POLYCYCLIC AROMATIC HYDROCARBONS IN SEDIMENTS AND ORGANISMS FROM KOREAN COAST

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Introduction

In recent years, there has been an increasing emphasis on the study of the environmental fate and effects of polycyclic aromatic hydrocarbons (PAHs). PAHs are well-known ubiquitous contaminants of the coastal marine environment [1]. This class of compounds in marine sediments and organisms has been widely studied [2] because of its carcinogenic and mutagenic character [3, 4]. These compounds have mainly anthropogenic origins [5], including combustion process of fossil fuels [6], domestic and industrial wastewater [5] and spillage of petroleum or petroleum products by ships [7]. Each source is characterized by a specific molecular pattern and it is, therefore, possible to identify which source generated these chemicals. PAHs derived from various sources transport to the marine environment via both waters and atmosphere. Most PAHs in water column tend to be adsorbed to particles and to be deposited to the underlying sediments. Degradation of PAHs in sediment is generally slow, particularly for the higher molecular weight PAH [8]. Aquatic organism may bioaccumulate and bioconcentrate environmental contaminants to more than 1 000 000 times of the concentrations detected in the water column. International monitoring programs for marine pollutants are carried out using bioindicators such as shellfish, particularly mussels (*Mytilus edulis*) and oysters (*Crassostrea gigas*) [9]. These bivalves are an effective trapping mechanism for many environmental pollutants such as PCBs, pesticides, PAHs and heavy metals because of their wide distribution, abundance, sedentary behavior, and pronounced ability to accumulate organic compounds at proportions that correspond to concentrations in their surroundings. Moreover, analysis of bivalve tissue gives an indication of the bioavailable fraction of environmental contamination and of direct exposure to chemicals. In the present study, we planned to monitor PAHs pollution in marine sediments and organisms collected from several coastal stations in Korea.

Materials and Methods

Surface sediments (0-5 cm) and organisms were sampled at 20 stations in Korean coast during a period of February to July 2000. Sediments were collected with a box-core sampler. Mussels (*Mytilus coruscus and Mytilus edulis*) and oysters (*Crassostrea gigas*), which were located on piers, rocks or buoys in the water column, were scraped with a rake. Both sediments and bivalve tissues were wrapped with an aluminium foil and frozen at -20°C. The freeze-dried sediments were sieved at 2 mm and then extracted in a soxhlet apparatus with 200 ml of toluene for 20 hours, then the volume was reduced to 1-2 ml in a rotary evaporator. The extract was transferred to *n*-hexane and then adjusted to a volume of 10 ml after internal standard (ES 2044, Cambridge Isotope Laboratories, Inc.) was spiked. Mussel and oyster samples were homogenized with an

ultra-disperser. Homogenized samples were freeze-dried and the internal standard (ES 2044, Cambridge Isotope Laboratories, Inc.) was spiked. They were decomposed in 200 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 after addition of water and 50 g of anhydrous Na_2SO_4. The extracts of sediments and bivalve tissues were purified using an activated silica gel column chromatography with successive elutants of *n*-hexane and 15% methylene dichloride in *n*-hexane. The contents of total organic carbon (TOC) in marine sediment were obtained using a CHN analyzer (Perkin Elmer 2400). For lipid determination, automatic extraction unit (Gerhardt and Variostat, Germany) was used. Further details of analytical methods and instrumental analysis procedures were based on previously used methods [10].

Results and Discussion

Descriptions and PAHs levels for sediment and organism samples present in Table 1. The wide range of sediment contamination levels can be partly explained by the great disparity of the sediments. They ranged from mud to coarse sand, and their organic carbon content ranged from 0.01 to 3.25%. In particular, Stations 1, 2 and 3 from East Sea were characterized by primarily sand (94.2-99.4% sand fraction). Wet weight for oysters (*Crassostrea gigas*) and mussels (*Mytilus coruscus and Mytilus edulis*) was a range of 1-22.5 g. Lipid in bivalves varied from 4.1 to 10.8%.

