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**Distribution and Origin Sources of Polycyclic Aromatic Hydrocarbons (PAHs) Pollution in Sediment of Sarawak Coastal Area.**

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**Abstract**

Alkyl and parent Polycyclic Aromatic Hydrocarbons (PAHs) compounds in marine sediment sample collected from ten locations along Sarawak coastal areas were extracted and analyzed by using gas chromatography-mass spectrometry. The source identification of PAH pollution in marine sediment of Sarawak coastal areas were identify by ratios technique of  $An/An+phen$ ,  $Fl/Fl+Py$ ,  $B[a]A/(B[a]A+Chry)$  and  $\sum MPhen/Phen$ . The  $\sum$  alkyl and parent PAHs concentration varies from 36.5 – 277.4 ng/g dry weight (d.w.) with a mean concentration of 138.2 ng/g d.w. The ratio values of PAHs pollution in marine sediment of Sarawak coastal areas are clearly indicating the PAHs pollutions are originated from petroleum (petrogenic) and petroleum combustion (pyrolytic). However, the origin sources of PAHs pollution in a few stations were uncertain due to mixing sources of PAHs.

**Abstrak**

Sebatian utama dan alkil hidrokarbon polisiklik aromatik (PAH) dalam sampel marin yang diambil dari sepuluh kawasan disepanjang perairan pantai Sarawak di ekstrak dan di analisa menggunakan gas chromatografi – spectrometri jisim. Kaedah nisbah sebatian  $An/An+phen$ ,  $Fl/Fl+Py$ ,  $B[a]A/(B[a]A+Chry)$  and  $\sum MPhen/Phen$  digunakan untuk mengenalpasti sumber pencemaran PAH.  $\sum$  kepekatan sebatian utama dan alkil PAH diantara 36.5 – 277.4 ng/g berat kering dengan purata kepekatan 138.2ng/g berat kering. Nilai nisbah pencemaran PAH dalam sediment diperairan Sarawak jelas menunjukkan sumber pencemaran berasal daripada sumber petroleum dan pembakaran petroleum. Walaubagaimana pun pencemaran PAH di beberapa kawasan tidak dapat dikenalpasti sumber pencemaran disebabkan oleh percampuran sumber pencemar.

Keywords: Sarawak coastal area, PAHs, sediment, origin source.

**INTRODUCTION**

The polycyclic aromatic hydrocarbons (PAHs) are a class of organic priority pollutants, ubiquitous in the aquatic ecosystems, which show lipophilic character, resistance to biodegradation and adverse health effects (carcinogenic activity) depending on the molecular weight and structure (Viguri, et al., 2002). PAHs are common organic contaminants and generally generated from the natural and anthropogenic processes. They can be introduced into the marine environment by various ways such as oil spill, urban runoff, domestic and industrial wastewater discharges (Hoffman et al. 1984; Pruell and Quinn, J.G., 1985; Elias et al. 2007), forest fire, coal burning, oil drilling and vehicle exhaust (Elias et al. 2009).

Sediments are deposited material consisting of organic matter in various stages of decomposition, particulate mineral matter and inorganic material of biogenic origin. They have been proven an efficient tool to identify environmental impacts. PAHs entering the aquatic environment, due to their hydrophobicity, rapidly become associated with sediments and suspended particles (Readman et al., 1984). Sediments may contain a high level of pollutants ready to pass on to benthic organism/fish and human through the food chain (Viguri, et al., 2002).

The major activities along the Sarawak coastal area are tourism, fishery activities and petroleum production. Study on PAHs contents along the Sarawak coastal is still limited. In this present study, organic contamination (PAHs) was selected because they are important to the public health and also for baseline data and/or information. The purpose of this study is to identify the distribution and possible source of these PAH compounds in sediment of Sarawak coastal area.

## METHODOLOGY

### *Sampling*

Ten sampling locations were selected during KL Paus 35-days cruise along the Sarawak's coastal area on July 2004. The sediment samples were collected using a Ponar grab sampler, and they were transferred into glass bottles with aluminium caps using a stainless steel spatula. The marine sediment samples were stored in glass bottles and stored at below 5°C before analysis. The sampling locations and coordinates for Sarawak coastal areas are shown in Table 1. Map of sampling stations of Sarawak coastal area was shown in Figure 1.

