

DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SURFACE SEDIMENTS OF THE STRAITS OF MALACCA

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Abstract: The individual compounds and sources of polycyclic aromatic hydrocarbon (PAHs) were studied in the surface sediments at 29 sampling sites in the Straits of Malacca along the areas of Umbai, Bandar Melaka, Tanjung Keling, and Sungai Udang during South West Monsoon on 8th July 2013. A total of 16 PAHs were determined and quantified by gas chromatography coupled with mass spectrometry (GC-MS). The total PAH concentrations in the surface sediments detected from this study ranged from 8.07 ng/g to 390.03 ng/g with the average of 133.5 ng/g. All sampling stations were dominated by the range of low molecular weight PAHs (3-ring), 44% and 28% from high molecular weight PAHs (4 -ring). The sources of PAHs were analyzed by employing diagnostic ratios (DR) of specific PAH compounds. The ratios in this study showed mixture of petrogenic and pyrogenic PAHs sources with a dominance of pyrogenic sources.

Keywords: PAHs, pyrogenic, petrogenic, diagnostic ratios, Malacca (Straits of Malacca).

Introduction

Coastal sediments can be considered as sinks and secondary sources of terrestrially derived materials and these materials can be partially found in depositional zones and some in deeper waters. Hence, sediments are loaded with anthropogenic derived materials, for example, polycyclic aromatic hydrocarbons (PAHs). As one of a class of organic contaminants PAHs can be accumulated in the environment extensively in different matrices due to its hydrophobic property with low solubility in water PAHs tend to settle in sediments and various organic components (Chiou *et al.*, 1998; Raoux *et al.*, 1999; Mastral *et al.*, 2003). United States Environmental Protection Agency (US EPA) categorized 16 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, perylene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3,cd]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i]perylene) as 'highlighted pollutants' due to their mutagenic, toxic, persistent and carcinogenic characteristics. With the bioavailability of PAHs

from sediments, fossil fuels and large organic particles, various types of marine biota may be affected by its acute toxicity in a long term (Neff, 2002; Sverdrup *et al.*, 2002; Reynaud & Deschaux, 2006; Zhang *et al.*, 2012; Gu *et al.*, 2013). In high amount of PAHs intake, fish and other organisms high up in the trophic chain may still be affected with toxic even though with their efficient metabolic mechanisms that able to excrete PAHs in a few days after the uptake (Neff, 2002; Van der Oost *et al.*, 2003; Neff *et al.*, 2005). As the input source from anthropogenic activities, petrogenic and pyrogenic sources are considered important. The pyrogenic sources include combustion processes mainly fossil fuel combustion and the petrogenic sources derived from byproducts of petroleum (Abrajano *et al.*, 2003). The pyrogenic input is largely prevalent in aquatic environments. Different chemical behavior and distribution in marine sediments determine the sources of PAHs whether from petrogenic or pyrogenic (Mastral *et al.*, 2003).

The assessment of PAHs for its pollution status and the bioavailability in the sediment is important in the long term aspects of economy

sustainability and also public health in general. Thus, the increasing level of contaminants in the environment, including PAHs has become a concern. Contamination of PAHs can be considered as a serious problem for the marine environment especially by the usage of fossil fuel as a source of energy in vehicles and abundant industries, and Malaysia being in a strategic location for oil tankers water route and disposal of used oils into the ocean are some of the main factors that contributed to the PAHs contamination around the coastal areas, rivers and oceans.

For identification and distribution of pollutants sources such as PAHs, several approaches have been used over the past years. PAHs occur in a mixture of hundreds of compounds which vary in concentration, which are closely related to sampling sites and environmental conditions. Apart from that, these abundant data normally contain an internal association with variables which are often in partially hidden structures and requires evaluations and interpretations. Hence, diagnostic ratios and chemometric techniques are found to be significant in analyzing

PAHs data in the ecosystem with different geographical and environmental situations. Different PAHs ratios are predicted to show a discrepancy with the sources most likely due to the various routes of PAHs formation under different combustion conditions. Pyrogenic sources PAHs are the result of pyrolysis process which creates a high molecular weight of parental PAHs. Petrogenic PAHs are also distinguished by the dominance of PAHs with low molecular weights (2-3 ring PAHs) and alkylated PAHs (Yunker *et al.*, 2002; Larsen & Baker, 2003; Zuo *et al.*, 2007; Liu *et al.*, 2009). Therefore, this research focuses on the sedimentary deposition of PAHs in the study area to deliver, firstly, the concentration levels of the specific PAHs compound, and secondly, to find possible sources of pollution exposure from various sources and the origin of PAHs.

