

The High Performance Liquid Chromatography (HPLC) Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) in Oysters from the Intertidal and Subtidal Zones of Chinhae Bay, Korea

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in marine environments. PAHs enter estuarine and nearshore marine environment via several routes such as combustion of fossil fuels, domestic and industrial effluents and oil spills. PAHs have been the focus of numerous studies in the world because they are potentially carcinogenic, mutagenic, and teratogenic to aquatic organisms and humans from consuming contaminated food. However, one can hardly find any available data on PAH content in marine organisms in Korea.

The present study was carried out in order to determine PAH content in oysters from the intertidal and subtidal zones of Chinhae Bay, which is located in near urban communities and an industrial complex, and the bay is considered to be a major repositories of PAHs. 16 PAHs were analyzed by High Performance Liquid Chromatography (HPLC) with uv/vis and fluorescence detectors in oysters: they are naphthalene (NPTHL), acenaphthylene (ANCPL), acenaphthene (ACNPN), fluorene (FLURN), phenanthrene (PHEN), anthracene (ANTHR), fluoranthene (FLRTH), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHRY), benzo(b)-fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DahA), benzo(g,h,i)perylene (BgHiP) and indeno(1,2,3,-cd)pyrene (I123cdP). The PAH contents in oysters from the intertidal and subtidal zones of Chinhae Bay ranged from < 0.1 to 992.0 $\mu\text{g}/\text{kg}$ (mean $69.8 \pm 9.8 \mu\text{g}/\text{kg}$).

Key words : polycyclic aromatic hydrocarbon, high performance liquid chromatography, oyster, Chinhae Bay.

1. Introduction

Nowadays in Korea, public concern about oil pollution is greatly increasing because there have been many oil tanker accidents (e.g. SEA PRINCE spilled 700 tons of bunker C on July of 1995, YEO-MYUNG HO spilled 48 tons of bunker C on August of 1995, CHEI 1 YOU-IL HO spilled 700 tons of bunker C on September of 1995, HONAM-SAPPHIRE spilled 1,200 tons of crude

oil on November of 1995) in southern and western coastal areas of Korea.

Polycyclic aromatic hydrocarbons (PAHs) consist of hydrogen and carbon arranged in the form of two or more fused benzene rings in linear, angular, or cluster arrangements with unsubstituted groups possibly attached to one or more rings (Eisler, 1987). Of aromatic hydrocarbons, PAHs are now becoming a public concern, because they are potentially carcinogenic, mutagenic and teratogenic

to aquatic organisms and humans from consuming contaminated food (Richards, 1982; Mix, 1984).

However, we can't find any available data on the levels of PAHs concentrated in marine organisms in Korea, even though it is urgent to accumulate a database on spatial and temporal distributions of PAHs in marine flora and fauna for environmental and sanitary reasons. Because PAHs are ubiquitous, humans are exposed to these chemicals as part of everyday living.

Through domestic and industrial effluents, oil spills, incomplete combustion of fossil fuels, forest and brush fires, terrestrial contributions and natural sources such as biosynthesis by plant and microorganisms, PAHs enter the marine environment. In addition, they are widespread in aquatic environment. However, oil spills and incomplete combustion of fossil fuels are major sources of PAHs (Neff, 1985; Rainio, 1986). They

are typically adsorbed by fine particulate material suspended in estuarine waters and sediment seafloor (Law, 1992).

The purpose of this study is to determine the PAH content of oysters (*Crassostrea gigas*) living in the intertidal and subtidal zones of Chinhae Bay in Korea, by developing the methodology of HPLC analysis of PAHs in oysters in the coastal areas of Korea.

2. Materials and Methods

2.1. Study area

The study area, Chinhae Bay (Fig. 1) with a total area of nearly 637 km², includes several smaller bays such as Masan Bay, Haengam Bay, Chindong Bay, etc. The depths of the study area