Table 1: Sampling stations and coordinates of the Sarawak coastal area.

Station	Latitude	Longitude	Water depth (m)	Distance from shore (nautical mile)	Surface water temperature
SR06	01° 45.93' N	110° 29.64' E	5.0	0.70	29.8
SR07	01° 55.05' N	110° 53.01' E	7.5	14.26	28.9
SR08	02° 30.76' N	111° 09.97' E	5.0	6.30	28.7
SR09	02° 56.18' N	111° 38.96' E	7.0	5.11	29.3
SR10	02° 59.77' N	112° 03.97' E	6.7	5.18	29.6
SR11	03° 07.92' N	112° 33.41' E	5.7	6.50	29.6
SR12	03° 13.96' N	113° 59.55' E	6.4	3.41	29.5
SR13	03° 34.94' N	113° 16.79' E	6.8	2.10	29.4
SR15	04° 26.90' N	113° 56.34' E	7.8	3.47	29.5
SR16	01° 53.19' N	109° 49.46' E	7.9	5.10	29.5

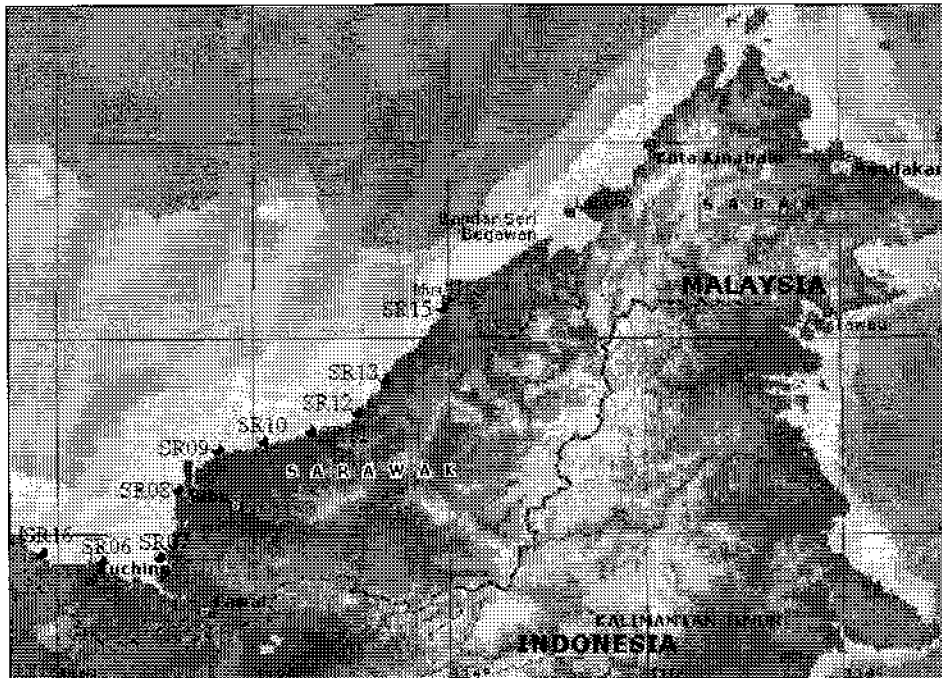


Fig. 1: Sampling stations of Sarawak coastal area.

#### *Soxhlet extraction of marine sediment sample*

Approximately 20 g wet weight of sediment samples were weighted in a glass beaker where about 30 g of  $\text{Na}_2\text{SO}_4$  was added to the sediment sample, mix together for a homogenous. Sample was added into the soxhlet apparatus and spike orto-terphenyl as internal standard for recovery assessment. The sample was soxhlet extracted using 250 ml (50:50 v/v) mixture of dichloromethane (DCM) and hexane. After 18 hours extraction, the extracted samples were dry up until 1ml using rotary cvaporator. About 1ml of extracted sample was fractionated into subfraction using silica-alumina column with 8 g of silica gel and 8 g of alumina. The silica gel and alumina should be deactivated with 0.16 ml and 0.4 ml deionzed water respectively. Copper granules were used to remove sulphur from the extract, which was then passed through a silica/alumina chromatographic column. Then 30 ml of hexane was eluted pass through into the silica-alumina column to elute aliphatic ( $\text{C}_{12} - \text{C}_{34}$ ) fraction. 40 ml mixture of DCM and hexane (50:50 v/v) was used to eluted the PAHs for fractionation 1 (F1) and followed by 40 ml of hexane-DCM (20:80) to elute the aromatic hydrocarbon compounds (PAH) for fractionation 2 (F2). The effluent was collected and concentrated to a few ml in a rotary evaporator after that collected concentrated samples were transferred into a vial, and reduced to 1 ml under a gentle nitrogen gas stream. The final solution was analyzed by GC-MS to determine the aromatic hydrocarbon compounds quantitatively.

