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Pollution Levels of 16 Priority PAHs in the Major Rivers of Southern Thailand

Abdulnaser Hajisamoh*

Chemistry Program, Faculty of Science Technology and Agriculture, Yala Rajabhat University, Yala, 95000 Thailand

Research Article

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***For Correspondence:**

Chemistry Program, Faculty of Science Technology and Agriculture, Yala Rajabhat University, Yala, 95000 Thailand.
Fax: +6673299629

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ABSTRACT

This study involved the determination of 16 priority PAHs in river water samples collected from the 4 major rivers in the area of southernmost of Thailand. Solid phase extraction (SPE) technique was successfully applied for PAHs extraction from water samples, as this technique offers several advantages over normal liquid-liquid extraction such as efficient isolation and pre-concentration. The extraction of water samples were carried out by validated C-18 SPE cartridges. The cartridge was dried by nitrogen gas before being eluted with a solvent mixture of hexane and acetone (1:1 ratio). The analytes were quantified by SPB-5 capillary column gas chromatograph (GC-FID). Percentage recovery of 16 PAHs standards were in the range of 70.24±4.22 to 115.37±6.15 % which were within the acceptable ranges of US-EPA protocol. The commonly detected PAH compounds in river water samples of this study were acenaphthylene, anthracene, fluoranthene and benzo[k]fluoranthene at the concentration range of 0.02-0.10, 0.02-1.83, 0.05-19.50 and 0.09-10.11 ug/mL, respectively. The PAHs presented in water samples were mostly comprised 4-5 fused benzene rings, which reflecting that anthropogenic sources are among the possible origin of these organic pollutants that discharged into the rivers. The detail of determinative method together with analytical results and possible sources of these pollutants will be presented.

INTRODUCTION

Polycyclic Aromatic hydrocarbons (PAHs) are classified as regional pollutants of concern in South East Asia and Pacific region according to RBA-PTS report [1]. These pollutants are not persistent as organochlorine compounds (OCs) and are being formed through several processes such as forest fire, incomplete combustion of coal, oil, petrol and wood [2, 3]. The United States Environmental Protection Agency (US-EPA) and the European Union Commission on health and consumer protection have placed 16 PAHs in a priority list to be concerned due their toxicity to the nature [4]. The widespread presence of PAHs in natural water, particularly rivers, is of significant concerns due to several PAHs are potent carcinogenic or mutagenic compounds, particularly benzo[a]pyrene.

Our study was designed to determine the levels of 16 PAHs in river waters of 4 major rivers, as these river waters were routinely used by local villagers for various purposes such as washing, bath and agricultural activities. Although some study have reported the quality of these river waters in terms of physical and inorganic parameters [5], but the comprehensive data on organic pollutant contaminations, especially PAHs are very scarce in this area. This study would be the first effort to determine current status of PAHs contaminations in the major rivers of southernmost of Thailand which is very important to the local communities settled along these rivers.

The following figure shows the southernmost border province area of Thailand and sampling locations in major rivers of present study.

