

## Residues and Bioaccumulation Patterns of Polycyclic Aromatic Hydrocarbons in Various Marine Organisms in Relation with Their Exposure Pathway

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Seventy four marine organisms, which are common edible species and commercially important items in Korea, were sampled at the local fisheries markets and were analyzed for polycyclic aromatic hydrocarbons (PAHs) using gas chromatography coupled to mass spectrometer detector (GC/MSD). The levels of sixteen PAHs in selected organisms from Korean coasts were in the range of 0.45-224 ng/g dry weight. Bivalvia species showed the highest contents of PAHs, followed by crustacea, filipino venus and fish species. The residues of PAHs in marine organisms from the coastal environments of Korea were slightly low or relatively moderate in comparison with those in other countries. The predominant compositions of PAHs in fish species were the lower-molecular-weight two- and three-ring aromatic groups with similar patterns of those in seawater samples. The PAHs compositions of bivalvia, crustacea, cephalopoda and gastropoda species were dominated by three- and four-ring aromatics with intermediate PAHs patterns of sediments and seawater. However, PAHs compositions in Filipino venus, which live in muddy flat, were relatively comparable to those in marine sediments. The PAH profiles in various marine organisms according to exposure pathway were compared to abiotic samples such as marine sediments and seawater using factor analysis. The PAH profiles in each biotic or abiotic samples showed similar distributions. The result suggests that PAHs bioaccumulation pattern in organisms from the marine ecosystems was governed by a variety of factors including exposure circumstance, habitat, diet and metabolites.

**Key words:** Marine organism, sediment, seawater, factor analysis, exposure pathway, bioaccumulation

### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are well-known ubiquitous contaminants in the coastal marine environment. These compounds have mainly anthropogenic origins, including combustion process of fossil fuels,<sup>1)</sup> domestic and industrial wastewater<sup>2)</sup> and spillage of petroleum or petroleum products by ships.<sup>3-4)</sup> Since they are carcinogenic and mutagenic,<sup>5-8)</sup> these compounds have been intensively studied in the marine environment.<sup>9-12)</sup>

Marine organisms may be exposed to PAH by contact with contaminated seawater and sediments, either on the seabed or through suspended sediments, or by

ingestion of contaminated prey.<sup>13)</sup> The different PAH profiles have been observed in organisms of various trophic levels.<sup>14-15)</sup> These differences were attributed to a partial biotransformation of the contaminants in the organisms of higher trophic levels.<sup>16)</sup> Therefore, these organisms reflect the pollution extent of PAHs and some species are used as bioindicators at different environmental conditions and foodweb.<sup>17-18)</sup>

Although PAHs have previously been determined in sediments and bivalves from some locations in the Korean coastal environments,<sup>19-21)</sup> there are few reported data on contaminations of PAHs in marine organisms including fish from Korean coasts.<sup>22)</sup> The main purpose of the current study was to measure the

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PAH residues in various marine organisms caught from Korean coasts and to elucidate relationships between PAHs accumulation patterns and exposure pathway in various organism species.

## 2. Materials and Method

### 2.1. Sample collection

Seventy four marine organism samples (38 species) were purchased at local fisheries markets from some locations distributed over Korean coastal areas from January 2002 to October 2003. These organisms are common edible species and are commercially important

seafood items in Korea. Marine organism samples can be classified by six groups with fish (24 species,  $n=38$ ), crustacea (5 species,  $n=9$ ), bivalvia (5 species,  $n=10$ ), filipino venus (*Ruditapes philippinarum*,  $n=7$ ), gastropoda (3 species,  $n=6$ ) and cephalopoda (2 species,  $n=4$ ). Biological information on selected marine organisms in this study was summarized in Table 1.

### 2.2. Sample preparation and analysis

Marine organism samples in a cooler box with ice or dry ice were immediately transported to the laboratory. The samples were homogenized with an ultra-disperser and then freeze-dried. After the internal standards of 7