### *Gas Chromatography–Mass Spectrometry (GC-MS) analysis*

The aromatic hydrocarbons and aliphatic compound were analyzed by GC-MS (Shimadzu QP5050A model) using selected ion monitoring (SIM) mode. A 30 m x 0.25 mm x 0.25  $\mu$ m ZB1 fused silica capillary column (Phenomenex) was used to identify them (Figure 4). Helium was used as carrier gas with a flow-rate of 3 ml/min. The initial injection and interface temperature of GC-MS was setup at 70°C and 270°C respectively. The column temperature was started at 70 °C, held for 2 min, then increased at 15 °C/min up to 300°C and the temperature will be maintained at 300°C for 12 minutes. The aromatic hydrocarbon analysis took about 1 h to be complete. The 24 of alkyl and parent PAHs were identification and quantification base on ion fragmentation and retention time compared to of that the external PAHs standard.

## **RESULTS AND DISCUSSIONS**

Twenty-four species of parent and alkyl PAH compounds were measured by using GCMS for source identification of PAHs pollution in sediment of Sarawak coastal area as shown in Table 2. The  $\Sigma$  Parent and alkyl PAHs concentration varies from 36.5 – 277.4 ng/g dry weight with a mean concentration of 138.2ng/g dry weight (Figure 2). The highest concentration of  $\Sigma$  PAHs was detected at station SR15 and the lowest at station SR08. The PAH concentrations could be characterized as low, moderate, high and very high ones when the  $\Sigma$ PAHs were 0–100, 100–1000, 1000–5000, and more than 5000 ng/g, respectively (Baumard et al., 1988a). PAHs pollution of Sarawak sediments were categorize as a low (< 100 ng/g) for six stations namely SR06, SR07, SR08, SR09, SR10 and SR11 and others stations were categorize as moderate pollution (100 – 1000 ng/g) as shown in Figure 2.

Isomer ratios of PAHs compound such as Anth/(Anth+phen), B[a]A/(B[a]A +Chry), Fl/(Fl + Py),  $\Sigma$ MPhen/Phen, and IP/(IP+BghiP) were used for source identification of the PAHs pollution in sediments of Sarawak. PAH isomer pair ratio values of Anth/(Anth+Phen) ratios less than 0.1 indicates source of PAH dominance of petroleum and ratios higher than 0.1 indicates dominance of combustion; Fl/(Fl+Py) ratio less than 0.4 represent petroleum source, 0.4 to 0.5 for petroleum combustion and more than 0.5 from combustion of coal, grasses and wood; B[a]A/(B[a]A+Chry) ratio value of less than 0.2 petroleum source, 0.2 to 0.35 petroleum and combustion and more than 0.35 combustion source; and IP/(IP+BghiP) ratio less than 0.2 for petroleum, 0.2 to 0.5 petroleum combustion and more than 0.5 combustion of coal, grasses and wood (Yunker et al., 2002).  $\Sigma$ MPhen/Phen ratio less than 1.0 imply petroleum combustion, 2 – 6 imply petroleum source (Garrigues, et al., 1995; Pereira, et al., 1999).

The ratio values for source identification of PAHs pollution in marine sediment samples of Sarawak coastal areas were shown in Table 2. The origin source of PAHs pollution of SR06, SR07, SR12 and SR15 stations were uncertain. This may be due to mixing of sources either petroleum product, petroleum (fossil fuel) combustion and combustion of coal, grasses and wood. Station SR08, SR10 and SR13 indicate the source of PAHs

pollution was originated from petroleum. The  $Fl/(Fl+py)$  ratio values of SR08, SR10 and SR13 stations are 0.044, 0.157 and 0.151, respectively. The ratio values of the  $Fl/(Fl+py)$  less than 0.4 imply the origin of PAHs was from petroleum source. This result was supported by  $B[a]A/(B[a]A+Chry)$  ratio values, which are 0.025, 0.026 and 0.022 for SR08, SR10 and SR13 stations, respectively. These ratio values of  $B[a]A/(B[a]A+Chry)$  are less than 0.2 indicating the origin source of PAHs pollution of those stations were originated from petroleum.

