

Level and Origin of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from Ulsan Bay, Korea

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Surface sediments (0~5 cm) were sampled from 22 stations in Ulsan Bay, one of the most highly industrialized regions in Korea, in November 2000. The sediment samples were analyzed for their polycyclic aromatic hydrocarbon (PAH) content using a gas chromatography coupled to a mass spectrometer detector (GC/MSD). The total PAH concentrations in the sediments varied from 14 to 7108 ng/g dry weight with a mean value of 1052 ng/g dry weight. The level of carcinogenic PAHs ranged from 6 to 2396 ng/g dry weight with a mean value of 433 ng/g dry weight. The highest PAH concentrations in the sediments from Ulsan Bay were found at Station U8, whereas the lowest levels were observed at Stations U2 and U17. The PAH distribution exhibited a decreasing gradient from the inner basin to the outer bay. The predominant contributors to the aromatic ring groups of the 16 PAHs were four- and five-ring groups, such as fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene, while two- and three-ring aromatics, like naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene, only exhibited a low concentration. The molecular indices for phenanthrene/anthracene and fluoranthene/pyrene were used to identify the origin of the PAH contamination in the sediments. The results indicated that the PAH contamination in Ulsan Bay was mostly pyrolytic in origin with a petrogenic input adjacent to Ulsan and Jangsuengpo harbor.

Key words : Surface sediment, PAHs, GC/MSD, pyrolytic, petrogenic

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are well-known ubiquitous contaminants of coastal marine environments¹⁾. PAHs have been widely studied in different aspects of the environment due to their carcinogenic and mutagenic activities in organisms and human beings^{2~5)}. These compounds are mainly detected in a marine environment with anthropogenic origins⁶⁾, including the combustion of fossil fuels⁷⁾, domestic and industrial wastewater⁶⁾, and petroleum or petroleum product spillage from ships^{8,9)}. PAHs derived from various sources are transported to a marine environment via water and the atmosphere. Then most PAHs in a water column tend to adsorb to particles, which are then deposited in underlying sediments¹⁰⁾. As such, PAHs have been extensively studied for their

geochemical value as markers that can identify the origins of sedimentary deposits in aquatic environments^{11,12)}. The aromatic compound distributions differ according to the production sources, chemical composition, and combustion temperature of the organic matter¹³⁾. The fingerprints of PAHs from a pyrolytic or petrogenic origin can thus be used to differentiate these origins through the use of molecular indices based on the ratios of the selected PAH concentration¹⁴⁾. The difficulties in identifying PAH origins, include the coexistence of many contamination sources and the occurrence of transformation processes before the deposition of the analysed sediments¹⁵⁾. Indeed, in marine ecosystems, PAHs can undergo degradation by photooxidation in a superficial water layer¹⁶⁾ or microbial activities within the sediment¹⁷⁾. The present study focused on the

levels and origins of PAH contamination in surface sediments from Ulsan Bay, Korea.

2. Materials and Methods

2.1. Study area

Ulsan Bay, with a total area of 6.3 km², is one of the most industrialized regions in Korea. The Ulsan petrochemical industrial complex, composed of over 100 plants, discharges up to 200,000 tons of effluent per day into Ulsan Bay via the Woihwang and Taehwa rivers. In addition, there are also many small, medium, and large-scale factories producing a whole range of products, such as automobiles, ships, etc. in the Ulsan area. However, the rapid industrialization of this area has also been accompanied by a significant environmental deterioration that has led to a variety of social and health problems.

2.2. Sampling and sample preparation

The surface sediments (0~5 cm) were sampled using a box-core sampler at 22 stations in Ulsan Bay in November 2000 (Fig. 1). The sediment samples were wrapped in aluminium foil and then frozen at -20 °C. Next, the samples were freeze-dried and sieved (2 mm). Ten grams of sediment was extracted using a Soxhlet apparatus with 200 mL of toluene (Ultra residue analysis, J. T. Baker) for 20 hours, then the volume was reduced to 1~2 mL in a rotary evaporator. The extracts were transferred to *n*-hexane (Ultra residue analysis, J. T. Baker) and then adjusted to a volume of 10 mL after being spiking with 7 species as internal standards (ES-2044, Cambridge Isotope Laboratories, Inc.). The extracts were purified using an activated silica gel (Art No. 7734, 70~230 mesh, Merck) column chromatography with successive elutants of *n*-hexane and 15 % methylene dichloride (Pesticide residue analysis, Cica-Merck) in *n*-hexane. The second fractions were concentrated to less than 1 mL and then left at room temperature for one day to evaporate to 100~200 μL. The residues were dissolved with 100 μL of *n*-nonane (Pesticide residue analysis, Fluka) and determined for PAHs.

