

A Fundamental Study on the Characteristics of Concentration Using a Blue Chitin Column for Polycyclic Aromatic Hydrocarbons in Water

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In order to evaluate the contribution of polycyclic aromatic hydrocarbons (PAHs) to mutagenicity of concentrates from water, the adsorption, elution and recovery behavior of 26 PAHs bearing 3 to 6 rings were investigated by the Blue Chitin column method. The adsorption rates of 22 PAHs, having three or more fused rings, to Blue Chitin were over 90%. Elution rates of PAHs with 4 and 5 rings and nitroarenes (NO₂-PAHs) adsorbed on Blue Chitin were 50–70% with 100 ml of methanol–ammonia (CH₃OH–NH₄OH) (50 : 1). However, elution rates of PAHs with 3 and 6 rings and aminoarenes (NH₂-PAHs) were 0–40% with 100 ml of the same mixed eluate. However, additional elution with 20 ml of dichloromethane (CH₂Cl₂) following the elution with 100 ml of CH₃OH–NH₄OH (50 : 1) raised the elution ratio by 10–30%. Elution employing CH₂Cl₂ was thus more effective for elution of PAHs adsorbed to Blue Chitin. Using this preconcentration method on a modified Blue Chitin column, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene and dibenz[*a,h*]anthracene in effluent water and fluoranthene, pyrene and benzo[*k*]fluoranthene in river water were detected. In summary, this preconcentration method using a modified Blue Chitin column was useful for concentration of PAHs and NO₂-PAHs with 4 and 5 rings from environmental water.

Key words—polycyclic aromatic hydrocarbons, Blue Chitin, preconcentration method, environmental water, GC-MS

INTRODUCTION

Municipal river water generally receives much of the waste water drained from the activities of human life; the effluent of sewage disposal plants, industrial waste plants and road runoff. Many studies have examined municipal river water which contains trace amounts of organic pollutants possessing principally frameshift type mutagenicity.^{1–9)}

Concentrates of municipal river water obtained using the Blue Rayon column concentration method, which is capable of adsorbing polycyclic aromatic hydrocarbons (PAHs) with three or more fused rings, have been shown to have frameshift type mutagenicity by Ames assay. They were also recognized as very mutagenic by Ames assay using new *Salmonella*

tester strains, which are highly sensitive to mutagenic nitroarenes (NO₂-PAHs) and aminoarenes (NH₂-PAHs). Thus, in this river water, some of the frameshift type-mutagenic materials may be NO₂-PAHs and NH₂-PAHs.

Large amounts of PAH derivatives enter the environment *via* the incomplete combustion of coal, oil, wood and paper. There have been many reports of PAHs detected in exhaust gas by incineration of refuse, vehicle traffic and waste water. However, there is little analytical data on PAHs in environmental water, especially river water.¹⁰⁾

Blue Chitin with higher selectivity and efficiency for concentrating PAHs than Blue Rayon was recently developed. The main characteristics of the adsorptive efficiency of Blue Chitin described were for heterocyclic amines such as 2-aminodipyrido[1,2-*a*:3',2'-*d*]imidazole (Glu-P-2), 2-amino-3-methylimidazo[4,5-*f*]quinoline (IQ), 2-amino-3,8-dimethylimidazo[4,5-*f*]quinoxaline (MeIQx), 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP), and 3-amino-1-methyl-5H-

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pyrido[4,3-*b*]indole (Trp-P-2). No description of application to polycyclic aromatic pollutants in water was presented.

The major purpose of the present study was to evaluate the exact contribution of PAHs to mutagenicity of concentrates from water, as obtained by Blue Chitin column method. In this paper, we report the adsorption, elution and recovery behavior by the preconcentration method of twenty-six PAHs bearing 3 to 6 rings from environmental water by Blue Chitin column.

