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# Evaluation of PCDDs/DFs origin in Sediments from Ulsan Bay, Korea

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Polychlorinated dibenzo-*para*-dioxins (PCDDs) and dibenzofurans (PCDFs) were measured in sediment samples at Ulsan Bay in Korea. PCDDs/DFs were detected in all the sediment samples. Recoveries of certified sediment materials (CRMs) were in the range of 69-117%, which satisfied EPA method 1613 protocols. Total concentrations of PCDDs/DFs in sediments ranged from 191 to 674 pg/g dry weight and I-TEQ levels in this bay ranged between 1.3 and 5.5 pg-TEQ/g dry weight. Dioxin contaminations among sampling stations at Ulsan bay had not great difference. PCDDs/DFs levels in the bay were similar to or lower than earlier data reported from the Korean coasts and other countries. TEQ values for PCDDs/DFs in all sediment samples were below the safety sediment value (20 pg-TEQ/g dry weight) for chronic toxicity assessment and seemingly moderate, but the total TEQ for the same sediments including PAHs exceeded the 20 pg-TEQ/g dry weight. This result indicates that the toxic potency assessment for aquatic environment of a bay should be considered to dioxin-like contaminants as well as PCDDs/DFs at the same time. Examination of homologue groups showed that octachlorinated dibenzo-*para*-dioxin (OCDD) had the highest proportions. For the congener distribution patterns, the most abundant congeners of PCDDs/DFs were comparable to those of combustion residues formed from various combustion processes. This finding reveals that the origin of PCDDs/DFs in sediments from Ulsan Bay is related to combustion processes. In order to assess the sources of PCDDs/DFs in sediments from Ulsan Bay, the congener-specific characterization using principal component analysis (PCA) was investigated. Four major factors were determined, and two of them were attributed to PCDDs/DFs in the inputs of airborne particulate matters. Other two factors can be explained by the influence of impurities of pentachlorophenol (PCP) and the direct discharge of industrial sewage and/or domestic wastewater, respectively. Consequently, the major origin of PCDDs/DFs in Ulsan Bay was the inputs of atmospheric particles generated from various combustion processes. Results showed that the congener-specific characterization using multivariate data analysis (PCA) was a useful technique for evaluation of PCDDs/DFs origins in marine sediments.

**Key words:** PCDDs/DFs, origin, Ulsan Bay, PCA, congener-specific characterization

## 1. Introduction

Polychlorinated dibenzo-*para*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are classes of tricyclic aromatic chemicals comprised of the elements of carbon, hydrogen, oxygen and chlorine. PCDDs and PCDFs (PCDDs/DFs) have in recent decades generated wide interest in both scientific and public settings as a result of the pronounced toxicity and persistence of members within these compound classes. PCDDs/DFs, especially the isomers with chlorines substituted in 2, 3, 7 and 8 positions are thought to pose a risk to human health due to their high toxicity, carcinogenic potency and potential effects on animal reproductive and immunological systems.[1-3] It has been reported recently that PCDDs/DFs exhibit endocrine disrupting potency.[4-5] In addition, there is growing evidence that these compounds are extremely harmful to marine and freshwater ecosystems, especially when they bioaccumulate through aquatic foodwebs.[6-8] Hence, the existence of PCDDs/DFs in marine sediments of waterways in industrialized and heavily populated areas is an environ-

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mental problem that has received considerable attention in recent years.

PCDDs/DFs are emitted into the environment by the various combustion sources and manufacturing processes, such as municipal solid waste incineration, motor vehicles, steel mills, and chemical production processes.[9-12] These contaminants derived from various sources are mainly transported to the aquatic systems through the atmospheric dry and wet deposition and/or directly via rivers. All PCDDs and PCDFs are characterized by extremely low water solubilities, have a tendency for being strongly bound or adsorbed onto surfaces of particulate matter.[13-14] Therefore, underlying sediments will work as conservative matrices that provide valuable information on the recent input of contaminants to the marine environment.[13,15] The similar homologue profiles at many environmental samples 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.[16-18] PCDDs/DFs from tetra- to octachlorinated compounds have 136 congeners. These congener distributions including the seventeen toxic 2,3,7,8-substituted congeners and non-toxic congeners have been used to identify the relationships between environmental samples and origins. However, the distributions and sources of PCDDs/DFs were mostly investigated using the homologue profiles or the value of toxic 2,3,7,8-substituted congeners until now. In several cases, it was difficult to estimate the origins of PCDDs/DFs from environmental samples. Hence, the examination including non-toxic congeners of PCDDs/DFs may provide more comprehensive information to identify origins of PCDDs/DFs in environmental samples.[19-23]

Multivariate statistical analyses have been utilized by many researchers to reduce the complexity of the data. Principal component analysis (PCA), the aim of which is the reduction of data dimensions and the interpretation of the data, has been applied successfully by several researchers to estimate relationships between pollutant sources and environmental samples.[24-26] In this study, the congener-specific characterization of PCDDs/DFs in marine sediments from Ulsan Bay was performed by PCA, to evaluate the origins of these contaminants in this bay.

The study area Ulsan Bay, which is located on the eastern coast of Korea, is one of heavily industrialized regions and the largest commercial harbor in Korea. Ulsan petrochemical industrial complex is composed of over 100 plants as well as many factories manufacturing products, automobiles, ships and related facilities. Hence, the rapid industrialization of this area has been accompanied by environmental deterioration which has led to social and environmental health problems. Studies on organochlorine pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenylethers (PBDEs) and heavy metals have been performed for the aquatic environment of Ulsan Bay by several authors.[27-31] However, there is relatively few data on dioxin contaminations in the environment of Ulsan Bay. This study represents a first effort to examine levels and origins of PCDDs/DFs in surface sediments from Ulsan Bay, Korea. The objective of this study is to evaluate toxic potency and source attributions of PCDDs/DFs at Ulsan Bay sediments in Korea using congener-specific characterization.

## 2. Materials and Method

### 2.1. Sampling

Surface sediments (0-5 cm) were sampled at 22 stations from Ulsan Bay in November 2000 (Fig. 1). Samples were collected using a box-corer sampler and then kept frozen at -20°C until extraction.