Materials and Methods

Sample Collection

The sampling sites are located along the Straits of Malacca, alongside areas such as Umbai, Bandar Melaka, Tanjung Keling, and Sungai

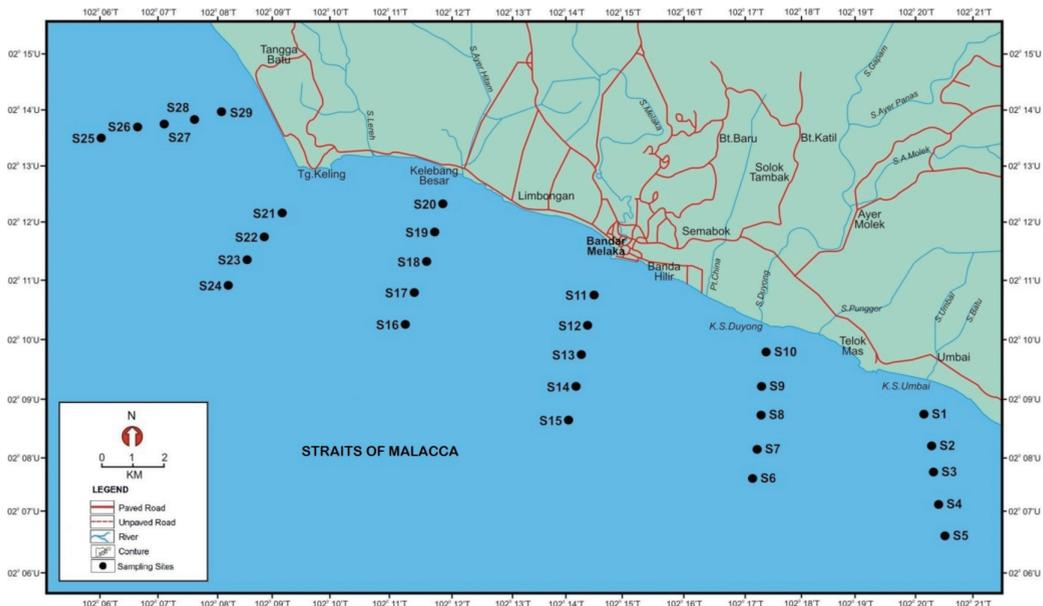


Figure 1: Map of sampling stations along the Straits of Malacca

Table 1: Coordinates and *in situ* parameters of sampling stations

Station	Longitude (N)	Latitude (E)	Depth (m)	Temperature (°C)	DO		Salinity	pH
					%	mg/l		
S1	102° 20.247	2° 8.782	4.3	29.5	93.6	3.06	30.41	7.66
S2	102° 20.314	2° 8.242	10.5	29.7	95.4	3.07	30.54	7.74
S3	102° 20.381	2° 7.702	11.8	29.6	97.4	3.07	30.59	7.84
S4	102° 20.448	2° 7.162	12.8	29.6	96.8	3.07	30.60	7.89
S5	102° 20.514	2° 6.628	7.9	29.7	95.6	3.08	30.67	7.84
S6	102° 17.171	2° 7.653	20.4	29.8	94.6	3.08	30.73	7.72
S7	102° 17.204	2° 8.187	20.7	29.7	95.8	3.10	30.87	7.89
S8	102° 17.237	2° 8.729	11.1	29.7	94.9	3.08	30.71	7.84
S9	102° 17.271	2° 9.272	10.2	29.7	95.8	3.08	30.68	7.84
S10	102° 17.304	2° 9.816	4.7	29.6	95.7	3.05	30.30	8.00
S11	102° 14.505	2° 10.775	6.3	29.7	94.5	3.08	30.62	7.89
S12	102° 14.379	2° 10.245	13.4	29.7	96.7	3.08	30.75	7.96
S13	102° 14.254	2° 9.716	22.2	29.8	92.8	3.09	30.82	7.89
S14	102° 14.129	2° 9.190	24.0	29.7	95.9	3.09	30.80	7.84
S15	102° 14.005	2° 8.667	32.5	29.8	93.8	3.06	30.87	7.56
S16	102° 11.222	2° 10.356	34.9	29.8	90.8	3.10	30.93	7.83
S17	102° 11.415	2° 10.867	27.5	29.8	94.4	3.10	30.91	7.89
S18	102° 11.606	2° 11.376	17.1	29.8	93.3	3.07	30.84	7.85
S19	102° 11.798	2° 11.884	6.5	29.6	93.9	3.08	30.71	7.83
S20	102° 9.530	2° 12.588	6.7	29.8	92.6	3.09	30.87	7.87
S21	102° 9.178	2° 12.179	35.7	29.8	93.5	3.09	30.88	7.98
S22	102° 8.828	2° 11.771	46.7	29.9	97.5	3.11	30.96	8.01
S23	102° 8.478	2° 11.364	42.3	29.9	95.5	3.11	31.00	7.97
S24	102° 8.121	2° 10.949	40.6	30.0	94.6	3.13	31.20	7.98
S25	102° 6.071	2° 13.510	38.1	30.0	97.4	3.11	31.00	8.00
S26	102° 6.604	2° 13.627	33.6	30.0	95.0	3.11	30.98	7.95
S27	102° 7.127	2° 13.741	32.8	30.0	97.4	3.11	30.97	8.03
S28	102° 7.651	2° 13.856	16.5	29.8	97.5	3.10	30.86	7.86
S29	102° 8.177	2° 13.971	7.3	29.8	97.6	3.10	30.88	7.96

Udang. The strait is the main shipping route connecting the Indian Ocean and the Pacific Ocean carrying along it various types of vessels. The state of Malacca covers an area of 1664 km² and commands a central position at the Straits of Malacca; this historical city has been listed as a UNESCO World Heritage Site. Other than that, around the sampling sites in Sungai Udang, the PETRONAS Malacca Refinery Complex that consists of two refining trains has been established in 1994 and 1999, owned by PETRONAS Penapisan (Melaka) Sdn. Bhd. and Malaysian Refining Company Sdn. Bhd. respectively. The refinery has the total capacity of 270,000 barrels of oil per day.