**Table 1.** Summary of biological characteristics of various marine organisms in Korea

| Local market | Species   | $n^a$ | Length (cm) | Height (cm) | Moisture (%) | Lipid (%) |
|--------------|---|-------|-------------|-------------|--------------|-----------|
| <b>Fish</b>  |   |       |             |             |              |           |
| Gangleung    | Korean flounder ( <i>Glyptocephalus stelleri</i> )  | 16    | 22          | 9.5         | 74           | 4.6       |
| Gangleung    | Roundnose flounder ( <i>Eopsetta grigorjewi</i> )   | 10    | 20          | 8           | 83           | 6.8       |
| Jumunjin     | Roundnose flounder ( <i>Eopsetta grigorjewi</i> )   | 12    | 28          | 10          | 75           | 13        |
| Pohang       | Roundnose flounder ( <i>Eopsetta grigorjewi</i> )   | 22    | 23          | 9           | 76           | 16        |
| Pohang       | Roundnose flounder ( <i>Eopsetta grigorjewi</i> )   | 20    | 22          | 10          | 76           | 3.1       |
| Jumunjin     | Alaska pollack ( <i>Theragra chalcogramma</i> )     | 9     | 34          | 5.5         | 76           | 12        |
| Jumunjin     | Alaska pollack ( <i>Theragra chalcogramma</i> )     | 10    | 38          | 6.8         | 75           | 5         |
| Jumunjin     | Sailfin sandfish ( <i>Arctoscopus japonicus</i> )   | 40    | 16          | 3.3         | 76           | 27.1      |
| Pohang       | Saury ( <i>Cololabis saira</i> )                    | 8     | 28          | 3           | 79           | 15        |
| Pohang       | Saury ( <i>Cololabis saira</i> )                    | 11    | 28          | 3.5         | 70           | 21        |
| Pohang       | Herring ( <i>Clupea pallasii</i> )                  | 6     | 27          | 6           | 77           | 46.9      |
| Busan        | Hairtail ( <i>Trichiurus lepturus</i> )             | 5     | 31          | 8           | 79           | 19.3      |
| Busan        | Mackerel ( <i>Scomber japonicus</i> )               | 5     | 42          | 6           | 81           | 48.2      |
| Tongyeong    | Anchovy ( <i>Engraulis japonica</i> )               | 60    | 4           | 1           | 77           | 12.2      |
| Tongyeong    | Common conger ( <i>Conger myriaster</i> )           | 10    | 32          | 3           | 81           | 31.8      |
| Yeosu        | Common Sea bass ( <i>Lateolabrax japonicus</i> )    | 2     | 38          | 11          | 71           | 14.7      |
| Yeosu        | Common Sea bass ( <i>Lateolabrax japonicus</i> )    | 13    | 43          | 5           | 75           | 20        |
| Yeosu        | Red tongue sole ( <i>Cynolossus joyneri</i> )       | 10    | 14          | 9           | 76           | 2.2       |
| Yeosu        | Red tongue sole ( <i>Cynolossus joyneri</i> )       | 10    | 24          | 2           | 79           | 3.5       |
| Yeosu        | Red tongue sole ( <i>Cynolossus joyneri</i> )       | 30    | 17          | 0.6         | 72           | 1.1       |
| Yeosu        | Sharp toothed eel ( <i>Muraenesox cinereus</i> )    | 10    | 33          | 4           | 81           | 14        |
| Yeosu        | Sharp toothed eel ( <i>Muraenesox cinereus</i> )    | 2     | 47          | 3           | 69           | 13        |
| Yeosu        | Silver fish ( <i>Pampus argenteus</i> )             | 7     | 19          | 10          | 81           | 18.1      |
| Mokpo        | Mi-iuy croaker ( <i>Michthys miiuy</i> )            | 2     | 85          | 16          | 80           | 13.1      |
| Mokpo        | Spanish mackerel ( <i>Scomberomorus niphonius</i> ) | 6     | 70          | 30          | 76           | 28.5      |
| Mokpo        | Flatfish ( <i>Paralichthys olivaceus</i> )          | 8     | 43          | 16          | 76           | 1.2       |
| Gunsan       | Flatfish ( <i>Paralichthys olivaceus</i> )          | 20    | 33          | 12.5        | 76           | 9.7       |
| Gunsan       | Flatfish ( <i>Paralichthys olivaceus</i> )          | 5     | 59          | 7           | 58           | 2.7       |
| Incheon      | Flatfish ( <i>Paralichthys olivaceus</i> )          | 2     | 64          | 26          | 82           | 6.2       |
| Mokpo        | Jacopever ( <i>Sebastes schlegeli</i> )             | 3     | 30          | 10          | 80           | 5         |

