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SOURCES AND COMPOSITION OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE RIVER AND ESTUARIAL SEDIMENT ALONG THE VICINITY OF KUALA KEDAH, MALAYSIA

(Sumber dan Komposisi Hidrokarbon Aromatik Polisiklik dalam Sedimen Sungai dan Muara di Sepanjang Persekitaran Kuala Kedah, Malaysia)

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Abstract

Sixteen surface sediment samples were taken along the vicinity of Kuala Kedah, especially the Kedah River and estuary areas. The surface sediments taken were identified and quantified by gas chromatography coupled with mass spectrometry (GC-MS). The knowledge and information gained from the study show that the concentration of individual Polycyclic Aromatic Hydrocarbon (PAH) compounds was known to be between 1.09 ng/g to 59.01 ng/g dry weight sediment. The river mouth sampling point was found to have the highest total PAHs concentration of 226.03 ng/g sediment dry weight. On the contrary, the S2 sampling point was found to have the lowest concentration of total PAHs with 7.20 ng/g sediment dry weight. Among all the incorporated sampling points, the highest number of an individual compound of PAHs found was that of benzo[ghi]perylene. On the other hand, acenaphthylene, which is another individual compound of PAHs, showed the lowest concentration. Apart from the estimation of the total and individual PAHs concentrations, the molecular indices and the Low Molecular Weight (LMW)/High Molecular Weight (HMW) of phenanthrene/anthracene and fluoranthene/pyrene were analyzed in this study to establish whether the sediment sources were pyrolytic or pyrogenic based. Lastly, based on the study of the sources of the PAHs, it was established that the study site’s sources consisted of mixed PAHs sources with a dominance of pyrogenic sources of fossil fuel combustion, vehicle engine combustion, open wood combustion and charcoal combustion; which were the main causes that contributed towards the diversity of sources in the sediments along the vicinity of Kuala Kedah river and estuary areas.

Keywords: PAHs, surface sediments, molecular indices, pyrogenic, pyrolytic

Abstrak

Enam belas sampel sedimen permukaan telah diambil di sekitar kawasan Kuala Kedah terutama di kawasan sungai dan muara. Sedimen permukaan yang di ambil ditentu dan dikuantifikasi oleh kromatografi gas-spektrometri jisim (GC-MS). Maklumat yang diperoleh daripada kajian menunjukkan bahawa kepekatan individu sebatian HAP adalah antara 1.09 ng/g hingga 59.01 ng/g berat kering sedimen. Kawasan persampelan di muara sungai didapati mempunyai jumlah kepekatan tertinggi HAP iaitu 226.03 ng/g berat kering sedimen. Sebaliknya, titik pensampelan S2 mempunyai kepekatan HAP terendah dengan 7.20 ng/g berat kering sedimen. Bilangan tertinggi individu HAP yang dijumpai adalah benzo[ghi]perilena untuk keseluruhan titik pensampelan. Sebaliknya, asenaftilena menunjukkan kepekatan yang paling rendah. Selain daripada anggaran jumlah dan kepekatan individu PAH, indeks molekul fenantrena/antrasena, benzo[a]antrasena/krisena, fluoranthena/pirena dan berat molekul rendah (BMR)/berat molekul tinggi (BMT) juga dianalisis dalam kajian ini untuk menentukan sama ada sumber sedimen adalah pirolitik atau pirogenik. Akhir sekali, berdasarkan penemuan sumber-sumber HAP, terbukti bahawa sumber di kawasan kajian adalah sumber bercampur yang didominasi oleh sumber pirogenik oleh pembakaran bahan bakar fosil, pembakaran enjin kenderaan, pembakaran kayu terbuka dan pembakaran arang adalah penyebab yang menyumbang ke arah kepelbagaian sumber di sedimen di sepanjang kawasan sekitaran dan sungai muara Kuala Kedah.

Kata kunci: HAP, sedimen permukaan, indeks molekular, pirogenik, pirolitik

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are pollutants of marine coastal sediments [1]. The US EPA Priority and European Union Pollutant List have included polycyclic aromatic hydrocarbons (PAHs) because they represent the major group of compounds that are carcinogenic, mutagenic and teratogenic [2, 3]. Petrogenic and pyrolytic are the most widely known anthropogenic sources and are usually widely distributed in marine environments [1]. Additionally, a lower molecular weight friction characterizes petrogenic pollution while the higher molecular weight of PAHs characterizes pyrolytic pollution [1]. Many studies have demonstrated that the sources of PAHs can be distinguished by the ratio of low molecular weight (LMW) PAHs to high molecular weight (HMW) PAHs [4-7].

