

Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Naphthalenes (PCNs) in Sediment of Hyogo Prefecture, Japan.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are known as environmental contaminants which occur in oil, coal and tar deposits, and are produced as byproducts of fuel burning. Some of PAHs may cause abnormal effect such as carcinogenicity, mutagenicity and teratogenicity. Polychlorinated naphthalenes (PCNs) have been used as cable insulation, wood preservatives, engine oil additives, electroplating masking compounds. In 2015, PCNs (including di- to octa-chlorinated naphthalene) was added to Annex A (elimination) and Annex C (reduction of unintentional production) of the Stockholm Convention. Both PAHs and PCNs are widespread environmental pollutants. However, there is little information about the concentration level of PAHs and PCNs in sediment of Hyogo prefecture [1,2]. In this study, PAHs and PCNs in sediment were investigated in Hyogo prefecture, Japan.

Materials and methods

Sampling points

The river and sea sediments were sampled for 3 years from 2015 to 2017. Sampling points (PAHs: R1, R2, R3, R4, R5, R6, R7, S1, PCNs: R1, R2, R4, R6, R7, R8, R9, S1) were shown in Figure 1.

Analytical procedure of PAHs

A 30 g of wet sediment sample was mixed with hydromatrix (Agilent) and copper (Kishida-kagaku, OSAKA, reduced, granular), transferred to accelerated solvent extraction (ASE) cell, and spiked with US EPA 16 PAH Cocktail (¹³C₆, CIL) as the surrogate. The sample was extracted with acetone/hexane (1:1) by ASE350 (Thermo Scientific, 100°C, 1500 psi, 2cycles). The extract was poured into a separatory funnel with pure water and sodium chloride, and solvent-exchanged by shaking. The hexane phase was separated from the extract by decantation. The hexane extract was dehydrated with anhydrous sodium sulfate and concentrated to 4 mL. Next, Sep-Pak Vac 12 cc (2 g) Silica Cartridge (Waters) was washed with hexane, and the part of the hexane concentrate (1 mL) was applied to the silica cartridge. The cartridge was eluted with 20 mL of 5% dichloromethane/hexane. The eluate was concentrated to approximately 3 mL with a rotary evaporator (25°C). The eluate was added to the reduced copper (Wako, powder) as necessary. Then the eluate was concentrated to 1 mL with nitrogen gas (25°C). After being added naphthalene-*d*₈, phenanthrene-*d*₁₀, perylene-*d*₁₂ as an internal standard, the measurement was performed using a GC/MS system consisting of 6890N (Agilent) gas chromatograph and JMS-800D (JEOL) high-resolution mass spectrometer. The capillary column was DB-17MS (30m, 0.25mm, 0.25µm). The target compounds were 27 PAHs (number of ring): Naphthalene (2), 2-Methylnaphthalene (2), Acenaphthylene (3), Acenaphthene (3), Fluorene (3), Phenanthrene (3), Anthracene (3), Fluoranthene (4), Pyrene (4), Benz[a]Anthracene (4), 5-Methylchrysene (4), Chrysene (4), Triphenylene (4), Cyclopenta[c,d]pyrene (5), Benzo[b]fluoranthene (5), Benzo[k]fluoranthene (5), Benzo[j]fluoranthene (5), Benzo[e]pyrene (5), Benzo[a]pyrene (5), Perylene (5), Dibenz[ah]Anthracene (5), Indeno[123cd]pyrene (6), Benzo[ghi]Perylene (6), Dibenzo[al]pyrene (6), Dibenzo[ae]pyrene (6), Dibenzo[ai]pyrene (6), Dibenzo[ah]pyrene (6). Quantification was carried out by isotope dilution method using a surrogated compound.

