

Distribution and Origin of Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Sediments Inside Hallim Harbor of Jeju Island, Korea

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

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

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

(Manuscript received 6 August, 2003 ; accepted 6 September, 2003)

The surface sediments inside Hallim Harbor, one of the major harbors of Jeju Island, were sampled 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 to suggest their possible origins. The concentrations of PAHs ranged from 19 to 496 ng/g on a dry weight basis with a mean value of 245 ng/g, and the levels were low to moderate in comparison with other areas in the world. Based on comparisons of individual and total PAH concentrations with effects-based and equilibrium partitioning-based on sediment quality guidelines, the potential for the biological effects were expected to be low. The sedimentary PAHs may be correlated with organic carbon and mud contents to some extent. 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 pyrolytic and petrogenic origins.

Key words : PAHs, Surface sediments, Hallim Harbor, Distribution, Origin indices

1. Introduction

Organic pollutants released into the environment may stimulate adverse effects in human beings and organisms.¹⁾ Polycyclic aromatic hydrocarbons (PAHs) with two or more fused aromatic rings, are a class of organic pollutants which give rise to this concern.²⁾ A small fraction of the PAHs generated and released into the environment by human activities has been shown to have both carcinogenic and mutagenic effects in organisms^{3,4)}. Thus, many studies have been made on them in different compartments of the environment.⁵⁾

PAHs can be introduced into the environment by various processes^{5~7)}: incomplete combustion at higher temperature of recent and fossil organic matter (pyrolytic origin), slow matura-

tion of organic matter under geochemical gradient conditions (petrogenic origin) and short-term diagenetic degradation of biogenic precursors (diagenesis). Most PAH inputs into the environment are linked to the anthropogenic activity that is thought to be the major source of these compounds, such as wastes from industrialized and urbanized areas, off-shore petroleum hydrocarbons production or petroleum transportation.

The PAHs derived from various sources are transported into a marine environment via the atmosphere and the water, where most of them in the water column are adsorbed by suspended particulate matter, and then deposited in underlying sediments⁸⁾, due to their relative insolubility in water and strong affinity for particulate matter.⁴⁾ It has been demonstrated that the distribution of PAHs in marine environments is influenced by a number of factors, including degradation by photooxidation in superficial water layers⁹⁾ and by microbial

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

activities into the sediments¹⁰⁾ based on their physical-chemical properties (resulting in the modification of the original distribution pattern of the emission sources), and particle size compositions and the organic carbon content of the sediments.¹¹⁾ However, PAH ubiquity in the sediments indicate that accumulation phenomena dominate degradation processes in sedimentary matrices.¹²⁾ It was demonstrated that organic rich coal and wood derived particles had concentrations of those several orders of magnitude higher than silica particles.¹³⁾

Many researchers have worked to elucidate possible origins of the PAHs in marine sediments. Each source (pyrolytic, petroleum and diagenetic hydrocarbons) is characterized by a specific molecular pattern, allowing the source of these compounds to be established.¹¹⁾ However, difficulties exist in identifying their origins in sedimentary medium, owing to the possible co-existence of several sources and their degradation processes in marine waters and sediments as mentioned above.⁵⁾ Molecular indices based on PAH physical-chemical behavior covariability were developed to assess the various origins of these pollutants (e.g., phenanthrene /anthracene vs. fluoranthene/pyrene).¹¹⁾ With simultaneous association of various molecular indices, it is possible to determine which process generated such hydrocarbons in the studied matrices.⁶⁾ The coast of Jeju Island has a good environmental condition as a spawning and habitat of fishes and shellfishes, because cold and warm currents cross, and seaweeds and sunken rocks are luxuriant. Recently, it has been reported that the biological productivity has been reduced and hazardous pollutants are being detected along the coast of Jeju Island.¹⁴⁾ However, there is no information on PAHs, although several studies on them have been carried out in other coastal environments of Korea since the middle of the 1990s.^{8,15-19)}

The present study is focused on surface sediment samples collected inside Hallim Harbor, one of the major harbors of Jeju Island. The interest of this work is to determine the concentration levels and the distribution, and to suggest possible origins of 16 PAHs recommended by US-Environmental Protection Agency (US-EPA) as priority pollutants to be monitored in the framework of environmental quality

control.

2. Materials and Methods

2.1. Study area

Hallim Harbor, located in the north-western part of Jeju Island, is the center of coastal fisheries in Bukjeju County, and is composed of a long stretched outerport bulwark and two innerport ones. It is a good place for fisheries because it is a seasonal migration route and hibernating place for warm current fishes, has a lot of seaweed, and underground seawater eruptions. Its total water area of the inner harbor is 4.42×10^5 m², and its water depth is about 4 m inside the bulwark, generally about 10-12 m outside one and about 20 m at the north-western part of the outside one.²⁰⁾ It has been shown that the pollution level inside Hallim Harbor including general contaminants (e.g., T-N, T-P and COD) and butyltin compounds based on antifouling paints was comparable to that in other coastal areas of domestic and foreign countries, suggesting that anthropogenic pollution is by no means low.^{20,21)}

2.2. Sample collection

Surface sediment sampling was taken three times (June, September and December, 2001) only inside the harbor because outside the harbor, rock masses are present in a wide range and sediments are not. The surface sediments (0-4 cm) were collected at 6 stations (Fig. 1) by SCUBA diving, considering physical (e.g. bulwark, mooring sites of ships, etc) and sedimentary environments inside the harbor. The collected sediment samples were added to a precleaned wide mouth jar (5 cm I.D. x 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.