In Malaysia, the marine environment is rapidly being exposed to threats from spills and grease contaminations [7, 8]. Previous studies that investigated the concentrations of PAHs around Malaysia, found PAHs that ranged from the lowest value of 2.1 ng/g in the Straits of Malacca near Port Dickson to the highest value of 1689 ng/g in the east coastal sea around Kelantan, Besut and Terengganu rivers [6, 7, 9]. Kuala Kedah's estuary faces outwards towards the Straits of Malacca, which is the main route for large ships travelling from the east to the west or vice versa. Hence, the objectives of this study are to determine the characteristics and possible sources of PAH compounds in Sungai Kedah, Kuala Kedah, Malaysia. Kuala Kedah is a district and parliamentary constituency in Kota Setar District, Kedah, Malaysia. It is a fishing port, located at the mouth of the Kedah River, and serves as a terminus for ferries to the tourist island of Langkawi. It is home to a fort, Kota Kuala Kedah, which was built in 1770.

Materials and Methods

Study area

A total of sixteen sampling stations were established along the Kedah River from Kuala Kedah, Kedah to the area near the capital city of Alor Setar, Kedah (Figure 1 and Table 1). Surface sediment was collected from each of these sampling stations using a PONAR grab. All the samples were then preserved in pre-cleaned glass jars. All the samples were frozen at 4 °C prior to analysis.

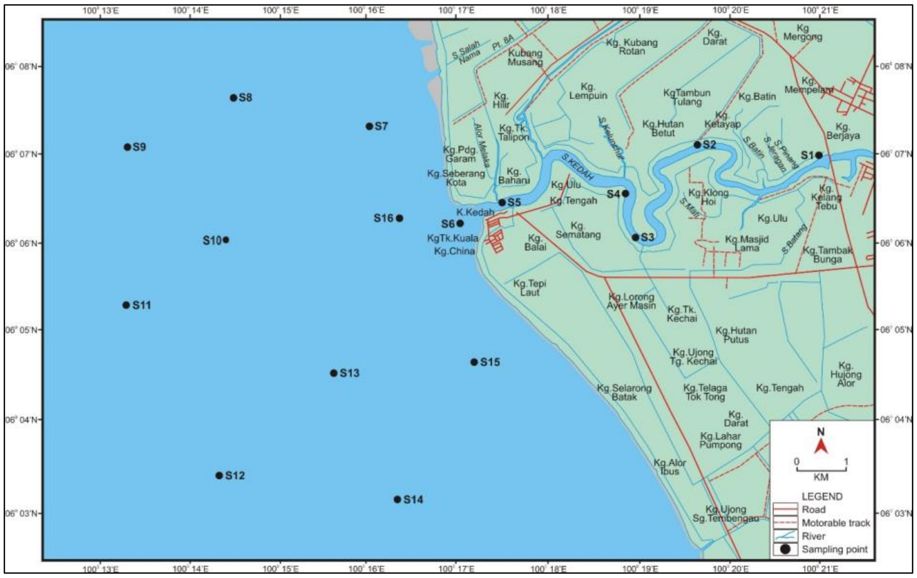

Figure 1. Sampling stations at the study area

Table 1. Description of sampling stations around Kuala Kedah, Kedah

Station	**Descriptions of Sampling Stations**	**Depth of Water Column (m)**	**Latitude (N)**	**Longitude (E)**
1	Residential Area	5.8	06º 7.007’	100º20.876’
2	Residential Area	3.6	06º 7.154’	100º19.687’
3	Residential Area	2.8	06º 6.043’	100º18.958’
4	Residential Area	4.9	06º 6.659’	100º18.708’
5	Residential Area	4.7	06º 6.529’	100º17.580’
6	River Mouth (Jetty Area)	3.0	06º 6.382’	100º17.123’
7	Coastal Area	0.8	06º 7.385’	100º16.019’
8	Open Sea	6.6	06º 7.657’	100º14.546’
9	Open Sea	11.6	06º 7.094’	100º 13.313’
10	Open Sea	2.4	06º 5.686’	100º 14.802’
11	Open Sea	13.7	06º 5.239’	100º 13.323’
12	Open Sea	12.1	06º 3.413’	100º 14.378’
13	Open Sea	4.7	06º 4.521’	100º 15.764’
14	Open Sea	8.5	06º 3.121’	100º 16.486’
15	Coastal Area	2.6	06º 4.681’	100º 17.278’
16	River Mouth	1.7	06º 6.043’	100º18.958’