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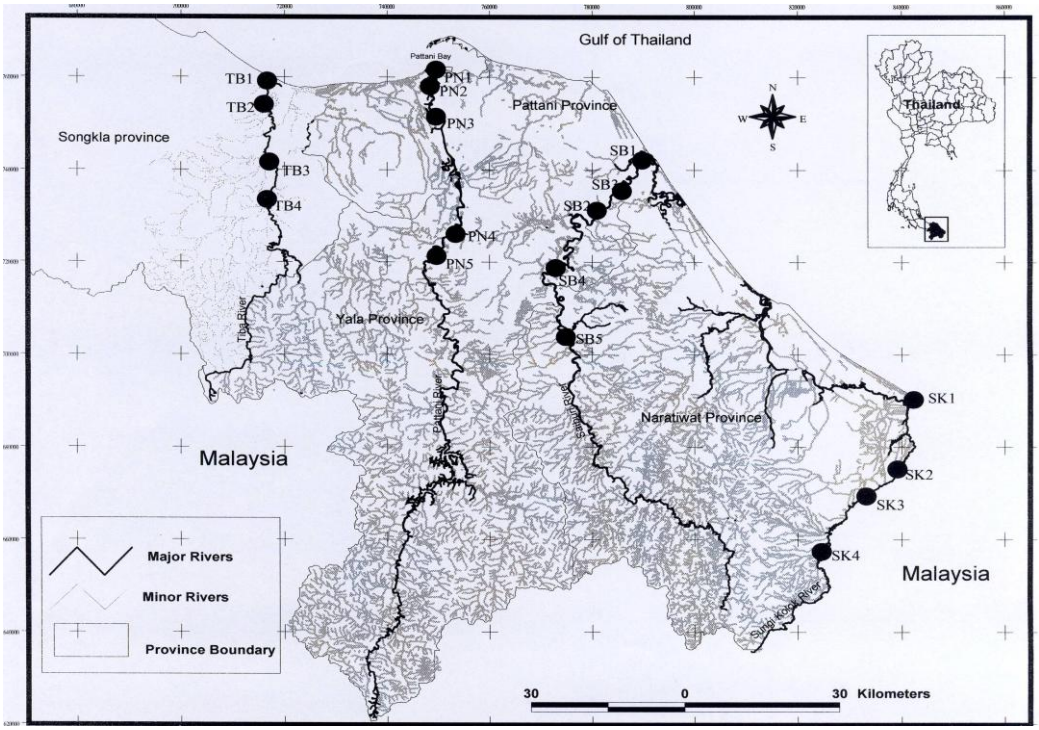

Figure 1: Map of study area and sampling locations in the major rivers

In our laboratory, the extraction of PAHs from water samples was performed by solid phase extraction (SPE) technique that has recently been modified and successfully applied for the determination of PAHs in water samples from the Pattani bay area [6]. This technique of extraction offers several advantages over normal liquid-liquid extraction such as efficient isolation, pre-concentration and volume of solvent use. This work aimed to determine the concentrations and distributions of 16 priority PAHs in the major rivers of southernmost of Thailand, namely, Saiburi river (SB), Pattani river (PN), Thepba river (TB) and Sungai Golok (SK) river and to study the current status of physical and chemical parameters of water in the respective rivers.

MATERIALS AND METHODS

All glassware and chemicals were prepared and maintained properly as stated in the US-EPA method 1664 [7]. Organic solvents and chemicals used were of AR grades and used without further purification. 200 ug/mL stock solutions were prepared and diluted into several concentration levels of working solutions for the purpose of method validations and instrument calibrations.

Sampling was carried out during June 2007-February 2008 and June 2009-Feburary 2010. Water samples were taken from different locations of the 4 majors as shown in figure 1. Sub-surface waters (about 1 m below surface) were collected using a 4.0 liter amber bottle and kept in ice chest before being transported into analytical laboratory for further analyses. Several physical and chemical parameters of water such as temperature, pH and dissolved oxygen (DO) were measured on cites. For turbidity, conductivity and total suspended solid (TSS) were determined using instruments in analytical laboratory. Total suspended solid content was determined by filtering water samples using 0.22 um membrane filter with the help of vacuum suction. The concentration of oil and grease was determined by gravimetric method and reported as hexane extractable material (HEM) and silica gel treated hexane extractable material (SGT-HEM).

Prior to extract, endcapped C-18 SPE cartridge was cleaned by eluting with 10 mL hexane and acetone (in 1:1 ratio) and conditioned with 10 mL methanol [8]. 1.0 L water sample was filtered using 0.22 um membrane filter and then acidified with 3 N HNO_3 to pH < 2. Simultaneous extraction of PAHs from water samples were carried out at the flow rate of 10 mL/min and manifold pressure of -15 inHg. After extraction, SPE cartridges were dried by nitrogen flow for 30 minutes. The dried cartridges were eluted with 3 mL solvent mixture of hexane: acetone (1:1 ratio). The eluent was then adjusted into exactly 1 mL by blowing down with a gentle stream of nitrogen gas and kept at 4 ^{o}C for further GC analyses.

