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Particle-Associated Polycyclic Aromatic Hydrocarbons in the Seawater from Gwangyang Bay, Korea

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Seawater particles sampled at 35 stations from Gwangyang Bay in March 2001 and polycyclic aromatic hydrocarbons (PAHs) were analysed using gas chromatography coupled to mass spectrometer detector (GC/MSD). Concentrations of total PAHs in seawater particles varied from 6.5 to 41.6 ng/L with a mean 16.4 ng/L. Concentrations of potentially carcinogenic PAHs varied from 0.42 to 19.3 ng/L with a mean value of 3.1 ng/L and occupied about 25±10% to total PAHs concentrations. The most contaminated seawaters by PAHs were found at the stations near industrial complex with static characteristics of poor seawater circulation, suggesting that PAHs is mainly generated from anthropogenic and terrestrial sources. Correspondence analysis was used to investigate source characteristics of PAHs in the studied bay. The results indicated that the PAHs contamination patterns in the inner part of the bay mainly were associated with combustion activities of high temperature from the adjacent industrial complex. The differences for PAHs compositions between seawater particles and marine sediments are more significant for the lower molecular weight compounds than the higher molecular weight compounds due to their high sensitivity to photooxidation and microbial degradation.

Key words: seawater particles, polycyclic aromatic hydrocarbons, correspondence analysis, lower molecular weight, higher molecular weight

1. Introduction

In recent years, there has been an increasing emphasis on the study of the environmental fate and effect of polycyclic aromatic hydrocarbons (PAHs). Since they have carcinogenic and mutagenic characters,[1-4] these compounds have been intensively studied in various environmental compartments such as air, soil, water, sediment, and biota.[5-9]

PAHs are ubiquitous environmental microcontaminants in the aquatic environment and derived mainly from anthropogenic activities. The main sources of these contaminants in the marine environment are a combustion of fossil fuels,[10] discharge of domestic and industrial wastewaters[5] and spillage of petroleum or petroleum products by ships.[11-12] PAHs generated from various sources transport to the marine environment through river inputs and atmospheric deposition. Most PAHs in water column tend to adsorb to particles and to be deposited to the underlying sediments.[7] The particle-associated PAHs in seawater can undergo transformation process before the deposition of the bottom sediments.[13] Photolysis and microbial degradation are regarded as two important processes for PAH removal from aquatic environments.[14-15] Indeed, PAHs in marine ecosystems can undergo degradation by photooxidation in the superficial surface water[16] and by microbial activities into the sediments[17]. Degradation of PAHs in sediment materials is generally slow, particularly for the higher-molecular-weight PAHs.[18]

The concentrations of dissolved PAHs in seawater are very low because of their hydrophobic nature based on high octanol-water and organic carbon adsorption partition coefficients.[19] PAHs in the marine ecosystem tend to be strongly adsorbed to particles and bioaccumulated in marine organisms. The primary pathway of exposure for sediment dwellers is the

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interstitial water[20)] and pelagic marine organisms such as fish seem to receive most direct PAH exposure from the seawater.[21)] The chronic introduction of PAHs in estuaries can affect threat to the pelagic and benthic ecosystem at various trophic levels.[22)] It is therefore very important to find the PAHs concentrations in the seawater to evaluate the risk assessment on the marine organisms exposed to particle-associated PAHs as well as to dissolved PAHs. Furthermore, the investigation on seawater pollution is necessary to grasp the present contamination degree and to design future strategies for environmental protection from PAHs contamination. Therefore, the objective of the study was to examine distributions and composition of particle-associated PAHs in the seawater from Gwangyang Bay, Korea.

2. Materials and Methods

2.1. Study area

Gwangyang Bay has an area of 230 km^2 with the depth around 5 m at the inner bay and 20 m at the central channel. The western part of this bay is somewhat hydrodynamically static with poor exchange of water and sluggish circulation. However, the major portion of Gwangyang Bay shows relatively good circulation through active water exchange with the current field of the South Sea.[23)] Tidal cycle is semi-diurnal with an average tidal exchange volume of 14 %.[24)] Freshwater flows into the bay mainly from Seomjin River at the northern end of the bay with annually 5.8 to 8.7×108 tons. This coastal area is surrounded by steel, petrochemical and related industrial complexs.