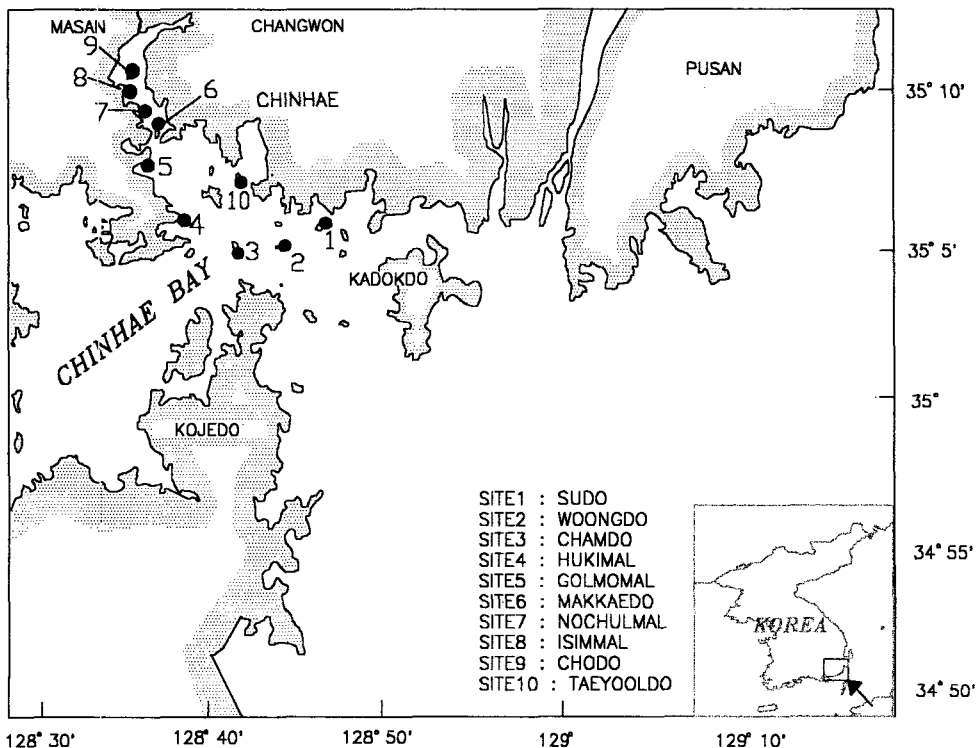


Fig. 1. Location of sampling sites in Chinhae Bay.

range from 5 m to 20 m.

Chinhae Bay is located in near the urban communities of Masan and Changwon industrial complex. There are many small and medium-sized factories producing textiles, metalworks, machines, electronics, petrochemical, products, automobiles, ships, etc. Accordingly, vast amounts of urban runoff, and domestic and industrial wastewater have been discharged into the bay and subsequently chronically contaminated the study area via several streams.

For many years, this area has been the recipient of various environmental injuries because of rapidly growing urban and industrial developments. The cities of Masan, Changwon and Chinhae surrounding Chinhae Bay to the north and east, are heavily populated areas. Total population around Chinhae Bay is over 1.1 million, and approximately 3×10^5 tons/day of municipal and industrial wastewater currently are discharged into the Chinhae Bay (Ministry of Environment, 1991). The COD load of 45 tons/day was measured to be mainly due to discharges from Masan and Changwon City (Lee, 1993).

As a matter of course, red tides and summer oxygen deficiencies have frequently occurred in this study area (Park, 1982; Hong, 1987).

2.2. Sampling of oysters

Oyster (*Crassostrea gigas*) samples were collected at 10 sites (Fig. 1) from the intertidal and subtidal zones of the Chinhae Bay, during October of 1996. Samples could not be found in site 1. To avoid contamination by the discharging water from the engine of the sampling boat used, care was taken while collecting samples.

Samples collected in the study area were wrapped in aluminum foil, placed in an icebox and brought to the lab, and then stored frozen in a refrigerator at -20°C for a couple of weeks prior

to analysis.

2.3. The extraction of PAHs

HPLC grades of hexane, acetone, diethylether, petroleum ether, methanol, dimethylsulfoxide, cyclohexane, etc. were used for all extraction procedures.

Glassware was washed in diluted detergent and rinsed twice with distilled water, followed by 90 min combustion at 560°C . Just before use, glassware was rinsed with cyclohexane (Smith, 1987).

For analysis, the oysters were partially thawed, and the shells were removed. The tissue of the oysters were homogenized with macerator. A sample of 20 g (wet wt) was taken from each homogenized oyster and was dried with anhydrous sodium sulfate (Na_2SO_4).

The hydrocarbons and the fats were Soxhlet-extracted with a mixture of hexane, acetone, diethylether, and petroleum ether (2.5 : 7.5 : 1 : 9, v/v) for 6 hours at $40 \sim 60^\circ\text{C}$ (Rainio, 1986). The solvent was then evaporated to near dryness at 40°C with a rotary evaporator.

A mixed solvent consisting of 150ml of methanol containing 7 g of potassium hydroxide was added to the fatty residue and the mixture was refluxed for saponification in darkness for 3 hours, and then 50ml of water was added. For digestive the methanol potassium hydroxide solution was cooled and separated with a separating funnel. Then the solution was replicated three times with 50ml of cyclohexane (Smith, 1984; Smith, 1987).

Soxhlet and refluxing apparatus were wrapped with aluminum foil to prevent hydrocarbons from being affected by light, because hydrocarbons can be altered by photochemical oxidation. (Lee, 1978; Tjessem, 1984; Barth, 1984; Berthou, 1985; Ducreux, 1986).

To separate PAHs from the aliphatic hydrocarbons, the liquid-liquid extraction procedure

developed by Natusch and Tomkins (1978) was applied. The dimethylsulfoxide (DMSO) layers, which contained the PAHs, were then combined. For clean up of PAHs, two volumes of water were added to the combined DMSO extracts.

The resulting solution was partitioned three times with equal volumes of cyclohexane. The cyclohexane layers were washed once with equal amounts of water (Rainio, 1986), and were dried nearly to a volume of 1.5ml with a rotary evaporator at 40°C, and then the sample was filtered through a 0.45µm PVDF filter (Whatman).

Finally the samples were concentrated to a final volume of approximately 1ml under a stream of nitrogen gas, and the sample vials were stored in the freezer prior to analysis by HPLC.

2.4. HPLC system employed in the study

The analysis of PAHs was carried out by reverse phased HPLC (Linear Instruments co.) using a gradient elution. The HPLC system for the analysis of PAHs consists of a binary solvent delivery system (Linear Instruments Model S-1100), an automatic gradient controller (Linear Instruments Model S-2000), an injector with a 20 µl sample loop fitted with a Spherisorb S5 ODS 2 column (4.6 mm. × 25 cm, 5µm particle size).