A Varian 3600 Cx gas chromatograph equipped with flame ionization detector (FID) was used for the analysis of 16 PAHs. 1 uL of final sample was injected (splitless for 2 minutes) with the help of 8200 Cx autosampler (sandwich injection technique). The analytes were separated on SPB-5 capillary column (30 m x 0.25 mm i.d. x 0.25 um film thickness). The column oven was programmed from 50 ^{o}C (maintained for 1 min) increased to 200 ^{o}C at 23.0 ^{o}C/min, from 200 ^{o}C to 230 ^{o}C at the rate of 4.7 ^{o}C/min

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and from 230 °C to the final temperature of 280 °C at the rate of 3.7 °C/min (held for 8.59 minutes). The temperature of injection port and detector were set at 250 °C and 300 °C, respectively. The instrument limit of detection (LOD) for 16 PAHs were ranging from 0.02 to 0.27 ug/mL. In most cases, the recovery results of validated SPE method for 16 PAHs standards mixture were within the acceptable ranges of US-EPA protocol (70% to 130 %).

Method blank was analyzed with each set of samples to verify the absence of interferences from either sorbent material or eluting solvent used. The standard mixtures of 16 PAHs used for calibration were routinely checked for area counts in order to maintain a proper concentration during sample quantifications.

RESULTS AND DISCUSSION

Partial results of the present study on water quality parameters and individual concentration of 16 priority PAHs detected in water samples are summarized in Table 1 and Table 2, respectively.

Table 1: Some parameters of water samples collected from the 4 major rivers

Major Rivers	pH	turbidity (NTU)	TSS (mg/L)	conductivity (uS/cm)	HEM (mg/L)	SGT-HEM (mg/L)	DO (mg/L)
1. Saiburi River (5 locations)	7.2-7.5 (7.3±0.1)	8.1-21.8 (16.3±6.5)	13.4-22.9 (18.3±4.3)	38-132 (65.3±44.7)	0.1-1.2 (0.6±0.5)	0.1-0.5 (0.2±0.2)	7.2-9.0 (7.9±0.7)
2. Pattani River (5 locations)	6.6-6.8 (6.7±0.1)	16.0-26.4 (19.9±4.3)	27.0-63.0 (39.5±14.9)	73-85 (78±4.5)	0.1-0.9 (0.5±0.4)	<0.1 (-)	6.1-6.4 (6.2±0.3)
3. Thepba River (4 locations)	6.8-9.1 (7.5±1.1)	7.4-46.9 (25.7±18.7)	13.2-31.8 (19.6±8.3)	22-157 (98±56.6)	0.7-2.2 (1.6±0.7)	0.7-2.2 (1.3±0.6)	6.0-7.3 (6.4±0.6)
4. Sungai Golok (4 locations)	6.6-6.9 (6.8±0.1)	24.1-74.7 (52.0±25.5)	45.2-81.1 (65.9±16.2)	40.2-157.0 (82.2±52.7)	0.1-0.3 (0.2±0.05)	0.1-0.2 (0.1±0.05)	7.2-8.4 (7.9±0.5)

(X±SD): mean and standard deviation values; temperature of water samples: 27.7 - 30.2 °C

Overall, the analytical results of water quality parameters in the respective rivers are still within the acceptable values according to the standard water quality criteria for natural inland water of Thailand (class II) [9]. pH values, for example, all water samples measured during this study were within the water quality range of pH 5.0-9.0. Other parameters such as TSS, temperature and dissolved oxygen (DO) were also within the allowable ranges as stated in the standard water quality criteria. For oil and grease in terms of HEM and SGT-HEM, Thepba river waters were found to be more contaminated than either Saiburi or Pattani River. Oil and grease detected in Thepba River were classified as non-polar hydrocarbons or SGT-HEM. However, the levels of oil and grease found in present study were not exceed the maximum level of 10 mg/L as recommended by Department of Pollution Control, the Ministry of Science Technology and Environment of Thailand. On the other hand, the pollution levels of oil and grease in Saiburi and Pattani River were found to be at trace levels.

