

Historical profiles of Polycyclic Aromatic Hydrocarbons (PAHs), sources and origins in dated sediment cores from Port Klang, Straits of Malacca, Malaysia

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Abstract—Polycyclic aromatic hydrocarbons and pentacyclic triterpanes (hopanes) were determined in 2 sediment cores collected from offshore of Klang River estuary and Old Port of Klang City, located in Straits of Malacca, Malaysia. Strait of Malacca is among the world's busiest waterways and Port Klang is one of the busiest, premier and largest ports in the Straits. The port has been an important trading post since the colonial era of the Portuguese, Dutch and the British Straits Settlements. Old Port of Klang is heavily influenced by urban population and runoff as well as massive shipping traffic. The highest concentration of polycyclic aromatic hydrocarbons was found in Old Port Klang with PAHs from 34 to 2426 ng/g while Offshore Klang showed total PAHs concentration from 7.37 to 32.97 ng/g. Also these concentrations are significantly elevated in upper layers in both cores. Sediment core collected in Old Klang port carries mixture of petrogenic and pyrogenic signatures with methylphenanthrene to phenanthrene (MP/P) ratio range from 0.63 to 1.11 while the core collected from an offshore station of the Klang river estuary revealed a highly pyrogenic signature as evidenced from the MP/P ratio of 0.22 to 0.83 indicating atmospheric transport and non-conservative behavior of the pollutant as the distance from the source increases. All sediment intervals showed PAHs concentration below the effects range-low (ER-L) sediment toxicity threshold values (total PAHs < 4000 ng/g) but indicative of polluted environment (> 1000 ng/g). Although results from pentacyclic triterpanes in this study revealed that hopane is not a conventional molecular marker for source identification of pyrogenic sources of PAHs, but apparently showed no significant of oil spills occurred in the study area. Results from the analysis of other alkyl substitute of PAHs such as ratio of Methyl Pyrene to Pyrene (MPy/Py), parent PAHs and hopanes as well as ratios such as Fl/Py and Ph/An indicated mostly pyrogenic source originated from street dust and asphalt in Klang valley including Kuala Lumpur. This indicates that the sedimentary environment around Port Klang mostly receives short and medium range transport materials via rivers and atmosphere, although heavy ship traffic and urban runoffs could easily be thought of receiving petrogenic input.

Key words: historical profile, PAHs, Hopane, Klang, Malaysia

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic contaminants that are area of concern due to its harmful effects to human and the environment (Neff, 1979). PAHs contain 2 or more fused benzene rings subjected to many studies worldwide (Youngblood and Blumer, 1975; Bohem and Quinn, 1979; Prahl and Carpenter, 1983; Mal-

donado et al., 1999; Zakaria et al., 2002) among others. PAHs are derived to the environment via various processes including combustion of fossil fuels (pyrogenic), biomass burning, crude oil and petroleum products release into the environment (petrogenic) and diagenesis. Since oil became the major energy source of the world in 20th century, the environment faced severe related pollutions such as PAHs through oil usage, transportation and infrastructure developments and has widespread implications (Wang and Stout,

2007; Chandru et al., 2008). Some PAHs are carcinogenic, mutagenic and disrupt human endocrine systems as consequences of human activities (Neff, 1979). PAHs with Lower Molecular Weight (2–3 rings) are more bio-available than Higher Molecular Weight (4–6 rings) with significant higher toxicity, mutagenic and carcinogenic characteristics. Marine organisms have different mechanisms for PAHs uptake. While mollusks uptake and accumulate the PAHs from water column, organisms such as benthic absorbs through feeding processes in sediments' layers. PAHs in marine organisms are subjected to various processes including accumulation, metabolism, excretion and depuration although fish are exceptions due to the Mixed Function Oxidize (MFO's) enzymes' function in the body.

Port of Klang is one of the major ports in the region located in the west coast of Peninsular Malaysia (Fig. 1a, b), about 50 Km from the capital city of Kuala Lumpur. The port was a major trading post since the colonial era of the Por-

tuguese, Dutch and the British settlements. The port was established in 1893 and played an important economic role in straits of Malacca and Southeast Asia. Due to global economic expansion, Port Klang has now grown into 3 major areas: the North, the South and the West Ports.

Malaysia has been experiencing extremely rapid economic growth in Southeast Asia since independent in 1957. Basically, there are two major possible sources of PAHs in the Port of Klang including combustion and petrogenic hydrocarbons. A Previous study in Port of Klang (Zakaria et al., 2002) reported high PAHs concentration with mix signature of petrogenic and pyrogenic origins, where crankcase oil was highly predominant. Sakari et al., (2008a) confirmed that mixture of petrogenic and pyrogenic pollution are abundant in Prai Straits, Malaysia. In Malaysia not only Port of Klang and Prai strait but also remote and not industrialized locations such as the East Coast showed pollution load from petroleum and its products (Sakari et al., 2008b). Possibly the

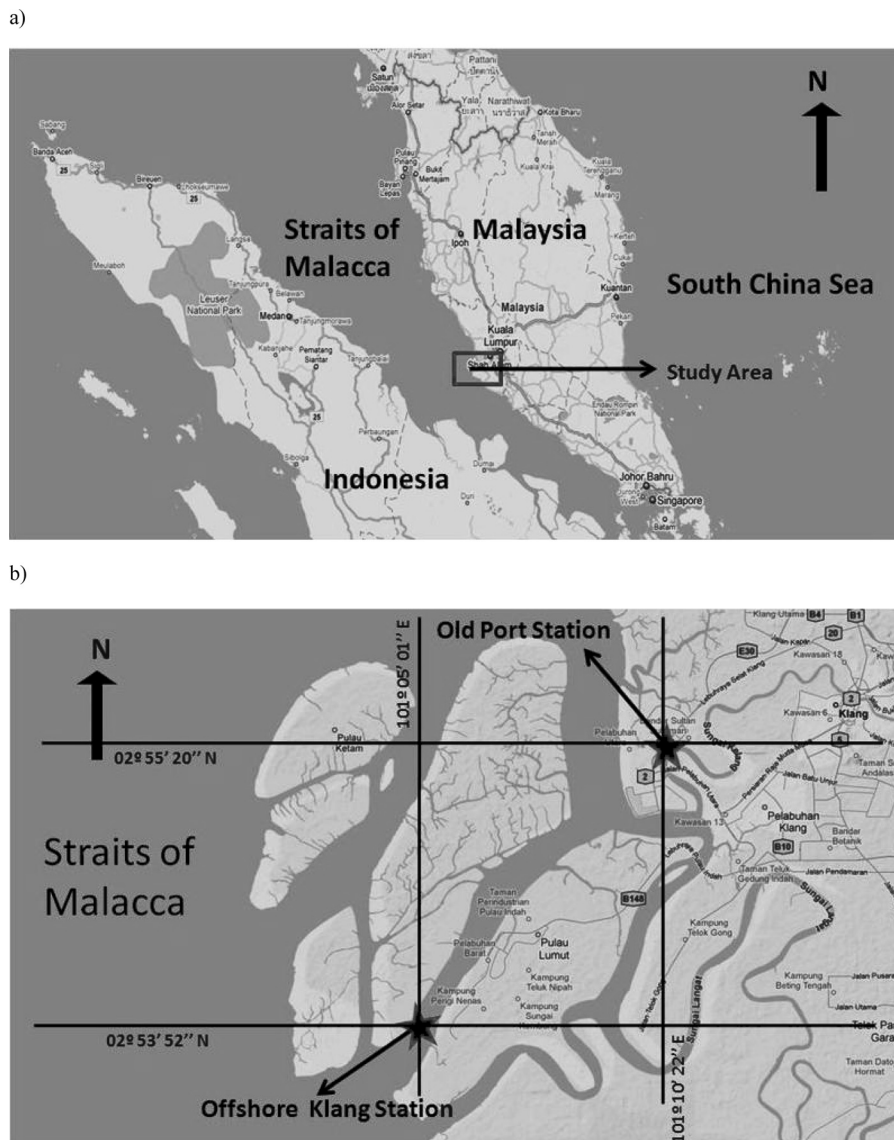


Fig. 1. Map of the study area; a) General view to Malaysia and the sampling locations, b) Sampling Locations (Star).

input of PAHs in the marine environment of Port of Klang is via lateral (Prahl et al., 1984) and atmospheric (Laflamme et al., 1978; Prahl and Carpenter, 1983) transport. Lateral transport of PAHs is via naturally occurring and anthropogenic particles where hydrophobic organic compounds absorbed onto the surface of particles for migration through the media such as water or air. While pyrogenic PAHs are strongly associated with soot particles for transport (Lake et al., 1979), petrogenic PAHs are deposited in to the marine environment by surface runoff, direct discharge and industrial effluents (Lake et al., 1979; Latimar and Quinn, 1996). PAHs from the time of formation to final sink are subjected to chemical, physical and biological processes, indicative of degradation in the environment.

