Spatial distribution of petroleum hydrocarbon in sediments of major rivers from east coast of peninsular Malaysia

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Abstract — Petroleum hydrocarbon pollution in the marine environment has been a major concern in recent years. A 50-year history of industrialization process in Malaysia is rapidly spreading to the East Coast regions. Some components of petroleum hydrocarbon had been demonstrated to disrupt endocrine systems in human. Very few measurement on compounds specific hydrocarbon has been made for the characterization and composition in the East Coast's rivers and estuaries. A total of 14 surface sediment samples were collected in August, 2006 from the Kelantan, Besut and Terengganu rivers. The samples were dried, soxhlet extracted, fractionated and injected into GC-FID and GC-MS for alkanes and polycyclic aromatic hydrocarbons (PAHs), respectively. In general, elevated concentrations hydrocarbons were found in all stations located in the vicinity of urban runoffs for all rivers. The concentrations of aliphatic hydrocarbons range from 1000 to 7168000 ng/g (dry wt.) and PAHs concentration ranged from 58 to 1689 ng/g (dry Wt.) for the rivers. The PAHs patterns in urbanized stations suggest the dominance of low molecular weight PAH components (2–4 rings). Based on MP/P ratio, the source of hydrocarbons influenced by the city runoffs are mostly petrogenic origin. The sources of hydrocarbons on the upstream and downstream stations have been to be of pyrogenic origin. In general, the concentrations of PAHs and alkanes for a number of stations in this study are comparable to more polluted sites in Malaysia. In conclusion, all three rivers showed low to moderate petroleum hydrocarbon contamination. These results suggested that immediate remedial measure in preventing further contamination has to be implemented by local, state and federal agencies.

Key words: spatial distribution, n-alkane, PAHs, east coast, Malaysia

Introduction

Malaysia has been experiencing rapid industrial development. The industrial process is now spreading to the East Coast of Peninsular Malaysia. With increasing industrial and commercial development, the East Coast will be experiencing greater pollution load from various anthropogenic activities especially from oil and gas industries and shipping industries. Petroleum hydrocarbon pollution is an increasing concern in recent years due to its wide usage as an energy source in most industrial and developing countries. Petroleum hydrocarbon generated from industrial processes and human activities are widespread contaminants and cause serious environmental problems because of their toxic, mutagenic and carcinogenic properties, persistence and bioaccumulation. Some components of petroleum hydrocarbon had been demonstrated to disrupt endocrine systems in human (Neff 79). Aliphatic and aromatic hydrocarbons found in the environmental samples are normally as a result of direct and indirect discharges via lateral and atmospheric transportations, especially into the marine environment (Prahl and Carpenter 1983).

The concentration of petroleum hydrocarbon pollution is directly related to anthropogenic activities. In general, aliphatic hydrocarbons consist of straight and saturated carbon chain starting from C_{10} to C_{40} containing odd and even carbon numbers indicating natural and anthropogenic hydrocarbons sources. United Nation Environment Program (UNEP, 1995) introduced guidelines to identify the levels of harmful ($>10 \mu g/g$) and harmless ($<10 \mu g/g$) aliphatic hydrocarbons in the marine sedimentary environment. Polycyclic Aromatic Hydrocarbons (PAHs) are another class of petroleum hydrocarbon pollutions beside the aliphatic, contain usually 2–7 benzene rings which some of which had been shown to disrupt human endocrine system. Some PAHs had also been shown to have carcinogenic and mutagenic effects to organisms. PAHs have different toxicities effects to organisms. LMW PAHs are more bioavailable but less toxic and carcinogenic, however high molecular weights PAHs are

less bioavailable but more toxic and carcinogenic. Marine organisms have been widely used by scientists as bioindicator to explain the effects and concentration of petroleum pollution in the environment. Marine organisms especially mollusks accumulate PAHs in their body via water while some others such as benthic take through the sediment. PAHs in organisms are subjected to processes such as uptake, distribution, accumulation, metabolism, excretion and depuration. Some higher marine organisms such as fish have ability to metabolize organic contaminants using specific enzymes such as mixed function oxidase's (MFO's). PAHs in the sediments of marine environment are also concern when it recovers from the sediment layers through bioturbation and physical movements from deeper levels.

Despite the potential for direct discharge of petroleum hydrocarbons into rivers, very little measurement and compound specific studies has been made for the characterization and composition in the East Coast's rivers and estuaries. A comprehensive study on compound-specific petroleum hydrocarbon pollution were conducted in major rivers in the East Coast and a total of 14 surface sediment samples were collected from the Kelantan, Besut and Terengganu rivers. The objective of this study is to investigate the spatial distribution of petroleum hydrocarbon pollution in sediments of the East Coast of Peninsular Malaysia.