### 2.2. Extraction and cleanup

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 (Ultra residue analysis grade, from J. T. Baker, USA) for 24 hours after being spiked with internal standards (EPA-1613LCS, from Wellington Laboratories, Canada). The extract was

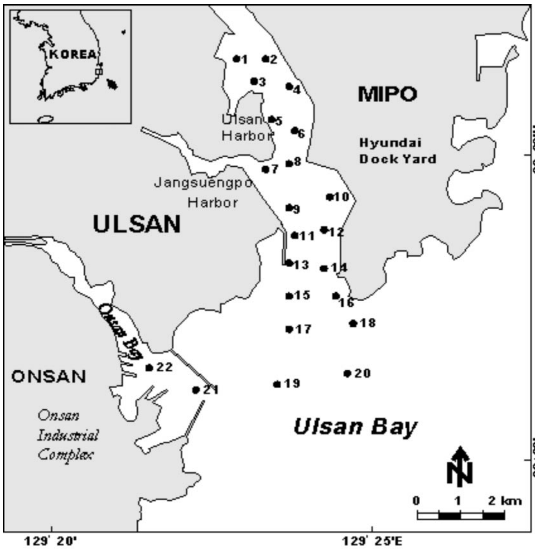



**Fig. 1.** Map showing the sampling stations of surface sediments from Ulsan Bay, Korea.

reduced to 1-2 mL in a rotary evaporator and transferred to *n*-hexane (Ultra residue analysis garde, from J. T. Baker, USA).

Samples were pre-cleaned up on a multi-layer silica-based adsorbents (70-230 mesh, from Neutral, Merck) column (15 mm in diameter, 300 mm in length) with 160 mL of *n*-hexane. The elution flow was set at 10 mL/min. The extract was 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% sulfuric acid impregnated silica gel 3 g, 44% sulfuric 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. After pre-cleaned up with a multi-layer silica gel column chromatography, samples were fractionalized with an activated neutral alumina (70-230 mesh, Neutral, Merck) column (12 mm in diameter, 250 mm in length) with successive eluants of 3% methylene dichloride (Pesticide residue analysis grade, from Cica-Merck, Japan) 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 grade, from Fluka, Switzerland) and determined for PCDDs/DFs.

### 2.3. High resolution gas chromatography/high resolution mass spectrometer analysis

The high resolution gas chromatography/high resolution mass spectrometer (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 SP 2331 (60 m length, 0.25 mm inner diameter, 0.25 μm film thickness, Supelco) and a DB-5MS (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness, J&W Scientific) were used for the separation of compounds. Two molecular ions ([M+] and [M+2]+) 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

**Table 1.** Instrumental conditions by HRGC/HRMS of PCDDs/DFs in surface sediments from Ulsan Bay, Korea

| | Tetra- to hexachloro DDs/DFs | Hepta- to octachloro DDs/DFs |
|---|---|---|
| Instrument | Agilent 6890 GC/JMS 700D MS | Agilent 6890 GC/JMS 700D MS |
| Column | SP-2331 (60 m, 0.25 mm inner diameter, 0.25 μm film thickness, Supelco) | DB-5MS (30 m, 0.25 mm inner diameter, 0.25 μm film thickness, J&W Scientific) |
| Injector type | Splitless | Splitless |
| Carrier gas | Helium, 1.2 mL | Helium, 1.2 mL |
| Injector temp. | 250°C | 280°C |
| Column temp. | 140°C (1 min)–10°C/min–200°C–2°C/min–250°C (28 min) | 150°C (1 min)–20°C/min–300°C (21.5 min) |
| Interface temp. | 250°C | 270°C |
| Chamber temp. | 260°C | 280°C |
| Ionization temp. | EI+, 38 eV, 500 μL | EI+, 38 eV, 500 μL |
| Injection volume | 2 μL | 2 μL |
| SIM | $M^+$ and $M^{+2}$ or $M^{+2}$ and $M^{+4}$ | $M^+$ and $M^{+2}$ or $M^{+2}$ and $M^{+4}$ |

**Table 2.** The recovery results (%) of SRMs for toxic 2,3,7,8-substituted PCDDs/DFs from marine sediment samples

| | DX-1 | DX-2 | Mean ± SD |
|---|---|---|---|
| 2,3,7,8-TCDD | 101 | 92.4 | 97 ± 4.3 |
| 1,2,3,7,8-PeCDD | 112 | 98.5 | 105 ± 6.8 |
| 1,2,3,4,7,8-HxCDD | 109 | 96.8 | 103 ± 6.1 |
| 1,2,3,6,7,8-HxCDD | 112 | 117 | 115 ± 2.5 |
| 1,2,3,7,8,9-HxCDD | 110 | 88.1 | 99 ± 11 |
| 1,2,3,4,6,7,8-HpCDD | 99.8 | 85.4 | 93 ± 7.2 |
| OCDD | 93.5 | 83.6 | 89 ± 4.3 |
| 2,3,7,8-TCDF | 91.4 | 82.9 | 87 ± 4.3 |
| 1,2,3,7,8-PeCDF | 85.6 | 80.2 | 83 ± 2.7 |
| 2,3,4,7,8-PeCDF | 104 | 105 | 105 ± 0.5 |
| 1,2,3,4,7,8-HxCDF | 85.9 | 82.6 | 84 ± 1.7 |
| 1,2,3,6,7,8-HxCDF | 88.6 | 85.1 | 87 ± 1.8 |
| 1,2,3,7,8,9-HxCDF | 80.3 | 78.9 | 80 ± 0.7 |
| 2,3,4,6,7,8-HxCDF | 82.6 | 77.6 | 80 ± 2.5 |
| 1,2,3,4,6,7,8-HpCDF | 75.6 | 75.4 | 76 ± 0.1 |
| 1,2,3,4,7,8,9-HpCDF | 77.8 | 102 | 90 ± 12 |
| OCDF | 68.9 | 72.1 | 71 ± 1.6 |

factor (RRF) method previously obtained four standard solutions injections (EPA-1613CVS, Wellington Laboratories, Canada), as recommended by the US EPA. Detailed instrumental conditions of HRGC/HRMS were summarized in Table 1.

### 2.4. Quality control

In order to assess the accuracy of the determinations by experimental procedure and instrument, the certified marine sediment materials collected from Great Lakes (DX-1 and DX-2, NWRI, Canada) were analyzed for 2,3,7,8-substituted PCDDs/DFs as Standard Reference Materials (SRMs) in this investigation. The recovery results were in the range of 69-117% which satisfied EPA method 1613 protocols.

Procedural blanks were processed in the same manner as real samples, and they were below 10% of analytes abundance. Blanks were run before and after the injection of standard solutions to check for any carryover. The calculated detection limits (S/N ratio=3) of individual PCDD/DF in marine sediments was 0.008 pg/g dry weight for tetra- and penta-chlorinated compounds, 0.02 pg/g dry weight for hexa- and hepta-chlorinated compounds and 0.04 pg/g dry weight for octachlorinated compounds.

