7.50	8.60	20.08	17.82	77.89	46.98	4.20	21.65	4.35	9.80	1.60	16.20	6.10	6.94	8.10	25.45
OCDF	1.40	0.50	1.60	2.31	6.40	10.40	8.10	56.24	28.40	7.00	18.60	3.10	3.80	2.60	14.80	5.70	4.97	5.40	4.00
PCDDs	59.86	7.10	28.56	67.37	103.37	155.86	109.62	563.50	493.19	45.91	121.59	62.47	78.13	26.52	96.33	94.59	90.37	68.64	83.70
PCDFs	23.85	11.08	8.35	27.89	42.28	46.47	43.87	240.54	161.61	17.11	70.96	36.38	30.90	12.22	57.83	55.32	56.93	43.48	64.38
Sum	83.71	18.18	36.90	95.26	145.65	202.33	153.49	804.04	654.80	63.02	192.55	98.84	109.03	38.74	154.16	149.91	147.29	112.12	148.08
I-TEQ	0.18	0.10	0.08	0.36	0.94	0.97	1.08	5.47	4.97	0.35	1.22	0.72	0.49	0.21	1.65	0.67	0.62	0.34	1.09

Table 2. Comparison of sediment PCDDs/DFs concentration measured in this study with literature values. The I-TEQ concentrations are recalculated from the original data

Locations	Concentration (pg/g dry weight)			References
	PCDDs	PCDFs	I-TEQ	
Korean coast	7~563	8~240	0.1~5.5	This study
Western Baltic Sea and Oder River Est. System	9~2,602	2~491	0.1~17.5	Dannenberg et al. (1997)
Umber Estuary, UK	1,915~2,777[a]	738~1,054[a]	14~24	Tyler and Millward (1996)
Black Rock Harbour, Bridgeport, CT, USA	18,226~19,946[b]	4,367~4,608[b]	223~250[b]	Norwood et al. (1989)
New Bedfore Harbord, MA, USA	1,707~7,564[b]	258~7,543[b]	10~761[b]	Norwood et al. (1989)
Chemieharbour, The Netherlands	2,484~5,752	39,123~89,395	434~923	Evers et al. (1989)
St. Laurensharbour, The Netherlands	3,670~31,994	3,065~19,956	352~1,849	Evers et al. (1989)
Frierfjorden, Norway	30,550~70,870	274,900~401,200	6,234~19,444	Oheme et al. (1989)
Venice Lagoon, Italy	16~13,642	49~126,561	0.5~2,857	Bellucci et al. (2000)

[a]As sum of all congeners; [b]Congeners with nondetected values are not considered.

for a management of environmental quality in Korean marine ecosystem.

Homologue profiles

The similar homologue profiles at many different stations make it difficult to identify a pattern, or 'fingerprint', which can associate environmental levels with a particular PCDDs/DFs source. The fingerprint method using homologue group profiles has been used by various authors to associate environmental levels and origins of PCDDs/DFs with particular sources (Fattore et al., 1997; Fiedler et al., 1996; Rose et al., 1994). Homologue profiles of PCDDs/DFs in marine sediments from Korean coasts were summarized in Fig. 3. All stations represented the similar homologue patterns. Octachlorinated dibenzo-*p*-dioxin (D8) was a predominant congener for all the stations. This pattern was in accordance with typical homologue profiles in marine sediments that a main source of PCDDs/DFs was atmospheric deposition of particulate matters generated from various combustion processes (Ballschmitter et al., 1986; Czuczwa and Hites, 1984). Indeed, atmospheric transformation seems to enrich octachlorinated dibenzo-*p*-dioxins in comparison to the less chlorinated homologues because of its lower photodegradation potential (Fattore et al., 1997). Therefore, the primary contribution of PCDDs/DFs contamination in Korean coast was likely to result from the atmospheric deposition from a large number of industrial activities by some local sources.

Relation between sediment PCDDs/DFs concentration, sediment organic carbon content and grain size distribution

The wide range of sediment contamination levels can be partly explained by the great disparity of the sediments. They range from mud to coarse sand, and their organic carbon content ranges from 0.0 to 3.24% (Table 3). In particular, Station 1, 2 and 3 where located at East Sea were characterized by a primarily sand (94.2~99.4% sand fraction) and PCDDs/DFs levels in these sampling stations showed the lowest values (0.08~0.18 pg-TEQ/g dry weight). This result can be indicated that sediment grain-size distribution is also one of the important factors governing PCDDs/DFs concentration and has to be considered. Indeed, fine grain-size sediments have been shown to accumulate hydrophobic organic contaminants at greater concentrations than coarse sands (Law and Andrulewicz, 1983).

Correlation between total PCDDs/DFs concentration and the percentage of TOC showed a positive relationship ($r^2=0.67$, $n=19$, $p<0.05$). This means that hydrophobic organic contaminants in sediments are mainly associated with the organic matter derived from the same source (Knezovich et al., 1987).