PAHs in the environment have definite behaviors which are controlled by several processes. Processes which can control the transport and degradation of PAHs in sediment include 1) partition of the compounds between aqueous (pore-water) and particulate phase, 2) microbial degradation, 3) uptake, metabolisms and depuration of PAHs by the benthos 4) photo-oxidation (surface sediment), chemical oxidation and 5) biosynthesis.

This study focused on the distribution, sources, origins and the historical profile of PAHs in the marine sediment samples from Port of Klang. The PAHs concentrations together with hopane biomarker signature were studied in two cores collected from Old Port of Klang and the estuary where the Klang River meets the Straits of Malacca. This study will give some insights of the lateral and atmospheric transport of the PAHs in the area; therefore the processes such as microbial degradation are not discussed.

Materials and Methods

Sample collection

Two cores were taken in January, 2007 at Old Port of Klang and the Klang River estuary in Straits of Malacca (02° 55'20"N, 101°10'22"E and 02°53'52"N, 101°05'01"E) using stainless steel gravity corers (i.d. 3 cm) equipped with compacted pre-cleaned plastic tube inserts to prevent cross contamination prior to slicing. The cores were taken so as to avoid collecting the samples where dredging activities had been conducted. The water column depth was ~4 and ~5 m and the cores reached to 21 and 42 cm in lengths. The core sediment in the pre-cleaned compacted plastic container was placed vertically and transferred immediately to the shore for slicing. The core was sliced in 3cm intervals from the top using pre-cleaned stainless steel sheets. Each sediment interval was transferred to a pre-cleaned stainless steel container and transported to the laboratory and stored at -18°C prior to further analysis. All glassware used for analysis was successively rinsed 3 times each with organic solvents including

methanol (MeOH), acetone and distilled hexane, capped with Aluminum Foil (Al Foil) and dried in oven at 60°C for 3 hours.

Chemical analysis

PAHs and hopanes authentic standards were purchased from Sigma Chemical Company (St. Louis, MO, The United States) and Chiron, Norway. All organic solvents used in the analysis were distilled in glass. Sediment samples were defrosted under the Al Foil cover at room temperature and homogenized using a pre-cleaned spatula. Five grams of the samples (dry weight basis) were dried with baked anhydrous sodium sulphate and placed in pre-cleaned cellulose thimbles and Soxhlet extracted for 11 hours by distilled dichloromethane. The extracts were subjected to activated copper and left overnight to remove the elemental sulfur which may interfere in the analysis. Precisely, 200 µl of the surrogate internal standards mixture containing (10 ppm each component), naphthalene-*d*8, anthracene-*d*10, benzo[*a*]anthracene-*d*12, and chrysene-*d*12) were spiked into the extracts. The solution was purified and fractionated by method previously described by Sakari et al., (2008 a,b). Briefly, the solution was transferred onto the top of silica gel column (i.d. 0.9 cm, length 9 cm) which was deactivated with 5% distilled H₂O to remove polar components. PAHs ranging from and 2–7 rings and Hopanes were eluted with 20 ml of 3 : 1 hexane/dichloromethane (v/v). Then, the solution was fractionated using fully activated silica column (i.d. 0.47 cm, length 18 cm) to obtain hopane and PAHs fractions using 4 ml hexane and 14 ml 3:1 hexane/dichloromethane (v/v), respectively. Hopane and PAHs fractions were individually evaporated to approximately 1 ml, transferred to 2 ml amber vial, and evaporated to dryness under a gentle stream of nitrogen. The Polycyclic aromatic hydrocarbon fraction was re-dissolved into an appropriate volume (200 µl) of iso-octane containing p-terphenyl-*d*14 was used as an internal injection standard (IIS). Hopanes standard mixture contains 17 α (H), 21 α (H)-30-norhopanes; 17 α (H), 22, 29, 30-trisnorhopane; 17 α (H), 21 β (H)-hopane; 17 β (H), 21 α (H)-30-norhopanes and 17 β (H), 21 β (H)-hopanes were used as Internal Injection Standard (IIS).

PAHs and Hopanes were analyzed using a Hewlett Packard 5972A quadrupole mass spectrometer integrated with a HP5890 gas chromatograph equipped with a J&W Scientific Durabond HP-5MS, 30 m fused silica capillary column, 0.25 mm i.d. and 0.25 µm film thickness, using helium as the carrier gas on a constant pressure at 60 kg/cm². GC-MS operating conditions were 70 eV ionization potential with the source at 200°C and electron multiplier voltage at ~1200 eV. The injection port was maintained at 300°C and the sample was injected with split mode followed by purge 1 min after the injection. For PAHs analysis, column temperature was held at 70°C for 2 min, then programmed at

30°C/min to 150°C, 4°C/min to 310°C and held for 10 minutes. A selected ion monitoring (SIM) method was employed after delay of 4 min. Individual PAHs were quantified by comparing the integrated peak area of the selected ion with the peak area of the IIS. Acenaphthene-*d*₈ and chrysene-*d*₁₂ were used as IIS for the quantification of PAHs ranging from phenanthrene to 1-methylphenanthrene and for PAHs from fluoranthene to Dibenzo (a, h) anthracene, respectively. Corrections for relative response at the corresponding mass/charge ratio were made by analyzing a PAH standard (phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, chrysene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, benzo[ghi]perylene) under the same instrumental conditions as the sample analyses. No 9 and 1-methylphenanthrene standards were available, therefore an estimated response factors for these compounds was based on a response for 9 and 1-methylphenanthrene. Since naphthalenes were difficult to quantify due to its high volatility, the present study focused on PAHs with three or more benzene-rings (i.e. phenanthrene—Dibenzo (a,h) anthracene). PAHs concentrations were recovery-corrected using the spiked surrogates and this procedure typically yields recoveries of PAHs in the range of 77% to 108%. The precision of the method was determined through four replicated analyses of the heavy residual oil sample. The relative standard deviation (RSD; n=4) of individual PAHs identified in sample extracts were <10%.

For hopane analysis, column temperature was held at 50°C for 2 min, then programmed at 6°C/min to 310°C and held for 15 minutes. A selected ion monitoring method (m/z=191) was employed after a delay of 4 minutes. The hopane compounds were identified based on peaks retention time in standard mixture solution.

Chronology experiments for determination of the age of the sediment core

For age determination experiments, the method that applied was comprehensively described by Mohamed et al., (2006); but in brief, an aliquot of 2 g of each sediment intervals from the core samples was dried in an oven in 50°C overnight, sieved in less than 250 μm mesh size and kept dry for analysis. Approximately 0.3 g of this sample was placed in 50 ml beaker and 1 ml (25 ppm) PbSO₄ was added as carrier. Then, 20 ml of HCl (8 M) was added to the sample, left for 2 h in hot plate at 60°C for digestion. Digested material was filtered to separate non-usable solids using glass filter paper (*i.d.*, 47 mm). Digested filtered was left in hot plate till dryness and yellow-brown colored paste remained. Thirty ml of HClO₄ was added to the paste and warmed-up for ion-exchange resin column chromatography in which 200 ml of HCl (1 M) was gradually added to dilute the samples in the column. Pb was extracted in the column and collected in clean beaker, dried for a day on hot plate till dryness or until

precipitate was formed as a white paste. Fifty ml of HNO₃ (1 M) was added to the paste and left in hotplate for 1–2 minutes, cooled to room temperature then a few drops of H₂SO₄ was added to precipitate the Pb. The precipitated Pb (PbSO₄) was left for 3 days in cool condition and filtered using glass paper filter (25 mm) and subsequently subjected to α,β-spectrometry for emission measurements and age determination. The following equation is used to achieve the sedimentation rate and the age of each layer.

$$A = A_0 e^{-\lambda(z/s)}$$

Where,

A is the activity of ²¹⁰Pb of the sediment in the laboratory (dpm/g)

A₀ is the activity of ²¹⁰Pb of the sediment in the date of sampling (dpm/g)

λ is the half life of ²¹⁰Pb, (e/t_{1/2}); 0.693/t_{1/2} ²¹⁰Pb (22.3 y) ≫ ≫ λ = 0.031

z is the depth of sediment

s is the sedimentation rate

e is Neperian Number

$$A = A_0 e^{-\lambda(z/s)}$$

$$\ln(A/A_0) = \ln(e^{-\lambda(z/s)})$$

$$\ln(A) - \ln(A_0) = -\lambda(z/s)$$

$$z = -\frac{s}{\lambda} [\ln(A) - \ln(A_0)]$$

=>y=mx (The equation of trendline from ²¹⁰Pb activity points through out the core);

$$\left(\text{where, } m = -\frac{s}{\lambda}\right) = > S_{(y/cm)} = -m\lambda$$

=>Age calculation:

Interval Deposition Time (y) = Thickness of core interval (cm) / Sedimentation rate (cm/y)

Age calculation at surface layer = Interval Deposition Time (y) - Zero(sampling year)

Age at layer (X)y = Interval Deposition Time of layer (X)y - Age of layer(X-1)y

Results

Twenty two individual polycyclic aromatic hydrocarbons ranging from 3 (dibenzothiophene) to 7 (Dibenzo (a,h) anthracene) rings and age (years) of each core interval were analyzed in 2 cores in this study. The results of PAHs data and aging experiments (the activity of ²¹⁰Pb) are shown in Table 1,2 and 3, respectively.