**Table 3.** Summary of total and toxic 2,3,7,8-substituted PCDDs/DFs (pg/g dry weight) in surface sediments from Ulsan Bay, Korea

| | Min | Max | Median | Mean |
|---|---|---|---|---|
| 2,3,7,8-TCDD | 0.054 | 0.219 | 0.099 | 0.104 |
| TCDDs | 7.92 | 81.28 | 24.70 | 28.22 |
| 1,2,3,7,8-PeCDD | 0.127 | 0.465 | 0.294 | 0.292 |
| PeCDDs | 6.06 | 34.02 | 15.15 | 16.41 |
| 1,2,3,4,7,8-HxCDD | 0.019 | 0.111 | 0.063 | 0.064 |
| 1,2,3,6,7,8-HxCDD | 0.050 | 0.179 | 0.140 | 0.132 |
| 1,2,3,7,8,9-HxCDD | 0.058 | 0.216 | 0.141 | 0.142 |
| HxCDDs | 12.42 | 34.23 | 25.51 | 24.79 |
| 1,2,3,4,6,7,8-HpCDD | 0.080 | 0.242 | 0.162 | 0.167 |
| HpCDDs | 17.98 | 56.59 | 36.76 | 37.69 |
| 1,2,3,4,6,7,8,9-OCDD | 0.053 | 0.334 | 0.177 | 0.194 |
| OCDD | 52.76 | 334.01 | 177.10 | 193.81 |
| 2,3,7,8-TCDF | 0.051 | 0.290 | 0.115 | 0.128 |
| TCDFs | 9.24 | 42.97 | 24.45 | 24.56 |
| 1,2,3,7,8-PeCDF | 0.042 | 0.251 | 0.103 | 0.113 |
| 2,3,4,7,8-PeCDF | 0.314 | 1.436 | 0.789 | 0.802 |
| PeCDFs | 10.49 | 68.00 | 26.26 | 28.52 |
| 1,2,3,4,7,8-HxCDF | 0.123 | 0.882 | 0.314 | 0.351 |
| 1,2,3,6,7,8-HxCDF | 0.072 | 0.616 | 0.180 | 0.214 |
| 1,2,3,7,8,9-HxCDF | 0.015 | 0.944 | 0.064 | 0.157 |
| 2,3,4,6,7,8-HxCDF | 0.037 | 0.369 | 0.168 | 0.189 |
| HxCDFs | 9.77 | 83.45 | 25.54 | 28.79 |
| 1,2,3,4,6,7,8-HpCDF | 0.053 | 0.255 | 0.117 | 0.131 |
| 1,2,3,4,7,8,9-HpCDF | 0.005 | 0.069 | 0.018 | 0.022 |
| HpCDFs | 10.59 | 59.12 | 23.74 | 27.50 |
| 1,2,3,4,6,7,8,9-OCDF | 0.006 | 0.053 | 0.023 | 0.026 |
| OCDF | 5.98 | 52.63 | 22.84 | 25.54 |
| I-TEQ | 1.3 | 5.5 | 3.2 | 3.2 |
| ΣPCDD/DF | 191 | 674 | 434 | 436 |

## 3. Results and Discussion

### 3.1. Levels and toxic potency assessment of PCDDs/DFs in sediments from Ulsan Bay

PCDDs/DFs were detected in all sediments analyzed. Total and toxic 2,3,7,8-substituted PCDDs/DFs concentrations in surface sediments at Ulsan Bay of Korea were summarized in Table 3 and Fig. 2. The international toxic equivalent factor (I-TEF) proposed by North Atlantic Treaty Organization (NATO) was used for the toxic equivalent (TEQ) concentration. PCDDs/DFs concentrations in surface sediments from Ulsan

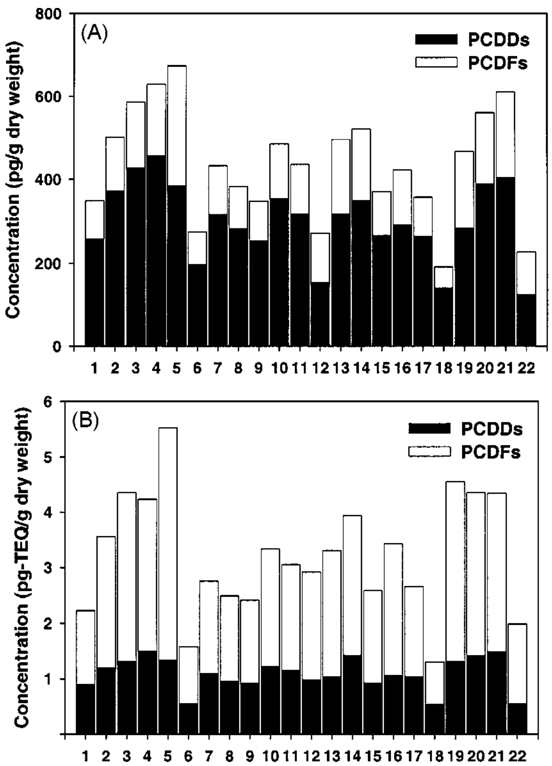



**Fig. 2.** Concentrations of total PCDDs/DFs (A) and toxic 2,3,7,8-substituted PCDDs/DFs (B) in surface sediments from Ulsan Bay, Korea.

Bay varied from 191 to 674 pg/g dry weight with an average of 436 pg/g dry weight. I-TEQ levels in this bay ranged between 1.3 and 5.5 pg-TEQ/g dry weight with an average of 3.2 pg-TEQ/g dry weight. Maximum concentration was found at Station 5 in the vicinity of Ulsan Harbor. However, in general, there were no great differences of dioxin contaminations among sampling stations from Ulsan Bay. A number of earlier studies have reported PCDDs/DFs levels in marine sediments from several Korean coasts. Ok et al.[32] studied sediments from Korean coasts, finding levels that ranged from 2 to 32 pg-TEQ/g dry weight. Moon et al.[33] found concentrations between 0.6 and 8.6 pg-TEQ/g dry weight in sediments from the southeastern coastal areas of Korea. Im et al.[34] also investigated dioxins in sediments from Masan Bay, and samples were in the range of 1-76 pg-TEQ/g dry weight. In the case of other countries, dioxin levels in sediments from Venice Lagoon, Italy varied between 0.01 and 37 pg-TEQ/g dry weight.[8] Eljarrat et al.[35] found that the sediments from the northwestern Mediterranean ranged from 0.4 to 39 pg-TEQ/g dry weight. Sakurai et al.[36] investigated that the PCDDs/DFs levels in Tokyo Bay of Japan varied from 18 to 52 pg-TEQ/g dry weight. In general, our results were similar to or lower than those reported in earlier studies from Korean coasts and other countries.

