한국환경분석학회지 제5권 (제1호) 33~39, 2002
J. of the Korean Society for Environmental Analysis

Levels and Patterns of Chlorobenzenes in Marine Sediments from Yeongil and Ulsan Bays of Korea

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Marine sediments (0-5 cm) were sampled at 42 stations from Yeongil and Ulsan Bays of Korea in November 2000. Samples were analyzed for eight chlorobenzene congeners using multi-layer silica gel column chromatography and gas chromatography coupled to mass spectrometer detector (GC/MSD). The levels of total chlorobenzenes in marine sediments from Yeongil and Ulsan Bays were 2.92 ± 1.65 ng/g dry weight and 11.16 ± 12.25 ng/g dry weight, respectively. The highest concentrations exhibited in the stations from inner basin adjacent to terrestial sources. This result indicates that the hazardous contaminants such as chlorobenzenes derived from anthropogenic activities. Chlorobenzene contaminations in Yeongil and Ulsan Bays of Korea were relatively moderate in comparison to other marine environment in the world. The dominant congener among chlorobenzene species was 1,2,4-trichlorobenzene in marine sediments from Yeongil and Ulsan Bays, whereas tetrachlorobenzenes and pentachlorobenzene occupied a low proportion. There was a high correlation among the chlorobenzene species in Ulsan Bay, while there was partially significant correlation in Yeongil Bay.

Key words: Marine sediment, Yeongil Bay, Ulsan Bay, chlorobenzene, GC/MSD, correlation

1. Introduction

In recent years, there has been an increasing emphasis on the study of the environmental fate and effects of organochlorine compounds. Chloro-benzenes are ubiquitous hydrophobic organic chlorinated compounds in the environment. They comprise a group of 12 congeners ranging from mono- to hexachlorobenzene according to the number and position of chlorine atom. These compounds are used as de-ordants, solvents and pesticides, as well as byproducts of agro- or petro-chemical related manufacturing processes, such as polychlorinated biphenyls (PCBs) and pentachlorophenol.[1)] However, unlike some organo-chlorine compounds, including PCBs and various pesticides, chlorobenzenes are not banned from production or use in any country until 1990s.[2)]

Hexachlorobenzene (HCB) of chlorobenzenes in the environment is predominantly industrial byproducts, which originate from the manufacture of chlorobenzene, carbon tetrachloride, trichloro-ethylene, tetrachloroethylene, polyvinyl chloride, and nitroso rubber. They are often synthetic precursors, byproducts or contaminants resulting from synthesis or degradation of other organic compounds. They also cover a wide range of volatility, some with vapor pressure comparable to various pesticides.[2)] HCB was found in all environment compartments such as water, air, soil, birds, fish, human milk, adipose tissue, and blood, as often as PCBs or organochlorine pesticides.[3-9)] HCB is bioaccumulated in species ranging from algae to catfish by 1,000-10,000.[10)] Its high bioaccumulative potential has resulted in its identification asprobably carcinogenic to humans.[1)] Also, HCB has been implicated as endocrine disrupting chemical in human and other animals. Therefore, its environmental persistence is an enough serious issue to the marine environment and may produce adverse health effects in organisms.

In addition, Angélique[11)] suggested that HCB should be classified as a dioxin-like compound with the possible impact on the toxic equivalent (TEQ), based on binding to the Ah (Aryl hydrocarbon) receptor, the dioxin-like effects, and the bioaccumulation in higher trophic levels. Thus, the traditional emphasis in investigations in environmental distribution has been only on HCB. However, other chlorobenzene congeners are common waste products, and because of their short half-lives in birds and fish, they are observed on site and event-specific bases during periods of heavy contamination.[12] Previous investigations have seldom quantified their con-centrations in environmental media despite the fact that many of these congeners are listed as priority pollutants owing to their toxicity and carcinogenicity.[13] In particular, there are few data on level of chlorobenzene congeners available in marine environment. Thus, prior to risk assessment of chlorobenzenes, the chlorobenzene contamination in marine environment of Korea needs to be investigated. The objective of this study is to investigate the levels and distribution patterns of chlorobenzenes including HCB in sediments collected from Yeongil and Ulsan Bays, Korea.

