The Polycyclic Aromatic Hydrocarbons in Benthos (including demersal fish) and Sediments from Pusan Coastal Water and Nakdong River Estuary, Korea

부산 연안과 낙동강 하구에 서식하는 저서생물과 퇴적물에 함유된 다환 방향족 탄화수소에 대한 연구

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Abstract

다환 방향족 탄화수소는 화석 연료의 불완전 연소나 기름 유출등으로 발생하며, 생물체에 농축되면 종양이나 돌연변이등의 심각한 독성 효과를 유발해 이미 세계 여러 나라에서 집중적인 연구의 대상이 되고 있다. 그러나 우리나라에서는 아직 이에 대한 연구가 부족하고 특히, 우리나라 연근해의 고유 어종에 대한 연구는 찾아보기 어렵다. 본 연구는 부산연안과 낙동강 하구에 서식하는 저서 생물과 퇴적물에 함유된 다환 방향족 탄화수소의 농도를 분석하여, 해양 생태계에 미칠 잠재적인 영향을 파악하는데 있다.

본 연구에서는 부산연안과 낙동강 하구에 서식한는 14종의 저서생물과 퇴적물에 함유된 16종류의 다환 방향족 탄화수소를 HPLC (High Performance Liquid Chromatography)를 이용하여 분석하였다. 본 연구결과 조사지역에 서식하는 저서동물의 근육조직과 퇴적물에 함유된 다환 방향족 탄화수소의 농도 범위는 각각 73.9 - 2605ng/g과 94.8 - 1863ng/g으로 조사지역의 해양 환경에서 다환 방향족 탄화수소에 의한 생태계의 직접적 피해 가능성은 희박하다. 그러나, 조사 지역에서 현재와 같은 기름 유출과 폐기물의 유입이 계속된다면, 해양 생태계는 급격히 파괴될 수 있으므로 해양 오염에 대한 예방 대책이 절실히 요구된다.

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1. Introduction

Polycyclic aromatic hydrocarbons are aromatic hydrocarbons with two or more fused carbon rings, which can have substituted groups attached to the rings. Compounds range from naphthalene ($C_{10}H_8$, two rings) to coronene ($C_{24}H_{12}$, seven rings). Crude oils contain 0.2 to 7% of PAHs. PAH content increases with specific gravity of the oil.

Concern about PAH stems from the carcinogenic and mutagenic potential of compounds such as benzene and benzo(a)pyrene, and the latter compound has been specifically related to the presence of tumours in Beluga whales from the Gulf of St. Lawrence in Canada (Martineau *et al*, 1988). Exposure to polycyclic compounds has also been associated with higher risks for cancer. The relation of skin cancer to the occupation of chimney sweeping was made in England during the late 18th century. By the early 20th century, soot, coal tar, and pitch were all known to be carcinogenic to humans. In 1918, benzo(a)pyrene was identified as a major carcinogenic agent; several other PAHs have since been similarly identified. Numerous toxic and carcinogenic effects on wildlife of PAHs have been documented (Eisler, 1987).

Hydrocarbons enter marine ecosystem from a number of sources including petroleum pollution, land run-off via rivers, refinery and sewage discharges, shipping losses and atmospheric deposition (Dunn and Fee, 1979; Howard and Fazio, 1980).

PAHs up to three condensed rings have been shown to serve as growth substrates. Compounds with more than three rings may be subject to cometabolic degradation (Cerniglia and Heitkamp, 1989). Probably the most important parameter affecting biodegradation is the redox character of the sediment of water system (Delaune *et al*, 1981).

The movement of oil from the water surface into the water column, by dissolution and emulsion, exposes the molecules and particles of oil to degradation and transport by living organisms (Atlas and Bartha, 1973; Cowell and Walker, 1977). Heavy and complex compounds are more resistant to microbial degradation and eventually settle into the bottom sediments. Oil particles and individual hydrocarbons (petroleum or pyrogenic origin) also adhere to particles (detritus, clay, microbes, phytoplankton) in the water and settle to the bottom where a variety of microbes metabolize the light and structurally simple compounds. About 40 to 80% of a crude oil can be degraded by microbial action (Peter, 1995).

