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Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Sediments from the Southeastern Coastal Areas of Korea

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Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) contents in marine sediments, which were sampled at 21 stations from the southeastern coastal areas of Korea in February 2000, were analyzed using high resolution gas chromatography coupled to mass specetrometer (HRGC/HRMS). The concentrations of these contaminants ranged from 44 to 855 pg/g dry weight and I-TEQ concentration varied from 0.6 to 8.6 pg/g dry weight for the investigation stations. The highest concentrations were found in sediments of Pohang coast. Examination of the homologue groups showed that octachlorinated dibenzo-*p*-dioxin (OCDD) and heptachlorinated dibenzofurans (HpCDFs) were predominant homologues in Busan, Jinhae and Ulsan coasts, whereas pentachlorinated dibenzofurans (PeCDFs) were dominant species in Pohang coast. In particular, the dioxin contribution of Pohang coast may be attributed to combustion process of the same point source. The investigation of the homologue profiles using cluster analysis indicated that there may be different dioxin sources in the studied stations. The relationship between the contents of PCDDs/DFs and the percentages of TOC in marine sediments was discussed.

Key words: PCDDs, PCDFs, homologue profiles, cluster analysis, TOC

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of tricyclic aromatic compounds substituted with one to eight chlorine atoms. This results in 210 different compounds(75 PCDDs and 135 PCDFs) according to a position and number of chlorine atoms. PCDDs/DFs are well-known ubiquitous contaminants in marine environment with high chemical stability and extremely poor water solubility. Many of the congeners bioaccumulate and are considered potential toxicants producing adverse effects to biota and humans such as carcinogenicity, chloracne, immunotoxicity, reproductive and developmental toxicity.[1-3] Seventeen congeners are more toxic than the others and these toxic congeners have chlorine atoms at the 2, 3, 7 and 8 positions.

PCDDs/DFs are inadvertently produced from various combustion sources and manufacturing processes, such as municipal solid waste incineration,[4] motor vehicles,[5] steel mills,[6] and chemical production processes.[7] These contaminants are mainly transported to 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.[8] Therefore, sediment is a deposition place that provides a valuable record of the recent input of contaminants to the marine environment. Especially, in the domestic case, the presence of PCDDs/DFs in sediments of waterways in industrialized and heavily populated areas is one of the environmental problems that have received considerable attention in recent years. Therefore, the objective of this investigation was to assess the contamination levels and source characteristics of PCDDs/DFs in sediments collected from southeastern coastal areas of Korea.

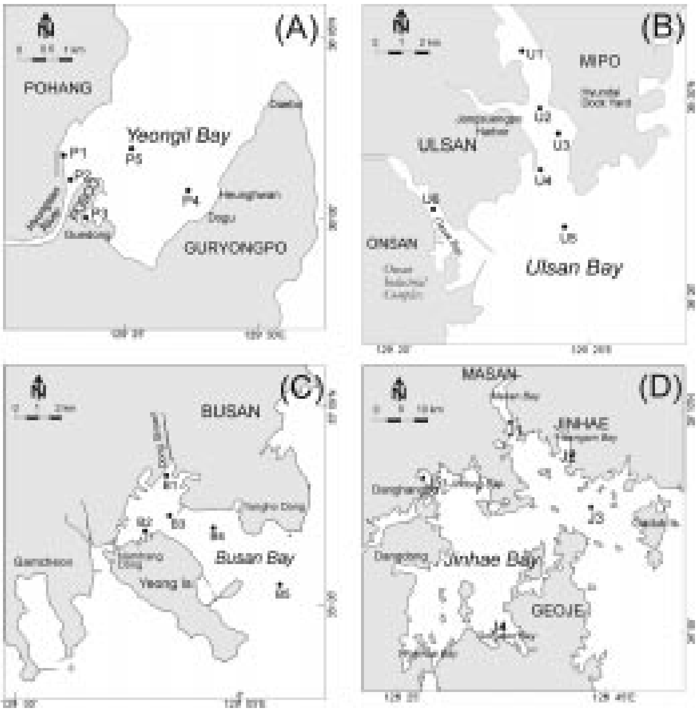

Fig. 1. Map showing the sampling stations of marine sediments from the southeastern coastal areas of Korea. (A) Pohang coast, (B) Ulsan coast, (C) Busan coast and (D) Jinhae coast.

