

Monitoring of PCDDs, PCDFs, DLPCBs and PAHs in marine organisms from the coastal areas of Korea

Hyo-Bang Moon¹, Hee-Gu Choi¹, Su-Jung Lee¹, Sang-Soo Kim¹, Minkyu Choi¹, Gon Ok²

¹National Fisheries Research & Development Institute, Busan

²Pukyong National University, Busan

Introduction

Monitoring of toxic organic contaminants is the fundamental work to study ecotoxicology. Bioaccumulative monitoring essentially can provide comprehensive information on the average variation in time and space of the concentrations of contaminants in the marine aquatic environments^{1,2}, assessing the extents and toxic effects of persistent organic chemicals for the coastal marine ecosystems. A large variety of organic chemicals, primarily anthropogenic pollutants, are transported into coastal marine ecosystems through various routes. Marine organisms may be exposed to toxic organic contaminants by contact with contaminated seawater and sediments, either on the seabed or through suspended sediments, or by ingestion of contaminated prey³. Due to low water solubility and high octanol/water partition coefficients (K_{ow}) in seawater, these chemicals can retain and concentrate in fatty tissues of these marine organisms such as migrate into fish, shellfish and invertebrates. In aquatic systems, the highly lipophilic and hydrophobic organic pollutants tend to bioconcentrate from water to aquatic animal and then biomagnify up through the multistep food chain^{4,5}. Hence, these organisms reflect the pollution extent of persistent toxic organic pollutants and some species are used as bio-indicators at different environmental conditions and foodweb⁶. Although several toxic microcontaminants have previously been determined in some locations for marine organisms from the Korean coastal environments^{7,8}, there are few reported data on levels of PCDDs/DFs, DLPCBs and PAHs in marine organisms, particularly shellfish, from the Korean coastal ecosystems. In this study, we planned to monitor the dioxins and dioxin-like contaminants pollution in marine environment of Korea.

Materials and Method

Sample collection: Mussels (*Mytilus coruscus* and *M. edulis*) and oysters (*Crassostrea gigas*) were collected along the Korean coastal areas from May 2001 to April 2002. These sampling stations were selected as potential pollution areas based on data of marine environmental contamination estimated through national marine environment monitoring network done by National Fisheries Research & Development Institute (NFRDI) since 1970s. Most of harbors in Korea were included in the sampling stations. In addition, there were subjected more extensive survey for mussels (*M. edulis*) in Busan coast and its adjacent areas (Gadeok Island). In particular, Busan coast has the largest port in Korea with three ports of North, South and Gamcheon. A number of point sources

were distributed over the coastal line. The sampling stations of marine organisms from the coastal areas of Korea were presented in Figure 1. Bivalve samples, which were located on piers, rocks or buoys in the water column, were scraped with a rake. Shells of mussels and oysters were carefully removed and bivalve tissues were wrapped with an aluminium foil and frozen at -20°C .