2.3. PAH analysis and quality control

The analytical procedures of PAHs in surface sediments followed Yim's method.¹⁶⁾ It consists of three steps: i) extraction of the components of interest from sediment samples, ii) clean-up of the extract, iii) qualitative and quantitative instrumental analysis with gas chromatography (GC) with a mass selective detector (MSD).

About 20 g of wet sediment sample and 30 g of anhydrous sodium sulfate (Yakuri Pure Chem., Japan) were well mixed and powered in

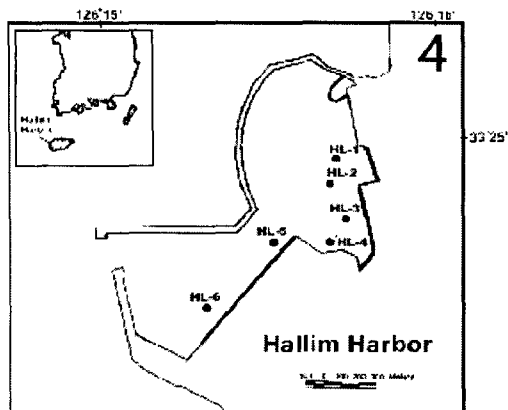


Fig. 1. Sampling stations of surface sediments inside Hallim Harbor of Jeju Island for the study of polycyclic aromatic hydrocarbons (PAHs) (■ : mooring site).

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 elemental 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 x 1 cm I.D.). The cleaned up fraction was reduced to a final volume of 1 mL by a high vacuum concentrator (Turbo Vap[®] 500), to which GC internal standard (hexamethylbenzene, 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 x 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 molecular ions of interest (electron impactor ionization at 70 eV). Three microliter samples were injected with a splitless mode. A 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 samples, were 55 ± 10 , 73 ± 7 , 78 ± 6 , $85 \pm 4\%$, respectively, which were within an acceptable range (40-120%).¹⁶⁾ 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 a 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.

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

2.4. 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 Ingram²²⁾ 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 μm and <63 μm (mud). The fraction >63 μm was dried and sieved using 1 ϕ (2 mm). Thus, the sediment particles were divided into three fractions, >2 mm, in the range of 63 μm ~2 mm and <63 μm , called gravel, sand and mud, respectively.

3. Results and Discussion

3.1. Distribution of PAHs

Total PAHs (as the sum of the 16 congeners

listed in Table 1) in surface sediments sampled three times (June, September and December, 2001) inside Hallim Harbor, ranged from 19 to 496 ng/g dw with a mean value of 245 ng/g dw (Table 2 and Fig. 2), indicating their variations with sampling station and time, which is considered to be influenced by several factors (e.g., their several source loads, ships activities, tidal currents, sedimentary environments, etc.). Relatively high and the lowest concentrations were detected at stations HL-2~HL-4 (mean value >300 ng/g dw) and at station HL-6 (mean value <50 ng/g dw), respectively.

Total concentrations of six PAHs (BaA, BbF, BkF, BaP, IcP and DaA) which are known as strong carcinogens⁷⁾, were in the range of 2~244 ng/g dw with a mean value of 93 ng/g dw (Table 2 and Fig. 3). They are distributed at higher levels at stations HL-2~HL-4 (mean value >100 ng/g dw) and at the lowest level at station HL-6 (mean value of 11 ng/g dw), like the distribution of total PAHs.

Among PAHs, the two compounds (Phe and Pyr) and the four compounds (Acy, Ace, Flu and DaA) were detected at higher and lower levels at all stations with their relative abundance (ratio of the sum of each PAH in parenthesis to total PAHs) of 18-33% and 3-8%, respectively.