The total of 29 surface sediment samples were collected using the Ponar grab sampler with six transects consisting five sampling sites each, except for the fourth transect which had

only four sites as shown in Figure 1. Sampling was conducted on 8th July 2013 during the South West Monsoon and the coordinates and their *in situ* parameters during sampling were measured simultaneously at each sampling point (Table 1). The surface sediment samples (upper 0 - 5 cm) were placed into glass containers that had been rinsed by solvents and then preserved in ice. Once transported to the laboratory, samples were stored at - 20 °C until further analysis.

Sample Analysis

This study focuses on the analysis of 16 PAHs, namely, naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), perylene (Per), fluoranthene (Fluo), pyrene (Pyr), benzo[a]anthracene (B[a]A), chrysene

(Chry), benzo[k]fluoranthene (BkF), benzo[a]pyrene (B[a]P), indeno[1,2,3,cd]pyrene (IcP), dibenzo[a,h]anthracene (DhA), and benzo[g,h,i]perylene (BgP). Solvents including methanol, dichloromethane (DCM), n-hexane, and deionized water were distilled in glass before use. The glassware was washed with Decon-90 and deionized-distilled water soaked overnight and rinsed successively with methanol, acetone and distilled hexane and muffled at 60 °C for 24 hours to get rid of any organic contaminants. Standards of 16 USEPA priority PAHs in a mixture solution (L20950018AL) were purchased from Dr. Ehrenstorfer GmbH, Germany and were injected individually into the gas chromatography coupled with mass spectrometer (GC-MS) as an external standard to identify and quantify the target PAHs in the sample. The samples were spiked with two surrogate standards (phenanthrene-d10 and chrysene-d12) as surrogate internal standards prior to injection into the GC-MS for quantification of all PAHs analyzed in this study. The silica gel columns (technical grade) with size 0.063–0.200 mm for column chromatography were purchased from Aldrich Chemistry, USA and were baked at 400 °C for 4 hours to remove organic contaminants and then activated at 200 °C for 2 hours.