Table 1. Sample description and total PAHs levels in sediments and organisms from Korean coast

St.	SEDIMENTS				ORGANISMS			
	Mud (<63 µm)	Sand (>63 µm)	TOC (%)	PAHs (ng/g)	Species	Wet weight (g)	Lipid (%)	PAHs (ng/g)
1	0.6	99.4	0.01	6.4	Mussel (*Mytilus coruscus*)	10.54	10.82	113.3
2	5.8	94.2	0.14	12.3	Mussel (*Mytilus coruscus*)	2.06	8.73	116.2
3	0.6	99.4	0.02	8.5	Mussel (*Mytilus coruscus*)	4.61	6.22	86.0
4	38.2	61.8	0.59	85.3	Mussel (*Mytilus coruscus*)	9.8	7.46	63.2
5	59.2	40.8	1.93	1214.2	Mussel (*Mytilus coruscus*)	8.46	10.18	81.6
6	94.7	5.3	1.26	273.3	Mussel (*Mytilus coruscus*)	7.16	7.24	258.6
7	88.8	11.2	1.47	171.3	Mussel (*Mytilus edulis*)	5.02	4.14	210.9
8	95.4	4.6	1.65	68.2	Oyster (*Crassostrea gigas*)	5.83	10.01	876.0
9	92.0	8.0	1.18	204.9	Mussel (*Mytilus edulis*)	16.94	6.29	116.0
10	84.0	16.0	3.24	176.7	Mussel (*Mytilus edulis*)	5.41	5.1	126.5
11	91.0	9.0	2.81	134.1	Mussel (*Mytilus edulis*)	8.29	10.08	79.9
12	97.0	3.0	1.01	121.1	Mussel (*Mytilus edulis*)	6.76	4.78	77.9
13	67.2	32.8	1.33	50.5	Mussel (*Mytilus edulis*)	18.86	7.64	104.3
14	64.4	35.6	0.65	37.4	Mussel (*Mytilus edulis*)	22.54	8.68	90.7
15	76.0	24.0	0.12	62.8	Oyster (*Crassostrea gigas*)	3.09	9.85	286.3
16	63.3	36.7	0.62	29.0	Oyster (*Crassostrea gigas*)	3.2	9.23	381.5
17	67.6	32.4	0.51	24.3	Oyster (*Crassostrea gigas*)	0.91	9.25	198.6
18	66.2	33.8	0.62	80.3	Oyster (*Crassostrea gigas*)	5.45	8.49	203.3
19	54.4	45.6	0.84	45.3	Oyster (*Crassostrea gigas*)	3.89	7.75	206.8
20	58.1	41.9	0.76	55.9	Oyster (*Crassostrea gigas*)	4.17	8.04	182.8

16 PAHs were detected in all sediment and organism samples. Concentrations of ΣPAH (sum of two- to six-ring PAHs) in sediments varied from 6.4 to 1214 ng/g dry weight. Station 5 from Pohang coast represents the highest level of ΣPAH. The lowest levels were observed at Stations 1, 2 and 3 from East Sea where grain-size was primarily sandy. This result indicates that grain-size distribution of sediment is an important factor governing PAHs concentrations and has to be considered. These experimental results were similar to PAHs levels in sediments from the southeastern coastal areas of Korea [11]. Concentrations of ΣPAH in organisms varied from 63.2 to 876 ng/g dry weight. The highest level was found at Station 8 from Jinhae coast, while the lowest level was Station 4 from Hupo coastal area.

The contributions of ring aromatic groups to sum of 16 PAHs in sediments and organisms from Korean coast were illustrated in Fig. 1. In the sediments, the contribution of 16 PAHs ring groups for each station showed similar patterns for most stations. The predominant contributions were four and five ring aromatics like fluoranthene, pyrene, benzo[a]anthracene, chrysene benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene, whereas two and three ring aromatics like naphthalene, acenapthylene, acenaphthene, fluorene, phenanthrene and anthracene showed a low concentration. The higher-molecular-weight five and six ring aromatics and more lipophilic and hydrophobic PAHs predominated in the sediment matrix, probably due to their higher persistence. These results indicate that the higher-molecular-weight aromatics seem to be preferentially adsorbed to particles and incorporated in the sediment. However, Stations 1, 2 and 3 from East Sea showed different contributions. PAHs contribution in sandy sediments from Stations 1, 2 and 3 was dominated by three and four ring aromatics, because adsorption ability of higher-molecular-weight PAHs to sandy sediments was relatively lower than muddy sediments. In the organisms, the contribution of four ring aromatics like fluoranthene, pyrene, benzo[a]anthracene and chrysene ranged between 50 and 77% in exception with Station 8. In particular, Station 8 from Jinhae coast with a high percentage of higher-weight-molecular five and six ring aromatics was characterized by the highest concentration in this study. The results suggest that the contamination of PAHs might be influenced by combustion process of high temperature and a local point source also might give the higher burden on PAHs contamination in the marine environment.
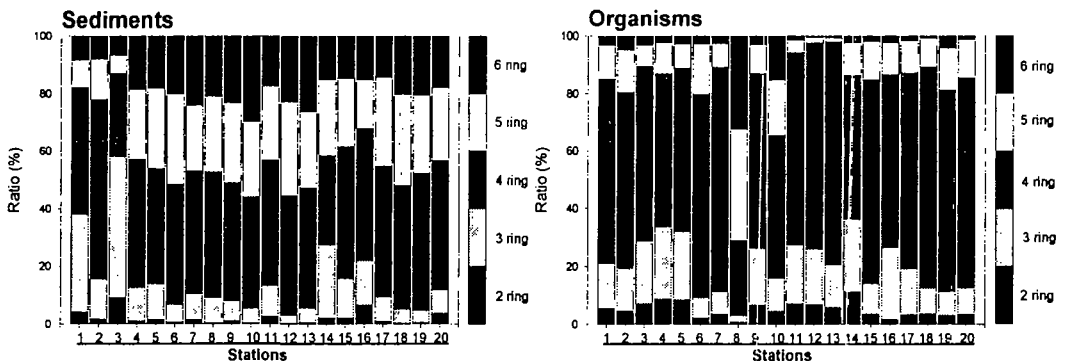