2.2. Experimental procedure

Surface seawaters were sampled at 35 stations from Gwangyang Bay in March 2001 (Fig. 1). Suspended particles were isolated by filtration through glass fiber filters (GFFs 47 mm, 0.7 μm, Whatman, England), dried in a desiccator and then weighed. The weight difference before and after filtering was used to determine a concentration of suspended particle. Particle samples were cut into a size of 1-2 cm, and then extracted with 100 mL of toluene (Ultra residue analysis, J. T. Baker, USA) for 5 hours under reflux after spiking with the 7 species internal standards (D_8-naphthalene, D_8-acenaphthylene, D_{10}-fluoranthene, D_{10}-phenanthrene, D_{10}-pyrene, D_{12}-benzo[a]pyrene and D_{12}-benzo[g,h,i]perylene, ES 2044, Cambridge Isotope Laboratories, Inc., USA). The extracts were filtered with glass wool and concentrated to 1-2 mL in a rotary evaporator. The residues were transferred to *n*-hexane (Ultra residue analysis, J. T. Baker, USA) and adjusted to a volume of 10 mL.

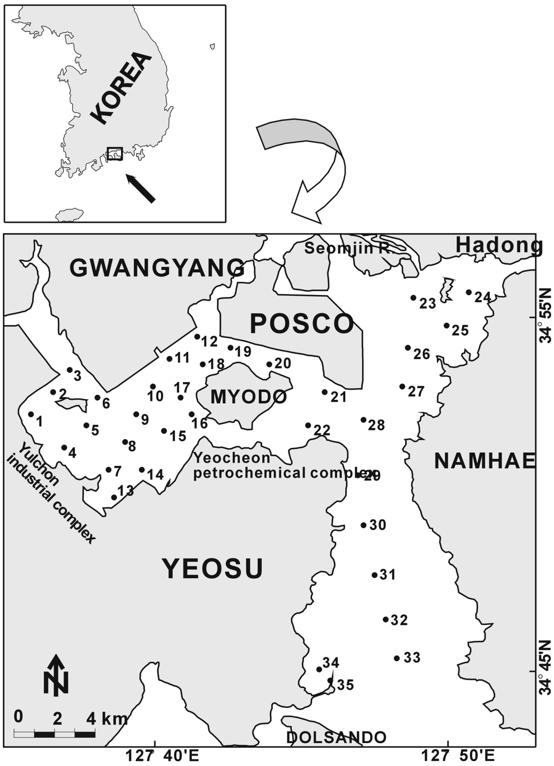

Fig. 1. Map showing the sampling stations in the surface seawater of Gwangyang Bay, Korea.

Particle samples were cleaned on an activated silica gel (Art No. 7734, 70-230 mesh, Merck, USA) column chromatography with successive elutants of *n*-hexane and 15% methylene dichloride (Dioxin analysis, Wako, Japan) in *n*-hexane. The elutants were concentrated to less than 1 mL, and left at room temperature for one or two days to evaporate to 50-100 μL. The residues were dissolved with 50 μL of *n*-nonane (Pesticide residue analysis, Fluka, Switzerland) and determined for PAHs.

2.3. GC/MSD analysis

The aromatic fraction was analysed by gas chromatography coupled with mass spectrometer. An Agilent 6890 GC equipped with a split/splitless injector was used (splitless time: 2 min; flow 70 mL/min). The injector temperature was maintained at 250°C. The GC temperature program was from 80°C (1 min) to 300°C (10 min) at 5°C/min. The carrier gas was helium at a constant flow rate of 1.2 mL/min. The capillary column used was a DB-5MS (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness, J&W Scientific, USA). The GC was coupled with a 5973N mass selective detector (MSD). The mass spectrometer was operated under the selected ion monitoring (SIM) mode using molecular ions of the investigated PAHs. The interface temperature was 250°C. 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)).