Materials and Method

Sample collection

The samples were collected during August, 2006. The map of sampling locations with detail data are shown in Fig. 1 (a, b, c and d) and Table 1, respectively. Fourteen surface sediment samples (top 2–4 cm representing recent input) were collected using Eckman dredge, placed into previously solvent-rinsed stainless steel containers. The samples were transported to the laboratory in ice and stored at −18°C prior to further analysis.

Chemical analysis

Authentic chemical standard for n-alkane and PAHs were purchased from Sigma Chemical Company (St. Louis, MO). All organic solvents used in the analysis were distilled in glass and the glassware were successively rinsed with methanol, acetone and distilled hexane. The glassware were then capped with clean aluminum foil and dried at 60°C for 2 hours and stored until further use.
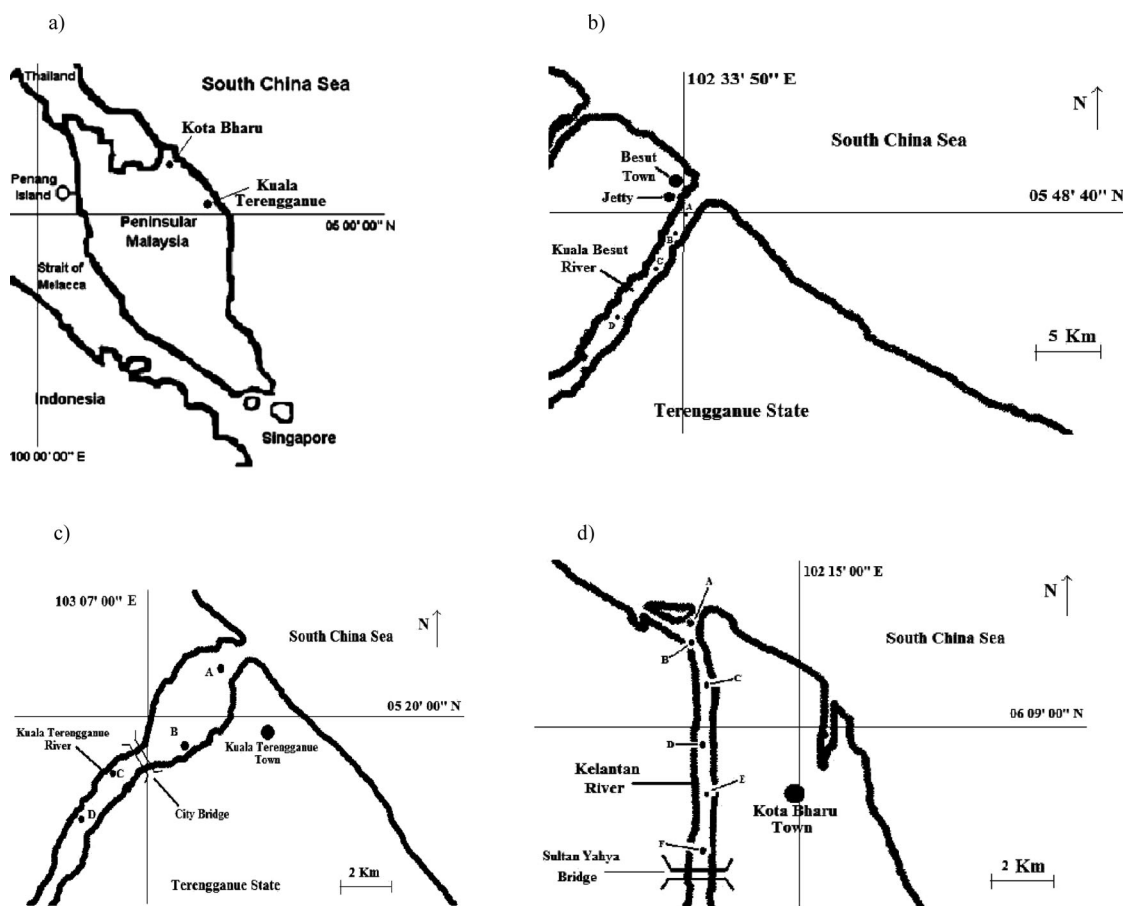
Sediment samples were defrosted at room temperature

Fig. 1. Study Area Map, (a)Peninsular Malaysia; (b) Besut River; (c) Terengganue River and (d) Kelantan River

Table 1. Sampling data; (a) Kelantan River; (b) Terengganue River and (c) Besut River

(a)