MATERIALS AND METHODS

Chemicals — Chemical sources were as follows:

acenaphthylene (Anl), acenaphthene (An), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (FA), pyrene (PY), benz[*a*]anthracene (B[*a*]A), chrysene (Chr), benzo[*a*]pyrene (B[*a*]P) and dibenz[*a,h*]anthracene (diB[*a,h*]A) were from Wako Pure Chemical Industries, Ltd.; benzo[*ghi*]perylene (B[*ghi*]P), 5-nitroacenaphthene (5-NAn), 3-nitrofluoranthene (3-NFA), 1-nitropyrene (1-NPY), 2,7-dinitrofluorene (2,7-diNFl), 1,3-dinitropyrene (1,3-diNPY), 1,6-dinitropyrene (1,6-diNPY), 1,8-dinitropyrene (1,8-diNPY), 2-aminofluorene (2-AFl), 1-aminoanthracene (1-AAnt), 2-aminoanthracene (2-AAnt), 3-aminofluoranthene (3-AFA) and 1-aminopyrene (1-APY) were from Aldrich Chemical Co. Inc.; benzo[*b*]fluoranthene (B[*b*]FA) and benzo[*k*]fluoranthene (B[*k*]FA) were from RK Chemical Co.; methanol (CH₃OH), ammonia (NH₄OH), dichlor-