2.3. GC/MS analysis

The aromatic fractions were analyzed using gas

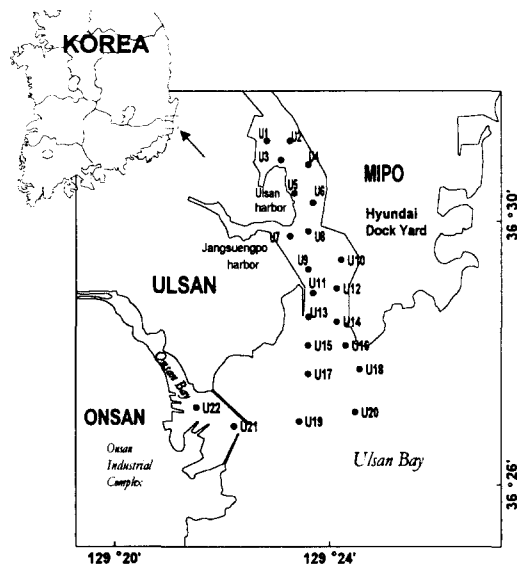


Fig. 1. Map showing sampling stations in Ulsan Bay, Korea.

chromatography coupled with mass spectrometry. An Agilent 6890 series II GC equipped with a split/splitless injector was used (splitless time : 2 min ; flow 70 mL/min). The injector temperature was maintained at 250 °C. The GC temperature program ranged from 80 °C (1 min) to 300 °C (10 min) at 5 °C/min. The carrier gas was helium at a constant flow rate of 1.2 mL/min. The capillary column used was a DB-5MS (30 m, 0.25 mm ID, 0.25 μm film thickness, J&W Scientific). The GC was coupled to a 5973N mass selective detector (MSD). The mass spectrometer was operated in the selected ion monitoring (SIM) mode using the molecular ions of the investigated PAHs (electron impact at 70 eV, 2000 V, 1.5 scan/s, dwell time/ion : 40 ms). The interface temperature was 250 °C. Each sample was analyzed for the presence of 16 non-alkylated PAH compounds (EPA 610), recommended by the US EPA as priority pollutants (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i]perylene). Blanks were run before and after the injection of the standards to check for any carryover. The sample recoveries were within a range of 73~94 %. The data pres-

ented in this investigation was not corrected for recoveries.

3. Results and Discussion

3.1. PAH levels

All sixteen PAHs were detected in each sediment sample. The total concentrations of the two- to six-ring PAHs varied from 14 to 7108 ng/g dry weight with a mean value of 1052 ng/g dry weight (Table 1). The Stations U7 and U8 near Ulsan and Jangsuengpo harbor exhibited the highest levels. In particular, the PAH concentrations in Ulsan Bay showed a decreasing gradient from the inner bay sampling stations to the outer stations, thereby suggesting a local source in the vicinity of Stations U7 and U8.

The total concentrations of the six potentially carcinogenic PAHs (benzo[a]anthracene, benzo[b]

fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene and dibenzo[a,h]anthracene)¹⁸⁾ varied from 6 to 2396 ng/g dry weight with a mean value of 433 ng/g dry weight. The highest concentrations of the carcinogenic PAHs were found at Stations U7 and U8. The PAH distribution exhibited a decreasing gradient from the inner stations (Station U1 to U14, mean value 1483 ng/g dry weight) to the outer stations (Station U15 to U20, mean level 324 ng/g dry weight). Accordingly, these results indicate that the inner basins are adjacent to a terrestrial source of PAHs with poor tidal flushing.

Although the number of PAHs analyzed will vary according to each study, the 16 PAHs investigated in the current study have been found in most estuarine or marine sediments. The PAHs in the sediments from Ulsan Bay revealed higher values than those from Kyeonggi Bay in Korea

Table 1. The levels of PAHs in sediments from Ulsan Bay, Korea (ng/g dry weight)