Stations SR09 and SR11 indicating sources of PAHs pollution were originated from the petroleum combustion. The ratio values of  $Anth/(Anth+phen)$ ,  $Fl/(Fl + Py)$ , and  $\Sigma MPhen/Phen$  are 0.136, 0.446 and 1.412, respectively. The ratio values of  $Anth/(Anth+phen)$ , more than 0.1 indicating combustion of petroleum, coal, wood and grass. The  $Fl/Fl + Py$  ratio values ranged from 0.4 to 0.5 indicating petroleum combustion (Yunker et al., 2002) and ratio values of  $\Sigma MPhen/Phen$ , 1.0 imply petroleum combustion (Garrigues, et al., 1995). Those ratios value clearly indicating that the sources of PAHs pollution for SR09 and SR 11 station were originated from petroleum combustion (pyrolytic).

The PAHs pollution in sediment sample from SR16 station was probably originated from combustion of forest, coal and grass. The ratio value of  $\Sigma MPhen/Phen$  is 2.88 indicating source of PAHs pollution from petroleum. However, the ratio values of  $Anth/(Anth+phen)$ ,  $Fl/(Fl + Py)$ ,  $B[a]A/(B[a]A+Chry)$  are 0.693, 0.706, 0.500 respectively, suggest the source of PAHs pollution from wood, coal and grass combustion. These clearly indicate the dominance source of PAHs pollution from wood, coal and grass combustion. The  $IP/IP+BghiP$  ratio was not calculated as Benzo(ghi)perylene compound was not detected.

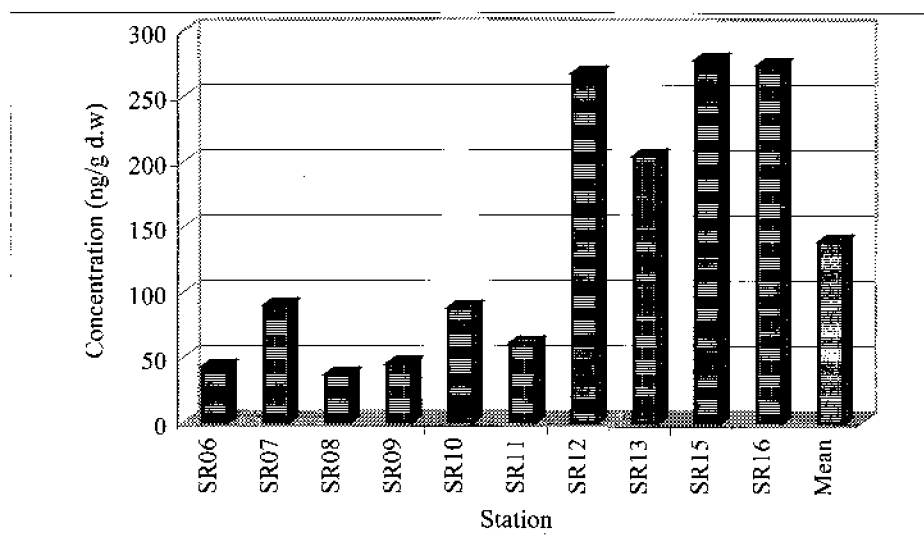


Fig 2: Total parent and alkyl PAHs concentration of Sarawak coastal area.

Table 2: Parent and alkyl PAHs concentration (ng/g d.w) in marine sediment samples collected from Sarawak coastal areas.