Table 1. PAHs specific compounds, characteristic, composition and ratios in core sediment collected from Old Port Klang.

PAHs Compounds Concentrations (ng/g)	Depth (cm)						
	0–3	3–6	6–9	9–12	12–15	15–18	18–21
Dibenzothiophene, DBT	5.32	22.69	0.00	13.10	0.00	2.30	3.17
Phenanthrene, Phen	2.32	184.97	82.33	143.70	19.74	11.26	49.67
Anthracene, Anth	2.33	0.00	25.92	28.39	12.01	6.60	13.56
3-Methylphenanthrene, 3-MP	0.82	38.96	17.48	27.83	4.15	2.89	6.72
2-Methylphenanthrene, 2-MP	0.73	50.19	22.55	28.25	5.45	5.24	8.82
2-Methylanthracene, 2-MA	0.43	11.41	7.16	5.79	2.04	3.05	2.98
9-Methylphenanthrene, 9-MP	0.49	35.95	15.13	21.93	4.25	2.41	7.25
1-Methylphenanthrene, 1-MP	0.55	28.26	13.20	17.37	4.32	2.00	8.53
Fluoranthene, Flu	0.90	121.98	81.53	65.11	10.44	6.63	20.14
Pyrene, Py	2.30	263.26	141.68	91.78	22.97	18.00	51.68
Benzo(a)Flourene, B(a)F	0.00	0.50	0.20	0.23	0.04	0.02	0.17
Benzo(b)Flourene, B(b)F	0.01	0.58	0.18	0.38	0.06	0.03	0.18
4-Methyl Pyrene, 4-MPy	0.01	1.09	0.63	0.71	0.10	0.16	0.14
2-Methyl Pyrene, 2-MPy	0.02	1.19	0.59	0.52	0.10	0.15	0.17
1-Methyl Pyrene, 1-MPy	0.03	1.19	0.88	0.63	0.19	0.27	0.22
Chrysene, Chry	0.50	90.05	53.10	27.32	6.02	4.71	16.07
Benzo (a) antharene, B(a)An	3.49	132.93	63.67	48.21	33.29	10.01	19.32
Benzo (k) fluoranthene, B(k)F	3.49	586.85	411.56	199.17	43.59	28.07	118.41
Benzo (e) acephenanthrylene, B(e)Ace	0.00	161.43	132.91	59.79	12.97	13.77	28.63
Benzo (e) pyrene, B(e)Py	7.29	470.50	359.89	179.78	43.03	32.21	79.28
Benzo (a) pyrene, B(a)Py	2.87	222.30	143.97	74.38	13.65	11.93	54.54
Dibenzo (a,h) anthracene, D(a,h)An	0.00	0.00	0.00	0.00	0.00	0.00	0.00
† Sediment age (year)	1999–2007	1990–1998	1981–1989	1972–1980	1963–1971	1954–1962	1945–1953
^a Total PAHs (ng/g)	33.89	2426.29	1574.56	1034.36	238.41	161.70	489.66
^b Total Parental PAHs (ng/g)	30.82	2258.05	1496.93	931.34	217.82	145.52	454.82
^c Total Alkyl PAHs (ng/g)	3.07	168.25	77.62	103.02	20.59	16.18	34.83
^d MPAHs/PAHs	0.10	0.07	0.05	0.11	0.09	0.11	0.08
^e MP/P	1.11	0.83	0.83	0.66	0.92	1.11	0.63
^f LMW PAHs (ng/g)	16.18	757.68	406.98	443.25	85.37	60.38	172.52
^g HMW PAHs (ng/g)	17.71	1668.62	1167.58	591.11	153.03	101.32	317.14
^h L/H PAHs	0.91	0.45	0.35	0.75	0.56	0.60	0.54
ⁱ TOC (mg/g)	65	71	59.5	55.9	51.4	51.4	61.2
^j Total PAHs/TOC (ng/g)	5.22	341.53	264.84	184.94	46.41	31.46	79.97
^k MPy/Py	0.03	0.01	0.01	0.02	0.02	0.03	0.01
^l Pyr/Fluo	2.55	2.16	1.74	1.41	2.20	2.72	2.57
^m Anth/(Anth+Phe)	0.50	0.00	0.24	0.16	0.38	0.37	0.21
ⁿ BaA/(BaA+Chry)	0.87	0.60	0.55	0.64	0.85	0.68	0.55
^o BeP/(BeP+BaP)	0.72	0.68	0.71	0.71	0.76	0.73	0.59
^p Flu/Pyr	0.39	0.46	0.58	0.71	0.45	0.37	0.39
^q Ph/An	1.00	NA	3.18	5.06	1.64	1.71	3.66

^a Total PAHs: sum of 22 PAHs ranging from Dibenzothiophene to Dibenzo (a,h) anthracene; ^b Total Parental PAHs: sum of Dibenzothiophene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)Flourene, Benzo(b)Flourene, Chrysene, Benzo (a) antharene, Benzo (k) fluoranthene, Dibenzo (a,h) anthracene, Benzo (e) pyrene, Benzo (a) pyrene and Benzo (e) acephenanthrylene; ^c Total Alkyl PAHs: sum of 3-Methylphenanthrene, 2-Methylphenanthrene, 2-Methylanthracene, 9-Methylphenanthrene, 1-Methylphenanthrene, 4-Methyl Pyrene, 2-MethylPyrene and 1-MethylPyrene; ^d MPAHs/PAHs: ratio of Alkyl PAHs to parent PAHs; ^e MP/P: ratio of sum of 3-Methylphenanthrene, 2-Methylphenanthrene, 9-Methylphenanthrene and 1-Methylphenanthrene to Phenanthrene; ^f LMW PAHs: sum of PAHs ranging from Dibenzothiophene to Pyrene; ^g HMW PAHs: sum of PAHs ranging from 1-methyl pyrene to Dibenzo (a,h) anthracene; ^h L/H PAHs: ratio of LMW over HMW PAHs; ⁱ TOC%: the percentage of Total Organic Carbon; ^j Total PAHs/TOC: ratio of Total PAHs over TOC percentage; ^k MPy/Py: ratio of sum of 4,2,1-Methylpyrenes to Methylpyrene; ^m Anth/(Anth+Phe): ratio of Anthracene to sum of Anthracene and Phenanthrene; ⁿ BaA/(BaA+Chry): ratio of Benzo(a)anthracene over sum of Benzo(a)anthracene and Chrysene; and ^o BeP/(BeP+BaP): ratio of Benzo(e)pyrene over sum of Benzo(e)pyrene and Benzo(a)pyrene; ^p Ratio of Fluoranthene to Pyrene; ^q Ratio of Phenanthrene to Anthracene; [†] Sediment age (year): was calculated using method described in "Methods" section.

Table 2. specific compounds, characteristic, composition and ratios in core sediment collected from Offshore Klang.