**Table 1.** (Continued)

| Local market          | Species   | <i>n</i> <sup>a</sup> | Length (cm) | Height (cm) | Moisture (%) | Lipid (%) |
|-----------------------|---|-----------------------|-------------|-------------|--------------|-----------|
| Incheon               | Jacopever ( <i>Sebastes schlegeli</i> )                           | 2                     | 30          | 10          | 78           | 14.2      |
| Jeju                  | Marbled rockfish ( <i>Sebastes marmoratus</i> )                   | 25                    | 18          | 6           | 77           | 11.8      |
| Jeju                  | Whitesaddled reeffish ( <i>Chromis notata</i> )                   | 50                    | 5           | 3           | 75           | 12.8      |
| Gunsan                | Korean pomfret ( <i>Pampus echinogaster</i> )                     | 8                     | 20          | 10          | 84           | 14.6      |
| Gunsan                | Armorclad rockfish ( <i>Sebastes hubbsi</i> )                     | 7                     | 28          | 7           | 78           | 8.3       |
| Gunsan                | Armorclad rockfish ( <i>Sebastes hubbsi</i> )                     | 20                    | 21          | 6           | 62           | 11.4      |
| Incheon               | Greening ( <i>Hexagrammos otakii</i> )                            | 10                    | 25          | 5           | 80           | 5.8       |
| Incheon               | Common mullet ( <i>Mugil cephalus cephalus</i> )                  | 2                     | 22          | 6           | 84           | 3.1       |
| <b>Crustacea</b>      |   |                       |             |             |              |           |
| Gangleung             | Atelecyclidae ortmann ( <i>Erimacrus isenbecki</i> )              | 24                    | 27          | 7.3         | 58           | 15        |
| Gangleung             | Atelecyclidae ortmann ( <i>Erimacrus isenbecki</i> )              | 30                    | 28          | 4.6         | 55           | 15        |
| Pohang                | Tanner crab ( <i>Chionoecetes opilio</i> )                        | 5                     | 55          | 20          | 72           | 14        |
| Pohang                | Tanner crab ( <i>Chionoecetes opilio</i> )                        | 7                     | 55          | 20          | 70           | 8.3       |
| Pohang                | Red tanner crab ( <i>Chionoecetes japonicus</i> )                 | 20                    | 40          | 17          | 78           | 15        |
| Pohang                | Red tanner crab ( <i>Chionoecetes japonicus</i> )                 | 30                    | 63          | 13          | 79           | 17        |
| Gunsan                | Shrimp large ( <i>Penaeus orientalis</i> )                        | 24                    | 14          | 2.5         | 71           | 1.5       |
| Incheon               | Blue crab ( <i>Portunus trituberculatus</i> )                     | 10                    | 18          | 10          | 79           | 2.4       |
| Incheon               | Blue crab ( <i>Portunus trituberculatus</i> )                     | 20                    | 17          | 15          | 69           | 6.3       |
| <b>Bivalvia</b>       |   |                       |             |             |              |           |
| Sokcho                | Mussel ( <i>Mytilus coruscus</i> )                                | 100                   | 11.6        | 4.5         | 78.9         | 4.6       |
| Ulsan                 | Mussel ( <i>Mytilus coruscus</i> )                                | 100                   | 3.8         | 1.4         | 75.8         | 10.1      |
| Gwangyang             | Mussel ( <i>Mytilus edulis</i> )                                  | 100                   | 7.4         | 3.8         | 63.8         | 7         |
| Asan                  | Oyster ( <i>Crassostrea gigas</i> )                               | 80                    | 3.4         | 2.4         | 46.3         | 10.3      |
| Incheon               | Oyster ( <i>Crassostrea gigas</i> )                               | 80                    | 4.8         | 2.7         | 45.5         | 8         |
| Jumunjin              | Farrer's scallop ( <i>Chlamys (Azumapecten) farreri farreri</i> ) | 70                    | 7           | 1.7         | 67           | 4.2       |
| Jumunjin              | Farrer's scallop ( <i>Chlamys (Azumapecten) farreri farreri</i> ) | 50                    | 7.8         | 1.9         | 65           | 4.5       |
| Yeosu                 | Japanese cockle ( <i>Fulvia mutica</i> )                          | 50                    | 18          | 7           | 71           | 3         |
| Mokpo                 | Grand jackknife clam ( <i>Solen (solen) grandis dunker</i> )      | 53                    | 8           | 1.7         | 55           | 3.5       |
| Mokpo                 | Grand jackknife clam ( <i>Solen (solen) grandis dunker</i> )      | 70                    | 5.8         | 1.2         | 76           | 2.6       |
| <b>Filipino venus</b> |   |                       |             |             |              |           |
| Mokpo                 | Filipino venus ( <i>Ruditapes philippinarum</i> )                 | 100                   | 3.3         | 1.4         | 81           | 3.9       |
| Mokpo                 | Filipino venus ( <i>Ruditapes philippinarum</i> )                 | 100                   | 3.7         | 1.4         | 84           | 2         |
| Mokpo                 | Filipino venus ( <i>Ruditapes philippinarum</i> )                 | 100                   | 3.6         | 1.3         | 81           | 2         |
| Mokpo                 | Filipino venus ( <i>Ruditapes philippinarum</i> )                 | 100                   | 3.6         | 1.4         | 82           | 2         |
| Mokpo                 | Filipino venus ( <i>Ruditapes philippinarum</i> )                 | 100                   | 3.7         | 1.4         | 80           | 2.7       |
| Mokpo                 | Filipino venus ( <i>Ruditapes philippinarum</i> )                 | 100                   | 4.1         | 1.6         | 81           | 2         |
| Mokpo                 | Filipino venus ( <i>Ruditapes philippinarum</i> )                 | 100                   | 4           | 1.5         | 84           | 2.1       |
| <b>Gastropoda</b>     |   |                       |             |             |              |           |
| Pohang                | Disk abalone ( <i>Nordotis discus discus</i> )                    | 10                    | 10          | 3           | 74           | 2.8       |
| Pohang                | Disk abalone ( <i>Nordotis discus discus</i> )                    | 10                    | 8.5         | 5.5         | 74           | 2.6       |
| Jeju                  | Abalone ( <i>Nordotis gigantea</i> )                              | 10                    | 15          | 12          | 67           | 3.9       |
| Jeju                  | Abalone ( <i>Nordotis gigantea</i> )                              | 7                     | 15          | 12          | 67           | 4         |
| Jeju                  | Topshell ( <i>Batillus cornutus</i> )                             | 15                    | 7           | 4           | 78           | 3         |
| Jeju                  | Topshell ( <i>Batillus cornutus</i> )                             | 5                     | 7           | 6           | 65           | 2.1       |
| <b>Cephalopoda</b>    |   |                       |             |             |              |           |
| Gangleung             | Common squid ( <i>Todarodes pacificus</i> )                       | 6                     | 28          | 15          | 79           | 4.1       |
| Gangleung             | Common squid ( <i>Todarodes pacificus</i> )                       | 8                     | 27          | 4.3         | 73           | 4.4       |
| Jumunjin              | Common squid ( <i>Todarodes pacificus</i> )                       | 10                    | 3           | 1.8         | 77           | 4.7       |
| Mokpo                 | Whiparm octopus ( <i>Todarodes pacificus</i> )                    | 7                     | 35          | 18          | 63           | 3.1       |

