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Research paper



Environmental Forensic Techniques in Identifying the Sources of 16 USEPA Priority Pollutants Polycyclic Aromatic Hydrocarbons (PAHs) at the Langat River, Selangor, Malaysia

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Abstract

Twenty-two surface sediment samples were collected from the Langat River, Selangor, Malaysia in January 2010. The concentration of 16 USEPA priority PAHs were determined and quantified by gas chromatography coupled with mass spectrometry detector (GC-MS). The 16 PAHs concentration ranged from 37.91 to 299.68 ng/g dry weight and are within low to moderate pollution range. Cluster analysis showed that SL08, SL09, SL10, SL15 and SL22 can be discriminated as having high pollution loading PAHs due to industrialized region and shipping boat traffic. In this work, Principal Component Analysis (PCA) and PCA association with Multiple Linear Regressions (PCA-MLR) to identify and apportion possible sources of PAHs. Three sources of PAHs were identified: (1) traffic emission (91.57%); (2) coal or wood combustion (6.63%); and (3) spillage of petroleum based products (1.80%). Langat River is highly contaminated by PAHs from pyrogenic sources, in particular 4 rings PAHs (28.87-79.52%) and 5 to 6 rings PAHs (2.69-57.44%).

Keywords: *Langat River; polycyclic aromatic hydrocarbons; cluster analysis; principal component analysis; multiple linear regressions*

1. Introduction

Many studies have been conducted by researchers around the world for identifying the Polycyclic Aromatic Hydrocarbons (PAHs) pollution in atmosphere, water column, sediment, soil as well as in organisms. Malaysia is not exempted as studies have had carried out on evaluating the current status of PAHs in the environment [1-6]. According to [7], Malaysia has transformed its development strategy in order to accommodate the world's market demands which from the agricultural-based economy to manufacturing industries in the 1990s. There was also continually increased in urban areas with the population in Malaysia exceeding 28.3 million (Population and Housing Census of Malaysia 2010). Such vast economic growth during the past two decades has significantly contributed to an increase in pollution and variety of waste. Among the organic pollutants that arise from these activities are PAHs. In general, PAHs was defined as compounds containing two or more fused aromatic benzene rings [8-9]. There are two types of anthropogenic sources of PAHs: (1) Pyrogenic sources that are derived from the combustion of fossil fuel (coal and petroleum) and in biomass, which are released into the environment as solid residues [10-12]. Pyrogenic PAHs consist of high molecular weight (HMW) molecules with 4 to 7 fused aromatic benzene rings. (2) Petrogenic sources originated from the crude oil and refined petroleum however its presence into the environment through accidental oil spills (transportation), off-shore oil exploitation and natural oil seeps in open sea [13-14]. Petrogenic PAHs are abundant with low molecular weight (LMW) molecules containing 2 to 3 fused aromatic benzene rings.

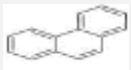
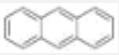
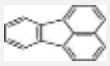
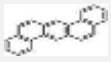
The United State Environmental Protection Agency (USEPA) has proposed 16 PAHs as priority pollutants (Table 1) due to great concern of their toxicity and carcinogenic potential towards animal and human health. Among the 16 PAHs, seven are probable carcinogens such as BaA, Chry, BaP, BbF, BkF, BahA and IP. PAHs have the ability to accumulate in the lipid of organisms due to its hydrophobic characteristic and thereafter will indirectly deteriorate human's health given the consumption of polluted organisms. Humans may also face the threat of contracting cancer. In addition, PAHs are also Endocrine Disrupting Compounds (EDC) owing to their ability to mimic human hormones [15-16]. There are several ways how PAHs can probably enter into the aquatic ecosystem; these can occur through atmospheric transportation via wind rise and volatilization, storm water carrying surface runoff during rainy season, direct discharge of effluent from sewage treatment plants, or accidental spillage of oil from traffic boats or ships [17-18]. When PAHs enter the water column it is eventually adsorbed onto particulate organic matter due to their hydrophobic nature and sediment to the bottom of the aquatic ecosystem with the aid of gravitational forces. Therefore, sediment is an excellent sample for PAHs alongside sedentary organisms found on seabed or ocean-bed [19].

This study sampled 22 stations in the Langat River located in the state of Selangor. It is the most developed area in Malaysia with

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good infrastructure such as highways and transportation. As a result of rapid growth of infrastructure in Selangor, Langat River also experienced land use change and subsequently results in rivers having to carry a significant load of matter in dissolved or particulate phases. Department of Environment, Malaysia reported that Langat River is seriously being contaminated by pollutants from sewage treatment plant, manufacturing industry, livestock farming, and agricultural activities [20].

Table 1: Molecular Structures of 16 USEPA Priority Pollutants

Compound	Molecular Structure	Molecular Weight	Number Of Rings
Naph		128	2
Acy		154	2
Flu		166	2
Ace		154	3
Phe		178	3
Ant		178	3
Fluo		202	3
Pyr		202	4
Chyr		228	4
BaA		278	4
BahA		278	5
BbF		252	5
BkF		252	5
BaP		252	5
IP		276	6
BghiP		276	6

Numerous scientific studies have been conducted on attributing PAH sources using diagnostic ratios. The diagnostic ratios involve manipulating the uniqueness of each PAH compound that profiles fingerprint tracer petrogenic or pyrogenic sources. The ratio of alkyl PAHs to parent PAHs is applied in diagnostic ratios for source differentiation of PAHs. This is possible due to the thermodynamically unstable alkylated PAHs that appear during combustion and stability of parent PAHs that are enriched during combustion [21].