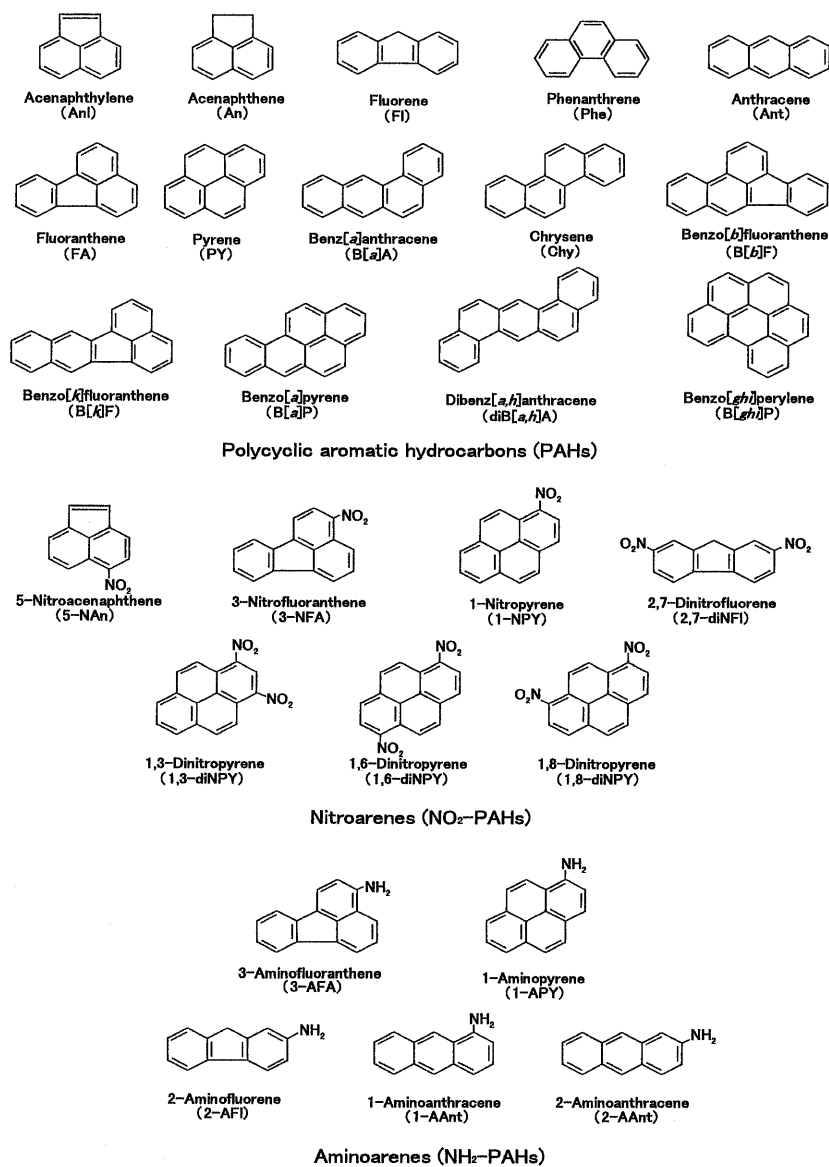


Fig. 1. Structure of PAHs

Table 1. GC-MS Conditions for Determination of PAHs

Column:	HP-5 Trace Analysis (5% PH ME Silicone) 30 m×0.25 mm i.d. 0.1 μ m film thickness
Temperature:	Column: 60°C (1 min)—15°C/min—140°C—10°C/min—300°C Injection port: 290°C Interface: 275°C Ion source: 200°C
Injection mode:	Splitless
Carrier gas:	He (40 cm/s, constant velocity)
Mass spectrometer:	Ionization energy: 70 eV Ionization current: 300 μ A
Injection:	1 μ l

omethane (CH₂Cl₂), cyclohexane (C₆H₁₂) and trifluoroacetic acid (CF₃COOH) were also from Wako Pure Chemical Industries, Ltd.

Mixed PAH standard solution (1 μ g/ml) was prepared by using individual solutions (100 μ g/ml) of PAH dissolved in CH₂Cl₂. However, the concentrations of 2,7-diNFl, 1,3-diNPY, 1,6-diNPY, 1,8-diNPY, 1-AAnt and 2-AAnt were 5 μ g/ml, respectively. The structures of these PAHs are shown in Fig. 1.

The column was prepared by placing 200 mg of Blue Chitin (Funakoshi, Ltd.) in a tube (14 mm i.d. × 6 mm). The adsorbent was in a powdered form containing 40 μ mol/g copper phthalocyanine trisulfonate.

Water Samples—The effluents from night soil and sewage treatment plants, septic tanks combined with aerobic treatment, and landfill sites were sampled in Gifu.

The surface water of the Katsura River, the Uji River and the Kizu River were sampled in September 1997. The surface water of the Nagara River, the Sakai River, the Arata River and the Kuwabara River were sampled in September 1998.

These water samples were analyzed as quickly as possible, and 20 l was filtered through a paper filter before concentration.

Preconcentration Method by Blue Chitin Column—Five liters of water spiked with 1 ml of mixed PAH standard solution was passed through a Blue Chitin column, which was washed as described previously,¹⁰⁾ at a flow rate of 20 ml/min with a peristaltic pump, and then the column was washed with 20 ml of water. The organics adsorbed in the column were consecutively eluted with 100 ml CH₃OH–NH₄OH (50:1) and 20 ml CH₂Cl₂ at a flow rate of 5 ml/min. The fractions with both CH₃OH–NH₄OH (50:1) and CH₂Cl₂ were mixed and evaporated to dryness with a rotary evaporator in a water bath at about 40°C. Concentrate was dissolved in 1 ml of CH₂Cl₂ for

Table 2. Properties of PAHs and Detection Limits by GC-MS Analysis

Compound	Molecular weight	Number of aromatic rings	Detection limit (pg)
Acenaphthylene	152.2	3	50
Acenaphthene	154.2	3	10
Fluorene	166.2	3	10
Phenanthrene	178.2	3	10
Anthracene	178.2	3	10
Fluoranthene	202.3	4	10
Pyrene	202.3	4	10
Benz[<i>a</i>]anthracene	228.3	4	50
Chrysene	228.3	4	20
Benzo[<i>b</i>]fluoranthene	252.3	5	20
Benzo[<i>k</i>]fluoranthene	252.2	5	20
Benzo[<i>a</i>]pyrene	252.3	5	20
Dibenz[<i>a,h</i>]anthracene	278.4	5	50
Benzo[<i>ghi</i>]perylene	276.3	6	50
5-Nitroacenaphthene	199.2	3	50
2,7-Dinitrofluorene	256.2	3	1000
3-Nitrofluoranthene	247.3	4	100
1-Nitropyrene	247.3	4	100
1,3-Dinitropyrene	292.3	4	1000
1,6-Dinitropyrene	292.3	4	1000
1,8-Dinitropyrene	292.3	4	1000
2-Aminofluorene	181.2	3	100
1-Aminoanthracene	193.3	3	500
2-Aminoanthracene	193.3	3	500
3-Aminofluoranthene	217.3	4	100
1-Aminopyrene	217.3	4	100

GC-MS analysis.