All the spike isotope compounds were detected without interfering peak. The average recoveries for all particle samples were in the range of 67-109%. Procedural blanks were processed in the same way as real samples, and they were below 10% of analytes abundance. Blanks were run before and after the injection of standards to check for any carryover.

3. Results and Discussion

3.1. Distributions of particle-associated PAHs

The particle-associated PAHs in the seawater from Gwangyang Bay were detected in all samples. Table 1 shows the concentrations of the sixteen PAHs in particles of seawater from Gwangyang Bay, Korea. The levels of ΣPAH (the sum of two- to six- ring aromatics) in seawater particles varied from 6.5 to 41.6 ng/L with a mean 16.4 ng/L. The highest level of ΣPAH was found in the seawater from Station 7 in the vicinity of Yulchon industrial complex. The lowest level of ΣPAH was found in Station 32 in the central channel of Yeosu and Namhae. Total concentrations of potentially carcinogenic PAHs[25] (ΣCPAH, the sum of benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene and dibenzo[a,h]anthracene) ranged from 0.42 to 19.3 ng/L with a mean value of 3.1 ng/L and occupied about 25±10% of the concentrations of ΣPAH.

Table 1. Summary of concentrations (ng/L) for each compound in particle-associated PAHs in seawater from Gwangyang Bay, Korea

	Min	Max	Median	Mean
Naphthalene	1.3	5.6	3.6	3.5
Acenaphthylene	0.02	0.29	0.09	0.10
Acenaphthene	0.56	3.5	2.8	2.6
Fluorene	0.08	9.3	1.4	1.6
Phenanthrene	0.27	1.6	0.68	0.73
Anthracene	0.03	0.56	0.08	0.11
Fluoranthene	0.21	2.4	0.57	0.72
Pyrene	0.10	2.4	0.49	0.67
Benzo[a]anthracene	0.01	1.8	0.23	0.36
Chrysene	0.10	3.3	0.68	0.90
Benzo[b]fluoranthene	0.20	6.6	1.0	1.5
Benzo[k]fluoranthene	0.06	2.3	0.37	0.50
Benzo[a]pyrene	0.07	4.1	0.89	1.4
Indeno[1,2,3-c,d]pyrene	0.05	3.8	0.51	0.71
Dibenzo[a,h]anthracene	0.02	0.73	0.15	0.22
Benzo[g,h,i]perylene	0.10	3.3	0.67	0.95
CPAH*	0.42	19.3	3.1	4.6
PAH**	6.5	41.6	14.5	16.4

CPAH*: the sum of six carcinogenic PAH.
PAH**: the sum of 16 PAHs.

The horizontal distribution of particle-associated PAHs in the seawater from Gwanayang Bay is presented in Fig. 2. The highest contaminated sites by PAHs were stations near Yulchon industrial complex (Stations 7 and 13) and near POSCO (Stations 20 and 21). The results suggested that industrial activities such as steel and petrochemical factories contributed largely to the PAHs contaminations in the Gwangyang Bay. Indeed, many authors reported that the steel mill and petrochemical complexes were the main sources of hazardous contaminants in the marine environment.[26-28]

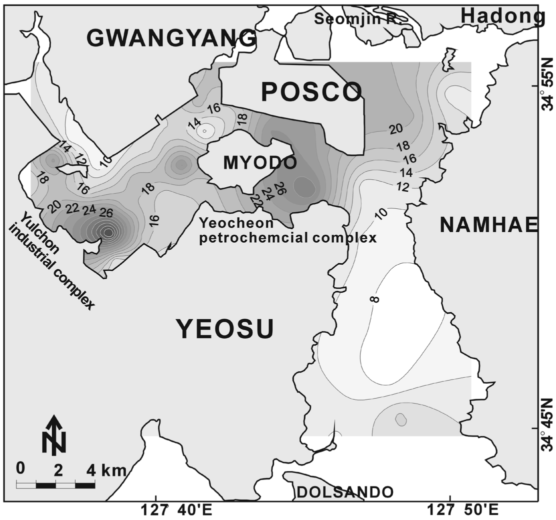

Fig. 2. Horizontal distribution (ng/L) of particle-associated PAHs in seawater from Gwangyang Bay, Korea.