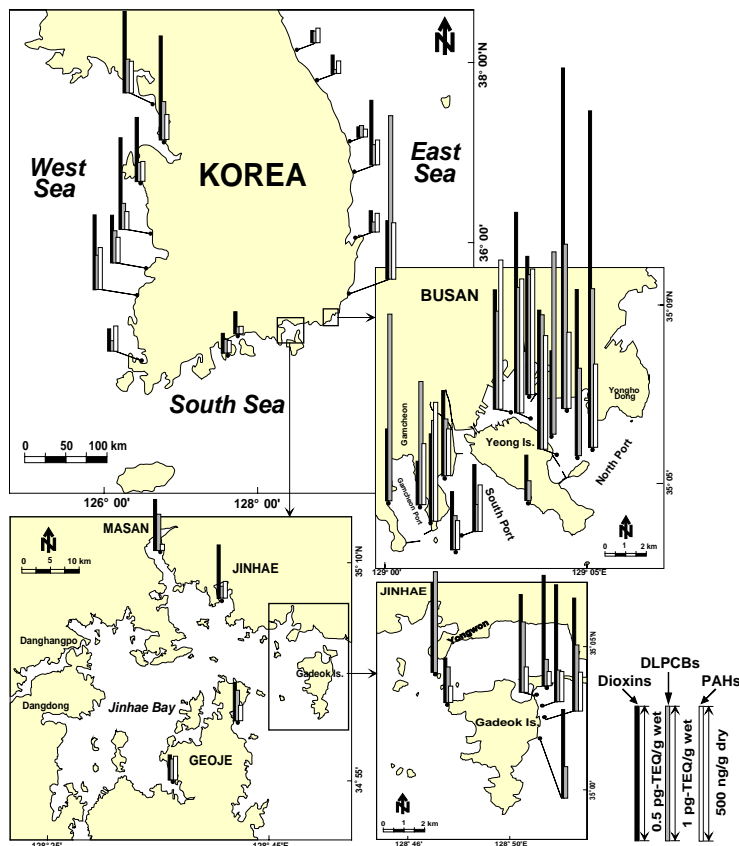


Figure 1: Map showing the sampling stations and the spatial distributions of target compounds in mussels (*Mytilus coruscus* and *M. edulis*) and oysters (*Crassostrea gigas*) from the coastal areas of Korea. The numbers indicate the sampling stations. Enlarged map shows the mussels sampling stations from Busan coast and the adjacent areas of Gadeok Island, Korea.

Sample preparation and analysis: Marine organism samples were pooled and then homogenized with an ultra-disperser. After the internal standards for PCDDs/DFs and DLPCBs spiked into homogenized samples (100 g), they were decomposed in 200 mL of 1 N KOH ethanolic solution (Dioxin analysis, Wako) for 2 hours by mechanical shaking. The digest was liquid-liquid extracted with twice using 150 mL of *n*-hexane after the addition of water and 50 g of anhydrous Na_2SO_4 . The extracts were reduced to small volume in a rotary evaporator and then adjusted to a volume of 10 mL. After pre-cleaned up with a multi-layer silica gel column chromatography containing AgNO_3 -silica gel, H_2SO_4 -silica gel and KOH-silica gel, the extract was cleaned up on an activated alumina column chromatography with successive elutants of 3% methylene dichloride 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 and determined for PCDDs/DFs and DLPCBs using HRGC/HRMS (JMS 700D, JEOL). Further details of the experimental procedure and instrumental analysis of PCDDs/DFs and DLPCBs are presented elsewhere^{8,9}. For the PAHs determinations, the extracts of marine organisms were purified with an activated silica gel column chromatography with successive eluants of *n*-hexane and 15% methylene dichloride in *n*-hexane. Instrumental analysis for PAHs was performed using gas chromatography coupled to mass spectrometry (GC/MS, Agilent 5973N).

Results and Discussion

Contamination levels: Concentrations of PCDDs/DFs, DLPCBs and PAHs in mussels and oysters from Korean coastal areas, Busan coast and the adjacent areas of Gadeok Island were summarized in Table 1. Most of PCDDs/DFs, DLPCBs and PAHs were detected in all bivalve samples from the studied areas. The result indicates that dioxins and dioxin-like contaminants are the widespread contaminant in the coastal marine environment of Korea. Total and TEQ concentrations of PCDDs/DFs in bivalves from all stations in this study ranged from 3.86 to 110 pg/g wet weight and from 0.03 to 1.40 pg-TEQ/g wet weight. The levels of total PCDDs/DFs from Korean coastal areas varied from 3.86 to 38.8 pg/g wet weight. TEQ concentrations of PCDDs/DFs also varied from 0.03 to 0.64 pg-TEQ/g wet weight. The contaminant levels in mussels from Busan coast ranged from 16.3–110 pg/g wet weight and the levels of TEQ ranged from 0.08 to 1.40 pg-TEQ/g wet weight. The residues of total PCDDs/DFs in mussels from Gadeok Island, which have been recently developed as very large port in Korea, were in the range of 16.9–44.0 pg/g wet weight and those of TEQ were in the range of 0.14–0.42 pg-TEQ/g wet weight.

The TEQ concentrations of DLPCBs in bivalves from all stations in this study ranged from 0.02 to 1.4 pg-TEQ/g wet weight. The levels of total DLPCBs from the Korean coastal areas varied from 0.02 to 1.22 pg-TEQ/g wet weight. The contaminant levels in mussels from Busan coast ranged from 0.15–1.4 pg-TEQ/g wet weight. The residues of DLPCBs in mussels from Gadeok Island were in the range of 0.2–0.74 pg-TEQ/g wet weight.

The concentrations of total PAHs in bivalves from all stations in this study ranged from 27.5 to 557 ng/g dry weight. The levels of total PAHs from Korean coastal areas varied from 27.5 to 211 ng/g dry weight. The contaminant levels in mussels from Busan coast ranged from 105–557 ng/g dry weight. The residues of total PAHs in mussels from Gadeok Island were in the range of 54.1–146 ng/g dry weight.

Table 1: Concentrations of PCDDs/DFs, DLPCBs and PAHs in marine organisms from the coastal areas of Korea

	Korean coast	Busan coast	Gadeok Island
PCDDs/DFs ^a	0.03 – 0.64	0.08 – 1.40	0.15 – 0.42
DLPCBs ^b	0.02 – 1.22	0.15 – 1.40	0.20 – 0.74
PAHs ^c	27.5 – 211	105 – 557	54.1 – 146

^a in the pg I-TEQ/g wet weight; ^b in the pg WHO-TEQ/g wet weight; ^c in the ng/g dry weight.

