PCDDs/Fs IN SURFACE SEDIMENTS FROM THE SOUTHEASTERN COASTAL AREA OF KOREA

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Abstract
This study was implemented to investigate PCDDs/Fs levels for 12 sediments from the southeastern coast (Gijang) of Korea. The levels of the total PCDDs/Fs were similar to those of the other 4 coastal areas previously reported in Korea. But the TEQ levels were lower than those of 3 out of 4 areas. The homologue profiles of PCDDs/Fs in all the samples were similar and in accordance with PCDDs/Fs homologue profile originated from PCP. As a result of the comparison with the homologue profiles of other 3 coastal areas (from some references) located near Gijang coast, the PCDDs/Fs homologue profile of the Ulsan coast was closely related to that of the Gijang coast ($r = 0.978$, $p < 0.001$). The city of Ulsan has a homologue profile of PCDDs/Fs originated from PCP and many PCDDs/Fs sources including waste incinerators and large steel, heavy chemical factories and petroleum refining facilities. So it is estimated that PCDDs/Fs emitted from these sources were transported by the wind direction and may be sunken in the Ulsan coast by atmospheric dry/wet deposition. Then it is likely that the deposited PCDDs/Fs were transported to the Gijang coasts by the ocean current.

Introduction
The contamination of the coastal environment by trace organic contaminants is of increasing concern these days. In particular, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) are ubiquitous environmental pollutants in coastal marine environments[1]. These chemicals are unintentional byproducts of incineration and manufacturing processes and mainly transported to the aquatic system through the atmospheric dry and wet deposition or directly via rivers[2]. So sediments are regarded as the final destination for non-polar organic contaminants such as PCDDs/Fs. By the release of the PCDDs/Fs, polluted sediments can act as a long-term reservoir with an adverse effect on the aquatic life and bioaccumulate in organisms through the food chain[3].
Therefore, the objective of this study is to investigate the contamination by PCDDs/Fs in surface sediments from the southeastern Korean coastal area of Gijang. Gijang is a highly important coast because of its high marine condition variation resulted from joining the two seas (East & South) of Korea. However, studies about PCDDs/Fs pollution in this area have not been performed even though several studies were done near this area[2, 3].

Materials and Methods
12 surface sediments (0~5 ㎝) were sampled from Gijang in August 2006 (Fig. 1). Near the Gijang area, several industrial cities are located. The cities of Pohang and Ulsan, located along the eastern coast (East Sea) near this sampling site, have contaminant point sources from large steel, heavy and petrochemical industries. And the city of Busan along the southern coast (South Sea) is the largest port in Korea. It is characterized by high contamination activities from ships and numerous municipal point sources along the coastal line. The East Sea joins the South Sea at the southeastern coastal area (Gijang) of Korea. So the Gijang area has a dynamic coastal condition that includes a complex ocean current and speed variation.
Sediment samples were dried at room temperature and sieved 63 ㎛. The experimental procedure and instrumental analysis based on the previous published papers[4, 5] were performed. The 10 g samples of dried sediments were extracted with 400 mL toluene for 16 hours by the Soxhlet apparatus. The extract was eluted with multi-layer silica gel column and with activated carbon-impregnated silica gel column (9 g). HRGC (HP 6890) with HRMS (Auto Spec Ultima-Micromass) system conditions were performed as follows: Determination of hepta- to octaCDDs/Fs were accomplished by using a 60 m of DB-5MS column (J&W Scientific; 0.25 ㎜ i.d. with 0.25 ㎛ film thickness). Similarly, SP-2331 (J&W Scientific; 60 m x 0.32 ㎜ i.d. with 0.20 ㎛ film thickness) fused silica capillary column was used to separate tetra- to hexaCDDs/Fs.
All multivariate statistical analyses were performed by SPSS 12.0K (SPSS inc., USA).