2. Materials and Methods

Surface sediments were sampled at 21 stations in Pohang, Busan, Ulsan and Jinhae coasts on the southeastern part of Korea, which are surrounded by heavily industrialized cities, in February 2000 (Fig. 1).

Sediment samples from the top 0-5 cm were collected using a box-corer sampler and then kept frozen at -20°C until extraction. They were freeze-dried and sieved through 2 mm. Twenty grams of sediments were extracted in a Soxhlet apparatus with 200 mL of toluene (Ultra residue analysis, J. T. Baker) for 24 hours, after being spiking of internal standard (EPA-1613 LCS, Wellington Laboratories). The extracts were reduced to 1-2 mL in a rotary evaporator and then were transferred to *n*-hexane (Ultra residue analysis, J. T. Baker). Samples were pre-cleaned up on a multi-layer silica based adsorbents (70-230 mesh, Neutral, Merck) column (15 mm inner diameter, 300 mm length) with 160 mL of *n*-hexane. The elution flow was set at 10 mL/min. The extracts were passed through adsorbents in the following order; anhydrous sodium sulfate 5 g, silver nitrate impregnated silica gel 4 g, silica gel 0.5 g, 22% sulfric acid impregnated silica gel 3 g, 44% sulfric acid impregnated silica gel 3 g, silica gel 0.5 g, 2% potassium hydroxide impregnated silica gel 2 g, and finally silica gel 0.5 g. The pre-cleaned samples was cleaned and separated with an activated neutral alumina (70-230 mesh, Neutral, Merck) column (12 mm inner diameter, 250 mm length) with successive eluents of 3% methylene dichloride (dioxin residue analysis, Cica-Merck) 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 30 μL of *n*-nonane (Pesticide residue analysis, Fluka) and determined for PCDDs/DFs.

The high resolution gas chromatography couples to mass spectrometer (HRGC/HRMS) analyses were carried using an HP 6890 gas chromatography coupled to a JMS 700 mass spectrometer at a resolution of 10,000 (10% valley) in selected ion monitoring (SIM) mode, and a SP-2331 (60 m, 0.25 mm inner diameter,

Table 1. The contents (%) of total organic carbon and grain size in sediments from the southeastern coastal areas of Korea

	POHANG	ULSAN	BUSAN	JINHAE
TOC (mean)	1.02-3.68 (1.67)	1.37-2.34 (2.0)	1.11-4.64 (1.9)	1.05-5.33 (2.35)
Grain size				
Mud (<63 m)	72-92.5 (82)	80.6-99.2 (90.5)	38.6-98.3 (81.8)	77.6-99.7 (94.3)
Sand (>63 m)	7.5-28 (18)	0.8-19.4 (9.5)	1.7-61.4 (18.2)	0.3-22.4 (5.7)

0.25 m film thickness, Supelco) and DB-5MS (30 m, 0.25 mm inner diameter, 0.25 m film thickness, J & W Scientific) was used for the separation of compounds. Two molecular ions (M^+ and $(M+2)^+$ or $(M+2)^+$ and $(M+4)^+$) 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 an relative response factors previously obtained four standard solutions injections (EPA-1613 CVS, Wellington Laboratories), as recommended by the US EPA.

Samples were injected splitlessly (2 μL portion of the total 30 μL) at the injector temperature of 260°C. Helium was used as carrier gas, and temperature was programmed as follows; 140°C, 1 min isothermal time, 20°C/min to 200, and then 5°C/min to 260 for tetra- to hexachlorinated compounds; 140°C, 1 min isothermal time, 20°C/min to 220°C, and then 8°C/min to 310 for hepta- to octachlorinated compounds.

The contents of total organic carbon (TOC) were obtained using a CHN analyzer (Perkin Elmer 2400), after the 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.

3. Results and discussion

3.1. Sample descriptions

Table 2. The concentrations (pg/g dry weight) of PCDDs/DFs in sediments from the southeastern coastal areas of Korea