GC-MS Analysis—The GC-MS analytical method for PAHs in water was according to US EPA Method 610.¹¹⁾ GC-MS was used with a Thermoquest GCQ. The GC-MS conditions are shown in Table 1. Table 2 shows the properties and limits of detection of these 26 different PAHs under these analytical conditions.

RESULTS

Adsorption of PAHs in Water to Blue Chitin

We used water spiked with a mixed PAH standard solution to study the adsorptive properties of 26 PAHs to a Blue Chitin column. The adsorptive amount was calculated by subtracting the flow-through amount from the amount of spiked PAHs. The amounts were given by GC-MS analysis of concentrates that were extracted with CH_2Cl_2 .

Adsorption of PAHs to Blue Chitin is shown in Table 3. Although the adsorption rates of AnI, An, Fl and 5-NAn were 60–80%, those of the other 22 PAHs were over 90%.

Elution Behavior of Adsorbed PAHs

According to the original method¹⁰⁾, PAHs adsorbed to a Blue Chitin column are eluted with a volume of 100 ml of $\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1). However, if the eluate volume can be to reduce, the operation time may be shorter. To check the appropriate amount of $\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1) for effective elution of adsorbed PAHs, the volume of eluate was set at 20, 50, 100 and 200 ml of $\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1).

Figure 2 shows the elution patterns of PAHs and NO_2 -PAHs with $\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1). Two elution patterns were recognized. One group was PAHs with 4 and 5 rings such as PY, B[a]P, etc.. Most of these PAHs were eluted at 50 to 100

Table 3. Adsorption of PAHs to Blue Chitin and Elution of the Adsorbed PAHs by the Blue Chitin Column Method

Compound	Adsorption rate to Blue Chitina ^{a)} (%)	Elution rate ^{b)} (%)				
		$\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1) ^{c)}	$\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1)+ CH_2Cl_2 ^{d)}	$\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1)+ C_6H_{12} ^{e)}	$\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1) + $\text{CH}_3\text{OH}-\text{CF}_3\text{COOH}$ (100 : 1) ^{f)}	CH_2Cl_2 ^{g)}
Acenaphthylene	78	0	0	0	0	0
Acenaphthene	75	0	2	2	2	2
Fluorene	79	0	8	4	4	7
Phenanthrene	94	3	34	5	6	24
Anthracene	95	3	27	4	7	23
Fluoranthene	98	60	81	62	64	28
Pyrene	97	58	82	60	62	24
Benz[a]anthracene	96	66	85	67	69	34
Chrysene	96	71	91	74	75	31
Benzo[b]fluoranthene	96	58	83	59	61	27
Benzo[k]fluoranthene	94	67	88	68	73	31
Benzo[a]pyrene	95	55	73	58	57	27
Dibenz[a,h]anthracene	95	60	75	60	62	29
Benzo[ghi]perylene	93	11	32	11	13	22
5-Nitroacenaphthene	66	59	66	60	62	27
2,7-Dinitrofluorene	100	59	63	62	62	0
3-Nitrofluoranthene	100	65	75	65	66	35
1-Nitropyrene	100	60	71	65	67	18
1,3-Dinitropyrene	100	63	70	67	67	16
1,6-Dinitropyrene	100	64	70	69	69	16
1,8-Dinitropyrene	100	68	70	68	68	15
2-Aminofluorene	100	15	17	16	16	0
1-Aminoanthracene	100	6	6	6	6	0
2-Aminoanthracene	100	8	8	8	8	0
3-Aminofluoranthene	100	42	43	42	42	0
1-Aminopyrene	100	22	23	22	22	0

a) Adsorption was calculated by subtracting the flow-through amount from the amount of spiked PAHs. b) Elution rates are expressed as percentage of elution amount to adsorption amount. c) PAHs adsorbed on the column were eluted with 100 ml $\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1). d) PAHs adsorbed on the column were eluted with 100 ml CH_2Cl_2 following the elution with 100 ml $\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1). e) PAHs adsorbed on the column were eluted with 100 ml C_6H_{12} following the elution with 100 ml $\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1). f) PAHs adsorbed on the column were eluted with 100 ml $\text{CH}_3\text{OH}-\text{CF}_3\text{COOH}$ (100 : 1) following the elution with 100 ml $\text{CH}_3\text{OH}-\text{NH}_4\text{OH}$ (50 : 1). g) PAHs adsorbed on the column were eluted with 100 ml CH_2Cl_2 .

