

Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Sediments inside Songsanpo and Seogwipo Harbors of Jeju Island, Korea

Sang-Hee Moon, Young-Don Lee*, Min-Gyu Lee** and Sang-Kyu Kam

Division of Civil and Environmental Engineering, Cheju National University, Jeju 690-756, Korea

**Marine and Environmental Research Institute, Cheju National University, Jeju 695-814, Korea*

***Division of Applied Chemical Engineering, Pukyong National University, Busan 608-739, Korea*

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The surface sediments inside Songsanpo and Seogwipo Harbors, major harbors of Jeju Island, were collected three times (June, September and December, 2001) and analyzed for 16 polycyclic aromatic hydrocarbons (PAHs) recommended by US-EPA as priority pollutants to assess their distribution levels and their biological effects on the marine organisms, and to suggest their possible origins. The concentrations of total PAHs inside Songsanpo and Seogwipo Harbors ranged from 41 to 288 ng/g on a dry weight basis with a mean value of 121 ng/g and from 14 to 268 ng/g with a mean value of 119 ng/g, respectively, and the levels were low as compared with those in other areas of the world. The sedimentary PAHs may be correlated with organic carbon and mud content to some extent. Based on comparisons of individual and total concentrations with effects-based sediment quality guidelines, the potential for the biological effects on the marine organisms were expected to be very low. From the examinations of the four PAH origin indices, such as LMW/HMW (low molecular weight 2-3 ring PAHs over high molecular weight 4-6 ring PAHs), phenanthrene/anthracene ratio, fluoranthene/pyrene ratio, chrysene/benzo[a]anthracene ratio, it can be concluded that the sediment PAH contaminations were ascribed to both of pyrolytic and petrogenic origins.

Key Words : PAHs, Surface sediments, Songsanpo Harbor, Seogwipo Harbor, Distribution, Origin indices

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants, deriving mainly from anthropogenic inputs¹⁾. Their widespread occurrence results largely from incomplete combustion of organic matter and consequently have numerous sources²⁾. Sources of anthropogenic combustion include combustion of fossil fuels, coal gasification and liquification processes, incineration of industrial and domestic wastes, production of coke, carbon black, coal tar pitch and asphalt, oil refinery and chemical engineering operations, aluminum manufacturing, etc^{3,4)}. Apart from combustion processes, another common

anthropogenic sources of PAHs is spillage of fossil fuels including unrefined (crude oil) and refined products (e.g. petrol)²⁾. PAHs also result from natural combustion sources such as forest fires, and certain compounds (perylene and retene) are thought to be produced diagenetically⁵⁾. Each individual source is characterized by a specific molecular pattern, allowing these compounds to be established^{6,7)}. PAH ratio profiles (e.g. phenanthrene/anthracene vs. fluoranthene/pyrene) have been commonly used as a means of differentiating those of pyrolytic and petrogenic origin⁸⁾.

The PAHs derived from various sources are transported to the marine environment via the water and the atmosphere, where most of them in the water column are adsorbed by suspended particulate matter, and then deposited in underlying sediments due to their relative insolubility and strong affinity for particulate matter⁹⁾. A number of factors determine the

Corresponding Author : Sang-Kyu Kam, Division of Civil and Environmental Engineering, Cheju National University, Jeju 690-756, Korea
Phone: +82-64-754-3444
E-mail: sakyukam@cheju.ac.kr

concentration and distribution of PAHs introduced in marine environment, including degradation by photo-oxidation in the superficial water layer¹⁰ and by microbial activities into the sediments¹¹ based on their physical-chemical properties (resulting in the modification of the original distribution pattern of the emission sources). Organic contaminants in coastal systems are present in several forms including bound to dissolved organic matter, adsorbed to suspended particulate matter, and associated with surface sediments¹². Organic carbon and particle size have been shown to influence the concentration and therefore distribution of PAHs in sediments^{7,8}. It has been demonstrated that organic rich coal and wood derived particles had concentrations of those several orders of magnitude higher than silica particles¹³.

Concern over PAHs in the aquatic environment results from their significant toxicity¹⁴. The low molecular weight (i.e. two and three ring) PAHs can be acutely toxic, however the major concern is for some of higher molecular weight PAHs that, when ingested by marine animals, can form metabolites that are active carcinogens⁹. The incidence of liver neoplasma and other abnormalities in bottom-dwelling fishes has been linked with their concentrations in the sediments over which they feed^{15,16}. In order to serve in protecting benthic organisms from the adverse toxic effects of PAHs and other sedimentary contaminants in Australia and New Zealand, their interim sediment quality guidelines have been published¹⁷, which, due to a paucity of their local toxicological data, are based on those developed for USA sediments from a large database of matching chemical and biological data¹⁸. In this approach, Effects-Range Low (ER-L) and Effects-Range Median (ER-M) sediment quality guidelines were derived from the lowest 10 percentile and 50 percentile of biological effects data, separating concentrations of contaminants into ranges that were rarely (<ER-L), occasionally (\geq ER-L, <ER-M) and frequently (\geq ER-M) associated with acute toxicological effects¹⁸. These guidelines have been shown to successfully predict toxicity¹⁹ and therefore, are useful as screening guidelines²⁰. In this study, the ER-L and ER-M guidelines were used to estimate the potential of adverse effects resulting from PAH contamination in the sediments inside Songsanpo and Seogwipo Harbors of Jeju Island. ER-L and ER-M guidelines were derived for 12 of the 16 PAH compounds listed as priority pollutants

by the US EPA¹⁸. Effects-range guidelines do not exist for the high molecular compounds benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene. In this paper, PAH results are presented for all 16 US EPA priority pollutant PAH compounds.

It has been reported that the biological productivity has been reduced, and the hazardous contaminants (e.g. butyltin compounds) are being detected in the coast of Jeju Island and their concentrations were comparable to those in other coastal areas of domestic and foreign countries, although its coast has a good environmental condition as a spawning and a habitat of fishes and shellfishes²¹⁻²³. The authors have reported that the concentrations of PAHs in sediments inside Hallim Harbor of Jeju Island, are low to moderate in comparison with other areas in the world²⁴. Songsanpo and Seogwipo Harbors are major harbors in Jeju Island located in the geographic east and south of Jeju Island, respectively, where there is no information on PAHs. Songsanpo Harbor, where many small-size fishing boats are anchored inside harbor, possesses the water surface area of 2.56×10^5 m² inside one. The water depth is in the range of 3.5-4 m and about 7.5 m inside and outside one. The sediments are mixed with gravel, sand and mud inside one, but are not present outside one, although rock masses are present in a wide area. Seogwipo Harbor, designated as a trade port by the Korea Maritime and Port Law, possesses the water surface area of 2.73×10^5 m² inside harbor and two small islands, Moon Island and Sae Island, which serve as a natural breakwater. The water temperature inside harbor is maintained constantly with the protruded breakwater of 280 m from the coastline to Sae Island and the breakwater of 125 m built at eastern open sea. The water depth inside one is in the range of 3-6 m, becoming deeper with going to the open sea in a parallel with the coastline, and 15 m outside one. The sediments are distributed in the similar way as Songsanpo Harbor.²⁵

The major objective of this study was to determine the concentration levels and the distribution of 16 PAHs recommended by US-Environmental Protection Agency (US-EPA) as priority pollutants to be monitored in the framework of the environmental quality control in surface sediments inside Songsanpo and Seogwipo Harbors of Jeju Island. The distribution and nature of PAHs were further investigated to identify possible origins of these contaminants, and the potential toxicological significance was evaluated by comparison

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with effects-based sediment quality guidelines.