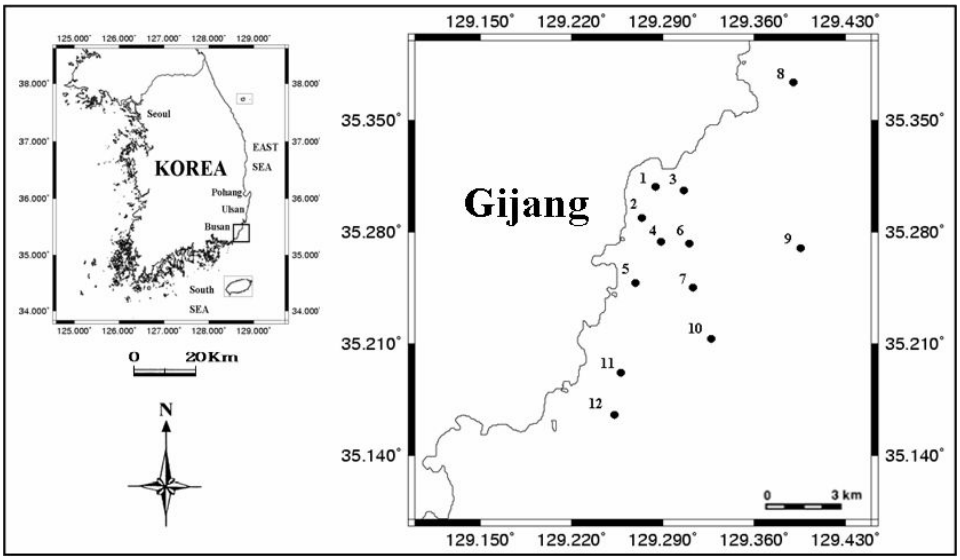

Fig.1. Map showing the sampling stations from the Southeastern coastal area (Gijang), Korea

Results and Discussion

PCDDs/Fs contents and homologue profiles in bulk sediments

Table 1 shows a broad range of total PCDDs/Fs levels in bulk sediments (387~2746 ng/kg dry weight; 1.4~11.7 pg WHO-TEQ/g dry weight). PCDDs/Fs results of a previous study[2] are also presented in Table 2 for comparison. The levels of the total PCDDs/Fs in this study are similar to previously reported results in the 4 coastal areas of Korea. But TEQ levels in this study are a little bit lower than 3 areas (the Jinhae, Pohang and Busan coast). The percentage of the total PCDDs (79.0±3.5%) was higher than that of the total PCDFs (21.1±3.5%). The OCDD was the most dominant homologue (60.7±3.9%) in all the sediment samples. Also, high chlorinated dioxins and furans were dominant (H7CDDs > O8CDF > H7CDFs). All samples had similar homologue distribution patterns and this similarity of PCDDs/Fs homologue profiles (RSD < ±3.87) suggests that the main sources or formation processes might be the same for all the samples.

Table 1. Concentrations of total PCDDs, PCDFs and WHO-TEQs in surveyed sites

Class / Conc.	Total PCDDs		Total PCDFs		Total PCDDs/Fs
	Range (Mean±SD)	Fraction (%) Range (Mean±SD)	Range (Mean±SD)	Fraction (%) Range (Mean±SD)	Range (Mean±SD)
ng/kg d.w.	374~2125 (1191±809)	75.0~88.7 (79.0±3.5)	82~604 (311±220)	11.3~25.0 (21.1±3.5)	387~2746 (1501±1014)
WHO-TEQ	0.3~1.6 (2.0±1.7)	14.8~73.2 (34.6±17.0)	0.9~7.8 (3.7±2.5)	26.8~85.3 (65.4±17.0)	1.4~11.7 (5.7±3.6)

Table 2. Comparison of the PCDDs/Fs concentrations in sediments from various coastal areas in Korea

Location	Year	Concentration	Reference
Gijang coast, Korea	2006	387~2746 ng/kg d.w. (1.4~11.7 pg WHO-TEQ/g d.w.)	This study
Jinhae coast, Korea	2000~ 2001	174~2663 ng/kg d.w. (1.4~41.7 pg WHO-TEQ/g d.w.)	Moon et al., 2003[2]
Ulsan coast, Korea		191~674 ng/kg d.w. (1.3~5.5 pg WHO-TEQ/g d.w.)	
Pohang coast, Korea		141~1265 ng/kg d.w. (2~16 pg WHO-TEQ/g d.w.)	
Busan coast, Korea		164~1991 ng/kg d.w. (1.23~22.7 pg WHO-TEQ/g d.w.)	

