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: $R1 \sim R15$, 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 (^{13}C , CIL) as a surrogate. The mixture was extracted with acetone: dichloromethane (1:1) using ASE350 (Thermo Scientific).



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	$:60 \degree C (1 \min) \rightarrow 10 \degree C /\min \rightarrow 250 \degree C \rightarrow 5 \degree C /\min \rightarrow$
	$300 \degree C \rightarrow 25 \degree C / min \rightarrow 320 \degree C (5 min)$
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)
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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

dichloromethane twice and then dehydrated with anhydrous sodium sulfate. The obtained extract was concentrated to 4 mL. Next, Sep-Pak Vac 12 cc (2 g) Silica Cartridge (Waters) was pre-washed with 10 mL of hexane, and part of the hexane concentrate (1 mL) was applied to the silica cartridge. The cartridge was eluted with 20 mL of dichloromethane:hexane (5:95). The eluate was concentrated to approximately 3 mL with a rotary evaporator and was added to the reduced copper (Wako, powder) as necessary. Then the eluate was concentrated to 1 mL with a gentle nitrogen stream. After adding perdeuterated PAHs (naphthalene- d_{10} , perylene- d_{12} , CIL) as an internal standard to the concentrate, the measurement was performed using HRGC/HRMS. Analytical conditions of the HRGC/HRMS are described in Table 1. The main target compounds were 27 PAHs (number of rings): naphthalene (2), 2-methylnaphthalene (2), acenaphtylene (3), acenaphthene (3), fluorene (3), phenanthrene (3), anthracene (3), fluoranthene (4), pyrene (4), benzo[a]anthracene (4), 5-methylchrysene (4), chrysene (4), triphenylene (4), cyclopenta[c,d]pyrene (5), benzo[b]fluoranthene (5), benzo[j]fluoranthene (5), benzo[a]pyrene (5), benzo[a]pyrene (6), dibenzo[at]pyrene (6), dibenzo[at]pyrene (6), dibenzo[at]pyrene (6), dibenzo[at]pyrene (6), dibenzo[at]pyrene (6), dibenzo[at]pyrene (6), and dibenzo[ah]pyrene (6). Quantification was carried out using the isotope dilution method with a surrogated compound.

Results and Discussion

Spatial distribution of PAHs

Average recoveries of surrogates were $75\pm11\%$ ~ $101\pm12\%$ (depending on the compound). The differences between analysis values and certified values of SRM 1941b (NIST) were small. Table 2 shows the concentration of PAHs. Duplicate measurements were performed for S1, and no significant variation was observed.

The range of Σ_{27} PAHs (Σ_8 PAHs/ Σ_{14} PAHs/ Σ_{16} PAHs) concentrations were from 15 (4.5/13/13) to 3,000 (1,400/2,100/2,500) ng/g-dry, and were found to be within the same range as the results of Lake Biwa, which is the largest lake in Japan



Figure 2 Concentration distribution by the number of rings

 $(\Sigma_8 PAHs; 24 \text{ to } 2,002 \text{ ng/g-dry})^2$; and Dokai Bay, Japan $(\Sigma_{14} PAHs; 1,050 \text{ to } 89,200 \text{ ng/g-dry})^3$. Excluding both R4 and R5, which are border Osaka prefecture, the concentration levels were within the range of Tokyo Bay, Japan $(\Sigma_{14} PAHs; 116 \text{ to } 987 \text{ ng/g-dry})^4$. This result may suggest a presence of PAH sources upstream of R5, areas in Osaka prefecture. The concentrations of R1, R3, R4, R5, R14 and S1 were relatively higher in Hyogo prefecture. It seems that these points have been affected by industrial activities.