2. Materials and Methods

2.1. Sample collection

The surface sediment sampling in Songsanpo and Seogwipo Harbors was taken three times (June, September and December, 2001) only inside harbor, because outside one, rock masses are present in a wide range and sediments are not. The surface sediment samples (0-4 cm) were collected at 6 stations in each harbor (Fig. 1) by SCUBA diving, considering physical (e.g. breakwater, mooring sites of ships, etc) and sedimentary environments inside harbor. The collected sediment samples were added to a pre-cleaned wide mouth jar (5 cm I.D.×6.5 cm long), placed in an ice box in the field, and transferred to the laboratory, where they were frozen at - 70 °C, until analysis.

2.2. PAH analysis and quality control

The analytical procedures of PAHs in surface sediments followed the Yim's method²⁶. About 20 g of wet sediment sample and 30 g of anhydrous sodium sulfate (Yakuri Pure Chem., Japan) were well mixed and powdered in a mortar, and then transferred to a thimble. A sub-sample was taken to calculate the percent of dry weight (dw) on which basis all the results are reported. The sediment sample was extracted for 15 hrs in a Soxhlet apparatus using 200 mL of methylene chloride (HPLC grade, Fisher Scientific Ltd., USA). Prior to extraction, four PAH surrogate standards (naphthalene-d₈, acenaphthene-d₁₀, chrysene-d₁₂, perylene-d₁₂; Chem Service, West Chester, PA) and the activated copper were added to the sample to allow the recoveries to be calculated and to eliminate the ele-

mental sulfur content from the extract, respectively. The extract was concentrated to about 1 mL in a hot water bath (60-70 °C) and the concentrated sample was reconstituted in 2 mL of n-hexane (HPLC Grade, Tedia Company Inc., USA).

The sample extract was cleaned up by being eluted with 25 mL of n-hexane: benzene (1:1 v/v) on slurry of alumina (1 g) and silica gel (3 g, Sigma Chem. Co., USA) packed into a glass column with stopcock (30 cm long×1 cm I.D.). The cleaned up fraction was reduced to the final volume of 1 mL by high vacuum concentrator (Turbo Vap[®] 500), to which GC internal standard (hexyamethylbenzene, Sigma Chem. Co., USA) was added.

The final fraction was analyzed by GC (HP 5890 series II) coupled to MSD (HP 5972) to determine the following 16 PAHs recommended by US-EPA as priority pollutants: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DaA), benzo[g,h,i]perylene (BgP), indeno[1,2,3-cd]pyrene (IcP). The injector temp. was maintained at 300 °C. The oven temp. started at 60 °C, held for 2 min, and increased to 240 °C at the rate of 10 °C/min, and then to 260 °C at the rate of 1 °C/min. The final temp. was increased to 300 °C at the rate of 10 °C/min and held for 8 min. The carrier gas was helium at a constant flow rate of 1.5 mL/min. A fused capillary column (DB-5 MS, 30 m long×0.25 mm I.D. x 0.25 μm film thickness, J&W Sci. Inc., USA) was used. MSD was operated under the selective ion monitoring (SIM) mode using the

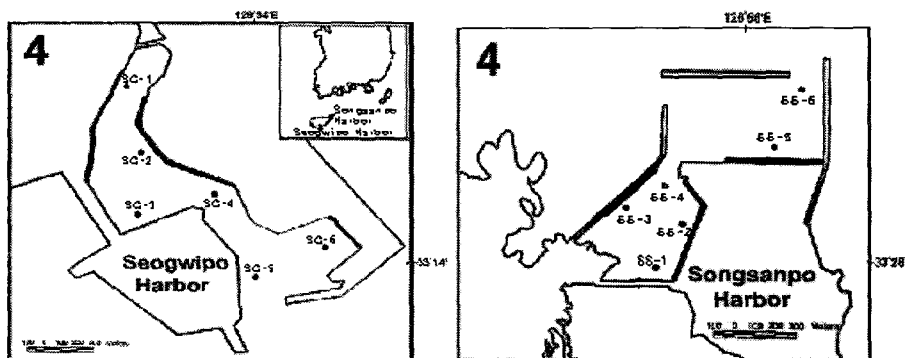


Fig. 1. Surface sediment sampling locations inside Songsanpo and Seogwipo Harbors of Jeju Island (■ : mooring site).

molecular ions of interest (electron impactor ionization at 70 eV). Three microliter sample was injected with splitless mode. Blank test was run before and after the injection of the sample and standards to check for any carryover.

The standard curve was obtained by using 2, 20, 200, 1000, 2000 ng/mL of mixed 16 PAH standard (Supleco, USA). All quantitation was performed by the method of internal standardization by using four surrogate standards at 200 ng/mL level. The response curves for the 16 PAHs were linear and the determination coefficients (r^2) were more than 0.99. Mean recoveries (\pm S.D.) of naphthalene-d8, acenaphthene-d10, chrysene-d12 and perylene-d12 which were added prior to the extraction of sediment sample, were 55 ± 10 , 73 ± 7 , 78 ± 6 , $85\pm 4\%$, respectively, which were within an acceptable range (40-120%)²⁶. Although the recovery of naphthalene-d8 was low compared to other surrogate standards due to several steps of concentration, the value was within an acceptable range. The method used in this study was verified using NIST SRM 1941a as a reference. As shown in Table 1, the recoveries of PAHs were in the range of 84.2-114.5% with the mean recovery of 96.2%. PAHs in procedural blanks were undetectable by GC/MSD. Thus, PAHs in surface sediments were not corrected for blank levels.

2.3. Organic carbon and particle size analysis

Organic carbon content was determined using the

CHN analyzer (Leuco CHN-900) after treatment with 1 N hydrochloric acid to remove inorganic carbon. Particle size analysis was conducted according to the procedure of Ingram²⁷) and was only briefly described here. The organic matter and inorganic carbon in sediments were eliminated using 15% hydrogen peroxide and 10% hydrochloric acid, respectively. The procedure was followed by rinsing with de-ionized water and repeated until no evidence of organic matter was visible upon addition of concentrated hydrogen peroxide. A wet sieving was carried using a 4 ϕ (63 μm) sieve and particles were divided into two fractions, $>63 \mu\text{m}$ and $<63 \mu\text{m}$ (mud). The fraction $>63 \mu\text{m}$ was dried and sieved using 1 ϕ (2 mm). Thus, the sediment particles were divided into three fractions, $>2 \text{ mm}$, in the range of $63 \mu\text{m} \sim 2 \text{ mm}$ and $<63 \mu\text{m}$, called as gravel, sand and mud, respectively.