	STATIONS																					
	U1	U2	U3	U4	U5	U6	U7	U8	U9	U10	U11	U12	U13	U14	U15	U16	U17	U18	U19	U20	U2	U22
Naphthalene	6.7	0.3	16.1	9.5	10.9	0.4	12.7	5.6	4.3	2.7	8.7	0.4	7.4	3.1	3.9	1.2	0.1	2.7	4.9	3.0	5.8	5.8
Acenaphthylene	2.4	0.1	2.8	1.5	2.7	0.4	6.3	6.9	1.4	0.8	3.2	0.3	2.1	0.8	1.1	0.5	0.1	4.2	2.1	2.9	10.1	7.2
Acenaphthene	5.7	0.2	9.8	3.9	20.1	5.6	87.5	109.7	8.5	8.8	14.2	0.8	7.1	2.6	2.2	0.9	0.1	3.0	2.3	2.8	5.4	4.0
Fluorene	8.4	1.1	12.1	5.4	16.7	6.3	65.6	104.2	7.0	7.3	11.2	1.4	8.6	3.4	3.3	1.4	0.6	3.0	3.7	3.5	1.6	3.2
Phenanthrene	55.9	2.1	88.9	40.0	120.7	64.9	534.8	758.3	69.4	67.3	101.9	18.5	74.6	27.7	26.1	13.3	0.9	37.5	26.0	27.6	5.5	21.3
Anthracene	13.3	0.4	18.5	4.1	23.5	8.3	74.2	114.9	11.3	9.6	16.2	2.8	14.4	5.5	5.3	2.6	0.2	4.4	6.0	5.5	1.6	4.9
Fluoranthene	95.4	3.4	117.4	67.3	159.5	150.5	551.9	980.7	85.8	153.9	128.8	40.7	96.7	53.0	51.7	30.7	1.7	70.5	48.2	53.9	8.9	37.3
Pyrene	85.7	3.0	138.1	55.7	172.9	130.3	585.5	1054.5	108.9	135.3	135.8	35.7	103.6	45.4	42.6	27.3	1.5	58.8	37.8	43.2	7.5	30.7
Benzo[a]anthracene	34.9	0.9	58.2	21.7	91.9	92.3	382.1	1020.4	51.8	92.7	68.5	21.8	51.8	28.5	26.2	16.7	0.8	33.7	24.1	29.2	4.2	20.0
Chrysene	48.1	1.7	75.2	32.7	112.6	95.3	450.1	825.0	63.1	96.9	88.2	24.4	68.0	33.6	33.7	20.1	1.0	37.9	19.5	34.2	4.2	26.5
Benzo[b]fluoranthene	76.7	1.8	118.5	45.6	180.8	153.2	606.4	546.4	89.7	156.3	126.8	41.7	99.5	59.6	61.3	35.4	1.9	69.3	60.1	61.8	11.1	51.3
Benzo[k]fluoranthene	24.4	0.6	37.7	15.8	59.6	49.4	207.8	500.1	30.3	51.3	42.9	13.4	32.6	18.7	18.8	11.1	0.6	21.6	18.0	19.6	4.4	16.4
Benzo[a]pyrene	113.8	1.4	62.9	26.2	93.9	98.8	378.1	152.9	45.9	90.7	60.2	18.9	54.0	39.0	37.9	13.6	1.7	30.6	21.1	23.6	4.4	31.1
Indeno[1,2,3-c,d]pyrene	43.1	0.9	73.5	28.0	129.4	133.4	439.7	72.2	58.5	136.7	87.7	34.0	69.2	52.4	54.5	30.6	1.5	60.9	56.6	56.7	9.1	148.5
Dibenzo[a,h]anthracene	8.9	0.2	15.7	5.8	27.0	24.8	96.4	104.4	13.7	24.1	17.3	6.9	15.8	9.0	9.0	5.9	0.3	10.9	9.1	9.5	4.2	8.4
Benzo[g,h,i]perylene	52.6	1.6	82.8	36.2	123.4	81.7	405.8	751.4	58.1	84.8	86.8	24.6	69.2	36.2	36.2	21.9	1.1	44.1	36.1	37.3	9.3	30.9
ΣPAH	676	20	928	399	1346	1096	4885	7108	708	1119	998	286	775	418	414	233	14	493	376	414	98	348
ΣCarcinogenic PAH	302	6	367	143	583	552	2111	2396	290	552	404	137	323	207	208	113	7	227	189	200	38	176

(values 9~1400 ng/g dry weight)¹⁹⁾ and comparable values to those from Penobscot Bay, USA²⁰⁾, Arcachon Bay²¹⁾ and the western Mediterranean Sea²²⁾, ranging from 290~8800 (mean 2600) ng/g dry weight, 32~4120 (mean 1918) ng/g dry weight, and 180~3200 (mean 1300) ng/g dry weight, respectively. Meanwhile, the PAHs in the sediments from Chesapeake Bay (0.6~180 ng/g dry weight)²³⁾ and the White Sea (13~208 ng/g dry weight)²⁴⁾ had lower values than those from Ulsan Bay, whereas the PAHs from Casco Bay²⁵⁾, San Francisco Bay, and Lazaret Bay²⁶⁾ were higher, ranging from 16~21,000 (mean 2900) ng/g dry weight, 2902~29,590 (mean 8186) ng/g dry weight, and 100~50,000 (mean 18,660) ng/g dry weight, respectively.