PAHs extraction

A total of 20 g of sediment sample was taken from each station and mixed with sodium anhydrous to eliminate the water content. The dried sample was put into a thimble extractor (30 mm x 150 mm) and extracted with dichloromethane for about 10 hours. About 250 mL of dichloromethane was put into a round bottom flask and was heated to 60 ^{o}C using a heater. After 10 hours, the extract was evaporated to near dryness by using a rotary evaporator. The residue was later diluted with dichloromethane and was transferred into a 5 mL vial. This residue is known as the Total Extractable Lipid (TEL). The TEL extracts were divided through two stages of silica gel column chromatography. The concentrated sample was then transferred into the silica gel column and washed with 2 mL (0.4 mL, 0.3 mL, 0.3 mL, 0.5 mL and 0.5 mL) hexane/dichloromethane (3:1), subsequently followed by 18 mL hexane/dichloromethane (3:1).

Hydrocarbons that ranged from n-alkanes to PAHs were then collected into a conical flask. Eluent from the first step chromatography was then concentrated by the rotary evaporator, and the PAH fraction was collected with 14 mL mixture of hexane/dichloromethane (3:1). The PAH fraction was labeled and stored in the freezer for further analysis. The PAH sample was then transferred to a 1 mL vial and injected to determine the concentration of PAH compounds. It then underwent the process of nitrogen blowdown evaporation and was refilled with distilled n-hexane prior to injection into the GC-MS (GC, 6890N coupled with 5975C MSD, Agilent, USA). The carrier gas used was helium at a fixed rate of 1 mL/min with a pressure of 158 kpa. An HP-5 fused silica capillary column (30 m × 0.25 mm i.d. and 0.25 um thickness) was used to separate the compounds in split-less mode at 270 °C. It was found that the GC temperature gradient was at 40 °C, then had increased at 8 °C/min to 150 °C, then at 5 °C/min to 310 °C, and finally had held for about 10 minutes. The GC-MS operating conditions were 70eV ionization potential with an MS source at 230 °C for 1.4 scans/sec, and an electron multiplier at 1400 V with the dwell time set to 40 sec. The interface temperature was 280 °C, while the injector temperature was maintained at 250 °C. The 18 PAHs were quantified based on their retention time and the ion m/z ratio of the native standard PAHs.

Quality control and assurance

To confidently confirm the precision of the sample analyses, several pre-detection steps were applied. Firstly, any cross-contamination that might have happened during the research was eradicated. This simultaneously involved the processing of blank and environmental samples. The validation of PAH peaks was determined based on the compatibility of the retention time of each and the abundance of quantification ions of individual PAHs with the 18 PAHs mixture, coupled with the surrogate standard. Apart from that, 5 points of external standard calibration curves (L20950018AL, Dr. Ehrenstorfer GmbH, Germany) were conducted in the range of 0.1 ppm-1.0 ppm, with a correlation coefficient higher than 0.990. The method detection limit (MDL) was also obtained to ensure the limit detection for each PAH. The MDL for naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[k]fluoranthene, benzo[e] pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene were 0.72, 1.22, 0.06, 2.08, 1.17, 1.05, 0.88, 1.11, 1.12, 1.17 and 0.72, respectively. The recoveries for phenanthrene and chrysene were 68.66% and 87.00%, respectively.

Results and Discussion

Composition of PAHs

Concentration of individual compounds ranged from 1.09 ng/g to 59.01 ng/g dry weight sediment as seen in Tables 2 and 3. The highest total PAH concentration was detected in S6, which was 226.03 ng/g dry weight sediment; while the lowest concentration was detected in S3, which was 7.20 ng/g dry weight sediment. This is because S6 is located at the river's estuary where all the sediments are transported *via* the river, which flows to the sea and as such the sediments are deposited here. Based on Figure 2, it was also observed that the total concentration of PAHs was lower in the residential areas in S1, S2, S3, S4 and S5, with the concentration value ranging from 7.20 ng/g-39.35 ng/g, compared to the jetty areas and the open sea, where the concentration value ranged from 13.91 ng/g-226.04 ng/g. This result is supported by Claudine et al. [10], who reported in their findings that PAHs in the residential areas are often lower than the jetty areas, which usually experience a high traffic of water vehicle activities.