The degree of sediment contamination by

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

PAHs	HL-1	HL-2	HL-3	HL-4	HL-5	HL-6
	Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)
Nap	4.4-20.0 (11.7)	8.5-16.6 (13.8)	9.3-94.0 (38.1)	10.5-11.4 (11.0)	8.4-41.4 (29.0)	2.5-13.5 (6.5)
Acy	ndc-5.0 (2.3)	nd-15.0 (10.0)	nd-4.4 (1.6)	0.9-11.6 (6.0)	nd-5.3 (2.4)	nd-0.4 (0.2)
Ace	nd-0.9 (0.4)	1.0-3.1 (2.0)	0.4-4.4 (1.9)	0.5-3.1 (2.0)	nd-7.8 (2.9)	0.3-1.5 (0.7)
Flu	nd-2.9 (1.8)	1.9-5.6 (3.9)	0.6-8.5 (4.0)	1.8-4.2 (3.0)	nd-5.3 (2.9)	0.5-0.9 (0.7)
Phe	4.4-18.6 (13.5)	20.7-43.0 (34.0)	33.2-66.2 (46.0)	15.4-43.8 (35.7)	9.9-65.5 (35.0)	4.7-9.2 (6.9)
Ant	2.3-18.1 (9.0)	3.5-28.0 (19.0)	6.6-12.8 (10.0)	7.4-27.3 (15.3)	2.3-12.9 (8.4)	0.3-1.3 (0.7)
Fle	8.4-16.5 (12.2)	18.8-25.1 (23.0)	20.0-37.1 (27.6)	25.8-42.8 (33.5)	10.7-30.8 (21.0)	2.0-7.0 (3.4)
Pyr	9.0-18.6 (14.0)	23.5-40.2 (35.5)	31.1-81.0 (50.6)	27.0-45.3 (36.8)	11.3-58.4 (33.4)	2.3-12.9 (7.1)
BaA	7.2-14.7 (9.8)	11.3-21.6 (16.4)	7.4-47.3 (25.2)	17.5-33.6 (23.2)	5.1-23.3 (14.2)	0.8-3.7 (1.9)
Chr	12.4-17.7 (14.7)	14.7-35.8 (27.9)	9.6-49.4 (30.1)	25.1-47.0 (34.7)	9.2-23.0 (18.4)	0.4-4.8 (2.0)
BbF	8.9-13.5 (10.1)	16.0-35.4 (23.5)	4.7-44.9 (24.9)	22.1-37.7 (27.5)	0.4-15.7 (7.5)	nd-4.2 (1.7)
BkF	8.7-14.7 (11.6)	14.2-38.9 (28.3)	nd-46.6 (22.7)	18.5-38.6 (26.6)	3.4-12.8 (9.5)	nd-4.2 (1.4)
BaP	11.8-13.4 (12.4)	16.3-49.4 (30.6)	1.5-55.9 (28.2)	24.3-49.4 (33.4)	4.4-15.3 (10.6)	nd-6.4 (2.3)
IcP	10.9-16.2 (12.8)	15.9-37.9 (28.6)	11.8-40.1 (24.9)	22.4-32.5 (25.4)	5.3-20.7 (12.4)	1.3-3.2 (2.0)
DaA	2.6-2.9 (2.7)	4.1-8.8 (7.0)	nd-9.4 (5.1)	5.9-9.0 (7.3)	1.8-5.0 (3.3)	0.9-2.7 (1.8)
BgP	6.7-14.2 (10.2)	17.3-42.1 (32.1)	7.5-40.9 (24.2)	24.4-36.5 (29.5)	7.6-20.4 (14.4)	0.6-7.8 (3.1)
ΣPAH ^a	128-197 (151)	191-446 (336)	275-496 (365)	272-467 (351)	156-326 (225)	19-72 (42)
ΣCar-PAH ^b	52-73 (61)	78-202 (150)	25-244 (131)	112-209 (149)	26-78 (57)	2-24 (11)

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

PAHs inside Hallim Harbor was compared with other marine aquatic systems (Table 3). Although the number of PAHs analyzed in this study may differ with study area, the 16 PAHs investigated in this study have been found in estuarine and marine sediments.⁸⁾ 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 extent.²³⁾

Comparing the contamination levels by the

mean value of total PAHs across the studies, the contamination levels inside Hallim Harbor appeared lower than those in Masan Bay¹⁶⁾, Kwangyang Bay¹⁷⁾ and Ulsan Bay⁸⁾ in Korea, Contou (Benin) in France⁵⁾, Northern Irish Sea-loughs¹¹⁾, the Baltic Sea²⁴⁾ and the Western Mediterranean Sea²⁶⁾, but higher than those in Kyeonggi Bay (Korea)¹⁷⁾ and Todos Santos Bay (Mexico)²³⁾. The value was comparable to those in Aquitaine (France)⁵⁾ and the Adriatic Sea.²⁵⁾

The contamination levels of carcinogenic PAHs inside Hallim Harbor by mean value

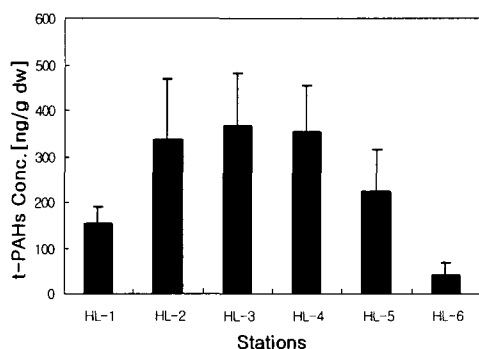


Fig. 2. Distribution of total PAHs (t-PAHs) in surface sediments of each station inside Hallim Harbor. The thick and thin bars indicate the mean concentration and standard deviation (SD), respectively.

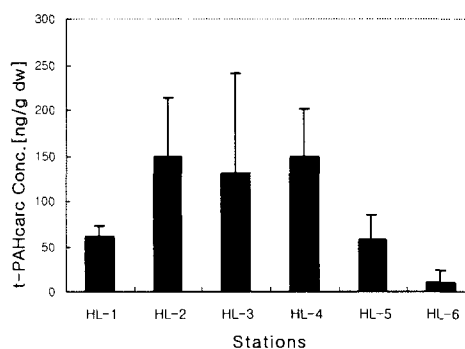


Fig. 3. Distribution of total carcinogenic PAHs (t-PAHcarc) in surface sediments of each station inside Hallim Harbor. The thick and thin bars indicate the mean concentration and standard deviation (SD), respectively.