A comparison of the effect-based and empirically-derived sediment quality guidelines with the individual PAH concentrations in Ulsan Bay, Korea is summarized in Table 2. When compared with NOAA's effects-based guidelines on organisms (Table 2), most of the compounds from Stations U7 and U8, which had the highest PAH concentrations in the current investigation, exceeded the effects range-low(ER-L), except for naphthalene, fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene, however, the levels did not exceed the effects range-medium(ER-M) values (Table 2).

Comparisons with other criteria, such as those based on the apparent effects threshold(AET) and empirical biota-sediment accumulation factors/equilibrium partitioning theory(WSSQC in Table 2), indicated relatively substantial margins of safety.

Consequently, the sediment contamination by PAHs in Ulsan Bay was seemingly moderate in comparison to that in other marine ecosystems. However, periodic monitoring of persistent organic pollutants(POPs), including carcinogenic PAHs, is still necessary to manage the environmental quality in the Ulsan coastal ecosystem.

3.2. PAH contributions in sediments

The contributions of aromatic ring groups to the overall level of the 16 PAHs in the sediments from Ulsan Bay are illustrated in Fig. 2. The contributions of the 16 PAH ring groups exhibited similar patterns for most stations. The predominant contributors were four- and five-ring aromatics, like fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene, whereas two- and three-ring aromatics, like naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene, only revealed low concentrations. Meanwhile, higher-molecular-weight five- and six-ring

Table 2. Comparison of effects-based and empirically-derived sediment quality guidelines with individual PAH concentrations (ng/g dry weight) in Ulsan Bay sediments

Compound (ng/g dry weight)	ER-L ²⁷⁾	ER-M ²⁷⁾	AET ²⁸⁾	WSSQC ²⁹⁾	Station U7	Station U8
Naphthalene	160	2100	500	2000	13	6
Acenaphthene	16	500	150	320	88	110
Fluorene	19	540	350	460	66	104
Phenanthrene	240	1500	260	2000	535	758
Anthracene	85	1100	300	4400	74	115
Fluoranthene	600	5100	1000	3200	552	981
Pyrene	670	2600	1000	20000	586	1055
Benzo[a]anthracene	260	1600	550	2200	382	1020
Chrysene	380	2800	900	2200	450	825
Benzo[a]pyrene	430	1600	700	1980	378	153
Dibenzo[a,h]anthracene	63	260	100	240	96	104
ΣPAH	4000	45000	22000		4885	7108

aromatics with more lipophilic and hydrophobic PAHs predominated in the sediment matrix, probably due to their higher persistence. These results indicate that the higher-molecular-weight aromatics were preferentially adsorbed and incorporated in the sediment.

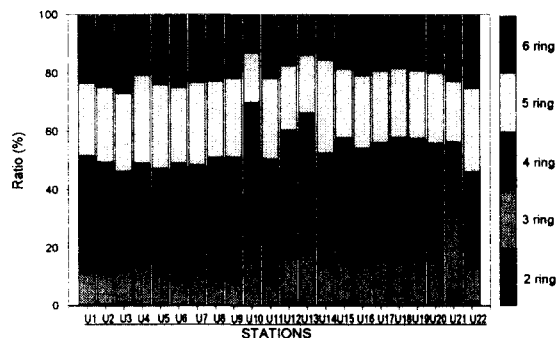


Fig. 2. Contributions of aromatic ring groups (two- to six-ring) to total concentrations of 16 PAHs in marine sediments from Ulsan Bay, Korea.

3.3. PAH origins

To estimate the origin of the PAH pollution at the investigated stations, molecular origin indices phenanthrene/anthracene versus fluoranthene/pyrene were plotted, refer Fig. 3. The ratio of phenanthrene/anthracene and fluoranthene/pyrene reveals useful information on the source of the PAH contamination³⁰. Due to their different physico-chemical properties, they behave differently according to the environment, thereby leading to different values. Since phenanthrene is more thermodynamically stable than anthracene, the phenanthrene/anthracene ratio is very high in PAH petrogenic pollution, yet lower in pyrolytic contamination cases³¹. Similarly, fluoranthene and pyrene are often associated during natural matrix analyses and considered to be typical pyrogenic products derived from the high-temperature condensation of lower molecular weight aromatic compounds. As such, a ratio of phenanthrene/anthracene < 10 and fluoranthene/pyrene > 1 indicates that the PAH contamination is due to a combustion process(pyrolytic origin)^{14,32}. Figure 3 clearly shows that the phenanthrene/anthracene ratios were lower than 10(values between 3.5 to 9.7) for all stations, The fluoranthene/pyrene ratios varied from 0.85 to 1.27, although at most stations

they were higher than 1, indicating that the PAH contamination was from a pyrolytic origin. However, the ratios from Stations U3, U5, U7, U9, U10, U11, and U13 close to Ulsan and Jangsuengpo harbor were lower than 1. Therefore, these results indicate that the PAH contamination at these stations was more from a petrogenic origin related to the usage or spillage of petroleum from transportation ships frequenting Ulsan and Jangsuengpo harbor.