Since PAHs have low solubility in water and tend to be transported with suspended sediment, most PAHs introduced into aquatic environments accumulate in bottom sediments. The length of time of PAH, as well as other organic pollutants, remain in the sediments usually depend on their rate of degradation in sediments (Delaune *et al.*, 1981).

Most data on benthic animals and sediment PAHs and their toxic effect have been reported in the U. S. and European countries. However, there are little data regarding PAH compounds concentrated in marine organisms and sediments in Korea except some (Lee, 1997; Kim *et al*, 1996; Kahng, 1995). Especially there in not any available one about PAH concentration in benthos and sediments from Pusan coastal water or Nakdong river estuary.

The basic purpose of this study is reporting preliminary data on the PAH contamination in benthos (including demersal fish) and sediments from Pusan coastal water and Nakdong River estuary in Korea. And this study may hopefully contribute to the first step of data accumulation about PAH contamination in the vicinity of Pusan harbor, Korea.

2. Materials and Methods

Pusan harbor, the largest one in Korea, has been a place for shipping, sport fishing and recreational activities. The harbor which has a couple of trbutaries, is semienclosed and has low water depths. As the city of Pusan has a population of about four million, there are many potential pollutant sources such as, domestic waste, oil spills, industrial waste, sea traffic, recreational boating, and stormwater inlets. Two sites were chosen in Suyong bay being a location of strong anthropogenic activities. The Nakdong river estuary was selected for the extended investigation.

Sediments and Benthos (including demersal fish samples) was sampled at total of seven sites in Pusan harbor, and three in Nakdong river estuary (Fig. 1).

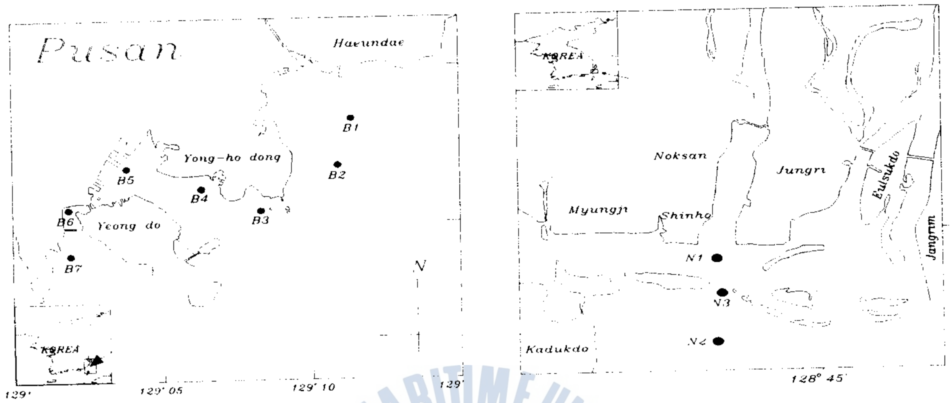


Fig. 1. Location of sampling sites in Pusan harbor (left) and Nakdor river estuary (right).

Using a commercial bottom trawl, 14 species of fish were collected; Sillaginidae (*Sillago sihama*), Gobiidae (*Acanthogobius flavimanus*, *Acanthogbius pflaumi*, *Petrogbius virgo*), Platycephalidae (*Platycephalus indicus*), Pleuronectidae (*Pleuronchthys cornutus*), Cynoglossidae (*Cynoglossus joyneri*), Liparidae (*Liparis tesselatus*), Callionymidae (*Callionymus lunatus*), Hexagrammidae (*Hexagrammos agrammus*, *Hexagrammos otakii*), Rajidae (*Raja kenojei*), Embiotocidae (*Ditrema temmincki*), Pholididae (*Pholis nubulosa*), *and* Congridae (*Conger myriaster*). Also some crabs (*Upogebia majar*, *Portunus trituberculatus*), a shrimp species (*Trachypenaeus curvirostris*), and a clam species (*Meretrix lusoria*) were collected. The sampling of benthos was performed in November, 1996, and in February, 1997.