Table 2. The concentration of individual PAHs found in sediment samples of Kuala Kedah

Compounds	**Concentrations (ng/g)**							
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**
Naphthalene	1.9	1.59	ND	2.49	5.92	4.27	1.12	2.26
Acenaphthene	ND	ND	ND	ND	2.18	2.08	ND	ND
Fluorene	1.26	ND	ND	1.14	3.55	3.73	ND	ND
Phenanthrene	5.83	4.05	4.78	5.39	9.55	10.56	2.59	4.40
Anthracene	ND	4.67	ND	6.21	11.01	1.52	2.99	ND
Fluoranthene	1.83	ND	1.14	1.32	2.75	20.81	1.83	3.99
Pyrene	1.46	ND	1.28	1.26	3.03	23.19	3.14	6.59
Benzo[k]fluoranthene	ND	ND	ND	ND	ND	39.4	ND	ND
Benzo[e]pyrene	3.23	1.21	ND	ND	ND	12.5	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND	ND	59.01	ND	ND
Benzo[ghi]perylene	ND	ND	ND	ND	1.36	48.96	1.69	3.41
a) Total PAHs	15.51	11.52	7.2	17.81	39.35	226.03	13.91	20.64
b) Total LMW PAHs	9.12	8.72	7.2	14.19	26.33	56.09	10.56	14.98
c) Total HMW PAHs	3.23	1.21	ND	ND	1.36	159.86	1.77	3.41
LMW/HMW	2.82	7.19	ND	ND	19.31	0.35	5.96	4.39

a) Total PAHs ranging from naphthalene to benzo[ghi]perylene,
b) Total of penanthrene, anthracene, fluorenthene and pyrene,
c) Total of benzo[k]fluoranthene, indeno-1,2,2-cd]pyrene, benzo[g,h,i]perylene, ND is not detected

Table 3. The concentration of individual PAHs found in sediment samples of Kuala Kedah

Compounds	**Concentrations (ng/g)**							
	S9	**S10**	**S11**	**S12**	**S13**	**S14**	**S15**	**S16**
Naphthalene	3.97	4.93	8.21	7.64	2.84	4.27	3.97	1.09
Acenaphthene	1.32	2.55	2.59	2.82	ND	1.91	1.72	ND
Fluorene	ND	1.78	2.64	2.11	1.13	2.03	1.65	ND
Phenanthrene	5.01	8.04	12.36	6.49	6.28	10.21	7.18	3.46
Anthracene	5.78	9.27	ND	ND	7.24	11.77	8.28	3.99
Fluoranthene	ND	3.91	4.51	3.35	1.91	2.73	1.44	1.79
Pyrene	5.29	5.73	8.41	4.26	2.56	3.34	1.55	3.79
Benzo[k]fluoranthene	ND	ND	1.25	1.26	ND	ND	ND	27.17
Benzo[e]pyrene	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	1.34	ND	ND	ND	ND	14.51
Benzo[ghi]perylene	ND	3.38	5.24	15.59	15.17	13.28	6.23	75.83
a) Total PAHs	22.03	39.6	46.55	43.79	37.13	49.55	32.02	131.63
b) Total LMW PAHs	16.08	26.96	25.28	14.11	17.98	28.06	18.45	13.03
c) Total HMW PAHs	ND	3.38	7.83	17.11	15.17	13.28	6.23	117.51
LMW/HMW	ND	7.97	3.23	0.82	1.18	2.11	2.96	0.11

a) Total PAHs ranging from naphthalene to benzo[ghi]perylene,
b) Total of penanthrene, anthracene, fluorenthene and pyrene,
c) Total of benzo[k]fluoranthene, indeno-1,2,2-cd]pyrene, benzo[g,h,i]perylene,
ND is not detected