Solvent A (acetonitrile) and solvent B (distilled water) were utilized as mobile phases. Gradients of Binary system, are programmed as follows; solvent A 70% for the initial condition, and then solvent A 80% at 12 min, solvent A 90% at 15 min, solvent A 100% at 20 min, followed by an isocratic hold until all PAH peaks were eluted. The flow rate was held constant at 1.5 ml/min under the condition of 0.5 bar pressure.

Each sample was injected by a 25µl syringe. Analytical blank tests were carried out between each sample run and no analytical contamination was observed for the HPLC system.

The peaks of PAHs were identified and quantified simultaneously using a fluorescence detector (Model LC 304 fluorescence detector) and uv/vis detector (Model 200 uv/vis detector). The fluorescence detector was excited at 270 nm and emitted at 400 nm, and the absorption of uv/vis detection was set at 254 nm.

The management of chromatograms, integration and calibration of data were carried out using Peaksimple Serial Data Program system (SRI Model 202).

3. Results and Discussion

















3.1. The analysis of PAHs in the standard solution and samples.

PAH assemblage in oysters analyzed by HPLC for this study consists of naphthalene (NPHTL), acenaphthylene (ANCPL), acenaphthene (ACNPN), fluorene (FLURN), phenanthrene (PHEN), anthracene (ANTHR), fluoranthene (FLRTH), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHRY), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DahA), benzo(g,h,i)perylene (BghiP) and indeno-(1,2,3,-cd)pyrene (I123cdP). The chemical formula, structure, and retention time of each compound of PAHs are summarized in Table 1.

In the present study, certified reference material was used for verification of PAHs and each PAH was identified on the basis of retention time marked in the chromatograms. The PAHs were quantified by comparison of the fluorescence and uv/vis detector responses of the samples with the corresponding peaks of the standard solution (Supelco : Lot No LA-53950).

Most of the parts of the separated of individual PAHs in HPLC systems with the standard solution was satisfactory; NPHTL, ANCPL, PHEN, ANTHR,

Table 1. The chemical formulas, structures and retention times (Rt) of PAHs analyzed in the study.

No.	COMPOUND (ABBREV)	ALTERNATIVE NAME	FORMULAR (MW)	STRUCTURE	Rt (min) ^a
				mw : molecular weight	
1	naphthalene (NPTHL)		C ₁₀ H ₈ (128)		5.12
2	acenaphthylene (ANCPL)		C ₁₂ H ₈ (152)		5.46
3	acenaphthene (ACNPN)		C ₁₂ H ₁₀ (154)		7.35
4	fluorene (FLURN)		C ₁₂ H ₁₀ (166)		7.50
5	phenanthrene (PHEN)		C ₁₄ H ₁₀ (178)		8.45
6	anthracene (ANTHR)		C ₁₄ H ₁₀ (178)		9.35
7	fluoranthene (FLRTH)		C ₁₆ H ₁₀ (202)		11.24
8	pyrene (PYR)		C ₁₆ H ₁₀ (202)		12.32
9	benzo(a)anthracene (BaA)	1,2 Benzanthracene	C ₁₈ H ₁₂ (228)		13.21
10	chrysene (CHRY)		C ₁₈ H ₁₂ (228)		15.03
11	benzo(b)fluoranthene (BbF)	3,4 Benzfluoranthene	C ₂₀ H ₁₂ (252)		18.15
12	benzo(k)fluoranthene (BkF)	11,12 Benzfluoranthene	C ₂₀ H ₁₂ (252)		18.31
13	benzo(a)pyrene (BaP)	3,4 Benzopyrene	C ₂₀ H ₁₂ (252)		19.22
14	dibenz(a,h)anthracene (DahA)	1,2,5,6 Dibenzanthracene	C ₂₂ H ₁₄ (278)		20.13
15	benzo(g,h,i)perylene (BgHiP)	1,12 benzperylene	C ₂₂ H ₁₂ (276)		21.12
16	indeno(1.2.3-cd)pyrene (I123cdP)	o-Phenyleneperylene	C ₂₂ H ₁₂ (276)		21.39

^aThe Retention times of PAHs analyzed were drawn from fluorescence detection, except ANCPL and BgHiP which were drawn from uv/vis detection.

