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Distribution of PAHs and n-alkanes in Klang River Surface Sediments, Malaysia

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ABSTRACT

Surface sediment samples were collected from five locations at the downstream of Klang River in January 2007 to examine the spatial distribution, composition, and sources of 19 parent polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbon (n-alkanes) using gas chromatography-mass spectrometry. The total concentrations of the 19 PAHs in the sediments were found to range from 1304 to 2187 ng g^{-1} sediment. Meanwhile, total concentrations of n-alkanes ranged from 17008 to 27116 µg g^{-1} sediment. The concentration of n-alkanes in the sediment was significantly correlated ($r = 0.991$, $p = 0.001$) with the content of sediment organic carbon. In this study, all the sediments exhibited phenanthrene/anthracene (PHE/ANT >15) fluoranthene/(fluorantene+pyrene) (FLT/FLT+PYR < 0.4), methylphenanthrenes/phenanthrene (MP/P >1), combustion PAHs/total PAHs (CombPAH/∑19PAH <0.3), terrigenous/aquatic ratio for hydrocarbons greater than 23. The also data showed that petrogenic and natural inputs were predominant at all the locations investigated. Multiple sources of n-alkanes and PAHs in the river sediments were also explained by low carbon preference index (CPI) values, different ratios of diploptene/$\sum C_{23}$-C_{25} n-alkanes, poor correlation between diploptene and $\sum C_{23}$-C_{25}, average chain length (ACL) of 29.54 ± 0.09, correlation between CPI and ACL ($r = 0.847$, $p = 0.035$), and high ratio of naphthalene/total PAHs.

Keywords: ACL, CPI, diploptene, Klang river, n-alkanes, PAHs

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in sediments and soils, yet they are virtually absent in living organisms (Laflamme and Hites, 1978; Hites *et al.,* 1980). PAHs are derived from natural or anthropogenic sources. Natural sources include: (a) forest and prairie fires (Blumer and Youngblood, 1975), (b) natural petroleum seeps, and (c) post-depositional transformations of biogenic pre-cursors over relatively short period of time (Wakeham *et al.,* 1980). Meanwhile, anthropogenic sources include: (a) combustion of fossil-fuel (Hites *et al*., 1977) and long-range atmospheric transport of PAHs adsorbed into soot or airborne particulate matter (Lunde

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and Bjorseth, 1977; Laflamme and Hites, 1978), (b) urban runoff containing PAHs derived from abrasion of street asphalt and automobile tyres and vehicular emissions (Wakeham *et al.,* 1980), and (c) spillage of petroleum and its refined products which contain complex assemblages of PAHs (Boehm *et al.,* 1991).

Polycyclic aromatic hydrocarbons (PAHs) form an important class of environmental contamination because some PAHs exhibit carcinogenic or mutagenic potentials (Boonyatumanond *et al.,* 2006). There are several reports of increased incidences of cancer in marine animals from the vicinity of oil spills (Al-Yakoob *et al.,* 1994; Colombo *et al*., 2005). Concerns over PAHs in the environment also arise also from the fact that many of them are persistent (IARC, 1983).

Much of the past work on the organic geochemistry of PAHs has concentrated on understanding their origins and some criteria have been developed to distinguish between different sources of PAHs, namely natural and anthropogenic. Phenanthrene/anthracene and Fluoranthene/pyrene ratios have been commonly used as a means of determining the dominant origins of PAHs (Gschwend and Hites, 1981; Sicre *et al.,* 1987; Colombo *et al.,* 1989; Budzinski *et al.,* 1997; Yang, 2000). The differences in both the reactivity and solubility of these two pairs of isomers have caused their respective ratios to unexpectedly remain constant and, therefore, provide a tracer of PAHs from origin through environmental transport to deposition in marine sediments (Yang, 2000).

The objectives of this study were to determine the distribution of PAHs and n-alkanes in the river surface sediment samples and investigate their sources in Klang River.