In order to evaluate a toxic potency for the marine coastal environment, Evers et al.[37] proposed the 20 pg-TEQ/g dry weight as a safety sediment value of chronic toxicity. In this study, concentrations for PCDDs/PCDFs in all the sediment from Ulsan Bay, Korea were below the safe sediment value.

Moon et al.[30] reported that PAH concentrations at sampling stations of Ulsan Bay were in the range of 14 to 7,108 ng/g dry weight, suggesting the wide contamination by PAHs. Of these sampling stations, some chemicals detected in Stations 7 and 8, which had the highest PAHs contaminations, exceeded the effects range-low (ERL) recommended by NOAAs effects-based guidelines on organisms.[38] This phenomena seems to be due to the differences of sources for two contaminants (PAHs and PCDDs/DFs). Indeed, the primary source of PAHs in sediments from Stations 7 and 8 in this bay derived from mostly petrogenic input. This result seems that toxic organic contamination in Ulsan Bay is responsible for PAHs than PCDDs/DFs based on the differences of contamination sources.

In addition, the induction-derived equivalency factors of individual PAH compound with respect to TCDD proposed by several researchers were roughly in the range of 0.001-0.00001.[39-41] So, TEQ value for PAHs by multiplying the concentrations with each factor proposed greatly exceeded the sediment safe value (20 pg-TEQ/g dry weight). Accordingly, TEQ value for PCDDs/DFs in all sediment samples was below the safe sediment value and seemingly moderate, but the total TEQ values for the same sediment exceeded the 20 pg-TEQ/g dry weight. Therefore, the toxic potency assessment for aquatic environment of the bay should be considered to a variety of hazardous organic contaminants including PAHs, dioxin-like PCBs and etc. at the same time.

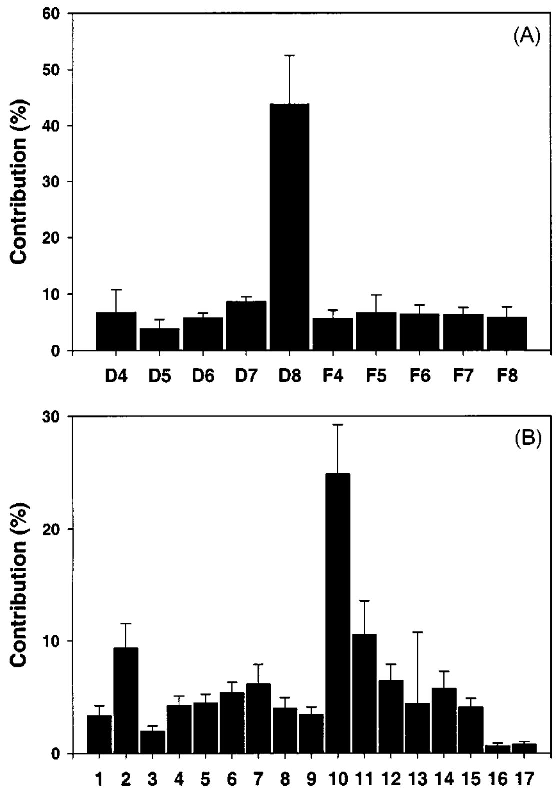
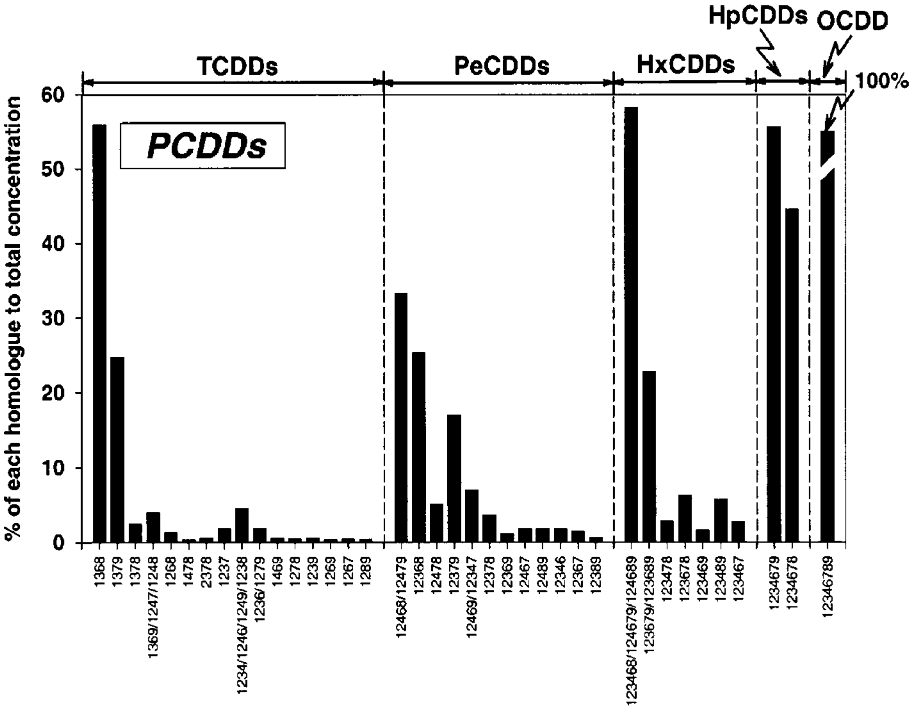



**Fig. 3.** Average normalized profiles of homologues (A) and toxic 2,3,7,8-substituted PCDDs/DFs (B) in surface sediments from Ulsan Bay, Korea. Vertical lines indicate standard deviations. D4: tetra CDDs, D5: penta CDDs, D6: hexa CDDs, D7: hepta CDDs, D8: octa CDD, F4: tetra CDFs, F5: penta CDFs, F6: hexa CDFs, F7: hepta CDFs, and F8: octa CDF. 1: 2,3,7,8-TCDD, 2: 1,2,3,7,8-PeCDD, 3: 1,2,3,4,7,8-HxCDD, 4: 1,2,3,6,7,8-HxCDD, 5: 1,2,3,7,8,9-HxCDD, 6: 1,2,3,4,6,7,8-HpCDD, 7: OCDD, 8: 2,3,7,8-TCDF, 9: 1,2,3,7,8-PeCDF, 10: 2,3,4,7,8-PeCDF, 11: 1,2,3,4,7,8-HxCDF, 12: 1,2,3,6,7,8-HxCDF, 13: 1,2,3,7,8,9-HxCDF, 14: 2,3,4,6,7,8-HxCDF, 15: 1,2,3,4,6,7,8-HpCDF, 16: 1,2,3,4,7,8,9-HpCDF, and 17: OCDF.

