

Spatial Distribution and Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments in Hyogo Prefecture, Japan

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in the environment. Anthropogenic sources of PAHs include the burning of fossil fuels, coal production, oil manufacturing, oil spills, tobacco smoke, and various forms of cooking. Some PAHs may cause abnormal effects such as carcinogenicity, mutagenicity, or teratogenicity. PAHs are widespread environmental pollutants, however, there is little information about the concentration of PAHs in sediments in Hyogo prefecture. In this study, the spatial distribution and risk assessment of PAHs in surface sediments were investigated in Hyogo prefecture, Japan.

Materials and Methods

Sampling points

River and sea sediments were sampled for 3 years from 2015 to 2017. Sampling points (river sediment: R1~R15, Sea sediment: S1) are shown in Figure 1.

Analytical procedure of PAHs

The analytical method for the PAHs was slightly modified from our previous report¹ in order to improve recovery ratios. A 30 g wet sediment sample was mixed with a hydromatrix (Agilent) and copper (Kishida-kagaku, reduced, granular), transferred to an accelerated solvent extraction (ASE) cell, and spiked with a US EPA 16 PAH Cocktail (¹³C, CIL) as a surrogate. The mixture was extracted with acetone: dichloromethane (1:1) using ASE350 (Thermo Scientific).

The extract was transferred into a separatory funnel containing purified water and sodium chloride. After shaking, it was let alone until dichloromethane phase separated from water. The solution was extracted with

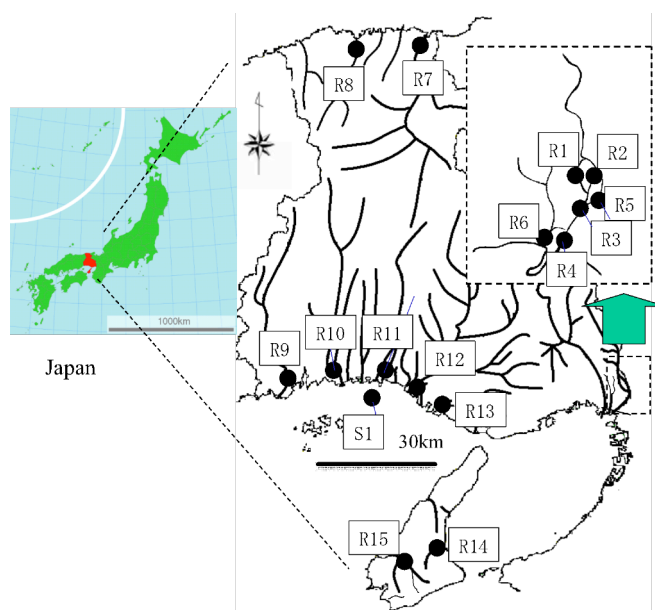


Figure 1 Sampling points of sediments in Hyogo

Table 1 Analytical conditions of HRGC/HRMS

Instrument	:HRGC 6890N (Agilent Technologies) HRMS JMS-800D (JEOL)
Capillary column	:DB-EUPAH 20 m, 0.18 mmID, 0.14µm film thickness
Oven temperature program	:60 °C (1 min) → 10 °C /min → 250 °C → 5 °C /min → 300 °C → 25 °C /min → 320 °C (5 min)
Inlet temperature	:325 °C
Inlet mode	:Splitless
Injection volume	:0.5 µL
Carrier gas	:Helium
Flow rate	:Constant flow (1.5 mL/min)
Ion source	:EI
Ion source temperature	:300 °C
Interface temperature	:330 °C
Ion current	:400 µA
Ionization volt.	:38 eV
Acquisition mode	:Selected ion monitoring (SIM)

Many kinds of PAHs were detected from sediments. Fluoranthene and pyrene were the most abundant compounds, and that was the same trend as in Dokai Bay and Tokyo Bay^{3,4}. S1 is the MOE's monitoring point. The concentrations of benzo[a]pyrene at S1 (88, 95 ng/g-dry) were within the range of the results of MOE's yearly surveys from 1992 until 2001 (17 to 270 ng/g-dry)⁵. As shown in Figure 2, the ratio of 4-ring, 5-ring, and 3-ring was high, which is consistent with previous studies^{6,7}.

Risk assessment

In order to assess the effect of the detected PAHs on benthic animals, we compared the concentration to the sediment quality guideline published by the National Oceanic Atmospheric Administration⁸, according to previous studies⁹. Concentrations of 2-methylnaphthalene, fluorene, and anthracene were higher than the 'effects range low' (ERL), but lower than the 'effects range medium' (ERM) threshold (Table 2). Furthermore, the mean of the ERM-Quotient, which is calculated by summing individual quotients (concentration/ERM) and dividing by the number of quotients¹⁰, of all the sites are much smaller than 1. Therefore, PAHs listed in Table 2 are not expected to produce substantial adverse effects on benthic animals in Hyogo Prefecture.

