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Distribution and Sources of PAHs in Saemangeum Reclaimed Tidal Lands of Central Korea

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Polycyclic aromatic hydrocarbons (PAHs) are an important group of organic micro-pollutants due to their widespread distribution in the environment. They are produced by incomplete combustion of fossil fuels as well as by digenetic processes during fossil fuel formation, while produced naturally by forest fires and possibly microbiological synthesis in relatively smaller amounts. PAHs have been the subject of much research during the last few decades due to their persistent properties. Especially, the higher molecular weight PAHs are hardly degradable and tend to accumulate in the different environmental compartments (Fires 1990). PAHs, like many other hydrophobic organic contaminants, are rapidly adsorbed to particles and incorporated within sediments in aquatic systems (Readman et al., 2002; Baun et al., 2002). The importance of sediments in determining fate and effects of a wide variety of contaminants has become apparent in recent years (Renner 1997). Most of the surveys of PAHs contamination in coastal sediments have been carried out in North America and Europe (Wang et al., 2001). Little information is available on PAHs contamination in Asia, where industrialization and urbanization have proceeded rapidly during the past several decades.

The wide scale reclamation of tidal flat distributed in the west and south coastal area in Korea have been completed to make the paddy field to cope with the food-shortage. The area of reclamation in the southwestern coastal area of Korea amounts to 157,000 ha. By 1999, 76,000 ha had already been developed while 60,000 ha are currently being developed. Recent changes in the agricultural situation such as over production of rice started to change land use from paddy to upland, even though the reclaimed tidal lands have been developed as paddy field to produce rice.

The objective of this study was to determine the concentrations, distribution, and sources of PAHs in Saemangeum reclaimed tidal lands of western seacoast, Korea, which is currently under construction. The levels of PAHs in the reclaimed tidal lands, can help the environmental risk assessment of those areas in many ways.

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MATERIALS AND METHODS

Total 24 samples were collected in February 1998 from 8 stations (3 samples from each station) in Saemangeum reclaimed tidal lands of western seacoast in Korea (Figure 1). Frozen aliquots of samples were air dried for three to four days. After drying the samples were ground using a mortar and pestle and sieved through a 0.5 mm sieve. All samples were stored at 4 ℃ in foil-wrapped vial until extraction. The 16 PAH compounds used in this study were naphthalene (Nap), acenaphthylene (A), acenaphthene (Ace), fluorene (F), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[ah]anthracene (DahA), benzo[ghi]perylene (BP), and indeno[1,2,3-cd] pyrene (IP). Authentic PAH standards and surrogate compounds were purchased from Supelco (Bellefonte, PA, USA).

Soxhlet extraction was performed using 5 g (equiv dry wt.) of spiked samples (surrogate standard: 4 ㎍/mL × 200 ㎕). The sample was extracted for 24 hr with 300 mL of methylene chloride. Based on EPA method 3540 (1992), the optimum time period for extraction was chosen to be 24 hour. The extract was concentrated in the condenser to 5 mL. The extract was treated with acid-activated copper powder to remove sulfur and then cleaned up on 5 g of silica gel in a glass column (25 × 1.3 cm i.d.). PAHs were eluted from the silica gel column with 100 mL methylene chloride: pentane (2:3, v/v) at a flow rate of 2 mL/min. The extracts were concentrated to 1 mL using a rotary evaporator before the addition of internal standards (4 ㎍/mL × 10 ㎕). The detection limits of this method for 16 PAHs ranged from 0.28 to 30.56 pg. The mean recoveries (%) for surrogates in sediment samples were 42–109%. The average recoveries of 16 PAHs varied from 39% (naphthalene) to 101% (benzo[ghi]perylene). Because the recovery of naphthalene was very low, the result of naphthalene was not concluded in this study.

GC-MS analyses were performed on an HP 5890 series Ⅱ gas chromatograph (Hewlett-Packard, USA) equipped with a DB 5 capillary column (JW, Folson, CA, USA: 30 m × 0.25 ㎜ film thickness). The injection was maintained at 270℃. The oven temperature program was: 50℃ (2 min) to 290℃ (20 min) at 5℃ min^{-1}. The carrier gas was helium at a constant flow rate of 1mL/min. The gas chromatograph was coupled to an HP 5972 mass selective detector (electronic impact mode: 70 eV). The interface temperature was 290℃.