### 3.2. Homologue and congener distributions of PCDDs/DFs in Ulsan Bay sediments

Profiles of total PCDDs/DFs and 2,3,7,8-substituted congeners in surface sediments from Ulsan Bay of Korea are shown in Fig. 3. All data were normalized to the total concentration of PCDDs/DFs. All stations represented the similar homologue patterns. The result suggests that this bay were influenced by the similar pollutant source. Total contribution of PCDDs was higher than those of PCDFs for all sediment samples. Regarding total PCDDs, OCDD had the highest occupation in all cases, followed by heptachlorinated dibenzo-*para*-dioxins (HpCDDs). In the case of PCDFs, all samples generally showed a similar contribution. For 2,3,7,8-substituted congeners, 2,3,4,7,8-PeCDF occupied the highest value in all samples, followed by 1,2,3,4,7,8-HxCDF > 1,2,3,7,8-PeCDD > 1,2,3,6,7,8-HxCDF > OCDD. The most toxic congener 2,3,7,8-TCDD relatively had a low value in all sediments studied.

Koester and Hites[42] suggested that atmospheric processes tend to favor the deposition of these higher chlorinated dioxins, which resulted in the higher concentrations in the environment. This phenomenon can be explained that the homologue profiles of PCDDs/DFs in the background river sediments caused by atmospheric deposition were mainly dominated by the higher chlorinated dioxins. Indeed, atmospheric trans-for-mation seems to enrich octachlorinated dibezo-*p*-dioxins in comparison to the less chlorinated homologues because of its lower photodegradation potential.[8] Hence, the PCDDs/DFs homologue patterns in sediments contaminated exclusively by atmospheric deposition are dominated by OCDD, while sediments contaminated directly by industrial discharges contain complex patterns of PCDDs/DFs congener. Zook and Rappe[43] also reported that the predominance of OCDD in many abiotic environmental samples is thought to reflect an enrichment process since OCDD is the least environmentally degraded of all PCDDs and is often the most abundant isomer present in snow, soil and sediments. However, it is remarkable that many abiotic samples such as marine sediments can resemble pentachlorophenol (PCP) homologue profiles, and hence the relative importance of these two dioxin sources (atmospheric deposition and PCP) may be unclear for environmental samples from certain locales. Baker and Hites[44] suggested that the photochemical synthesis of OCDD from PCP in atmospheric condensed water is the most significant source of OCDD to the environment. For these reason, the characterisation including other congeners will be necessary for the more comprehensive information on relationships between source and environmental samples.[23,45]



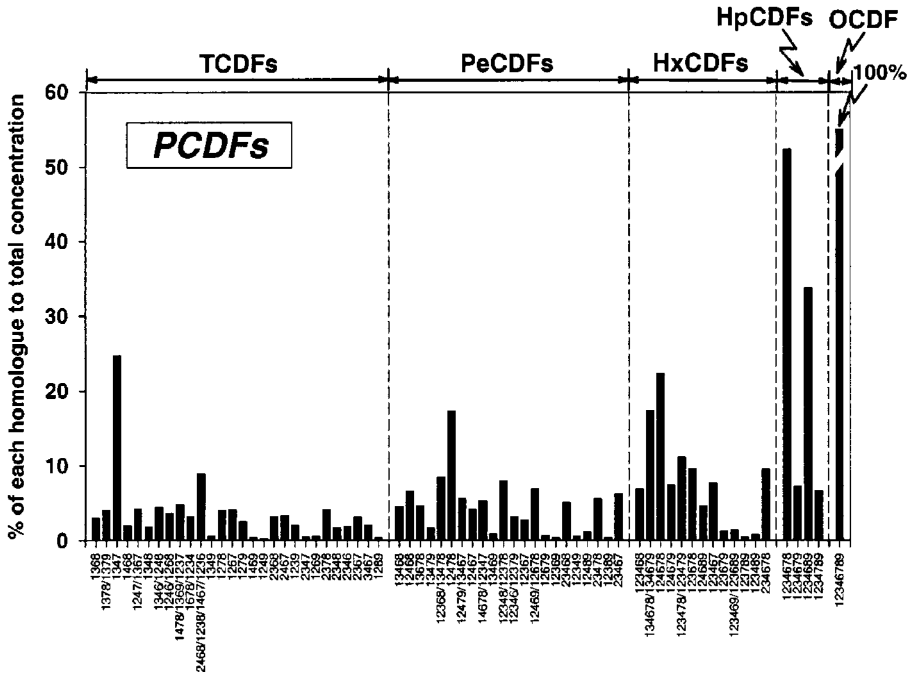




**Fig. 4.** Average congener profiles of PCDDs and PCDFs in marine sediments from Ulsan Bay, Korea. Each congener were normalized by total concentration of each homologue. Congener group which coelutes on SP-2331 and DB-5MS columns is described by '/'.

### 3.3. Congener-specific characterisation of PCDDs/DFs in sediments from Ulsan Bay, Korea

Average congener distributions of PCDDs/DFs in sediments from Ulsan Bay, Korea are presented in Fig.

4. Each congener was normalized to total concentrations of each homologue. The 1,3,6,8-TCDD and 1,3,7,9-TCDD were dominant species in TCDD homologues and the 1,2,4,6,8/1,2,4,7,9-, 1,2,3,6,8- and 1,2,3,7,9-PeCDD were predominant species in the PeCDDs. 1,2,3,4,6,8/1,2,4,6,7,9/1,2,4,6,8,9-HxCDD was the most abundant species in HxCDD congener groups. Wehrmeier et al.[46] showed that typical isomer patterns of isomers of PCDDs/DFs formed as trace byproducts from various combustion conditions. In this study, the TCDD isomer pattern is dominated by the 1,3,6,8- and 1,3,7,9-TCDD. The most abundant PeCDD isomers (in decreasing order) were 1,2,3,6,8-, 1,2,4,7,9-, 1,2,3,7,9- and 1,2,4,6,8-PeCDD. The 1,2,3,4,6,8-HxCDD was the isomer with highest concentrations in combustion residues, only small amounts of other HxCDD isomers were found. Therefore, the congener patterns of PCDDs/DFs in surface sediments from Ulsan Bay were similar to those of combustion processes, indicating that these contaminants mainly derived from various combustion processes in studied areas.