Baker and Hites[6] proposed that a significant source of OCDD (and a lesser extent of the H7CDDs) to the environment might be photochemical synthesis of OCDD from pentachlorophenol (PCP) in condensed water in the atmosphere. PCP itself is believed to be sufficiently volatile (vapor pressure around 0.1 Pa) under ambient conditions, so it may be emitted to the atmosphere from treated products, such as wood and textiles. General PCDDs/Fs profiles[7] from PCP-treated products are characterized by OCDD dominant and relatively high concentrations of PCDFs. The ratio of the ΣPCDDs to ΣPCDFs concentrations (D/F ratio) ranges from 1~10.
In this study, the D/F ratio was 3.95±1.24 for all the samples and OCDD was dominant, indicating the possibility of PCP-oriented contamination in this area.

Origin of PCDDs/Fs in Gijang sediments of this study
To investigate the origin of PCDDs/Fs in Gijang coastal sediments of this study, the homologue profiles of sediments in three coastal areas[3] (the Pohang, Busan and Ulsan coast) located near the Gijang coast were compared with that of Gijang coastal sediments (Fig. 2). As a result of correlation analysis, the homologue profiles of Gijang coastal sediments were closely related to that of Ulsan coastal sediment ($r = 0.978$, $p < 0.001$). Ulsan coastal sediment also had an OCDD dominant pattern and high D/F ratio, regarding it as a PCP originated pattern like in the Gijang area. PCP is mainly used as a preservative of timber and biocide in Korea. In the city of Ulsan, it is estimated that about 23 hundred of tons of waste timber per year have been treated by waste incinerators and there are other dense resources of PCDDs/Fs such as large steel, heavy chemical factories and petroleum refining facilities (Fig. 3). The main wind direction is to the northwest in Ulsan, so the main wind transports PCDDs/Fs emitted from the above sources and they seem to be sunken in the Ulsan coast by atmospheric dry/wet deposition. So, PCDDs/Fs of surface sediments in Ulsan might be transported to the Gijang area through ocean current, especially, point 8 near the Ulsan coast. Therefore, the homologue profiles of Gijang sediments are closely related to that of the Ulsan coastal sediment.

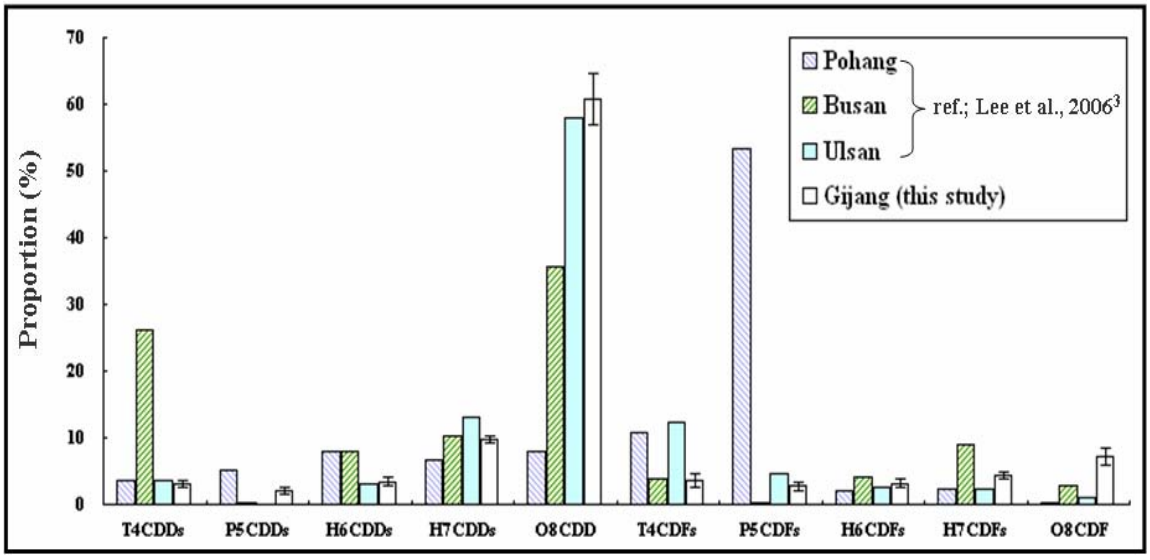

Fig. 2. PCDDs/Fs homologue profiles for Pohang, Busan, Ulsan and Gijang (this study) coast

