Characterization of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in different particle size fractions of marine sediments

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Fine sediment particles have high levels of PCDD/Fs that could affect marine organisms.

Abstract

The distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) was examined according to particle size in marine sediments, with a particular focus on fine particulates. Samples from different coastal sites were fractionated into five size groups (<2, $2-5$, $5-10$, $10-20$, and $20-63$ µm diameter) by gravitational split-flow thin fractionation. Despite the different size profiles and PCDD/F contents of the sediments at each site, PCDD/F levels in fractionations tended to increase as the particle size decreased; the PCDD/F levels in the finest particles were up to 16 times higher than in the coarsest particles, which was associated with their organic carbon contents. Log normalization showed high levels of PCDD/Fs in the fine silt particles ($2-10$ µm), which are consumable by aquatic biota. Because of the different toxicity and bioavailability of PCDD/Fs in different sediment particle sizes, it is important to study particle actions to understand their effects on the aquatic ecosystem.
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1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are produced as byproducts of combustion and manufacturing processes (Alcock and Jones, 1996; UNEP, 1999; WHO, 1989). The PCDD/Fs released from these activities are transported to other regions through the air and water (Alcock and Jones, 1996; WHO, 1989). Their production and dispersal is a significant ecotoxicological problem because they are highly persistent, hydrophobic, and can have detrimental effects on organisms including humans.

Sediments are known to be an important and final sink for non-polar organic contaminants, including polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and PCDD/Fs. These hydrophobic compounds are characterized by large octanol–water partition coefficients (log K_{ow} of approximately $4-8$), which promote their accumulation in sediments. Therefore, to understand their accumulation and eventual fate, it is important to study their presence in sediments, particularly since contaminated sediments can be consumed by marine organisms, such as fish, burrowing invertebrates, and filtering organisms (Connolly, 1991; Harkey et al., 1994). Of these, benthic organisms, which ingest sediment particles to obtain nutrition, may have a particularly high body burden of contaminants.

The environmental conditions in aquatic systems determine the accumulation and circulation of these contaminants. Physical and textural properties of the water column and marine sediments determine their interactions and the interactions between abiotic and biotic surfaces (Brannon et al., 1991;

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Cornelissen et al., 1997; Gschwend and Wu, 1985; Kukkonen and Landrum, 1996). The particle size of sediments is particularly important in this regard. Adsorption/desorption experiments have shown that PAHs and PCBs, for instance, distribute preferentially in the fine particles (Brannon et al., 1991; Kukkonen and Landrum, 1996). Thus, the fate and migration of non-polar organic contaminants depend on the particle size of sediments rather than the bulk sediment itself. Many studies of PCDD/Fs in sediments, however, have focused on the spatial distribution of bulk sediments. Also, the studies that have examined the effect of particle size have only compared sandy and muddy sediments, which were defined as having particles of diameter greater than and less than 63 μm respectively. However, particles of diameter 63 μm are too coarse to be consumed by benthic organisms.

In this study, we examined the distribution of PCDD/Fs in mud-sized (<63 μm) marine sediments. The marine sediments from three different coastal areas of Korea (Pohang, Ulsan, and Busan) were separated by size using a newly developed gravitational split-flow thin fractionation technique, and the PCDD/F levels were analyzed as a function of the particle size. This type of analysis is important for understanding the transport of PCDD/Fs in the ocean and the bioavailability of these compounds for marine creatures.

2. Materials and methods

2.1. Sediment collection

Marine sediments were collected near three different coastal areas as shown in Fig. 1. The cities of Pohang and Ulsan, located along the southeastern coast, have large steel and heavy industries, respectively, with the latter including car manufacturing, shipbuilding, and petrochemical industries. The city of Busan is the largest port in Korea, characterized by high contamination due to the transportation activities of ships and numerous municipal point sources along the coastal line. These cities have been developed industrially since the mid-1960s. The sediment sample from Busan in Fig. 1(C) was collected from a zone between the Busan coast and Geoje Island. The sampling point was on the west side of Busan near Gaduck Island, which features fishing villages. The sampling point was to the east of Geoje Island, which has two large shipyards. The core sampler with which sediments were collected used gravity to allow unrestricted flow of water through its core tube during descent. Surface sediments (~10 cm depth) were used for investigation and samples were stored below −20 °C until the particle fractionation and instrumental analysis.