Analytical Procedure

Approximately 20 g of each wet sample were homogenized with a stainless steel spoon, and dried with anhydrous sodium sulphate (Merck KGaA, Germany). After that, it was Soxhlet-extracted with 250 mL dichloromethane (DCM) (Merck KGaA, Germany) for 6–8 hours. The DCM extract containing the organic pollutants was transferred to a 250 mL round bottom flask, and the extract was reduced by rotary evaporator to a small volume and then undergo the two-step silica gel chromatography column process to be purified and fractioned into aliphatic and aromatic. This separated most of the organic pollutants, including n-alkanes, linear alkyl benzenes (LABs), Polychlorinated Biphenyls (PCBs), pesticides and PAHs from other unwanted polar compounds. The

concentrated sample extracts were transferred onto the top of the silica gel column (first step of column chromatography) then rinsed with 2 mL n-hexane/dichloromethane (3:1) followed by another 18 mL of mixture n-hexane/dichloromethane (3:1). Hydrocarbons ranging from n-alkanes to PAHs were diluted through the column and collected in a pear-shaped flask.

The second step of column chromatography was performed to separate the n-alkane and hopane, LAB and PAH fractions. The eluent from the first step of column chromatography was concentrated to 1–5 mL by a rotary evaporator and further concentration was performed using a gentle stream of purified nitrogen to near dryness. The PAH fraction as the third fraction was treated with 16 mL DCM:n-Hexane (1:3). After that, the volume of the PAHs fraction was reduced using a rotary evaporator to near dryness and was transferred into a 2 mL vial. Then it underwent a nitrogen blow down evaporation and was refilled with distilled n-hexane prior to the injection into the GC-MS (GC, 6890N coupled with 5975C MSD, Agilent, USA). The carrier gas was helium at a fixed rate of 1 mL/min with a pressure of 158 kpa. A HP-5 fused silica capillary column (30 m × 0.25 mm i.d. and 0.25 μm thickness) was used to separate the compounds in split-less mode at 270 °C. The GC temperature gradient was at 40 °C which was then increased from 8 °C/min to 150 °C, then, at 5 °C/min to 310 °C and finally held for about ten minutes. The GC-MS operating conditions were 70eV ionization potential with a MS source at 230 °C for 1.4 scans/sec, electron multiplier at 1400 V and the dwell time set at 40 seconds. The interface temperature was at 280 °C while the injector temperature was maintained at 250 °C. The 16 PAHs were quantified based on their retention time and the ion m/z ratio of native standard PAHs.

Results and Discussion

Distribution and Concentration of PAHs

The total PAHs concentration from the sum of 16 EPA priority pollutants in surface sediments

Table 2: Summary table of PAH concentrations (ng/g) based on dry weight of the surface sediments