2. Materials and Methods

2.1. Study areas

Yeongil Bay with a total area of 120 km^2 is one of the most industrialized regions of Korea. There are steel industrial complex and the large number of related facilities in this area. Effluents containing various contaminants discharge into this bay through Hyungsan River. Ulsan Bay with a total area of 6.3 km^2 is also one of the most industrialized regions of Korea. The Ulsan petrochemical industrial complex, composed of over 100 plants, discharges effluents of up to 200,000 tonnes per day into Ulsan Bay, via the Woihwang and Taehwa Rivers. In addition, there are many small, medium and large-scaled factories producing products, automobiles and ships in this area. Subsequently, the rapid industrialization of these two areas has been accompanied by marine environmental deterioration which led to social and environmental health problems.

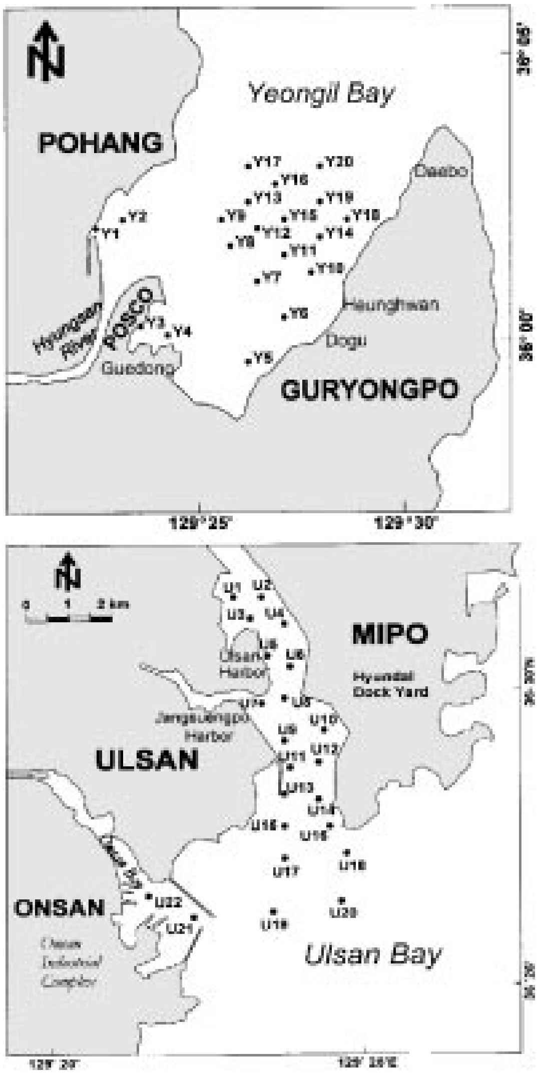

Fig. 1. Map showing sampling stations of marine sediments from Yeongil (upper map) and Ulsan (lower map) Bays of Korea.

2.2. Sampling and sample preparations

Surface sediments (0-5 cm) were sampled from 42 stations in Yeongil and Ulsan Bays of Korea in November 2000 (Fig. 1). Sediments were collected using a box-corer sampler and then kept frozen at -20 until extraction. The freeze-dried sediments were sieved at 2 mm and then extracted in a Soxhlet apparatus with 200 mL of toluene (Ultra residue analysis, J. T. Baker, USA) for 24 hours after the spike of internal stan-

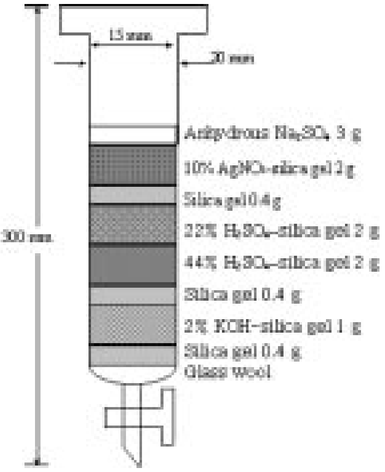

Fig. 2. Clean-up column chromatography of multi-layer silica gel for chlorobenzenes.

dards. The volume was reduced to 1-2 mL in a rotary evaporator. The extract was transferred to n-hexane (Ultra residue analysis, J. T. Baker, USA) and adjusted to a volume of 10 mL.

Samples were cleaned up a multi-layer silica based adsorbent (70-230 mesh, Neutral, Merck) column (15 mm inner diameter, 300 mm length) with 120 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 3 g, silver nitrate impregnated silica gel 2 g, silica gel 0.4 g, 22% sulfuric acid impregnated silica gel 2 g, 44% sulfuric acid impregnated silica gel 2 g, silica gel 0.4 g, 2% potassium hydroxide impregnated silica gel 1 g, and finally silica gel 0.4 g (Fig. 2).