*n*<sup>a</sup>: sample numbers.

species (ES 2044, Cambridge Isotope Laboratories, Inc.) had been spiked into freeze-dried samples, they (approximately 3 g) were digested in 150 mL of 1 N KOH ethanolic solution for 2 hours by mechanical shaking. The digest was liquid-liquid extracted with twice using 150 mL of *n*-hexane (Ultra residue analysis, J. T. Baker) after the addition of water and 50 g of anhydrous Na<sub>2</sub>SO<sub>4</sub>. The extracts were reduced to a small volume in a rotary evaporator and then adjusted to a volume of 10 mL.

The extracts of marine organisms were cleaned up using an activated silica gel (Art no. 7734, 70-230 mesh, Merck) column successively eluted with *n*-hexane and 15% methylene dichloride (Dioxin analysis, Wako) in *n*-hexane. The second fraction was concentrated to less than 1 mL, and left at a room temperature for one day to evaporate to 100-200  $\mu$ L. The residues were dissolved in 100  $\mu$ L of *n*-nonane (Pesticide residue analysis, Fluka) and analyzed for PAHs with GC/MSD (Agilent 5973N, USA). Further details of the experimental procedure and instrumental analysis of PAHs were presented elsewhere.<sup>21-22)</sup>

The sixteen non-alkylated PAH compounds recommended by US EPA were analyzed in each sample (naphthalene (NaP), acenaphthylene (AcPy), acenaphthene (AcP), fluorene (Flu), phenanthrene (PhA), anthracene (AnT), fluoranthene (FluA), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InP), dibenzo[a,h]anthracene (DbA) and benzo[g,h,i]perylene (BghiP)).

### 2.3. QA/QC

All the spiked internal standards were detected with no interfering peak. The average recoveries showed 76  $\pm$  7% for two-, 75  $\pm$  6% for three-, 82  $\pm$  7% for four-, 87  $\pm$  4% for five-, and 92  $\pm$  6% for six-ring aromatic groups. In order to assess the accuracy of the determinations by experimental procedure and instrument, the certified mussel homogenate (1974a, NIST, USA) was analyzed as Standard Reference Materials (SRMs) in this study. Average recoveries for two-, three-, four-, five-, and six-ring aromatic groups were 67%, 78%,

84%, 91% and 92%, respectively. 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.

## 3. Results and Discussion

### 3.1. PAHs residues in various marine organisms

The moisture and lipid contents (dry weight basis) in all marine organisms were in the range of 46-84% and 1.1-48%, respectively. In particular, fish species showed the wide range of lipid contents with 1.1-48%. The sixteen PAHs were detected in all organisms samples collected from the Korean coastal areas. The levels of  $\Sigma$ PAH (the sum of individual PAH) in marine organisms from Korean coasts were in the range of 0.45-224 ng/g dry weight.

PAHs residues in fish species from the Korean coastal areas were characterized by the wide extent of bioaccumulation. Concentrations of  $\Sigma$ PAH in fish species varied from 0.45 to 56.0 (mean value 10.0) ng/g dry weight total concentrations of potentially carcinogenic PAHs ( $\Sigma$ CPAH; the sum of BaA, BbF, BkF, BaP, InP and DbA)<sup>23)</sup> varied from 0.05 to 5.56 (mean value 1.0) ng/g dry weight. The highest contents were detected in jacobever (*Sebastes olivaceus*) from Incheon coast. Sailfin sandfish (*Arctoscopus japonicus*) from Jumunjin coast and roundnose flounder (*Eopsetta grigorjewi*) from Pohang coast also showed relatively high contents of PAHs. Residues of  $\Sigma$ PAH in crustacea species were in the range of 1.40-71.8 (mean value 20.0) ng/g dry weight and  $\Sigma$ CPAH were in the range of 0.12-49.8 (mean value 7.98) ng/g dry weight. The levels of  $\Sigma$ PAH in bivalvia species ranged from 13.9 to 224 (mean value 103) ng/g dry weight and  $\Sigma$ CPAH ranged from 2.41 to 39.2 (mean value 18.4) ng/g dry weight. Mussels (*Mytilus coruscus*, 224 ng/g dry weight) from Gwangyang coast and oysters (*Crassostrea gigas*, 137 ng/g dry weight) from Incheon coasts was characterized by the highest content of PAHs. Also, farrer's scallop (*Chlamys (Azumapeden) farreri farreri*) from Jumunjin coast revealed a relatively high level of PAHs in this study. Filipino venus