MATERIALS AND METHODS

Sampling Locations

Surface sediments were collected from five locations in Klang River which is located in the west coast of Peninsular Malaysia in January 2007 *(Fig. 1)*. The sediment samples were collected using the Ekman Dredge sampler. The sediment cake was placed on a stainless steel pan and the top 0-3 cm layer was taken using a pre-cleaned stainless steel scoop. After that, the samples were placed in ice and transported to the laboratory and stored at -35°C until further analysis.

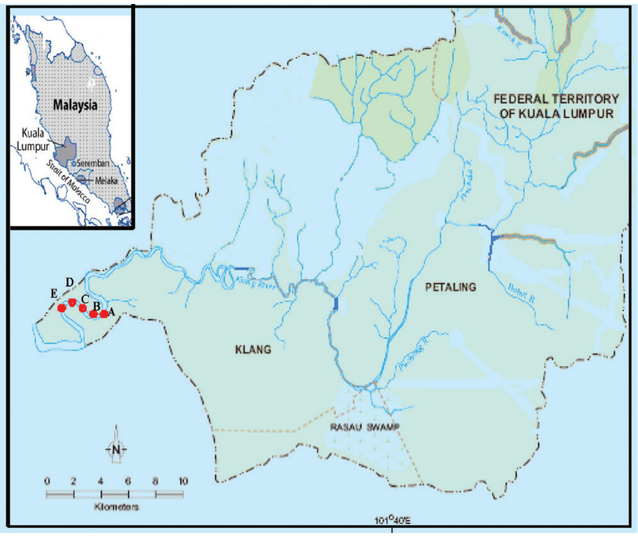

Fig. 1: Map of the sampling sites in the Klang River, Malaysia

Laboratory Analysis

Analytical procedure for PAHs and n-alkanes

Based on the dry weight of the samples, 5 g of each sediment was homogenized using a mortar and pestle in sodium sulphate to remove remaining water. The samples were then purified and fractionated according to the method described earlier (Zakaria *et al.,* 2002). Briefly, the soxhlet extractor was used for the extraction of lipid from the samples using 270 ml of distilled dichloromethane for 10 hours. About 100 µl of the PAH surrogate internal injection standard mixture, where 10 ppm of each component containing naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, was added for quality control of the PAH analyses. The eluate was purified and fractionated using two-step silica gel column chromatography. The first step silica gel chromatography was accomplished through 5% H_2O deactivated silica gel column (1 cm i.d. × 9 cm, ~6 g, 100–200 mesh; F.C.923, Davison Chemical). Hydrocarbons ranged from n-alkanes to PAHs were eluted with 20 ml of dichloromethane/hexane (1:3 v/v). The second step column chromatography was a fully activated silica gel (0.47 cm i.d.×18 cm, ~3 g, 60–200 mesh; Sil-A-200; Sigma). Alkanes were eluted with 4 ml of hexane and subsequently PAHs were eluted with dichloromethane/hexane (1:3, v/v). Normal and isoprenoid alkanes were determined using capillary gas chromatograph which was equipped with flame ionization detector. The PAHs analyses were carried out using quadrupole mass spectrometer integrated with gas chromatograph.

Each PAH fraction was evaporated to approximately 1 ml, transferred to a 1.5 ml amber ampoule and evaporated to dryness under a gentle stream of nitrogen and re-dissolved in 100 µl of isooctane containing *p*-terphenyl-d_{14} as an internal injection standard (IISTD) for the PAHs analysis. The PAHs analyses were done using Agilent technologies 5973A quadrupole mass spectrometer integrated with an Agilent 6890 gas chromatograph.

Each n-alkane fraction was evaporated to approximately 1 ml, transferred to a 1.5 ml amber ampoule and evaporated to dryness under a gentle stream of nitrogen and re-dissolved in 100 µl of isooctane. It was sealed by teflon and after sonication, while volatile organic carbons (VOCs) were formed in the head space. Meanwhile, the n-alkane analyses were carried out using the Agilent technologies 5973A quadrupole mass spectrometer, which was integrated with an Agilent 6890 gas chromatograph.

