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Distribution of Polycyclic Aromatic Hydrocarbons in Sediments inside Jeju Harbor of Jeju Island

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) with two or more fused aromatic rings, are a well-documented contaminants in aquatic environments throughout the world. PAHs can be introduced into the environment by various processes: incomplete combustion at higher temperature of recent and fossil organic matter (pyrolytic origin), slow maturation of organic matter under geochemical gradient conditions (petrogenic origin) and short-term diagenetic degradation of biogenic precursors (diagenesis). 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(Guinan et al., 2001). 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.

The present study is focused on surface and core sediment samples collected inside Songsan Harbor, one of major harbors in Jeju Island. The interest of this work is to determine the concentration levels and the distribution, and to suggest possible origin of 16 PAHs recommended by US-Environmental Protection Agency (US-EPA) as priority pollutants to be monitored in the framework of the environmental quality control. The distribution and nature of PAHs were further studied to identify the possible origins of these contaminants, and the potential toxicological significance was evaluated by comparison with effects-based sediment quality guidelines.

2. Materials and Methods

Jeju Harbor, located at north-central part of Jeju Island, is the largest one in Jeju Island. Inside Jeju Harbor, the water area and water depth are 7.904×10^4 m and in the range of 1.5 x 14.3 m, respectively. The surface and core sediments sampling

was taken three times (June, September and December, 2001) only inside harbor because outside harbor, rock masses are present in a wide range and sediments are not. The surface (0-4 cm) and core(14 cm) sediments were collected at 6 stations (Js-1~Js-6) and 1 stations (Jc) by SCUBA diving, respectively, considering physical (e.g. bulwark, mooring sites of ships, etc) and sedimentary environments inside harbor. For core sediment sampling, a 9 cm I.D. x 30 cm long PVC barrel was used and the sediment samples were extruded and sectioned every 2 cm according to the depth. 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 transfered to the laboratory, where they were frozen at – 70℃, until analysis.

The analytical procedures of PAHs in surface and core sediments followed the Yim's method (1998). They consist 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 mass selective detector (MSD). The following 16 PAHs recommended by US-EPA as priority pollu-tants: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]flu-oranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene.

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 Ingram (1971), and thus the sediment particles were divided into three fractions, >2 mm, in the range of 63 μm~ 2 mm and <63 μm, called as gravel, sand and mud, respectively.

Radiodating analysis of core sediments were carried out at the Korea Basic Science Institute. About 3-4 g of dried and ground sediment samples were trans-ferredto plastic scintillation vial, and then assayed for ^{210}Pb and ^{137}Cs by well-type purity Germanium (HPGe) detector with ultra low background cryostat and 10 lead shield.

3. Results and Discussion

3.1. Distribution of PAHs

Sixteen individual PAHs were identified comprising 2-6 ring aromatics. The total PAHs in surface sediments inside Jeju Harbor ranged from 104 to 3554 ng g-1 dry weight (dw) with the mean value of 853 ng g-1. Station Js-1 represents localized region of high contamination of 3313-3554 ng g-1, compared to other stations (104 to 682 ng g-1). The spatial distribution of total PAHs inside Jeju Harbor shows a general trend of increased concentrations towards the harbor ends.

Total PAHs at core sediments varied in the range of 171-526 ng g-1(mean 374 ng g-1). With depth, total PAHs of 273-349 (mean 316) at near surface increased to 460-526 ng g-1 (mean 492 ng g-1) at a depth of 6-8 cm, then decreased. In order to obtain the sediement age in core sediments used in this study, sedimentation rates were estimated based on ^{210}Pb activity. However, ^{210}Pb activity in both core sediments were nearly the same with depth, thus they are could not obtained.

3.2. Relationships among sedimentary PAHs, organic carbon and particle size distribution

In order to evaluate the distribution of sedimentary organic carbon and particle size distribution to total PAHs, the relationship between each of them was investigated. Relatively good correlation coefficients (r) were obtained between total PAHs, and each of organic carbon content (r= 0.757, 0.802) and mud distribution (r= 0.737, 0.742) for surface and core sediments, respectively. However, no correlations were obtained for sand and gravel.

3.3. Identifying the origin of PAHs

In order to estimate the origin of sediment contamination by PAHs in this study, we examined the four indices, the ratio of sum of the low molecular weight 2-3 ring PAHs over sum of the high molecular weight 4-6 ring PAHs (LMW/HMW), the raios of Phe(.phenanthrene)/Ant(anthracene), Fle(fluoranthene)/Pyr(pyrene) and Chr (chrysene)/BaA(benzo[a]anthracene).

It is generally accepted that pyrogenic PAHs are characterized by the dominance of HMW over LMW. In contrast, petroleum hydrocarbons in crude oil and light refined products are dominated by LMW. It can be known that this index values varied according to sampling station and sampling time, but the values for the majority of the sediment samples were lower than 1, indicating pyrolytic origin contamination.

The ratios of Phe/Ant and Fle/Pyr, based on thermodynamic principle, are generally used to differentiate the pyrolytic and petrogenic origins of PAHs. Phe is more thermodynamically stable than Ant, so a Phe/Ant ratio <10 is characteristic of PAH pyrolytic. Pyr is more stable than Fle hence pyrolytic products are usually characterized by a predominance of Fle over Pyr at ratios >1. The values of Phe/Ant ratio were <10 for most of sediment samples, indicating that most of sediment samples collected in this study were contaminated by pyrolytic PAHs. In contrast, the values of Fle/Pyr were in the range of 0.30-1.50 for the surface and core sediments, making the discrimination of PAHs origin difficult.

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 an inversion of this tendency, i.e., Chr/BaA ratio = 1. The values of Chr/BaA ratio obtained from the sediment samples of each station with sampling time, were >1 in most of sediment samples.

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

3.4. Potential toxicological significance

In order to estimate the potential of the PAHs contamination in surface and core sediments inside Jeju Harbor to cause adverse effects in biota, their levels were compared with the values ER-L and ER-M derived by NOAA. Any of individual PAH and total PAHs in this study did not exceed the ER-L values, except for Js-1. At Js-1, Flu, Phe and Ant exceeded the Er-L values and the other individual and total PAHs approaches to Er-L values. In conclusion, PAHs in surface and core sediments inside Jeju Harbor are distributed at lower levels that does not show the biological effects on marine organisms, except for Js-1 located at Sanji stream.

4. Conslusions

Levels of total PAHs (16 US EPA priority pollutants) in surface and core sediments inside Jeju Harbor, were in the range of 104-3554 ng g-1 (mean 853 ng g-1) and 171-526 ng g-1. respectively. One station located at Sanji stream inside Jeju Harbor showed a localized region of high contamination, compared to the other stations., The spatial distribution showed a general trend of increased concentrations towards the bay ends. The core sediments inside Jeju Harbor were disturbed, thus their sediment ages could not be obtained. The sedimentary PAHs may be relatively highly correlated with organic carbon content and mud distribution, but no correlations were obtained between PAHs and gravel or sand. The sediment PAH contamination in this study were ascribed to both of pyrogenic and petrogenic origins, by the examination of the four PAH origin indices, namely LMW/HMW, Phe/Ant ratio, Fle/Pyr ratio and Chr/BaA. The sediment PAH levels in this study except for one station mentioned above do not pose the biological effects on marine organisms in comparisons with numerical effects-based sediment quality guidelines derived by NOAA.

References

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