The purified samples were concentrated to less than 1 mL, and left at a room temperature for one day to evaporate to 50-100 L. The residues were dissolved with 50 L of n-nonane (Pesticide residue analysis, Fluka, Switzerland) and determined for chlorobenzenes.

2.3. Identification and quantification

Target chlorobenzenes used in this investigation were as follows; 1,2,3-, 1,2,4- and 1,3,5-isomers of trichlorobenzene (1,2,3-TrCB, 1,2,4-TrCB and 1,3,5-TrCB), 1,2,4,5-, 1,2,3,4- and 1,2,3,5-isomers of tetrachlorobenzene (1,2,4,5-TeCB, 1,2,3,4-TeCB and 1,2,3,5-TeCB), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB). We selected eight congeners ranging from tri- to hexachlorobenzene based on persistent ability to retain them on marine sediment materials, and analyzed them our chromatographic system. This method could not separately quantify the 1,2,3,5- and 1,2,3,4-tetrachlorobenzene and they were therefore quantified together as a compound. Isotope labelled compounds ($^{13}C_6$-1,2,3-TrCB, $^{13}C_6$-1,2,3,4-TeCB, $^{13}C_6$-PeCB and $^{13}C_6$-HCB; MCBS, Wellington Laboratories, Canada) were used as internal standards.

An Agilent 6890 GC (Agilent, USA) equipped with a split/splitless injector was used (splitless time: 2 min; flow: 70 mL/min). Samples were injected splitlessly (2 mL portion of the total 50 mL) at the injector temperature of 250°C. The GC temperature program was from 50°C (1.5 min), 3°C/min to 170°C, and then 10°C/min to 300°C (5 min). The carrier gas was helium at a constant flow rate of 1.3 mL/min. A HP-1 (30 m, 0.25 mm inner diameter, 0.25 mm film thickness, Hewlett Packard, USA) capillary column was used for the separation of chlorobenzene compounds. The GC was coupled to a 5973N mass selective detector (MSD). The mass spectrometer was operated under the selective ion monitoring (SIM) mode using two molecular ions ($M^{\cdot+}$ and $(M+2)^{\cdot+}$) for each degree of chlorinaion were monitored in the electron impact (EI) ionization mode at 70 eV. The interface temperature was 230°C.

Procedural blanks were porcessed in the same manner as real samples, and they were below 10% of analytes abundance. Blanks were run before and after standards to check for carryover. Sample recoveries were in the range of 81-95%. The data presented in this investigation were not corrected for recoveries. The calculated detection limit (S/N ratio=3) for individual chlorobenzene in marine sediment was estimated at 0.01 ng/g dry weight.

3. Results and Discussion

3.1. Levels of chlorobenzene in marine sediments

Table 1. The concentrations (ng/g dry weight) of chlorobenzenes in marine sediments from Yeongil Bay, Korea

	1,3,5-TrCB	1,2,4-TrCB	1,2,3-TrCB	*TeCBs	1,2,3,4-TeCB	PeCB	HCB	Sum
Y1	0.03	1.07	0.28	0.06	0.07	0.13	1.02	2.66
Y2	0.02	0.67	0.15	0.03	0.04	0.07	0.35	1.32
Y3	0.02	4.54	0.77	0.05	0.12	0.15	0.41	6.07
Y4	0.06	5.70	0.61	0.11	0.19	0.30	0.97	7.95
Y5	0.01	1.61	0.47	0.02	0.03	0.04	0.27	2.45
Y6	0.01	0.98	0.24	0.02	0.03	0.04	0.26	1.58
Y7	0.04	2.44	0.65	0.13	0.06	0.10	0.33	3.75
Y8	0.02	0.99	0.20	0.07	0.06	0.10	0.52	1.95
Y9	0.05	1.72	0.33	0.25	0.12	0.22	0.50	3.19
Y10	0.01	1.37	0.21	0.04	0.04	0.08	0.39	2.14
Y11	0.03	2.41	0.30	0.07	0.06	0.08	0.34	3.29
Y12	0.01	0.81	0.10	0.07	0.05	0.09	0.42	1.54
Y13	0.03	0.89	0.21	0.13	0.09	0.18	0.53	2.05
Y14	0.09	1.57	0.23	0.04	0.05	0.08	0.38	2.44
Y15	0.02	2.60	0.65	0.08	0.07	0.10	0.38	3.90
Y16	0.04	1.19	0.21	0.08	0.06	0.11	0.43	2.13
Y17	0.01	0.28	0.08	0.03	0.02	0.05	0.24	0.71
Y18	0.02	2.08	0.31	0.05	0.06	0.08	0.31	2.90
Y19	0.02	1.82	0.36	0.09	0.08	0.13	0.50	3.00
Y20	0.02	2.31	0.49	0.07	0.07	0.11	0.37	3.44

*TeCBs: the sum of 1,2,3,5-TeCB and 1,2,4,5-TeCB.