Analytical procedure for the total organic carbon (Toc)

The analytical procedure used in this study was described by Nelson and Sommers (1996). Briefly, the sediment samples were dried overnight at 60°C in an oven and then homogenized using mortar and pestle. Sample preparation was carried out to eliminate inorganic carbon. For this purpose, 1-1.5 g of the sample was mixed with 1-2 ml of HCl 1 M to eliminate all carbonates and then dried for about 10 hours at 100-105°C to get rid of Hydrochloric Acid. The TOC% was then determined using LECO CR-412 Carbon Analyzer with the furnace temperature of 1350°C and the oxygen boost time of 60s.

RESULTS AND DISCUSSION

Total Concentration of PAH

All PAH concentrations and TOC values are presented in Table 1. ∑PAH concentrations were normalized with TOC to eliminate the grain size effect. The range of ∑PAH/TOC was from 46 to 108 ng mg^{-1}.

TABLE 1
PAHs concentration (ng g $^{-1}$) and related parameters in the surface sediments from the Klang River

	Stations			
Compounds	A	B	C	D
Nap	1201.81	1654.04	2167.76	1861.72
DBT	0.81	1.09	N.D	N.D
Phe	11.14	15.09	2.05	10.77
Ant	0.23	0.21	0.04	0.17
3MPhe	2.38	4.70	0.78	3.16
2MPhe	2.93	5.16	0.53	2.62
2MAnt	N.D	0.76	N.D	N.D
9MPhe	2.48	4.21	0.84	3.11
1MPhe	3.82	4.44	0.59	2.55
Fluo	4.87	10.22	3.31	10.13
Pyr	15.74	36.56	5.16	23.35
1MPyr	16.33	7.89	N.D	3.94
Chry	3.81	1.6	N.D	3.52
BaAnt	3.57	2.23	N.D	3.32
BkFluo	8.98	0.49	N.D	N.D
BeAcep	N.D	13.51	N.D	N.D
BePyr	22.89	12.77	5.58	19.63
BaPyr	2.36	N.D	N.D	2.02
Per	N.D	N.D	N.D	N.D
DBahAnt	N.D	N.D	N.D	N.D
∑19PAHs	1304	1775	2187	1950
LMW/HMW	16.7	22.65	202.45	33.94
MP/P	1.45	1.23	1.34	1.1
PHE/ANT	49.33	73.38	53.96	62.93
FLT/(FLT+PYR)	0.24	0.22	0.39	0.3
CombPAH/∑19PAHs	0.06	0.04	0.005	0.03
Nap/∑19PAHs	0.92	0.93	0.99	0.95
TOC	28.16	12.35	23.6	17.92
∑19PAHs/TOC	46.31	143.72	92.67	108.82

∑19PAHs = Sum of (Naphtalene, Dibenzothiophene, Phenanthrene, Anthracene, 3-Methylphenanthrene, 2-Methylphenantrene, 2-Methylanthracene, 9-Methylphenanthrene, 1-Methylphenantrene Fluoranthene, Pyrene, 1-Methylpyrene, Chrysene, Benzo[a]Anthracene, Benzo[k]Fluoranthene, Benzo[e]Acephenanthrene, Benzo[e]Pyrene, Benzo[a]Pyrene, Dibenzo[a-h]Anthracene).
LMW/HMW = (Nap+ DBT+ Phe+ Ant+ 3Mphe+ 2Mphe+ 2MAnt+ 9MPhe+ 1MPhe+ Flu)/(Pyr+ 1MPyr+ Chr+ BaAnt+ BkFluo+ BeAcep+ BePyr+ BaPyr+ Per+DBahAnt).
MP/P = (3MPhe+2MPhe+9MPhe+1MPhe)/Phe.
PHE/ANT = Phenanthrene/Anthracene.
FLT/(FLT+PYR) = Fluoranthene/(Fluoranthene+Pyrene).
CombPAH = (Pyr+ 1MPyr+ Chr+ BaAnt+ BkFluo+ BeAcep+ BePyr+ BaPyr+ Per+DBahAnt).
Nap/∑19PAHs = Naphtalene/ ∑19PAHs.
TOC = Total organic carbon in unit of mg g $^{-1}$.
∑19PAHs/TOC in unit of ng mg $^{-1}$.
N.D = non detected