2.2. Particle fractionation with GSF technique

The particle fractionation was conducted by the gravitational split-flow thin (SPLITT) fractionation (or GSF) technique. SPLITT fractionation (or SF) is a continuous and rapid separation technique which is able to fractionate macromolecules, cells, and particulate materials (Moon et al., 2002b). It is carried out in a thin rectangular channel with splitters laying at both the inlet and outlet. Fig. 2 shows a schematic diagram of the GSF channel in which particles entering the upper channel inlet continuously are initially pushed toward the upper channel wall by relatively high speed carrier flow stream and simultaneously, they begin migrating toward the channel outlets. In the GSF channel, gravitational force plays a role of differentiating particles across the channel based on particle settling velocity. It results in an elution of particles larger than a certain diameter (or cut-off diameter) at the lower outlet of the channel and the remainder of smaller diameter at the upper outlet. The control of cut-off diameter can be made with a proper selection of flow rates used in GSF

operation. The details were found from elsewhere (Moon et al., 2002b, 2004). The pinched inlet GSF (or PI-GSF) utilized in this study is the modified technique of the conventional GSF to obtain high separation efficiencies by reducing the channel inlet thickness. By applying the pinched inlet channel design to the GSF channel, particles leaving the inlet splitter can be quickly transported and efficiently pushed against the upper wall of the GSF channel by the carrier stream so that the number of particles expected to deviate from the ideal trajectory during sample injection is decreased by some degree.

About 30.0 g of dried sediment sample at 105 °C was initially treated with a 63 μm in pore sieve in wet conditions, and the fraction of sediment smaller than 63 μm (the fraction S) was used for the PI-GSF fractionation. The separation of the sediment fraction S was conducted with ultrapure water (>18 MΩ) containing 0.02% NaN_3 as a bactericide and 0.1% FL-70 from Fisher Scientific (Fairlawn, NJ). After sieving, the solution was filtered through a membrane filter that had a pore size of 0.2 μm. Filtered fine particles were added to the fraction S for another PI-GSF, and the filtered solution was diluted to about a total of 5 L of 0.02% NaN_3 solution which was utilized as a carrier solution in PI-GSF. At the end of the SPLITT processes, 1 L of the carrier solution was taken for dioxin analysis. From this operation, we could obtain fractionated sediment groups according to the following sizes; >63 μm, 20−63 μm, 10−20 μm, 5−10 μm, 2−5 μm and <2 μm.

2.3. Analysis of PCDD/Fs

Dried and separated sediments were used for PCDD/Fs analysis. Pre-treatment was conducted according to US EPA method 8290. Each sample was extracted by a Soxhlet apparatus with toluene after spiking a cocktail of $^{13}C_{12}$-labelled PCDD/Fs as the internal standards (Wellington Laboratories, Canada). The extracts were washed with H_2SO_4 and neutralized by following H_2O saturated by hexane. Sample clean up was performed using multi-layer (with layers of neutral, basic, neutral, acidic, and neutral silica) silica and an alumina column. Finally, samples were concentrated with N_2 gas and $^{13}C_{12}$-labelled PCDD/Fs recovery standards were added prior to the instrumental analysis.

The analysis of PCDD/Fs was conducted via high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS, HP 6890 series II/JMS 700T) and followed US EPA method 1613. The DB5-MS column (60 m length, 0.25 mm i.d., 0.25 μm film thickness) was used with helium as the carrier gas. The temperature program of GC was as follows; 140 °C for 4 min → increase at 15 °C/min → 220 °C for 3 min → increase at 1.5 °C/min → 240 °C for 2 min → increase at 4 °C/min → 310 °C for 6 min. Samples were injected with splitless mode and the MS was operated under positive EI conditions: 38 eV electron energy at a resolving power of 10,000. The single ion monitoring (SIM) mode with the monitoring of two ions among M+, M + 2, M + 4 were used. The quantification of tetra- to octa-CDD/Fs followed with these criteria: (1) isotope ratios within ±15% of theoretical values and (2) signal to noise ratio ≥2.5. Recoveries of $^{13}C_{12}$-labelled PCDD/Fs internal standards in environmental samples ranged from 50 to 120%.