PAHs Compounds (ng/g)	Depth (cm)															
	0-3	3-6	6-9	9-12	12-15	15-18	18-21	21-24	24-27	27-30	30-33	33-36	36-39	39-42		
DBT	0.35	0.63	0.01	0.00	0.31	0.59	0.00	1.47	1.19	2.01	2.81	0.75	2.80	2.72		
Phen	0.54	0.46	0.42	0.57	0.61	0.86	0.46	1.76	1.70	2.38	3.51	1.09	3.46	3.36		
Anth	0.34	0.11	0.06	8.16	0.25	0.53	0.09	1.24	1.50	0.13	0.12	0.55	1.86	2.00		
3-MIP	0.16	0.14	0.07	0.04	0.22	0.10	0.13	0.21	0.09	0.05	0.07	0.03	0.11	0.08		
2-MIP	0.09	0.06	0.06	0.15	0.01	0.02	0.06	0.02	0.07	0.02	0.02	0.02	0.04	0.04		
2-MAnt	0.02	0.01	0.01	0.13	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01		
9-MIP	0.15	0.06	0.06	0.01	0.09	0.18	0.05	0.33	0.56	0.05	0.01	0.18	0.67	0.64		
1-MIP	0.05	0.04	0.04	0.08	0.00	0.01	0.04	0.01	0.05	0.70	0.69	0.01	0.03	0.03		
Flu	0.77	1.14	0.73	0.16	0.16	0.64	1.00	0.36	1.09	0.39	0.42	0.36	1.19	0.65		
Pyr	0.93	5.00	0.97	1.89	0.22	0.59	1.04	0.40	5.52	0.45	0.49	0.41	4.31	1.08		
B(a)F	0.87	0.04	0.05	0.07	0.05	0.12	0.06	0.19	0.34	0.44	0.40	0.13	0.43	0.42		
B(b)F	0.30	0.18	0.32	0.11	0.00	0.02	0.10	0.30	0.67	0.50	0.63	0.41	0.45	1.68		
4-MIPy	0.67	0.71	0.08	0.16	0.00	0.02	0.11	0.00	0.02	0.02	0.01	0.01	0.01	0.03		
2-MIPy	0.08	0.15	0.19	0.23	0.01	0.02	0.26	0.02	0.04	0.03	0.03	0.02	0.03	0.07		
1-MIPy	0.19	0.10	0.12	0.09	0.01	0.04	0.09	0.29	0.32	0.46	0.04	0.03	0.66	0.07		
Chry	0.30	0.26	0.36	0.36	0.07	0.14	0.32	0.08	0.10	0.11	0.10	0.08	0.10	0.30		
B(a)Ant	0.40	0.22	0.38	0.57	0.05	0.12	0.18	0.23	0.12	0.31	0.23	0.09	0.13	0.16		
B(k)F	2.35	2.78	2.53	3.65	0.58	2.28	3.37	1.31	0.78	1.24	1.09	1.25	0.79	1.75		
B(e)Ace	0.47	0.00	0.70	0.65	0.00	0.39	0.56	0.00	0.00	0.00	0.00	0.00	0.00	0.22		
B(e) Py	2.90	3.59	2.17	2.61	3.19	2.45	2.82	4.65	0.00	0.00	0.00	1.67	2.48	2.76		
B(a)Py	1.90	0.80	0.84	0.97	1.53	3.74	1.00	7.68	10.95	14.98	15.06	3.82	13.41	14.05		
D(a,h)Ant	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		
r Sediment age (year)	2001-2007	1994-2000	1987-1993	1980-1986	1973-1979	1966-1972	1959-1965	1952-1958	1945-1951	1938-1944	1931-1937	1924-1930	1917-1923	1910-1916		
^a Total PAHs (ng/g)	13.83	16.49	10.19	20.68	7.37	12.84	11.73	20.56	25.12	24.27	25.73	10.90	32.97	32.12		
^b Total Parental PAHs (ng/g)	12.42	15.22	9.56	19.78	7.02	12.46	11.00	19.67	23.95	22.94	24.85	10.61	31.42	31.15		
^c Total Alkyl PAHs (ng/g)	1.41	1.27	0.63	0.90	0.35	0.39	0.73	0.88	1.17	1.33	0.87	0.29	1.56	0.97		
^d MPAHs/PAHs	0.11	0.08	0.07	0.05	0.05	0.03	0.07	0.04	0.05	0.06	0.04	0.03	0.05	0.03		
^e MP/P	0.83	0.64	0.54	0.51	0.52	0.37	0.59	0.32	0.46	0.34	0.22	0.22	0.24	0.23		
^f LMW PAHs (ng/g)	3.40	7.66	2.43	11.20	1.87	3.52	2.87	5.79	11.77	6.19	8.14	3.39	14.47	10.60		
^g HMW PAHs (ng/g)	10.43	8.83	7.75	9.47	5.50	9.33	8.87	14.77	13.35	18.08	17.59	7.51	18.50	21.52		
^h L/H PAHs	0.33	0.87	0.31	1.18	0.34	0.38	0.32	0.39	0.88	0.34	0.46	0.45	0.78	0.49		
ⁱ TOC (mg/g)	65	71	59.5	55.9	51.4	51.4	61.2	45.6	72.1	77.2	65.2	82.2	85.7	69.1		
^j Total PAHs/TOC (ng/g)	2.13	2.32	1.71	3.70	1.43	2.50	1.92	4.51	3.48	3.14	3.95	1.33	3.85	4.65		
^k MPy/Py	1.01	0.19	0.40	0.25	0.12	0.12	0.44	0.77	0.07	1.15	0.18	0.13	0.16	0.16		
^l Pyr/Fluo	1.20	4.38	1.34	12.20	1.42	0.92	1.04	1.12	5.07	1.13	1.16	1.15	3.62	1.67		
^m Anth/(Anth + Phe)	0.39	0.19	0.13	0.93	0.29	0.38	0.16	0.41	0.47	0.05	0.03	0.34	0.35	0.37		
ⁿ BaA/(BaA + Chry)	0.57	0.45	0.51	0.61	0.43	0.47	0.36	0.74	0.54	0.74	0.69	0.53	0.56	0.35		
^o BeP/(BeP + BaP)	0.60	0.82	0.72	0.73	0.68	0.40	0.74	0.38	0.00	0.00	0.00	0.30	0.16	0.16		
^p Flu/Pyr	0.84	0.23	0.75	0.08	0.70	1.09	0.96	0.89	0.20	0.88	0.86	0.87	0.28	0.60		
^q Ph/An	1.60	4.31	6.63	0.07	2.45	1.61	5.13	1.42	1.14	17.95	28.88	1.98	1.86	1.68		

See Table 1 for compound abbreviations and definitions on "a to r".

Table 3. Lead (^{210}Pb) clean activity, sedimentation rate and age of two sedimentary cores collected from Old Port and Offshore of Klang

Core Name	Core length (cm)	Pb clean activity (cpm) ^a	Pb clean activity (cpm)	Sedimentation rate (cm/y)	Core age (y)
		Surface layer	Deep layer		
Klang City	21	0.51	0.24	0.35	60
Offshore Klang	42	0.45	0.21	0.49	102

^a Clean Activity of the ^{210}Pb (Count Per Minute)

Reports of the 1st Core: Old Klang Port (nearshore)

Old port of Klang is located in the busiest part of the city where a vital bridge connects the town into two parts by Klang River as shown in Fig. 1. The collected core is representing the age of sediment since 1945 in the deepest part and 2007 in top surface sediment sample. The highest and lowest concentration of total PAHs, ΣPAHs occurred during 1990–1998 and 1999–2007, respectively. In addition, the era of 1954–1962 shows the lowest PAHs during the past 62 years. Interestingly, total PAHs in study area is controlled by vehicular emission, Gross Domestic and National Products (GDP and GNP) data and population growth (Fig. 2 a, b, c) from the increasing trend of those parameters in this country (Malaysian National Census Council, 2008). During late 1940's the country was busy with the WWII and slightly elevated bulk PAHs rather than early 1950's where showed least level of PAHs during ceasefire. On 1957, when Malaysia become independent, the country start development plans followed by rapid development of the country, frequently used energy sources such as fossil fuel consumption therefore the bulk amount of PAHs started increasing trend till the end of 20th century. Malaysia in recent decades showed magnificent and extraordinary rapid development in the Southeast Asia. Although sudden drop of PAHs during the modern era (1999–2007) was irregular and it is discussed in coming sections of this paper.

The sorptive properties of PAHs are closely controlled by the organic particulate fraction of suspended and deposited sediments (Baker et al., 1986). PAHs concentration was found to be closely resembled with the amount of organic compound (TOC, 51.4–71.0 mg/g) throughout the core and relatively comparable. Increasing TOC is directly related to increase in the land based input of organic matter due to increasing economic development in the country. Comparing these harmonic changes with exponential and rapid increase of PAHs concentration approves the increasing levels of pollution load to the study area.

Also, specific compound analysis of PAHs in this core showed high concentration of parent PAHs such as phenanthrene, flouranthene, pyrene, chrysene, benzo(a)anthracene, benzo(k)flouranthene, benzo(e)acephenanthrylene, Benzo(e)pyrene and Benzo(a)pyrene (Fig. 3a,b). These ele-

vated concentrations together with severe low L/H PAHs ratio below unity indicate the pyrogenic sources of PAHs along the core. The ratio of total 3, 2, 9, 1-methylphenanthrene to phenanthrene (MP/P) range from 0.63 to 1.11 with an average value of 0.87 again confirms the pyrogenic sources of PAHs. It is noted that the dominant of petrogenic source contribution to the pollution in this station throughout the last 62 years occurred in 2 periods. The first period occurred during 1954–1962 when Malaysia became independent in 1957 and rapid development began, thereafter, the second era is happening now with MP/P ratio value of 1.11 where Zakaria et al., 2002 reported the widespread input of petrogenic PAHs in this country. Although MP/P is considered for changes via microbial degradation while the source of pollution is petrogenic; through this core the results showed only a mixture of pyrogenic and petrogenic or slightly petrogenic which is not considered for biodegradation. The Historical profile of PAHs in this core also showed the phenomenon of sub-surface maxima where the highest PAHs value was placed in sub-layer of the core ($\Sigma\text{PHs} \sim 2426 \text{ ng/g}$) and severe depletion in surficial sediments ($\Sigma\text{PAHs} \sim 34 \text{ ng/g}$).

Reports of the 2nd Core: Klang River Estuary in Straits of Malacca (Offshore)

As shown in Table 2, total concentration of PAHs varies from 7.37 to 32.97 ng/g. The latter results indicate that there were very little changes in PAHs concentration throughout the core. This can be attributed to a constant input of PAHs to the study area (Fig. 4).