For PCDFs, the congener abundances of all sediment samples were similar except some species. The 1,3,4,7- and 2,4,6,8/1,2,3,8/1,4,6,7/1,2,3,6-TCDF were predominant congeners in TCDF homologue and 1,2,4,7,8-, 1,2,3,6,8/1,3,4,7,8- and 1,2,3,4,8/1,2,3,7,8-PeCDF were present in higher proportions in PeCDFs. HxCDF congener patterns were dominated by 1,2,4,6,7,8- and 1,3,4,6,7,8/1,3,4,6,7,9-HxCDF. They were generally characterized by a small amount of 1,9-substituted congeners.

### 3.4. Origin attribution of PCDDs/DFs in sediments from Ulsan Bay of Korea using multivariate data analysis

Although the examination of congener profiles can explain the relationships among congeners within each homologue, it is difficult to identify the relationships among all congeners of different homologues, including OCDD and OCDF.[45] Hence, principal component analysis (PCA) has been used to investigate the similarities, differences, and relationships of the variations in PCDDs/DFs profiles among all congeners.[23,45,46] In this study, the 106 chromatographic peaks resolved by two used columns of 136 congeners from tetra- to octachloro compounds were subjected to PCA. Some inseparable congeners by two columns were only available as sums. The variance of each peak was normalized to total values of PCDDs/DFs congeners. The eigenvectors were varimax-rotated to clearify the interpretability of the results. Multivariate statistical analysis of marine sediment samples was carried out using SPSS Windows 10.0 (SPSS Co.).

The factors 1, 2, 3, and 4 accounted for 48%, 17%, 8%, and 7% of the total standardized variance, respectively. Since each of other factors described for less than 3%, the number of major factors was determined to be four. The loading plots for PCDDs/DFs congeners with three factors (factor 2, 3 and 4) against factor 1 are shown in Fig. 4. The description for calculated factors and congeners with a strong correlation to each factor is also summarized in Table 4.

Most of congeners within each homologue group were located close inner or near the circles except some species as shown in Fig. 4. These results indicated that the congener profiles of primary sources for each sediment sampling station are similar and that most of the congeners within each homologue behave identically in marine environment. This finding was comparable to those investigated on congener distributions of PCDDs/DFs in atmospheric deposition samples from Kanto region, Japan.[45]

The loading factor 1 showed the higher correlation

**Table 4.** Descriptions for calculated factors

| Factors | Contribution (%) | Congeners with a high correlation to each factor |
|---|---|---|
| 1 | 48 | Most of TCDFs, PeCDFs and HxCDFs |
| 2 | 17 | Most of TCDDs and PeCDDs, 1347F, 1278F, 1267F, 1269F |
| 3 | 8 | Most of HxCDDs and HpCDDs, OCDD, 12369D, 12489D, 2378F, 1289F, 123489F, 1234678F, 234689F, OCDF |
| 4 | 7 | 1478D, 2378D, 12368D, 1468/1238/1467/1236F, 2368F, 2467F, 2348F, 2346F, 2367F, 3467F |

values for most of TCDFs, PeCDFs, and HxCDFs (Fig. 4 and Table 4). Ok et al.[47] found that congener patterns of PCDDs/DFs in ambient air from urban, industrial and residential areas of Korea were dominated by TCDFs, PeCDFs and HxCDFs. Eitzer and Hites[48] also reported to contain tetra- to hexa-CDFs as the higher contributor for dioxin contaminations in atmosphere of Bloomington, Indiana. Hence, the loading factor 1 might be explained by inputs of air particulate matters generated from various sources, although the composition of PCDDs/DFs in aerial matters may change through the processes of deposition to underlying sediments. Indeed, atmospheric deposition of air particles has been considered to be one of the major routes of PCDDs/DFs inputs to bottom sediments from Korean coasts.[33,49] However, it must be noted that this contribution does not necessarily imply direct air particle deposition of these contaminants to this bay. Namely, this finding can be included transportation by other input pathways of airborne PCDDs/DFs such as soil run-off, riverine inputs, and resuspension of bed sediments.

Factor 2 had the high loading values for most of TCDDs and PeCDDs, which occupied the higher proportions for dioxins in atmosphere in addition to the lower chlorinated PCDFs. These congeners with a high relationship to factor 2 also derived from inputs of atmospheric particulate matters such as factor 1. Then, the differences of two factors might be explained by the ratio of gas and particle phase PCDDs/DFs in ambient air. One possible interpretation for this finding is that the ratio of the vapor versus the particle phase of PCDDs/DFs in atmosphere decreases as the degree of chlorination increases[47-48] and that transport, degradation, and deposition processes primarily depend on these phases.[42,50] Therefore, the attribution by air particulate matters of PCDDs/DFs contaminations in sediments from Ulsan Bay of Korea can be statistically explained by 65%, which was described the sum of the contribution for factor 1 and 2.

Factor 3 had a high loading value for most of HxCDDs and HpCDDs, OCDD, 1,2,3,6,9-PeCDD, 1,2,4,8,9-PeCDD, 2,3,7,8-TCDF, 1,2,8,9-TCDF, 1,2,3,4,8,9-HxCDF, 1,2,4,6, 8,9-HxCDF, and OCDF. Miles et al.[51] and Hagenmeier

