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Distribution of Certain Chlorobenzenes in Seawater from Youngil Bay, Korea

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Surface seawater was sampled from 20 stations in Youngil Bay, Korea in November 2000. The samples were analyzed for eight chlorobenzenes(CBs) out of a total of 12 in the congener series using a gas chromatography coupled to a mass spectrometer detector(GC/MSD). The total CB levels varied from 1.3 to 6.1 ng/L with a mean of 4.0 ng/L. Trichlorobenzene groups (sum of 1,3,5-, 1,2,4-, and 1,2,3-trichlorobenzene) were the predominant class among the four congener groups, while tetrachlorobenzenes(sum of 1,2,3,5-, 1,2,4,5-, and 1,2,3,4-tetrachlorobenzene) and pentachlorobenzene showed a low presence. The total CB levels exhibited similar patterns for all the stations. A significant positive correlation was observed between the individual CB compounds in the particulate samples, while the dissolved samples revealed a strong correlation between the heavier molecular weight CBs.

Key words : surface seawater, chlorobenzenes(CBs), GC/MSD, contributions, correlation

1. Introduction

Organochlorine compounds are widely used in the chemical industry either as solvents or intermediates for synthesis. The chlorobenzenes (CBs) included in these chemicals comprise a group of 12 compounds ranging from mono- to hexachlorobenzene according to the number and position of the chlorine atoms. These compounds are mainly used as deodorants, solvents, and pesticides and are often the byproducts of the manufacturing processes related to agro-or petro-chemicals[1]. Unlike some organochlorine(OC) compounds, including polychlorinated biphenyls (PCBs) and various pesticides, CBs are not banned from production or use in any country. However, hexachlorobenzene(HCB) has been identified in human tissue samples as often as PCB or OC pesticides[2]. Its high bioaccumulative potential also means that it is probably carcinogenic to humans[1]. Recently, HCB has been implicated as an endocrine disrupting chemical in humans and other animals. In addition, Angélique[3] suggested that HCB has a possible toxic equivalent(TEQ) impact of 2,3,7,8-tetrachloro dibenzo-*p*-dioxin(2,3,7,8-TCDD). Accordingly, based on its ability to bind to an Ah(aryl hydrocarbon) receptor, its dioxin-like effects, and bioaccumulation in higher trophic levels, HCB should be classified as a dioxin-like compound. Furthermore, its action mechanism resembles that of mono-ortho substituted PCBs, which also have phenobarbital- like properties and are included in the TEQ concept. However, based on the limited information available it has estimated that HCB is about 10,000 times less potent than 2,3,7,8-TCDD. Studies have already been conducted on HCB in various environmental compartments, such as water, air, soil, birds, fish, human milk, adipose tissue, and blood[4~9], yet the emphasis of these investigations has only been on the environmental distribution of HCB. As such, the concentrations of other chlorobenzene compounds have seldom been quantified in environmental media despite the fact that many of these compounds are listed as priority pollutants owing to their toxicity and carcinogenicity[10]. In particular, there is relatively few data on the level of chlorobenzene compounds in marine environments. Accordingly, the current study is the first investigation of chlorobenzene compound levels in seawater from a Korean marine environment.

2. Materials and Methods

2.1. Sampling and Sample Preparations

Surface seawater was sampled from 20 stations in Youngil Bay in November 2000(Fig. 1). The samples were filtered through glass fiber filters (GF/F 47 mm, Whatman) and divided into dissolved and particulate phases.

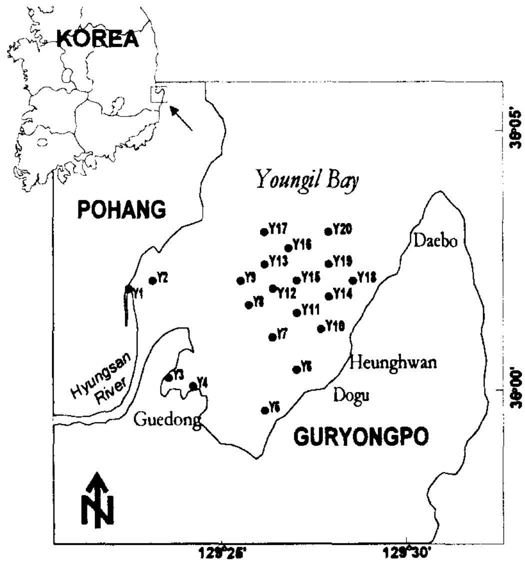

Fig. 1. Map showing sampling stations in Youngil Bay, Korea.

The dissolved water samples were liquid-liquid extracted with methylene dichloride(Pesticide residue analysis, Cica-Merck) and *n*-hexane(Ultra residue analysis, J.T.Baker) after being spiked with 4 species as internal standards.