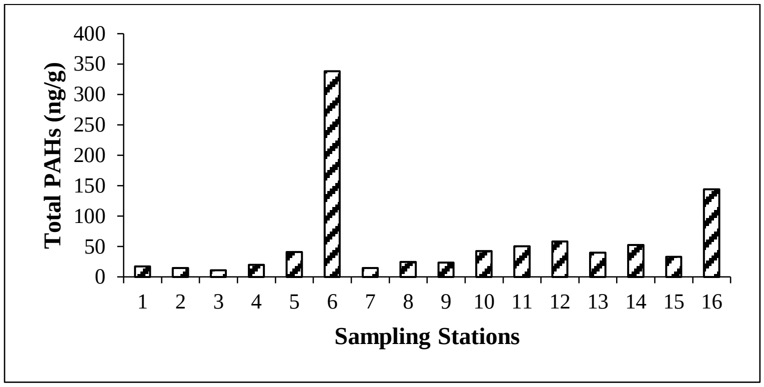

Figure 2. Total PAHs concentration (ng/g) for all sampling stations in Kuala Kedah

According to Baumard et al. [11], the four pollution levels based on total PAHs can be defined as: 0 ng/g-100 ng/g PAHs in the sediment which is classified as low, 100 ng/g-1000 ng/g classified as being moderate, 1000 ng/g-5000 ng/g classified as high, and a concentration of >5000 ng/g, which is classified as very high. Based on these levels, the range concentration of PAHs detected in the area of research in Kedah River can be considered as being in the low to moderately polluted range (11.16 ng/g-338.04 ng/g). The surface sediment samples from these sampling points were dominated by benzo[ghi]perylene and phenanthrene, with the values of 25% and 14% respectively (Figure 3). The lowest occurring compound was benzo[e]pyrene, with a total occurrence of 2% and a total concentration of 16.94 ng/g dry weight sediment.

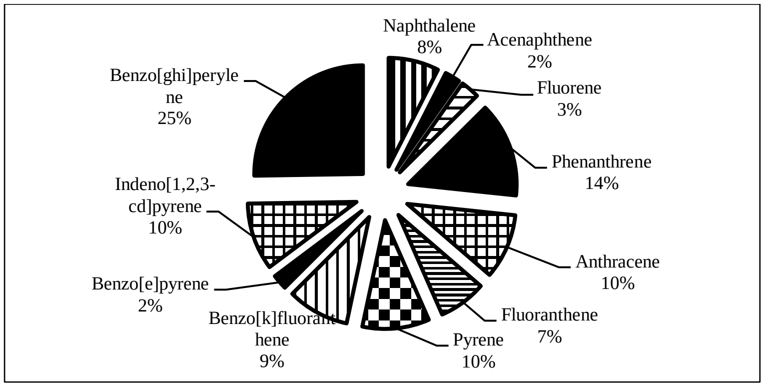

Figure 3. Percentage of individual compounds of PAHs found in Kuala Kedah sediment samples

Molecular ratio index

Figure 4 illustrates the general molecular index of fluoranthene/pyrene against phenanthrene/anthracene. Molecular ratios of Phenanthrene/Anthracene and Fluoranthene/Pyrene were determined in order to differentiate between PAHs of dissimilar origin, where the Phenanthrene/Anthracene ratio is temperature-dependent and consists of approximately 3 of the emissions from the combustion of various fuels [12]. Phenanthere/Anthracene ratios of less than10 are related to the combustion processes, while values more than 10 are derived from petroleum sources or are diagenetic [11]. From our research, S1 indicated a petroleum source while S3, S8, S11 and S12 indicated mixed sources, while other stations indicated combustion sources, which makes pyrolytic source the dominant source based on this ratio. LMW/HMW ratios greater than 1 indicate dominance of petrogenic inputs, and LMW/HMW lesser than 1 indicate pyrogenic inputs [13, 14]. Figure 5, on the other hand, shows that for the Low Molecular Weight (LMW)/High Molecular Weight (HMW) index, the stations that obtained values less than 1 (pyrolytic) are S3, S4, S6, S9, S12 and S16, while the rest attained values of more than 1 (petrogenic). Low molecular PAHs can be observed in Table 2, which comprise of 2-3 fused aromatic benzene rings, compared to high molecular weight of PAHs with 4-6 fused aromatic benzene rings, which suggest that the source of sediment is petrogenic [3, 15]. Based on all the molecular ratio indices used, it can be clearly seen that the major sources of PAHs in the sediment were mixed sources, which were dominated by both petrogenic and pyrolytic sources.