Table 3. Comparison of total and carcinogenic PAH concentrations (ng/g dw) in surface sediments of this study with those in other areas

PAH	Location	n ^c	Range (Mean)	References
ΣPAH ^a	Inside Hallim Harbor, Jeju Island, Korea	16	19-467 (245)	This study
	Ulsan Bay, Korea	16	14-7108 (1052)	Moon et al. ⁸⁾
	Kwangyang Bay, Korea	13	171-1014 (408)	Yoo ¹⁸⁾
	Kyeonggi Bay, Korea	24	9-1400 (120)	Kim et al. ¹⁷⁾
	Masan Bay, Korea	24	151-1110 (562)	Yim ¹⁶⁾
	Todos Santos Bay, Mexico	16	8-813 (96)	Macias-Zamora et al. ²³⁾
	Northern Irish Sea-loughs	13	83-22960 (1930)	Guinam et al. ¹¹⁾
	Contou (Benin), France	14	25-1411 (487)	Soclo et al. ⁵⁾
	Aquitaine, France	14	4-853 (256)	Soclo et al. ⁵⁾
	Baltic Sea	15	720-1900 (1200)	Witt ²⁴⁾
	Adriatic Sea	12	18-580 (200)	Caricchia et al. ²⁵⁾
Western Mediterranean Sea	31	180-3200 (1300)	Lipiatou and Saliot ²⁶⁾	
ΣPAHcarc ^b	Inside Hallim Harbor, Jeju Island, Korea	6	2-244 (93)	This study
	Ulsan Bay, Korea	6	6-2396 (205)	Moon et al. ⁸⁾
	Masan Bay, Korea	6	51-910 (205)	Yim ¹⁶⁾
	Kyeonggi Bay, Korea	6	(9)	Kim et al. ¹⁷⁾
	Todos Santos Bay, Mexico	6	1-301 (25)	Macias-Zamora et al. ²³⁾

^asum of PAHs analyzed; ^bsum of six carcinogenic PAHs (BaA, BbF, BkF, BaP, IcP and DaA; ^cnumber of PAHs analyzed in each study

were lower than those in Masan Bay¹⁶⁾ and Ulsan Bay⁸⁾, but higher than those in Kyeonggi Bay¹¹⁾ and Todos Santos Bay (Mexico).²³⁾

Consequently, it is considered that the contamination levels by PAHs inside Hallim Harbor are low to moderate in comparison with

those in other areas in the world.

3.2. Biological by PAH contamination in sediments

As part of on-going studies associated with the NOAA (National Oceanic and Atmospheric Administration) National Status and Trends Program, NOAA has derived effects range-low (ER-L) and effects range-medium (ER-M) values for predicting the potential for adverse effects of persistent chemicals.²⁷⁾ From the results, NOAA has determined the distribution of sediment concentrations which were associated with any degree of biological effects to freshwater, estuarine and marine organisms. The 10th percentile and the 50th percentile of the distribution were identified as ER-L value and ER-M value, respectively. Although these values are not intended for use as regulatory guidelines, they provide useful benchmarks for assessing the biological effects of contaminated sediment.¹⁶⁾ The NOAA's ER-L and ER-M values for individual PAH and total PAHs are presented in Table 4.

As shown in Table 4, individual PAH and total PAHs in this study did not exceed the

ER-L values. As compared with other criteria, such as those based on apparent effects thresholds (AET)²⁸⁾ and empirical biota-sediment accumulation factors/equilibrium partitioning theory (e.g., WSSQC²⁹⁾ in Table 4), the surface sediment contamination by PAHs indicates substantial margins of safety. In conclusion, PAHs in surface sediments inside Hallim Harbor are distributed at lower levels that do not show the biological effects on marine organisms.

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

It was that the factors affecting the distribution of organic chemicals are particle size distribution, organic matter content and mineral composition, etc.³⁰⁾ In order to evaluate the distribution of sedimentary organic carbon and particle size to total PAHs concentration (Table 5), the relationship between each of them was investigated (Fig. 4 and 5). 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, ship activity, surrounding environment, etc.

Table 4. Comparison of effects-based and empirically-derived sediment quality guidelines with individual PAH concentration (ng/g dw) inside Hallim Harbor

PAH (ng/g dw)	ER-L ^a	ER-M ^a	AET ^b	WSSQC ^c	This study
Nap	160	2100	500	2000	4.4-9.4
Ace	16	500	150	320	nd-7.8
Flu	19	540	350	460	nd-8.5
Phe	240	1500	260	2000	4.4-16.2
Ant	85	1100	300	4400	2.3-28.0
Fle	600	5100	1000	3200	2.0-42.8
Pyr	670	2600	1000	20000	2.3-81.0
BaA	260	1600	550	2200	0.8-47.3
Chr	380	2800	900	2200	0.4-49.4
BaP	430	1600	700	1980	nd-55.9
DaA	63	260	100	240	nd-9.4
ΣPAH	4000	45000	22000		19-496

^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 value (Long et al.²⁷⁾); ^bapparent effects threshold (Long and Morgan²⁸⁾); ^cWashington State Sediment Quality Criteria (1991)²⁹⁾

Table 5. Total PAHs concentration, organic carbon content and particle size distribution in surface sediments inside Hallim Harbor