	Total concentration			I-TEQ concentration		
	PCDDs	PCDFs	Sum	PCDDs	PCDFs	Sum
P1	241.7	344.9	586.6	1.67	4.18	5.85
P2	165.5	275.7	441.2	1.46	3.10	4.56
P3	294.3	432.7	727.0	2.44	6.18	8.62
P4	230.2	344.9	575.1	1.68	4.18	5.86
P5	190.3	292.2	482.5	1.32	3.09	4.41
U1	46.8	24.3	71.1	0.23	0.44	0.67
U2	54.2	25.6	79.8	0.41	0.36	0.77
U3	257.6	67.4	325.0	0.60	0.56	1.16
U4	76.7	35.0	111.7	0.36	0.55	0.91
U5	38.7	15.7	54.4	0.34	0.23	0.57
U6	34.6	40.2	74.8	0.22	0.76	0.98
B1	110.1	89.7	199.8	0.70	1.49	2.19
B2	252.8	103.7	356.5	0.81	1.02	1.83
B3	500.6	290.0	790.6	2.00	3.94	5.94
B4	213.6	67.3	280.9	0.62	0.59	1.21
B5	291.9	87.0	378.9	0.75	0.83	1.58
J1	60.4	104.5	164.9	0.71	2.00	2.71
J2	344.9	122.5	467.4	1.09	1.28	2.37
J3	97.8	26.0	123.8	0.25	0.25	0.50
J4	663.2	192.1	855.3	1.51	1.66	3.17
J5	76.5	57.7	134.2	0.68	1.16	1.84

The TOC and grain size in surface sediments is summarized in Table 1. The contents of TOC ranged from 1.02 to 4.64% for all sediment samples. Sediments were primarily muddy (about 84-94%) for all stations. Mud contents in sediments of Busan and Jinhae coasts were higher than those of Pohang and Ulsan coasts.

3.2. PCDDs/DFs in sediments

PCDDs/DFs were detected in all sediment samples. Table 2 shows the concentration of PCDDs/DFs in sediments from the southeastern coastal areas of Korea. Total and I-TEQ concentrations of PCDDs/DFs represented the highest value in Pohang coast. Total concentrations of PCDDs/DFs analysed for Pohang coast were in the ranges of 441-727 pg/g dry weight with 4.4-8.6 pg/g dry weight for I-TEQ concentration. Total PCDDs/DFs in sediments from Busan coast vared from 200 to 791 pg/g dry weight with 1.2-5.9 pg TEQ/g dry weight. In Jinhae coast, total concenraions ranged between 124 and 855 pg/g dry weight with 0.5-3.2 pg-TEQ/g dry weight. The Ulsan Bay showed the lowest level of PCDDs/DFs, ranging from 44 to 325 pg/g dry weight with 0.6-1.2 pg-TEQ/g dry weight.

Homologue profiles of PCDDs/DFs in marine sediments for four coasts are summarized in Fig. 2. Busan, Ulsan and Jinhae coasts showed the similar patterns. In these coasts, the predominant homologues were octachlorinated dibenzo-p-dioxin (OCDD) and heptachlorinated dibenzofurans (HpCDFs). However, in the Pohang coast, pentachlorinated dibenzofurans (PeCDFs) was the predominant homologue and the concentration of dibenzofurans was higher compared with that of dibenzo-p-dioxins. These results indicated that the contamination of this bay was attributed to PCDDs/DFs generated from combustion process of stationary source.[9]

3.3. Source characteristics

In order to evaluate source characteristics of PCDDs/DFs in the sediment samples, we used cluster analysis based on multivariate statistical analysis. Data for cluster analysis used homologue groups of total PCDDs/DFs. Results of cluster analysis and representative homologue profiles of cluster groups are summarized in Fig. 3. The eight sampling stations of J3, J4, U3, B5, U4, B2, B4 and J2 form a distinct group. Representative homologue profile (B5) of this group showed that the predominant congeners were the high molecular weight such as hepta- and octachlorinated compounds. In particular, the OCDD showed the highest contribution in this group. This pattern is in accor-