3. Results and Discussion

3.1. Distribution of PAHs

Table 2 and 3 show the range of PAH concentrations in the surface sediments sampled three times (June, September and December, 2001) inside Songsanpo and Seogwipo Harbors, respectively. Sixteen individual PAHs were identified comprising 2-6 ring unsubstituted complexes. The concentrations of total PAHs (as the sum of the 16 congeners listed in Table 1) inside Songsanpo and Seogwipo Harbors ranged from 41 to

Table 1. Comparison of NIST SRM 1941a's certified value with this study's value ($\mu\text{g}/\text{kg dw}$)

PAHs	Abbreviation	Certified value ^a	This study (mean \pm SD, n=4)	Mean percent of certified value
Naphthalene	Nap	1010 \pm 140	850 \pm 35	84.2
Acenaphthylene	Acy	-	-	-
Acenaphthene	Ace	-	-	-
Fluorene	Flu	97.3 \pm 8.6	106 \pm 15	108.9
Phenanthrene	Phe	489 \pm 23	468 \pm 18	95.7
Anthracene	Ant	184 \pm 14	165 \pm 10	89.7
Fluoranthene	Fle	981 \pm 78	912 \pm 7	92.9
Pyrene	Pyr	811 \pm 24	760 \pm 9	93.7
Benzo[a]anthracene	BaA	427 \pm 25	398 \pm 25	93.2
Chrysene	Chr	380 \pm 24	435 \pm 23	114.5
Benzo[b]fluoranthene	BbF	740 \pm 110	815 \pm 35	110.1
Benzo[k]fluoranthene	BkF	361 \pm 18	386 \pm 12	104.9
Benzo[a]pyrene	BaP	628 \pm 52	563 \pm 23	89.6
Dibenzo[a,h]anthracene	DaA	73.9 \pm 9.7	68 \pm 7	92.0
Benzo[g,h,i]perylene	BgP	525 \pm 67	474 \pm 27	90.3
Indeno[1,2,3-cd]pyrene	IcP	501 \pm 72	445 \pm 15	88.8

^aThe uncertainty is based on a 95% confidence interval for the true concentration.

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Table 2. Range and mean concentrations (ng/g dw) of individual PAHs in surface sediments inside Songsanpo Harbor

PAHs	Ss-1	Ss-2	Ss-3	Ss-4	Ss-5	Ss-6
	Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)
Nap	10.2-21.1 (13.9)	1.1-12.1 (7.7)	4.2-14.2 (9.7)	6.4-11.4 (8.2)	6.3-26.5 (15.1)	7.0-21.0 (13.1)
Acy	nd ^c -1.1 (0.4)	nd-0.6 (0.3)	0.4-3.2 (2.0)	nd-5.9 (3.5)	1.3-3.2 (1.9)	2.2-5.2 (3.3)
Ace	nd-1.7 (0.6)	0.1-0.4 (0.2)	0.2-2.7 (1.1)	0.5-4.9 (2.1)	0.6-5.7 (3.4)	nd-3.8 (1.4)
Flu	nd-3.9 (1.8)	nd-1.5 (0.8)	1.2-1.6 (1.5)	nd-3.5 (2.0)	5.5-6.9 (6.1)	1.9-3.4 (2.6)
Phe	10.0-31.7 (17.4)	1.8-11.3 (7.6)	10.9-19.2 (14.0)	7.1-36.3 (23.0)	18.4-45.8 (27.7)	13.8-28.4 (20.6)
Ant	1.4-4.6 (2.7)	0.2-2.1 (1.1)	2.7-8.9 (5.8)	2.4-13.4 (7.2)	0.8-6.7 (3.8)	2.9-8.2 (5.4)
Fle	5.5-17.7 (12.5)	2.6-3.3 (3.1)	7.0-19.3 (14.3)	3.5-34.1 (15.1)	4.6-34.1 (12.2)	11.9-20.1 (15.0)
Pyr	6.5-21.4 (14.3)	3.6-7.0 (5.6)	10.8-18.2 (15.1)	3.7-27.3 (13.0)	5.4-18.6 (12.5)	13.1-15.8 (14.4)
BaA	2.6-9.3 (5.7)	1.4-4.2 (2.4)	5.2-13.0 (8.9)	1.3-21.5 (9.8)	2.5-9.6 (7.1)	5.9-17.2 (11.6)
Chr	3.7-15.4 (9.5)	1.1-6.4 (3.7)	6.5-16.5 (11.0)	2.7-26.6 (12.3)	3.6-12.8 (7.5)	6.1-13.9 (10.2)
BbF	4.2-13.7 (8.8)	1.5-3.3 (2.4)	5.9-11.4 (8.3)	1.7-21.6 (9.7)	3.4-10.3 (7.9)	4.3-16.1 (10.9)
BkF	2.2-9.8 (6.7)	0.7-4.3 (1.9)	3.8-9.7 (6.1)	1.5-19.4 (8.4)	1.4-8.9 (6.0)	4.9-16.4 (10.6)
BaP	2.9-10.0 (6.8)	1.3-3.5 (2.1)	6.9-12.7 (9.7)	2.3-22.3 (10.2)	1.6-7.7 (4.5)	6.0-13.9 (10.0)
IcP	4.7-10.4 (7.3)	0.8-2.6 (1.8)	8.3-11.2 (9.6)	2.2-19.5 (9.7)	3.4-4.9 (4.1)	4.8-17.2 (11.9)
DaA	nd-3.0 (1.5)	nd-0.9 (0.3)	2.5-3.0 (2.7)	nd-5.3 (2.7)	1.4-17.8 (7.0)	2.2-4.1 (3.2)
BgP	4.4-10.3 (7.3)	1.6-4.8 (3.3)	7.7-10.3 (9.2)	2.7-18.4 (9.0)	3.4-6.2 (4.9)	6.7-16.5 (12.1)
∑PAHs ^a	63-167 (117)	41-51 (44)	97-167 (129)	43-288 (146)	85-169 (132)	98-209 (156)
∑Car-PAHs ^b	18-56 (37)	8-16 (11)	35-61 (45)	9-110 (51)	14-54 (37)	28-81 (58)

^asum of above 16 PAHs; ^bsum of six carcinogenic PAHs (BaA, BbF, BkF, BaP, IcP and DaA); ^cnot detected.