The extracts were reduced to 1-2 mL in a rotary evaporator and adjusted to a volume of 10 mL. The particulate samples were dried at room temperature and then cut into 1-2 cm pieces. After being spiked with 4 species as internal standards, the samples were extracted with toluene(Ultra residue analysis, J.T.Baker) for 5 hours under reflux. The extracts were filtered and reduced to 1-2 mL in a rotary evaporator. The residues were transferred to *n*-hexane and adjusted to a volume of 10 mL. The dissolved and particulate samples were then purified using a multi-layer silica gel (Art No. 7734, 70-230 mesh, Merck) column chromatography containing an $AgNO_3$-silica gel, H_2SO_4-silica gel, and KOH-silica gel with *n*-hexane. The elutants were concentrated to less than 1 mL and left at room temperature for one day to evaporate to 50-100 μL. The residues were dissolved with 50 μL of *n*-nonane (Pesticide residue analysis, Fluka) then the CB compounds were determined using the GC/MSD.

2.2. Instrumental analysis

The compounds of interest included the 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) (CBS, Wellington Laboratories). The compounds used as the internal standards were $^{13}C_6$-1,2,3-TrCB, $^{13}C_6$-1,2,3,4-TeCB, $^{13}C_6$-PeCB, and $^{13}C_6$-HCB(MCBS, Wellington Laboratories).

Eight compounds, ranging from tri- to hexachlorobenzene and selected due to their persistent retention in the seawater samples, were analyzed using the chromatographic system. However, the system was unable to separately quantify the 1,2,3,5- and 1,2,3,4-tetrachlorobenzene, therefore, they were quantified together as a compound. Blanks were run before and after the injection of the standards to check for any carryover. The sample recoveries were within a range of 77 ~ 100 %. The data presented in this investigation was not corrected for recoveries. The detailed conditions used to analyze the CBs by the GC/MSD are shown in Table 1.

The particulate organic carbon(POC) was determined using a CHN analyzer(Perkin Elmer 2400) after eliminating the calcium carbonate through the addition of 1 N HCl. The dissolved organic carbon(DOC) was determined using a DC 180 elemental analyzer(Rosemount Analytical Inc.).

Table 1. Conditions for analysing CBs using GC/MSD

Items	Conditions
Instrument	Agilent 6890 II GC/5973N MSD
Column	Hewlett Packard, HP-1(30 m×0.25 mm×0.25 μm)
Oven	50 ℃(1.5 min) - 3 ℃/min - 170 ℃ - 10 ℃/min - 300 ℃(5 min)
Carrier gas	Helium, 1.3 mL/min, Constant flow
Injector type	Splitless
Ionization mode	EI+
Ionization energy	70 eV
Injector temperature	250℃
Ion source temperature	260℃
Interface temperature	250℃
Injection volume	2 μL
Selective ion monitoring	M^+, $(M+2)^+$

3. Results and Discussion

3.1. Sample Characterization

The suspended solids(SSs), DOC, and POC found in the seawater from Youngil Bay are summarized in Table 2. The SS concentrations varied from 11.4 to 18.3 mg/L, with a mean of 14.1 mg/L. The DOC and POC contents ranged from 1.1 to 1.7 mg/L and 0.1 to 0.5 mg/L, respectively. The mean concentration of TOC was 1.7 mg/L. The SSs, DOC, and POC exhibited similar concentrations at all stations.

Table 2. Characterization of seawater samples from Youngil Bay(mg/L)

Items	Range	Median	Mean
SS	11.4-18.3	14.0	14.1
DOC	1.1-1.7	1.4	1.4
POC	0.1-0.5	0.3	0.3
TOC*	1.4-2.1	1.7	1.7

TOC* means the sum of DOC and POC.

3.2. Distributions of Chlorobenzene Compounds in Seawater

Table 3 shows the levels of CB compounds in the seawater from Youngil Bay, Korea. Eight CB compounds were detected in all samples. In the dissolved samples, the levels ranged from 0.63 to 4.42 ng/L with a mean of 2.44 ng/L. In the particulate matter samples, the levels varied from 0.64 to 2.3 ng/L with a mean of 1.55 ng/L. As such, the dissolved CB levels were higher than the particulate CB levels in all the seawater samples. The CB levels in the seawater from Youngil Bay ranged from 1.3(Station Y18) to 6.1 ng/L(Station Y16) with a mean of 4.0 ng/L. Generally, the concentration of CBs in Youngil Bay exhibited a uniform distribution between 2.5 and 5.0 ng/L, except for Stations Y18 and Y16. Accordingly, this indicates that was no specific source for CB compounds in Youngil Bay.