However, diagnostic ratios have several limitations. There will conflicts between ratios were certain ratio will showed pyrogenic sources but other ratio were concluded different result. One the other hand, diagnostic ratios are not sensitive enough to be applied in determine the multiple point source of pollution. The inconsistencies from the usage of diagnostic ratios to identify pyrogenic and petrogenic sources of PAHs have resulted to the further confirmation using PCA. Recently, there have been advances in investigating the possible sources of PAH contamination. Instead of using only limited number of compounds in diagnostic ratios, PCA 'looks' at all the compounds which would prevent misinterpretation of collected data. Multivariate statistical tools such as Cluster Analysis (CA), Principal Component Analysis (PCA) and Multiple Linear Regression (MLR) can be used in the analysis to avoid misinterpretation and are unbiased approaches in the analysis of complex environmental data [22]. These approaches have seen successfully applied in evaluating surface water and freshwater quality [23-24]. However, lately its usage have been extended to the determination of the source of organic contaminants such as PAHs and fecal sterol in the environment [14, 20, 25-28]. This paper reports the assignment of the possible sources of anthropogenic PAHs by using PCA followed by the apportionment of PAH sources in surface sediment of Langat River, Selangor using PCA-MLR.

2. Materials and Method

2.1. Sample Preparation

Sampling was conducted from the 11th to 13th October 2010 at the Langat River which is located in Selangor, Peninsular Malaysia. The 120 km long river flows from the Nuang Mountain down to the Straits of Malacca. Sediment samples were collected in triplicates from 22 locations along Langat River (Figure 1). Description of each sampling location is shown in (Tables 2). Sediment samples were collected using the Eckman Dredge Sediment Sampler and the sediment cake was placed in a stainless steel pan. Surface layer of the sediment sample (0-5 cm) was sectioned using pre-cleaned stainless steel scoop. This study focused on surface sediment as an indicator to provide a good representation of the current active input of terrestrial material into the river. The samples were then wrapped with aluminium foil and kept in a zip log bag to reduce any cross-contamination and temporarily stored in a cooler box with dry ice during its transportation to the laboratory. Upon reaching the laboratory, the sample is stored in the fridge (-4^{0}C) until further analysis.

2.2. Chemical and Reagents

All solvents were purchased from Fisher Scientific (M) Sdn. Bhd. This study focused on the analysis of sixteen PAHs namely naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), dibenzo[a,h]anthracene (BahA), indeno[1,2,3-cd]pyrene (IP) and benzo[g,h,i]perylene (BghiP). The native standards were purchased from Sigma-Aldrich and were injected individually into the GC-MS under the same instrumental conditions to identify and quantify the target PAH in the sample. Five deuterated PAHs standards (naphthalene-d8, acenapthene-

d10, phenanthrene-d10, cyrsene-d12 and perylene-d12) were spiked as Surrogate Internal Standard (SIS), *p-terphenyl-d14* was used as Internal Injection Standard (IIS) and spiked to the sample prior to injection into the GC-MS for quantification of all PAHs analysed in this study. SIS and IIS standard PAHs was purchased from Sigma-Aldrich. The silica gel 60 with size 0.063-0.200 mm for column chromatography (70-230 mesh ASTM) were purchased from MERCK Sdn. Bhd, German and was baked at 400^{0}C for 4 hours to remove organic contaminants and activated at 200^{0}C for 2 hours.



Fig. 1: Map f Sampling Stations at the Langat River, Selangor, Malaysia

Table 2: Sampling Locations for Sediment Samples of Langat River

Station Code	Latitude (N)	Longitude (E)
SL01	03^{0}02'5.23"	101^{0}46′23.7″
SL02	03^{0}00'53.7"	101^{0}46′31.9″
SL03	02^{0}58'58.4"	101^{0}47′19.1″
SL04	02^{0}57'22.5"	101^{0}47′4.75″
SL05	02^{0}56'30.6"	101^{0}47′6.48″
SL06	02^{0}55'25.4"	101^{0}45′55.5″
SL07	02^{0}54'47.9"	101^{0}45′11.9″
SL08	02^{0}54'11.9"	101^{0}43′12.4″
SL09	02^{0}54'10.1"	101^{0}41′54.8″
SL10	02^{0}52'26.0"	101^{0}41′22.7″
SL11	02^{0}50'24.0"	101^{0}40′42.6″
SL12	02^{0}49'39.9"	101^{0}39′13.8″
SL13	02^{0}48'39.7"	101^{0}38′38.4″
SL14	02^{0}47'50.8"	101^{0}37′27.4″
SL15	02^{0}48'32.9"	101^{0}36′12.9″
SL16	02^{0}49'26.5"	101^{0}35′50.2″
SL17	02^{0}49'44.2"	101^{0}34′56.8″
SL18	02^{0}48'35.7"	101^{0}32′59.0″
SL19	02^{0}49'4.81"	101^{0}32′10.5″
SL20	02^{0}50'34.1"	101^{0}31′31.5″
SL21	02^{0}51'32.6"	101^{0}31′42.6″
SL22	02^{0}51'55.0"	101^{0}29′34.9″