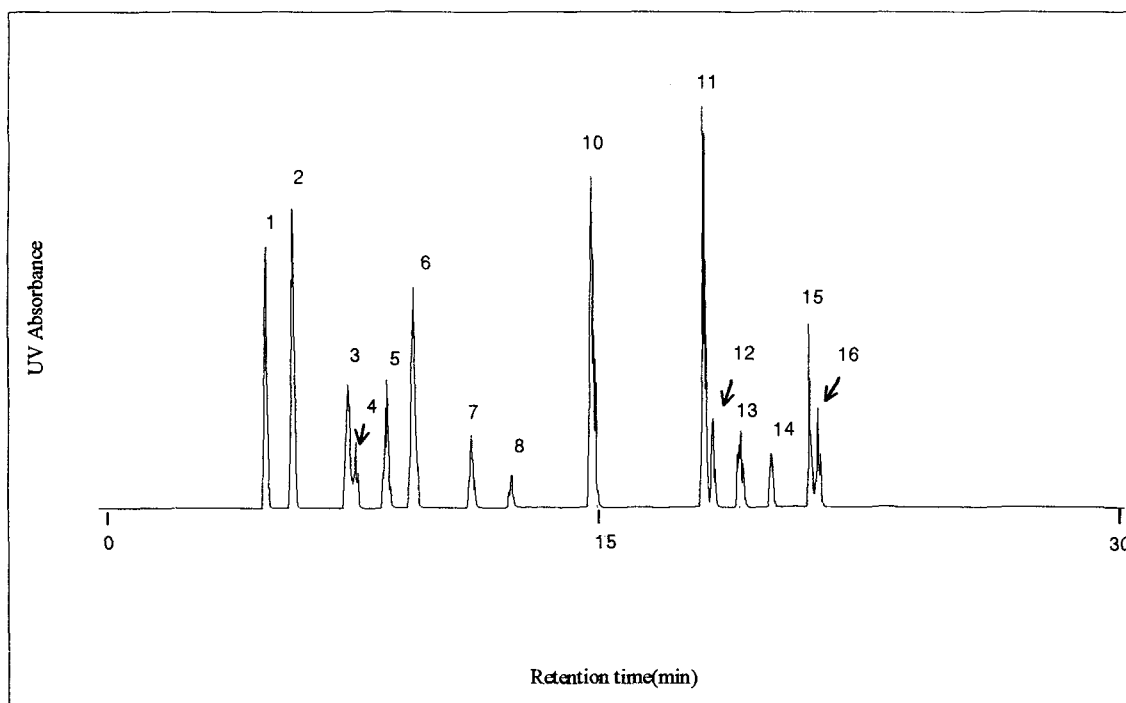


Fig. 2. Chromatogram of PAH standard solution by HPLC with uv/vis detection. BaA was not eluted at 254 nm. The PAHs were numbered identically with those represented in Table 1.

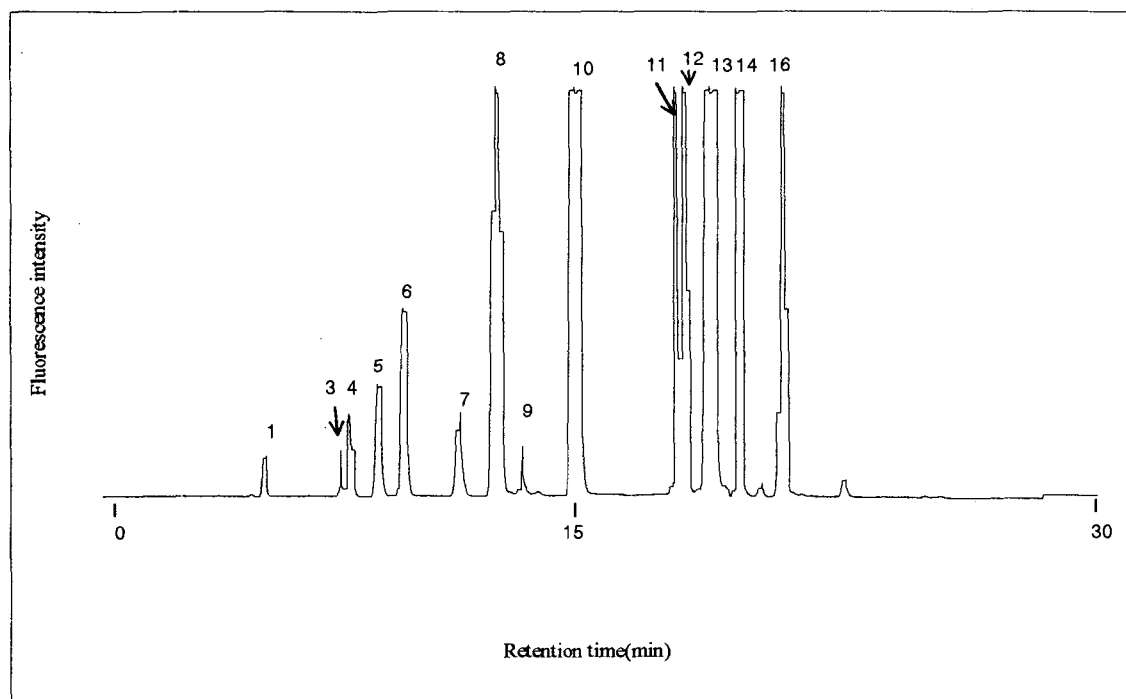


Fig. 3. Chromatogram of PAH standard solution by HPLC with fluorescence detection. ANCP and BghiP were not eluted under the wavelength setting (excitation 270 nm; emission 400 nm). The PAHs were numbered identically with those represented in Table 1.

FLRTH, PYR, BaA, CHRY, BaP and DahA were almost completely separated, while ACNPN, FLURN, BbF, BkF, BghiP, and I123cdP were not sharply separated with both fluorescence and uv/vis detection (Fig. 2 & 3).

When standard solution was analyzed with the uv/vis detector at 254 nm, the compound sets of ACNPN and FLURN, BbF and BkF, BghiP and I123cdP were not sharply separated with each other, and BaA could not be eluted.

ANCPL and BghiP were not eluted in the standard solution by the fluorescence detector under the wavelength set (Excitation: 270, Emission: 400), and the compound sets of ACNPN and FLURN, BbF and BkF were not separated well in uv/vis detection either. However, the

peaks of the rest of the PAHs could be clearly separated. BghiP can not be eluted with I123cdP by fluorescence detection (Fig. 3).