Table 2. The concentrations (ng/g dry weight) of chlorobenzenes in marine sediments from Ulsan Bay, Korea

	1,3,5-TrCB	1,2,4-TrCB	1,2,3-TrCB	*TeCBs	1,2,3,4-TeCB	PeCB	HCB	Sum
U1	0.58	43.38	3.89	0.43	0.50	1.38	8.12	58.3
U2	0.06	3.62	0.66	0.09	0.18	0.51	2.60	7.73
U3	0.26	20.49	2.22	0.22	0.26	0.75	4.38	28.6
U4	0.18	10.68	1.10	0.12	0.19	0.38	1.34	14.0
U5	0.23	17.20	1.99	0.18	0.23	0.46	2.11	22.4
U6	0.07	5.90	0.52	0.11	0.15	0.29	1.21	8.24
U7	0.10	10.47	1.29	0.21	0.28	0.58	1.99	14.9
U8	0.05	3.57	0.36	0.15	0.13	0.33	1.25	5.84
U9	0.06	4.67	0.49	0.06	0.11	0.17	0.78	6.34
U10	0.03	2.59	0.31	0.06	0.08	0.20	0.62	3.90
U11	0.06	5.86	0.66	0.10	0.16	0.27	1.21	8.32
U12	0.05	3.39	0.47	0.06	0.09	0.21	0.84	5.11
U13	0.08	8.05	1.07	0.12	0.22	0.37	1.75	11.7
U14	0.04	3.70	0.49	0.06	0.11	0.20	0.95	5.54
U15	0.07	4.25	0.49	0.10	0.16	0.33	1.70	7.10
U16	0.03	2.15	0.22	0.04	0.07	0.11	0.59	3.21
U17	0.06	4.63	0.57	0.09	0.15	0.21	0.95	6.64
U18	0.04	3.80	0.41	0.06	0.09	0.12	0.58	5.09
U19	0.08	5.47	0.54	0.10	0.17	0.27	1.47	8.12
U20	0.04	3.10	0.37	0.07	0.14	0.22	1.42	5.35
U21	0.05	3.69	0.53	0.09	0.17	0.32	1.73	6.58
U22	0.03	1.57	0.21	0.03	0.07	0.11	0.53	2.56

*TeCBs: the sum of 1,2,3,5-TeCB and 1,2,4,5-TeCB.

Table 3. Correlation coefficients (r) for individual chlorobenzene congener in marine sediments from Yeongil and Ulsan Bays, Korea

	1,3,5-TrCB	1,2,4-TrCB	1,2,3-TrCB	[1]TeCBs	1,2,3,4-TeCB	PeCB	HCB
				YEONGIL BAY			
1,3,5-TrCB		0.316	0.124	0.420	0.424	0.463^{*}	0.304
1,2,4-TrCB	0.992^{***}		0.826^{***}	0.217	0.811^{*}	0.629^{**}	0.354
1,2,3-TrCB	0.975^{***}	0.988^{***}		0.221	0.551^{*}	0.375	0.133
TeCBs	0.930^{***}	0.950^{***}	0.947^{***}		0.592^{**}	0.709^{***}	0.302
1,2,3,4-TeCB	0.905^{***}	0.925^{***}	0.960^{***}	0.966^{***}		0.953^{***}	0.642^{**}
PeCB	0.929^{***}	0.940^{***}	0.942^{***}	0.969^{***}	0.962^{***}		0.724^{***}
HCB	0.932^{***}	0.938^{***}	0.929^{***}	0.933^{***}	0.929^{***}	0.980^{***}	
				ULSAN BAY			

[1] TeCBs: the sum of 1,2,3,5-TeCB and 1,2,4,5-TeCB.

$^{*}0.01<p<0.05$, $^{**}0.001<p<0.01$, $^{***}p<0.001$.

