HISTORICAL RECORD OF POLYCYCLIC AROMATIC HYDROCARBONS IN CORE SEDIMENTS FROM THE SOUTHEASTERN COASTAL AREAS OF KOREA

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are well-known ubiquitous contaminants of the coastal marine environment [1]. PAHs have been widely studied in the different compartments of the environment because of their carcinogenic and mutagenic activities in organisms and human being [2, 3]. They have been intensively studied for their geochemical interest as markers in identifying sedimentary deposits origin in the aquatic environment [4]. These compounds have mainly anthropogenic origins [5], including combustion process of fossil fuels [6], domestic and industrial wastewater [5] and spillage of petroleum or petroleum products by ships [7]. Each source is characterized by a specific molecular pattern and it is, therefore, possible to identify which source generated these chemicals. PAHs derived from various sources transport to the marine environment via both waters and atmosphere. Most PAHs in water column tend to be adsorbed to particles and to be deposited to the underlying sediments. Degradation of PAHs in sediment is generally slow, particularly for the higher molecular weight PAH [8]. Vertical profiles of residues in dated sediment cores have been used as historical records of pollution [6, 9]. Several studies have examined vertical profiles of persistent organic contaminants such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and PAHs in sediment cores and found that the depositional histories of these compounds are often preserved in the sediment bed [10, 11]. It is important to identify and characterize their past and current input fluxes and to know how the coastal areas have responded to changing inputs historically, to help establish strategies that will effectively control the inputs of PAHs to the marine environment. In the present study, we construct the depositional history of PAHs in sediment cores in order to assess possible sources, distributions, and trends of these compounds in several coasts of Korea.

Materials and Methods

Sediment cores were sampled from Pohang, Onsan, Busan and Masan coasts of Korea in 2000. The core samples were sliced into 2 cm thickness. Each disk was freeze-dried and frozen at -20°C until analysis. The freeze-dried sediments extracted in a soxhlet apparatus with 200 ml of toluene for 20 hours, then the volume was reduced to 1-2 ml in a rotary evaporator. The extract was transferred to *n*-hexane and then adjusted to a volume of 10 ml after internal standard (ES 2044, Cambridge Isotope Laboratories, Inc.) was spiked. The extracts of core sediments were purified using an activated silica gel column chromatography with successive elutants of *n*-hexane and

15% methylene dichloride in *n*-hexane. The second fraction was concentrated to less than 1 ml, and left at a room temperature for one day to evaporate to 100-200 µl. The residue was dissolved with 100 µl of *n*-nonane and determined for PAHs using GC/MSD (Agilent 5973N). Further details of analytical methods and instrumental analysis procedures were based on previously used methods [12]. Sedimentation rates were estimated by the ^{210}Pb method and the ^{137}Cs method. Both estimating results were similar and the value obtained using the ^{210}Pb method was used in this study.

Results and Discussion

Maximun concentrations of 16 PAHs were detected at depths of 3 cm (approximately year 1980) in Pohang coast, 3 cm (approximately year 1997) in Onsan coast, 5 cm in Busan coast and 19 cm (approximately year 1956) in Masan coast (Fig. 1). The trends of vertical profile in Pohang and Onsan coasts showed a similar pattern. Busan coast was characterized by the constant vertical profile of ^{210}Pb estimating values. It seems that the strong disturbance by hydrodynamic mixing and/or the activity of benthic organisms existed in this station. Hence, the vertical profile of PAHs showed a constant distribution in this sampling station. Sedimentation and accumulation rates of PAHs in sediment cores from several coasts of Korea present in Table 1. Onsan coast represented the highest sedimentation rate, followed by Masan and Pohang coast. However, the flux of PAHs showed the highest value in Pohang coast.

Table 1. Sedimentation rate of particle and accumulation rates of PAHs concentration in core sediments from the southeastern coastal areas of Korea

Locations	Sedimentation rate (cm/year)	PAHs concentration (0-5 cm, ng/g dry)	Accumulation rate (ng/cm^2/year)
Pohang coast	0.12 ± 0.01	19 218	1153 ± 96
Onsan coast	1.39 ± 0.19	282	196 ± 27
Busan coast	NA	156	NA
Masan coast[13]	0.44 ± 0.04	127	28 ± 3

NA : not available.

The contributions of ring aromatic groups to sum of 16 PAHs in core sediments showed similar patterns. The predominant contributions were four ring aromatics like fluoranthene, pyrene, benzo[a]anthracene and chrysene for all stations.

To grasp the PAHs origin, the molecular indices were plotted phenanthrene/anthracene versus fluoranthene/pyrene (Fig. 2). The ratio of phenanthrene/anthracene and fluoranthene/pyrene allows us to give useful information on source of PAHs contamination [14]. The ratio of phenanthrene/anthracene<10 and fluoranthene/pyrene>1 indicates that the contamination by PAHs is due to combustion process (pyrolytic origin) [15]. Pohang and Busan coasts represented the coexistence of pyrolytic and petrogenic origin of PAHs contamination. Masan coast showed pyrolytic origin of PAHs by combustion process from local source, whereas Onsan coast showed petrogenic origin of PAHs by oil contamination. Consequently, four different sampling stations represented local source characteristics of each coast for PAHs contaminations.