288 ng/g dw with a mean value of 121 ng/g dw and from 14 to 268 ng/g dw with a mean value of 119 ng/g dw, respectively. The distribution of total PAHs showed no distinct spatial trends inside both harbors (Fig. 2), which is considered to be influenced by several factors (e.g., their several source loads, ships activities, tidal currents, sedimentary environments, etc.). Mean total PAHs were distributed in similar concentrations (117-156 ng/g dw) at all the stations except for the station Ss-2 (44 ng/g dw) inside

Songsanpo Harbor, but were distributed in relatively high concentrations at the stations Sg-3 and Sg-4 (> 190 ng/g dw) and in low concentrations at three stations (Sg-2, Sg-5 and Sg-6) (< 70 ng/g dw) inside Seogwipo Harbor. Total concentrations of six PAHs (BaA, BbF, BkF, BaP, IcP and DaA) which are known as strong carcinogens¹⁴⁾, were in the range of 8-110 ng/g dw (mean value of 40 ng/g dw) inside Songsanpo Harbor and 1-119 ng/g dw (mean value of 37 ng/g dw) inside Seogwipo Harbor, and their

Table 3. Range and mean concentrations (ng/g dw) of individual PAHs in surface sediments inside Seogwipo Harbor

PAHs	Sg-1	Sg-2	Sg-3	Sg-4	Sg-5	Sg-6
	Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)
Nap	12.4-35.3 (23.5)	2.5-14.0 (7.9)	6.1-20.7 (11.0)	5.6-19.8 (14.1)	3.3-9.3 (7.2)	0.7-24.1 (13.5)
Acy	nd ^c -4.4 (1.8)	nd-4.0 (3.0)	0.5-9.8 (5.3)	nd-7.3 (3.9)	nd-1.8 (0.6)	nd-2.0 (0.7)
Ace	nd-2.3 (0.9)	nd-0.7 (0.2)	0.2-5.6 (2.1)	1.5-16.3 (7.5)	0.1-1.5 (0.6)	0.2-1.6 (0.8)
Flu	nd-5.0 (2.8)	0.7-2.9 (1.8)	1.3-6.6 (3.5)	5.3-12.3 (7.8)	nd-1.5 (0.5)	nd-4.4 (1.8)
Phe	2.7-28.2 (17.9)	1.1-12.8 (6.3)	16.6-45.7 (27.1)	20.7-40.5 (32.6)	1.6-12.9 (8.8)	2.4-23.5 (11.4)
Ant	0.4-8.4 (3.9)	0.9-5.1 (2.8)	2.2-6.8 (5.1)	2.3-16.1 (8.9)	0.3-2.8 (1.6)	2.1-8.2 (6.0)
Fle	3.8-15.1 (10.1)	1.6-2.2 (2.0)	5.0-49.6 (21.4)	11.0-42.2 (25.1)	12.5-9.0 (4.7)	1.5-13.2 (5.6)
Pyr	4.4-16.2 (11.1)	2.3-3.5 (2.9)	6.4-47.6 (21.0)	8.0-40.7 (23.4)	3.2-9.6 (5.4)	2.1-13.3 (6.2)
BaA	0.7-8.1 (4.9)	0.6-2.7 (1.7)	3.8-15.2 (8.6)	8.3-15.6 (12.3)	0.2-4.4 (2.0)	0.6-7.6 (3.1)
Chr	1.2-13.2 (7.6)	0.7-2.4 (1.5)	5.3-22.3 (14.3)	13.9-21.6 (18.3)	0.4-4.8 (2.3)	0.2-12.8 (4.4)
BbF	1.0-10.8 (6.6)	0.4-1.7 (1.2)	6.4-24.3 (13.5)	12.8-23.6 (19.6)	0.3-4.4 (2.3)	1.3-7.4 (4.3)
BkF	0.9-6.9 (4.7)	0.6-1.5 (1.1)	4.8-22.6 (11.3)	13.6-19.2 (15.6)	0.2-3.0 (1.2)	0.7-4.1 (2.4)
BaP	2.0-8.5 (5.2)	1.1-3.1 (1.8)	6.5-26.9 (16.6)	5.4-22.4 (14.0)	0.5-3.9 (1.8)	nd-6.0 (2.1)
IcP	2.2-11.3 (7.0)	1.4-4.6 (2.7)	7.6-22.9 (14.6)	11.7-19.1 (16.4)	nd-4.8 (2.7)	nd-6.1 (2.4)
DaA	nd-3.2 (2.1)	1.0-4.5 (2.2)	2.4-5.4 (3.7)	2.8-28.9 (12.3)	nd-1.5 (0.9)	nd-2.4 (0.8)
BgP	1.0-14.1 (7.4)	0.9-1.7 (1.4)	7.8-22.0 (14.7)	7.9-22.3 (14.2)	nd-5.1 (2.6)	nd-8.3 (2.9)
∑PAHs ^a	43-191 (118)	18-52 (39)	108-265 (194)	218-268 (246)	14-79 (46)	15-144 (66)
∑Car-PAHs ^b	7-49 (31)	8-16 (11)	31-109 (68)	77-105 (90)	1-22 (11)	2-34 (13)

^asum of above 16 PAHs; ^bsum of six carcinogenic PAHs (BaA, BbF, BkF, BaP, IcP and DaA); ^cnot detected.

distribution patterns were the same as those of total PAHs (Fig. 3).

The mean concentration for individual PAH compound at each station inside both harbors has been calculated as the contribution of it to the total PAHs shown in Fig. 4, in order to evaluate the relative abundance of individual PAH compounds. The results show that Nap and Phe among low molecular weight (2-3 ring) PAH compounds and Fle and Pyr among high molecular weight (4-6 ring) PAH compounds, are more

abundant, at both harbors. In addition, it can be found that the relative abundance of individual PAH compounds, varies rather greatly according to the sampling station, suggesting that the sediment PAH contamination at each station derives from different sources.

The degree of sediment contamination by PAHs inside both harbors was compared with other marine aquatic systems (Table 4). Although the number of PAHs analyzed in this study may differ with study area, the 16 PAHs investigated in this study have been

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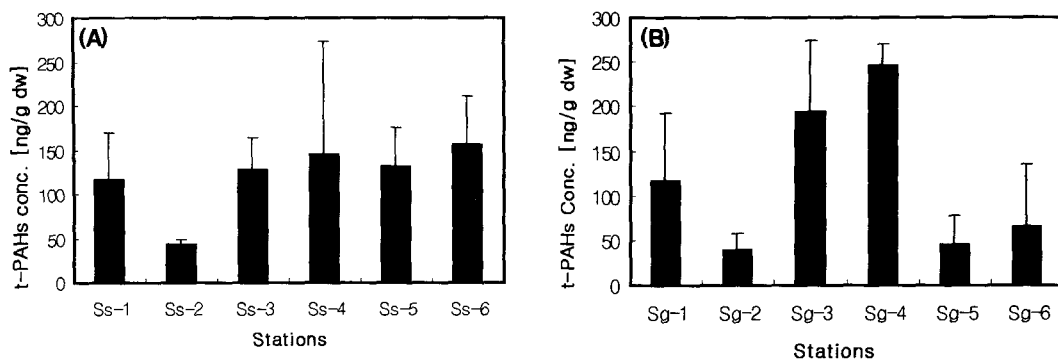


Fig. 2. Distribution of total PAHs (t-PAHs) in surface sediments of each station inside Songsanpo (A) and Seogwipo (B) Harbors. The thick and thin bars indicate the mean concentration and standard deviation (SD), respectively.