2.3. Analytical Procedures

The collected samples were analysed according to procedures described elsewhere [1, 3, 6]. Briefly, 20 g of samples were weighed precisely and freeze dried for 3 to 4 days to remove any moisture in the samples. Dried sediment samples were then spiked with 100 µL of 10 ppm deuterated surrogates (Naphthalene-d8, Acenapthene-d10, Phenanthrene-d10, Cyrsene-d12 and Perylene-d12) for recovery of PAHs. Homogenised sample were then transferred into the cellulose thimble and placed into a Soxhlet Extraction Chamber. The extraction was carried out using 250 ml dichloromethane (DCM) for 9 hours. Activated copper was added into the extract and left overnight to remove sulphur. The volume of extracted sample was then reduced to 1 ml using rotary evaporator. Subsequently, the concentrated sample was fractionated using the 1st step column chromatography (9 cm and 0.9 cm i.d.). The hydrocarbon fraction is eluted with 20 ml of 3:1 v/v Hexane: DCM. The 1st step column chromatography was prepared prior to the fractionation with 5% deactivated silica gel to remove polar compounds and captured the hydrocarbon fraction. Subsequently, the eluted hydrocarbon fraction underwent further fractionation through the 2nd step column chromatography (18 cm and 0.9 cm i.d) which was prepared using fully activated silica gel. The PAHs fraction was eluted with 16 ml 3:1 v/v Hexane: DCM. The volume of the PAHs fraction was reduced using rotary evaporator to near dryness and was transferred into 2 ml vial. Then the fraction inside the vial was dried gently using nitrogen blow down and reconstituted with 100 µL of isooctane prior to its injection into Gas Chromatography-Mass Spectrometry (GC-MS). All PAHs fractions were analysed using 6890 N Agilent gas chromatograph coupled with 5973 N Agilent mass spectrometer (Agilent Technologies, USA) and 7683 Agilent auto sampler.

The carrier gas was helium at a constant flow rate of 1 mL/min with constant pressure of 100 kg/cm2. The compounds were separated using HP-5 fused silica capillary column (30 m × 0.25 mm i.d. and 0.25 µm thicknesses, Agilent Technologies) in split less mode at 270°C. The quantification of the compounds was carried out in the selected ion monitoring (SIM) mode. The GC temperature gradient was: 70°C for two minutes then increase 30°C/min to 150°C, then at 4°C/min to 310°C and finally held for 10 min. The GC-MS operating condition was 70 eV ionisation potential with the temperature source at 200°C for 1.4 scans/sec, with the electron multiplier at 2000 V and the dwell time set at 40 sec. The interface temperature was 290°C while the injector temperature was maintained at 270°C. Individual 16 PAHs was quantified based on their retention time and the ion m/z ratio of native standard PAHs.

2.4. Quality Control and Quality Assurance

In order to ensure high accuracy and precision during analysis of samples, several pre-cautionary steps have been applied: (1) All surface sediment samples were analysed in triplicates and their relative deviations (n=3) was calculated < 20%. (2) Blank samples, spiked blank samples and environmental samples were processed together to eliminate any cross-contamination during analysis. (3) The condition of GCMS was optimised prior to the injection of samples. The confirmation of PAH peaks were performed based on the compatibility of each retention time and abundance of quantification ions of individual PAHs with 16 PAHs mixture, coupled with p-terphenyl-d14 as Internal Injection Standard (IIS), and Surrogate Internal Standard (SIS). In addition, five points internal calibration curves were built in the range of 0.1- 1.0 ppm for PAHs with correlation coefficients higher than 0.993. The recovery ranged from 60% to 110% for all 16 target analytes. PAH concentrations were corrected using their recoveries.

2.5. Data Analysis

Diagnostic ratios of PAHs are an established method for interpreting PAHs composition and determine the origin of PAH sources [29-30]. The ratios of individual PAH concentration gives some indications about the different sources of PAH compounds. There were several diagnostic ratios of some molecular mass that have been applied in this study, namely; (i) Ant/ (Ant+Phe), (ii) Fluo/ (Fluo+Pyr), and (iii) BaA/ (BaA+Chry). Normal distribution tests

were carried out in order to observe the distribution of 16 priority pollutant PAHs. The test included W (Shapiro-Wilk) test, Anderson- Darling test, and Lilliefors test. Variables with normal distribution analysed further while those showing other than normal distribution underwent relevant transformations. In this study Cluster Analysis, PCA and MLR were performed for the data set of individual PAHs at 95% confidence level for all sampling locations using the XL-STAT 2010 Excel add-in. The mean of total 16 PAHs in each sampling station were hierarchically clustered in order to examine the dissimilarity (or similarity) between variables and cases. PCA is a widely used multivariate analytical tool employed to interpret relationships of all measured parameters (16 PAHs) and to identify all sources of pollution [23, 31-32]. PCA was applied in this study for two purposes; to reduce the number of variables from the complex dimensionality of the sample data and to identify relationships among the variables in the data set by displaying the correlation among the original variables [30]. PCA-MLR was used then to apportion PAH sources where PCA scores act as an independent variables while normalized PAH concentrations (dry weight) are the dependent variables [26, 33].