Station	Total PAHs (ng/g dw)	Organic carbon (%)	Particle size distribution (%)		
			Gravel	Sand	Mud
HL-1	128-197 (151)	1.0-1.6 (1.3)	11-52 (26)	38-54 (45)	10-43 (29)
HL-2	191-446 (336)	2.1-3.4 (2.8)	7-9 (8)	25-43 (34)	50-66 (58)
HL-3	275-496 (365)	1.8-3.8 (3.0)	14-56 (42)	16-28 (22)	21-57 (36)
HL-4	272-467 (351)	1.4-2.2 (1.7)	9-25 (18)	35-57 (45)	23-48 (37)
HL-5	156-326 (225)	1.4-2.8 (2.0)	33-56 (46)	35-61 (46)	2-15 (8)
HL-6	19-72 (42)	1.4-1.7 (1.6)	76-89 (83)	12-23 (16)	0-1 (1)
	19-496 (245)	1.0-3.8 (2.1)	7-89 (37)	12-61 (34)	0-66 (28)

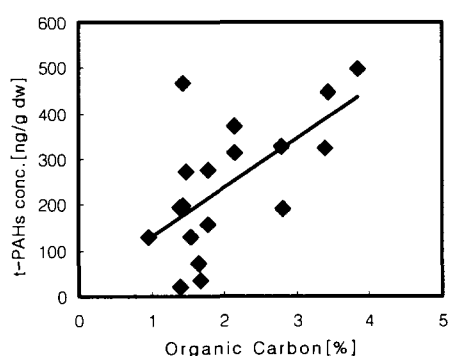


Fig. 4. Relationship between total PAHs concentration and organic carbon content in surface sediments inside Hallim Harbor.

Relatively good correlation coefficients (r) were obtained between total PAHs, and organic carbon and mud ($r = 0.621, 0.557$ for organic carbon and mud, respectively). However, very low ($r = 0.227$) and negative ($r = -0.559$)

correlations were obtained for sand and gravel, respectively. Similar results were found in Kyeonggi Bay¹⁷⁾ ($r = 0.754, -0.361, 0.274, 0.339$ for organic carbon, sand, silt and clay, respectively) and Kwangyang Bay¹⁸⁾ ($r = 0.520, -0.395, 0.389$ for organic carbon, 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 al.²³⁾ 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 al.¹¹⁾ also reported that high correlations between total PAHs concentration and % silty/clay (corresponding to mud content in this study) were observed for both Lame ($r = 0.806$) and Strangford ($r = 0.781$) loughs in surface

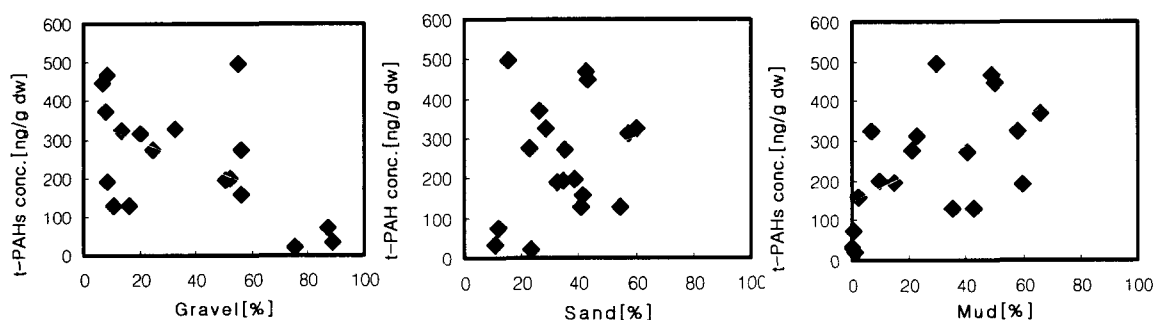


Fig. 5. Relationship between total PAHs concentration and particle size (gravel, sand and mud) in surface sediments inside Hallim Harbor.

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^{31,32}, 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 contents, although the correlation between them is not high because of several factors, such as sedimentary environments and presence of multiple sources of chemicals, etc..

3.4. 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 6, which were used by other investigators from various environments.^{5,11,16,33}

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

molecular weight (HMW) 4-6 ring PAHs (Flu, Pyr, BaA, Chr, BbF, BkF, BaP, IcP, DaA, BgP) over the low molecular weight (LMW) 2-3 ring PAHs (Nap, Acy, Ace, Flu, Phe, Ant). 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.^{11,16,33}

The values for this index obtained from the sediment samples of each station with sampling times, are shown in Table 6 and Fig. 6. It can be known that these index values varied according to sampling station and sampling time, but the values for the majority of the sediment samples were lower than 1 (values between 0.10 and 0.82), indicating pyrolytic origin contamination. Only, three sediment samples from the stations HL-3, HL-5 and HL-6 collected in December, 2001, revealed values higher than 1 (values between 1.38 and 3.00), indicating these three samples were contaminated by petrogenic PAHs. Especially, the value equal to 3.0 in the HL-6 sample collected at the time, seemed to indicate that the petrogenic contamination source was greater than the other two samples.