The fluorescence detector was much more sensitive than the uv/vis detector for the analysis of PAHs. Therefore, the fluorescence detector was used for the purpose of quantification of each PAH. However, the peaks of ANCPL and BghiP were quantified using the uv/vis detector at 254 nm, because the two peaks were not eluted by the fluorescence detector, as mentioned before.

The representative chromatograms of PAHs of oysters analyzed by fluorescence detector were presented in Fig. 4. The concentrations of PAHs in oysters analyzed and quantified by the HPLC system are summarized in Table 2 and 3.

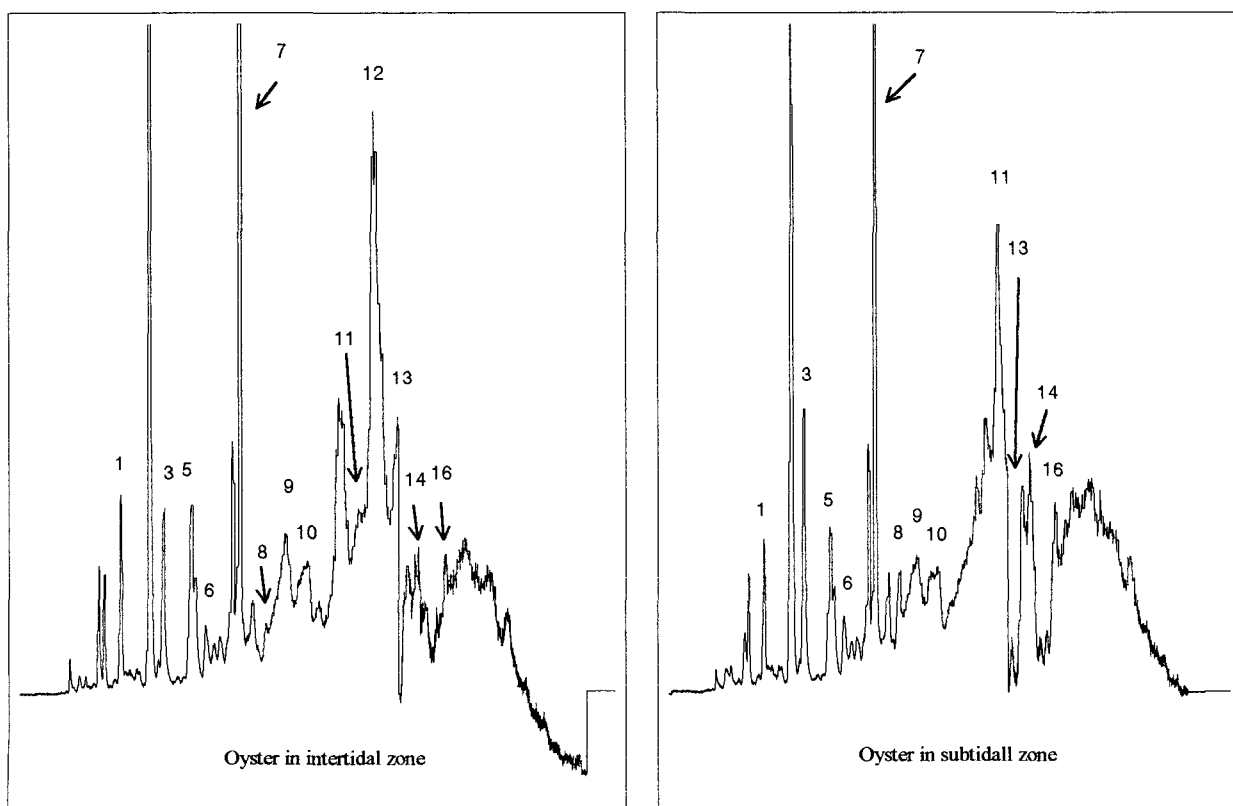


Fig. 4. Chromatograms of PAHs in oysters by HPLC with fluorescence detector at site 3.

Table 2. The concentration ($\mu\text{g}/\text{kg}$ wet wt) of PAHs in oysters from the intertidal zone determined by fluorescence detection (Excitation 270 nm : Emission 400 nm).

Site	NPThL	ANCPL*	ACNPN	FLURN	PHEN	ANTHR	FLRTH	PYR	BaA	CHRY	BbF	BkF	BaP	DahA	I123cdP	Total PAHs
Site 2	85.0	99.5	410.0	-	5.0	2.5	11.5	0.1	100.5	0.1	10.5	6.0	1.0	0.2	0.5	732.4
Site 3	155.0	38.5	586.5	-	9.5	5.0	32.0	0.1	146.5	0.1	2.0	15.0	3.0	0.2	0.5	993.8
Site 4	117.0	1.0	434.0	-	8.5	14.0	28.5	0.1	146.0	0.5	-	7.5	1.5	0.4	0.5	868.4
Site 5	92.5	142.5	667.0	-	8.5	11.5	29.0	0.1	102.0	2.5	-	16.0	3.5	1.0	0.5	1,076.6
Site 6	97.5	47.0	294.0	-	6.0	6.5	19.5	0.5	53.0	0.2	23.0	-	2.0	0.5	0.5	550.2
Site 7	62.5	49.5	695.0	-	8.5	6.0	19.0	0.1	112.5	0.1	29.0	-	1.0	-	0.5	983.2
Site 8	93	125.5	400.5	-	7.5	4.0	17.5	0.15	50.5	0.1	-	1.0	0.5	0.5	0.5	702.3
Site 9	111.5	96.5	297.5	-	8.0	13.0	33.5	0.5	48.5	0.1	-	1.0	1.0	-	0.5	611.6
Site 10	132.5	84.5	830.0	-	7.0	14.5	43.0	-	603.0	1.5	-	28.5	3.5	1.0	1.5	1,750

- : Concentration below the detection limits or not detected.