In addition, compound specific analysis of PAHs showed that some compounds such as benzo(a)pyrene and benzo(e)pyrene contributed higher concentration among others (table 2), indicative of pyrogenic and long range transport as the sampling location has no lateral connection via rivers or canals to the source of PAHs production (Prahl and Carpenter, 1984).

As a supportive evidence, the ratio of MP/P in this core (MP/P ~ 0.22 – 0.83 ; average ~ 0.43) together with depleted ratio of L/H (average ~ 0.53) represents highly pyrogenic input in the study area and most likely it was derived via atmospheric input due to well-mixed concentrations of PAHs,

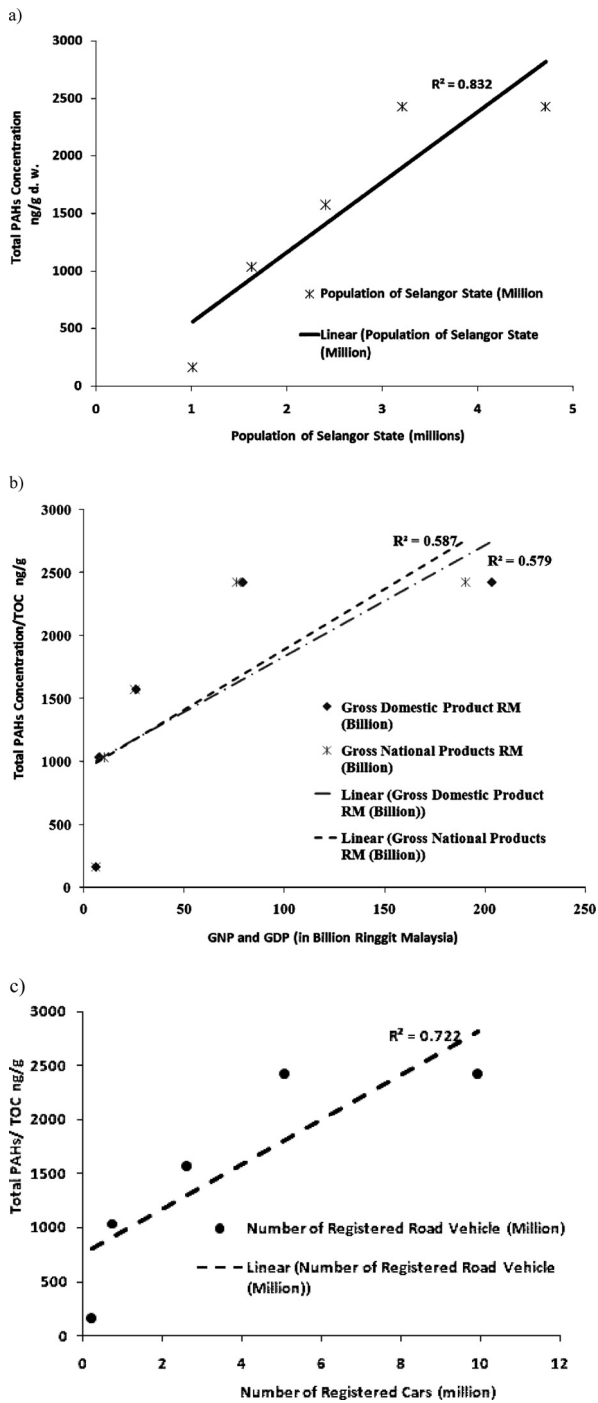


Fig. 2. Socio-economic and PAHs data in historical trend of Old Port of Klang, Data is obtained from Department of Statistics, Malaysia.

- (a) Regression of population vs. Σ PAHs/TOC (ng/g)
- (b) Regression of GNP and GDP vs. Σ PAHs/TOC (ng/g)
- (c) Regression of Registered Cars vs. Σ PAHs/TOC (ng/g)

low input, insignificant riverine discharge and high salinity (salinity~28‰) (Prahl and Carpenter, 1983). Normally, pyrogenic PAHs that originated from combustion sources have great affinity for particulate matter such as soot particles and can move in great distances by wind and lateral transport. These sorptive characteristics of PAHs to particu-

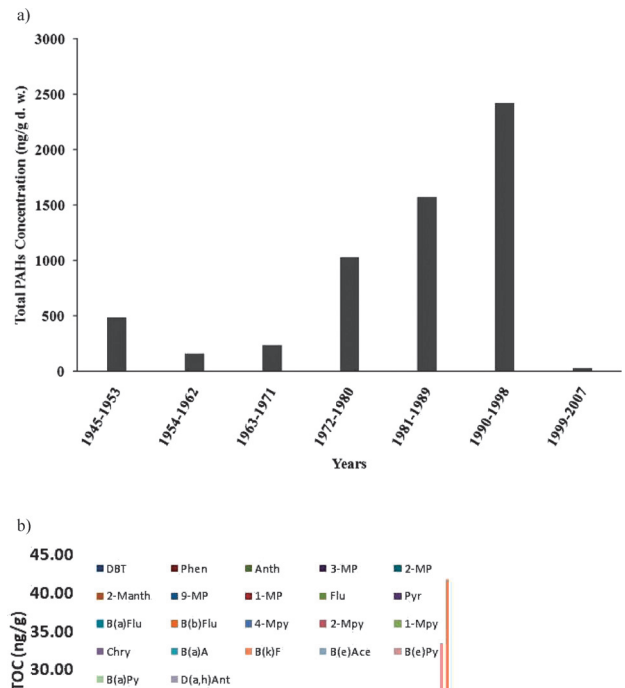


Fig. 3. PAHs compounds in Old Port Klang. a) Total PAHs ; b) specific compounds of PAHs. See Table 1 for compound abbreviations.

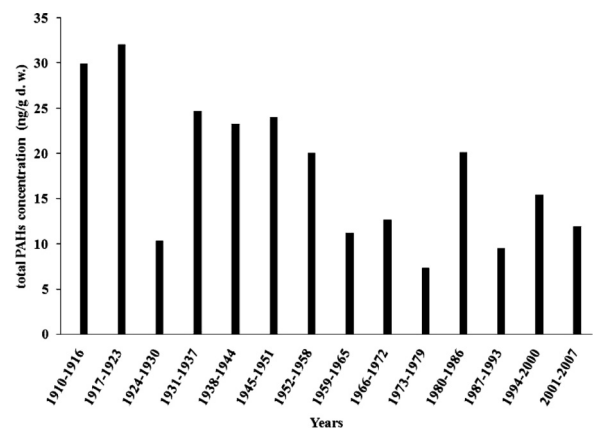


Fig. 4. Total PAHs concentration in Offshore Klang. See Table 1 for compound abbreviations.

lates and organic matter also refer to partitioning behavior (Pereira et al., 1999; Murakami et al., 2008). Also sub-surface layer in this core showed higher value of Σ PAHs rather than most upper layers but the maximum concentration observed during the period of 1917–1923 where Σ PAHs/TOC~3.85 ng/g and TOC~85.7 mg/g sub-surface maxima

were not so prominence.

Discussions

Sources of PAHs in the study area

In this study we have applied several ratios to identify the sources of pollution using alkylated or substitute and parent PAHs values. MP/P and L/H ratios had been utilized quite frequently in the past for examples; Prahl and Carpenter, 1983; Garrigues et al., 1995; Budzinski et al., 1997, Zakaria et al., 2002, Boonyatumanond et al. 2006, among others.. They found that MP/P ratio is fluctuating from 0.5 to 1 for combustion derived PAHs in the sediments and 2–6 in sediment dominated by petrogenic fossil fuel. MP/P ratio around 4.0 was also being reported to be derived from used crankcase oil (Pruel and Quinn, 1988), values close to 1.0 for street and urban dust samples (Takada et al., 1990, 1991) and around 0.5 for atmospheric fallout (Takada et al., 1991). Previous studies also pointed out that MP/P ratio vary with different sources where it is higher for coal combustion sources than that of the petroleum sources (Lee et al., 1977; Takada et al., 1990, 1991). Figure 5 (a and b) shows the MP/P ratio in dated sediment for both cores. Figure 5 (a) shows the MP/P ratio in dated sediment for the core taken near shore of Old Klang Port. The results from the Old Port of Klang indi-

cate that the MP/P ratio range from 0.63 to 1.11 with an average of 0.87 indicating that the sources of PAHs were a mixture of petrogenic and pyrogenic origin (Fig. 5a). Likewise, Offshore core showed that MP/P ratio was in the range of 0.22 to 0.83 with an average of 0.43 clearly suggesting that the source of the PAHs were come from pyrogenic origin (Fig. 5b). Furthermore, Fig. 5 (c), and (d) shows correlations of Σ PAHs (normalized to organic carbon) and MP/P ratio of Old Klang Port and Klang River Estuary in Straits of Malacca. The results show that there is a decreasing trend of Σ PAHs (normalized to organic carbon) and MP/P ratio of 1 to 2 orders of magnitude as we move away from sources.