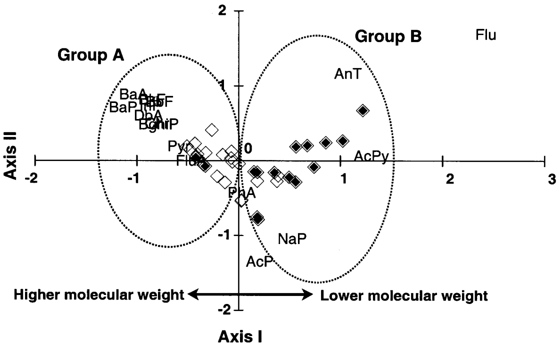

Fig. 3. Correspondence analysis of the particle-associated PAH compositions in seawater from Gwangyang Bay, Korea. Circles in the plot were grouped by their molecular weight of PAHs. Stations from 1 to 22 (◇) are located at the inner part and stations from 23 to 35 (◆) are located at the central channel of the bay.

In addition, it seems that poor water circulation in the high contaminated sites near industrial complex of this bay accelerated the PAHs contamination in the bay, indicating that toxic organic contaminants such as PAHs can be trapped and then accumulated in the marine sediments and organisms in this coastal zone. The lowest contaminations of PAHs were measured in seawater from Yeosu waterway. These sites with non-contaminated freshwater inputs from Seomjin River are far away the industrial complex and good water circulation.

3.2. Source characteristics

The PAHs distributions among the sampling stations were compared using the correspondence analysis on the percentage corresponding to the sixteen PAHs compositions. The relationship plot on the factorial plane is shown in Fig. 3. Statistical analysis of particle-PAHs was performed using MVSP (Multi-variate statistical package) Windows 3.0 software (Kovach Computing Services, UK).

Axes I and II represent 64% and 25% of total variance of the original data, respectively. Two groups (Group A and B) was distinguished according to the molecular weight of PAHs. Group A was characterised by a high contribution of the higher molecular weight aromatics, while group B included the lower molecular weight aromatics. The stations from inner part belonged to Group A and stations from the central channel belonged to Group B. The results indicated that the PAHs contaminations in the inner part of the bay mainly were associated with a combustion activity of high temperature from steel mill, petrochemical complex and related industrial facilities. Furthermore, the coastal zone showed the higher contamination by PAHs than those of the other part of the bay as mentioned above. Actually, some authors reported that higher molecular weight PAHs are generated mainly by high temperature combustion such as industrial pyrolysis, ship and automobile exhausts, forest fires, urban coal and oil heating.[29-30] Accordingly, these results indicate that the high contamination of PAHs in inner basins is due to adjacent to a terrestrial source of PAHs with poor tidal flushing.

3.3. Comparison of PAHs compositions in seawater particles and marine sediments

PAHs data were normalised to the total PAHs by expressing each compound value as a percentage of the sum of the sixteen PAH concentrations. In general, the composition of particle-associated PAHs was dominated by the lower molecular weight compounds such as two and three-ring aromatics, even though the higher

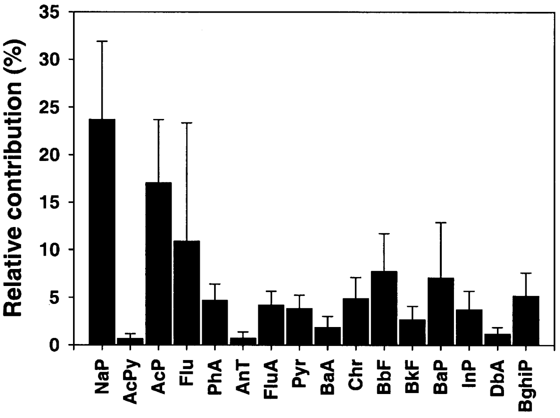

Fig. 4. Normalised profiles to total concentrations of particle-associated PAHs in seawater from Gwangyang Bay, Korea. Vertical lines represent the standard deviations for a contribution of each PAH compound.