Analytical procedure of PCNs

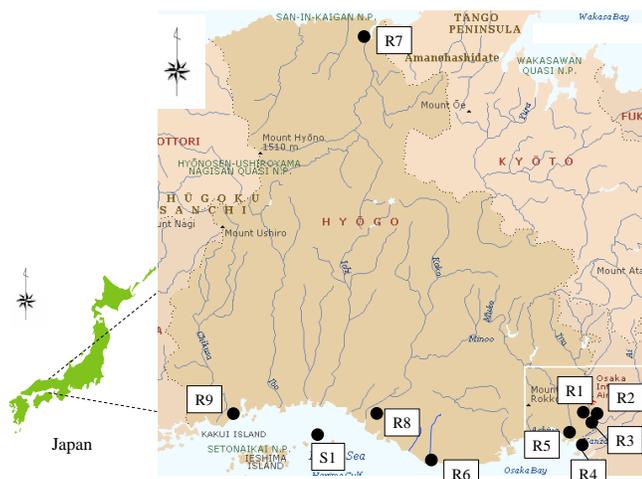


Figure 1: Sampling points of sediment in Hyogo

The method of ASE and concentration was the same as that of PAHs. MBP-3, MBP-15 ($^{13}\text{C}_{12}$, Wellington) and Tetra-Octa PCN Mixture ($^{13}\text{C}_{10}$, CIL) were used as a surrogate. The part of the hexane concentrate (1 mL) was cleaned with sulfuric acid, Sep-Pak Plus Silica cartridge (Waters) and Carboxen 1000 Reversible tube (Supelco, 100 mg). Connected columns (1st Sep-Pak Plus Silica, 2nd Carboxen 1000) were loaded sulfuric acid treated sample, washed with hexane (50 mL) and 20% DCM/ hexane (60 mL). After Sep-Pak Plus Silica was removed, the PCNs fraction was eluted using 80 mL toluene with reverse direction [3]. To the eluate was added the reduced copper as necessary, and was concentrated to 0.1 mL with nitrogen gas. After being added MBP-8, 28, 70, 101, 170 ($^{13}\text{C}_{12}$, Wellington) as an internal standard, the analyte was determined by the same method as PAHs. The capillary column was HT8-PCB (60m, 0.25mm). The target congeners were mono- to octa-chlorinated naphthalenes.

Results and discussion

PAHs

Average recoveries of surrogate were 49-89% (depending on compound). Method detection limit (MDL) was ranged from 0.1 to 24 ng/g-dry (depending on compound). The difference between analysis value and certified value of SRM 1941b (NIST) was small. Figure 2 shows the concentration distribution by the number of rings. For convenience, Dibenz [ah] Anthracene / Indeno [123cd] pyrene was calculated as 5-ring. Many kinds of PAHs were detected from sediment, but fluoranthene and pyrene were the most abundant compound. Compared to the number of rings, the ratio of 4-ring and 5-ring was high. The range of ΣPAHs concentration were from 15 to 1500 ng/g-dry, and it was found to be within the range of the result of Tokyo Bay (329 to 2598 ng/g-dry) [4]. The concentrations of R1, R3, R4 and S1 were relatively higher in Hyogo prefecture. It seems that these points were affected by households and industries. It is known that the sources of PAHs were originated from crude and refined petroleum, combustion of fossil fuel such as petroleum and coal and biomass such as grass and wood etc. Some molecular ratios of specific hydrocarbons have been developed to distinguish PAHs sources generated from different sources. Phenanthrene (Phen), anthracene (Ant), fluoranthene (Flth) and pyrene (Pyr) were normally used to obtain these ratios [5]. The results of these ratios in this study were shown in Figure 3. Ant / (Ant + Phen) ratio and Flth / (Flth + Pyr) were ranged from 0.07 to 0.21 and 0.49 to 0.53, respectively, which may suggest that the majority of PAHs in sediment of Hyogo prefecture was derived from combustion of fossil fuel and biomass. There are few cases of investigating PAHs in sediment of Hyogo prefecture, and we plan to expand the survey area and estimate the origin.

PCNs

Average recoveries of surrogate were 33-57% (depending on homologue). Method detection limit (MDL) was ranged from 0.003 to 0.01 ng/g-dry (depending on homologue). PCNs was not detected at R6, R7, R8, R9. The concentration of ΣPCNs at R1, R2, R4 and S1 were 1.7, 0.34, 4.5 and 0.37 ng/g-dry, respectively. It was found to be within the range of national survey (0.032 to 28 ng/g-dry)[1]. Figure 4 shows the concentration of ΣPCNs homologue in sediment (R4 and S1). Tri- to penta- chlorinated naphthalenes were major homologue. In 2008, Ministry of the Environment, Japan, investigated the concentration of PCNs in S1 sediment, and the average value of ΣPCNs was 0.36 ng/g-dry [1]. Since the value has not changed so much, the possibility of new contamination is considered to be small. It has been recognized that PCNs show dioxin-like toxicities because of their structural similarity to dioxins. The 2,3,7,8-tetrachlorodibenzo-p-dioxin relative potency factors (RPFs)