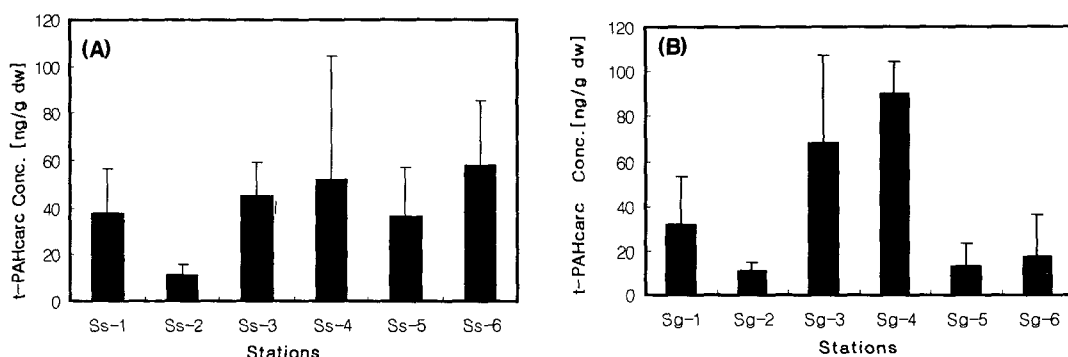


Fig. 3. Distribution of total carcinogenic PAHs (t-PAHcarc) in surface sediments of each station inside Songsanpo (A) and Seogwipo (B) Harbors. The thick and thin bars indicate the mean concentration and standard deviation (SD), respectively.

found in estuarine and marine sediments²⁸. It was reported that the alkylated PAHs which were not measured in this study, did not affect the mean value of total PAHs in some areas, although they represent a contribution to total PAHs to some extent²⁹.

Comparing the contamination levels by mean value of total PAHs across studies, the contamination levels inside both harbors appeared lower than those in Masan Bay²⁶ and Kwangyang Bay³⁰ in Korea, Adriatic Sea³⁵, Contou (Benin) and Aquitaine in France³², were much lower than Ulsan Bay (Korea)²⁸, Western Mediterranean Sea³⁶, Baltic Sea³⁴, Western Baltic Sea³³ and Northern Irish Sea-loughs⁸, and were comparable to those in Kyeonggi Bay (Korea)³¹ and Todos Santos Bay (Mexico).²⁹ Especially, the contamination levels in this study were a half lower as compared with those inside Hallim Harbor²⁴, one of major harbors of Jeju Island. Consequently, it is considered that the sediment contamination levels by PAHs inside both harbors

show a clean environment in comparison with those in other areas in the world.

3.2. Relationships among sedimentary PAHs, organic carbon and particle size

It has been reported that the wide range of sediment contamination levels can be partly explained by the great disparity of the sediments³³, PAHs in the sediments are mainly associated with the organic matter^{37,38}, and PAH sediment content depends on the particle size distribution^{8,39}. In order to evaluate the distribution of sedimentary organic carbon content and particle size distribution to total PAH concentrations (Table 5), the correlation between each of them was investigated (Table 6). As shown in Table 5, the organic carbon content and particle size distribution differed greatly with the station and sampling time, which is considered to be influenced by tidal currents, shipping activities, surrounding environments, etc.

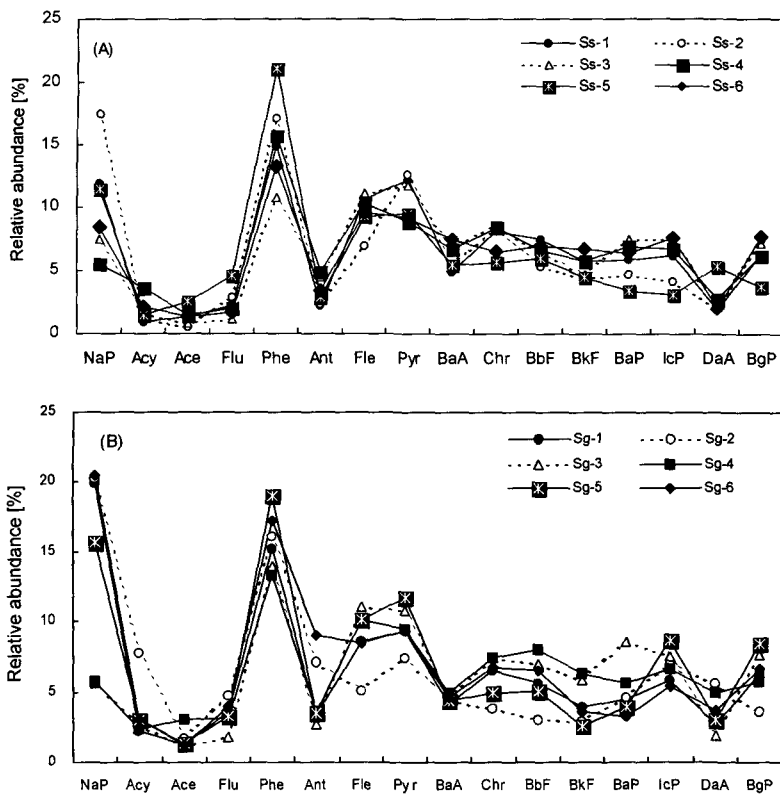


Fig. 4. Relative abundance of individual PAH compound to the total PAHs calculated from the mean concentration for each station inside Songsanpo (A) and Seogwipo (B) Harbors.