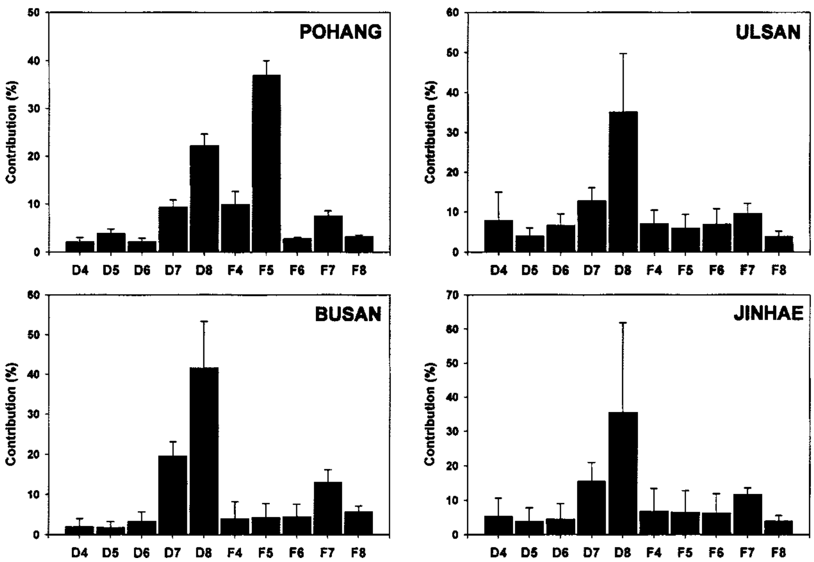

Fig. 2. Average normalized compositions of dioxin homologues in sediments from the southeastern coastal areas of Korea. Vertical lines indicate standard deviations. D4: tetra CDDs, D5: penta CDDs, D6: hexa CDDs, D7: hepta CDDs, D8: octa CDD, F4: tetra CDFs, F5: penta CDFs, F6: hexa CDFs, F7: hepta CDFs, and F8: octa CDF.

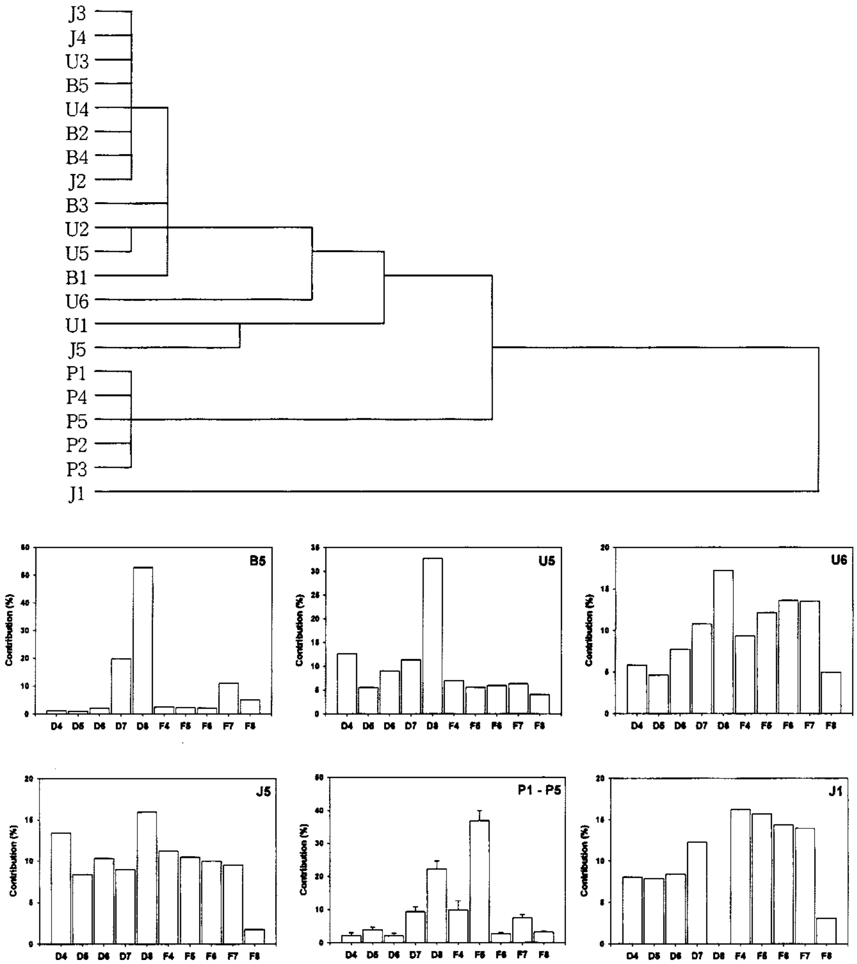

Fig. 3. Dendrogram of cluster analysis and representative homologue profiles of each group. Vertical lines in homologue profiles (P1-P5) indicate standard deviations. Vertical lines in representative homologue profile (P1-P5) indicate standard deivations. D4: tetra CDDs, D5: penta CDDs, D6: hexa CDDs, D7: hepta CDDs, D8: octa CDD, F4: tetra CDFs, F5: penta CDFs, F6: hexa CDFs, F7: hepta CDFs, and F8: octa CDF.

dance with typical homologue profile of PCDDs/DFs in marine sediments and atmosphere from previously published papers.[10-11] Indeed, atmospheric transformation seems to enrich OCDD in comparison to the less chlorinated homologues because of its lower photodegradation potential.[12] Therefore, the primary contribution of PCDDs/DFs contamination in these stations was likely to result from atmospheric deposition from combustion process by some local sources.