Sampling Station	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26	S27	S28	S29
Mean	17.98	2.92	1.49	2.48	0.50	1.70	0.52	1.58	13.00	6.04	21.50	19.18	4.86	1.53	1.37	1.94	2.46	4.85	7.64	13.26	16.73	19.13	1.09	1.73	2.34	5.02	22.30	22.51	24.38
Median	9.23	0.00	1.05	1.28	0.21	0.47	0.13	0.24	4.99	0.89	14.50	5.04	2.81	0.51	0.17	0.28	0.46	1.41	2.80	3.17	8.05	5.20	0.86	0.48	1.80	3.84	16.54	5.00	15.11
Standard Deviation	21.42	4.86	1.58	3.37	0.74	2.39	0.87	2.46	16.92	8.92	27.72	30.17	5.90	1.87	2.39	3.09	3.81	6.60	10.36	21.43	20.16	25.94	1.53	2.72	2.84	5.32	18.41	35.38	23.18
Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Maximum	67.76	16.96	4.32	10.92	2.51	8.11	2.77	9.12	48.08	29.55	90.99	95.25	18.47	6.54	9.11	11.71	10.92	22.15	35.63	68.29	55.74	75.42	5.45	10.42	10.34	18.40	60.91	110.49	72.60
∑ PAHs	287.65	46.75	23.85	39.74	8.07	27.15	8.34	25.33	208.03	96.65	344.06	306.93	77.68	24.47	21.92	30.99	39.36	77.65	122.17	212.08	267.63	306.02	17.48	27.67	37.50	80.31	356.86	360.17	390.03
LMW	160.13	24.52	9.63	10.26	6.66	8.34	6.58	18.70	153.78	30.68	242.37	250.45	24.60	10.06	10.03	23.00	21.77	38.20	41.90	145.86	179.30	215.04	6.52	21.36	21.42	15.60	48.43	302.39	210.67
HMW	127.26	34.55	18.96	24.47	11.19	16.45	6.73	11.60	55.00	70.50	102.14	58.41	54.27	15.46	20.99	16.65	22.56	43.77	83.51	66.95	88.05	91.65	15.93	15.41	21.05	58.93	294.23	59.73	166.69
LMW/HMW	1.26	0.71	0.51	0.42	0.60	0.51	0.98	1.61	2.80	0.44	2.37	4.29	0.45	0.65	0.48	1.38	0.97	0.87	0.50	2.18	2.04	2.35	0.41	1.39	1.02	0.26	0.16	5.06	1.26
Sand (%)	43.00	79.00	90.00	94.00	90.00	42.00	10.00	46.00	30.00	40.00	60.00	85.00	6.00	65.00	68.00	93.00	20.00	40.00	60.00	24.00	10.00	97.00	78.00	98.00	85.00	95.00	89.00	20.00	30.00
Silt (%)	46.00	11.00	10.00	6.00	10.00	40.00	79.00	22.00	42.00	39.00	23.00	10.00	78.00	19.00	20.00	7.00	65.00	28.00	22.00	46.00	69.00	0.00	20.00	0.00	0.00	0.00	0.00	75.00	50.00
Clay (%)	11.00	10.00	0.00	0.00	0.00	18.00	11.00	32.00	28.00	21.00	17.00	5.00	16.00	16.00	12.00	0.00	15.00	32.00	18.00	30.00	21.00	0.00	2.00	0.00	0.00	0.00	0.00	5.00	22.00
TOC (%)	0.94	1.43	0.71	1.15	1.36	1.09	1.28	0.47	1.49	1.69	2.06	3.21	1.37	0.98	0.41	0.48	1.62	1.46	0.65	1.50	1.35	0.85	0.76	0.56	0.43	0.32	0.54	0.81	1.34

LMW: Low Molecular Weight; HMW: High Molecular Weight; TOC: Total Organic Carbon

of Malacca Strait is shown in Table 2. The total amount of PAHs varies from 8.07 to 390.03 ng/g dry weight with a mean concentration of 133.54 ng/g dry weight. Maximum PAHs level was found in site S29 with 390.03 ng/g ∑ PAHs and the second highest was from site S28 with 360.17 ng/g. These sites are all located at the Sungai Udang transect where the refineries were spotted at the nearby mainland along with vessels and boating activities. Site S11 is located at the river mouth of Sungai Melaka of Bandar Melaka, which explains the higher concentration of ∑ PAHs, 344.06 ng/g. Pollutants from this site might be from the crowded population of residents together with their activities along the coastal area. Heavy industrial with many factories are located along the coastline either in urban and suburban area which contributed to the discharged of the wastes enriched with combustion-derived PAHs into the coastline of Malacca. Furthermore, anthropogenic inputs such as oil spillage, river run off from the rain which contain atmospheric dust and municipal wastewater, settled in the sediments contaminated by PAHs with mixed pattern of pyrogenic and petrogenic origins. For individual compounds, the highest PAH was Ace with 20% of the total PAHs while the lowest was Acy with only 0.38% of the total PAHs. The surface sediment samples from this sampling area were mostly dominated by Ant and Phe with values of 20% and 17%, respectively. The dominance of Naph, Phe, Ant and Fluo (12-20%) were expected from the