Table 4. Comparison of total PAH concentrations (ng/g dw) in surface sediments of this study with those in other areas

Location	n ^a	Range (Mean)	References
Inside Songsanpo Harbor	16	41-288(121)	This study
Inside Seogwipo Harbor	16	14-268(119)	This study
Inside Hallim Harbor	16	19-467 (245)	Moon et al. ²⁴⁾
Ulsan Bay, Korea	16	14-7108 (1052)	Moon et al. ²⁸⁾
Kwangyang Bay, Korea	13	171-1014 (408)	Yoo ³⁰⁾
Kyeonggi Bay, Korea	24	9-1400 (120)	Kim et al. ³¹⁾
Masan Bay, Korea	24	151-1110 (562)	Yim ²⁶⁾
Todos Santos Bay, Mexico	16	8-813 (96)	Macias-Zamora et al. ²⁹⁾
Northern Irish Sea-loughs	13	83-22960 (1930)	Guinam et al. ⁸⁾
Contou (Benin), France	14	25-1411 (487)	Soclo et al. ³²⁾
Aquitaine, France	14	4-853 (256)	Soclo et al. ³²⁾
Western Baltic Sea	18	3-30100 (3847)	Baumard et al. ³³⁾
Baltic Sea	15	720-1900 (1200)	Witt ³⁴⁾
Adriatic Sea	12	18-580 (200)	Caricchia et al. ³⁵⁾
Western Mediterranean Sea	31	180-3200 (1300)	Lipiatou and Saliot ³⁶⁾

^anumber of PAHs analyzed in each study.

Relatively good correlation coefficients (r) were obtained between total PAH concentrations, and organic carbon (0.587, 0.578 for Songsanpo and Seogwipo

Harbors, respectively) and mud content (0.661, 0.507). However, very low ($r=0.239, 0.211$) and negative ($r=-0.325, -0.262$) correlations were obtained for sand and

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Table 5. Total PAH concentrations, organic carbon content and particle size distribution in surface sediments inside Songsanpo and Seogwipo Harbors

Harbor	Station	Total PAHs (ng/g dw)	Organic carbon (%)	Particle size distribution (%)		
				Gravel	Sand	Mud
Songsanpo Harbor	Ss-1	63-167 (117)	2.1-3.7 (2.6)	14-42 (26)	45-83 (67)	3-12 (7)
	Ss-2	41-51 (44)	0.3-1.5 (0.9)	81-89 (86)	10-18 (13)	1-1 (1)
	Ss-3	97-167 (129)	5.8-6.4 (6.0)	12-22 (16)	70-79 (75)	7-11 (9)
	Ss-4	43-288 (146)	3.5-7.3 (6.0)	13-47 (35)	40-80 (54)	6-11 (8)
	Ss-5	85-169 (132)	2.6-3.8 (3.3)	17-74 (47)	26-72 (51)	4-9 (7)
	Ss-6	98-209 (156)	2.4-3.1 (2.9)	30-72 (56)	22-55 (35)	5-15 (9)
			24-220 (121)	0.3-7.3 (3.6)	12-89 (44)	10-83 (49)
Seogwipo Harbor	Sg-1	43-191 (118)	3.4-5.8 (4.7)	23-29 (26)	53-69 (61)	8-18 (13)
	Sg-2	18-52 (39)	0.3-0.5 (0.4)	15-58 (31)	40-83 (67)	2-3 (2)
	Sg-3	108-265 (194)	4.0-4.9 (4.3)	4-35 (19)	60-88 (70)	3-21 (11)
	Sg-4	218-268 (246)	3.5-5.2 (4.1)	4-65 (33)	32-83 (60)	2-13 (7)
	Sg-5	14-79 (46)	2.7-3.8 (3.1)	47-67 (55)	28-44 (38)	5-10 (8)
	Sg-6	15-144 (66)	1.2-3.0 (2.2)	55-79 (64)	21-37 (31)	0-8 (4)
			14-268 (118)	0.3-5.8 (3.1)	4-79 (38)	21-88 (55)

Table 6. Correlation between total PAH concentrations and each of organic carbon content and particle size distribution in surface sediments inside Songsanpo and Seogwipo Harbors

Statistics *	Harbor	Organic carbon	Particle size distribution		
			Gravel (n=18)	Sand (n=18)	Mud (n=18)
r	Songsanpo	0.587	-0.325	0.239	0.661
	Seogwipo	0.578	-0.262	0.211	0.507

Pearson's sample distribution; $p < 0.05$.

gravel content, respectively (Table 6). The similar results were found in Kyeonggi Bay³¹⁾ ($r=0.754$, -0.361 , 0.274 , 0.339 for organic carbon, sand, silt and clay, respectively), Kwangyang Bay³⁰⁾ ($r=0.520$, -0.395 , 0.389 for organic carbon, sand and mud, respectively), and Hallim Harbor of Jeju Island²⁴⁾ ($r=0.621$, -0.559 , 0.227 and 0.557 for organic carbon, gravel, sand and mud, respectively), in Korea.

Many studies about the relationship between total PAHs or other hydrophobic chemicals and organic carbon or particle size were made in marine or riverine surface sediments of different compartments in the world, except for the studies mentioned above. Micias-Zamora et al²⁹⁾ reported that relatively high correlation ($r=0.782$) was observed between total PAHs and organic carbon in Todos Santos Bay (Mexico), suggesting that PAHs distribution generally followed that of organic matter content. Guinam et al⁸⁾ also reported that high correlations between total PAHs

concentration and % silty/clay (corresponding to mud content in this study) were observed for both Larne ($r=0.806$) and Strangford ($r=0.781$) loughs in surface sediments of two northern Irish sea-loughs. However, in the case of the relationship between total PAHs and organic carbon, high correlation was found in Larne lough ($r=0.900$) and no correlation was found in Strangford lough, suggesting that the productive and varied benthic community in Strangford lough contributes to the organic carbon level in the benthic sediment masking any relationship which may exist between total PAHs and organic carbon. It has been reported that other hydrophobic chemicals including n-hydrocarbon, DDTs, PCBs, etc. were distributed at low correlations with organic matter content^{40,41)}, suggesting that the reasons for this may be related to the presence of multiple sources of chemicals and/or to large inputs of relict sediments by rain, although the exact reason was still unclear. From the results obtained in this study

and other studies, it can be concluded that the distribution of PAHs may be correlated with organic carbon and mud content, although the correlation between them is not so high because of several factors such as sedimentary environments and presence of multiple sources of chemicals, etc.

3.3. Identifying the origin of PAHs

In order to estimate the origin of sediment contamination by PAHs in this study, we examined the four indices shown in Table 7, LMW/HMW ratio (sum of the low molecular weight 2-3 ring PAH concentrations versus sum of the high molecular weight 4-6 ring PAH concentrations), Phe/Ant ratio, Flt/Pyr ratio and Chr/BaA ratio, which were used by other investigators from various environments^{2,7,8,26,32}.

It is generally accepted that pyrogenic PAHs are characterized by the dominance of high molecular

weight (HMW) 4-6 ring PAHs over the low molecular weight (LMW) 2-3 ring PAHs. In contrast, petroleum hydrocarbons in crude oil and light refined products are dominated by the lowest molecular weight PAHs with only trace levels of the penta- and hexa-aromatics present^{2,7,8,26}.