(*Ruditapes philippinarum*) from Mokpo coastal areas showed the residue ranges of 6.3-23.1 (mean value 17.4) ng/g dry weight and of 1.0-6.5 (mean value 4.8) ng/g dry weight for  $\Sigma$ PAH and  $\Sigma$ CPAH, respectively. For gastropoda species, the levels of  $\Sigma$ PAH varied from 1.31 to 18.2 (mean value 8.87) ng/g dry weight and  $\Sigma$ CPAH varied from 0.19 to 4.27 (mean value 1.81) ng/g dry weight. Cephalopoda species showed similar residues of PAHs with gastropoda species.

The comparison of  $\Sigma$ PAH residues in various marine organisms from the coastal areas of Korea were presented in Fig. 1. Bivalvia species showed the highest contents with a wide range of PAHs in this study. Filter-feeding marine bivalves can absorb xenobiotics adsorbed on a small grain-size fraction of particles. PAHs migrated with particles into organism are accumulated to a greater extent. Hence, bivalvia such as oysters and mussels have been used bio-monitoring species for PAHs contamination in the coastal environment of Korea and other countries.<sup>21),24-25)</sup> Crustacea and filipino venus revealed a similar distribution of PAHs. The contents of PAHs in other organisms were relatively lower values than those of other organisms species in this study. In particular, fish species with high trophic level in marine ecosystem showed the low concentrations. It could be explained by high metabolism of fish relative to other organism species. Fish have a greater metabolic capacity than other species, particularly bivalve organisms. This indicates that PAHs migrated into fish can be eliminated by the biotransformation and/or biodegradation with a greater efficiency.<sup>14-15)</sup> Actually, Baumard et al.<sup>16)</sup> reported that marine organisms with high trophic levels can partly biotransform some contaminants such as PAHs.

### 3.2. Status of PAHs residues in marine organisms from the coastal environment of Korea

In order to investigate status of PAHs residues in marine organisms from the Korean coastal areas, PAHs residues in bivalves such as mussels and oysters and fishes were compared with those in other countries. First, the comparison of PAHs residues in bivalves in this study with those in other countries were

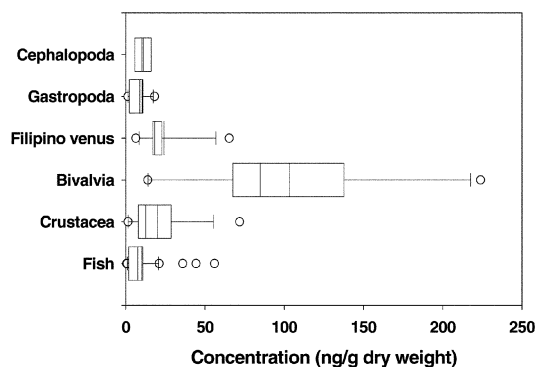


Fig. 1. Comparison of  $\Sigma$ PAHs residues in various marine organisms from the coastal areas of Korea.

summarized in Table 2. Although the number of PAHs analyzed in other studies may differ, the sixteen PAHs have found in bivalve samples from most estuaries and coastal waters in the world. PAHs residues in bivalves from the Korean coastal areas were in the range of 14-224 ng/g dry weight. These values were similar to PAHs residues in oysters (*Crassostrea gigas*) from Jinhae Bay of Korea.<sup>19)</sup> 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.<sup>26-28)</sup> Recently, Stella et al.<sup>30)</sup> reported that PAHs residues in mussels from Sanremo, Zinola, Voltri, Paraggi coastal areas of Italy varied from 88 to 283 ng/g dry weight. For several regions of France, PAHs concentrations in mussels ranged between 25 and 552 ng/g dry weight.<sup>11),31)</sup> These PAHs residues 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 weight,<sup>29)</sup> from Cornigliano of Italy were in the range of 1,489-2,640 ng/g dry weight,<sup>30)</sup> from Arcachon Bay of France were in the range of 279-2,420 ng/g dry weight,<sup>11)</sup> and from Kiel area of France were in the range of 342-38,800 ng/g dry weight.<sup>31)</sup>

There is little information on the level of PAHs in fish in the world. Although the number of PAHs, fish species and sample types (muscle or liver) analyzed in