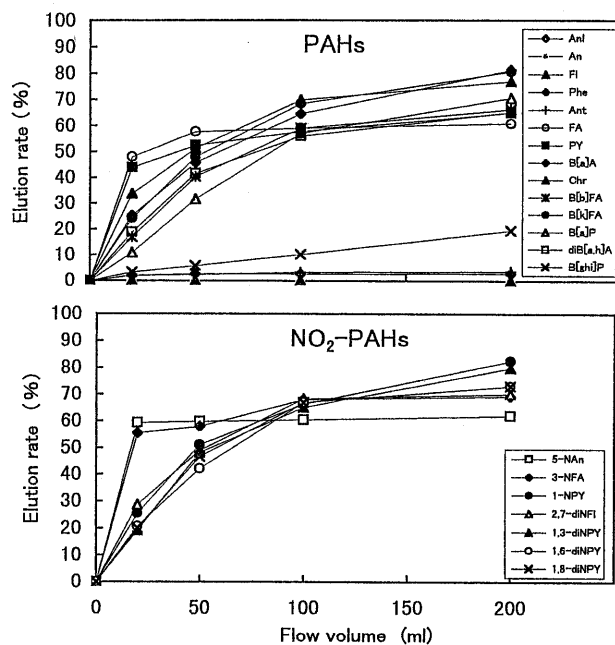


Fig. 2. Elution Pattern of PAHs and NO₂-PAHs Adsorbed on a Blue Chitin Column, with CH₃OH-NH₄OH (50 : 1)

ml CH₃OH-NH₄OH (50 : 1) and plateaued at from 100 to 200 ml. The elution rates were 60–80% at 200 ml. The other group was PAHs with 3 and 6 rings, and the elution rates were 0–20% at 200 ml. The elution patterns and rate of NO₂-PAHs were almost the same as those of PAHs in the first group.

From these results, we confirmed that the volume of CH₃OH-NH₄OH (50 : 1) as eluate for effective elution of PAHs adsorbed to a Blue Chitin column was appropriate at 100 ml.

Elution Solvent for Adsorbed PAHs

In the elution of PAHs adsorbed to Blue Chitin, elution rates of analogs with 3 and 6 rings and NH₂-PAHs were low (0–40%) with 100 ml of CH₃OH-NH₄OH (50 : 1). We therefore assumed that these compounds were still adsorbed to the Blue Chitin and therefore eluted with 100 ml of either CH₂Cl₂, C₆H₁₂ or CH₃OH-CF₃COOH (100 : 1), which are known to easily dissolve hydrophobic PAHs.

The elution rate with each solvent is shown in Table 3. Elution with 100 ml of C₆H₁₂ or CH₃OH-CF₃COOH (100 : 1) was not effective since only a small increase in the elution rate was noted. Elution rates of 11 PAHs (except Anl, An and Fl) and NO₂-PAHs (3-NFA and 1-NPY) with 100 ml CH₂Cl₂ increased by about 10–30%, however, CH₂Cl₂ alone was not effective, since under

these conditions the elution rates of PAHs, NO₂-PAHs and NH₂-PAHs were 0–35%. These results suggested that additional elution with 100 ml CH₂Cl₂ following the elution with 100 ml CH₃OH-NH₄OH (50 : 1) was effective for quantitative recovery of the adsorbed PAHs.

Considering these findings, CH₂Cl₂ was the most suitable as the additional eluate, and a check was carried out to deduce the appropriate volume. Since an elution volume from 20 to 100 ml showed no increase in elution rate, a 20 ml volume was selected as optimal. We then confirmed that elution with 20 ml CH₂Cl₂ following elution with 100 ml CH₃OH-NH₄OH (50 : 1) offered a better recovery than elution with only 100 ml CH₃OH-NH₄OH (50 : 1).