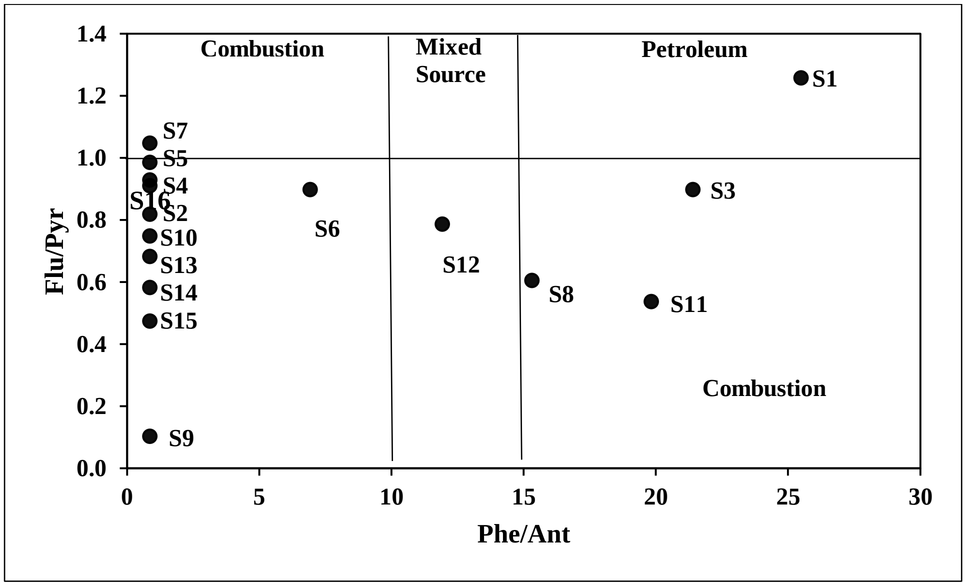

Figure 4. Fluoranthene/Pyrene against Phenanthrene/Anthracene molecular index

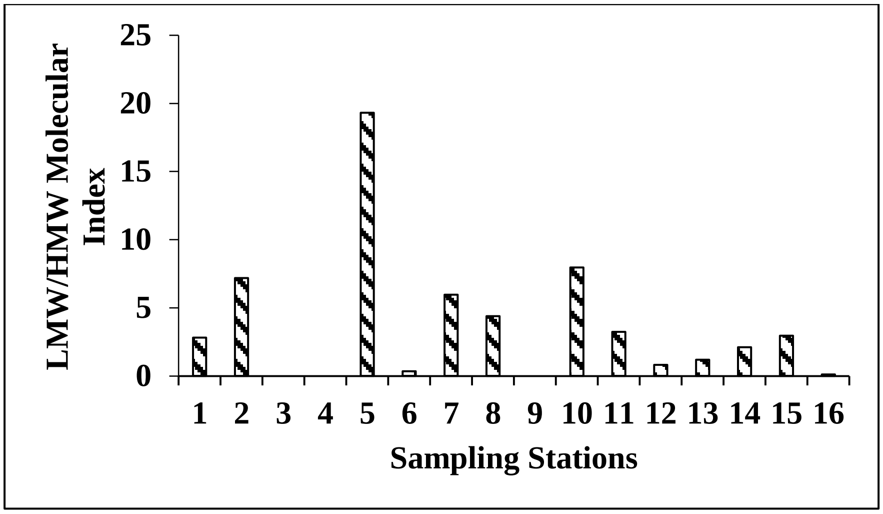

Figure 5. LMW/HMW molecular index

A pyrolytic source is a source that originates from anthropogenic contamination, coming from the combustion of trees, woods, vehicle's engine as well as organic combustion [15]. The sampling locations along the river of Sungai Kedah which originated from the Alor Setar area to the Kuala Kedah area, are primarily residential areas. However, there is also an industrial area known as *Kawasan Perusahaan* Mergong Barrage that could have contributed to the combustion source in the sediment. Apart from that, the road system network that circulates around Kuala Kedah and the Alor Setar area also caters to a significant number of vehicles that emit petroleum combustions to the atmosphere. These can be deposited into the water column and form the sediments at the bottom [17, 18]. A petrogenic source is that which originates from petroleum contamination sources [19].

Conclusion

The total concentrations of all the PAHs in this study ranged from 7.02 ng/g to 226.03 ng/g, which can be categorized under low to moderate pollution levels [11]. Based on the molecular index calculations of Fluoranthene/Pyrene, Phenanthere/Anthracene and LMW/HMW, the PAH concentrations and their possible sources found in this study mostly originated from PAH contaminations that were caused by the combustion of trees, woods, vehicle engine combustions and organic combustions.

Acknowledgement

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