**Table 2.** Comparison of PAHs concentrations (ng/g dry weight) in mussels (or oysters) measured in this study with those in different locations in the world

| Locations            | <i>n</i> <sup>a</sup> | Concentrations | References                       |
|----------------------|-----------------------|----------------|----------------------------------|
| Korean coasts        | 16                    | 14-224         | This study                       |
| Jinhae Bay, Korea    | 16                    | 0.1-992        | Lee et al. <sup>19)</sup>        |
| Kara Sea, Russia*    | 18                    | 250-940        | Sericano et al. <sup>26)</sup>   |
| Carolinas, USA       | 18                    | 300            | Lauenstein et al. <sup>27)</sup> |
| Great Lake, USA      | 24                    | 270-650        | O'Connor <sup>28)</sup>          |
| Pacific Sea, Mexico* | 16                    | 750-6,910      | Botello et al. <sup>29)</sup>    |
| Sanremo, Italy       | 10                    | 139-252        | Stella et al. <sup>30)</sup>     |
| Zinola, Italy        | 10                    | 140-207        | Stella et al. <sup>30)</sup>     |
| Voltri, Italy        | 10                    | 127-283        | Stella et al. <sup>30)</sup>     |
| Cornigliano, Italy   | 10                    | 1,489-2,640    | Stella et al. <sup>30)</sup>     |
| Paraggi, Italy       | 10                    | 88-258         | Stella et al. <sup>30)</sup>     |
| Arcachon Bay, France | 18                    | 279-2,420      | Baumard et al. <sup>11)</sup>    |
| Biomar, France       | 18                    | 25-390         | Baumard et al. <sup>11)</sup>    |
| Kiel, France         | 16                    | 342-38,800     | Baumard et al. <sup>31)</sup>    |
| Warnemünde, France   | 16                    | 89-552         | Baumard et al. <sup>31)</sup>    |
| Peenemünde, France   | 16                    | 99-374         | Baumard et al. <sup>31)</sup>    |

<sup>a</sup>*n* = number of PAH compounds analysed in each study.

\*PAHs were analysed in oyster species.

other studies may differ, the sixteen PAHs have found in most samples regardless of species and sample types of fish. PAHs residues in fish in this study were similar or slightly low values compared to PAH levels in lake trout sampled from Great Lakes.<sup>32)</sup> Solé et al.<sup>33)</sup> reported that 14 PAHs levels in deep-sea fish gadiform (*Mora moro*) from Mediterranean Sea varied from 0.2 to 0.6 ng/g wet weight in muscle and varied from 6.9 to 16 ng/g wet weight in liver. These residues in muscle were slightly lower than those in this study. However, the PAH levels in yellowtail flounder (*Pleuronectes ferruginea*) tissues from Grand Bank were in the range of 0.5-34 ng/g wet weight.<sup>17)</sup> These values revealed an order of about 10-20 times greater than those reported here. Also, other reports<sup>16),26),35-36)</sup> seemed to be relatively greater than in this study despite the difference of sample type. Consequently, PAHs residues in marine organisms from the Korean coastal areas was low or moderate level in comparison with marine environments from other countries.

### 3.3. Relations between accumulation patterns of PAHs and exposure pathway of various marine organisms

The PAH profiles in various marine organisms according to their exposure pathway were compared by factor analysis corresponding to the PAH distributions in marine sediments and seawater samples. PAH data in marine sediments and seawater sampled from Korean coastal areas were used in this investigation.<sup>21),36)</sup> The relationship plots between 16 variables (the individual PAH of 16 species) and marine biotic and abiotic samples on the factorial plane were presented in Fig. 2.

The two factors accounted for 46.7% and 17.2% of the total variance on the variable (PAH compound) map ((A) in Fig. 2), respectively. It could be noted that each factor is significantly correlated with different aromatic groups. The higher-molecular-weight aromatic compounds were mostly correlated with loading factor 1, while the lower-molecular-weight aromatic compounds were mostly correlated with loading factor 2. The first group represented the lower-molecular-weight three and four ring aromatics, the most water soluble PAHs such as AcP, AcPy, Pyr and FluA. The another group comprised the higher-molecular-weight PAHs such as BbF, BkF, BaA and BghiP.

The two factors accounted for 75.4% and 8.5% of total variance on the biotic and abiotic sample map ((B)

