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# Monitoring of Some Chlorobenzenes in Marine Sediments and Bivalves from Several Coastal Regions of Korea

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Marine sediments and bivalves were sampled at 20 stations from coastal regions of Korea, to investigate the levels and patterns of some chlorobenzene isomers. Total chlorobenzenes were in the range of 0.32-3.55 ng/g dry weight in marine sediments and 0.26-0.84 ng/g wet weight in bivalves. Hexachlorobenzene levels in marine sediments and bivalves were lower than or comparable to those levels of reported in other countries. Isomeric patterns of some chlorobenzenes in marine sediments and bivalves were slightly different. However, the predominant isomer in marine sediments and bivalves was 1,2,4-trichlorobenzene. Hexachlorobenzene contribution to total concentrations was higher in sediments than in bivalves.

Key words: Sediment, Bivalve, Chlorobenzene, Isomer, Hexachlorobenzene

## Introduction

Monitoring of toxic organic contaminants is the fundamental work to assess the environmental fate and toxic effect of these chemicals for the coastal marine ecosystems. In addition, monitoring can provide comprehensive information on the temporal and spatial variations of these contaminants in the marine environment (Herve et al., 1988; Law et al., 2002). National Fisheries Research & Development Institute (NFRDI) has been determined the presence of toxic metals and persistent organic pollutants (POPs) in the marine environment of Korea. The results on monitoring of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs) and tributyltin (TBT) in the marine sediments and bivalves from coastal regions of Korea have been recently reported elsewhere (Moon et al., 2001a; 2001b; 2001c; Choi et al., 2002; Moon et al., 2004). In this study, we present the concentration and composition of some chlorobenzenes in the marine environmental samples from various regions in Korea.

Chlorobenzenes are widespread organic contaminants in the marine environment. They comprise a group of 12 isomers ranging from mono- to hexachlorobenzene according to the number and position of chlorine. These compounds are mainly used as de-ordants, solvents and pesticides, as well as by-products of manufacturing processes (Newhook and Meek, 1994). Unlike some organochlorine pesticides, however, chlorobenzenes are not banned from production or use in any country until 1990s (Lane et al., 1992). Previous investigations have seldom quantified the chlorobenzene isomers in environmental media despite the fact that many of these congeners are listed as priority pollutants owing to their toxicity and carcinogenicity (Harper et al., 1992). In particular, there are few data on level of chlorobenzene isomers available in marine environments of Korea. The objective of this study is to investigate the levels and isomeric patterns of chlorobenzenes in the marine sediments and organisms from several Korean coastal regions.

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## Materials and Methods

Surface sediments (0-4 cm) and bivalves were sampled at 20 stations from the coastal regions of Korea during February-July 2000 (Fig. 1). Sediments were collected with a box-core sampler. Mussels (*Mytilus coruscus* and *M. edulis*) and oysters (*Crassostrea gigas*), which were located on piers, rocks, and buoys, were scraped with a rake. The

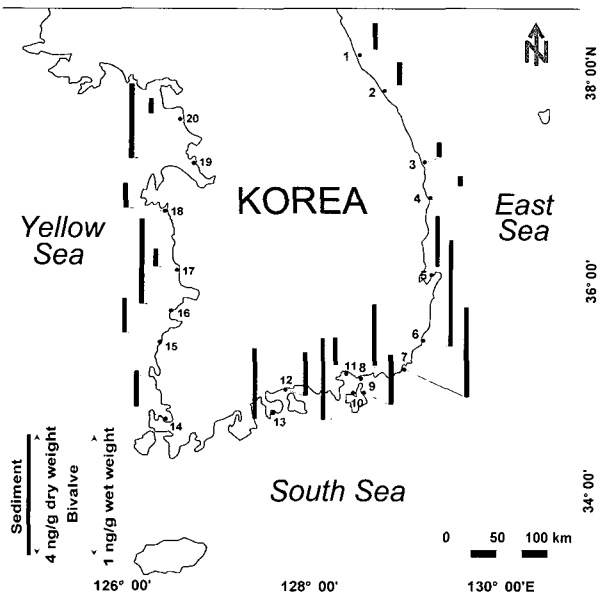


Fig. 1. The sampling stations and total concentrations of some chlorobenzenes in marine sediments and bivalves from coastal regions of Korea.

shells of the bivalves were removed. Both sediments and bivalve tissues were wrapped with an aluminum foil and frozen at -20℃ until analysis. Detailed procedure of sample preparation has been described in Moon et al. (2001d; 2002). In brief, sediments were extracted with Soxhlet apparatus with toluene (Ultra residue analysis, J.T. Baker, USA). Organisms were homogenized with an ultra-disperser. They were decomposed in 200 mL of 1 N KOH ethanolic solution by mechanical shaking. The digest was liquid-liquid extracted with *n*-hexane (Ultra residue analysis, J. T. Baker, USA). Both extracts of sediments and bivalves were cleaned up on a multi-layer silica gel column chromatography. The purified samples were concentrated to less than 1 mL, and left at a room temperature for one day to evaporate to 50-100 $\mu$L. Samples were determined for chlorobenzenes with gas chromatography coupled to mass spectrometer detector (GC/MSD). Analytical details and instrument parameters have been presented by Moon et al. (2001d; 2002).