	Kelantan River					
	A (Estuary)	B	C	D	E	F (Upstream)
Time	9:55 AM	10:20 AM	11:00 AM	11:20 AM	12:20 PM	12:50 PM
GPS location	N06°13.053′	N06°12.114′	N06°11.218′	N06°10.201′	N06°08.271′	N06°07.540′
	E102°13.953′	E102°13.886′	E102°13.984′	E102°14.975′	E102°13.877′	E102°14.018′
Dissolved Oxygen (mg/l)	6.36	5.53	5.50	5.08	6.22	5.01
Conductivity	15390.00	13120.00	924.00	584.00	72.70	79.00
Salinity (ppt)	10.80	6.80	0.40	0.30	0.00	0.00
Turbidity (NTU)	38.70	20.60	98.60	111.00	57.00	81.00
Secchi Disk (m)	0.50	0.70	0.25	0.15	0.40	0.20

(b)

	Terengganu River			
	A (Estuary)	B	C	D (Upstream)
Time	14:25	14:55	16:07	16:45
GPS location	N05°20.321°	N05°19.770′	N05°19.533′	N05°19.423′
	E103°08.216′	E103°07.910′	E103°06.306′	E103°05.310′
Dissolved Oxygen (mg/l)	4.35	4.20	3.70	3.51
Conductivity	8590.00	4918.00	686.00	38.00
Salinity (ppt)	4.80	2.33	0.30	0.00
Turbidity (NTU)	5.00	6.00	11.60	7.30
Secchi Disk (m)	1.70	<1.0	1.40	1.50

(c)

	Besut River			
	A (Estuary)	B	C	D (Upstream)
Time	18:40	18:10	17:40	17:06
GPS location	N05°48.397′	N05°48.876′	N05°15.227′	N05°15.227′
	E102°33.518′	E102°33.500′	E102°33.655′	E102°33.655′
Dissolved Oxygen (mg/l)	5.10	5.92	5.58	4.82
Conductivity	4.076×10^{-3}	9.70	18.45	21.66
Salinity (ppt)	2.10	5.40	10.90	12.90
Turbidity (NTU)	15.00	8.00	6.00	6.00
Secchi Disk (m)	2.10	1.40	1.10	1.45

and homogenized with pre-cleaned spatula. Five grams of the samples 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. Exactly $200\,\mu$l 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 Yim et al. (2005) and Boonyatumanond et al. (2006). 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 H_2O to remove polar components. n-alkanes (C_{16} to C_{36}) and PAHs ranging from and 2–7 rings 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 alkane and PAHs fractions using 4 ml hexane and 14 ml 3 : 1 hexane/dichloromethane (v/v), respectively.

Aliphatic and polycyclic aromatic hydrocarbon fractions were individually evaporated to approximately 1 ml, transferred to 2 ml amber container, and evaporated to dryness under gently stream of nitrogen blow-down. Aliphatic hydrocarbon fraction then re-dissolved into $100\,\mu$l of iso-octane.

Normal alkanes analyzed using Hewlett Packard 5980 Gas Chromatograph (GC) with Flame Ionization Detector (FID). A J&W Scientific Durabond DB-5, 30 m fused capillary column, 0.25 mm i.d. and 0.25 μm film thickness used with helium as the carrier gas at 200 kPa. The injection port maintains at 300°C and samples injects with split less mode followed by 1 min purge after the injection. Column temperature holds at 70°C for 1 min then planned at 30°C/min to 150°C, 5°C/min to 310°C and hold for 10 min. The detector temperature remains at 310°C. A scan mode method was employed to identify the normal alkane peaks comparing to the standard solution which was injected prior to the sample's injection at the same machine and instrument conditions. The normal alkane standard (10 ppm of each compound) including some of even carbon number alkane (C_{16}, C_{18}, C_{20}, C_{24}, C_{26}, C_{28}, C_{32} and C_{36}) used as external standard. An appropriate volume of 1 μl of alkane standard was injected before the samples injection and the peaks were identified using retention time of peaks from the standard solution.

Polycyclic aromatic hydrocarbon fraction also re-dissolved into an appropriate volume (200 μl) of iso-octane containing p-terphynyl-d_{14} was used as an internal injection standard (IISTD) for PAHs analysis. PAHs analyses were made 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/cm^2. GC-MS operating conditions were 70 eV ionization potential with the source at 200°C and electron multiplier voltage at ~2000 eV. The injection port was maintained at 300°C and the sample was injected with split less mode followed by purge 1 min after the injection. 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 method was employed after a delay of 4 min. PAHs were monitored at m/z=178 (phenanthrene, anthracene), m/z=192 (methylphenanthrenes), m/z=202 (fluaranthene, pyrene), m/z=228 (benz(a)anthracene, chrysene), m/z=252 (benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene), m/z=276 (indeno[1,2,3-cd]pyrene, benzo(ghi)perylene. Individual PAHs were quantified by comparing the integrated peak area of the selected ion with the peak area of the IISTD. Acenaphthene-d_8 and chrysene-d_{12} were used as IISTD for the quantification of PAHs ranging from phenanthrene to 1-methylphenanthrene and for PAHs from fluoranthene to Dibenzo (a, h) antharacene, 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 2-, 3- or 9-methylphenanthrene standards were available, therefore an estimated response factors for these compounds was based on a response for 1-methylphenanthrene. Similarly, benz[a]anthracene benzo[j]fluoranthene+ benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene concentrations were based on the chrysene/triphenylene, benzo[b]fluoranthene and benzo[ghi]perylene response, respectively. 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) antharacene). PAHs concentrations were recovery-corrected using the spiked surrogates and were in the range of 70% to 130% recoveries. 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%.