2.4. Analysis of organic carbon in sediment samples

Measurement of the carbon content in solid samples was performed by weighing a portion of the sample in a ceramic boat using a solid sample module (SSM-5000A, Shimadzu). The boat with the sample was placed into a combustion furnace containing an oxidation catalyst and heated to 950 °C. The carbon compounds in the sample combusted to form CO_2, which was then swept from the combustion tube to a non-dispersive infrared (NDIR) detector using oxygen as the carrier gas. The total carbon (TC) quantification was performed by comparing the sample response to a known carbon standard, glucose. Measurement of total inorganic carbon (IC) content in solid samples was also performed in the same manner, except that dilute H_3PO_4 was added to the sample. The ceramic boat was then heated to 250 °C and CO_2 was detected by the NDIR detector. Finally, the total organic carbon (OC) concentration was calculated by subtracting the IC from the TC results. All samples were analyzed in duplicate.
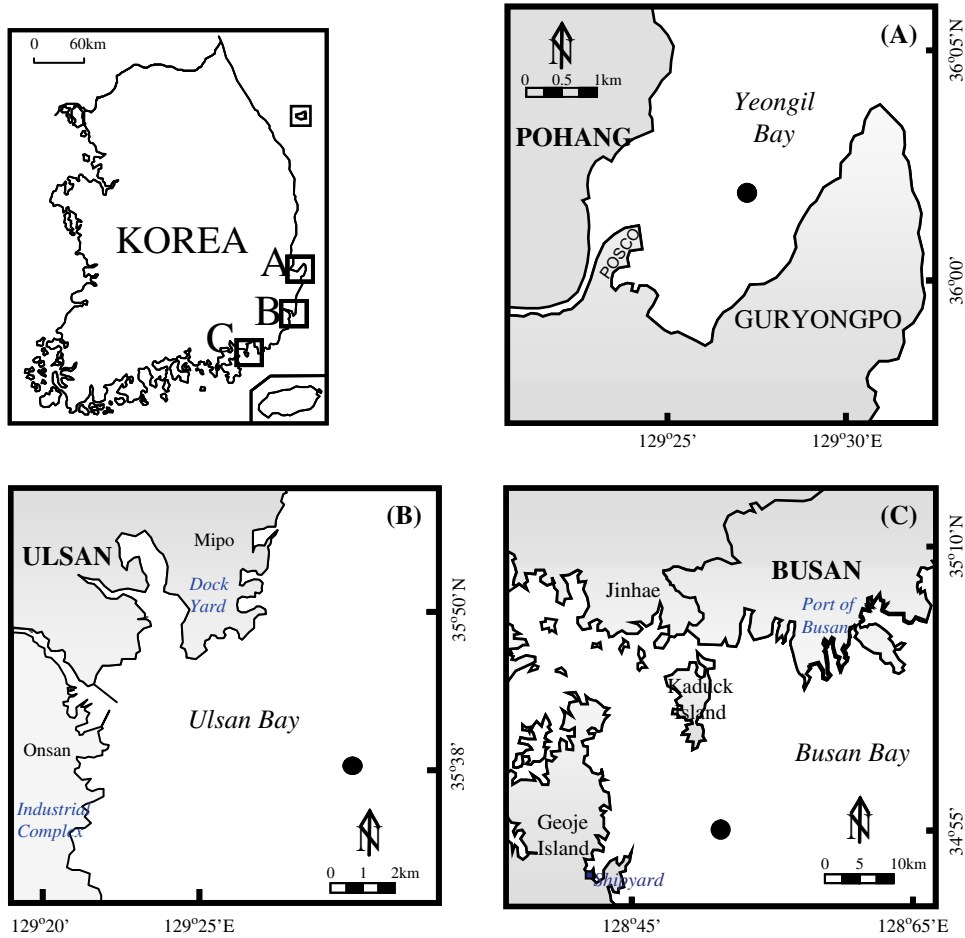
Fig. 1. Location of the sediment sampling sites. Black circles (•) indicate the core sediment sampling site. (A) Pohang coast, (B) Ulsan coast, (C) Busan coast.

3. Results and discussion

The densities of the bulk sediments were 2.3 (Pohang), 2.2 (Ulsan), and 2.3 g/m³ (Busan). The separation efficiencies for this study, based on the number of fractionated particles within the cut-off diameters, were over 80%, with 87.2% as the average efficiency. As in the previous study (Moon et al., 2004), the PI-SPLITT technique gave a higher separation efficiency than the conventional SPLITT technique, because of reduced overlap in the diameters of the size groups. In particular, the efficiency of separation within 2 μm of the cut-off diameter was at least 90% and as high as 97.7% for the PI-SPLITT technique. The loss of particles in the carrier solution was negligible.