3. Results and Discussion

3.1. Distribution and Compositional Patterns of Pahs in Surface Sediment

The concentration of 16 PAHs and their diagnostic ratios are presented in (Table 3). Total concentration of 16 PAHs, expressed as Σ16PAHs ranged from 37.91 to 299.68 ng/g with a mean of 139.351 ng/g dry weight. Figure 2 showed the total concentration of Σ16PAHs in 22 sampling locations at Langat River. In this study, cluster analysis was applied to characterise pollution loading of PAHs in surface sediment samples by using Σ16PAHs. The agglomerative hierarchical analysis was applied by using Ward's method [34] to identify similarities among Σ16PAHs at different sampling locations. Figure 3 indicated three clusters ($p < 0.05$) labelled as Cluster 1, Cluster 2 and Cluster 3 for High Pollution Loading (HPL), Low Pollution Loading (LPL), and Moderate Pollution Loading (MPL) respectively. It is observed that SL08, SL09, SL10, SL15 and SL22 (Cluster 1) have been discriminated as High Pollution Loading group due to the contribution from rapidly growing industrial areas located near urban sampling locations. These findings are consistent with the study conducted by [3], that showed evidence that SL08, SL09 and SL10 areas have been receiving high concentration of PAHs due to increase in human activities in those areas. In [35] had reported that downstream of Langat River were highly populated with small industrial factories and also act as busy pathway for shipping boats. As such, significant evidence for high concentration of PAHs in SL15 and SL22 may be due to the direct discharge of waste generated from shipping activities and surface runoff.

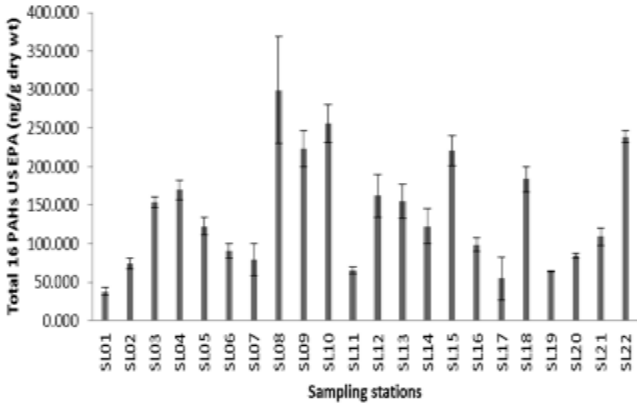


Fig. 2: Total 16 Pahs (Ng/G) of Surface Sediment at Langat River Based on Dry Weight

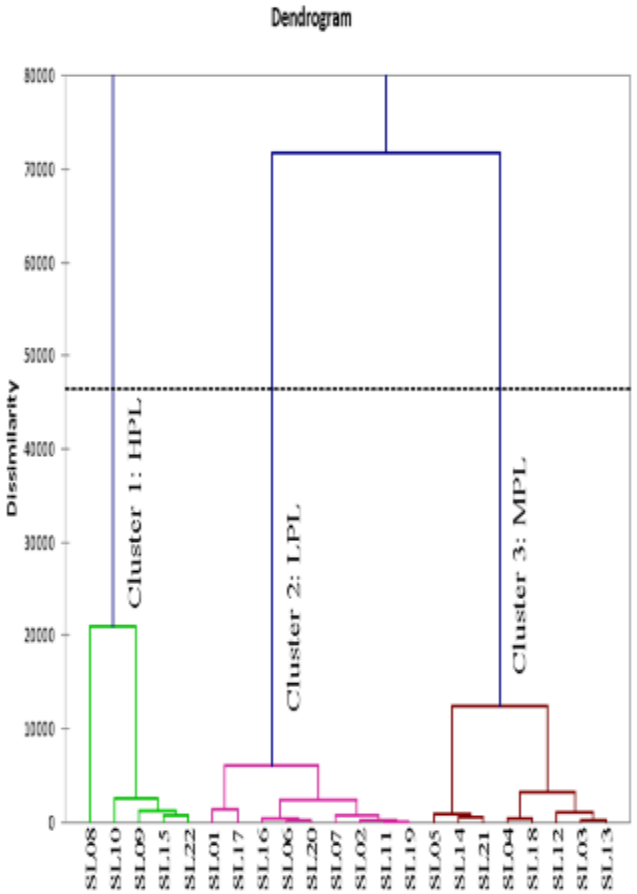


Fig. 3: Dendrogram of Clustering of Sampling Stations According to Total Concentration of Pahs Analyzed In Surface Sediment Samples of Langat River Using Wards' Method

In order to determine the current status of PAH pollution in the Langat River, concentration of PAHs in Langat River were compared with the data obtained by [36], where 0-1000 ng/g of PAH in sediment is considered as low to moderately polluted while 1000-10000 ng/g is considered as being moderate to highly polluted. The results of this study indicated that PAHs from Langat River fall within low to moderate pollution range and is similar to the study that have been successfully carried out by [1] which showed that Malaysia riverine falls under that pollution range. Most of the sampling locations in Langat River are dominated by high molecular weight PAHs (HMW) which consist of 4 to 6 fused aromatic benzene rings compared to low molecular weight of PAHs (LMW) of 2 to 3 fused aromatic benzene rings. Based on Figure 4, most of the sampling locations in Langat River have higher proportion of 4 rings (28.87-79.52%) compared to 5 to 6 rings (2.69-57.44%) except for station SL22 which was detected to have a high distribution of 2-3 rings PAHs. Fundamentally, petrogenic PAHs are abundant in LMW PAHs while pyrogenic PAHs are dominated by HMW PAHs (e.g combustion of fossil fuel and biomass) [37-38]. These results suggested that the PAHs contamination in Langat River sampling stations mostly originated from pyrogenic sources. This is supported by [3] who reported that surface sediments in Langat River were dominated by high molecular weight PAHs while low molecular weight PAHs were abundant in the water column. This is due to the different intrinsic hydrophobic characteristics between HMW PAHs and LMW PAHs [38]. Generally, PAHs that enter the aquatic environment will be attached to particulate organic matter thus, allowing them to travel long distances before being deposited to the bottom of the sediments due to gravitational forces [9].