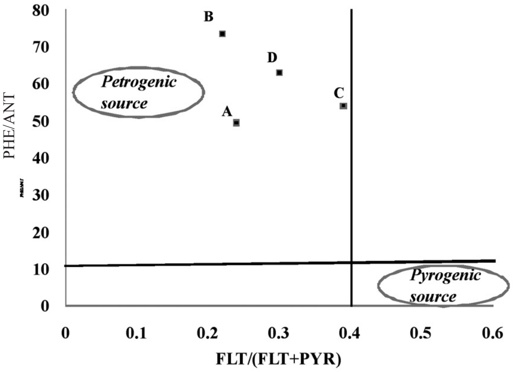

Fig. 2: Values of PHE/ANT and FLT/ (FLT/PYR) ratios for the sediments from Klang River

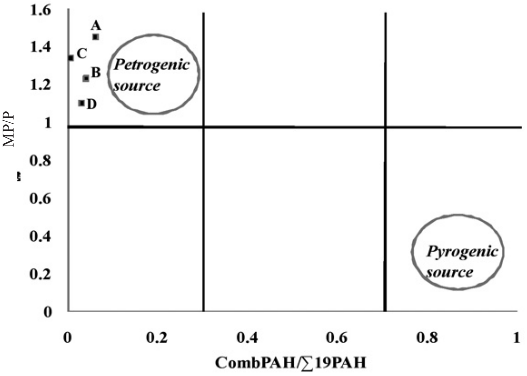

Fig. 3: Values of MP/P and CombPAH/∑19PAH ratios measured in the sediments from the Klang River

The total concentration of the 19 PAHs found in the sediments (expressed as ∑PAH) was found to range from 1300 to 2200 ng g^{-1}. In this study, the sediment PAH concentrations at all the stations investigated were dominated by naphthalene. Meanwhile, the naphthalene concentrations ranged from 1200 to 2167 ng g^{-1}. This is most likely due to the fact that naphthalene occurs at elevated concentrations in woody material (Wilcke *et al.,* 2000). It is believed that naphthalene originated from natural sources in the Klang River sediments. Lower molecular weight versus higher molecular weight ratio has been applied in several studies to distinguish between petrogenic and pyrogenic PAH sources (Bence *et al.,* 1996; Wang *et al.,* 1999; Mai *et al.,* 2002). The results of this study suggest petrogenic inputs to surface sediments in the Klang River.

Source Identification of PAH

As compared to pyrogenic sources, petrogenic sources are characterized by high ratios of phenanthrene/antracene (PHE/ANT >15) and methylephenanthrenes/phenanthrene (MP/P >1), in association with lower ratios of fluoranthene/pyrene (FLT/FLT+PYR<0.4) and combustion PAH/ total PAH (CombPAH/∑19PAH <0.3) (Budzinsky *et al.,* 1997; Benner *et al.,* 1989: 1990; Yunker *et al.,* 2002; Hwang *et al.,* 2003).

Fig. 2 shows that the values of PHE/ANT ranged from 53 to 74, whereas FLT/FLT+PYR ranged from 0.22 to 0.39 in the sediment samples of the Klang River. In addition, the values of MP/P ratio were found to range from 1.1 to 1.45, while the CombPAH/∑19PAH ratio ranged from 0.005 to 0.06, as shown in *Fig. 3*. The results suggest petrogenic inputs of PAHs in the sediments derived from the study area. Among the influencing factors are rapid tourism development, direct effluent discharges into the river, drainage from port areas, and contaminants from ships (Unlu and Alpar, 2006).

n-alkane Concentrations

The hydrocarbon concentrations and related parameters are shown in Table 2. To eliminate the grain size effect, n-alkane concentrations were normalized with TOC. There was found significant positive correlation (r = 0.991, p = 0.001) between n-alkane concentration and TOC at the 99% confidence level *(Fig. 4)*, indicating changes in n-alkane concentration can be depended on TOC contents.