Compound	Stations												
	SR06	SR07	SR08	SR09	SR10	SR11	SR12	SR13	SR15	SR16			
Naphthalene	2.4	2.8	1.6	4.8	6.6	1.5	3.3	0.3	10.0	6.5			
1-Methyl Naphthalene	1.5	1.2	1.0	1.8	3.6	1.4	2.4	n.d	6.9	7.1			
1-Ethyl Naphthalene	n.d	n.d	n.d	1.8	n.d	n.d	n.d	n.d	8.3	n.d			
2,3,6-Trimethyl Naphthalene	0.8	1.2	n.d	1.0	2.0	0.8	1.9	n.d	5.4	n.d			
Acenaphthylene	n.d	0.1	n.d	0.1	n.d	0.2	0.1	n.d	0.2	n.d			
Acenaphthene	0.1	n.d	n.d	0.1	0.2	0.1	0.1	n.d	0.5	n.d			
Fluorene	2.1	3.0	0.5	2.2	4.8	1.9	3.7	n.d	23.5	n.d			
Phenanthrene	13.2	26.4	3.5	4.6	9.3	10.1	77.1	9.7	25.5	21.8			
Anthracene	n.d	n.d	0.2	0.7	0.2	0.1	0.1	n.d	44.6	49.3			
2-Methyl Phenanthrene	4.5	6.4	5.4	5.1	11.1	4.5	14.4	17.3	28.6	27.5			
1-Methyl Phenanthrene	1.1	1.6	1.5	1.3	3.0	1.2	6.8	4.8	8.3	6.3			
3,6-Dimethyl Phenanthrene	n.d	n.d	n.d	n.d	n.d	6.0	10.7	26.6	28.2	29.1			
Fluoranthene	9.5	10.6	0.4	6.3	3.2	5.5	28.3	1.4	38.9	3.3			
Pyrene	5.2	11.6	8.8	7.8	17.1	7.0	16.8	7.9	46.5	1.4			
1-Methyl Pyrene	n.d	n.d	n.d	n.d	n.d	n.d	12.8	30.1	n.d	n.d			
Chrysene	0.2	14.1	11.6	0.5	22.7	4.5	25.4	46.3	0.2	0.3			
Perylene	n.d	n.d	n.d	n.d	n.d	7.4	18.4	31.1	n.d	120.0			
Benz[a]anthracene	0.2	0.1	0.3	n.d	0.6	0.1	13.4	1.0	0.2	0.3			
Benzo[b]fluoranthene	0.1	0.1	n.d	0.1	0.2	0.2	14.6	10.4	0.5	n.d			
Benzo[k]fluoranthene	1.4	0.1	0.2	0.8	0.2	2.6	0.5	13.8	0.5	0.3			
Benzo[a]pyrene	0.2	2.9	0.1	0.2	0.2	0.3	0.3	1.0	n.d	0.3			
Indeno [1,2,3-cd]pyrene	0.1	0.4	n.d	0.2	n.d	0.1	4.8	0.7	0.2	n.d			
Dibenz[a,h]anthracene	n.d	6.6	1.1	5.0	1.4	4.8	11.0	n.d	n.d	n.d			
Benzo[g,h,i]perylene	n.d	n.d	0.2	0.1	0.8	0.2	0.3	1.4	0.2	n.d			
$\Sigma$ Parent and Alkyl PAHs	42.6	89.3	36.5	44.6	87.1	60.3	267.2	203.9	277.4	273.3			
Ant/(Ant+Phen) ratio	n.c	n.c	0.054	0.136	0.021	0.008	0.002	n.c	0.636	0.693			
Fl/(Fl+Py) ratio	0.646	0.478	0.044	0.446	0.157	0.441	0.628	0.151	0.456	0.706			
B[a]A/(B[a]A +Chry) ratio	0.500	0.009	0.025	n.c	0.026	0.017	0.345	0.022	0.500	0.500			
$\Sigma$ MPhen/Phen ratio	0.420	0.304	1.943	1.412	1.511	1.169	0.414	5.036	2.558	2.888			
IP/(IP+BghiP) ratio	1.000	1.000	n.c	0.667	n.c	0.250	0.947	0.333	0.500	n.c			

## CONCLUSION

Six stations from Sarawak coastal areas namely SR06, SR07, SR08, SR09, SR10 and SR11 were very low in PAHs pollution. However, SR12, SR13, SR15 and SR16 indicating moderate PAHs pollution with  $\Sigma$  parent and alkyl PAH concentration higher than 200 ng/g dry weight.

The origin source of PAHs pollution of SR06, SR07, SR12 and SR15 stations were uncertain may be due to mixing source of PAHs. Stations SR08, SR10 and SR13 indicating the source of PAHs pollution originated from petroleum (petrogenic). However, PAHs pollution for SR09 and SR 11 stations originated from petroleum combustion (pyrolytic) and SR 16 station was dominated by combustion of forest, coal and grass.

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