Eight chlorobenzene congeners were detected in all sediment samples. Table 2 and 3 show the concentrations of chlorobenzenes in marine sediments from Yeongil and Ulsan Bays of Korea, respectively. In Yeongil Bay sediments, the levels of trichlorobenzenes (the sum of 1,3,5-TrCB, 1,2,4-TrCB and 1,2,3-TrCB) varied from 0.37 to 6.56 ng/g dry weight with a mean 1.52 ng/g dry weight. The levels of tetrachlorobenzenes (the sum of 1,2,3,5-TeCB, 1,2,4,5-TeCB and 1,2,3,4-TeCB) ranged between 0.04 and 0.44 ng/g dry weight (mean 0.14 ng/g dry weight). Pentachlorobenzene and hexachlorobenzene residues in marine sediments were in the ranges of 0.04-0.30 ng/g dry weight (mean 0.11 ng/g dry weight) and 0.24-1.02 ng/g dry weight (mean 0.45 ng/g dry weight), respectively. The highest levels of total chlorobenzenes in Yeongil Bay were found in Stations Y3 (6.07 ng/g dry weight) and Y4 (7.95 ng/g dry weight) located close to a steel industrial complex. These sampling stations were relatively likely to reveal the higher levels due to the effects of contamination source generated from various combustion processes. Many authors reported that this plant was the main source of hazardous contaminants in marine environment.[14-15]

In Ulsan Bay sediments, the levels of trichlorobenzenes varied from 1.81 to 47.9 ng/g dry weight (mean 8.79 ng/g dry weight). The levels of tetrachlorobenzenes ranged between 0.10 and 0.93 ng/g dry weight (mean 0.28 ng/g dry weight). Pentachlorobenzene and hexachlorobenzene residues in sediments were in the range of 0.11-1.38 ng/g dry weight (mean 0.35 ng/g dry weight) and 0.53-8.12 ng/g dry weight (mean 1.73 ng/g dry weight), respectively. The highest level of total chlorobenzene in Ulsan Bay was found in Station U1 (58.3 ng/g dry weight) located at Taehwa river mouth. The chlorobenzene distribution exhibited a decreasing gradient from the inner sampling stations (Stations U1 to U14, mean value 14.4 ng/g dry weight) to the outer stations (Station U15 to U20, mean value 5.92 ng/g dry weight). Accordingly, these results indicate that the inner basins are adjacent to a terrestial source of chlorobenzenes with a poor tidal flushing.

Comparison of average chlorobenzene concentrations in sediments from Yeongil and Ulsan Bays are shown in Fig. 3. Chlorobenzene contaminations in sed-

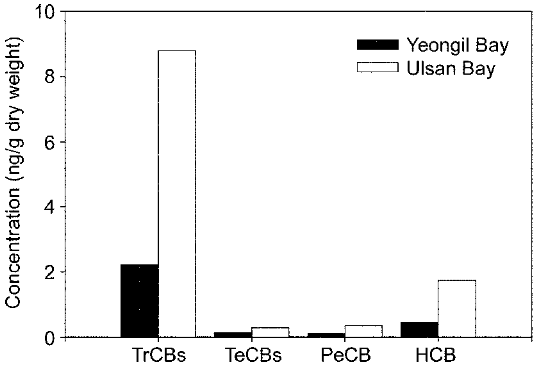

Fig. 3. Comparison of average chlorobenzene concentrations in marine sediments from Yeongil and Ulsan Bays. TrCBs; 1,3,5-, 1,2,4- and 1,2,3-trichlorobenzene, TeCBs; 1,2,3,5-, 1,2,4,5- and 1,2,3,4-tetrachlorobenzene, PeCB; pentachlorobenzene and HCB; hexachlorobenzene.

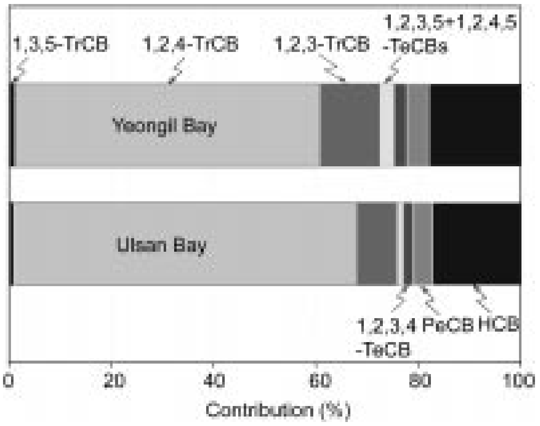

Fig. 4. Contributions of individual chlorobenzene congener in marine sediments from Yeongil and Ulsan Bays of Korea.

iments of Ulsan Bay were 2-4 times higher than those of Yeongil Bay.