Table 3: PAH concentrations (ng/g) based on dry weight and diagnostic ratios of the surface sediments from the 22 sampling stations at Langat River, Selangor.

Sampling Location	SL 01	SL 02	SL 03	SL 04	SL 05	SL 06	SL 07	SL 08	SL 09	SL 10	SL 11	SL 12	SL 13	SL 14	SL 15	SL 16	SL 17	SL 18	SL 19	SL 20	SL 21	SL 22
Naph	0.44	0.54	0.49	1.08	0.00	0.49	0.61	0.63	8.07	1.44	0.32	1.75	0.89	2.22	2.93	1.01	0.56	0.00	0.79	1.28	0.24	0.65
Acy	0.11	0.89	0.50	2.54	2.95	0.49	2.02	3.54	1.39	5.80	3.80	4.32	3.59	3.21	3.78	1.35	2.06	3.80	0.11	0.18	1.92	2.58
Ace	0.11	0.44	0.28	0.78	0.00	0.49	0.60	0.69	1.00	0.55	0.12	0.53	0.16	1.94	1.18	1.29	0.56	0.00	0.11	0.18	0.58	1.22
Flu	2.65	3.34	2.99	6.13	3.15	4.30	3.64	7.19	6.89	6.29	1.13	5.16	4.40	4.00	6.02	3.94	3.37	4.05	3.24	4.03	3.30	7.46
Phe	2.05	4.57	3.31	12.34	5.31	10.90	5.66	22.45	9.65	11.49	1.87	8.16	6.66	5.66	9.72	3.50	2.12	5.04	2.98	3.51	3.53	18.53
Ant	3.13	2.51	2.82	5.71	3.54	3.75	3.63	4.66	5.19	5.22	4.19	4.58	4.40	3.57	4.19	3.17	4.19	4.54	3.82	4.82	3.53	4.19
Fluo	3.80	5.81	4.81	12.46	10.83	5.97	6.65	18.26	11.44	11.04	5.58	14.92	10.67	7.47	12.27	6.67	4.41	10.36	5.38	7.16	7.86	14.12
Pyr	5.16	9.23	7.19	14.64	24.61	10.90	9.86	19.92	20.75	14.09	8.90	42.83	19.86	9.23	14.06	11.90	6.84	17.12	7.52	9.93	11.39	28.56
BaA	2.95	8.91	5.93	14.66	11.02	6.55	8.44	36.30	22.51	28.11	6.34	14.07	15.83	14.24	22.98	11.12	3.70	19.15	5.54	9.18	11.32	26.75
Chry	0.11	1.61	0.86	0.78	0.00	0.49	0.00	9.37	6.49	4.06	0.12	0.00	0.16	3.49	9.88	1.60	0.56	6.04	0.11	0.18	7.98	20.85
BbF	3.55	9.45	6.50	15.68	10.43	8.35	8.03	35.94	24.09	38.50	8.47	16.15	21.74	19.56	28.11	14.10	5.01	25.18	7.25	11.77	9.27	29.46
BkF	3.55	9.45	6.50	15.68	10.43	8.35	7.02	35.94	24.09	38.50	8.47	16.15	21.74	19.56	28.11	14.10	5.01	25.18	7.25	11.77	12.66	29.46
BaP	3.70	4.88	4.29	10.25	6.10	4.30	3.22	12.84	10.58	9.64	5.96	8.67	8.85	7.20	12.92	3.44	5.79	12.40	4.83	6.89	4.47	12.53
IP	0.11	0.44	0.28	10.26	1.77	0.49	1.34	0.16	0.98	0.55	0.12	0.00	5.93	1.24	16.17	4.22	0.56	14.68	4.55	0.18	7.90	16.85
BahA	0.11	2.51	1.31	5.66	3.35	3.19	3.01	10.81	6.02	6.45	2.98	3.76	4.53	4.13	6.87	2.88	0.56	5.53	2.91	0.18	3.05	4.84
BghiP	6.41	9.94	8.17	40.86	29.16	21.96	15.66	80.99	63.62	74.03	7.02	21.10	25.82	15.99	41.30	14.26	9.37	30.34	7.68	13.22	19.92	20.81
Ant/(Ant+Phe)	0.60	0.35	0.46	0.32	0.40	0.26	0.39	0.17	0.35	0.31	0.69	0.36	0.40	0.39	0.30	0.48	0.66	0.47	0.56	0.58	0.50	0.18
BaA/(BaA+Chry)	0.96	0.85	0.87	0.95	1.00	0.93	1.00	0.79	0.78	0.87	0.98	1.00	0.99	0.80	0.70	0.87	0.87	0.76	0.98	0.98	0.59	0.56
Fluo/(Fluo+Pyr)	0.42	0.39	0.40	0.46	0.31	0.35	0.40	0.48	0.36	0.44	0.39	0.26	0.35	0.45	0.47	0.36	0.39	0.38	0.42	0.42	0.41	0.33

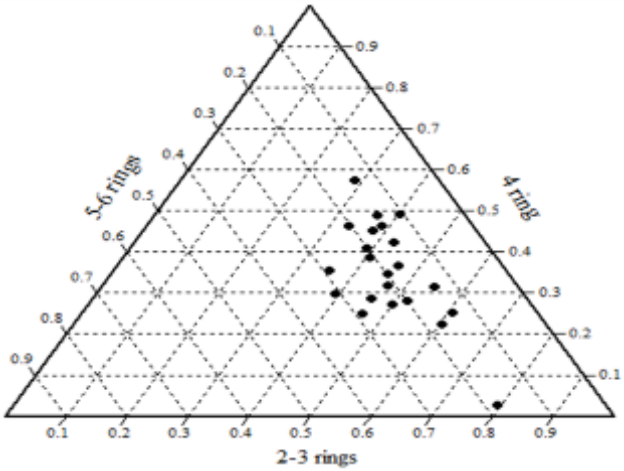


Fig. 4: Triangular diagram of percentage concentration for the 16 PAHs in surface sediment