3.3. Contributions of Chlorobenzene Congener Groups in Surface Seawater

The contributions of CB congener groups to the total eight compounds(tri- to hexa-CB) identified in the dissolved and particulate matter samples in the seawater from Youngil Bay, Korea are presented in Fig. 2. In the dissolved samples, TrCB groups were the predominant contributors(72.9±8.6 %), HCB occupied 23.0±7.2 %, and the contributions of TeCBs(1.5±0.4 %) and PeCB(2.6±1.3 %) were low. While in the particulate samples, TrCB groups were the predominant contributors(64.7±2.9 %), HCB occupied 29.6±2.7 %, and the contributions of TeCBs(2.2±0.3 %) and PeCB(3.5±0.5 %) were low. The TrCB presence in the dissolved CBs was higher than that in the particulate CBs. In contrast, the HCB content was higher in the particulate samples than in the dissolved samples. Accordingly, these results indicate that the higher-molecular-weight CB compounds were preferentially adsorbed to the particulate matter and incorporated in the sediment.

3.4. Correlation Analysis

A regression analysis was carried out to investigate the relationship between the individual

Table 3. The levels of chlorebenzene isomers in seawater from Youngil Bay, Korea(ng/L)

	STATIONS																			
	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10	Y11	Y12	Y13	Y14	Y15	Y16	Y17	Y18	Y19	Y20
	Dissolved chlorobenzenes																			
1,3,5-TrCB	0.02	0.03	0.03	0.02	0.02	0.01	0.01	0.02	0.03	0.02	0.05	0.07	0.01	0.01	0.01	0.01	0.02	0.03	0.02	0.01
1,2,4-TrCB	1.38	0.83	1.21	1.40	1.58	1.39	2.52	2.11	1.45	1.21	2.04	1.55	1.78	2.54	1.28	0.32	0.87	3.43	3.32	1.33
1,2,3-TrCB	0.14	0.06	0.08	0.10	0.08	0.07	0.08	0.13	0.18	0.05	0.08	0.17	0.16	0.42	0.17	0.03	0.13	0.11	0.19	0.13
TrCBs	1.54	0.93	1.31	1.51	1.68	1.47	2.61	2.26	1.66	1.28	2.17	1.79	1.95	2.97	1.46	0.35	1.02	3.56	3.53	1.48
1,2,3,5+1,2,4,5-TeCB	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.00	0.01	0.01	0.01	0.01
1,2,3,4-TeCB	0.03	0.01	0.03	0.02	0.03	0.02	0.02	0.02	0.03	0.01	0.02	0.02	0.03	0.03	0.02	0.01	0.02	0.03	0.02	0.02
TeCBs	0.04	0.02	0.04	0.03	0.04	0.03	0.04	0.03	0.05	0.02	0.03	0.03	0.04	0.04	0.03	0.01	0.04	0.04	0.03	0.03
PeCB	0.08	0.04	0.07	0.05	0.08	0.04	0.07	0.05	0.12	0.03	0.03	0.06	0.06	0.05	0.05	0.04	0.06	0.08	0.07	0.04
HCB	0.57	0.43	0.86	0.44	0.68	0.49	0.52	0.40	0.68	0.33	0.46	0.49	0.53	0.50	0.49	0.22	0.58	0.73	0.55	0.40
SUM	2.22	1.42	2.28	2.02	2.49	2.03	3.23	2.74	2.52	1.65	2.69	2.37	2.58	3.57	2.03	0.63	1.70	4.42	4.19	1.96
	Particulated chlorobenzenes																			
1,3,5-TrCB	0.01	0.02	0.03	0.03	0.02	0.06	0.02	0.02	0.05	0.02	0.03	0.04	0.01	0.02	0.02	0.01	0.03	0.01	0.01	0.03
1,2,4-TrCB	0.40	0.68	0.81	1.02	0.72	1.18	0.94	0.96	1.21	0.87	1.06	0.79	0.69	0.73	0.96	0.43	1.05	1.01	0.43	1.18
1,2,3-TrCB	0.02	0.10	0.11	0.10	0.09	0.18	0.11	0.13	0.16	0.09	0.14	0.12	0.09	0.09	0.12	0.01	0.12	0.12	0.07	0.17
TrCBs	0.43	0.79	0.95	1.15	0.84	1.41	1.07	1.12	1.42	0.98	1.23	0.95	0.80	0.84	1.09	0.45	1.21	1.14	0.52	1.38
1,2,3,5+1,2,4,5-TeCB	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.02
1,2,3,4-TeCB	0.01	0.02	0.02	0.03	0.02	0.03	0.02	0.03	0.03	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.01	0.03
TeCBs	0.01	0.02	0.03	0.04	0.03	0.05	0.03	0.04	0.05	0.04	0.04	0.03	0.03	0.02	0.03	0.01	0.04	0.04	0.02	0.04
PeCB	0.02	0.04	0.05	0.06	0.04	0.09	0.05	0.07	0.10	0.07	0.07	0.05	0.05	0.04	0.04	0.02	0.06	0.06	0.03	0.06
HCB	0.18	0.33	0.47	0.52	0.36	0.67	0.47	0.56	0.72	0.53	0.56	0.60	0.37	0.37	0.43	0.16	0.59	0.42	0.27	0.55
SUM	0.64	1.18	1.50	1.77	1.27	2.22	1.62	1.79	2.30	1.62	1.90	1.63	1.24	1.27	1.59	0.64	1.89	1.66	0.84	2.04
Total CBs	2.87	2.60	3.78	3.80	3.75	4.25	4.84	4.52	4.82	3.27	4.59	4.00	3.82	4.84	3.62	1.27	3.59	6.08	5.03	4.00