Table 1 shows the resulting particle distributions of fractions and the PCDD/F profiles according to the particle sizes in each sample. All sediments contained only a few percent of particles larger than 63 μm and were composed mostly of
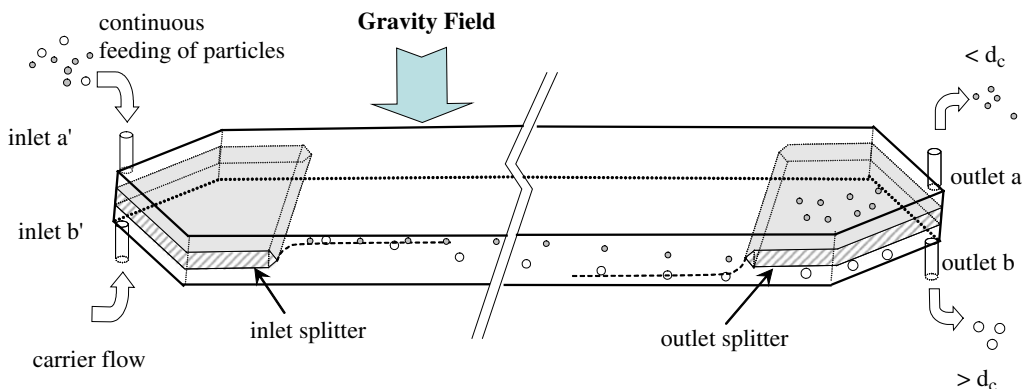

Fig. 2. Schematic diagram of the gravitational split-flow thin fractionation channel.

Table 1
Weight percentages and PCDD/F concentrations (pg/g dry weight) fractionated by the Pinched-SPLITT technique

Station	Pohang						Ulsan						Busan					
Size (µm)	>63	20−63	10−20	5−10	2−5	<2	>63	20−63	10−20	5−10	2−5	<2	>63	20−63	10−20	5−10	2−5	<2
Sediment weight (%)	8.4	17.9	19.5	21.1	15.8	17.4	4.0	6.0	14.0	21.0	42.5	12.5	1.7	8.0	7.0	13.3	25.3	44.7
TCDDs	<0.10	3.33	2.59	4.81	9.94	12.61	14.77	8.51	5.73	5.43	10.86	21.45	23.59	9.86	18.61	3.43	3.96	19.05
PeCDDs	2.51	5.56	4.63	1.95	11.19	20.79	<0.10	<0.10	3.82	<0.10	<0.10	18.14	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
HxCDDs	14.53	8.67	7.66	5.84	19.22	17.60	47.54	5.96	3.16	6.26	14.84	26.15	<0.20	<0.20	<0.20	<0.20	<0.20	23.06
HpCDDs	12.77	6.16	4.65	4.25	19.99	13.50	103.50	16.43	10.66	19.89	23.54	28.33	<0.20	<0.20	<0.20	<0.20	2.13	27.84
OCDD	9.55	5.66	5.14	5.48	23.28	24.94	74.57	47.98	26.68	34.97	120.02	134.35	13.82	2.64	3.10	1.52	7.59	78.59
TCDFs	1.79	10.33	2.67	7.47	19.11	56.52	36.25	3.19	5.03	8.70	8.60	36.43	3.91	1.99	<0.01	2.75	<0.10	2.92
PeCDFs	5.79	54.40	24.85	39.04	132.12	232.40	17.78	7.61	5.02	6.32	6.06	16.99	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
HxCDFs	<0.20	1.57	0.87	1.41	4.07	10.95	24.02	32.00	3.41	<0.20	5.46	32.68	<0.20	0.94	<0.20	<0.20	5.32	5.61
HpCDFs	4.82	1.31	1.71	1.48	4.90	6.34	35.98	1.81	5.37	6.30	15.91	28.59	<0.20	8.06	7.38	2.57	8.40	<0.20
OCDF	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	7.86	2.16	2.79	1.21	5.87	<0.50	<0.50	1.07	<0.50	<0.50	2.16	3.96
ΣPCDD/Fs (I-TEQ)	0.10	2.00	0.95	1.46	5.78	9.26	5.91	1.14	1.56	2.13	1.38	3.22	3.21	0.09	3.46	0.08	0.40	0.56
ΣPCDD/Fs	51.75	96.99	54.77	71.72	243.81	395.66	362.26	125.65	71.66	89.10	211.14	343.11	41.31	24.55	29.08	10.27	29.56	161.03

fine particles (<63 µm) such as silt and clay. However, the distributions of these fine particles were somewhat different between the various sites. The Pohang sediment showed a comparatively even distribution among the subfractions, whereas over 50% of the total particles in the Ulsan and Busan sediments were composed of fine silt and clay particles (<5 µm). This difference may be due to the fact that the sampling at the Pohang site was conducted closer to the bay than the Ulsan and Busan sites. Additionally, the differences in sediment composition may have been the result of different geographies and characteristics of the mud belt deposited by the ocean currents. Indeed, the mean particle size of Korean coastal sediments increases from the West Sea to the East Sea (Kim et al., 2001).