PAH analysis were run on a SYKAM HPLC (Model S1100) equipped with 25cm × 7mm ODS silicagel column in series packed with 35-75μm Bondapak C_{18}-Porasil B. Binary solvent gradient program was applied. In order to test the efficiency of the extraction and clean-up method for PAHs, recovery experiments were performed with spiked samples. Naphthalene, phenanthrene, anthracene, fluoranthene, and pyrene were added to the samples at the concentration of 4-20㎍. So the recoveries varied 49-97 %, the average recovery was 78 %.

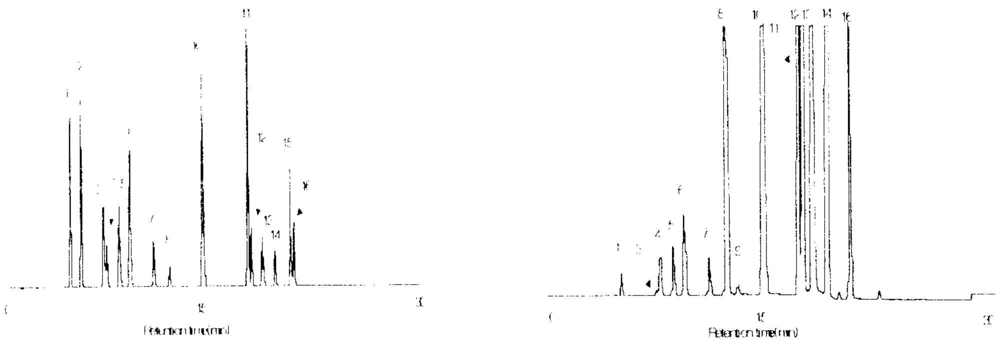


Fig. 2. The chromatogram of PAH standard solution by HPLC with UV/vis. detection (left) and fluorescence detection (right).

Samples were injected by 20㎕ syringe. 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 management of chromatograms, integration and calibration of data were carried out using Peaksimple Serial Data Program system (SRI Model 202).

The standard PAHs solution was prepared from EPA and that was 98% or better purity. Composite PAHs of the standard solution are naphthalene, NAP(1); acenaphthylene, ANPL(2); acenaphthene, ANPN(3); fluorene, FLU(4); phenanthrene, PHEN(5); anthracene, ANT(6); fluoranthene, FLUT(7); pyrene, PYR(8); benzo(a) anthracene, BaA(9); chrysene, CHRY(10); benzo(b)fluoranthene, BbF(11); benzo(k) fluoranthene, BkF(12); benzo(a) pyrene, BaP(13); dibenzo(a,h)anthracene, DahA(14); benzo(g,h,i)perylene, BghiP(15); ideno (1,2,3-cd)pyrene, $I_{123cd}P$(16); Standard material was stored at 5℃ in a refrigerator. The solvents, cyclohexane, methanol, dimethylsulfoxide, ether, petroleum ether, acetone were initially purchased as AR grade chemicals. All glassware were immersed in a 10% sulfuric acid solution for at least 24h. They were then thoroughly washed out using a deionized water and oven dried overnight at 300℃ and rinsed with cyclohexane before use.

3. Results and Discussion

Total PAH concentration in bottom sediments from Pusan coastal water and Nakdong river estuary ranged from 94.8 to 1,862.7 ng/g (wet wt) with the mean value of 412.7 ng/g (wet wt). The highest concentration was detected at site B6, the discharging area of waste water from Ja-Gal-Chi market, while the lowest was detected occurred at site N1, Nakdong river mouth. The concentrations of individual PAH components varied from <0.1 (detection limit) to 1,193.2μg/kg (wet wt). However, they were very unevenly distributed according to sites. Naphthalene, acenaphtylene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, ideno(1,2,3-c,d)pyrene and dibenzo(a,h)anthracene were detected in most of the samples, while acenaphthene, fluorene, chrysene, and benzo(g,h,i)perylene were not. The concentrations of PAHs were highest in sediment from the site B6. Especially, the fluoranthene at site B6 showed one order of magnitude higher than those at the other sites (Fig. 3).