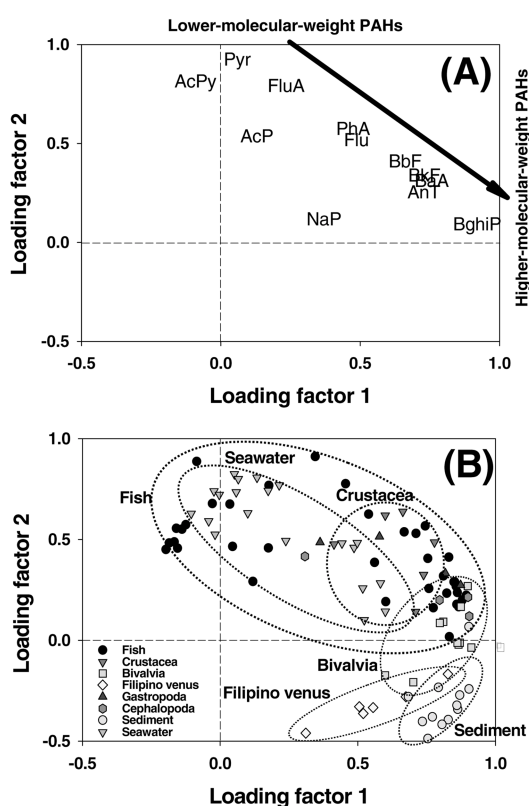


Fig. 2. Factor analysis of the sixteen PAH distribution for the biotic and abiotic samples from the Korean coastal areas. (A): Variable map for relative sample matrix PAHs concentrations as variables. (B): Sample map for the fishes, crustacea, bivalvia, filipino venus, gastropoda, cephalopoda, sediment and seawater.

in Fig. 2), respectively. Six groups among the samples (defined by six circles) were to be distinguished and were related to PAH compositions in various marine organism. The first and second groups were integrated by variables of fish and seawater samples, respectively. The third cluster was integrated by variables of crustacea species such as crab and shrimp. The fourth one comprised variables of bivalvia samples. Fifth and sixth groups integrated by variables of sediment and filipino venus samples. Most of the PAHs within the same sample types were located closely together near the circumference. This result suggested that the PAH profiles in the same marine samples are similar and that most of the PAHs within the same samples behave identically in the marine environment.

The representative profiles of PAHs in each marine environmental sample were presented in Fig. 3. The contributions of ring aromatic groups to total PAHs in marine sediments were predominant in heavier molecular weight like FluA, Pyr, BaA, Chr, BbF, BkF and BaP. This was due to their higher persistence and adsorption into sediment matrix based on more lipophilic and hydrophobic character.<sup>37-38)</sup> While the PAHs compositions in seawater samples were dominated by the lower-molecular-weight two- and three-ring aromatics such as NaP, Flu, PhA and FluA.

The predominant PAHs in fish species were the lower-molecular-weight compounds such as two- and three-ring aromatics-NaP, AcP, Flu and PhA-in accounting for more than about 70% of the total PAHs. Hydrophobic contaminants such as PAHs tend to rapidly adsorb on particles and decrease as the octanol-water partition coefficient ( $K_{ow}$ ) increases. PAHs solubilities decreases with increasing molecular weight.<sup>39)</sup> Therefore, the lower-molecular-weight PAHs are preferentially dissolved, while the higher-molecular-weight compounds are preferentially absorbed onto or associated with particles. Thus, the uptake of these contaminants is governed by its bioavailability, and fish is often enriched in the lower-molecular-weight PAHs relative to the sediment (Porte and Albaigés, 1993; Djomo et al., 1996). Contrasting with fish species, the predominant contributors of bivalvia species were four-ring aromatics such as Pyr, FluA and Chr. The variations of the PAH profiles between fish and other organisms could be related to metabolic differences. Fish have a greater metabolic capacity relative to other organisms and biotransformation of the higher-molecular-weight PAHs with a greater efficiency.<sup>39-40)</sup> Hence, the PAH accumulation in fish tissue is mainly governed by the lower-molecular-weight PAHs.

The predominant PAHs in tissues of cephalopoda, crustacea and gastropoda species were three- and four-ring aromatic compounds like AcP, PhA, FluA and Pyr although there was a slight difference among organism species. The differences of PAH profiles in these marine organisms relative to fish could result from exposure pathway, different diets and biotransformation