3.1. PCDD/F contents in bulk sediments

There was a broad range of total PCDD/F levels in bulk sediments (7.88−156.96 pg/g dry weight; 0.12−3.82 pg I-TEQ/g dry weight). The Busan sediment had lower PCDD/F levels than the other two sediments, likely due to the presence of large steel and heavy chemical factories along the waterfront in Pohang and Ulsan. High levels of contaminants have already been reported in these regions (Moon et al., 2002a; Oh et al., 2003). Our results imply that the Busan was less contaminated by terrestrial effluents than the Pohang and Ulsan, this difference might instead be due to the fact that the distance between the sampling point and the shore was the greatest for the Busan site.

The three sediment samples showed different PCDD/F homologue profiles, indicating different sources of PCDD/Fs at each site (Fig. 3). The PCDD/F distribution of the Ulsan sample was characterized by a high portion of OCDD, and HpCDDs > TCDFs > PeCDFs followed. This is not surprising because OCDD is dominant in sediments that act as a main sink of PCDD/Fs. This is generally due to the low
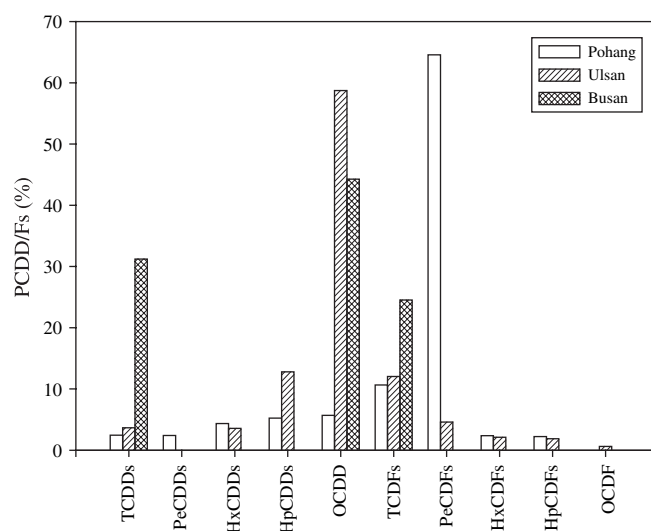

Fig. 3. Distributions of PCDD/Fs in bulk sediments at the various sampling sites.

solubility of OCDD in water (Muir et al., 1992), atmospheric input from a variety of combustion processes (Czuczwa and Hites, 1984, 1986; NIER, 2003; Sakurai et al., 2000), and photochemical synthesis from pentachlorophenol (Baker and Hites, 2000; Hagenmaier and Brunner, 1987). Therefore, the homologue profile indicates contamination of the Ulsan sediment by atmospheric input and/or discharge of pentachlorophenol. In contrast, the PCDD/F profile of the Pohang sediment was dominated by PeCDFs collected in an area close to a steel mill. Indeed, the Pohang coast is known to have high levels of PeCDFs (Kim et al., 2002; Moon et al., 2002b) due to the melting of metal, which releases low chlorinated dibenzofurans, especially TCDFs and PeCDFs (Antonsson et al., 1989; Tysklind et al., 1989). The Busan sediment contained low concentrations of PCDD/Fs with detectable amounts of OCDD, TCDDs, and TCDFs. Because industrial and shipping activities near the sediment sampling point are relatively low, the contamination may be due to discharges from neighboring islands. The presence of these low chlorinated dioxins/furans have been reported in discharge of domestic wastewater and industrial sewage (Moon et al., 2002b; Wu et al., 2001).

3.2. Distribution of PCDD/Fs in marine sediments of different particle sizes

The concentrations of total PCDD/Fs in sediment fractions showed a unimodal distribution with the peak in the clay-sized (<2 μm) fractions (Table 1). Notably, the sand-sized (>63 μm) fraction of the Ulsan sample had a slightly higher PCDD/F level than the clay-sized fraction. The PCDD/F levels in the finest particle size fraction of the Ulsan sample, however, were 2–16-fold higher than in all other fractions. In particular, the PCDD/F level in the finest particle size fraction of the Busan sample was 20-fold higher than that of the bulk sediment. This supports our previous findings that the fine sediment particles possess relatively high concentrations of PCDD/Fs. Other researchers have also found that silt and clay particles were more contaminated by these compounds than sand or coarse particles; differences in PCDD/F contamination between sandy (>63 μm) and muddy (<63 μm) sediment particles were also observed on the Korean coasts (Moon et al., 2002b). A study by Piérard et al. (1996) also confirmed that PCBs preferentially concentrate in silt/clay fractions even though their samples had varying compositions in terms of particle size. As found with the PCDD/Fs in the Ulsan sediments, pesticides such as atrazine and bifenox (Gao et al., 1997) were also concentrated in fine particles, with a bimodal distribution in clay (<2 μm) and fine sand (63–200 μm) fractions. On the other hand, a study of the sequestration of PAHs in weathered sediments found the opposite trend, in which the larger sized particles were in the low density fractions and vice versa (Persson et al., 2002).