Spatial distributions of dioxins and dioxin-like contaminants: The spatial distributions of PCDDs/DFs in mussels and oysters from Korean coastal areas were presented in Figure 1. In general, West coasts showed the higher contamination status than East and South coasts in comparison of PCDDs/DFs residues in bivalves from three coasts of Korea. PCDDs/DFs residues in mussels from Busan coast showed the 2–3 times greater than other studied stations. The national survey for PCDDs/DFs contents in mussels and oysters were comparable to those of Gadeok Island. In Busan coast, North Port had the higher concentration of PCDDs/DFs in mussels in comparison with those from three ports of Busan coast. The distributions of DLPCBs in bivalve from the surveyed stations were similar to PCDDs/DFs distribution patterns. DLPCBs residues in Station 6 (Ulsan Bay) from East coast showed the higher contamination than other stations from three coasts of Korea. For the spatial distributions of PAHs, the South and West coasts showed higher contamination status than East coasts in comparison of PAHs residues in bivalves from three coasts of Korea. PAHs residues in mussels from Busan coast showed the 3–5 times greater than other studied stations. The national survey for PAHs contents in mussels and oysters were comparable to those of Gadeok Island. In Busan coast, North Port had the higher concentration of PAHs in mussels in comparison of those from three ports of Busan coast.

Comparison of PCDDs/DFs, DLPCBs and PAHs levels with other countries: PCDDs/DFs residues in mussels from Korean coastal areas varied from 0.03 to 1.4 pg-TEQ/g wet weight. These values were slightly higher than or comparable to those from the southern coast of Korea¹⁰ and from Seoul city of Korea¹¹. PCDDs/DFs levels in mussels collected from Adriatic Sea, Italy¹² were lower than those in this study. However, PCDDs/DFs levels in shellfish from rural beach, Tokyo Bay and Shinji Lake of Japan were 3.56 pg-TEQ/g wet weight and in the range of 1.72–2.21 pg-TEQ/g wet weight, respectively^{13,14}. In addition, PCDDs/DFs levels in shellfish from Taiwan, in oysters from Mississippi of USA, in mussels from Catalonia of Spain, and in bivalves from Huelva of Spain were comparable to and higher than those in this study^{15–18}.

PAHs residues in mussels and oysters from Korean coastal areas were in the range of 28–557 ng/g dry weight. These values were similar to PAHs levels in oysters (*Crassostrea gigas*) from Jinhae Bay of Korea with a range of 0.1–992 ng/g dry weight¹⁹. In addition, PAHs levels in mussels and oysters from Kara Sea of Russia, Carolinas and Great Lake of USA were in the range of 250–940 ng/g dry weight^{20–22}. For several regions of France, PAHs concentrations in mussels ranged between 25 and 552 ng/g dry weight²³. These PAHs values in mussels from different locations in the world were comparable to those measured in this study. However, PAHs residues in mussels from the several locations of other countries were 10–100 times higher than PAHs levels in mussels measured in this study. PAHs concentrations in mussels from Pacific Sea of Mexico were in the range of 750–6,910 ng/g dry weight²⁴, from Cornigliano of Italy were in the range of 1,489–2,640 ng/g dry weight²⁵, from Arcachon Bay of France were in the range of 279–2,420 ng/g dry weight²³, and from Kiel area of France were in the range of 342–38,800 ng/g dry weight²³. Consequently, the contamination status of toxic organic contaminants including dioxins in marine organisms from the Korean coastal areas is likely to be moderate in comparison with marine environment from other countries.

Congener profiles of PCDDs/DFs, DLPCBs and PAHs: Marine bivalves such as mussel and oyster are accumulated by the bio-concentration of contaminants adsorbed in the sedimentary or suspended particles and dissolved in the seawater and by the magnification of preys they feed on.

The homologue profiles of PCDDs/DFs in marine organisms from the coastal areas of Korea showed the similar patterns. In general, PCDFs revealed the higher contributions to the total concentrations in comparison with those of PCDDs. Tetra-chloro compounds such as TCDFs and TCDDs had the highest occupation in all homologues, while the high chlorinated compounds showed low contribution. However, OCDD had relatively high contributions because these bivalves are characterized by filter-feeding habit of suspended particles with the high OCDD concentrations. For toxic 2,3,7,8-substituted congeners of PCDDs/DFs, 2,3,4,7,8-PeCDF occupied the highest value in marine organisms, followed by 2,3,7,8-TCDD>2,3,7,8-TCDF>1,2,3,7,8-PeCDF.