As for individual PAHs (Figure 5 and Figure 6), BghiP, BbF, BkF, BaA and Pyr were pre-dominant of the surface sediment samples in Langat River and have approximately 19.46%, 12.01%, 12.09%, 10.93% and 10.93% respectively of the total PAHs. BghiP, BbF and BkF are basically tracer of incomplete combustion of vehicle exhaust [40-42] that are dispersed by atmospheric transport and eventually accumulate in soils and aquatic environment. In addition, Flu, Phe, and Ant contribute 3.26%, 5.36% and 3.01% respectively and are usually due to combustion of coal or wood [33, 42-43]. These could be attributed to forest fire that normally occurs in Malaysia's forest initiated by human activities or hot weather. In this study, Naph contributes 0.89% of PAH pollution in Langat River and is commonly found in petroleum products [28, 44-45]. This is reasonable because downstream areas of Langat River were found to have high concentration of PAH due to anthropogenic sources (e.g ships and small boats). Previous study conducted by [1] identified used crankcase oil as the major petrogenic sources of PAHs in Malaysia's aquatic environment. The mixture between petrogenic (used crankcase oil) and pyrogenic (unburned fuel) sources are usually present and presumably come from derivation of combustion products in the engine system itself.

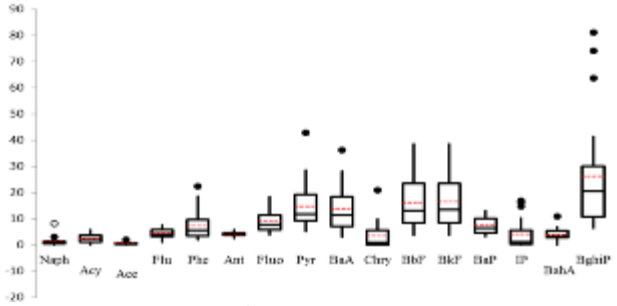


Fig. 5: Box Plot for Individual PAH Compounds

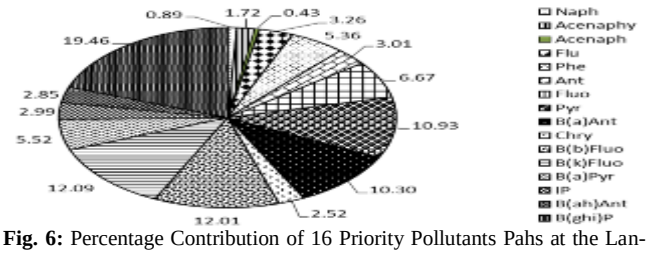


Fig. 6: Percentage Contribution of 16 Priority Pollutants Pahs at the Langat River.

3.2. Identification of the 16 PAH Sources Using Diagnostic Ratios

In this study, three specific PAH ratios were calculated to identify the origin and potential sources of PAHs in surface sediment samples from Langat River. The ratios are of Ant/(Ant+Phe), BaA/(BaA+Chry), and Fluo/(Fluo+Pyr) which are indicative of molecular mass 178, 202, and 228 respectively. In order to distinguish between PAH sources whether it originated from combustion (pyrogenic sources) or petroleum product (petrogenic sources), these ratios are often applied by numerous researchers such as [29, 39, 53, 60]. Based on diagnostic ratios applied by [36], Ant/(Ant+Phe) < 0.1 indicates petrogenic sources while Ant/(Ant+Phe) > 0.1 are pyrogenic sources. In this study, all values for sampling locations ranged from 0.17 to 0.69. Therefore, the ratios it strongly suggest the PAHs are of pyrogenic sources. Overall, Ant (178) is less persistant in the environment because it will undergo rapid photochemical reaction in the atmosphere compared to Phe (178).

Therefore Fluo/(Fluo+Pyr) ratio was introduced due to its higher persistence in environment [28]. The ratio developed by [61],where Fluo/(Fluo+Pyr) ratio < 0.4 acts as an indicator for raw petroleum sources, 0.4 to 0.5 were attributed to petroleum combustion while Fluo/(Fluo+Pyr) > 0.5 implied grass, wood and coal combustion. In surface sediment samples of Langat River, the ratio ranged from 0.26 to 0.48. Nine out of twenty two samples showed values within 0.4 to 0.5 indicating petroleum combustion. Another 13 samples showed value less than 0.4 and are typically of raw petroleum sources. As for BaA/(BaA+Chry) ratio < 0.2 indicates petroleum sources while values 0.2 to 0.35 implied mixture of petrogenic and pyrogenic sources, and BaA/(BaA+Chry) ratio > 0.35 acts as an indicator of PAHs combustion. Calculated PAH ratio revealed that BaA/(BaA+Chry) ratio ranged from 0.56 to 1.0, mainly due to pyrogenic sources (Table 4)

Table 4: Pearson's correlation coefficient (r) between Σ16PAH concentrations and diagnostic ratios.