The recoveries of the 26 PAHs were as follows: Anl, An, Fl, 1-AAnt and 2-AAnt were 0–10%, Phe, Ant, B[ghi]P, 2-Afl, 1-APY, 3-NFA and 3-AFA were 10–60%, and the 14 other compounds were more than 60%. In particular, the recoveries of PAHs and NO₂-PAHs with 4 or 5 rings were over 70%. However, recoveries of NH₂-PAHs and PAHs with 3 or 6 rings were low. Hence, since the preconcentration method using a Blue Chitin column was useful for PAHs with 4 or 5 rings and NO₂-PAHs, we focused on these types of PAHs to elicit their occurrence in a water environment.

Occurrence of PAHs in Effluent from Various Treatment Plants and River Water

The presence of PAHs in effluents from 4 different treatment plants and water from 8 different rivers located in Gifu and Osaka was investigated. Five liters of sample water was treated by the Blue Chitin column preconcentration method. The total ion chromatograms, obtained by GC-MS¹¹⁾ of the mixed PAH standard solution, the sewage plant effluent, and the water from the Sakai River are shown in Fig. 3. These results are collected in Tables 4 and 5.

Eight types of PAH were detected in the effluent from a night soil treatment plant. The detection levels were 10–18 ng/l, with the highest level being shown by FA. Three PAHs were detected in the effluent from sewage treatment plants; they were detected at levels of 8–17 ng/l, with FA the highest. FA was detected in the water of 7 rivers and PY was detected in the water of 5 rivers; their levels were 3–17 ng/l.

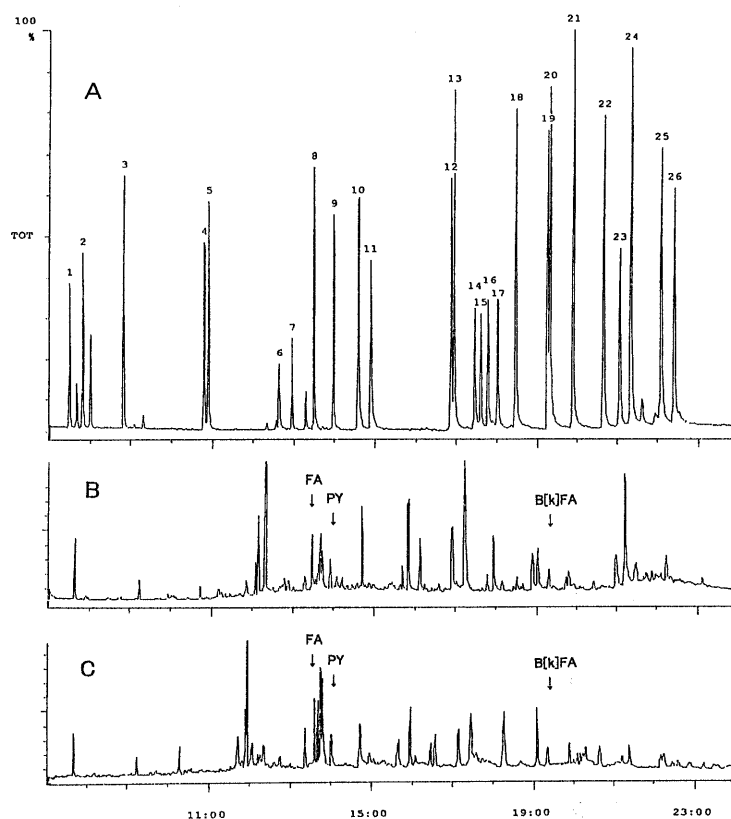


Fig. 3. Total Ion Chromatograms of Standard Solutions of 26 PAHs and Concentrates from Effluent Water and River Water