The concentration of PAHs in sediments of Pusan coastal water and Nakdong river are recently unknown. Mackie *et al.*(1980), regarded the areas which the total PAH concentration in sediments varies within 50-140μg/kg dry weight as unpolluted, and those containing 1,930-2,850μg of total PAH/kg dry weight as heavily polluted. The total PAH levels, 140.2 - 1,862.7μg/kg (wet wt; having water portion of 40～70 %) in sediments from coastal areas of Pusan harbor correspond to that of polluted areas. In Table 1 and 2, we can find that study area was more polluted with PAHs than Kyeonggi Bay, but a little less than Chinhae Bay, and moderate in comparison with other urbanized coastal areas around the world.

The dominant PAH compounds in all sediments were naphthalene, acenaphtylene, and fluoranthene. The concentrations of dominant PAH compounds in Pusan coastal water showed to be higher than those in Nakdong estuary (Fig. 4).

Of the individual PAHs examined, the four- and five ring PAHs such as fluoranthene, pyrene, plus benzo(b)fluoranthene and benzo(a)pyrene were the dominant PAHs in the sediments. The concentrations of naphthalene, acenaphtylene,

Table 1. List of PAH concentrations (ng/g dry wt) in sediments from various studies.

Sites	n	Average	Range	Reference
Pusan Harbor, Korea[1]	16	463	140 - 1,860	This study
Nakdong river estuary, Korea[2]	16	241	95 - 390	This study
Kyeonggi Bay, Korea	24	130	9 - 1,400	Kim *et al.*(presenting)
Chinhae Bay, Korea	27	1,500	150 - 3,400	Kang(1995)
San Diego Bay, USA	36	3,000	80 - 20,000	Anderson *et al.*(1996)
Casco Bay, USA	23	2,900	16 - 21,000	Kennicutt *et al.*(1994)
Penobscot Bay, USA	12	2,600	290 - 8,800	Johnson *et al.*(1985)
Washington coast, USA	13	200	29 - 460	Prahl and Carpenter(1983)
Boston Harbor, USA	12	50,700	83 - 718,000	Shiaris and Jampard(1986)
Passaic River, USA	19	150	0.22 - 8,000	Huntley *et al.*(1995)
Chesapeake Bay, USA	15	52	0.56 - 180	Foster and Wright(1988)
Manukau Harbor, New Zealand	10	820	16 - 5,300	Holland *et al.*(1993)
Baltic Sea	15	1,200	720 - 1,900	Witt(1995)
Adriatic Sea	9	130	27 - 530	Guzzella and De Paolis(1994)
Adriatic Sea	12	200	18 - 580	Caricchia *et al.*(1993)
Western Mediterranean Sea	31	1,300	180 - 3,200	Lipiatou and Saliot(1991)

n: number of PAH compounds analyzed in each study.
[1] wet weight (having water portion of 40-70 %).
[2] wet weight (having water portion of 40-60 %).

Table 2. The concentrations (ng/g dry wt) of individual PAH compounds in sediment measured in Korea so far.

Compounds	Pusan*	Nakdong*	Chinhae Bay[1]	Incheon Harbor[2]	WSSQC[3]	ER-L[a]	ER-M[b]	AET[c]
Acenaphthene	-	-	106	23	320	150	650	150
Anthracene	11.6	2.1	88	43	4,400	85	960	300
Benzo[a]anthracene	6.3	6.3	178	64	2,200	230	1,600	550
Benzo[a]pyrene	8.1	2.3	241	-	1,980	400	2,500	700
Chrysene	-	-	48	92	2,200	400	2,800	900
Dibenz[a,h]anthracene	7.5	1.1	69	9	240	60	260	100
Fluoranthene	1,193	110	162	300	3,200	600	3,600	1,000
Fluorene	-	-	137	66	460	35	640	350
2-methylnaphthalene	-	-	135	69	760	65	670	300
Naphthalene	96.8	91.5	129	84	2,000	340	2,100	500
Phenanthrene	32.1	14.3	96	220	2000	225	1,380	260
Pyrene	75.7	4.5	122	240	20,000	350	2,200	1,000
Total PAHs	1,860	387	3,362	1,400		4,000	35,000	22,000

* Wet weight (having water portion of 40-70 %).
ER-L[a] : effects range-low, ER-M[b] : effects range-median.
AET[c] : apparent effects thresholds. [1] Kang (1995). [2] Kim (presenting).
[3] Washington state sediment quality criteria (1991).