Although the homologue profiles are similar for all the sampling sites in this study, the two main groups (Fig. 3) were divided according to the levels of PCDDs/Fs concentration in PCA (Principle Component Analysis). The samples in Group 1 (sampling sites: 1~6) had low concentration levels (387~600 ng/kg dry weight; 1.4~3.2 pg WHO-TEQ/g dry weight), but those of Group 2 (sampling sites: 7~12) had relatively higher concentration levels (2202~2746 ng/kg dry weight; 7.2~11.7 pg WHO-TEQ/g dry weight) than Group 1. The levels of the total PCDDs/Fs of Group 2 were 4~7 times higher than those of Group 1. The depth of surface sediments and severe marine condition variation such as ocean current and speed in the region might affect the levels of PCDDs/Fs between Group 1 and 2. The difference of depth in surface sediments between Group 1 (20~40 m) and 2 (60~85

m, except point 8) cause the different PCDDs/Fs concentration levels. Namely, PCDDs/Fs in the surface sediments of Ulsan (or from the other sources) may be transported to the Gijang area by the ocean current. So it is likely that the fine sediment particles which contain high PCDDs/Fs concentration swept away from the coastal area by the tide and settled in the outer coast.

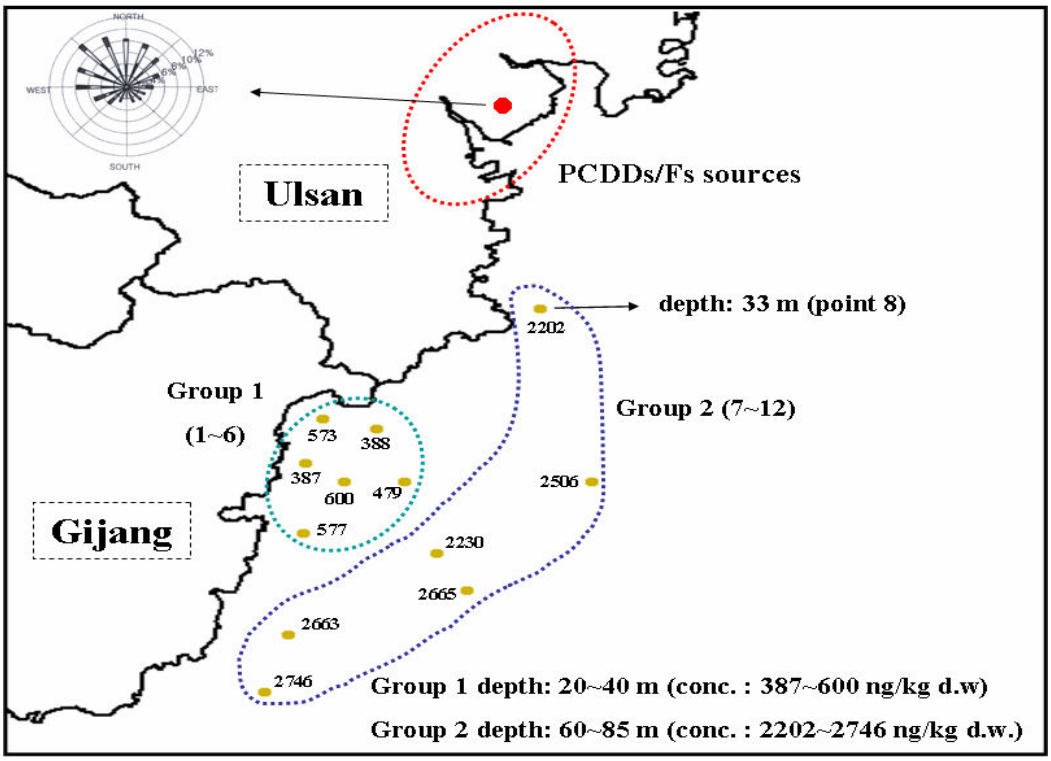

Fig. 3. The topography of Gijang and Ulsan region and sampling depth of Group 1 and 2

But the conclusive evidence for supporting this discussion is the exiguous because research about the identification of deposited PCDDs/Fs transported by the ocean current has never been studied and the PCDDs/Fs analysis according to particle size is needed. Therefore, a further investigation such as PCDDs/Fs transport by ocean current and particle size distribution with depth should be performed to explain these phenomena conclusively.

Acknowledgements

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