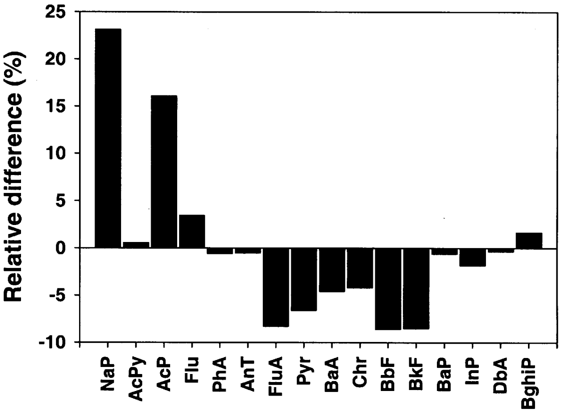

Fig. 5. Differences of PAHs compositions in seawater particles versus marine sediments from Gwangyang Bay, Korea. Data was calculated as the differences of mean contribution for PAHs compositions in seawater particles and marine sediments.

molecular weight PAHs such as benzo[b]fluoranthene and benzo[a]pyrene occupied rather high proportions (Fig. 4). These PAHs compositions in this study were similar to those of measured in a different location previously.[31)]

In order to investigate the effect of certain degradation in seawater column, the PAHs compositions of seawater particles and marine sediments were compared. PAHs data observed in marine sediment from the same sampling stations of Gwangyang Bay were used in this investigation.[32)] Differences of the sixteen PAHs composition between seawater particles and marine sediments is presented in Fig. 5. Lower molecular weight compounds such as two and three ring aromatics showed positive values while higher molecular weight compounds of four and five ring aromatics were negative values. Namely, the sixteen PAHs composition in seawater particles was dominated by lower molecular weight aromatics in comparison with that of sediments. In contrast, the higher molecular weight PAHs were the predominant species in the marine sediments and occupied the higher contributions than those of seawater particles. The difference of PAH composition for these materials was likely to be environmental persistence and decomposition activities of individual PAH in the marine environment. In general, PAHs persistence in the environment increases with increasing molecular weight. Approximately 80% of low molecular weight PAHs input can be lost by volatilisation from surface seawater into atmosphere.[33)] Furthermore, microbial degradation and/or biotransformation is thought to be the major environmental processes contributing to the decomposition of PAHs in the aquatic ecosystem.[34-35)]

Some studies have proposed that a variety of bacteria can degrade certain PAHs completely to CO_2 and metabolic intermediates.[36-37)] A large number of bacteria that metabolise PAHs have been isolated (*Pseudomonas sp., Alcaligenes denitrificans, Rhodococcus sp., Mycobacterium sp.*). These species are widespread microorganisms in the marine environment of Korea including Gwangyang Bay,[38-39)] suggesting that there has a possibility on biodegradation of PAHs in the studied bay. In this study, the differences for PAHs compositions between two matrices were more significant for the lower molecular weight PAHs than the higher molecular weight PAHs such as indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene due to their high sensitivity to photooxidation and microbial degradation. It means that the higher molecular weight aromatics seem to be adsorbed preferentially to particles in the seawater and incorporated and accumulated in the underlying sediments without degradation.

4. Conclusions

Surface seawater was sampled at several stations in Gwangyang Bay to examine distributions and composition of particle-associated PAHs. Concentrations of PAHs varied from 6.5 to 41.6 ng/L and carcinogenic PAHs varied from 0.42 to 19.3 ng/L with a occupation of about 25% to total PAHs. The highest contamination were found in the seawater from the inner part near industrial complex with static characteristics of poor seawater circulation. It seems that the PAHs contamination pattern in this site mainly were associated with a combustion activity of high temperature from the adjacent industrial complex. The differences for PAHs compositions between seawater particles and marine sediments are more significant for the lower molecular weight compounds than the higher molecular weight compounds due to their high sensitivity to photooxidation and microbial degradation.

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