RESULTS AND DISCUSSION

PAH with three and more rings tend to be strongly adsorbed to the soil. Strong sorption coupled with very low water solubility and very low vapor pressures make leaching and volatilization insignificant pathway of PAH dissipation (Park et al. 1990). PAHs concentrations in Saemangeum reclaimed tidal lands varied to a

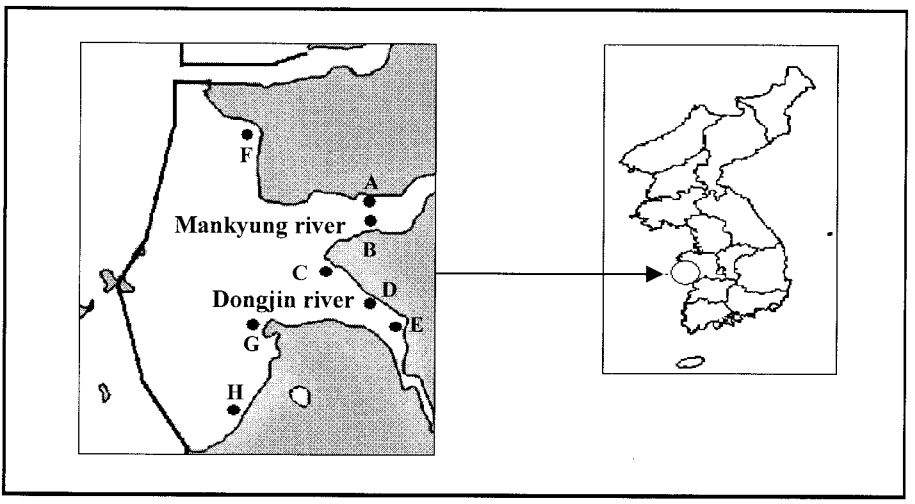

Figure 1. Map showing sampling sites in Saemangeum reclaimed tidal lands. The thick solid line is sea wall.

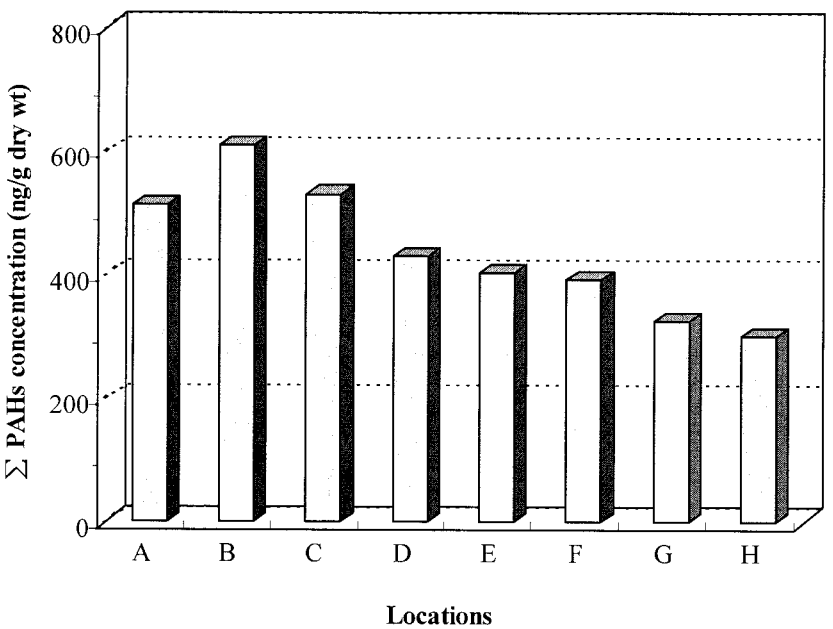

Figure 2. Distribution of ∑ PAHs in Saemangeum reclaimed tidal lands.