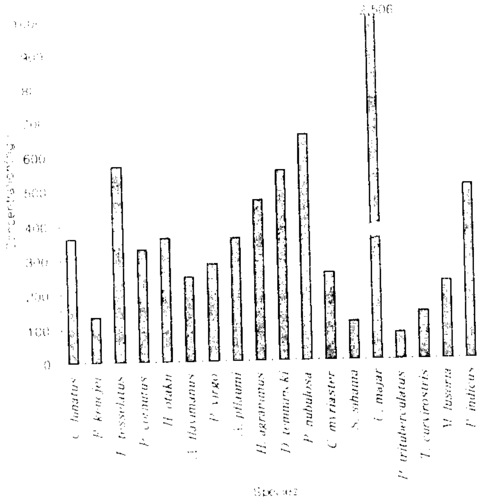
phenanthrene, and anthracene varied from site to site. The persistence of PAHs in aquatic sediments seems to be related to their molecular weight (Readman *et al.*, 1982). Thus, low molecular compounds tend to be volatile and subjected to rapid microbial degradation, hence they have short residence time. On the other hand, high molecular PAH compounds have a high particle affinity and low microbial degradation rate and hence tend to accumulate in sediments.

PAHs of bottom sediments in Pusan coastal water and Nakdong river estuary were one order of magnitude less (0.6 - 8.1) than those from contaminated estuaries in the U. S. (Kim *et al.*, 1996) and NOAA's effects range low (ERL) criteria except the fluoranthene at site B6. Thus, PAHs would not be expected to be a primary cause for biological/ ecological degradation in the study area.

Total PAHs level of each fish muscle was in the range of 73.9 - 859μg/kg (wet wt) from Sillaginidae *Sillago sihama* and Pholididae *Pholis nubulosa.* And those of shellfish were 81.8 - 2506μg/kg (wet wt) from Crab *Portunus trituberculatus* and Crab *Upogebia major.* With regard to the distribution and relative concentrations of the sixteen compounds investigated, naphthalene, acenaphtylene, phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene, and anthracene were detected more frequently (80-95% of the specimens), and their concentrations were quite high (10-1,419μg/kg, wet wt); benzo(a)anthracene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene were present in 24% of the specimens and showed lower concentration within the range of 0.4 - 16.9 μg/kg (wet wt), with an average concentration of 1.2 μg/kg wet wt.

Acenaphthene, fluorene, and chrysene were never detected. Benzo(a)pyrene was present in 92% of the samples at concentrations from 0.1 to 7.4μg/kg (wet wt) with an average of 3.2 μg/kg, which is considerably lower than 128-543μg/kg detected by Bourcart and Mallet (1975) in the common mussel from the Gulf of Naples, but similar to that detected in the mussels and oyster from Chinhae Bay by Lee (1997), and in the mussels from the Adriatic Sea by Amodio-Cocchieri *et al.* (1990) in the mussels from Laguna Veneta, Northeast Italy by Fossato *et al.* (1979).

The highest concentration of total PAHs was detected in branchia tissue of Hexagrammidae *Pleuronchthys cornutus* at site B3. A major Crab *Upogebia majar* showed the highest contamination of PAHs among the benthos. PAH concentration in