The values for this index obtained from the sediment samples of each station with sampling time inside both harbors, are shown in Fig. 5. It can be known that this index values varied according to sampling station and sampling time, but the values for the majority of the sediment samples were lower than 1 (i.e., the values are in the range of 0.09-0.97 and 0.26-0.94 for Songsanpo and Seogwipo Harbors, respectively), indicating pyrolytic origin contamination. Only, three sediment samples (two Ss-2 samples and one Ss-5 sample) for Songsanpo Harbor (the values between 1.01 and 1.77) and four sediment samples (one sample at

Table 7. The PAH origin indices at each station inside Songsanpo and Seogwipo Harbors

Harbor	Station	LMW/HMW ^a	Phe/Ant	Flt/Pyr	Chr/BaA
Songsanpo Harbor	Ss-1	0.37-0.64(0.49) ^b	4.73-7.63(6.44)	0.67-1.18(0.90)	1.44-1.72(1.61)
	Ss-2	0.09-1.44(0.85)	5.38-10.93(8.50)	0.47-0.72(0.58)	0.79-2.29(1.53)
	Ss-3	0.35-0.36(0.36)	2.07-3.96(2.73)	0.65-1.18(0.91)	0.77-1.95(1.33)
	Ss-4	0.33-0.97(0.68)	2.71-4.54(3.39)	0.94-1.25(1.06)	1.14-2.10(1.49)
	Ss-5	0.55-1.77(1.01)	2.83-15.57(9.60)	0.85-1.08(0.94)	0.64-1.43(1.15)
	Ss-6	0.33-0.49(0.43)	3.48-4.82(4.03)	0.91-1.13(1.04)	0.61-1.17(0.94)
Seogwipo Harbor	Sg-1	0.57-1.51(0.95)	3.36-7.58(5.97)	0.86-0.94(0.90)	1.40-1.81(1.62)
	Sg-2	0.33-1.94(1.07)	0.97-5.43(2.55)	0.60-0.79(0.69)	0.51-1.30(0.97)
	Sg-3	0.26-0.94(0.51)	2.59-20.88(8.75)	0.78-1.08(0.97)	1.41-2.24(1.71)
	Sg-4	0.31-0.70(0.47)	1.29-17.46(7.73)	1.03-1.37(1.15)	1.38-1.59(1.52)
	Sg-5	0.56-1.30(0.91)	4.59-6.85(5.99)	0.73-0.93(0.82)	1.09-2.80(1.68)
	Sg-6	0.66-5.58(2.34)	1.01-3.08(1.73)	0.64-0.99(0.78)	0.21-1.69(0.77)

^athe ratio of sum of the low molecular weight 2-3 ring PAHs over sum of the high molecular weight 4-6 ring PAHs; ^bthe value in the parenthesis indicates the mean of the range.

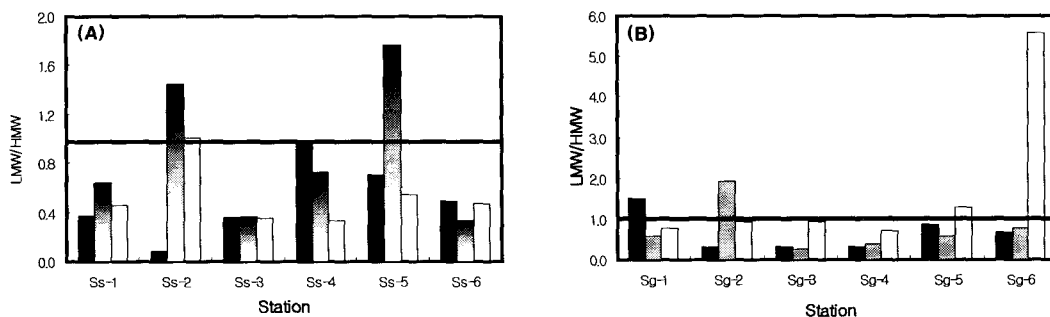


Fig. 5. The ratio of low molecular weight (LMW) PAHs to high molecular weight (HMW) PAHs at each station inside Songsanpo (A) and Seogwipo (B) Harbors. The 1st, 2nd and 3rd bars at each station indicate the ratio of LMW/HMW at surface sediments collected in June, September and December, 2001, respectively.

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the stations Sg-1, Sg-2, Sg-5 and Sg-6) for Seogwipo Harbor (the values between 1.30 and 5.59), revealed the values higher than 1, indicating these samples were contaminated by petrogenic PAHs. Especially, The value equal to 5.59 in Sg-6 sample collected in December, 2001, seemed to indicate that the petrogenic contamination source was greater than the other samples.

Ratios between individual PAH compounds are used to identify the processes from which PAHs originate^{9,42}. The ratios of Phe/Ant and Fle/Pyr, based on thermodynamic principle, are generally used to differentiate the pyrolytic and petrogenic origins of PAHs^{8,30,32,33}. Phe and Ant are two structural isomers. Because of their different physical-chemical properties, they could behave differently in the environment and could lead to different values for their Phe/Ant ratio that would lead to different values for their Phe/Ant ratio that would give useful information on the PAH origin^{32,43}. Phe is more thermodynamically stable than Ant, so a Phe/Ant ratio <10 is characteristic of PAH pyrolytic⁸. Fle and Pyr are often associated and considered typical pyrogenic products generated from high temperature condensation of low molecular weight aromatic compounds^{8,32}. During the combustion process, Pyr is more stable than Fle hence pyrolytic products are usually characterized by a predominance of Fle over Pyr at ratios >1^{8,32,33}. Pyr is more profuse in petroleum-derived PAHs. The values of these two indices obtained inside both harbors are shown in Table 7. In most of sediment samples, the values of Phe/Ant ratio were lower than 10 (2.07-9.20 for Songsanpo Harbor, 0.97-7.59 for Seogwipo Harbor), except for three sediment samples (one Ss-2 sample (10.99) and two Ss-5 samples (15.57, 10.41) for

Songsanpo Harbor and two sediment samples (one Sg-3 sample (20.88) and one Sg-4 sample (17.46) for Seogwipo Harbor, indicating that most of sediment samples collected in this study were contaminated by pyrolytic PAHs. In contrast, the values of Fle/Pyr were lower than 1 (0.47-0.98 for Songsanpo Harbor, 0.64-0.99 for Seogwipo Harbor) for most of sediment samples except for five samples for each harbor, indicating pyrolytic origin contamination. To investigate this further, both ratios were plotted against each other (Fig. 6). As shown in Fig. 6, it is difficult to discriminate the PAH origins with the values of these two indices. It is considered that the sediment PAH contamination inside both harbors is caused by both pyrolytic and petrogenic origins. This fact was also found in surface sediments around Kwangyang Bay, Korea, where in most of sediment samples, the values of Phe/Ant ratio and Fle/Ant ratio were higher than 10 and were higher than 1, respectively³⁰.