Until recent, there were few data on level of chlorobenzene congeners available in marine environment because the traditional emphasis on investigations in environmental distribution has been only on HCB. Hence, HCB concentrations were only compared with other countries in this study. HCB levels in marine sediments from Yeongil Bay (0.45 ± 0.21 ng/g dry weight) and Ulsan Bay (1.73 ± 1.66 ng/g dry weight) were slightly low or comparable to those in Ise Bay (2.2 ± 1.8 ng/g dry weight), Lake Huron (2 ng/g dry weight) and Lake Erie (3 ng/g dry weight).[16] HCB levels in sediments from Mediterranean Sea ranged from 0.01 to 39.4 ng/g dry weight,[17] Kaohsiung coast in Taiwan (12.1-31.4 ng/g dry weight)[18] and Lake Ontario (100 ± 59 ng/g dry weight)[19] with an order of about 10~50 times greater than those reported here. In the other hand, HCB levels in sediments from Western Baltic Sea (values between 0.01 and 0.23)[20] showed lower values than those in this investigation. Consequently, it means that chlorobenzenes contaminations in Yeongil and Ulsan Bays of Korea were relatively moderate in comparison to other marine environment in the world.

3.2. Congener patterns of chlorobenzene in marine sediments

The contributions of individual congener to the sum of eight chlorobenzenes in sediments from Yeongil and Ulsan Bays of Korea are illustrated in Fig. 4. Composition of chlorobenzenes in sediments showed relatively similar patterns for Yeongil and Ulsan Bays. The predominant contributors for total chlorobenzenes in this investigation were 1,2,4-TrCB in trichlorobenzenes, whereas tetrachlorobenzenes and pentachlorobenzene occupied low proportions. These patterns were comparable to a review by Lee et al.[18] concerning contributions of individual chlorobenzene in surficial sediments from Kaohsiung coast, Taiwan.

The contributions of lower chlorobenzenes such as trichlorobenzenes in sediments from Ulsan Bay were slightly greater than those of Yeongil Bay due to usage as a primary solvent of trichlorobenzenes in a petrochemical manufacturing process, whereas the higher chlorobenzenes such as penta- and hexachlorobenzene in Yeongil Bay were slightly greater than Ulsan Bay due to high temperature pyrolysis from a steel manufacture process.[21]

3.3. Correlation

A correlation analysis was carried out to investigate the relationship within each congener group of chlorobenzenes (Fig. 4). This statistical approach is based on the fact that each pollution source produces a characteristic chlorobenzene pattern, so the correlation analysis can give an idea whether they all originate from the same source or not. In Ulsan Bay, there was a highly positive correlation (n=22, r=0.91-0.99, p<0.001) among the chlorobenzenes species. This finding can be explained by the similar contamination source of chlorobenzenes for Ulsan Bay of Korea. In Yeongil Bay, there was partially a significant correlation such as 1,2,3,4-TeCB and PeCB (r=0.95, p<0.001), 1,2,4-TrCB and 1,2,3-TrCB (r=0.83, p<0.001), 1,2,4-TrCB and 1,2,3,4-TeCB (r=0.81, p<0.001), PeCB and HCB (r=0.72, p<0.001), while correlation coefficients between other chlorobenzene congeners relatively showed the lower value. This seems that chlorobenzene contamination in Yeongil Bay derived from various source.

4. Conclusion

Marine sediments were sampled at several stations from Yeongil and Ulsan Bays of Korea, to examine levels and patterns of chlorobenzene in marine sediments. The highest concentrations exhibited in the stations from inner basin adjacent to terrestial sources. This indicated that the hazardous contaminants such as chlorobenzenes derived from anthropogenic activities. The levels of total chlorobenzenes in marine sediments from Ulsan Bay were 2-4 times higher than those of Yeongil Bay. Chlorobenzene contaminations in two bays were relatively moderate in comparison to other marine environment in the world. The dominant congener among chlorobenzene classes was 1,2,4-trichlorobenzene, whereas tetrachlorobenzenes and pentachlorobenzene occupied a low proportion. There was a high correlation among the chlorobenzene species in Ulsan Bay, while there was partially significant correlation in Yeongil Bay.

Acknowledgement

We are greatful to Mr. Seong-Ryul Jeong for the assistance of pretreatment and analysis of chlorobenzenes.

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