A: PAH standards. 1, acenaphthylene; 2, acenaphthene; 3, fluorene; 4, phenanthrene; 5, anthracene; 6, 2-aminofluorene; 7, 5-nitroacenaphthene; 8, fluoranthene; 9, pyrene; 10, 1-aminoanthracene; 11, 2-aminoanthracene; 12, benz[*a*]anthracene; 13, chrysene; 14, 3-aminofluoranthene; 15, 3-nitrofluoranthene; 16, 1-aminopyrene; 17, 1-nitropyrene; 18, 2,7-dinitrofluorene; 19, benzo[*b*]fluoranthene; 20, benzo[*k*]fluoranthene; 21, benzo[*a*]pyrene; 22, 1,3-dinitropyrene; 23, 1,6-dinitropyrene; 24, 1,8-dinitropyrene; 25, dibenz[*a,h*]anthracene; 26, benzo[*ghi*]perylene; B: sewage treatment plant; C: Sakai River

Table 4. Concentrations of PAHs in the Effluent of Purification Plants

Compound	(ng/l)			
	Night soil treatment plant	Sewage treatment plant	Septic tanks combined with aerobic treatment	Landfill sites
Fluoranthene	18	17	16	8
Pyrene	8	10	4	<2
Benz[<i>a</i>]anthracene	10	<10	<10	<10
Chrysene	11	<4	<4	<4
Benzo[<i>b</i>]fluoranthene	11	<4	<4	<4
Benzo[<i>k</i>]fluoranthene	13	8	<4	5
Benzo[<i>a</i>]pyrene	15	<4	<4	5
Dibenz[<i>a,h</i>]anthracene	17	<10	<10	<10
2,7-Dinitrofluorene	<200	<200	<200	<200
3-Nitrofluoranthene	<20	<20	<20	<20
1-Nitropyrene	<20	<20	<20	<20
1,3-Dinitropyrene	<200	<200	<200	<200
1,6-Dinitropyrene	<200	<200	<200	<200
1,8-Dinitropyrene	<200	<200	<200	<200

Table 5. Concentrations of PAHs in River Water

Compound	(ng/l)							
	Nagara R.		Tributary of Nagara R.			Tributary of Yodo R.		
	Upstream	Downstream	Sakai R.	Arata R.	Kuwabara R.	Katsura R.	Uji R.	Kizu R.
Fluoranthene	<2	3	17	4	5	4	3	3
Pyrene	<2	3	10	7	4	3	<2	<2
Benz[<i>a</i>]anthracene	<10	<10	<10	<10	<10	<10	<10	<10
Chrysene	<4	<4	<4	<4	<4	<4	<4	<4
Benzo[<i>b</i>]fluoranthene	<4	<4	<4	<4	<4	<4	<4	<4
Benzo[<i>k</i>]fluoranthene	<4	<4	6	<4	7	<4	<4	<4
Benzo[<i>a</i>]pyrene	<4	<4	<4	<4	<4	<4	<4	<4
Dibenz[<i>a,h</i>]anthracene	<10	<10	<10	<10	<10	<10	<10	<10
2,7-Dinitrofluorene	<200	<200	<200	<200	<200	<200	<200	<200
3-Nitrofluoranthene	<20	<20	<20	<20	<20	<20	<20	<20
1-Nitropyrene	<20	<20	<20	<20	<20	<20	<20	<20
1,3-Dinitropyrene	<200	<200	<200	<200	<200	<200	<200	<200
1,6-Dinitropyrene	<200	<200	<200	<200	<200	<200	<200	<200
1,8-Dinitropyrene	<200	<200	<200	<200	<200	<200	<200	<200

DISCUSSION

Some of the frameshift type-mutagenic materials contained in municipal river water appear to be PAHs such as NO₂-PAHs or NH₂-PAHs. However, little information exists on how wide the range of PAHs in environmental water is.

Many analytical studies of PAHs in water¹²⁻¹⁴ have been reported, and although some report the mutagenicity of the water, the preconcentration method for water samples for Ames assay and for analysis of PAHs has differed,¹⁵ and the preconcentration method has not been applied quantitatively.⁷ No detail has been described about adsorption, elution and recovery behaviors with a preconcentration method such as a Blue Chitin column.