	Σ16 PAHs	Fluo/(Fluo+Pyr)	BaA/(BaA+Chry)	Ant/(Ant+Phe)
Σ16 PAHs	0.00	0.12^{ns}	-0.47^{ns}	-0.74^{ns}
Fluo/(Fluo+Pyr)		1.00	-0.17^{ns}	0.01^{ns}
BaA/(BaA+Chry)			1.00	0.36^{ns}
Ant/(Ant+Phe)				1.00

In order to estimate sources of PAHs in Langat River, Ant/(Ant+Phe) was plotted against Fluo/(Fluo+Pyr), and BaA/(BaA+Chry) was plotted against Fluo/(Fluo+Pyr) [62,27,28] in (Figure 7a and 7b). Results showed several similarities among 11 sampling locations (SL02, SL05, SL06, SL9, SL11, SL12, SL13, SL16, SL17, SL18, and SL22) due to petrogenic pollution sources and other samples (SL01, SL03, SL04, SL7, SL08, SL10, SL14, SL15, SL19, SL20, and SL21) were being defined as pyrogenic sources. In order to evaluate the correlation between Σ16PAHs and diagnostic ratios, calculations were carried out using Pearson's correlation. Results shown in Table 5 indicate that there are no significant correlation between Σ16PAHs and the applied diagnostic ratios. From this, it is reasonable to say that, diagnostic ratios are not very convincing in distinguishing petrogenic and pyrogenic sources of PAHs in Langat River sediment samples.

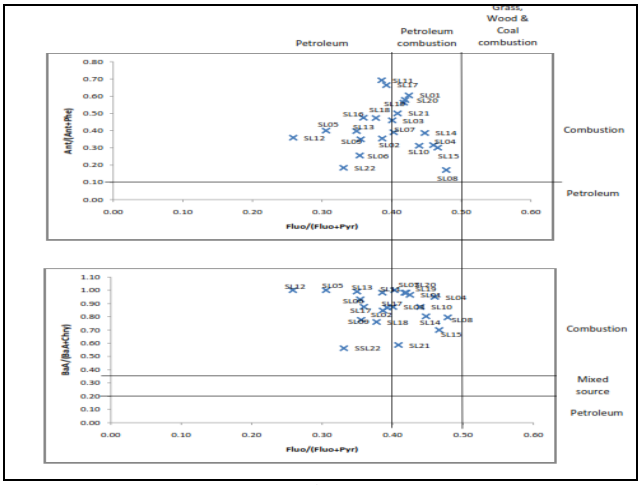


Fig. 7: Diagnostic PAH ratios of (a) Ant/(Ant+Phe) plotted against Fluo/(Fluo+Pyr) and (b) B(a)Ant/(B(a)Ant+Chry) plotted against Fluo/(Fluo+Pyr)

3.3. Source Estimation by Principal Component Analysis (PCA) Coupled with Multiple Linear Regression (MLR)

PCA provides information on the most significant parameters associated with the 16 priority pollutant PAHs [22, 23]. The principal components with eigenvalues greater than one were identified and in order to obtain the relationship between the principal components and individual PAHs, which are indicated by their factor loadings, PCA with Varimax rotation were performed. The varimax rotation in PCA was used to increase the weight of the significant factor loadings and reduce the weight of the non-significant ones [24, 47-49]. Table 5 presents the three significant Varimax Factors (VF) that are responsible for the 16 PAHs. Loading values exceeding 0.75 are also highlighted (bold). Values above 0.75 are considered to have strong loading while moderate loading fall within 0.5-0.75 [20].

Table 5: Loading of individual 16 PAHs after Varimax rotation (high loading > 0.75 are shown in bold; moderate loading 0.5-0.75 in italic bold) for the surface sediment samples from 22 sampling station at the Langat River

	VF1	VF2	VF3
Naph	0.289	-0.143	**0.810**
Acy	**0.751**	0.050	-0.270
Ace	0.106	0.479	***0.676***
Flu	**0.763**	0.347	0.417
Phe	**0.753**	0.361	0.193
Ant	**0.757**	-0.166	0.101
Fluo	**0.906**	0.246	0.004
Pyr	***0.636***	0.101	-0.158
BaA	**0.883**	0.351	0.204
Chry	0.397	**0.824**	0.184
BbF	**0.874**	0.320	0.179
BkF	**0.869**	0.337	0.174
BaP	**0.839**	0.378	0.059
IP	0.214	0.345	-0.173
BahA	**0.860**	0.235	0.160
BghiP	**0.878**	-0.064	0.302
Eigenvalue	9.648	1.509	1.371
Explained variance (%)	52.024	15.523	10.751

Cumulative (%)	50.024	67.548	78.299

PCA identified the values of total percentage variance for VF1, VF2, and VF3 as 52.02%, 15.52 %, and 10.75% respectively. VF1 corresponds to the strong factor loading of the following compounds: Fluo, B(a)Ant, B(b)Fluo, B(k)Fluo, B(a)Pyr, B(ah)Ant, and B(ghi)P. B(ghi)P which are presumably released from traffic emission [50,51] and are tracers for aerosol from automobile exhaust [43, 52]. Fluo, B(a)Ant, B(b)Fluo, B(k)Fluo, B(a)Pyr, and B(ah)Ant have high molecular weight and are found in diesel engine emission and gasoline engine emission [53]. After considering all possible contributions of PAH contamination, VF1 is seen to have been the result of traffic emission sources. Based on the visual survey, which was carried out prior to sampling, it is clear that Langat River is mostly polluted by anthropogenic sources especially in areas which are highly populated. VF2 is strongly loaded with Chry which is a high molecular weight PAH consisting of four fused aromatic rings.