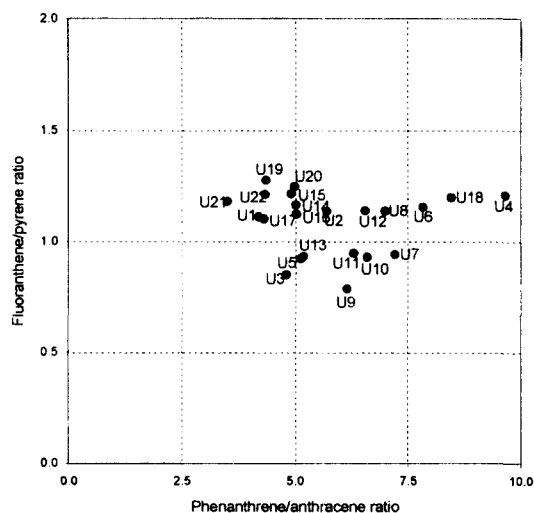


Fig. 3. Source origin for phenanthrene/anthracene ratio against fluoranthene/pyrene ratio in marine sediments from Ulsan Bay, Korea. Phenanthrene/anthracene < 10 and fluoranthene/pyrene > 1 indicate pyrolytic origin. Phenanthrene/anthracene > 10 and fluoranthene/pyrene < 1 indicate petrogenic origin.

To evaluate the source characteristics of the PAHs in the sediment samples, a cluster analysis was performed based on each of the 16 PAH compounds identified at the 22 stations. The results of the cluster analysis are summarized in Fig. 4. The six sampling stations of U11, U13, U5, U3, U9, and U7 were found to form a distinct group, which was in accordance with the phenanthrene/anthracene versus fluoranthene/pyrene ratios indicating the characteristics of a petrogenic origin.

Consequently, the origins of the PAH contamination in the sediments from Ulsan Bay were confirmed to be basically pyrolytic with a

harbor.

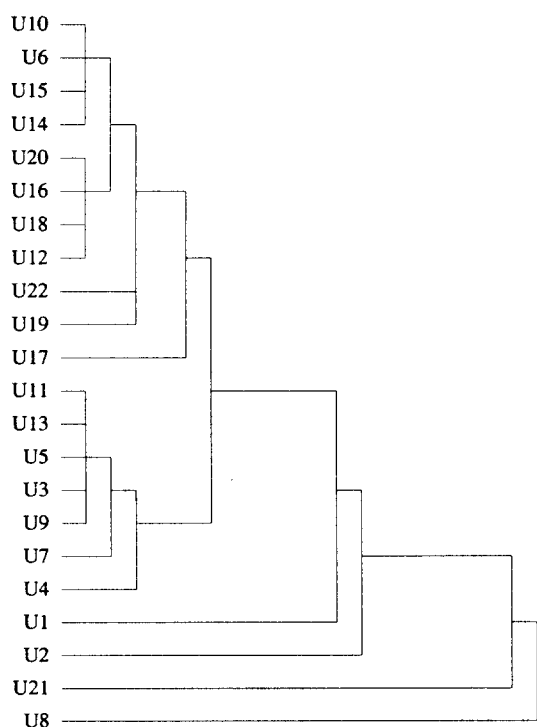


Fig. 4. Dendrogram of hierarchical cluster analysis in sediments from Ulsan Bay.

4. Conclusions

Surface sediments (0~5 cm) were sampled from 22 stations in Ulsan Bay, Korea to investigate the level and origin of PAH contamination. The total concentrations for the 16 PAHs measured ranged between 14 and 7108 ng/g dry weight, with a mean concentration of 1052 ng/g dry weight. The concentrations of carcinogenic PAHs ranged from 6 to 2396 ng/g dry weight with a mean value of 433 ng/g dry weight. The PAH distribution exhibited a decreasing gradient from the inner basin to the outer stations. Four- and five-ring aromatic groups, such as fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene, occupied a high proportion. The origins of the PAH contamination in the sediments from Ulsan Bay were found to be strongly pyrolytic with a petrogenic input adjacent to Ulsan and Jangsuengpo harbor.

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