Table 4. Pearson product-moment correlation coefficients for CB compounds in seawater from Youngil Bay, Korea

	1,3,5-TrCB	1,2,4-TrCB	1,2,3-TrCB	1,2,3,5+ 1,2,4,5-TeCBs	1,2,3,4-TeCB	PeCB	HCB
				DISSOLVED			
1,3,5-TrCB		0.027	-0.079	-0.126	-0.028	-0.029	0.079
1,2,4-TrCB	0.690**		0.412	0.129	0.457*	0.282	0.332
1,2,3-TrCB	0.782***	0.766***		0.38	0.428	0.181	0.139
1,2,3,5+ 1,2,4,5-TeCBs	0.693**	0.909***	0.733***		0.641**	0.692*	0.587***
1,2,3,4-TeCB	0.852***	0.845***	0.885***	0.876***		0.725***	0.864***
PeCB	0.769***	0.768***	0.835***	0.837***	0.952***		0.735***
HCB	0.859***	0.788***	0.893***	0.763***	0.957***	0.899***	
				PARTICULATE			

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

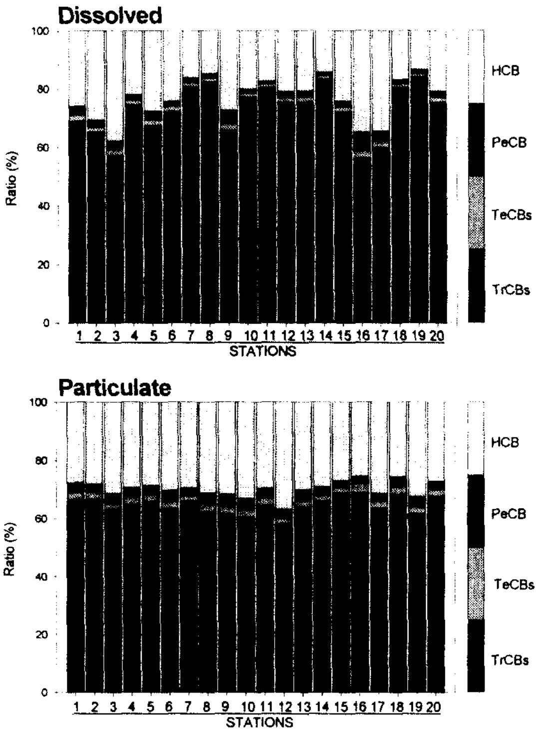

Fig. 2. Contributions of chlorobenzene congener groups in dissolved and particulate phase of seawater from Youngil Bay, Korea. TrCBs : sum of 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene, TeCBs: sum of 1,2,4,5-, 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene, PeCB : pentachlorobenzene, and HCB : hexachlorobenzene.

CB compounds(Table 4). This statistical approach is based on the fact that each pollution source produces a characteristic CB pattern, therefore, the analysis can reveal whether or not the CBs all originated from the same source. In the particulate matter samples, there was a highly positive correlation between the CB species. In particular, the high-molecular-weight compounds, such as PeCB and HCB, exhibited a higher correlation than the low-molecular-weight compounds. In contrast, in the dissolved samples, there was no correlation between the lower-molecular-weight TrCBs. However, a significant correlation was found between the tetra- to hexa-CBs. These results appeared to be related to the physical and chemical properties of each compound.

Furthermore, there was no apparent significant correlation between the concentration of the dissolved CBs and the DOC(r^2=0.29) or the particulate CBs and the POC(r^2=0.02). This was most likely because the primary source of organic carbon in a marine environment is marine phytoplankton.

4. Conclusions

Surface seawater was sampled from 20 stations in Youngil Bay to investigate the level of chlorobenzene(CB) contamination. The total CB compound levels ranged from 1.3 to 6.1 ng/L. The contributions of congener groups to the total eight CB compounds found in the seawater exhibited similar patterns for all stations. A positive correlation was observed between the individual CB compounds in the particulate samples, while the dissolved samples exhibited a high correlation between heavier molecular weight CBs.

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