* : Concentration determined by uv/vis detection (uv = 254 nm).

Table 3. The concentration ($\mu\text{g}/\text{kg}$ wet wt) of PAHs in oysters from the subtidal zone determined by fluorescence detection (Excitation 270 nm : Emission 400 nm).

Site	NPThL	ANCPL*	ACNPN	FLURN	PHEN	ANTHR	FLRTH	PYR	BaA	CHRY	BbF	BkF	BaP	DahA	I123cdP	Total PAHs
Site 2	43.0	62.5	295.5	-	3.5	1.0	0.5	0.1	175.5	0.5	9.5	1.0	1.0	0.1	0.5	594.2
Site 3	119.5	74.0	922.0	-	8.0	5.5	32.0	0.5	61.0	0.1	24.5	-	2.5	0.5	0.2	1,250.2
Site 4	85.0	150.5	490.0	-	9.5	12.5	32.5	0.5	61.5	0.5	-	1.5	2.0	0.4	0.5	846.8
Site 5	170.5	72.5	493.0	-	11.0	7.5	25.5	0.2	63.0	0.2	-	6.0	5.5	0.2	1.0	855.2
Site 6	83.5	68.5	343.0	-	5.5	11.5	28.5	0.5	77.0	0.5	-	13.0	2.5	1.0	0.5	635.4
Site 7	108.5	76.5	370.0	-	10.5	7.5	19.5	0.1	123.0	0.5	1.0	41.0	8.0	0.1	0.2	766.4
Site 8	64.5	181.5	538.0	-	6.0	3.5	22.0	-	122.5	0.2	-	1.0	1.0	1.0	0.5	941.7
Site 9	95.5	56.5	617.0	-	6.5	9.0	26.0	-	65.5	0.3	-	1.0	1.0	-	0.5	878.8
Site 10	112.0	53.5	619.0	-	7.5	8.5	31.0	0.2	314.0	1.0	-	16.0	1.0	1.5	1.5	1,166.7

- : Concentration below the detection limits or not detected.

* : Concentration determined by uv/vis detection (uv = 254 nm).

3.2. Mean concentrations of PAH compounds

The predominant group of PAH compounds in oysters from the intertidal zone consisted of ACNPN ($512.7 \pm 63.1 \mu\text{g}/\text{kg}$), NPThL ($105.2 \pm 9.1 \mu\text{g}/\text{kg}$), ANCPL ($88.2 \pm 12.2 \mu\text{g}/\text{kg}$) and BaA ($151.4 \pm 57.9 \mu\text{g}/\text{kg}$). The second dominant group of PAHs consisted of FLRTH ($25.9 \pm 3.27 \mu\text{g}/\text{kg}$), BbF ($16.1 \pm 6.1 \mu\text{g}/\text{kg}$), ANTHR ($8.6 \pm 1.6 \mu\text{g}/\text{kg}$), PHEN ($7.6 \pm 0.27 \mu\text{g}/\text{kg}$) and BkF ($10.7 \pm 3.7 \mu\text{g}/\text{kg}$). And the least dominant group of PAHs

consisted of BaP ($1.9 \pm 0.3 \mu\text{g}/\text{kg}$), PYR ($0.2 \pm 0.1 \mu\text{g}/\text{kg}$), DahA ($0.5 \pm 0.1 \mu\text{g}/\text{kg}$), I123cdP ($0.6 \pm 0.1 \mu\text{g}/\text{kg}$), CHRY ($0.5 \pm 0.2 \mu\text{g}/\text{kg}$) and FLURN (not detected).

The same pattern of concentration of PAHs was shown in the oysters from the subtidal zone as from the intertidal zone; the predominant group consisted of ACNPN ($520.8 \pm 63.1 \mu\text{g}/\text{kg}$), NPThL ($98.0 \pm 12.1 \mu\text{g}/\text{kg}$), ANCPL ($88.4 \pm 15.1 \mu\text{g}/\text{kg}$) and BaA ($118.1 \pm 27.8 \mu\text{g}/\text{kg}$). The second dominant group consisted of FLRTH ($24.2 \pm 3.3 \mu\text{g}/\text{kg}$), BkF ($10.1 \pm 4.9 \mu\text{g}/\text{kg}$), BbF (11.7 ± 7.0