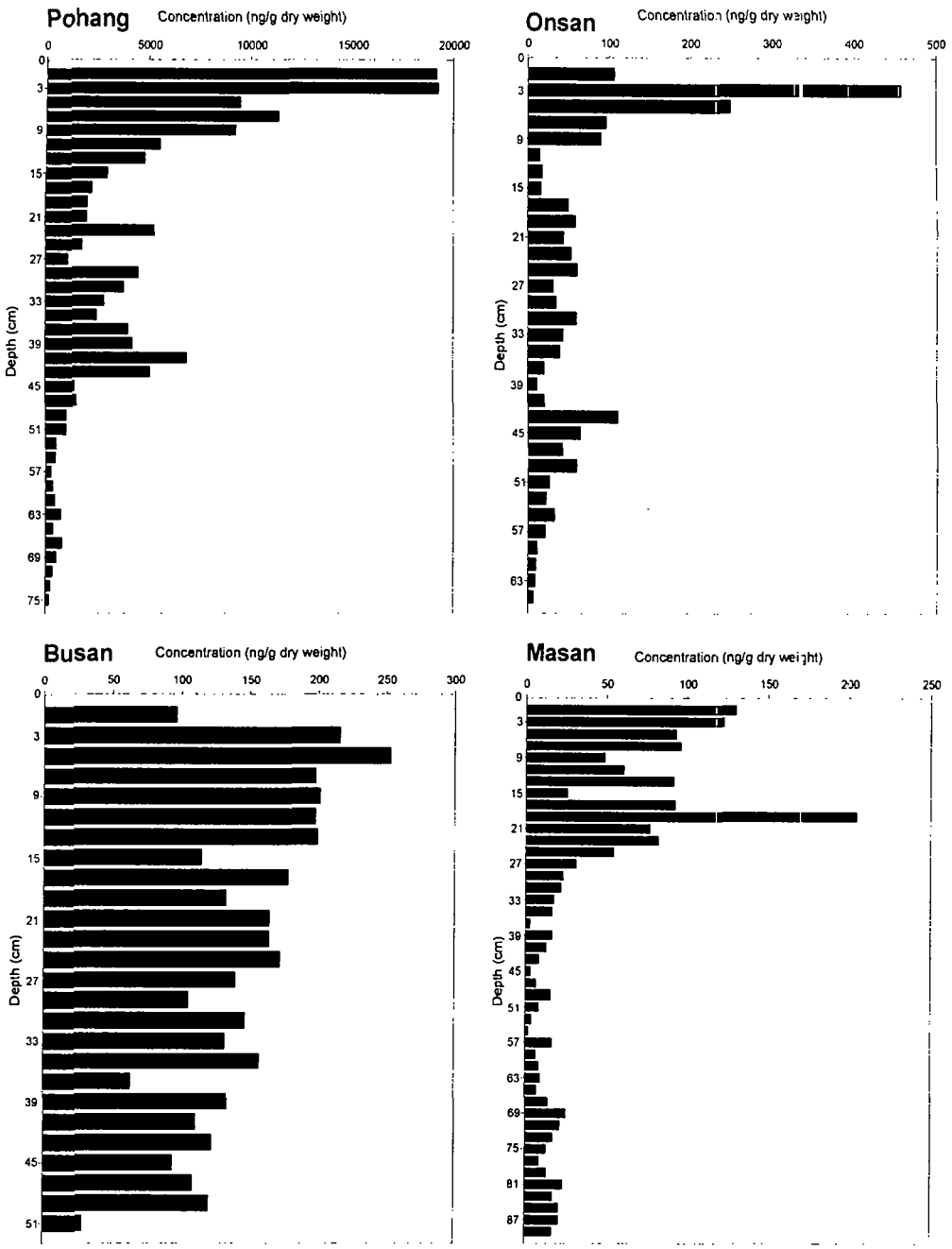

Fig. 1. Vertical profiles of PAHs concentrations in the sediment cores for the four different sampling stations of Korea.

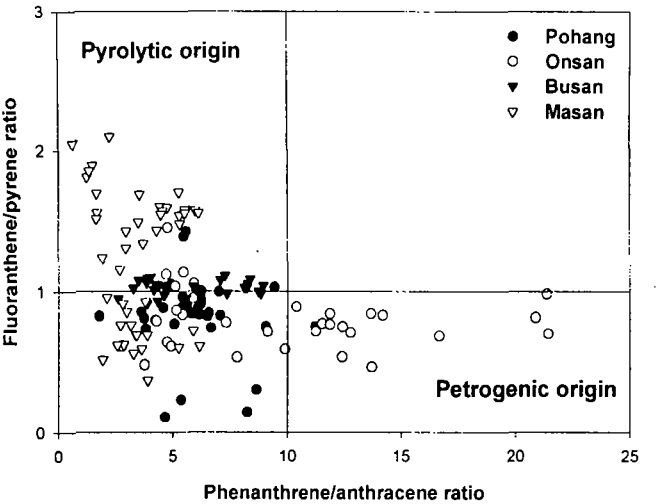

Fig. 2. The plots between phenanthrene/anthracene ratio versus fluoranthene/pyrene ratio in core sediments from the southeastern coastal areas of Korea.

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