Chr and BaA are derived from processes of organic matter combustion at high temperature, with the values of Chr/BaA ratio lower than 1. In contrast, low maturation of organic matter during burial in the sedimentary matrix could lead an inversion of this tendency, i.e., Chr/BaA ratio=1^{32,44}. In addition, it has been reported that chrysenic derivatives are more stable than benzenanthracenic ones because of the possibility of the latter ones to convert to the former ones³². The values of Chr/BaA ratio obtained from the sediment samples of each station with sampling time, are shown in Table 7 and Fig. 7. It can be known that this index values for most of sediment samples, were higher than 1 (1.04-2.10 for Songsanpo Harbor, 1.09-2.80 for Seogwipo Harbor) except for four sediment samples (one sediment sample at Ss-2 (0.79), Ss-3 (0.77), Ss-5

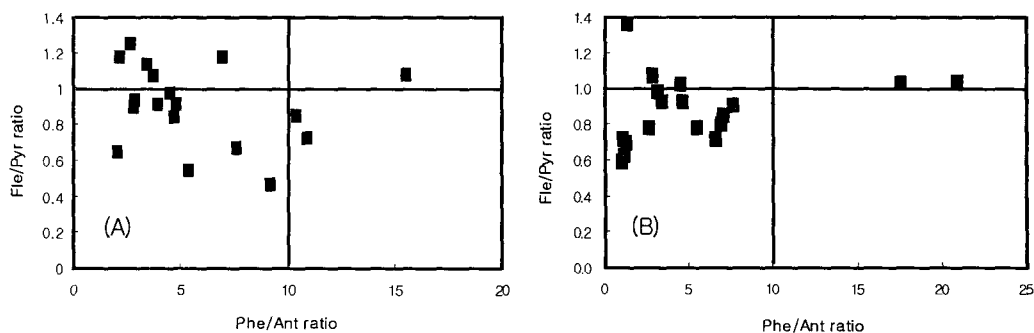


Fig. 6. Plot of Fle/Pyr against Phe/Ant for surface sediments inside Songsanpo (A) and Seogwipo (B) Harbors.

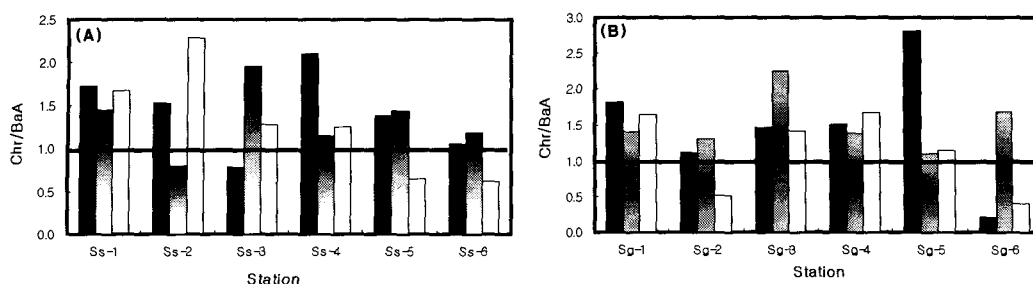


Fig. 7. The ratio of chrysene (Chr) to benzo[a]anthracene (BaA) at each station inside Songsanpo (A) and Seogwipo (B) Harbors. The 1st, 2nd and 3rd bars at each station indicate the ratio of Chr/BaA at surface sediments collected in June, September and December, 2001, respectively.

(0.64) and Ss-6 (0.61) station, respectively) for Songsanpo Harbor and three sediment samples (one Sg-2 sample (0.51) and two Sg-6 samples (0.21, 0.57)) for Seogwipo Harbor, showing petrogenic PAH contamination for most of sediment samples.

From the examination of above four PAH origin indices, it is difficult to discriminate one of pyrolytic and petrogenic PAH origins, although two sediment samples (one Ss-5 sample collected in September and one Ss-6 sample collected in December) shows a distinct petrogenic and pyrolytic PAH origin, respectively. It can be concluded that the sediment PAH con-

tamination inside both harbors is ascribed to both of pyrolytic and petrogenic origins, but not to just one.

3.4. Potential for biological/ecological effects

As mentioned in 3.1, the sediment contamination levels by PAHs inside both harbors is low in comparison with those in other areas in the world.

In order to estimate the potential of the sediment PAH contamination inside both harbors to cause the adverse effects in biota, the effects-based guidelines (ER-L and ER-M) developed by US NOAA¹⁸⁾ and applied in Australia and New Zealand¹⁷⁾, were com-

Table 8. Comparison of effects-based and empirically-derived sediment quality guidelines with individual and total PAH concentrations (ng/g dw) inside Songsanpo and Seogwipo Harbors

PAH (ng/g dw)	ER-L ^a	ER-M ^a	This study	
			Songsanpo Harbor	Seogwipo Harbor
Nap	160	2100	1.1-26.5	0.7-35.3
2-methyl NaP	70	160	-	-
Acy	44	640	nd-5.9	nd-9.8
Acc	16	500	nd-5.7	nd-16.3
Flu	19	540	nd-6.9	nd-12.3
Phe	240	1500	1.8-45.8	1.1-45.7
Ant	85	1100	0.2-13.4	0.3-16.1
∑ LMW PAHs	552	3160	3-70	4-90
Fle	600	5100	2.6-34.1	1.5-50.0
Pyr	670	2600	3.6-27.2	2.1-47.6
BaA	260	1600	1.3-21.5	0.2-15.6
Chr	380	2800	1.1-26.6	0.2-22.3
BaP	430	1600	1.3-22.3	nd-26.9
DaA	63	260	nd-17.8	nd-28.9
∑ HMW PAHs	1700	9600	17-216	6-199
∑ PAHs	4000	45000	41-288	14-268

^aThe PAH concentrations observed or predicted by different methods to produce biological effects were ranked. The 10th percentile and the 50th percentile of the distribution were identified as the effects range-low (ER-L) value and the effects range-medium (ER-M) value¹⁸⁾.

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pared with those in this study, and the results were presented in Table 8. As shown in Table 8, any of individual PAH, total LMW PAHs, total HMW PAHs and total PAHs in this study did not exceed the ER-L values, indicating substantial margins of safety. In conclusion, the PAHs in surface sediments inside both harbors are distributed at very low levels that does not show the biological effects on marine organisms.

4. Conclusions

Analysis of PAHs in surface sediments inside Songsanpo and Seogwipo Harbors of Jeju Island provided a useful tool in assessing PAH contamination levels, biological effects on marine organisms, and possible PAH origins. The PAHs inside both harbors appeared to be distributed in similar concentrations and may be correlated with organic carbon and mud content in sedimentary matrices to some extent. The sediment PAH contamination was low in comparison with those in other areas of the world and do not appear to impose biological effects on marine organisms. By the examinations of several PAH origin indices, it is difficult to discriminate the PAH origins and it can be concluded that the sediment PAH contamination were ascribed to both pyrolytic and petrogenic origins.

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