Diverse factors control the distribution of pollutants in aquatic system, including the quantity and quality of organic matter in the water body and sediments, the characteristics of the contaminants, and the texture of the sediments. Depending on their specific properties, even similar organic materials have different capacities to sequester contaminants (Kukkonen et al., 2003; Persson et al., 2002; Rockne et al., 2002). In addition, even contaminants having similar properties, can behave differently in an aquatic system (Harkey et al., 1994; Oh et al., 2002; Wu et al., 2001). The characteristics of sediments, therefore, play a considerable role in the movement of these contaminants, while the organic matter in the sediment affects their sorption. Gschwend and Wu (1985) reported that PCB partitioning depends on ionic strength, which influences the release of sediment organic carbon. PAH distributions were also associated with the clay fraction containing organic matter as a major sorbent (Brannon et al., 1991).

In the present study, we tried to determine the factor controlling PCDD/F distributions in different particle sizes. The particle sizes themselves did not correlate significantly with the distributions of PCDD/Fs; rather, their organic carbon content appeared to be linked to the distributions of PCDD/Fs (Fig. 4). The organic carbon contents in the sediments were between 0.238% and 4.456%, whereas the amounts of inorganic carbon were very low. Like the PCDD/Fs, organic carbon was also more associated with small particles. Regression plots show that the presence of PCDD/Fs correlates well with the organic carbon content of the sediment particles. Although the relationship between PCDD/Fs and the presence of organic carbon were relatively weak for all particle sizes, within the muddy sizes (<63 μm), the correlations were significant at a 95% confidence level ($r^2 > 0.7$). Normally, fine particles such as muddy fractions exhibit an abundance of organic matter and a large surface to volume ratio. Organic carbon in sediment particles acts as an important adsorbent for organic contaminants; it controls the sorption and desorption of these highly hydrophobic compounds between water and sediment particles. Therefore, these fine particles can adsorb non-polar organic compounds more readily, and this tendency is related to the bioavailability of contaminants to marine organisms.
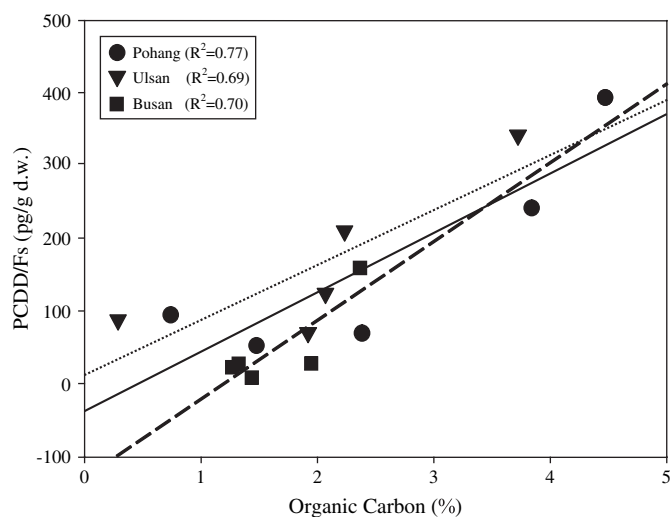

Fig. 4. Linear regressions of PCDD/F concentrations (pg/g dry weight) vs. total organic carbon (%) in sediment groups less than 63 μm diameter at $P = 0.05$. Black circles (●), triangles (▼), and squares (■) indicate the results of analysis for Pohang, Ulsan, and Busan coasts, respectively.

Persson et al. (2002) recently reported that the influence of soot carbon was more significant than that of organic carbon. However, other experimental results suggest the importance of particulate density and the presence of detrital plant debris rather than soot carbon (Kukkonen and Landrum, 1996; Persson et al., 2002). Larsen et al. (2003) showed that the movement of 1,2,7,8-TCDD in sediments was related to the surface area as well as the content of organic material. Different studies have identified different determining factors for the profiles. Our current results suggest that organic carbon in the sediments, like dissolved organic carbon in water columns (Cornelissen et al., 1997; Muir et al., 1992), is responsible for trapping contaminants.