In previous studies, Chry is usually found in coal or wood combustion emission [42- 43, 54]. Thus, it is suggested that VF2 is dominated by coal or wood combustion sources. VF3 is dominated by Naph which is identified as typical tracers for spillage of petroleum based products (from waterway transportation industry) and defined as petrogenic sources [1, 56]. According to these results, VF1, VF2, and VF3 are possible sources of PAHs from traffic emission, coal or wood combustion and spillage of petroleum based products respectively. Further analysis of data was conducted to determine the percentage of contribution from the three possible sources of PAHs [41]. MLR was performed on the factor score of the PCA-Varimax rotation as independent variables and the 16 PAHs as dependent variables. According to method described elsewhere [26] PCA-MLR is the best estimation tool to predict the mean percentage of possible sources on samples that has a wide range of individual PAHs.

This was proven in Figure 8 showing the correlation between PCA-MLR predictions value and the observed Σ16PAHs were within the 95% confidence level with best correlation to each other (r^2 = 0.9883). Thus, mean contribution percentage for each possible sources are 91.57% for traffic emission sources, 6.63% attributed from coal or wood combustion and 1.80% contribution from spillage of petroleum based products (Figure 9). In a nutshell, possible major sources of PAHs in Langat River were contributed from traffic emission categorized as pyrogenic sources. Smoke from vehicles is easily spread via atmospheric transportation and wet or dry deposition [56] reported that atmosphere is the main transport pathway of PAHs and act as an important medium of pollutant transfer. After smoke is being released into the atmosphere, it is absorbed onto soot particles and deposited onto the road surface or soil and thereafter transported into the aquatic environment via urban runoff [57, 60]. On the other hand, possible minor contributors of PAHs contaminating the Langat River come from spillage of petroleum based products. These types of petrogenic sources were detected at several sampling locations downstream of Langat River.

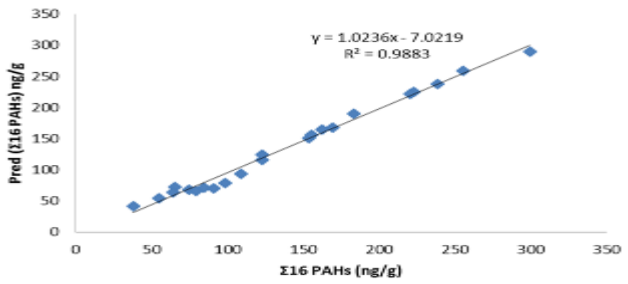


Fig. 8: Correlation of the value of Σ16PAHs between PCA-MLR predictions.

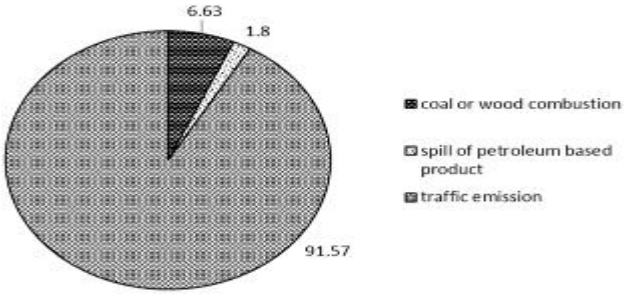


Fig. 9: Possible sources of PAHs based on PCA-MLR prediction

A previous study by [1] stated that Malaysian sediments receive a mixture of petrogenic and pyrogenic sources from illegal disposal of crankcase oil and leakage of crankase oil from vehicle onto road surfaces. Besides active shipping and boating activities found at downstream of Langat River, improperly managed landfills are also sighted where untreated leachate was directly discharged into the river (Figure 10). Normally, the most common design of landfills is the open land-filling [61, 63] situated near rivers or towns. Landfill sites receive solid wastes from domestic and industrial sectors and it is believed that the generated leachate from the landfills contain mixtures of petrogenic and pyrogenic PAHs.

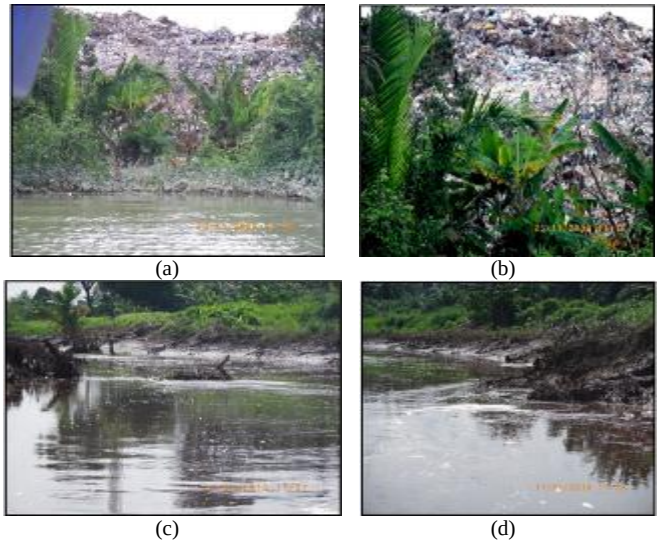


Fig. 10: Photos of Landfill Sites Situated Near the River Bank Downstream of Langat River. (a) and (a) November, 23, 2009 Sedu Landfill, Semenyih,(c) and (d) January, 11, 2010 Blackish Colour of River Water Due to the Improper Management of Landfill Arising from Direct Discharge of Untreated Leachate.

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