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Spatio-temporal distribution and characteristics of PAHs in sediments from Masan Bay, Korea

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Abstract

The distribution of polycyclic aromatic hydrocarbons (PAHs) has been investigated in the surface and core sediments from Masan Bay, Korea. Total PAHs in the surface sediments ranged from 207 to 2670 ng/g dry weight with a mean value of 680 ng/g. Qualitative similarity and quantitative difference between inner and outer bay indicate that the main sources of PAHs are located in the inner bay and outer bay is also affected by the same sources. Vertical distribution of PAHs revealed that three distinctive stages could be differentiated with the help of PCA analysis. The highest concentration (industrialization stage) appeared between late 1950s and 1980, which was 10 years later than other developed countries. A strong pyrolytic source fingerprint has been detected with slight influence of petrogenic sources, and diagenetic PAH, perylene also contributed. Total organic carbon normalized PAHs (sum of 13 PAHs, 8.85–88.0 μg/g OC) were under the threshold effects concentration (TEC, 290 μg/g OC).

Keywords: PAHs; Sediment; Core; Source; PCA; Masan Bay

1. Introduction

Masan Bay is one of the most extensively studied areas in Korea for its long history of contamination (MOMAF, 2002). For many years, this area has been the recipient of various environmental damages because of rapidly growing urban and industrial development. Masan, Changwon and Chinhae cities surrounding Masan Bay to the north and east, are heavily populated areas, and hundreds of industrial plants which are mainly concentrated in the Masan and Changwon cities discharge significant amounts of organic pollutants into the bay. Masan Bay (Fig. 1) is semi-enclosed embayment and there are strong semi-diurnal tidal currents along the deep channel at the bay mouth, while very weak currents are observed in the inner bay where most pollutants are loaded in. Average water depth range from less than 5 m in the inner bay, to 5–20 m in the central part. In summer time, red tides events frequently occur, which lead to anoxic condition of bottom sediments (MOMAF, 2002).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitously distributed contaminants. Natural processes like forest fire can produce PAHs but anthropogenic activity like combustion of fossil fuel, spillage of oils are generally considered to be the major source of PAH input into the environment (Blumer and Youngblood, 1975). PAHs are mainly transported to the marine environment by two routes: atmospheric deposition and the rivers. Other input sources are urban runoff of domestic and industrial wastewater, spillage of petroleum or petroleum products by ships (Boehm and Farrington, 1984). Once introduced into marine environment, PAHs are accumulated in sediments because of their hydrophobicity and strong affinity for organic matter. Because of their large adsorption capabilities, fine-grained sediments represent a major repository for contaminants and a record of the temporal changes in

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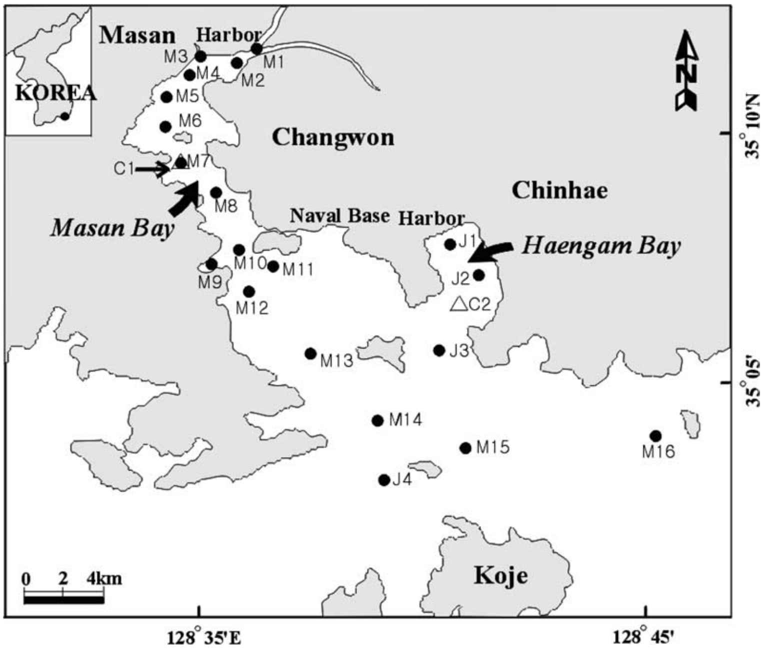

Fig. 1. Sampling locations of surface sediments (M1–M16 and J1–J4) and core samples (C1 and C2) collected from Masan Bay.

contamination. Thus they can be used for historical reconstruction (Latimer and Zheng, 2003). To guarantee reliable dating, the cored material must be undisturbed, fine-grained, and collected in an area with a relatively fast sedimentation rate (Hites et al., 1980). Masan Bay sediments can provide such conditions where anoxic environments and fast sedimentation prevails. This study will focus on (1) to determine the current status and temporal trends of PAHs contamination; (2) to elucidate the possible sources of PAHs in Masan Bay.

2. Materials and methods

2.1. Sample collection

The sampling sites are shown in Fig. 1. Surface sediment, sediment core samples were collected in August 1997. Surface sediments (top 2 cm) were collected from 20 sites in Masan Bay. Sediment cores (60–80 cm) were sampled at C1 and C2 by SCUBA diving using 150×18 cm i.d. PVC barrel. After collection, core was extruded and sectioned every 1–2 cm according to the depth. Resulting sediment samples were frozen at −20 °C until subsequent analysis.

2.2. Analytical procedures

The analytical procedures of PAHs in sediments followed the method of Sloan et al. (1993) after some modifications (Yim et al., 2002; Hong et al., 2003). Briefly, wet sediment samples (approximately 20 g) were well mixed and dried with 50 g of sodium sulfate. The chemically dried samples were spiked with 300 ng of deuterated surrogates (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) and extracted by Soxhlet apparatus for 6–8 h with 200 ml of methylene chloride. The sample extracts were extensively cleaned up by a Si/Al column chromatography and HPLC with size exclusion column (Krahn et al., 1988). Terphenyl-d_{14} was used as GC internal standard.

A 30 m × 0.25 mm i.d. DB-5MS capillary column was used in a Hewlett-Packard Model 5890 GC with Hewlett-Packard Model 5972 MSD. The mass spectrometer was operated under the selected ion monitoring mode using the molecular ions of the studied PAHs (electron impact at 70 eV, 2000 V, 1.4 scan/s). Quantification was performed using the molecular ion (mass-to-charge ratio). Peaks were confirmed based on retention time and secondary ions. The oven temperature was programmed to start initially at 60 °C (1.5 min), increased to 300 °C at 4 °C/min, and held for 10 min. Injector temperature was set at 300 °C and transfer line at 280 °C.

Quantitation of 24 target compounds were based on the relative response factor of each PAH to the surrogate standards spiked before extraction. The response factors of the different compounds were measured by injecting a Standard Reference Material (SRM) 2260 (24 aromatic hydrocarbons in toluene) (National Institute of Standards and Technology [NIST], Gaithersburg, MD, USA) solution spiked with the same solution containing the perdeuterated PAHs as the one used for spiking the sediments. Nonalkylated and methylated PAHs were analyzed. The studied PAHs ranged