TABLE 2

Hydrocarbon concentrations (µg g $^{-1}$) and related parameters in the surface sediments of the Klang River

Compounds	Stations				
	A	B	C	D	E
nC_{10}	31.1	N.D	N.D	N.D	N.D
nC_{12}	5.0	N.D	N.D	N.D	N.D
nC_{14}	26.4	27.4	N.D	N.D	31.1
nC_{15}	36.6	32.0	N.D	46.1	8.6
nC_{16}	57.2	51.3	8.3	51.5	78.1
nC_{17}	81.4	67.5	10.7	62.0	81.2
Pristane	129.9	130.2	20.8	98.9	93.3
nC_{18}	68.5	43.9	12.8	45.9	89.0
Phytane	N.D	N.D	N.D	N.D	N.D
nC_{19}	54.2	42.9	11.0	40.8	63.7
nC_{20}	60.4	35.9	22.7	38.4	74.4
nC_{21}	118.7	68.7	53.0	78.6	186.2
nC_{22}	260.7	128.3	164.4	164.4	451.8
nC_{23}	569.8	234.3	442.4	370.5	900.7
nC_{24}	2101.4	406.6	863.8	683.1	1459.7
nC_{25}	1717.9	636.1	1533.5	1129.5	2154.5
nC_{26}	2320.9	836.5	2118.7	1537.9	2632.0
nC_{27}	2998.8	1036.6	2611.1	1961.3	3118.1
nC_{28}	2894.0	1015.3	2549.9	1867.5	2927.4
nC_{29}	3171.1	1248.0	2680.5	2157.2	3127.7
nC_{30}	2629.6	906.5	2391.7	1647.9	2648.9
nC_{31}	2848.5	979.9	2262.2	2001.5	2727.4
nC_{32}	1887.8	700.8	1486.7	1250.9	1896.9
Diploptene	194.5	151.4	131.6	157.7	158.7
nC_{33}	1500.8	668.0	1102.9	1043.3	1403.4
nC_{34}	759.4	289.9	610.1	498.6	735.4
nC_{35}	434.7	200.2	297.5	331.9	300.1
nC_{36}	156.5	N.D	N.D	N.D	N.D
TOC	28.16	12.35	23.6	17.92	30.49
CPI	1.09	1.21	1.09	1.21	1.11
∑HC/TOC	951.4	781.9	899.7	949.1	889.4
SHC/TOC	6.11	11.53	0.92	8.31	5.70
LHC/TOC	320.26	264.33	320.08	341.52	294.30
TAR_{HC}	52.38	22.93	348.40	41.09	51.73
$Di/\sum C_{25-33}$	0.016	0.033	0.013	0.019	0.013
Di/TOC	6.9	12.26	5.58	8.80	5.20
ACL	29.54	29.65	29.43	29.59	9.47

SHC/TOC= µg of $(nC_{15}+nC_{17}+nC_{19})$/ mg of TOC. LHC/TOC = µg of $(nC_{27}+nC_{29}+nC_{31})$/ mg of TOC.
∑HC/TOC in unit of (µg mg $^{-1}$). $nC_{31}/Terr = nC_{31}/(nC_{27}+nC_{29}+nC_{31})$.
TAR_{HC} = terrigenous/aquatic ratio = $(nC_{27}+nC_{29}+nC_{31})/(nC_{15}+nC_{17}+nC_{19})$.
CPI = carbon preference index = ½ ×$[(nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33} \div nC_{24}+nC_{26}+nC_{28}+nC_{30}+nC_{32}) + (nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33} \div nC_{26}+nC_{28}+nC_{30}+nC_{32}+nC_{34})]$. TOC= Total organic carbon (mg g $^{-1}$).
$Di/\sum C_{25-33}$ = diploptene/$(nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33})$.
Di/TOC = diploptene/TOC, in unit of (µg mg $^{-1}$). N. D = non detected
ACL = average chain length

$$\mathbf{ACL=}\ \frac{27(nC_{27})+29(nC_{29})+319nC_{31})+33(nC_{33})}{nC_{27}+nC_{29}+nC_{31}+nC_{33}}$$