Secondly, Fig. 3 clearly shows that the alignment of five samples from Pohang coast of Stations P1, P2, P3, P4 and P5 was separated from the others. In particular, Pohang coast is an area with heavy pollution due to combustion process from steel mill.[13-14] The samples from Pohang coast were characterized by the presence of pentachlorinated dibenzofurans (PeCDFs). It may suffer from certain point source of contamination. Furthermore, the absolute levels were high in the investigation area, so these sampling stations seem to be influenced by toxic contaminants generated from combustion process of steel mill. Many authors reported that this plant was the main source of hazardous contaminants in marine environment.[7),15]

Other stations of B1, U6, U1, J5 and J1 were mostly located at the river or stream mouth. Therefore, it might be affected by domestic wastewater and industrial sewage that discharged directly into rivers without any treatment. Homologue profile of these stations shows that the lower chlorinated chemicals (tetra- and pentachlorinated CDDs and CDFs) occupied the high ratio compared with other stations. This finding indicated that the contribution of PCDDs/DFs in these stations might result from contaminant load via river rather than atmospheric deposition of particulates generated from combustion process of high temperature.

3.4. Correlations

A regression analysis was carried out to investigate the relationship between the concentrations of PCDDs/DFs and the percentages of TOC (Fig. 4). There was no significant correlation for all samples. That is because the primary source of TOC in marine sediments is marine phytoplankton. In general, the C:N atomic ratio of marine phytoplankton varies from 3 to 9.[16] Namely, the TOC contribution in the stations that C:N atomic ratios were higher than 9 (black circles in Fig. 4) can be regarded as land-derived particulate matter.[17] In the case of these stations, the relationships for PCDDs/DFs and TOC showed a highly positive correlation ($n=9$, $r^2=0.86$, $p<0.001$). This result suggests that PCDDs/DFs in marine sediments were derived from terrestrial and anthropogenic activities.

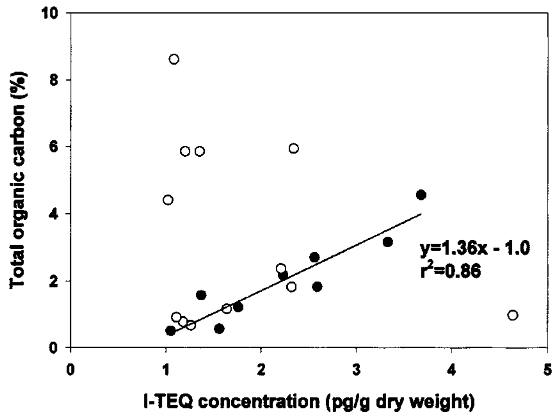

Fig. 4. The relationship between PCDDs/DFs concentration and TOC in the sediments. Black (●) and white (○) circles indicate C:N atomic ratio>9 and C:N atomic ratio<9, respectively.

4. Conclusion

Results can be summarized as follows:

1. Total concentrations of PCDDs/DFs in sediments from the coastal areas of Korea ranged from 44 to 855 pg/g dry weight and I-TEQ concentration varied from 0.6 to 8.6 pg/g dry weight. Pohang coast was characterized by the highest contamination in the investigation coasts.

2. Busan, Ulsan and Jinhae coasts showed a similar homologue pattern for total PCDDs/DFs concentrations. The predominant homologue for total concentrations was octachlorinated dibenzo-p-dioxin (OCDD) and heptachlorinated dibenzofurans (HpCDFs).

3. In the Pohang coast, the predominant homologue of total PCDDs/DFs was pentachlorinated dibenzofurans (PeCDFs) and the concentration of dibenzofurans was higher compared with that of dibenzodioxins. And this coast represented very similar homologue pattern. These results indicate that the dioxin contamination of this coast was generated from combustion process of the same point source.

4. A regression analysis of PCDDs/DFs and TOC contents showed significantly high correlation in the stations that C:N atomic ratio is higher than 9.

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