A major purpose of this study was to evaluate the exact contribution of PAHs to mutagenicity of water concentrates, obtained by the Blue Chitin column method. We thus needed to know the concentration characteristics of PAHs in water using a Blue Chitin column in order to achieve the purpose of this study. Accordingly, we carried out a quantitative and fundamental study on adsorption, elution and recovery of 26 PAHs bearing 3 to 6 rings from environmental water using a Blue Chitin column as the preconcentration method.

The adsorption rates of 22 of 26 PAHs to Blue Chitin were more than 90%, but those of 4 other PAHs (Anl, An, Fl and 5-NAn) were 60—

80%. These results compliment the previous report by Hayatsu *et al.*¹⁰ and indicate that Blue Chitin selectively adsorbs compounds bearing more than 3 rings.

In the Hayatsu method, 100 ml CH₃OH-NH₄OH (50 : 1) was used for elution of polycyclics adsorbed to Blue Chitin. This amount of eluate was confirmed since most adsorbed PAHs were eluted with this volume. However, several compounds were not eluted, even with more than 100 ml. This suggested that these compounds remained attached to the surface of the Blue Chitin resin.

We thus compared the elution characteristics using CH₂Cl₂, C₆H₁₂ and CH₃OH-CF₃COOH (100 : 1) to completely elute the PAHs still adsorbed on Blue Chitin. Effective elution of PAHs was expected using a hydrophobic eluate such as C₆H₁₂ or CH₃OH-CF₃COOH (100 : 1), since PAHs are hydrophobic, a property which is enhanced with increasing molecular weight. It was recognized that the highly hydrophobic solvent CH₂Cl₂ was effective as an additional eluate for PAHs with 4 and 5 rings.

The elution mechanism of PAHs using CH₃OH-NH₄OH (50 : 1) and CH₂Cl₂ suggested that hydrophilic PAHs and a portion of the hydrophobic compounds were eluted with CH₃OH-NH₄OH (50 : 1) as the first eluate, and hydrophobic compounds were eluted with CH₂Cl₂ as the second eluate. The adsorption of PAHs to Blue Chitin is based on interaction between the

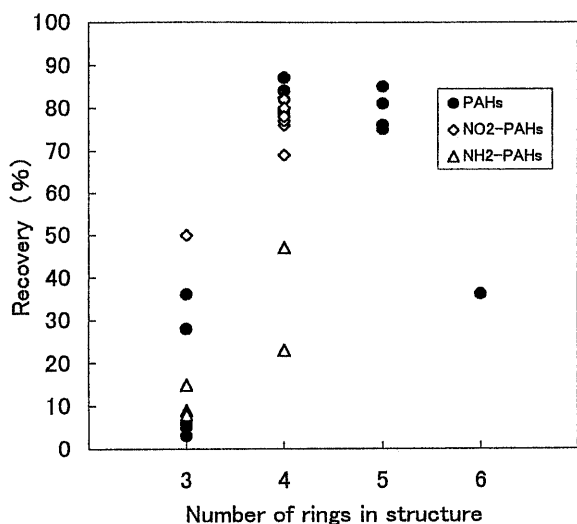


Fig. 4. Relationship between Recovery and Number of Rings in Structure

π -electron of PAHs and phthalocyanine copper on Blue Chitin.

The relationship between recovery of PAHs by the Blue Chitin column method and structural characteristics such as the presence of nitro or amino and the number of cyclic rings is shown in Fig. 4. This method may be efficient for highly hydrophobic compounds since good recovery was in the order PAHs \geq NO₂-PAHs > NH₂-PAHs, and 4 rings = 5 rings > 3 rings in terms of number of cyclic rings. These characteristics corresponded to the adsorption and elution behavior of PAHs from Blue Chitin. Thus, PAHs with 4 and 5 rings showed high recovery, but recovery decreased with addition of hydrophilic nitro and amino groups.

Detection of PAHs such as fluoranthene and pyrene in the effluent of treatment plants and river water in the present paper indicates that the source of pollution derived from human activities and roads.

This paper demonstrated the characteristics of adsorption and elution of 26 PAHs using the

Blue Chitin column method. These findings should be useful for evaluation of the contribution of PAHs to mutagenic concentrates from environmental waters.

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