unburned fossil fuels in the fresh topmost layer of the sediments compared to the presence of PAHs in higher molecular weight of PAHs in the lower layers. However, the pollutant levels suggested by Baumard *et al.* (1998) can be used to categorize the relative contamination level into four categories: (a) low, 0 – 100 ng/g; (b) moderate, 100 – 1000 ng/g; (c) high, 1000 – 5000 ng/g; and (d) very high, > 5000 ng/g based on the total PAHs. From these categories, the total amount of PAHs in these particular sampling sites is considered moderate. There are a few factors that control the concentration of PAHs in surface sediment such as microbial degradation of PAHs, differential resuspension and redeposition of PAHs and sediment, and vertical mixing due to biological or physical processes which could be more active in tropical areas and may contribute to lower PAHs concentration (Booyatumamond *et al.*, 2006). All of these factors can be linked as the Straits of Malacca, is the main shipping channel between the Indian Ocean and the Pacific Ocean with thousands of vessels passing through it each year.

In order to assess the current status of PAHs pollution in the Straits of Malacca, the concentrations of PAHs were compared with data from previous studies. For areas along the Straits of Malacca, the total of PAHs concentration levels found in the sediments in the ten sampling stations from Johor to Kedah, Malaysia ranged from 209.8 to 611.0 ng/g (Elias *et al.*, 2007), 391.0 to 554, 204 ng/g from Prai

Straits, Penang (Sakari & Zakaria, 2013), 34.0 to 2426 ng/g from Old Port Klang (Sakari *et al.*, 2010), 7.37 to 32.97 ng/g from offshore Port Klang (Sakari *et al.*, 2010), 176.61 to 4447.14 ng/g from near shore Malacca (Sakari *et al.*, 2011) and 1.71 to 714.37 ng/g from offshore Malacca (Sakari *et al.*, 2011). From the previous studies mentioned, the results of this study show that the PAHs from the sampling stations are within the low to moderate pollution range. According to Zakaria *et al.* (2002), tropical rainforest climate plays a role in the lower concentration of PAHs in that environment by the dilution of PAHs in the sediment that resulting extra sediment load where sediment washout is caused by consistent heavy rainfall in Malaysia. Therefore, a large amount of particle matters from rivers enter the higher salinity area resulting in active sedimentation in the estuary.

The PAHs with concentrations that are susceptible to co-varying in the environment were identified in this study on the basis of the correlation factor values. This statistical approach is based on the fact that each pollution source produces a characteristic PAHs pattern; the correlation of all the individual PAHs can give an overview of whether it all originates from the same source. Significant correlations were noted between Phe/Ant ($r^2 = 0.9997$, $p < 0.01$), Flu/Phe ($r^2 = 0.9523$, $p < 0.01$), Flu/Ant ($r^2 = 0.9522$, $p < 0.01$), Chry/DhA ($r^2 = 0.9520$, $p < 0.01$), BaA/Chry ($r^2 = 0.9186$, $p < 0.01$), Naph/Flu ($r^2 = 0.9179$, $p < 0.01$) and Acy/Flu ($r^2 = 0.9009$, $p < 0.01$). This indicates that Phe, Ant, Flu, Chry, DhA, BaA, Naph and Acy might originate from the same source.

Comparison of PAHs Concentration by Number of Ring

The PAHs composition of sediments collected from these sampling sites are shown in Figure 2. According to the number of aromatic rings, the 16 PAH compounds were divided into 2-ring, 3-ring, 4-ring, 5-ring, and 6-ring. For individual PAHs in sediments, 3-ring PAHs was the most abundant with 44% occurrences and the second highest was for the 4-ring PAHs

with 29% occurrences. The dominance of the 3- and 4-rings compounds suggests that there are a possibility of major petrogenic and minor pyrogenic input in that area (Walker *et al.*, 2005). High amount of low molecular weight PAHs with two to three aromatic rings could be a sign of fresh petroleum input of petroleum hydrocarbons from petrogenic sources. While for pyrogenic sources is highly related with the abundance of high molecular weight PAHs, for example, PAHs with more than three aromatic rings (Zakaria *et al.*, 2002). Some carcinogenic 5-ring PAHs were detected in all sites in this study. The importance of high molecular weight PAHs have also been commonly observed in the sediments from the river and marine environments (Tolosa *et al.*, 2004; Chen *et al.*, 2012).