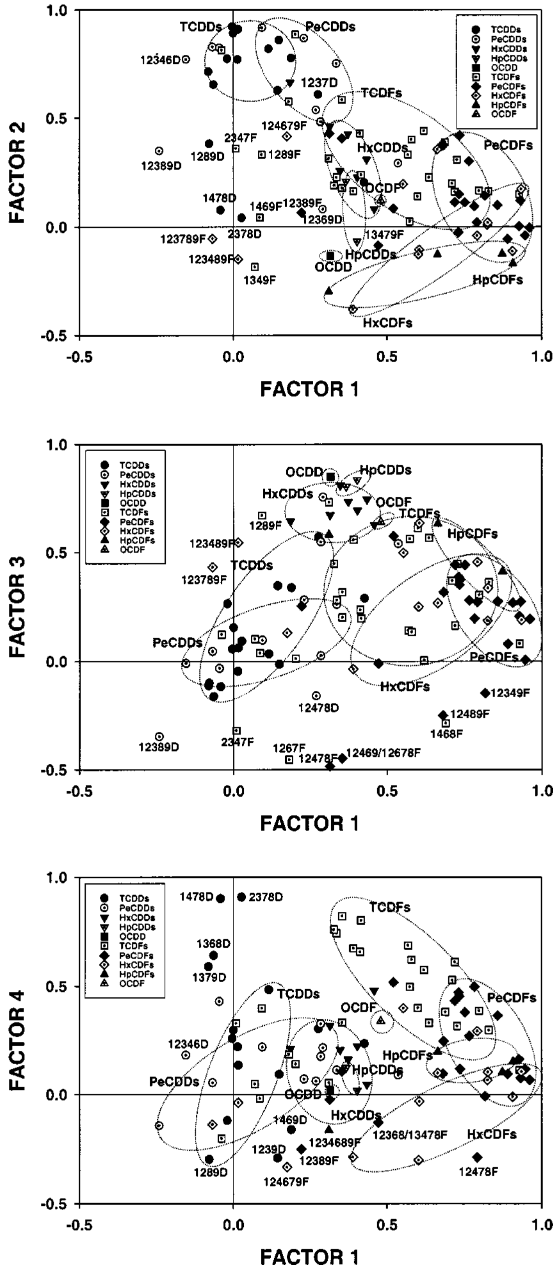



**Fig. 4.** The loading plots for PCDDs/DFs congeners with three factors against factor 1. D: PCDDs, F: PCDFs, number: the position of chlorine (',' is omitted). Congeners eluted on analytical capillary column is expressed by '/'.

and Brunner[52] showed that the congener distributions of PCDDs/DFs by the impurities of PCP are characterized by HxCDDs, HpCDDs, OCDD, 1,2,4,6,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,8,9-HpCDF, and OCDF. These congeners were very similar to congeners with a strong correlation to factor 3.

Factor 4 had a high loading value for 2,3,7,8-TCDD, 2,4,6,8/1,2,3,8/1,4,6,7/1,2,3,6-TCDF, 2,3,6,8-TCDF, 2,4,6,7-TCDF, 2,3,4,8-TCDF, 2,3,4,6-TCDF, 2,3,6,7-TCDF and 3,4,6,7-TCDF. The specific congeners, which correlated with factor 4, were dominated by tetrachloro-DDs/DFs. Fattore et al.[8] reported that the presence of low chlorinated compounds of dioxins such as TCDFs may suffer from some point source of contamination. Moon et al.[33] investigated dioxin congener distributions from sediments located at the river or stream mouth. Results showed the lower chlorinated compounds, especially tetra-CDDs/CDFs, were predominant congeners at sampling stations studied, suggesting that these congeners might be affected by domestic wastewater and/or industrial sewage that discharged into the river and/or bay without any treatment rather than inputs of particulate matters generated from combustion processes of high temperature.

Consequently, the primary attribution of PCDDs/DFs contamination sediments from Ulsan Bay was confirmed to be the inputs of aerial deposition with a slight PCP and/or discharge from a point source.

## 4. Conclusions

Surface sediments were sampled from Ulsan Bay of Korea, to evaluate toxic potency and the origin of PCDDs/DFs. The total PCDDs/DFs levels ranged between 191 and 674 pg/g dry weight and I-TEQ concentrations varied from 1.3 to 5.5 pg/g dry weight. Our results were comparable to or lower than previously reported levels from the Korean coasts and other countries. TEQ values for PCDDs/DFs in all sediment samples were below the safety sediment value (20 pg-TEQ/g dry weight) and seemingly moderate, but the total TEQ for the same sediments including PAHs exceeded the 20 pg-TEQ/g dry weight. This result indicates that the toxic potency assessment for aquatic environment of a bay should be considered to dioxin-like contaminants as well as PCDDs/DFs at the same time. The most abundant congeners of PCDDs/DFs were similar to those of combustion byproducts formed from various combustion processes. Four major factors were determined using congener-specific characterisation with the aid of principal component analysis (PCA), and two of them were attributed to PCDDs/DFs in the inputs of airborne particulate matters. Other two factors can be explained by the influence of impurities of pentachlorophenol (PCP) and direct discharge of industrial sewage and/or domestic wastewater, respectively. This study showed that congener-specific characterisation using multivariate data analysis (PCA) was a useful tool for evaluation of PCDDs/DFs origins in marine sediments and also reassumed that the major origin of PCDDs/DFs in sediments from Ulsan Bay come from the inputs of airborne particulate matters formed as various combustion processes.

## References


1) K. D. Courtney and J. A. Moore, *Toxicol. Appl. Pharmacol.*, **1971**, 20, 396-403.
2) L. Zeise, Huff, J., Salmon, A. and Hooper, K. *Adv. Mod. Environ. Toxicol.*, **1990**, 17, 293-342.
3) J. E. Huff, *Chemosphere*, **1992**, 25, 173-176.
4) P. Mocarelli, Brambilla, P., Gerthoux, P. M., Patterson, D. G. J. and Needham, L. L. *Lancet*, **1996**, 348, 409.
5) S. Safe, *Terat. Carcin. Mut.*, **1998**, 17, 285-304.
6) D. W. Kuehl, P. M. Cook, A. R. Batterman, D. B. Lothenbach, B. C. Butterworth and D. L. Johnson, *Chemosphere*, **1985**, 14, 427-437.
7) H. J. Geyer, I. Scheuntert, K. Rapp, A. Kettrup, F. Korte, H. Greim and K. Rozman, *Toxicology*, **1990**, 65, 97-107.
8) W. Z. Wu, K. W. Schramm and A. Kettrup, *Wat. Res.*, **2001**, 35, 1141-1148.
9) K. Olie, P. L. Vermeulen and O. Hutzinger, *Chemosphere*, **1977**, 8, 455-459.
10) S. Marklund, C. Rappe, M. Tsyklind and K. E. Egebäk, *Chemosphere*, **1987**, 16, 29-36.
11) M. Tsyklind, G. Söderström, C. Rappe, L.-E. Hägerstedt and E. Burström, *Chemosphere*, **1989**, 19, 705-710.
12) O. Hutzinger, M. J. Blumich, M. V. D. Berg and K. Olie., *Chemosphere*, **1985**, 14, 581-611.
13) J. E. M. Beurskens, G. A. J. Mol, H. L. Barreveld, B. van Munster and L. Winkels, *Environ. Toxicol. Chem.*, **1993**, 12, 1549-1566.
14) A. O. Tyler, G. E. Millward, P. H. Jones and A. Turner,

*Estuar. Coast. Shelf Sci.*, **1994**, 39, 1-13.