The ratios of Phe/Ant and Flu/Pyr, based on thermodynamic principle, are generally used to differentiate the pyrolytic and petrogenic origins of PAHs.^{5,6,11,18,33} 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 give useful information on the PAH origin.^{5,34} Phe is more thermodynamically stable

Table 6. The PAH origin indices at each station inside Hallim Harbor

Station	LMW/HMW ^a	Phe/Ant	Flu/Pyr	Chr/BaA
HL-1	0.10-0.50 (0.35) ^b	1.03-1.93 (1.57)	0.63-0.94 (0.84)	1.21-1.87 (1.60)
HL-2	0.20-0.32 (0.27)	0.49-4.44 (2.20)	0.57-1.07 (0.78)	1.30-2.03 (1.66)
HL-3	0.14-1.78 (0.73)	2.59-10.11 (5.45)	0.25-0.93 (0.67)	1.05-1.50 (1.28)
HL-4	0.16-0.32 (0.24)	1.10-3.94 (2.38)	0.84-0.96 (0.91)	1.40-1.72 (1.52)
HL-5	0.12-1.38 (0.72)	2.93-5.10 (4.13)	0.53-0.94 (0.72)	0.99-1.82 (1.48)
HL-6	0.23-3.00 (1.35)	5.34-19.61 (13.45)	0.67-0.87 (0.75)	0.46-1.30 (0.82)
	0.10-3.00 (0.61)	0.49-19.61 (4.86)	0.25-1.07 (0.78)	0.46-2.03 (1.39)

^athe ratio of sum of the low molecular weight 2-3 ring PAHs over sum of the highmolecular weight 4-6 ring PAHs;

^bthe value in the parenthesis indicates the mean of the range

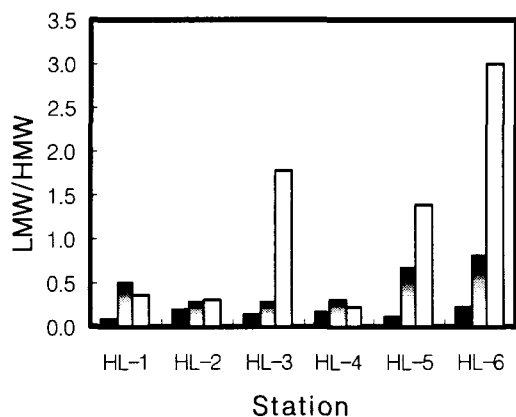


Fig. 6. The ratio of low molecular weight (LMW) PAHs to high molecular weight (HMW) PAHs at each station inside Hallim Harbor. The 1st, 2nd and 3rd bars at each station indicate the ratio of LMW/HMW at surface sediments collected in June, September and December, 2001, respectively.

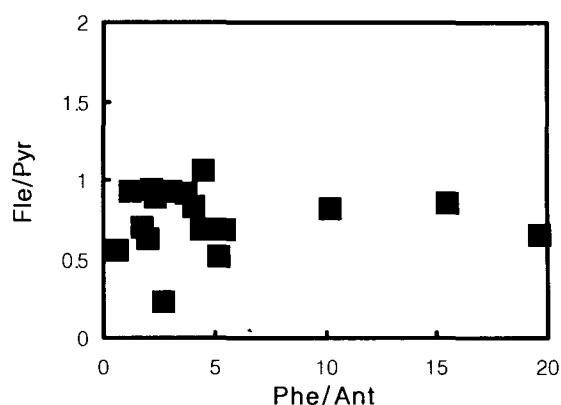


Fig. 7. Plot of Fle/Pyr against Phe/Ant for surface sediments inside Hallim Harbor.

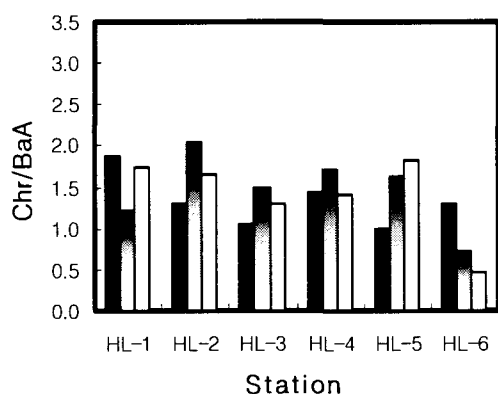


Fig. 8. The ratio of chrysene (Chr) to benzo [a]anthracene (BaA) at each station inside Hallim Harbor. The 1st, 2nd and 3rd bars at each station indicate the ratio of LMW/HMW at surface sediments collected in June, September and December, 2001, respectively.

than Ant, so a Phe/Ant ratio <10 is characteristic of PAH pyrolytic.¹¹⁾ Fle and Pyr are often associated and considered typical pyrogenic products generated from high temperature condensation of low molecular weight aromatic compounds.^{5,11)} 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 .^{5,11,35)} Pyr is more profuse in petroleum-derived PAHs. The

values of these two indices obtained from the surface sediments inside Hallim Harbor are shown in Table 6. The values of Phe/Ant ratio were in the range of 0.49-5.10 for most of the sediment samples, except for three sediment samples (from the station HL-3 collected in December, 2001 and from the station HL-6 collected in September and December, 2001) which showed values of 10.11, 15.30 and 19.61, indicating that most of the sediment samples collected in this study were contaminated by pyrolytic PAHs. In contrast, the values of Fle/Pyr were in the range of 0.25-0.96 for the majority of sediment samples, except for that (1.07) from station HL-2 collected in June, 2001, indicating petrogenic origin contamination. To investigate this further, both ratios were plotted against each other (Fig. 7). As shown in Fig. 7, it is difficult to discriminate the PAH origins with the values of these two indices. It is considered that the sediment contamination by PAHs inside Hallim Harbor is caused by both pyrolytic and petrogenic origins. This fact was also found in surface sediments around Kwangyang Bay, Korea, where in most of the sediment samples, the values of Phe/Ant ratio and Fle/Ant ratio were higher than 10 and 1, respectively.