The present findings showed that major rivers in southernmost of Thailand were slightly contaminated with several kinds of PAHs varying from location to location along respective rivers, particularly acenaphthylene, anthracene, fluoranthene, chrysene and benzo[k]fluoranthene which were found at the concentration range of 0.02-0.10, 0.02-1.83, 0.05-19.50, 0.27-6.47 and 0.09-10.11 ug/mL, respectively. This finding also showed that Sungai Golok river was more polluted with PAHs than other 3 major rivers of the present study.

We found that 15 out of 16 priority PAH compounds quantified were detected in this study. The PAH pollutants presented in river waters were mostly comprised 4-5 fused benzene rings, which reflecting that anthropogenic sources are among the possible origin of these organic pollutants that discharged into the rivers. Overall, the major rivers of southernmost of Thailand are classified as natural inland water Class II which required several treatments before being further used.

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Table 2: The concentrations of 16 priority PAHs in water samples collected from sampling locations of the respective rivers

16 priority PAH compounds	PAHs concentrations (ug/mL) detected in 4 major rivers			
	Saiburi River (5 locations	Pattani River (5 locations)	Thepba River (4 locations)	Sungai Golok (4 locations)
1. NAP	ND	0.05*	0.62*	0.05-1.05 (0.36)
2. ACE	ND	0.02-0.07 (0.05)	0.03-0.10 (0.05)	0.05-0.07 (0.06)
3. ACN	ND	0.02-1.92 (1.28)	0.02*	0.04-0.12 (0.08)
4. FLU	ND	0.09-0.12(0.11)	1.2*	0.10-0.55 (0.21)
5. PHE	ND	1.57-3.40 (2.70)	ND	3.48-7.52 (3.88)
6. ANT	0.02-1.83 (0.77)	0.06*	0.02-0.05 (0.04)	0.06-0.16 (0.08)
7. FLA	0.05-19.50 (5.37)	0.52-2.47 (1.30)	0.05-1.75 (0.99)	2.40-5.76 (4.13)
8. PYR	2.18-3.60 (2.89)	0.25*	ND	0.02-1.97 (0.85)
9. B[a]A	ND	1.72-5.78 (3.75)	0.30-8.50 (4.40)	2.05-6.08 (3.82)
10. CHR	0.27*	0.47-1.32 (0.89)	2.12-6.30 (3.57)	1.80-6.47 (3.64)
11. B[b]F	2.40-7.31 (5.27)	ND	ND	1.98-3.72 (2.85)
12. B[k]F	0.09-10.11 (4.06)	0.70-3.02 (1.64)	ND	0.35-2.10 (0.99)
13. B[a]P	ND	2.60-6.80 (4.70)	ND	1.98*
14. I[123cd]P	ND	0.89-1.53 (1.21)	ND	ND
15. D[ah]A	ND	ND	ND	ND
16. B[ghi]P	2.7*	ND	ND	ND
Total PAHs	4.74-42.35	8.60-26.43	2.25-16.70	12.38-35.57
(X ± SD)	(18.36 ± 12.04)	(17.63 ± 7.80)	(9.05 ± 7.88)	(20.95 ± 5.67)

( ): mean concentration value, * : detected at one location only, ND: not detected (below detection limit), 1. NAP: naphthalene, 2. ACE: Acenaphthylene, 3. ACN: Acenaphthene, 4. FLU: Fluorene, 5. PHE: Phenanthrene, 6. ANT: Anthracene, 7. FLA:Fluoranthene, 8. PYR: Pyrene, 9. B[a]A: Benzo[a]anthracene, 10. CHR: Chrysene, 11. B[b]F: Benzo[a]fluoranthene, 12. B[k]F: Benzo[k]fluoranthene, 13. BaP: Benzo[a]pyrene, 14. I[123cd]P:Indo[123-cd]pyrene, 15. D[ah]A:Dibenzo[ah]anthracene, 16. B[ghi]P:Benzo[ghi]perylene

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