To identify the location of PAHs production in term of locality scientists use FI/Py ratio, where values between 1.3–1.7 indicates remote sites and values of <1.0 shows the vicinity to urban centers (Gschwend and Hites, 1981; Helfrich and Armstrong, 1986). A core sample collected from Old Port of Klang showed FI/Py ratio ranging from 0.36 to 0.70 with average value of 0.47 while the Offshore Klang core revealed the range of 0.08–1.08 with average value of 0.65. These results showed strong evidence that the sources of PAHs are closer to urban hinterlands of the Port Klang. Although industrial activities in the surrounding areas of Kuala Lumpur can generally contribute to PAHs production, but due to distance and dilution factors those pollution sources may become insignificant as evidenced by FI/Py

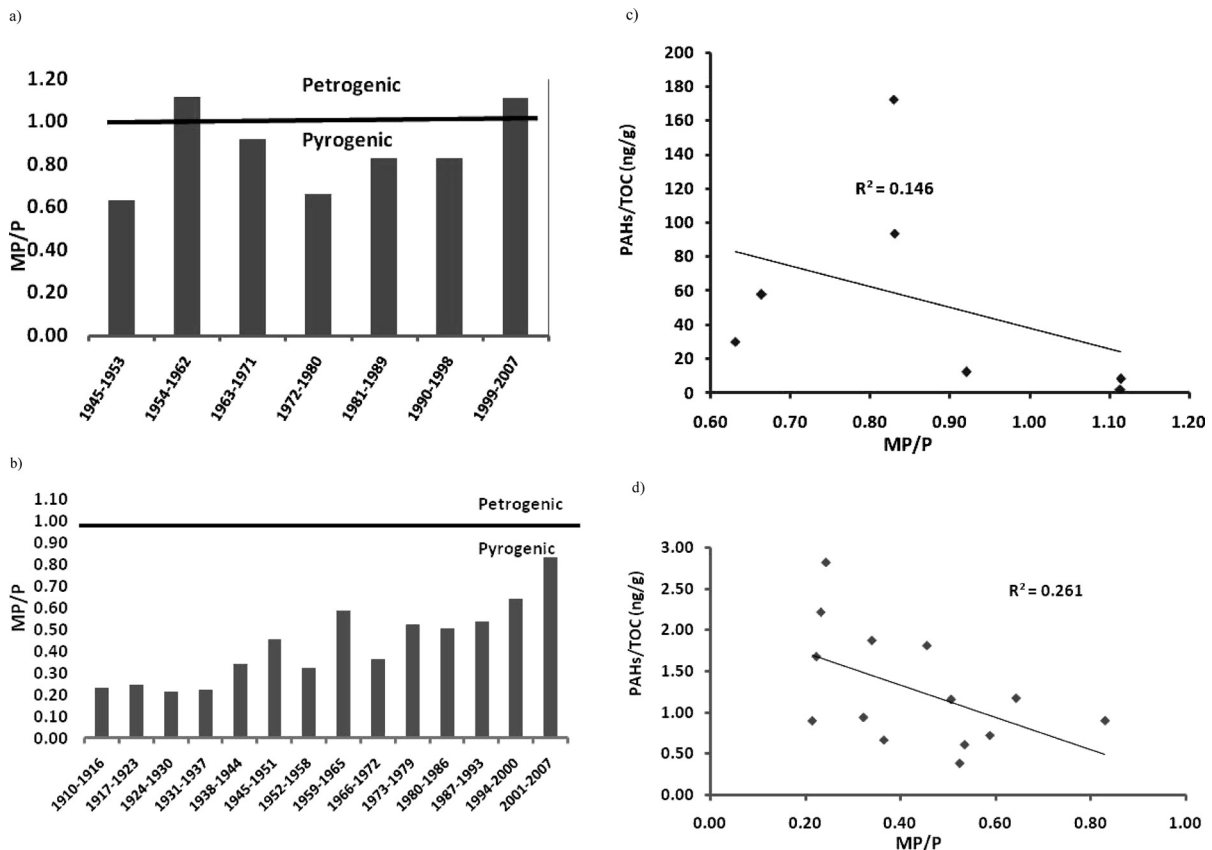


Fig. 5. MP/P ratio in both cores. a) Old Port Klang b) Offshore Klang, please see Table 1 and 2 for definition of MP/P ratio.

ratios. In addition, Ph/An ratio can also be utilized to show the location of PAHs production where values >15 indicate remote area while values <10 show near-urban sites (Zhang et al., 1993). The examination of this ratio for both cores was in agreement with Fl/Py except for the specific dated sample of 3–6 cm depth (correspond to period between 1990–1998) where value indicates that the origin of PAHs production was of remote location. A possible explanation for this observation can be attributed to the dry conditions brought about by El Nino in 1997. In other words, dry conditions in 1997 may have less flushing and riverine inputs resulting in skewed Fl/Py ratio in sedimentary environments. However, in the following year (1998–2001) with the effects of El-Nino diminishing, the flushing effect had significantly increased and shifted or washed away the most recent input elsewhere. This physical process may have removed significant amounts of PAHs making the overall depletion of total concentrations of PAHs as indicated in Table 1 and 2.

The L/H PAHs ratio was also applied to identify the sources of PAHs. Pyrogenic PAHs are characterized by high abundance of HMW compounds (4–6 benzene rings) and unsubstituted (parent) compounds, whereas most petrogenic PAHs are dominated by alkyl substituted and LMW (2–3 benzene rings) PAHs (Garrigues et al., 1995; Budzinski et al., 1997). Values of L/H PAHs ratio in this study revealed harmonic changes 0.35 to 0.91 with MP/P in Old Port of Klang. As MP/P in this core changes, the L/H fluctuates and definitely indicate the pyrogenic source as stated before from the MP/P value (Fig. 6a). This ratio (L/H) in Offshore Klang was shown in Fig. 6b. The values from the core collected from Offshore Klang were changing from 0.31 to 1.18 that is consistent with MP/P ratio of this core. Specific compound analysis results of PAH compound from both core samples in regression with total PAHs (Fig. 6c and d, Old Port Klang and Fig. 6e, Offshore Klang) showed predominance of parent and HMW PAHs and severe depletion in alkyl substituted and LMW PAHs. These values are showing evidence of pyrogenic sources of PAHs and supported by strong correlations between total and the individuals HMW and/or parent PAHs.

It is also observed that high concentration of Benzo(k)fluoranthene in all core layers are leading the total PAHs specially in samples collected from Klang City. It's confirmed that high concentrations of Benzo(k)fluoranthene in environmental samples is a signature for biomass burning (Rogge et al., 1998; Omar et al., 2006). Watershed of Klang River is situated in the middle of Kuala Lumpur and Selangor State development area where everyday, urbanization, industrial and transportation development need for clear-cutting of the forest and consequently biomass burning. It seems that high concentration of Benzo(k)fluoranthene leads the total PAHs is the highest PAH in both cores of this study (see Table 1 and 2).

Pentacyclic triterpanes (hopanes)

Sediment samples for the two cores in Klang area were analyzed for pentacyclic triterpanes as the molecular marker to identify the sources of petroleum pollution using methods previously described in Zakaria et al., (2000) and Zakaria et al., (2001). The hopanes signature of Middle East and South East Asia crude oil (MECO and SEACO) were obtained from Zakaria et al., 2001. In Malaysia, petroleum products are formulated by mainly 2 types of crude oil (MECO and SEACO, where mostly MECO is used for production lubricating and engine oil (Zakaria et al., 2002). The recognition of reference oil including MECO and SEACO are based on ratios of C_{29}/C_{30} and $\sum C_{31}-C_{35}/C_{30}$ ratio. The values of these ratios are shown in Table 4. A combination of both ratios in a cross-plot graph were applied (Zakaria et al., 2000) to distinguish the origins of the oil pollution C_{29}/C_{30} vs. $\sum C_{31}-C_{35}/C_{30}$ diagram as are shown in Fig. 7 a,b.

As shown in Fig. 7a (Old Port) and 7b (Offshore) the groupings of the ratios for the majority of the samples are found in a very specific area in the X axis as reported in Zakaria et al., 2000. In addition, the C_{29}/C_{30} for Old Port of Klang has an average of ca. 1.25; and for the Offshore Klang, the average is ca. 1.19, On the other hand, the dominant area for Y axis location indicative of $C_{31}-C_{35}/C_{30}$ are vary (Old Port of Klang average~4.70; Offshore Klang average~6.25). Unique location of the sampling station as shown in Fig. 7 affords similarity in their origins but hopanes may not be an effective indicator for pyrogenic sources when all core samples in this study were highly pyrogenic. This hypothesis was consistent with the findings reported by Boonyatumanond et al., 2006 where combustion of petroleum products to some extent destroyed the hopanes structure. Hopane biomarkers was proven to be excellent molecular markers for lubricating oil and are persistent as the crankcase oil was not subjected to extreme temperatures that render its destruction. The used crankcase oil with undamaged hopanes would be laterally transported to the marine environment via surface runoff (Zakaria et al., 2002).