Estimation of PAH sources

It is known that PAHs originate from crude and refined petroleum, and combustion of fossil fuels such as petroleum, coal, and biomass (such as grass and wood etc.). Some molecular ratios of specific hydrocarbons have been studied to differentiate PAHs generated from different sources¹¹. Phenanthrene (Phen), anthracene (Ant), benzo[a]anthracene (BaA), chrysene (Chr), indeno[123cd]pyrene (IDP), benzo[ghi]perylene (BghiP), fluoranthene (Flth), and pyrene (Pyr) were used to obtain these ratios. Ant/(Ant+Phen), BaA/(BaA+(Chr and Triph)), IDP/(IDP+BghiP), and Flth/(Flth+Pyr) were plotted against Flu/(Flu+Pyr) and compared with previously reported source data¹². The results of these ratios are shown in Figure 3(a,b,c). Ant/(Ant+Phen), BaA/(BaA+(Chr and Triph)), IDP/(IDP+BghiP), and Flth/(Flth+Pyr) ratio were ranged from 0.09 to 0.75, 0.18 to 0.43 (except 0), 0.18 to 0.53 (except 0), and 0.47 to 0.63, respectively, which suggests that the majority of PAHs in Hyogo prefecture sediments have been derived from fossil fuel combustion, biomass, and petroleum. Although the cause was unknown, the ratios of Flth/(Flth+Pyr) at R1 and Ant/(Ant+Phen) at R5 were relatively high (Figure 3(a,b,c)).

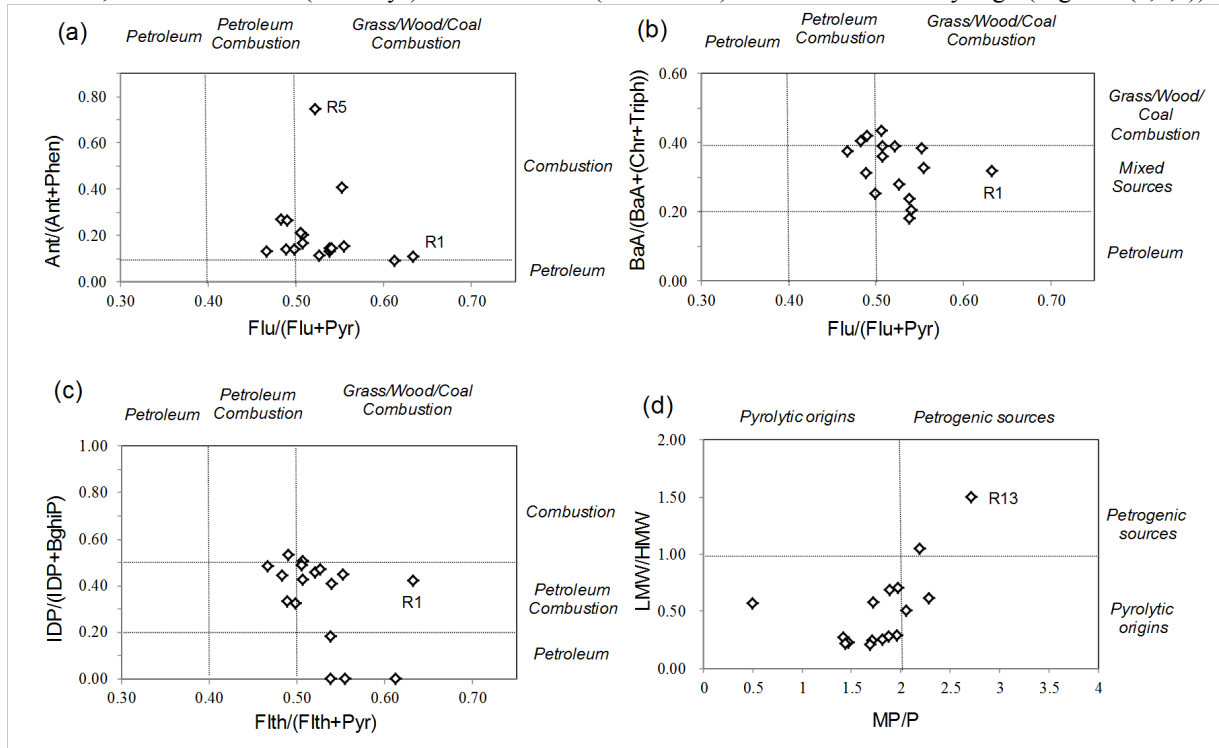


Figure 3: Estimation of potential sources of PAHs in sediments
(The chrysene and triphenylene peaks could not be isolated.)

Further investigation is necessary for more detailed analysis. Lower LMW/HMW (low-molecular-weight parent PAHs (2 and 3 rings of 16 EPA priority PAHs)/high-molecular-weight parent PAHs (4, 5, and 6 rings of 16 EPA

priority PAHs)) and MP/P (1-, 2-, 3-, and 9-methylphenanthrene/phenanthrene) ratios are observed in pyrolytic sources^{6,10,16}. Commonly, a ratio of LMW/HMW <1 suggests a pollution of pyrolytic origin^{10,11,14}. MP/P ratios in combustion mixtures are generally <1, whereas unburned fossil fuel mixtures exhibit a range values from 2 to 6^{12,14,16}. As shown in Figure 3(d), the LMW/HMW and MP/P ratios were 0.24 to 1.5 and 0.5 to 2.7, respectively, which indicates that the origin of the PAHs was pyrogenic except for a few points. The ratio of LMW/HMW and MP/P was relatively high at R13, suggesting the presence of petrogenic sources.

TEQ of PAHs

The total toxic equivalent (Σ TEQ) was calculated using the toxic equivalent factor (TEF) according to the USEPA^{17,18}. TEFs for benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[ah]anthracene, and indeno[123cd]pyrene have been calculated as 0.1, 0.001, 0.1, 0.01, 1, 1, and 0.1, respectively. Σ TEQ values calculated for sediment samples of Hyogo prefecture varied from 0.6 to 160 ng-TEQ/g-dry, lower than the sediments of Meiliang Bay, China (94 to 856 ng-TEQ/g-dry); and the soils of South Chattanooga, USA (<50 to 113,900 ng-TEQ/g-dry)^{19,20}.

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