Identification of PAHs Sources by Diagnostic Ratios

The interpretation of PAHs sources was determined by many researchers using a large number of different parent and alkyl PAHs ratios. Those ratios are usually restricted to PAHs within a given molecular mass to reduce confounding factors such as water solubility, volatility and absorption (McVeety & Hites, 1988). The diagnostic ratios used in this study were the low molecular weight (LMW)/ high molecular weight (HMW), Flu/(Flu+Pyr)

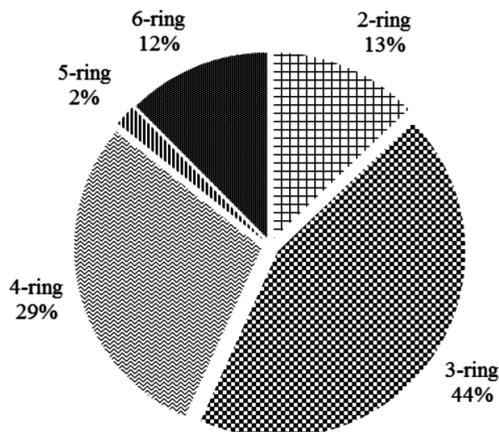


Figure 2: Relative distribution (%) of 2-, 3-, 4-, 5-, and 6-ring PAHs in the sediments

(Magi *et al.*, 2002), Flu/Pyr (Magi *et al.*, 2002), Phe/Ant (Soclo *et al.*, 2000), IcP/(IcP+BgP) (Yan *et al.*, 2006), and B[a]A/(B[a]A+Chr) (Wu *et al.*, 2011). Ratios of Phe/Ant and Flu/Pyr were estimated in order to differentiate between PAHs of dissimilar origin. The Phe/Ant ratio is temperature-dependent and is approximately 3 of the emissions from the combustion of various fuels (Gschwend & Hites, 1981). LMW/HMW ratios > 1 indicate dominance of petrogenic inputs and LMW/HMW < 1 indicate pyrogenic inputs (Magi *et al.*, 2002; Soclo *et al.*, 2000). The LMW/HMW ratios in this study showed a mixture of both petrogenic and pyrogenic sources with the dominance of pyrogenic. Generally, the predominance of Flu/Pyr is resulted from pyrogenic origin, especially from coal combustion (Simo *et al.*, 1997). In this study area, the average PAHs ratio is 1.2 for Phe/Ant and 0.8 for Flu/Pyr, indicating a pyrogenic origin of the predominant PAH compounds. PAHs in the sediment samples in this study are mainly from the combustion of biomass, coal, and petroleum (Figure 3), a strong indication

of anthropogenic impacts in the environment (Yunker *et al.*, 2002). For Flu/(Flu+Pyr) the petroleum boundary ratio appears close to 0.4 and the ratio between 0.4 to 0.5 is an indication of combustion from petroleum whereas a ratio > 0.5 implies on combustion of grass, wood or coal. The present result of Flu/(Flu+Pyr) ranged from 0.13 to 0.37 in 15 stations suggesting that sediments from the study area are predominated caused by petroleum contamination. For more detailed classification of the pollution sources, the isomer IcP/(IcP+BgP) and B[a]A/(B[a]A+Chr) (Figure 3) are used to distinguish among petroleum, liquid fossil fuel combustion (vehicle and crude oil) and biomass burning. However, the pattern is not coherent with that of IcP/(IcP+BgP) and B[a]A/(B[a]A+Chr), with total of 18 stations suggesting they derived from a petroleum contamination source for IcP/(IcP+BgP) and only 7 stations for ratio B[a]A/(B[a]A+Chr) are derived from petroleum contamination source. This indicates that different PAH compounds underwent different degradation pathways from source to receptor (Zhang *et al.*, 2005).