The Tm/Ts ratios for Old Port of Klang (average~1.49) and Offshore Klang (average~1.15) were compared with the findings reported by Zakaria et al., 2003. The ratios indicate that the sources were originated from Asphalt and Street Dust. Frequent rainfall and flash flood exacerbate flushing of road surface materials into the estuaries and marine environment via drains, canals and rivers. Hence strong signatures of asphalt and pyrogenic sources were found in the sedimentary environments of Old Port Klang. Further supportive evidence for the asphalt signature of hopanes origins in Old Port of Klang is confirmed by $C_{31}-C_{35}/C_{30}$ ratio where the value is the nearest number to reference material sources which were analyzed and reported previously by Zakaria et al., 2003. On the other hand, Tm/Ts signature in the Offshore Klang revealed that the sediment composition has presumably origi-

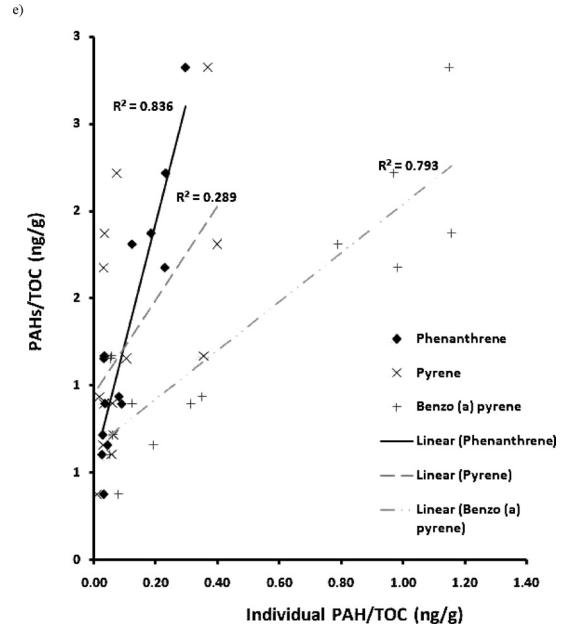
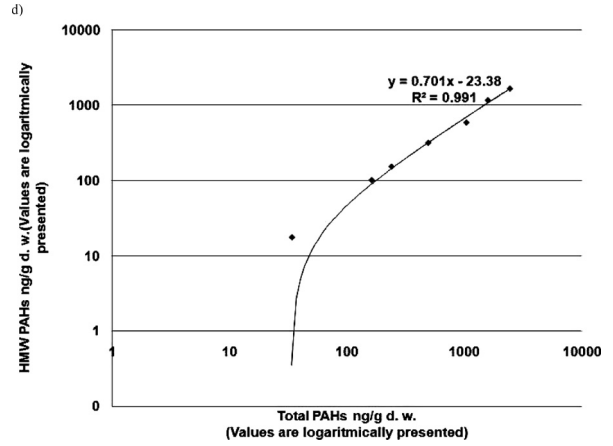
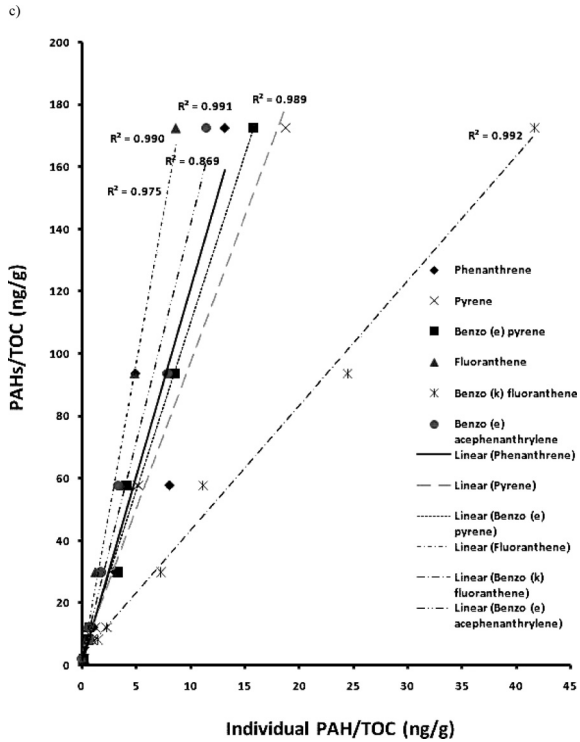
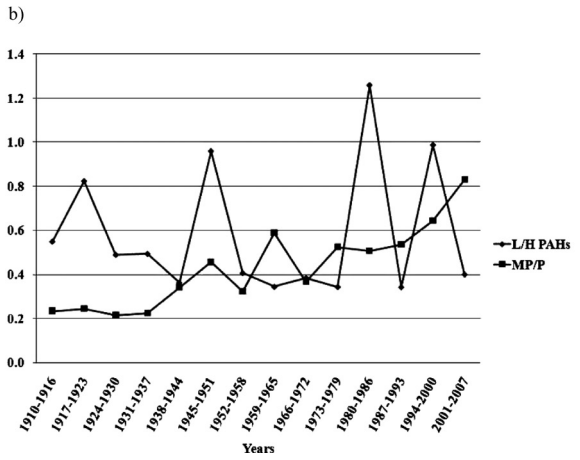
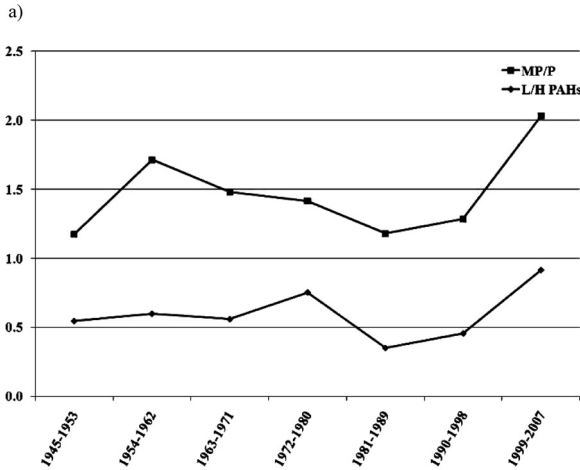


Fig. 6. Ratio of L/H in two cores, a) Old Port of Klang, b) Off-shore Klang; Regression between total PAHs and individual PAHs, c,d) Old Port of Klang e) Offshore Klang ; Please see Table 1, 2 for definition of ratios.

nated from the urban terrestrial locations and other anthropogenic sources. Theoretically, the street dust was blown away by wind currents and transported via dry deposition and atmospheric transport and deposited to the offshore locations.

Strong PAHs Input in the Marine Environment of Old Port Klang (Near Shore)

The historical trend of PAHs input to the marine environment of Old Port of Klang revealed interesting findings. The PAHs concentration rapidly increased from 1945 to 1999 and abruptly decreased thereafter (modern input) (Table 1). There are several explanations for the exponential increase of the PAHs concentration within the Old Port Klang. First, Malaysia experienced phenomenal economic and population growth in late 70's and 80's especially in the hinterlands or

Table 4. Hopanes composition in two sedimentary cores collected from Old Port of Klang and Offshore Klang.

a)		Old Port of Klang			
		Sediment age			
Hopane Ratio		1999–2007	1990–1998	1963–1972	1945–1953
^a C_{31-35}/C_{30}		4.35	3.87	5.70	4.90
^b C_{29}/C_{30}		1.27	1.24	1.20	1.32
^c Oleanane/ C_{30}		0.00	0.00	0.00	0.00
^d Tm/Ts		0.91	1.46	2.97	0.64

b)		Offshore Klang Core						
		Sediment age						
Hopane Ratio		2001–2007	1994–2000	1980–1986	1952–1958	1938–1944	1924–1930	1910–1916
C_{31-35}/C_{30}		0.00	6.24	9.46	2.73	6.14	6.39	5.08
C_{29}/C_{30}		0.00	1.20	0.81	0.87	1.20	1.19	0.38
Oleanane/ C_{30}		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tm/Ts		^e ND	0.82	1.96	1.73	0.14	1.04	1.22

^aRatio of sum 17α , 21β (H)- C_{31} homohopane to 17α , 21β (H)- C_{35} homohopane relative to 17α , 21β (H)-hopane

^bRatio of 17α , 21β (H)-30 norhopane to 17α , 21β (H)-hopane

^cRatio of Oleanane relative to 17α , 21β (H)-hopane

^dRatio of 17α -22, 29, 30-trisnorhopane relative to 18α -22, 29, 30-trisnorhopane