## Results and Discussion

Eight chlorobenzene isomers were detected in all environmental samples. Table 1 summarizes the concentrations of chlorobenzene isomers in marine sediments and bivalves from coastal regions of Korea. Spatial distributions of total chlorobenzenes (the sum of eight isomers) in marine sediments and bivalves from several coastal regions of Korea were presented in Fig. 1. In sediments, the levels of total chlorobenzenes varied from 0.32 to 3.55 ng/g dry weight with a mean 1.57 ng/g dry weight. The highest level of chlorobenzenes was at Station 6 from Ulsan coast due to the effect of contamination sources. Some chlorobenzenes, trichlorobenzene in particular, have been used as a primary solvent in a petrochemical manufacturing process (Lee et al., 2000). Relatively lower levels were observed at Stations 1 to 4 from East Sea, where the sediment type was primarily sand. The result indicates that the grain-size composition in the sediments can be one of the important factors governing the levels of organic contaminants.

In bivalves, the levels of total chlorobenzenes varied from 0.26 to 0.84 ng/g wet weight with a mean 0.48 ng/g wet weight. High levels of chlorobenzenes were found at Station 4 from Hupo coast and Station 6 from Ulsan coast. However, in general, there were no significant differences (Student *t*-test, $p>0.05$) of chlorobenzene contamination among the sampling stations from Korean coastal regions. The levels of

Table 1. Summary of some chlorobenzene congeners in marine sediments and bivalves from coastal regions of Korea

| | Sediment (ng/g dry weight) | | Bivalve (ng/g wet weight) | |
|---|---|---|---|---|
| | Range | Mean | Range | Mean |
| 1,3,5-TrCB | 0.001-0.077 | 0.010 | 0.006-0.078 | 0.023 |
| 1,2,4-TrCB | 0.159-2.63 | 0.868 | 0.001-0.370 | 0.186 |
| 1,2,3-TrCB | 0.014-0.730 | 0.106 | 0.001-0.105 | 0.018 |
| 1,2,3,5+1,2,4,5-TeCBs | 0.005-0.226 | 0.052 | 0.001-0.088 | 0.029 |
| 1,2,3,4-TeCB | 0.001-0.223 | 0.049 | 0.001-0.115 | 0.037 |
| PeCB | 0.014-0.328 | 0.096 | 0.009-0.316 | 0.096 |
| HCB | 0.098-1.13 | 0.390 | 0.030-0.206 | 0.092 |
| SUM | 0.32-3.55 | 1.57 | 0.26-0.84 | 0.48 |

chlorobenzenes in marine bivalves were lower than those in sediments, and this suggests that there was no specific bioaccumulation of these contaminants in the coastal regions of Korea.

There were few data on level of chlorobenzene isomers available in marine environment. Only, HCB concentration was compared with other countries in this study, because the survey on environmental distribution has been traditionally focused on HCB among chlorobenzene isomers. HCB levels in marine sediments in this study were in the range of 0.10-1.13 ng/g dry weight (mean 0.39 ng/g dry weight). These values were slightly low or comparable to those in Ise Bay (Japan), Lake Huron, Lake Erie (USA) (Masunaga et al., 1991). However, HCB levels in sediments from Mediterranean Sea (Tolosa et al., 1995), Kaohsiung coast (Lee et al., 2000) and Lake Ontario (Durrsma et al., 1989) revealed as about 10-50 times higher than those measured in this study.

HCB levels in marine bivalves in this study were in the range of 0.03-0.21 ng/g wet weight (mean 0.09 ng/g wet weight). These values were comparable to the residues in the bivalves from southeastern coasts of Korea (Kim et al., 2002), Norwegian coast (Green and Knutzen, 2003) and Black Sea (Kurt and Ozkoc, 2004). However, HCB residues in mussels from several regions of Greenland showed the higher values than those of Korean coasts (Cleemann et al., 2000). Consequently, it means that chlorobenzene contamination in Korean coastal regions were comparable to other coastal regions of the world.

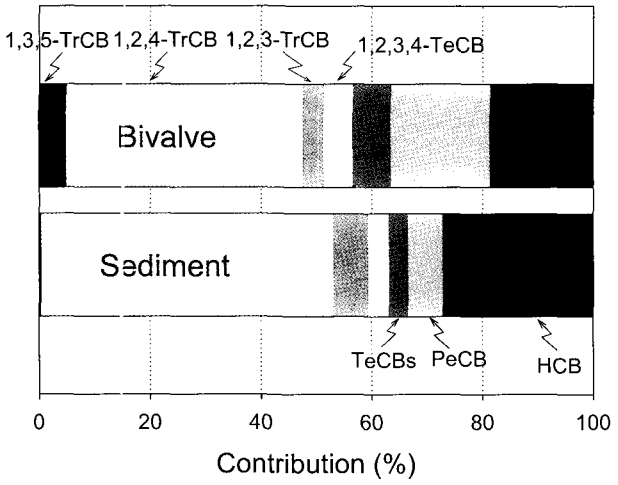


Fig. 2. Average contribution of individual chlorobenzene congener to the total concentrations in marine sediments and bivalves from coastal regions of Korea. TeCBs means the sum of 1,2,3,5- and 1,2,4,5-TeCBs.

The average contribution of individual chlorobenzene isomer to total chlorobenzenes in sediments and bivalves was presented in Fig. 2. The compositions of chlorobenzenes in marine sediments and bivalves were slightly different. However, the predominant congener in all sediments and bivalves was 1,2,4-TrCB. HCB contribution in sediments was higher than that of bivalves, while PeCB contribution was lower in sediments than bivalves.

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