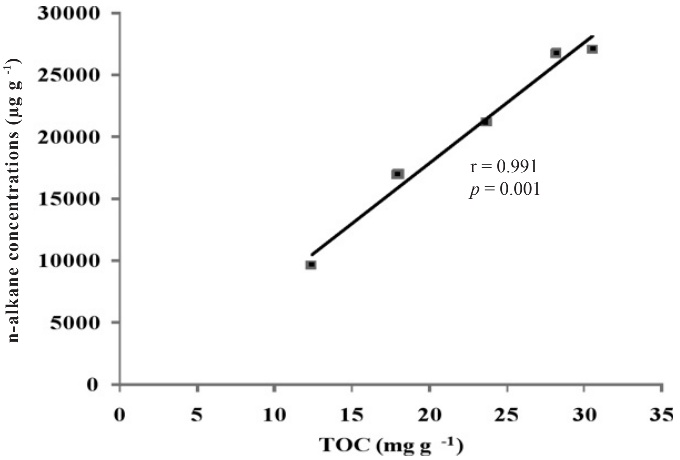

Fig. 4: Correlation between polycyclic aromatic hydrocarbons and total organic carbon in the sediments

n-alkanes were found to range between C_{10} and C_{36}. Total n-alkane concentrations were abundant ranging from 9600 to 27200 µg g $^{-1}$ in sediments of different stations. The long-chain n-alkanes (LHC, $>C_{23}$) were found in higher concentrations when compared to the short-chain n-alkanes (SHC, < C23) and the distribution patterns showed large contributions from even (C_{26}, C_{28}, C_{30}) and odd carbons (C_{27}, C_{29}, C_{31}). For LHC n-alkanes, the C_{27} and C_{29} are diagnostic of waxes from trees and shrubs and n-C_{31} is diagnostic of grass waxes (Jeng, 2007). Our results indicate that the sediments received contribution of the n-alkanes from grass, tree and shrub waxes in the banks of Klang River. This can possibly be attributed to the fact that vegetation types form the main influence on the chain length of terrigenous leaf lipids (Cranwell, 1973). It has been suggested that plants produce longer-chain compounds in warmer climates (Poynter *et al.,* 1989; Simoneit *et al.,* 1991).

Carbon Preference Index (CPI) of n-alkanes

In organic geochemistry, CPI is used to indicate the degree of diagenesis of straight-chain geolipids and it is also a numerical representation of how much of the original chain length specificity has been preserved in geological lipids (Meyers and Ishiwatari, 1995). In addition, it is also useful in determining the degree of biogenic versus petrogenic input (Mazurek and Simoneit, 1984). Hydrocarbons compose of a mixture of compounds originating from land plant material which shows a predominance of odd-numbered carbon chains with CPI~5–10 (Rieley *et al.,* 1991; Hedges and Prahl, 1993), whereas petrogenic inputs have a CPI approximating 1.0 (Farrington and Tripp, 1977; Eganhouse and Kaplan, 1982; Nishimura and Baker, 1986; Saliot *et al.,* 1988; Pendoley, 1992). Meanwhile, the CPI values close to one are also thought to indicate greater inputs from marine micro-organisms and/or recycled organic matter (Kennicutt *et al.,* 1987). The CPI values of the n-alkanes were found to vary from 1.09 to 1.21 in sediments at different locations (Table 2). This finding indicates that the sediments are contaminated by petrogenic hydrocarbons. However, it is important to highlight that exceptions exist in some cases. For example, Zhou *et al.* (2005) obtained low CPI values of n-alkanes during a warm-wet period in the sediment core samples in the Dingnan region in southern China. In addition, the CPI ratios ranging from 1-1.5 had been obtained in the sediment core samples taken from Chini Lake in Malaysia in the tropical environment (Riyahi Bakhtiari *et al.* full article in preparation for publication). They concluded that the CPI ratio ranging from 1-1.5 indicate greater inputs from higher plants in the study areas. A possible explanation for this might be the fact that plants produce longer-chain compounds in warmer climates (Poynter *et al.,* 1989; Simoneit *et al.,* 1991). Another possible explanation for this is that higher plants produce the same alkonoic acids < C_{20} as microbiota with additional homologs from C_{20} to C_{34} (Simoneit and Mazurek, 1982). These higher plant n-fatty acids are biosynthesized by elongation of low molecular weight homologues which result in predominantly even carbon number n-alkanoic acids (Kolattukudy *et al.,* 1976). The n-alkanes with an even number of carbon atoms can only result from the coupling of fatty acids containing an even and an odd number of carbon atoms. Therefore, due to the fact that the odd carbon number fatty acids are relatively rare, only the odd carbon number n-alkanes are virtually predominant in plants (Bird and Lynch, 1974). The plant wax n-alkanes show a C_{max} in the range of C_{25} to C_{33}, which are dependent on the plant species as well as the season and locality (e.g. Eglinton and Hamilton, 1967; Simoneit and Mazurek, 1982; Mazurek *et al.,* 1991; Rogge *et al.,* 1993d; Stephanou and Stratigakis, 1993; Abas and Simoneit, 1998). As compared to the CPI range of Chini Lake sediments (1-1.5), the sediment from the Klang River has a relatively smaller range from 1.09 to 1.21. One possible cause can be the multiple sources of n-alkanes in the study area. Moreover, the n-alkanes in the Klang river may include high CPI n-alkanes from the plant waxes, but low CPI n-alkanes from microbial or petrogenic sources. These findings seem to be consistent with the data previously reported by some researchers (Pearson and Eglinton, 2000; Reddy *et al.,* 2000).