Congener profiles of DLPCBs in marine organism showed the similar patterns. PCB 126 had the highest occupation (>70%) in all organism samples analyzed, followed by PCB 169 and PCB 156. Generally, non-*ortho* PCBs were the higher contributions to total DLPCBs concentrations than mono-*ortho* PCBs.

PAHs profiles in marine organisms from the coastal areas of Korea showed a little different composition. However, in general, the four ring aromatics like fluoranthene, pyrene, benzo[a]anthracene and chrysene were the predominant species for all collected organism samples.

References

1. Herve S., Heinonen P. and Paukku R. (1988) *Chemosphere* 17, 1945–1961.
2. Law R.J., Kelly C.A., Baker K.L., Langford K.H. and Bartlett T. (2002) *Mar. Pollut. Bull.* 44, 903–911.
3. Hellou J. and Warren W.G. (1996) *Mar. Environ. Res.* 43, 11–24.
4. Clark T., Clark K., Paterson S., Mackay D. and Norstorm R. (1988) *Environ. Sci. Technol.* 22, 120–127.
5. Jones P., Ankley G., Best D., Crawford R., DeGalan N., Giesy J., Kubiak T., Ludwig J., Newsted J., Tillitt D. and Verbrugge D. (1993) *Chemosphere* 26, 1203–1212.
6. Escartín E. and Porte C. (1999) *Mar. Pollut. Bull.* 38, 1200–1206.
7. Kim G.B., Maruya K.A., Lee R.F., Lee J.H., Koh C.H. and Tanabe S. (1999) *Mar. Pollut. Bull.* 38, 7–15.
8. Moon H.B., Choi H.G., Kim S.S. and Lee P.Y. (2002) *J. Fish. Sci. Technol.* 4, 51–57.
9. Moon H.B., Choi H.G., Kim S.S., Jeong S.R., Lee P.Y. and Ok G. (2002) *J. Kor. Soc. Environ. Anal.* 5, 225–235
10. Hashimoto S., Cho H.S. and Morita M. (1998) *Chemosphere* 37, 951–959.
11. Kim K.S., Kim J.G. and Kim M.Y. (2000) *J. Kor. Soc. Environ. Eng.* 22, 1345–1355.
12. Bayarri L., Frignani M., Raccanelli S. and Carraro C. (2000) *Mar. Pollut. Bull.* 40, 65–76.
13. 12. Sakurai T., Kim J.G., Suzuki N., Matsuo T., Li D.Q., Yao Y., Masunaga S. and Nakanishi J. (2000) *Chemosphere* 40, 627–640.
14. Hashimoto S., Horiguchi T., Shibata Y. and Morita M. (1999) *Chemosphere* 39, 2661–2669.
15. Hsu M.S., Ma E., Cheong P.S., Chou U., Chen S.Y., Chang C.F., Chou S.S., Cheng C.C., Yu C.Y., Liao C.H. and Ling Y.C. (2002) *Organo. Comp.* 57, 73–76.
16. Fiedler H., Cooper K.R., Bergek S., Hjelt M. and Rappe C. (1997) *Chemosphere* 34, 1411–1419.
17. Abad E., Llerena J.J., Saulo J., Caixach J. and Rivera J. (2002) *Chemosphere* 46, 1435–1441.
18. Bordajandi L.R., Herrero L., Abad E., Rivera J. and Gonzalez M.J. (2002) *Organo. Comp.* 57, 69–72.
19. Lee K.S., Noh I., Lim C.S. and Chu S.D. (1998) *J. Kor. Soc. Environ. Sci.* 2, 57–68.
20. Sericano J.L., Brooks J.M., Champ M.A., Kennicutt M.C. and Makeyev V.V. (2001) *Mar. Pollut. Bull.* 42, 1017–1030.
21. Lauenstein G.G., Cantillo A.Y. and O'Connor T.P. (2001) *Sci. Total Environ.* 285, 79–87.
22. O'Connor T.P. (2002) *Environ. Res.* 53, 117–143.
23. Baumard P., Budzinski H., Garrigues P., Dizer H. and Hansen P.D. (1999) *Mar. Environ. Res.* 47, 17–47.
24. Botello A.J., Garcia-Ruelas C. and Ponce-Velez G. (2002) *Environ. Contam. Toxicol.* 69, 486–493.
25. Stella A., Piccardo M.T., Coradeghini R., Redaelli A., Lanteri S., Armanino C. and Valerio F. (2002) *Anal. Chimica Acta.* 219, 1–13.