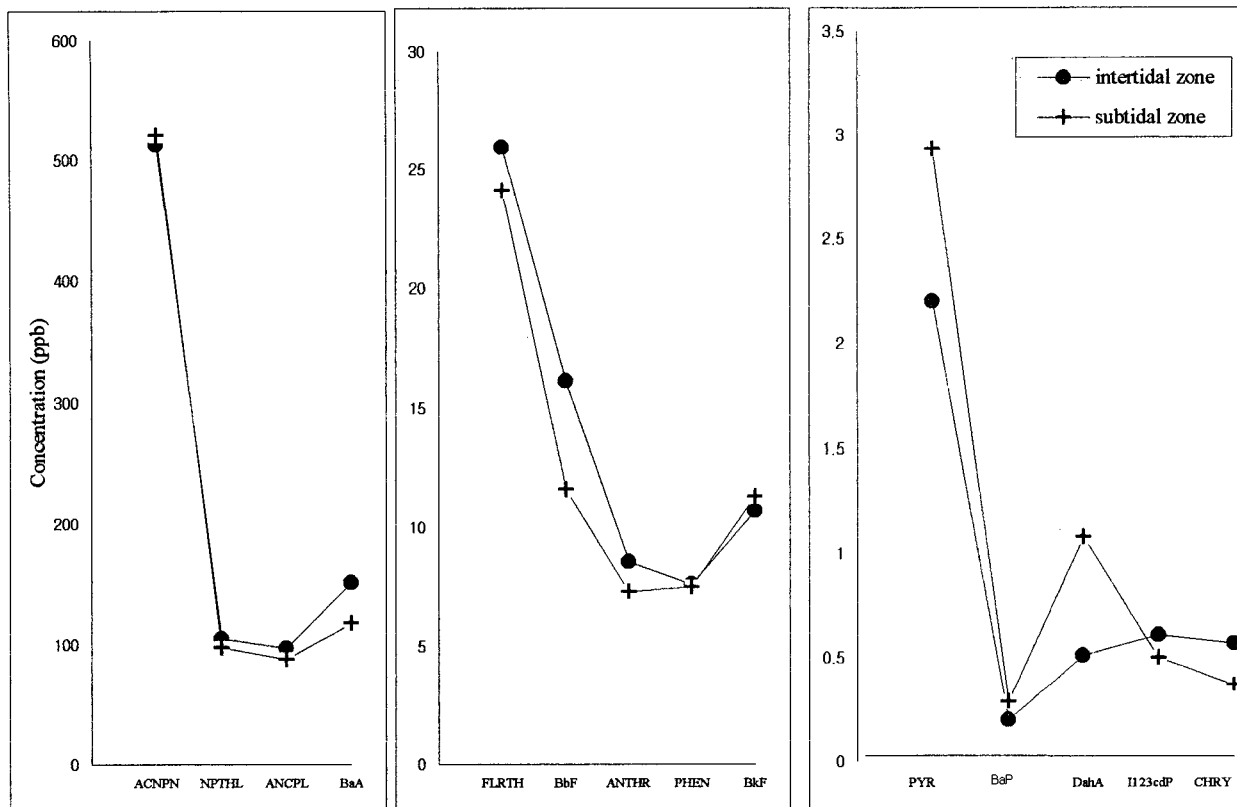


Fig. 5. The mean concentrations of PAH compounds in oysters from the intertidal and subtidal zones.

$\mu\text{g}/\text{kg}$), ANTHR ($7.3 \pm 1.22 \mu\text{g}/\text{kg}$), PHEN ($7.6 \pm 0.8 \mu\text{g}/\text{kg}$). And the least dominant group of PAHs consisted of BaP ($2.7 \pm 0.8 \mu\text{g}/\text{kg}$), PYR ($0.2 \pm 0.1 \mu\text{g}/\text{kg}$), DahA ($0.5 \pm 0.1 \mu\text{g}/\text{kg}$), I123cdP ($0.6 \pm 0.1 \mu\text{g}/\text{kg}$), CHRY ($0.3 \pm 0.1 \mu\text{g}/\text{kg}$) and FLURN (not detected).

In summary, ACNPN was the most dominant PAH compound both in intertidal and subtidal zones.

Any difference in concentration of PAHs could not be found between the intertidal and subtidal zone (Fig. 5).

3.3. Total PAH concentrations in oysters in the study area.

Total PAH concentrations on the average in

oysters were as follows: $576.0 \pm 209.1 \mu\text{g}/\text{kg}$ in oysters from the intertidal, and $889.0 \pm 473.7 \mu\text{g}/\text{kg}$ from the subtidal zone.

Although methodological differences make a comparison difficult, it is somewhat worthwhile comparing our data with other reports in other parts of the world in order to diagnose the pollution level of PAHs in marine organisms in the study area. Unfortunately, there is no available data on PAHs in oysters in the domestic marine environment.

A comparison is shown in Table 4. The NPTHL concentration in the blue oyster of the Finnish Archipelago Sea (Rainio, 1986) was reported to be $41.0 \mu\text{g}/\text{kg}$, which is half as much as that in the oysters in Chinhae Bay, Korea.

Rainio (1986) also reported that ANTHL in

Table 4. Comparison of PAH contents in oysters in Chinhae Bay with marine organisms from other studies.

N A : Not analyzed, - : Not detected, Units in $\mu\text{g}/\text{kg}$

PAHs	Chinhae Bay	Finland A	Italy B		Australia C	U.S.A D		England E
	Oyster*	Mussel	Mussel	Razor fish	Oyster	Mussel	Oyster	Porpoise
NPThL	105	41	-	20	3	N A	N A	4.4
ANCPL	88	N A	60	25	-	N A	N A	N A
ACNPN	512.7	N A	35	27	0.4	N A	N A	N A
FLURN	-	N A	5	17	0.2	N A	N A	N A
PHEN	7.6	-	4	2	2	N A	N A	2.1
ANTHR	8.6	14	5	2	0.3	N A	N A	6
FLRTH	26.0	-	21	22	0.2	N A	N A	1.5
PYR	0.2	-	24	-	0.2	2	58	1.9
BaA	151.4	-	29	4	< 1	< 0.2	8	N A
CHRY	0.6	-	13	13	< 1	< 0.2-0.3	< 2-15	N A
BbF	16.1	N A	46	26	-	< 0.2-0.3	< 2-15	N A
BkF	10.7	N A	4	25	< 0.02	N A	N A	N A
BaP	2.2	-	5	5	< 0.01	< 0.5	2	N A
DahA	0.5	N A	20	-	< 1	N A	N A	N A
BghiP	N A	N A	22	7	< 0.1	< 0.2-0.3	< 2-15	N A
I123cdP	0.6	N A	2	4	< 0.1	N A	N A	N A