15) D. Dannenberg, R. Andersson and C. Rappe, *Mar. Pollut. Bull.*, **1997**, 34, 1016-1024.
16) C. L. Rose, W. A. McKay and P. F. Ambidge, *Chemosphere*, **1994**, 29, 1279-1292.
17) H. Fiedler, C. Lau, L.-O. Kjeller and C. Rappe, *Chemosphere*, **1996**, 32, 421-432.
18) E. Fattore, E. Benfenati, G. Mariani and R. Fanelli, *Environ. Sci. Technol.*, **1997**, 31, 1777-1784.
19) E. H. G. Evers, J. W. van Berghem and K. Olie, *Chemosphere*, **1989**, 19, 459-466.
20) E. H. G. Evers, H. J. C. Klamer, R. W. P. M. Laane and H. A. J. Govers, *Environ. Toxicol. Chem.*, **1993**, 12, 1583-1598.
21) C. S. Creaser, A. R. Fernandes, S. J. Harrad and E. A. Cox, *Chemosphere*, **1990**, 21, 931-938.
22) L. O Kjeller and C. Rappe, *Environ. Sci. Technol.*, **1995**, 29, 346-355.
23) T. Sakurai, N. Suzuki, S. Masunaga and J. Nakanishi, *Chemosphere*, **1998**, 37, 2211-2224.
24) B. Jimenez, L. M. Hernandez, M. J. Gonzalez, E. Eljarrat, J. Rivera and M. C. Fossi, *Environ. Sci. Technol.*, **1998**, 32, 3853-3861.
25) D. A. Bright, W. J. Cretney, R. W. Macdonald, M. G. Ikonomou and S. L. Grundy, *Environ. Toxicol. Chem.*, **1999**, 18, 1097-1108.
26) T. Sakurai, N. Suzuki and M. Morita, *Chemosphere*, **2002**, 46, 1359-1365.
27) Y. B. Kim, S. Y. Jo, J. H. Jeong, S. I. Lee and G. H. Jeong, *J. Kor. Soc. Environ. Sci.*, **1998**, 2, 69-78.
28) H. G. Choi, S. S. Kim, H. B. Moon and P. Y. Lee, *J. Kor. Soc. Oceanogr.*, **2001**, 36, 93-100.
29) J. S. Khim, K. T. Lee, K. Kannan, D. L. Villeneuve, J. P. Giesy and C. H. Koh, *Arch. Environ. Contam. Toxicol.*, **2001**, 40, 141-150.
30) H. B. Moon, H. G. Choi, S. S. Kim and P. Y. Lee, *J. Kor. Soc. Environ. Sci.*, **2001**, 10, 113-119.
31) H. B. Moon, H. G. Choi, S. S. Kim, S. R. Jeong and P. Y. Lee, *J. Kor. Soc. Oceanogr.*, **2001**, 36, 101-108.
32) G. Ok, H. B. Moon, S. H. Ji and Y. H. Han, *Organo. Comp.*, **1999**, 43, 209-212.
33) H. B. Moon, H. G. Choi, S. S. Kim, C. K. Kang, P. Y. Lee and G. Ok, *J. Kor. Soc. Environ. Anal.*, **2002**, 5, 41-47.
34) S. H. Im, K. Kannan, M. Matsuda, J. Giesy, P. John and T. Wakimoto, *Environ. Toxicol. Chem.*, **2002**. 21, 245-252.
35) E. Eljarrat, J. Caixach, J. Rivera, M. D. Torres and A. Ginebreda, *Environ. Sci. Technol.*, **2001**, 35, 3589-3594.
36) T. Sakurai, J. G. Kim, N. Suzuki, T. Matsuo, D. Q. Li, Y. Yao, S. Masunaga and J. Nakanishi, *Chemosphere*, **2000**, 40, 627-640.
37) E. H. G. Evers, R. W. P. M. Laane, G. J. J. Groeneveld and K. Olie, *Oragano. Comp.*, **1996**, 28, 117-120.
38) E. R. Long, D. D. MacDonald, S. L. Smith and F. D. Calder, *Environ. Manage*., **1995**, 19, 81-97.
39) K. L. Willett, P. R. Gardinali, J. L. Sericano, T. L. Wade and S. H. Safe, *Arch. Environ. Contam. Toxicol.*, **1997**, 32, 442-448.
40) J. H. Clemons, L. M. Allan, C. H. Marvin, Z. Wu, B. E. McCarry, D. W. Bryant and T. R. Zacharewski, *Environ. Sci. Technol.*, **1998**, 32, 1853-1860.
41) C. Klimm, A. M. Hofmaier, K. W. Schramm and A. Kettrup, *Organo. Comp.*, **1999**, 40, 39-42.
42) C. J. Koester and R. A. Hites, *Environ. Sci. Technol.*, **1992**, 26, 1375-1382.
43) D. R. Zook and C. Rappe, **1994**. "*Environmental sources, distribution, and fate of polychlorinated dibenzodioxins, dibenzofurans, and related organochlorines*" pp. 90-93, A. Schecter, Plenum Press, New York and London.
44) J. I. Baker and R. A. Hites, *Environ. Sci. Technol.*, **2000**, 34, 2879-2886.
45) I. Ogura, S. Masunaga and J. Nakanishi, *Chemosphere*, **2001**, 45, 173-183.
46) A. Wehrmeier, D. Lenoir, K. W. Schramm, R. Zimmermann, K. Hahn, B. Henkelmann and A. Kettrup, *Chemosphere*, **1998**, 36, 2775-2801.
47) G. Ok, S. H. Ji, H. B. Moon, H. S. Y. S. Kim and H. S. Yang, *Organo. Comp.*, **1999**, 43, 393-396.
48) B. D. Eitzer and R. A. Hites, *Environ. Sci. Technol.*, **1989**, 23, 1389-1395.
49) H. B. Moon, H. G. Choi, S. S. Kim, S. R. Jeong and P. Y. Lee, *J. Fish. Sci. Technol.*, **2001**, 4, 51-57.
50) T. F. Bidleman, *Environ. Sci. Technol.*, **1988**, 22, 361-367.
51) W. F. Miles, J. Singh, N. P. Gurprasad and G. P. Malis, *Chemosphere*, **1985**, 14, 807-810.
52) H. Hagenmaier and H. Brunner, *Chemosphere*, **1987**, 16, 1759-1764.