Average Chain lLh (ACL)

The higher plant n-alkane average chain length (ACL) describes the average number of carbon atoms per molecule based on the abundance of the odd-carbon-numbered higher plant n-alkanes (Poynter and Eglinton, 1990). It has been found that the modal carbon number of a higher plant n-alkane distribution is broadly related to the latitude (Poynter *et al*., 1989; Poynter and Eglinton, 1990), with higher modal carbon numbers occurring at lower latitudes. Furthermore, the distribution of ACL has been linked to the geographical distribution of fluvial and eolian inputs and source regions (Poynter and Eglinton, 1990). In other words, for coastal marine sediments, ACL in a given area can be considered a constant if all these factors are the same. The ACL values were found to range from 28.3 to 29.9 in the surface sediments of NW Africa at ~0–40° N (Huang *et al.,* 2000). It has been reported that the ACL values increased from 29.9 to 30.8 for the north to south latitudinal transect (5–30° S latitude) of the Holocene sediment in the SE Atlantic (Rommerskirchen *et al.,* 2003). This means a change of ~0.04 ACL unit for crossing 1° latitude (Jeng, 2006). The ACL values of Chini Lake sediment core samples (Latitude 03° 26′ N) yield an average of 29.68 ± 0.15, indicate an increment of 0.038 ACL units for crossing 1° latitude compared to that in surface sediments of NW Africa ranging from ~0–40° N (Riyahi Bakhtiari *et al.* full article in preparation for publication). This suggests a predominant input of biogenic (recent) hydrocarbons. In this study, the ACL values of the Klang River sediment samples (Latitude 02° 56′ N) yield an average of 29.54 ± 0.09 indicate an increment of 0.034 ACL units for crossing 1° latitude when compared to the surface sediments of NW Africa ranging from ~0–40° N. The sediment samples of Chini Lake showed a higher increment. This could probably be attributed to the river sediment being contaminated by petrogenic hydrocarbons because petrogenic hydrocarbons are expected to have low ACL values in the C_{25}–C_{33} range (Jeng, 2006).