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 to an

inversion of this tendency, i.e., Chr/BaA ratio = 1.^{5,35}) In addition, it has been reported that chrysenic derivatives are more stable than benzantracenic ones because of the possibility of the latter ones converting to the former ones.⁵⁾ The values of Chr/BaA ratio obtained from the sediment samples of each station with sampling time, are shown in Table 6 and Fig. 8. It can be known that these index values were in the range of 1.05-2.03 in most of the sediment samples, except for three sediment samples (from the station HL-5 collected in June, 2001 and from the station HL-6 collected in September and December, 2001) which showed the values of 0.99, 0.71 and 0.46, indicating that most of the sediment samples collected in this study were contaminated by petrogenic PAHs.

From an examination of the above four PAH origin indices, it can be concluded that sediment contamination by PAHs is ascribed to both pyrolytic and petrogenic origins, but not to just one.

4. Conclusions

The surface sediments sampled three times (June, September and December, 2001) at 6 stations inside Hallim Harbor of Jeju Island, Korea were analyzed to assess the distribution levels of 16 PAHs recommended by US-EPA and to suggest their possible origins. The sediment PAH concentrations in this study were in the range of 19-496 ng/g dw with a mean value of 245 ng/g dw. The levels were low to moderate, as compared with other areas in the world and do not appear to impose biological effects on marine organisms. The PAH distribution in surface sediments may be correlated with organic carbon and mud contents in sedimentary matrices to some extent. From the examinations of several PAH origin indices, it can be concluded that the sediment contamination by PAHs were ascribed to both pyrolytic and petrogenic origins.

Acknowledgements

This work was supported by the Brain Korea 21 Project of Cheju National University, 2002.

References

- 1) Mitra, S., R. M. Dickhut, S. A. Kuehl and K. I. Kimbrough, 1999, Polycyclic aromatic hydrocarbons (PAHs) source, sediment deposition patterns, and particle geochemistry as factors influencing PAH distribution coefficients in sediments of the Elizabeth River, VA, USA, *Mar. Chem.*, 66, 113-127.
- 2) Barrosa, E. N., G. Gold-Bouchot, O. Zapeta-Perez and J. L. Sericano, 1999, Polynuclear aromatic hydrocarbons in american oysters *Crassostrea virginica* from the Terminos Lagoon, Campeche, Mexico, *Mar. Pollut. Bull.*, 38, 637-645.
- 3) Lehr, R. E. and D. M. Jerina, 1977, Metabolic activation of polycyclic aromatic hydrocarbons, *Arch. Toxicol.*, 39, 1-6.
- 4) Woodhead, R. J., R. J. Law and P. Matthiessen, 1999, Polycyclic aromatic hydrocarbons in surface sediments around England and Wales, and their possible biological significance, *Mar. Pollut. Bull.*, 38, 773-790.
- 5) Soclo, H. H., P. Garrigues and M. Ewald, 2000, Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas, *Mar. Pollut. Bull.*, 40, 387-396.
- 6) Neff, J. M., 1979, Polycyclic Aromatic Hydrocarbons in the Aquatic Environment, Sources, Fates, and Biological Effects, Applied Sciences, London, Great Britain, 262pp.
- 7) McElroy, A. E., J. W. Farrington and J. M. Teal, 1999, Bioavailability of polycyclic aromatic hydrocarbons in the aquatic environment, In Vanarasi, U. (ed.), *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*, CRC Press, Boca Raton, FL, 1-40pp.
- 8) Moon, H. B., H. G. Choi, S. S. Kim and P. Y. Lee, 2001, Level and origin of polycyclic aromatic hydrocarbons (PAHs) in sediments from Ulsan Bay, Korea, *Environ. Sci.*, 10(S-3), 113-119.
- 9) Mill, T., W. R. Mabey, B. Y. Lan and A. Baraze, 1981, Photolysis of polycyclic aromatic hydrocarbons in water, *Chemosphere*, 10, 1281-1290.
- 10) Cerniglia, C. E. and M. A. Heitkamp, 1989,

