LEVELS AND PATTERNS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN SEDIMENTS FROM KOREAN COAST

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are very stable chemicals and have very long residence times in the environment and in organisms, including humans. Their adsorption on the particle and hydrophobicity promotes 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, reduce reproduction, liver toxicity, decreased growth rate and behavioral changes [1,2,3]. 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 on the recent input of contaminants to the marine environment. The objective of this investigation was to assess the contamination levels and patterns of PCDDs/DFs in sediments of Korean coast.

Materials and Methods

Surface sediments were sampled at 19 stations in Korean coast during the period of February to July 2000 (Fig. 1). Sediments were collected with a box-corer sampler and then kept frozen at -20℃ until analysis. They were freeze-dried and sieved through 2 mm. 20 g 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 spiked. 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 elutants 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 using HRGC/HRMS (JMS 700D, JEOL). Further details of the fractionation procedure and instrumental analysis procedures are presented elsewhere [9,10]. 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.

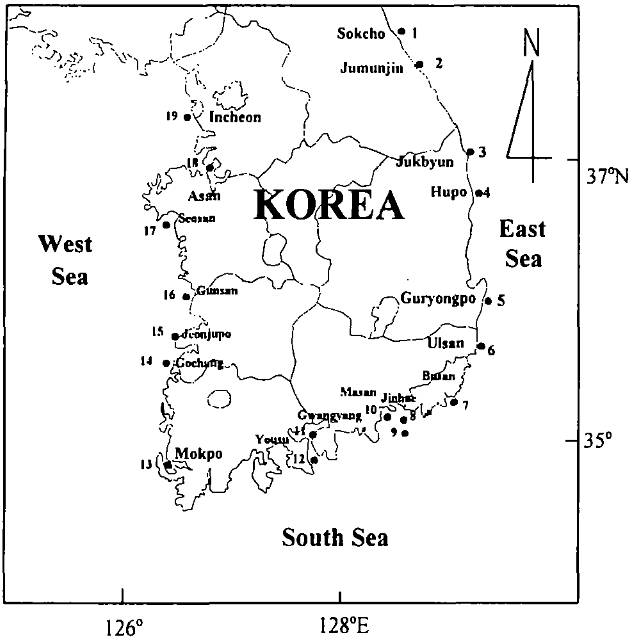

Fig. 1. Map showing sampling stations of sediments collected from Korean coast.

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 levels in sediments from the southeastern coasts of Korea [11].

Homologue profiles

Homologue profiles of PCDDs/DFs in marine sediments from Korean coasts were summarized in Fig. 3. All stations represented similar homologue patterns. Octachlorinated dibenzo-*p*-dioxin (OCDD) was a predominant congener for all stations. This pattern was in accordance with typical homologue profiles in marine sediments in which a main source of PCDDs/DFs was atmospheric deposition of particulate matters generated from various combustion processes [12, 13]. Indeed, atmospheric transformation seems to enrich octachlorinated dibenzo-*p*-dioxins in comparison to the less chlorinated homologues because of its lower photodegradation potential [14]. Therefore, the primary contribution of PCDDs/DFs contamination in Korean coast was likely to result in 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 2). 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 important factor 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 [15].

Correlation between total PCDDs/DFs concentration and the percentage of TOC showed a significantly 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 [16].

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Table 1. Total and I-TEQ concentration of PCDDs/DFs (pg/g dry weight) in surficial 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. Total organic carbon (TOC) content and the grain size fraction in surficial 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 (%)	0.01.	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 (<63µm, %)	0.6	5.8	0.6	38.2	59.2	94.7	92.0	88.8	95.4	91.0	84.0	97.0	67.2	64.4	58.1	54.4	66.2	67.6	63.3
Sand (>63µm, %)	99.4	94.2	99.4	61.8	40.8	5.3	8.0	11.2	4.6	9.0	16.0	3.0	32.8	35.6	41.9	45.6	33.8	32.4	36.7