3.3. Normalized distribution of PCDD/Fs in different particle sizes

The relative homologue distributions of PCDD/Fs have been shown to vary widely in the atmosphere according to their molecular weights and degrees of chlorination. Highly chlorinated compounds are more concentrated in coarse particles, and the less chlorinated compounds are present more in smaller particles (Oh et al., 2002). This is due to the different vapor pressures of PCDD/Fs, which depend on their extent of chlorination. Fig. 5 displays the log normalized distribution patterns of PCDD/F homologues according to particle size. Although the homologue profiles of the Pohang sediments
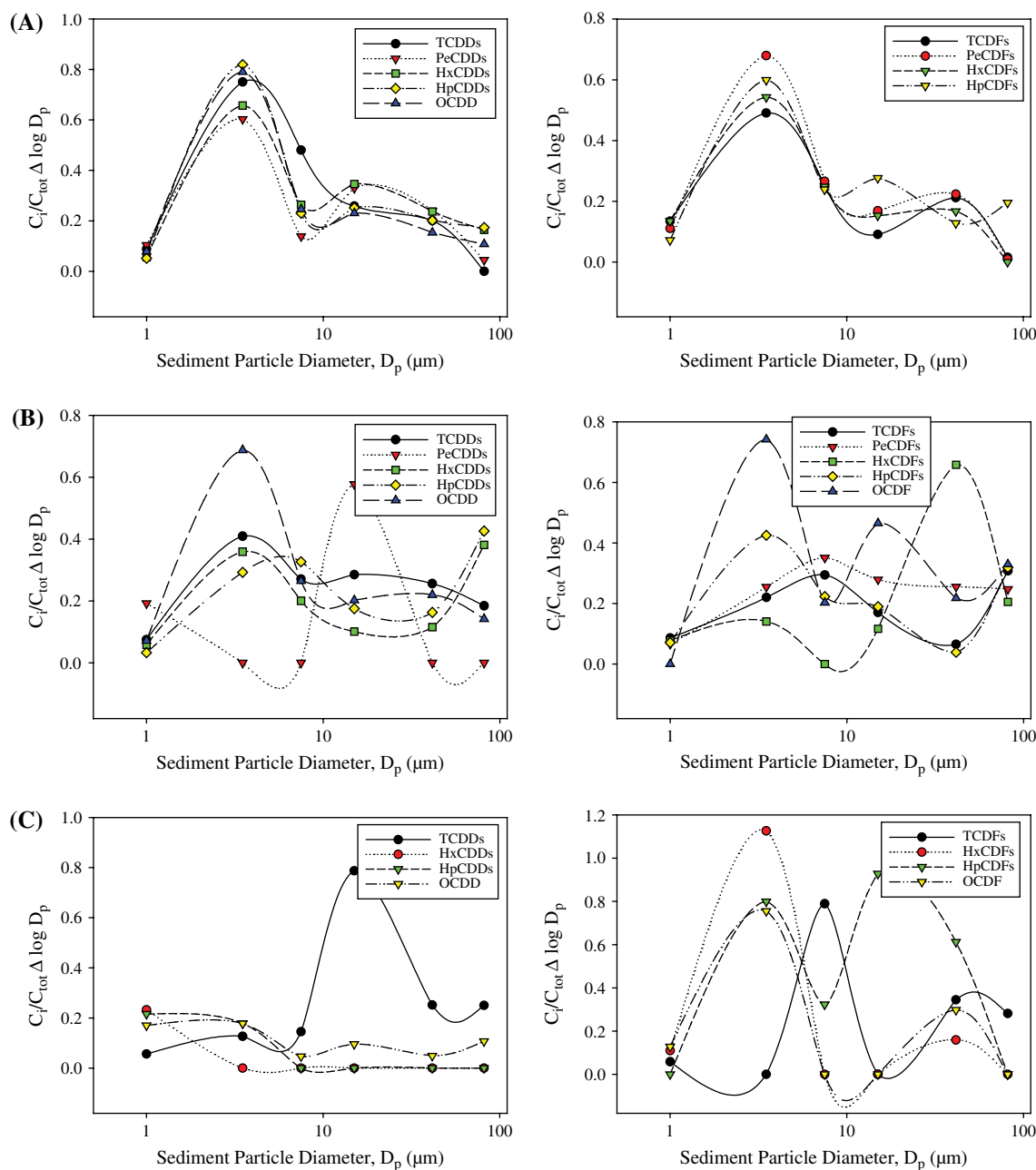

Fig. 5. Log normalized distribution patterns of PCDD and PCDF homologue concentrations according to particle size in sediment samples from the coasts at (A) Pohang, (B) Ulsan, and (C) Busan.

were similar, the Ulsan and Busan homologue profiles were not. It was difficult to find distinctive profiles in this plot with regard to the chlorination degrees as same as those of atmospheric PCDD/Fs.