Both ACL and CPI were calculated using the n-alkanes data derived from higher plants. Therefore, they are expected to be correlated (Jeng 2006). The correlation between the ACL and CPI values of the sediment samples were tested and the data are presented in *Fig. 5*. The results show a significant positive correlation at 95% confidence level in the sediment samples (r = 0.847,

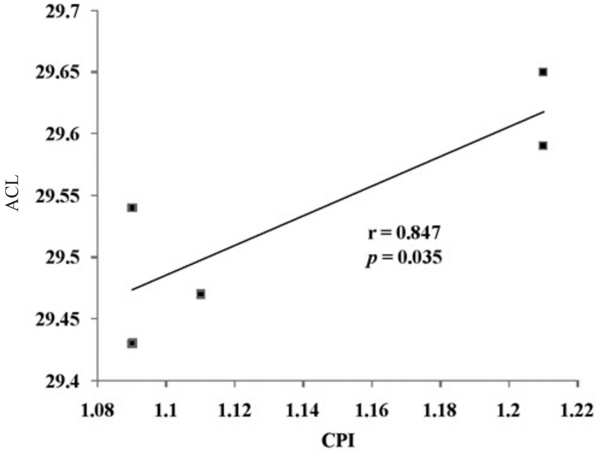

Fig. 5: Correlation between ACL and CPI n-alkanes in Klang River sediments

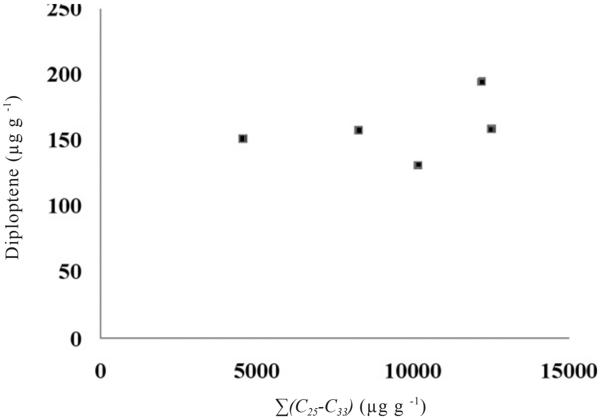

Fig. 6: Plots of diploptene versus $\sum(C_{25}$-$C_{33})$ *n-alkanes for Klang River sediments*

p = 0.035). Therefore, it could be inferred that the CPI ranging from 1-1.5 could be attributed to the mixed petrogenic and natural sources of n-alkanes in the Klang River sediments.

Diploptene (hop-22(29)-ene)

The concentrations of diploptene in the sediment samples (ranging from 131.6 to 194.5 µg g $^{-1}$) are shown in Table 2. Meanwhile, the values of Di/$\sum$ (C_{25}-C_{33}) ratio were found to range from 0.013 – 0.033.

Diploptene is derived from terrestrial higher plants and it is also formed by bacteria (Rohmer *et al.,* 1984). If higher plants are the sole source of diploptene, a strong correlation between diploptene and terrestrial higher plants n-alkanes can be expected. The correlation between diploptene and $\sum$ (C_{25}-C_{33}) was examined in the sediments *(Fig. 5)*. However, there was no significant correlation (r = 0.391, *p* = 0.515) found between diploptene and $\sum C_{23}$-C_{25} n-alkanes (odd carbon only) for the sediments *(Fig. 6)*. This was most likely because the sediments received multi inputs of hydrocarbons and hence contained different ratios of diploptene to $\sum C_{23}$-C_{25} n-alkanes. These findings are in agreement with those of the previous research (Jeng, 2007).

CONCLUSIONS

The results of this study suggest petrogenic and natural sources inputs of hydrocarbons in the study area. These were shown by the high Nap/∑19PAHs and LMW/HMW ratios, as well as the ratios of PHE/ANT >15, MP/P >1, FLT/FLT+PYR < 0.4 and CombPAH/∑19PAH <0.3 for PAHs. Therefore, it is concluded that the downstream sediments in the Klang River contain n-alkane from both petrogenic and natural sources. These could be expressed by predominance of LHC, $>C_{23}$ as compared to SHC, < C23, the CPI values of the n-alkanes (i.e. from 1.09 to 1.21), the ACL values of 29.54 ± 0.09, the positive correlation between ACL and CPI values (r = 0.847, *p* = 0.035), different ratios of diploptene /$\sum C_{23}$-C_{25} n-alkanes in the stations, as well as no correlation (r = 0.391, *p*= 0.515) between diploptene and $\sum C_{23}$-C_{25} n-alkanes.

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