Fig. 1. Contributions of ring aromatic groups (two to six ring aromatics) to total concentrations of 16 PAHs in sediments and organisms from Korean coast.

Several molecular indices such as phenanthrene/anthracene ratio, fluoranthene/pyrene ratio [12] and LMW (low molecular weight; groups with three and four aromatic rings)/HMW (high molecular weight; groups with five and six aromatic rings) ratio [13] were used to identify the origin of PAHs contamination in marine sediments. From these indices, the majority of Korean coast is characteristic of pyrolytic and petrogenic contaminants with strong pyrolytic input.

The PAHs which concentrations are susceptible of covarying in the environment were identified in this study on the basis of the correlation factor values [14]. In the sediments, there was a highly positive correlation between the concentrations of PAH species. In particular, high-molecular-weight five and six ring aromatics showed higher correlation factors than low-molecular-weight two and three ring aromatics. This indicates that PAHs contamination in analyzed sediments derived from the same source. In the organisms, there is no correlation within lower molecular weight PAHs unlike marine sediments. However, the relationships within four to six ring aromatic PAHs showed a significant correlation. This finding is thought to be relation with a metabolism of organisms. In the marine environment, the majority of heavier molecular weight PAHs was strongly adsorbed with particulate matter because of hydrophobic and persistent character of PAHs. Filter-feeding marine bivalves such as oysters and mussels can be absorbed xenobiotics adsorbed on a small grain-size fraction of particles through digestive system. PAHs migrated with particle into organism are accumulated to a greater extent. Therefore, heavier molecular weight PAHs in organism matrix is thought to be a high correlation relative to low molecular weight PAHs.

References
1. Kennish, M.J. (1992) Ecology of Estuaries: Anthropogenic Effects. CRC Press, Boca Raton, FL.
2. Neff, J. M. (1979) Polycyclic aromatic hydrocarbons in the aquatic environment. Applied Science. London. UK.
3. Mix, M. M. (1986) Marine Environmental Research. 20, 141.
4. Lehr, R.E. and Jerina, D. M. (1977) Archieve Toxicology. 39, 1-6.
5. Wakeham, S. G., Schaffner, C. and Giger, W. (1980) Geochemical Cosmochimia Acta. 44, 403-413.
6. Hites, R. A., LaFlamme, R. E. and Farrington, J. W. (1977) Science. 198, 829-831.
7. Pettersen, H., Naf, C. and Broman, D. (1997) Marine Pollution Bulletin. 34, 85-95.
8. Readman, J.W., Mantoura, R.F.C., Rhead, M.M. and Brown, L. (1982) Estuarine Coastal Shelf Science. 14, 369-389.
9. Phillips, D.J.H. (1978) Environmental Pollution. 16, 167-229.
10. Ok, G., Moon, H.B., Ji, S.H. and Han, Y.H. (1998) J. of the Korea Society for Environmental Analysis. 1(3), 265-274.
11. Moon, H.B., Choi, H.G., Kim, S.S., Kim, P.J., Lee, P.Y. and Ok, G. (2000) Organohalogen Compounds. 46, 423-426.
12. Mille, G., Chen, J. Y. and Dou, H. J. M. (1982) International Journal of Environmental Analytical Chemistry. 11, 295-304.
13. Soclo, H. H., Garrigues, PH. and Ewald, M. (2000) Marine Pollution Bulletin. 40, 387-396.
14. Bourbon, P., Esclassan, J., Giroux, M., Vandaele, J., Lepert, J. C. and Svoya, L. (1986) Polluting Atmospherique. 36-42.