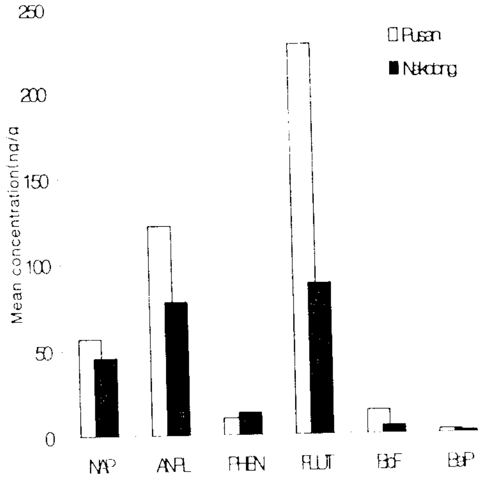
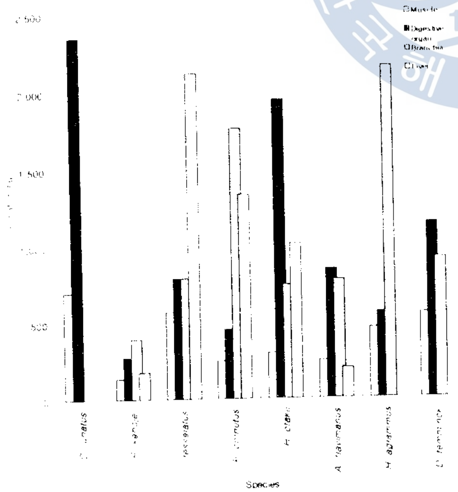


Fig. 3. Total concentrations of PAH compounds in sediments of the study areas (left).

Fig. 4. The mean concentrations of selected PAHs in sediments from Pusan coastal region vs. Nakdong river estuary (right).



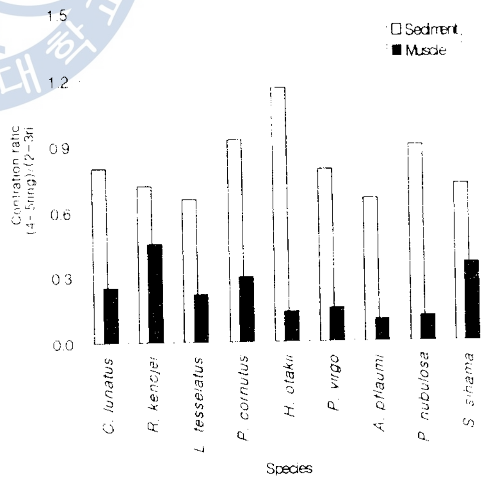


Fig. 5. The mean concentrations of total PAHs from selected fishes muscle, digestive organ, branchia, and liver (left).

Fig. 6. The concentration ratio of 4~5 ring to 2~3 ring PAHs in sediments and fish muscle (right).

the liver, digestive organ, and branchia were one or three order magnitude higher than muscle from the selected fishes (Fig. 5). Same result was presented at pike perch and burbot from Finnish archipelago sea by Rainio *et al* (1986).

In a laboratory experiment, ringed seals were exposed to petroleum (by ingestion or immersion) and hydrocarbon, it was shown that concentrations declined less rapidly in muscle than in liver or blubber tissues (Engelhardt *et al.*, 1977). Actually, Lyes (1979) found in a laboratory experiment that some tissues have an inherently greater affinity for contaminants and hydrocarbon concentrations may be greatest in digestive tissues even when uptake is entirely from contaminated water.

All the PAHs detected from benthos and sediments in this study can be found in other studies for urban airborne particulates derived from municipal incinerators, motor vehicle exhaust, and industrial operations (Baek and Choi, 1996; Davies *et al.*, 1976; Sawicki *et al.*, 1960). These particles with associated PAHs can eventually be deposited in coastal waters and thus become available to benthos.

4-5 ring PAHs in sediment and fish were compared with 2-3 ring (Fig. 6). The ratio (4-5 ring / 2-3 ring PAHs) of fishes muscle was 2-5 times lower than those of sediments at same regions. It would be due to the different routes uptaking high and low molecular weight PAHs, and/ or special enzyme systems of fishes.

Because PAH toxicity occurs at levels that can also induce cancer, concerns about the carcinogenic potential predominate. Consequently, PAHs that are not carcinogenic are less studied than those that are carcinogenic.

This study is the first survey of polycyclic aromatic hydrocarbons in benthos and sediments from Pusan coastal water and Nakdong river estuary. The determination of PAHs in the benthos and sediments may be a gear for detection of petroleum comtamination in the marine environment. Although the concentrations of PAHs in the study area are currently not to be acutely toxic, those may increase with oil spill accidents and sewage disposal. As this study presents preliminary data for the PAH levels in marine environment of Pusan coastal water and Nakdong river estuary. It suggests a need for an increasing effort in controlling sources of pollution in the study areas.

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