congeners) ranged from 288.6 to 648.0 ng/g dry weight with a mean value of 439.3 ng/g. In the mouth of the Mankyung River (station A, B, and C), ∑ PAHs ranged from 413.5 to 648.0 ng/g (mean: 552.6 ng/g). In the vicinity of Dongjin

River (station D and E), $\sum$ PAHs ranged from 380.9 to 496.4 ng/g (417.6 ng/g) and remaining stations (station F, G, and H) contained $\sum$ PAHs between 288.9 and 421.6 ng/g (340.5 ng/g). PAHs concentrations were significantly higher in the Mankyung River area (A, B, and C) probably due to industrial wastewater than compared to the other parts (D, E, F, G, and H). The highest concentration was found at station B (559.3 to 648.0 ng/g; mean: 610.6 ng/g), the innermost site in Mankyung River; the lowest concentration occurred at station H (288.6 to 314.8 ng/g; mean: 302.3 ng/g) in the southern end of Dongjin River. Especially, the data found for the near A, B, and C sites located near Mankyung River were, hence, indicative of a polluted environment. It is believed that the sources of this pollution are of anthropogenic origin due to a high urbanization of the Chonju, and a large industrial activity of the Iksan and Kunsan seashore. This area is the seat for such as agricultural chemical manufacturing, hazardous waste disposal, industrial wastewater treatment, and steel manufacturing from Kunsan, Chonju, and Iksan industrial complex area. The presence of these industries yields a huge amount of particulate matter, which is directly let in the atmosphere as smokes, as well as a great mass of waste. This mass, together with the wastes coming from the various processes and treatment installations, must have been disposed in a sea area.

No significant correlation was observed among the concentration of $\sum$ PAHs and CEC ($r = 0.42$), OC ($r = 0.23$), and clay content ($r = 0.51$) of reclaimed tidal lands (Figure 3). It is suggested, therefore, that the observed distribution of PAHs in sediments was not governed by soil characteristics, but by the localized sources of inputs.

There are various ways in which PAHs are introduced into the environment. It is generally accepted that industrial activities constitute the main source of PAHs, but it is difficult to identify which PAHs have been introduced from pyrolytic origin or petrogenic ones. The two dominant PAHs found in Saemangeum reclaimed tidal lands are fluoranthene and pyrene. They formed 24.6 to 45.7% (mean: 37.3%) and 2.7 to 33.9% (mean: 23.7%) of the $\sum$ PAHs. Pyrene, benzo(a)pyrene, and benzo(a)anthracene are considered as car exhausts indicators (Kayali et al. 1995) and their high level found in this study indicates that traffic plays an important role in reclaimed tidal lands of western seacoast in Korea. Indeed, phenanthrene in 3-ring PAHs), fluoranthene in 4-ring PAHs, and benzo(b)fluoranthene in 5-ring PAHs have also a relatively high contribution compared with the rest of PAHs (Figure 4). The predominance of high-molecular-weight PAHs (5 to 6 ring) is less often observed. The low-molecular-weight PAHs (3 to 4 ring) formed about 88% of the $\sum$ PAHs. It is important to note that PAH distribution in atmospheric particles were mainly low-molecular-weight components (Sicre et al. 1987). Transport became the predominant source of environmental pollution at the city of Chonju, Iksan and Kusan area in Korea during recent 9 to 10 years contributing up to 60% of air pollution of the city (Statistical Yearbook of Environment, Korea 2000). The amount of cars was doubled during this period. At the same time air