^e ND: Not Detected

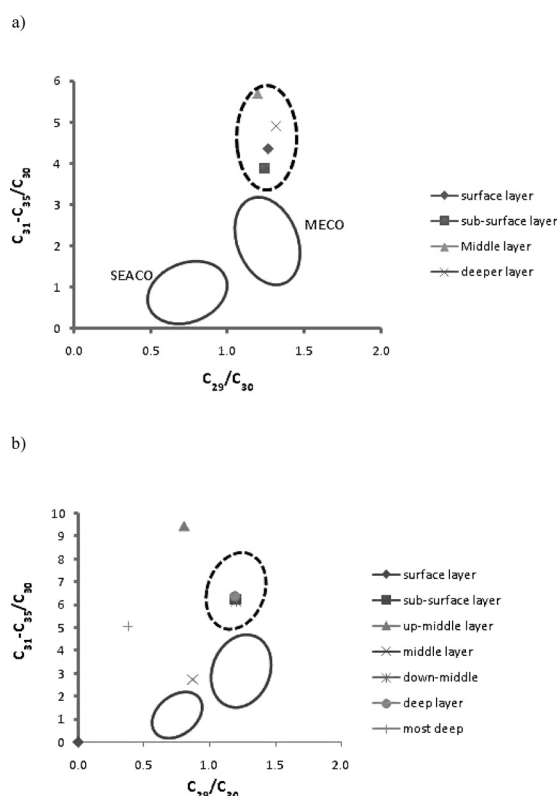


Fig. 7. Hopane graph in a) Old Port of Klang and b) Offshore Klang, Please see Table 3 for definitions of ratios. Solid circles are data from Zakaria et al, 2002 and dashed circle for present study.

metropolitan areas of the Klang Valley where Kuala Lumpur is the engine of the economic and industrial growth (Fig. 2b). Second, the tremendous increase of the PAHs concentration can significantly be contributed to the climate and environmental conditions, where high humidity, heavy rainfall, suspended riverine (due to land clearings for development) and airborne particles was constantly flushed to surrounding aquatic environments of the Old Port Klang and became the final sink. This phenomenon was discussed in detail by Waibel (1976) and recently was reported by Ikenaka et al., (2005) where flood contributes in high PAHs concentration in Lake Suwa, Japan. The sudden drop in PAHs concentration for the Old Port Klang will be further elaborated in section 3.7 of this paper.

Predominant Pyrogenic Input of PAHs in Old Port Klang and Offshore Klang area

PAHs pollution is very dynamic in terms of their sources and trends in the marine environment. Such observations may be contributed to different socio-economic and environmental conditions of a particular place and regions. For instance, PAHs sources in more industrialized countries are generally originated from combusted materials (e.g. in Japan, Takada et al., 2008, in press) and for less industrialized countries petrogenic materials became the predominant inputs (e.g. in Indonesia, Lukman et al., 2007 and in Malaysia, Zakaria et al., 2002). In core sediments, many studies have been conducted to identify major sources of PAHs in the environment. Christensen and Zhang, (1993) studied Lake Michigan

and have identified a combination of sources including combusted coal, petroleum and wood as the source from collected sediment cores. Combusted derived PAHs occurs very frequently in the environment such as pioneering study by Wakeham et al., (1979), and supported by other scientists in recent years (Su et al., 1998; Luo et al., 2006; Barra et al., 2006; Vane et al., 2007). On the other hand, very few studies had also indicated the predominant input of petrogenic sources of PAHs in the surface sediment (e.g. Witt and Trost, 1998; Zakaria et al., 2002; Boonyatumanond et al., 2006; Liu et al., 2000; Philips et al., 1997; Yunker et al., 1996; Boehm et al., 1998; Kennicutt et al., 1995 and Eganhouse and Gorsett, 1991). The current study revealed that major inputs of the core sediment samples were of pyrogenic signatures. A most probable explanation for this phenomenon was due to water mass movement in the river redistributes the petroleum hydrocarbons to the various locations. When the water mass became stagnant and the retention time increases, active deposition of the particulates by the force of gravity became predominant over the water mass movement. Finally, the petroleum hydrocarbons and products would be stored in physically stable reservoirs such as riversides, dams or river's meander. This is probably one of the many reasons why petrogenic PAHs are not well homogenized in the marine environment and constantly vary from location to another (Zakaria et al., 2002).

Modern Inputs of Petroleum and Pyrogenic Hydrocarbons in Old Port Klang

The concentrations of PAHs for the core dated from 1945 to 1953 were relatively higher than that of the period from 1963 to 1971 (Table 2). During the period of late 1950's, soon after independence and the 2nd World War the country was experiencing rapid re-construction and population growth. Also, during the peak period of the WWII, transports and spillage of hydrocarbon fuels increased the inputs in the coastal marine environments. Such rapid and sudden change had brought about significant magnitude of environmental disturbances which led to a big pulse in hydrocarbon input to the urban centers such as the busy Old Port Klang areas. However, during the decades of 1960's onwards until 1999, the country experienced rapid urbanization and industrialization. Hence, saw further increase in the hydrocarbon inputs for the whole country in general and in the Old Port Klang area in particular.

In 2003, the Malaysian Marine Department reported 127 oil spill incidents from 1976 due to heavy oil tankers traffic in Strait of Malacca. Surprisingly, the signatures for oil spills were absent for both cores. Based on previous reports of the oil spills incidences in the Straits of Malacca, major spills normally occurred in offshore locations where tanker traffic was at the heaviest and did not influence the input for the inshore locations. Further studies should be conducted to

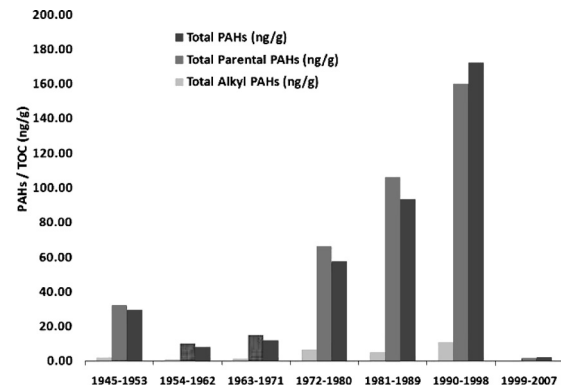


Fig. 8. PAHs in Historical Trend in Old Port of Klang, Please see Table 1 and 2 for definitions of ratios.

confirm this statement.

Another interesting observation in this study is that the concentrations of PAHs in the upper section of the cores representing most recent modern inputs were very low (Fig. 8). This is in contrast with recent reports of surficial PAHs concentration in about the same location previously reported by Zakaria et al., 2002. In the Zakaria et al., 2002 studies, the samples were collected from 1997 to 1999 and therefore it is interesting to note that period after the study the PAHs concentration began to drastically drop. Possible explanations for the decrease might be due to redistribution of surface sediments by active the movement of water mass and intense flushing activities during the El Nino events of 1997 to 2003. This was confirmed by intense precipitation (total annual rainfall of 3181.7 mm) and extraordinary meteorological and hydrological conditions such as flooding and landslides during this period.

The other possible explanation for this observation could be due to less input of combustion PAHs from internal combustion engines. Modern engines are equipped with lean burning technology with marked reduction of smoke and soot particles.

Another contributing factor could be the environmental regulations in Malaysia where pollution in general is regulated through policy instruments such Environmental Quality Act of 1974, Malaysian Water Quality Criteria, among others. Such regulations could somehow reduce pollutants input to the Malaysia aquatic environments in general including that of hydrocarbon pollution. In support of the above findings, Gevao et al., (1997) also found dramatic decrease of PAHs since 1970s in core samples collected from Eastwaite Water from the English Lake district because of the immediate stop of coal combustion for heating purposes in home and industries due to regulatory issues.

Studies in cores usually reveal such sudden increase or decrease of PAHs concentrations (Hurt and Quinn, 1979; Gschwend and Hites, 1981; Hites et al., 1977; Pereira et al., 1999; Wakehame et al., 1979; Prahl and Carpenter, 1983;

Rose and Rippey, 2002; Youngblood and Blumer, 1975; Taylor and Lester, 1995; Witt and Trost, 1998; Viguri et al., 2007; Nudi et al., 2007 and Liu et al., 2005) due to regulation, rapid urbanization, heavy industrialization, motorization, oil incidents, war events and natural phenomena.

In conclusion, the results of this study indicate the total PAHs concentration are controlled by vehicular emission, GNP, GDP, population growth and biomass burnings. High concentration of parent PAHs such as Phen, Fluo, Chry, B(a)A, B(k)F, B(e)An, B(e)P and B(a)P associated with low L/H and depleted MP/P showed pyrogenic input near the sources of PAHs production. This study also revealed that hopane was not a conventional molecular marker for the origin and identification of pyrogenic PAHs, where high temperature of combustion processes destroys the molecular structure of pentacyclic triterpanes. We found that asphalt and street dust are the most probable main contributors of pyrogenic PAHs that flushed onto the marine environment by daily heavy rainfall as well as atmospheric transport. It is interesting to note that no signature of 127 oil spills in Straits of Malacca were found in this research indicating no long term survival of spilled oil in coastal area as a result of these tanker spills. Dramatic decrease of PAHs in recent years maybe due to final sink re-location during the El Nino phenomenon and consequent floods in the region. Modern engines that are equipped with lean burning technology resulting in marked reduction of smoke and soot particles. Regulations may also contribute to the overall reduction of the pollutants but further study is needed to confirm this statement.

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