Conclusions

Results can be summarized as follows:

1. PCDDs concentrations in marine sediments collected from Korean coasts ranged from 7 to 563 pg/g dry weight and PCDF levels varied from 8

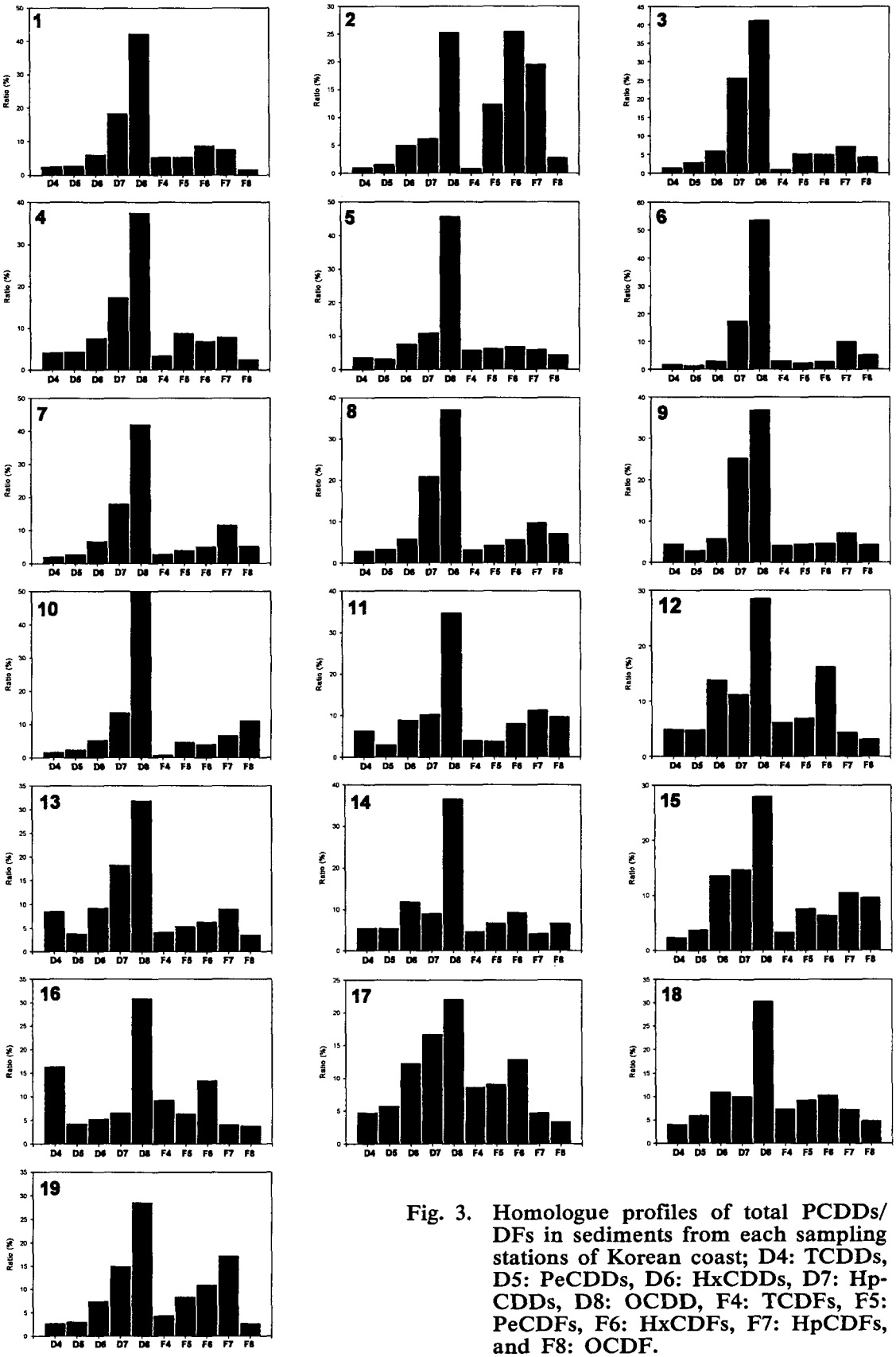

Fig. 3. Homologue profiles of total PCDDs/DFs in sediments from each sampling stations of Korean coast; D4: TCDDs, D5: PeCDDs, D6: HxCDDs, D7: HpCDDs, D8: OCDD, F4: TCDFs, F5: PeCDFs, F6: HxCDFs, F7: HpCDFs, and F8: OCDF.

Table 3. Total organic carbon (TOC) content and the grain size fraction in sediments from collected each sampling station of Korean coast

	Stations																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
TOC (%)	n.d.	0.14	0.02	0.59	0.93	1.26	1.47	2.81	1.65	3.24	1.01	1.33	0.65	0.76	0.84	0.62	0.51	0.62	0.12
Mud (<63 μm) (%)	0.589	5.841	0.569	38.23	59.24	94.68	91.96	88.83	95.42	91	83.95	96.99	67.16	64.43	58.09	54.37	66.16	67.63	63.3
Sand (>63 μm) (%)	99.41	94.16	99.43	61.77	40.76	5.321	8.042	11.17	4.585	9.002	16.05	3.008	32.84	35.57	41.91	45.63	33.84	32.37	36.7

n.d.=not determined.

to 240 pg/g dry weight. I-TEQ levels were 0.1 to 5.5 pg/g dry weight. Station 8 from the South Sea represented the highest value, whereas Station 2 and 3 from the East Sea showed the lowest levels.

2. All stations showed a similar homologue profile of PCDDs/DFs. Octachlorinated dibenzo-*p*-dioxin (OCDD) was a predominant congener. The primary contribution of PCDDs/DFs contamination in Korean coasts was atmospheric deposition of particulate matters generated from various combustion processes by some local sources.
3. Grain size and total organic carbon (TOC) distribution are one of the important factors governing PCDDs/DFs levels in this study.

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