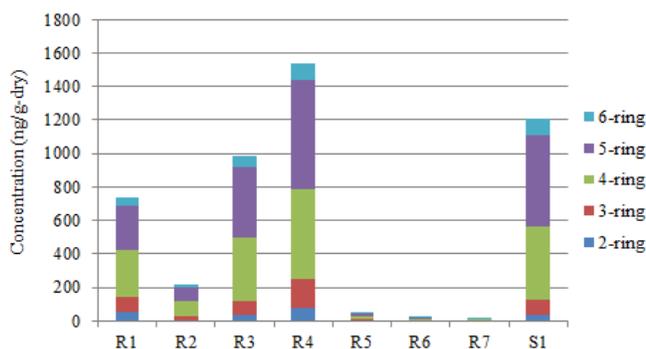


Figure 2: Concentrations of PAHs in sediment

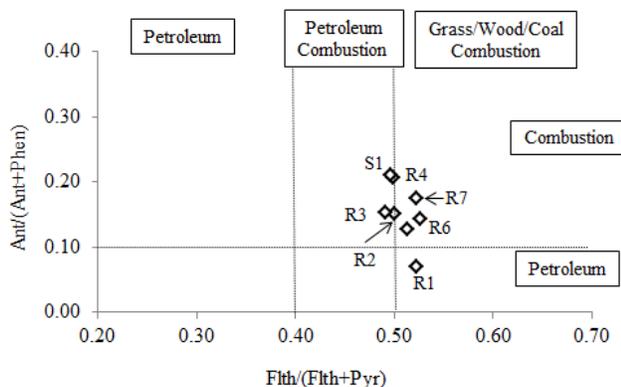


Figure 3: Estimation of potential source of PAHs in sediment

of individual congeners of PCNs have been estimated using their ethoxyresorufin-O-deethylase (EROD) activity or aryl hydrocarbon receptor (AhR)-mediated activity [6,7,8,9]. Many kinds of congeners were detected at R4 and referred to the previous reports [10,11]. The dioxin-like toxicities of PCNs at R4 samples were estimated using these RPFs [6,7,8,9,12]. The concentration of each congener of R4 was quantified, and it was estimated that total TEQ was 0.54 pg-TEQ/g-dry (Table 1). The TEQ of total (PCDDs+PCDFs) and of total Co-PCBs at R4 sediment were 54 and 23 pg-TEQ/g-dry, respectively, which revealed that the TEQ of PCNs was very small. In future, we will improve the recoveries of surrogate and expand the survey area.

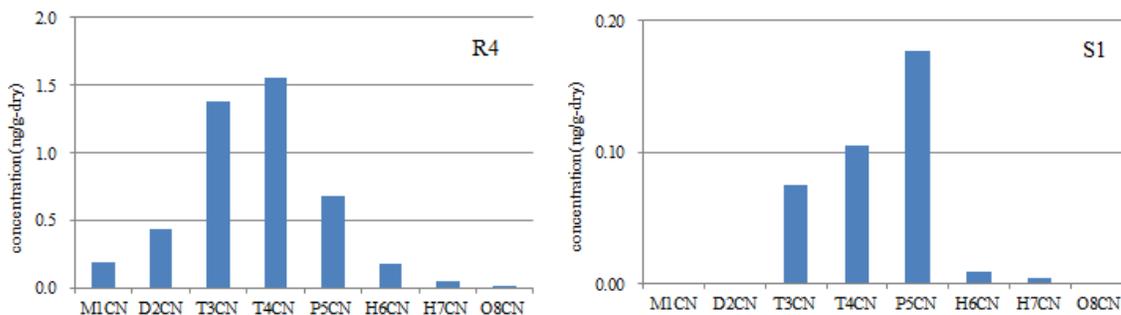


Figure 4: Concentrations of PCNs homologue in sediment (ng/g-dry) (left: point R4, right: point S1)

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Table 1: Concentrations and estimated TEQ of PCNs in R4 sediment

congener	IUPAC no.	RPFs	concentration (ng/g-dry)	estimated TEQ (ng-TEQ/g-dry)
2-	2	1.8×10^{-5}	0.058	0.0000010
1-	1	1.7×10^{-5}	0.18	0.0000031
1,4-/1,6-	5/7	1.8×10^{-8}	0.54	0.000000097
1,3-	4	2.0×10^{-8}	0.078	0.000000016
2,3-	10	2.7×10^{-5}	0.015	0.00000041
1,2,5,8-	38	8.5×10^{-6}	0.29	0.0000025
1,2,6,8-	40	8.5×10^{-6}	0.018	0.00000015
2,3,6,7-/ 1,2,4,8-	48/35	2.1×10^{-5}	0.12	0.0000025
1,2,3,6,7-	54	1.7×10^{-4}	0.009	0.0000015
1,2,3,7,8-	56	4.6×10^{-5}	0.009	0.00000041
1,2,4,5,6-	57	1.6×10^{-6}	0.077	0.00000012
1,2,3,4,6-	50	6.8×10^{-5}	0.044	0.0000030
1,2,3,4,6,7- /1,2,3,5,6,7-	66/67	2.5×10^{-3}	0.062	0.00016
1,2,3,4,5,7-/ 1,2,3,5,6,8-	64/68	1.0×10^{-3}	0.046	0.000046
1,2,3,6,7,8-	70	2.1×10^{-3}	0	0
1,2,4,5,6,8-/1,2,4,5,7,8-	71/72	3.5×10^{-6}	0.066	0.00000023
1,2,3,4,5,6-	63	2.0×10^{-3}	0.037	0.000074
1,2,3,5,7,8-	69	2.0×10^{-3}	0.075	0.00015
1,2,3,4,5,6,7-	73	3.0×10^{-3}	0.032	0.000096
total	-	-	-	0.00054