PAH compounds Samping point																						
	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	S1-1	S1-2	ERL	ERM [₽]	8PAH ^c	14PAH ^d	16 EPA ^e
Naphthalene	63	12	43	70	105	5.0	5.7	2.7	2.9	4.7	5.7	4.3	1.4	34	6.4	55	49	160	2100		•	0
2-Methylnaphthalene	18	11	21	53	104	3.3	3.4	1.9	2.2	3.9	4.0	3.2	1.0	29	7.6	34	22	70	670		•	
Acenaphtylene	11	1.0	13	35	26	0.4	ND	0.6	ND	ND	0.6	1.4	ND	10	1.4	14	23	44	640		•	0
Acenaphthene	3.0	2.4	5.9	13	13	ND	ND	0.3	1.1	ND	ND	0.4	0.3	4.9	1.8	9.6	7.0	16	500		•	0
Fluorene	8.7	4.4	12	26	45	0.7	2.1	0.8	1.8	3.6	2.6	1.1	1.1	13.9	4.1	18	19	19	540		•	0
Phenanthrene	83	13	79	125	178	4.1	9.4	5.1	8.1	9.6	6.5	7.7	4.4	84	13	72	89	240	1500		•	0
Anthracene	10.0	2.2	20	46	524	0.7	1.4	1.0	1.3	6.6	1.2	1.1	0.4	10	2.2	26	23	85.3	1100		•	0
Fluoranthene	194	14	142	220	361	3.7	10.5	8.1	5.5	10.5	3.9	5.9	2.1	109	8.9	146	172	600	5100	0	•	0
Pyrene	113	14	138	235	331	3.7	9.0	7.8	4.7	8.5	3.1	6.7	1.3	98	7.6	152	167	665	2600	0	٠	0
Benzo[a]Anthracene	35	3.0	54	91	109	0.5	2.1	2.9	0.3	3.4	0.7	1.9	ND	31	1.5	71	78	261	1600	0	•	0
Chrysene and Triphenylene	74	6.8	84	135	171	1.4	6.7	5.2	1.5	5.5	1.4	3.1	ND	81	6.0	99	102	384	2800	0	•	0
5-Methylchrysene	ND	ND	2.2	2.8	2.2	ND																
Cyclopenta[c,d]pyrene	5.8	ND	5.9	14	12	ND	3.9	0.0	9.2	10												
Benzo[b]fluoranthene	55	5.5	66	127	141	1.3	6.5	3.7	1.2	5.2	2.3	2.2	0.5	60	5.1	113	113					0
Benzo[k]fluoranthene	29	2.8	35	68	80	0.8	3.0	2.3	0.9	3.2	1.4	1.2	0.2	29	3.1	64	67			0		0
Benzo[j]fluoranthene	25	1.9	29	54	66	0.3	2.5	1.0	ND	1.7	0.5	0.8	ND	23	1.6	47	51					
Benzo[e]pyrene	48	4.6	63	111	114	0.8	3.3	2.4	ND	2.9	0.3	2.4	0.0	37	4.0	70	70			0		
Benzo[a]pyrene	43	4.3	55	109	105	1.6	4.2	3.5	2.4	4.9	1.8	2.4	0.5	38	4.2	95	88	430	1600	0	•	0
perylene	36	7.8	87	300	229	1.5	16	3.5	ND	2.3	ND	1.9	1.4	110	6.4	75	81					
Dibenz[ah]Anthracene	6.8	ND	7.5	20	17	0.1	19	ND	ND	ND	ND	ND	ND	6.8	ND	18	17	63.4	260		•	0
Indeno[123cd]pyrene	53	3.3	54	113	121	0.8	4.3	1.8	ND	3.4	0.1	1.4	ND	52	2.5	107	98					0
Benzo[ghi]Perylene	73	6.7	73	141	144	1.7	19	1.8	ND	4.2	1.0	1.5	0.3	58	3.7	94	103			0		0
Dibenzo[al]pyrene	0.0	ND																				
Dibenzolaejpyrene	6.3	ND	7.8	19	13	ND	6.9	ND	17	15												
Dibenzolaijpyrene	ND																					
Dibenzolanjpyrene	ND																					
Σ ₈ PAHs ^u	607	57	644	1111	1415	14	58	34	15	43	14	25	4.5	480	39	792	847					
Σ ₁₄ PAHs ^d	662	88	673	1177	2089	25	73	40	32	61	31	39	13	550	65	809	857					
Σ ₁₆ PAHs ^e	853	96	881	1573	2470	26	103	48	32	73	32	42	13	719	72	1153	1216					
Σ ₂₇ PAHs	991	120	1097	2128	3011	32	128	56	34	84	37	51	15	928	91	1405	1465					
Mean ERM-Quotient ^f	0.026	0.005	0.030	0.057	0.108	0.001	0.008	0.002	0.002	0.003	0.002	0.002	0.001	0.026	0.004	0.040	0.041					
a EBI =Effects range low																						

Table 2 Concentrations of PAHs in sediment (ng/g-dry)

b ERM=Effects range-medium c Lake Biwa Environmental Research Institu

c Lake Biwa Environmental Research Institute's survey(2015) d Kadokami et al(2013).

d Kadokami et al(201 e 16 EPA priority PAH

f A mean ERM -Quotientd is calculated by summing individual quotients (concentration/ERM) and dividing by the number of quotients IND Not detected 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 Administration, according to previous studies. 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 quotients.', 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 sources⁴⁰. 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)), and IDP/(IDP+BghiP) were plotted against Flth/(Flth+Pyr) and compared with previously reported source data⁴⁰. 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. Commonly, a ratio of LMW/HMW <1 suggests a pollution of pyrolytic origin^{mitit}. 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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