A Rainio, (1986) in Finnish Archipelago Sea. B Cocchieri, (1990) in Gulf of Naples. C Pendoley (1992) in Rowley Shelf. D Pancirov & Brown (1977) in New Jersey. E Law & Whinnett (1992) at UK waters

* represented as mean concentrations in the intertidal zone from Chinhae Bay.

blue mussels was $14.0 \mu\text{g}/\text{kg}$, which is two times that of mussels in Chinhae Bay. The concentration of the other PAHs could not be compared because Rainio did not analyze the concentration of a couple of PAHs.

Using HPLC fitted with uv/vis detector, Cocchieri et al. (1990) analyzed PAHs in mussels and razor fishes collected in the Gulf of Naples, which is located in Mediterranean coast, and it could be much contaminated by anthropogenic activity. Comparing the PAHs in the Gulf of Naples with our work, ACNPN, ACNPL, NPThL, PHEN, ANTHR and BaA were reported in lower concentrations in the Gulf of Naples than Chinhae Bay; While PYR, CHRY, BbF, DahA and I123cdP in the Gulf of Naples were generally higher than those in Chinhae Bay. As a whole, however, oysters in Chinhae Bay generally showed to have very similar contents of PAHs to those in mussels and razor fishes in the Gulf of Naples.

According to Cocchieri, the total PAH content observed in common mussels in the Gulf of Naples is much higher than that in unpolluted areas ($< 0.5 \sim 148.0 \mu\text{g}/\text{kg}$), but relatively lower than those in heavily polluted areas ($534.0 \sim 1,060.0 \mu\text{g}/\text{kg}$ wet wt). The total PAH content in oysters ($550.0 \sim 1,250.0 \mu\text{g}/\text{kg}$) in Chinhae Bay falls in the criterion of the heavily polluted area.

Pendoley (1992) analyzed the concentrations of PAHs in oysters in Rowley Shelf, Australia by HPLC with fluorescence detection. The PAHs ranged from < 2.0 to $3.0 \mu\text{g}/\text{kg}$ (wet wt), which were two to three orders of magnitude lower than those in Chinhae Bay.

Pancirov and Brown (1977) analyzed PAH concentration in mussels and oysters from New Jersey. The concentrations of BbF and BaP in oysters from New Jersey were very similar to those in oysters from Chinhae Bay. Although most PAHs including the predominant group of

this study were not analyzed in mussels and oysters in New Jersey.

There is little data on PAHs in marine mammals. However, Law and Whinnett (1992) reported the mean concentration of PAHs in muscle tissue of harbour porpoises (*Phocoena phocoena*), which is shown in Table 4.

The concentration of PAHs in muscle tissue of harbour porpoises ranged from 1.5 to 4.4 $\mu\text{g}/\text{kg}$. The level of NPTHL, PHEN, ANTHR, FLRTH and PYR analyzed were definitely lower than those in oysters in Chinhae Bay, even though content of a pollutant in marine mammals can't be directly compared with that in invertebrates.

In summary, the level of PAHs in oysters in Chinhae Bay is thought to be very much similar to these in severely polluted areas in other parts of the world, as can be definitely seen in Table 4.

4. Conclusion

Acenaphthene (ACNPN) was the most dominant PAH compound in oysters in the study area, and all the PAH compounds analyzed in oysters from the intertidal and subtidal zones can form three groups: the predominant group: acenaphthene (ACNPN), naphthalene (NPTHL), acenaphthylene (ANCPL) and benzo(a)anthracene (BaA); the second dominant group: fluoranthene (FLRTH), benzo(b)fluoranthene (BbF), anthracene (ANTHR), phenanthrene (PHEN) and benzo(k)fluoranthene (BkF); and the least dominant group: benzo(a)pyrene (BaP), pyrene (PYR), dibenz(a,h)anthracene (DahA), indeno(1,2,3-cd)pyrene (I123cdP), chrysene (CHRY) and fluorene (FLURN).

Total concentration of 15 PAHs in oysters from the intertidal zone was $918.7 \pm 120.2 \mu\text{g}/\text{kg}$; and from the subtidal zone was $880.9 \pm 72.7 \mu\text{g}/\text{kg}$. The PAH contents in the study area generally seem to be higher than those in organisms living

in polluted area like in the Gulf of Naples, Italy.

In conclusion, Chinhae Bay is thought to be a heavily polluted area by PAHs, however, further study about seasonal variations of PAHs in oysters as well as the PAH levels in various kinds of marine organisms would be needed for monitoring the area regarding PAH contamination.

The sources of PAH contamination in Chinhae Bay may be from fossil fuel combustion such as soot and smoke from nearby cities and industrial complexes, from domestic and industrial wastewaters and finally from engine or fuel oil spilled from the vessels navigating in and out of the Bay. The tool for the exact identification for the sources of PAHs in marine environment needs to be devised in further studies.

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