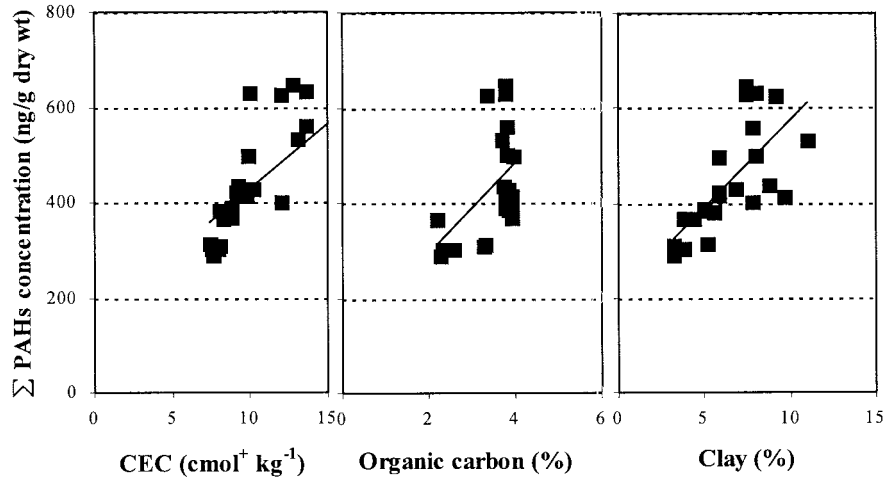

Figure 3. The relationship among ∑ PAHs and CEC, OC, and Clay content in Saemangeum reclaimed tidal lands.

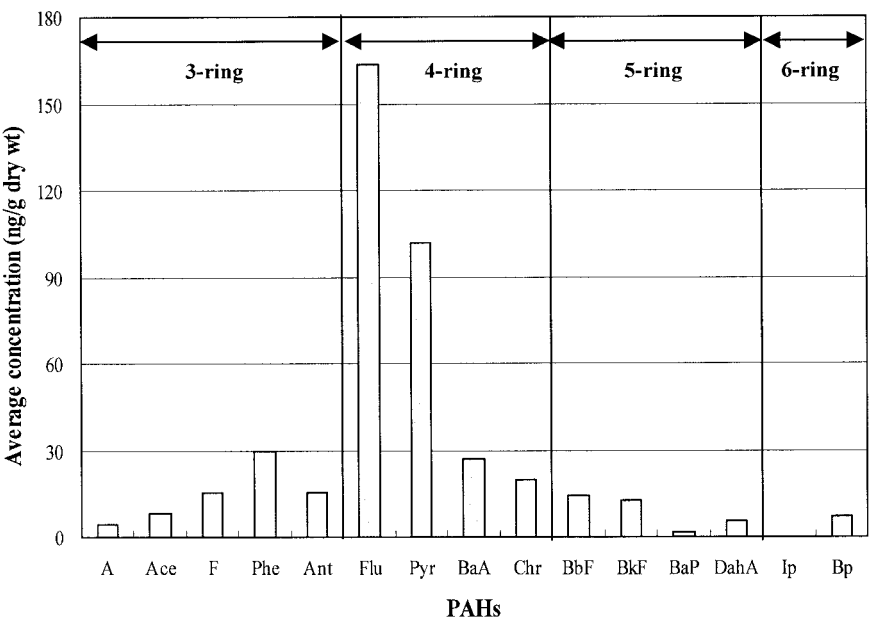

Figure 4. Spatial distribution of 3-ring to 6-ring PAHs.

Table 1. Comparison of PAHs concentration measured in this study with those in other country (ng/g dry wt).

Site	Reference	Mean	Range
Taranto Gulf, Italy	Storelli and Marcotrigiano 2000	2014	335- 5193
Adriatic Sea	Caricchia et al. 1993	200	18- 580
Western Mediteranean	Lipiatou and Saliot 1991	1300	180- 3200
Casco Bay, USA	Kennicutt et al. 1994	2900	16-21000
Kyeonggi Bay, Korea	Kim et al. 1999	120	9-1400
Baltic Sea	Witt 1995	1200	720-1900
This study	.	439	289- 648

pollution load from stationary sources declined three times due to the recessed economical situation. Therefore, traffic could be one of the main reasons for enhanced PAHs concentrations in Saemangeum reclaimed tidal lands of Mankyung River districts.

The comparison with published data from other aquatic systems (Table 1) showed that PAH concentrations in Saemangeum reclaimed tidal lands were lower than those detected in some areas of urbanized estuaries in other countries, but were also about an order of magnitude greater than those reported for the Taranto Gulf, western Mediteranean and Casco Bay.

Consequently, at their present levels, PAHs in Saemangeum reclaimed tidal land considered to be moderate in comparison with other aquatic system. However, periodic monitoring of persistent, sediment-associated contaminants such as PAHs should be instituted as an indicator of agricultural environment in reclaimed tidal lands.

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