By examining the change in PCB distribution according to the number of chlorine atoms in particles between 15 and 800 μm, Piérard et al. (1996) found that PCB homologues in sediments showed similar distributions as the atmospheric PCDD/Fs; highly chlorinated PCBs with more than five chlorine atoms were enriched in the smallest particles (<15 μm). However, that study examined particle sizes larger than in the current study. Furthermore, Bush et al. (1994) did not observe a difference in the distribution pattern of PCB congeners between coarse (>420 μm) and fine (<420 μm) particles. Our previous study (Moon et al., 2002b) also found different homologue profiles, as seen by Piérard et al. (1996), despite the preferential distribution of total PCDD/Fs in fine particles. The reasons for these differences in profiles are not clear, yet some explanations seem to be possible: various environmental conditions around sediment collection sites, low levels of PCDD/Fs, and the differences in particles sizes examined in the various studies. Further studies are needed to clarify the relationships between the PCDD/F distribution and sediment particle size, such as PCDD/F sorption according to particle size.

Many benthic organisms take in nutrition from fine particles through filtering. In the case of selective feeders, such as *Diporeia* and Zebra mussels, the effective size range for ingestion is 2–20 μm (Beninger and St-Jean, 1997; Moore, 1976). Fig. 6 shows an elevated level of total PCDD/Fs within this range that would be bioavailable to these organisms (2–10 μm). In addition, turbulence can remobilize these fine particles in the water column (Karlckhoff and Morrls, 1985), increasing the chance that the aquatic biota interact with various substances. However, all of the following contribute to the complicated bioavailability of PCDD/Fs: the feeding behaviors of organisms (Gossiaux et al., 1998; Harkey et al., 1994), uptake affinities for PCDD/Fs in aquatic environments (Loonene et al., 1994), microdechlorination of PCDD/Fs by microorganisms (Peter et al., 1995), and textures of sediment/water (Lyytikäinen et al., 2003). Even hydrophobic organic compounds such as PCBs and PAHs with similar log K_{ow} values had different distributions and availability to the biota (Harkey et al., 1994; Moon et al., 2002b). It is therefore difficult to estimate the relative contribution of each factor.

4. Conclusions

The current study determined the PCDD/F contents in sediments of varying particle sizes. Like other persistent organic pollutants, the major proportion of PCDD/Fs was found in the finest fractions of the sediments. The distribution correlated with the organic carbon contents, indicating that organic carbon acts as a reservoir for contaminants. The distribution of homologues in the different particle sizes was unrelated to the degree of chlorination. Although the bulk concentrations of contaminants in sediments are important, we have demonstrated that it is the fine particles that pose an increased risk for marine organism exposure to PCDD/Fs. Indeed, estimation of the bioavailability of sediment-bound PCDD/Fs to benthic organisms is more reliable when based on the ingestible fine particles rather than the bulk sediment. Studies on the effects of particle size and other factors controlling the bioavailability of sedimentary PCDD/Fs can enhance our understanding of their threat to the aquatic environment.

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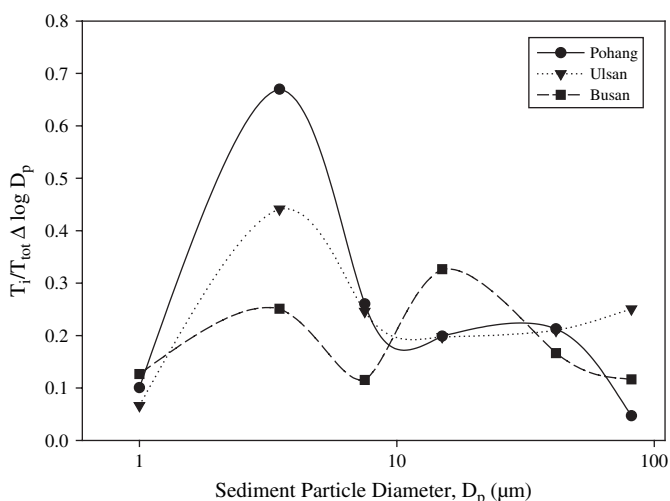

Fig. 6. Log normalized distribution patterns of total PCDD/Fs for different particle sizes.

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