- Microbial degradation of PAH in the aquatic environment, In Vanarasi, U. (ed.), *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*, CRC Press, Boca Raton, FL, 41-68pp.
- 11) Guinan, J., M. Charlesworth, M. Service and T. Oliver, 2001, Sources and geochemical constraints of polycyclic aromatic hydrocarbons (PAHs) in sediments and mussels of two northern Irish Sea-loughs, *Mar. Pollut. Bull.*, 42, 1073-1081.
 - 12) Smith, J. N. and E. M. Levy, 1990, Geochronology of polycyclic aromatic hydrocarbon contamination in sediments of the Saguenay Fjord, *Environ. Sci. Technol.*, 24, 874-879.
 - 13) Ghosh, U., J. S. Gillette, R. G. Luthy and R. N. Zare, 2000, Microscale location, characterization and association of polycyclic hydrocarbons on harbour sediment particles, *Environ. Sci. Technol.*, 34, 1729-1736.
 - 14) Kam, S. K., L. S. An, E. I. Cho and K. S. Choi, 1999, Contamination and bioaccumulation of butyltin compounds inside Cheju Harbor of Cheju Island, Korea, *The East China Sea*, 2, 125-144.
 - 15) Lee, K. S., I. Noh, C. S. Lim and S. D. Chu, 1998, The high performance liquid chromatography (HPLC) analysis of polycyclic aromatic hydrocarbons in oysters from the intertidal and subtidal zones of Chinhae Bay, Korea, *Environ. Sci.*, 2, 57-68.
 - 16) Yim, U. H., 1998, Contamination of polycyclic aromatic hydrocarbons (PAHs) in Masan Bay, Korea, MS Thesis, Seoul National University, 99pp.
 - 17) Kim, G. B., K. A. Maruya, R. F. Lee, J. H. Lee and C. H. Koh, 1999, Distribution and sources of polycyclic aromatic hydrocarbons in sediments from Kyeonggi Bay, Korea, *Mar. Pollut. Bull.*, 38, 7-15.
 - 18) You, Y. S., 2000, A study on the pollution of polycyclic aromatic hydrocarbons (PAHs) in sediments around Kwangyang Bay, MS Thesis, Yosu National University, 69pp.
 - 19) Park, J. H., S. Y. Kim, S. H. Ji and G. Ok, 2002, Distribution characteristics and origin of PAHs in sediments from Nakdong River estuary and adjacent coast, Abstract of 2002 KSfEA Autumn Meeting, Cheju National University, 29-30 November, 151-155pp.
 - 20) Jeju-Do, 1997, Report on implementation of environmental index for environment-friendly development in Jeju Island, 245-268pp.
 - 21) Kam, S. K., H. J. Kim, C. G. Hu, Y. C. Choi and M. G. Lee, 2003, Distribution of butyltin compounds in surface sediments inside Hallim Harbor of Jeju Island, *J. Environ. Sci.*, 12(7), 753-762.
 - 22) Ingram, R. L., 1971, Sieve analysis, In Carver, R. E. (ed.), *Procedures in Sedimentary Petrology*, Wiley Interscience, Athens, GA, 47-67pp.
 - 23) Macias-Zamora, J. V., E. Mendoza-Vega and J. A. Villaescusa-Celaya, 2002, PAHs composition of surface marine sediments: a comparison of potential local sources in Todos Santos Bay, B.C., Mexico, *Chemosphere*, 46, 459-468.
 - 24) Witt, 1995, Polycyclic aromatic hydrocarbons in water and sediment of the Baltic Sea, *Mar. Pollut. Bull.*, 31, 237-248.
 - 25) Caricchia, A. M., S. Chiavarini, C. Cremisini, F. Marrini and R. Morabito, 1993, PAHs, PCBs, and DDE in the Northern Adriatic Sea, *Mar. Pollut. Bull.*, 26, 581-583.
 - 26) Lipiatou, E. and A. Saliot, 1991, Fluxes and transport of anthropogenic and natural polycyclic aromatic hydrocarbons in the western Mediterranean Sea, *Mar. Chem.*, 32, 51-71.
 - 27) Long, E. R., D. D. MacDonald, S. L. Smith and F. D. Calder, 1995, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments, *Environmental Management*, 19, 81-97.
 - 28) Long, E. R. and L. G. Morgan, 1990, The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Programs, NOAA Technical Memorandum NOS OMA 52, NOAA Office of Oceanography and Marine Assessment, Ocean Assessment Division, Seattle, WA, 173pp.
 - 29) Washington State Sediment Quality Criteria, 1991, *Sediment Management Standards*,

- WAC, Dept. of Ecology, Washington State, April 1991, 173-204pp.
- 30) Lambert, S. M., 1967, Functional relationship between in soil and chemical structure, J. Agric. Food Chem., 15, 572-576.
- 31) Macias- Zamora, J. V., 1996, Distribution of hydrocarbons in recent marine sediments off the coast of Baja California, Environ. Pollut., 2, 45-53.
- 32) Ramirez-Alvarez, N., 2001, Distribution of de los alquil benceno lineales (ABL), trazados de la frontera Mexico-USA a Punta Banda, Ensenada, Baja California, MS Thesis, 76pp.
- 33) Baumard, P., H. Budzinski, P. Garrigues, H. Dixer and P. D. Hansen, 1999, Polycyclic aromatic hydrocarbons in recent sediments and mussel (*Mytilus edulis*) from the Western baltic Sea: occurrence, bioavailability and deasonal variations, Mar. Environ. Res., 47, 17-47.
- 34) Gschwend, P. M. and R. A. Hites, 1981, Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States, Geochim. Cosmochim. Acta, 45, 2359-2367.
- 35) Parlanti, E., 1990, Utilisation des hydrocarbures comme traceurs d'origine de la matiere organique sedimentaire en milieu marin, Etude du Golfe du Lyon et du Golfe de Gascogne (Programme Ecomarge), Ph. D Thesis Nr 495, University Bordeaux I, Bordeaux, France, 289pp.