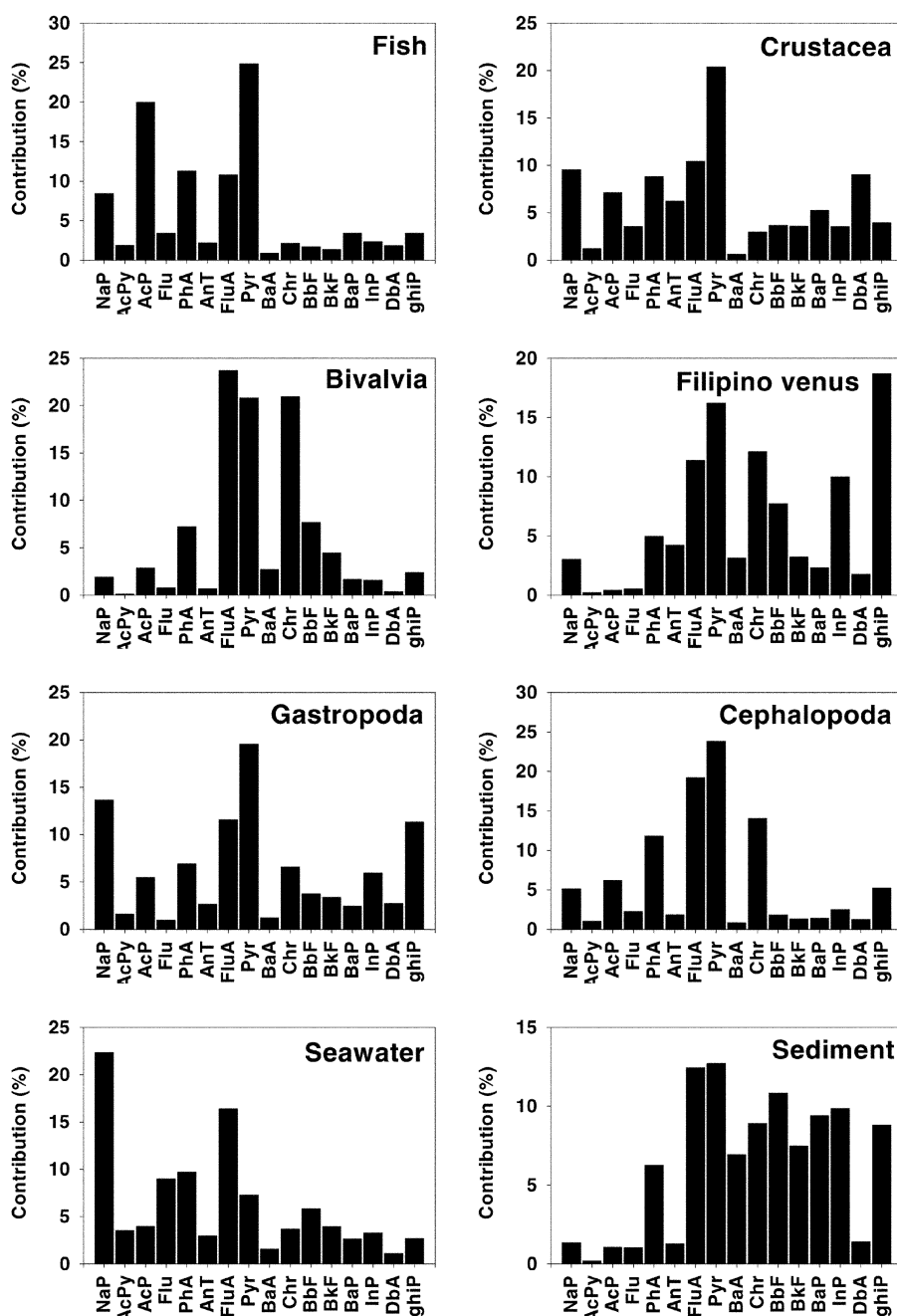


Fig. 3. Representative PAHs profiles in fish, crustacea, bivalvia, filipino venus, gastropoda, cephalopoda, seawater and sediment from the coastal areas of Korea.

capacities of the organisms in addition to a different bioavailability of the compounds.<sup>14-15)</sup> Namely, these marine species were accumulated by the bioconcentration of contaminants adsorbed in the sediment particle and dissolved in the water and by the biomagnification

of preys they feed on. Therefore, the PAH profiles in cephalopoda, crustacea and gastropoda tissues were characterized by intermediate between those observed in the sediments and in the seawater.

The contributions for PAHs compositions in filipino

venus samples increased with increasing molecular weight. These compositions were different with other bivalve samples and relatively comparable to those in marine sediments. This finding also seems to be associated with exposure environments. Indeed, filipino venus species primarily live in muddy flat and grow up by the digestion of organic matter in surrounding sediments. Consequently, PAHs bioaccumulation pattern of marine organism species in marine environment was governed by a variety of factors including exposure circumstance, habitat, diet and metabolites.

#### 4. Conclusions

Various marine organisms were sampled at the local market from Korean coastal areas, to investigate residues and bioaccumulation patterns of polycyclic aromatic hydrocarbons (PAHs). The levels of sixteen PAHs in selected organisms from Korean coasts were in the range of 0.45-224 ng/g dry weight. The residues of PAHs according to organism species showed the highest content in bivalvia species, followed by crustacea, filipino venus and fish species. The residues of PAHs in bivalves and fishes in this study were slightly low or relatively moderate to other countries. The predominant contributors in fish species were the lower-molecular-weight PAHs with similar patterns of PAHs in seawater. The PAHs compositions of bivalvia, crustacea, cephalopoda and gastropoda species were dominated by three- and four-ring aromatics with intermediate PAHs patterns of sediments and seawater. However, PAHs compositions in filipino venus, which live in muddy flat, were relatively comparable to those in marine sediments. The PAH profiles in various marine organisms according to exposure environments were compared with abiotic samples such as marine sediments and seawater using factor analysis. The PAH profiles in each sample species or matrices samples showed similar distributions. This result suggests that PAHs bioaccumulation pattern in organisms from the marine ecosystems was governed by a variety of factors including exposure circumstance, habitat, diet and metabolites.

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