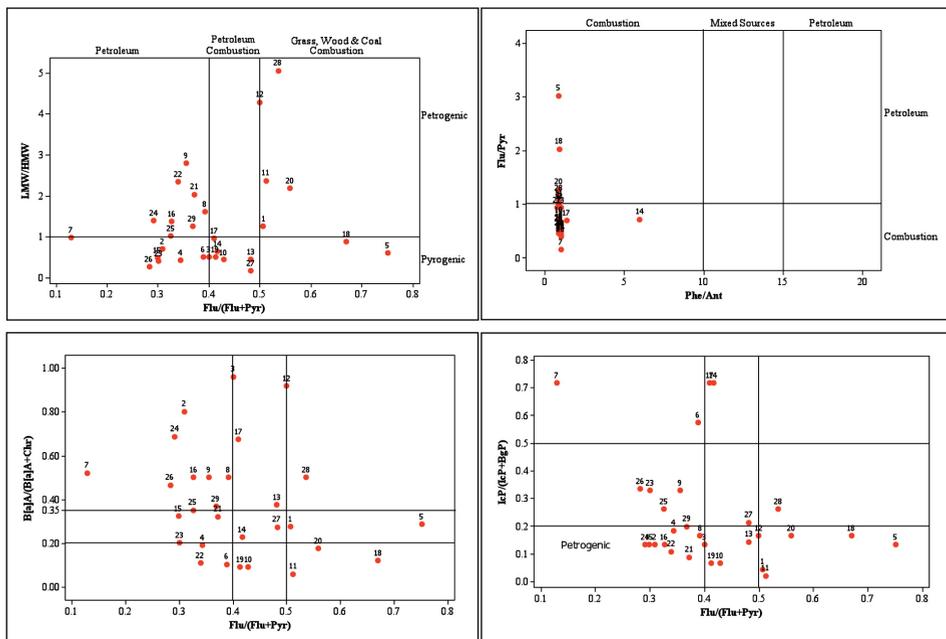


Figure 3: Plot diagrams between LMW/HMW against Flu/(Flu+Pyr), Flu/Pyr against Phe/Ant, Flu/(Flu+Pyr) against Ant/(Ant+Phe), IcP/(IcP+BgP) against Flu/(Flu+Pyr), and B[a]A/(B[a]A+Chr) against Flu/(Flu+Pyr)

Other than that, the ratios of BaA/(BaA+Chr) is more sensitive to weathering processes such as photo-degradation and long distance transport, where the water is shallower in surface sediments to allow light to penetrate (Yan *et al.*, 2006).

Total Organic Carbon (TOC) and Particle Grain Size

The particle grain size value in this study area consists of mostly sand. With the average percentage of 58%, the highest value is at S22 with 97% of sand (Table 2). High values of TOC is recorded on S11 and S12 with the values of 2.06% and 3.21% respectively, which are from the area of Sungai Melaka river mouth. Previous studies showed that concentrations of PAHs in sediments are positively correlated with the TOC content (Prah & Carpenter, 1983; Evans *et al.*, 1990; Zhang *et al.*, 2004; Guo *et al.*, 2007). In this study, total PAHs concentration and TOC are significantly correlated ($r^2 = 0.327$, $p < 0.01$) as shown in Table 3. In addition, high correlation between total PAHs and LMW ($r^2 = 0.897$, $p < 0.01$) shows the sources of pollution are due to combustion, fresh release of oil and oil derivatives (Sakari & Zakaria, 2013).

Conclusion

The concentrations of PAHs at the Straits of Malacca ranges from 8.07 ng/g to 390.03 ng/g and can be described as low to moderate and they are still within the safe range. The source determination of PAHs in sediments in the study area was determined based on individual compound distribution and diagnostic ratio

application. The results from the individual distributions of PAHs suggested a mixture of probable petrogenic and pyrogenic inputs with the domination of LMW PAHs with 2 – 3 fused aromatic benzene rings (13 % and 44%) compared to HMW PAHs with 4 – 6 rings. Data PAHs isomer pair ratios of LMW/HMW, Flu/(Flu+Pyr), Flu/Pyr, Phe/Ant, IcP/(IcP+BgP), and B[a]A/(B[a]A+Chr) suggested that PAHs mainly descended from mixture of petrogenic and pyrogenic origins with the predominance of pyrogenic inputs.

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Table 3: Total PAHs, LMW, HMW, particle size and TOC correlation table

Variables	∑ PAHs	LMW	HWM	Sand (%)	Silt (%)	Clay (%)
LMW	0.897					
HMW	0.771	0.412				
Sand (%)	-0.198	-0.253	-0.036			
Silt (%)	0.189	0.270	-0.007	-0.956		
Clay (%)	0.103	0.135	0.015	-0.718	0.500	
TOC (%)	0.327	0.449	0.030	-0.286	0.273	0.293

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