Results

Aliphatic and polycyclic aromatic hydrocarbon compositions and related ratios in the studied area are shown in Table 2 and 3, respectively.

Discussions

Kelantan River: The Alkanes Distribution and Characterization

Total aliphatic hydrocarbon concentrations ranged from 3000 to 4565000 ng/g (dry Wt.). There is no correlation between the sampling locations and the concentration of aliphatic hydrocarbons. The highest and lowest alkane concentrations are recorded in the middle of the river and upstream, respectively. Elevated concentrations of the hydrocarbons could be attributed to input from urban runoffs, shipping and boating activities. However, the levels of hydrocarbons showed lower values that had been previously reported from surficial sediment samples in industrialized location of Penang, Malaysia (Zakaria et al., unpublished information). Low molecular weight (LMW) and high molecular weight (HMW) normal alkane which are used as a source identifier is shown Fig. 2. The ratio of low to high (L/H) ratio range from 0.04 to 4.00. Low L/H ratio in the estuary could be attributed to higher plant, sedimentary bacteria and marine animals inputs whereas the slightly higher L/H ratio in the middle and the upstream could be attributed to fresh oil inputs (Fig. 3). One other ratio that can be used for source identification of aliphatic hydrocarbon pollution is Carbon Preference Index (CPI) which was defined as a ratio of odd to even carbon Odd number carbon is normally attributed to natural sources whereas even number carbons are attributed to an-

Table 2. Aliphatic Hydrocarbon Composition for Surficial Sediment of Selected Major Rivers from East Coast of Peninsular Malaysia. See Table 3 for definition of

Study Area Sampling Stations	Besut River Estuary				Terengganu River Estuary				Kelantan River Estuary					
	A	B	C	D	A	B	C	D	A	B	C	D	E	F
Total LMW Alkane (μg/g)[a]	395	531	425	2330	6205	4678	1504	52	102	151	2966	3	3	2
Total HMW Alkane (μg/g)[b]	1112	2523	1130	4412	578	2489	1001	57	440	3259	1598	0	0	1
Ratio of LMW to HMW[c]	0.35	0.21	0.37	0.52	10.73	1.87	1.50	0.91	0.23	0.04	1.85	4	4	4
SUM (C_{17}, C_{19}) (μg/g)	13	194	9	34	1	92	4	27	1	1	1	1	1	1
Total Odd Number Hydrocarbon (μg/g)[d]	318	647	243	136	1852	1620	1271	80	15	162	3517	1	2	1
Total Even Number Hydrocarbon (μg/g)[e]	1188	2407	1312	6606	4932	5548	1233	28	527	3249	1047	2	2	2
Total n-Alkane (μg/g)[f]	1507	3054	1555	6743	6784	7168	2505	109	542	3411	4565	4	3	3
CPI[g]	0.26	0.26	0.18	0.02	0.37	0.29	1.03	2.77	0.02	0.04	3.35	0.48	0.96	0.83
Major Hydrocarbon[h]	C_{32}	C_{32}	C_{32}	C_{26}, C_{32}	C_{26}	C_{16}, C_{26}	C_{20}	C_{33}	C_{28}	C_{36}	C_{27}	C_{26}		
n-Alkane/C_{16}	217	3054	156	1814	10	3	160	109	542	3411	83	222	203	111
1/CPI	3.72	3.71	5.39	48.52	2.66	3.42	0.96	0.36	33.55	20.00	0.29	2.045145	1.040743	1.192669
C_{31}/C_{19}	2.85	0.37	0.13	0.99	138.57	0.99	1.05	0.09	0.99	11.78	0.99	0.00	0.00	0.00
ACLi	27.30	29.56	26.76	32.92	25.52	30.88	26.31	32.95	32.86	29.64	26.07	27.82	27.09	27.11

[a]Total LMW Alkane: Sum of C_{16} to C_{26} aliphatic hydrocarbons; [b]Total HMW Alkane: Sum of C_{27} to C_{36} aliphatic hydrocarbons; [c]Ratio of LMW to HMW: Ratio of Low Molecular Weight aliphatic hydrocarbon to High Molecular Weight; [d]Total Odd Number Hydrocarbon: Sum of natural origin hydrocarbon from C_{17} to C_{35}; [e]Total Even Number Hydrocarbon: Sum of anthropogenic origin hydrocarbon from C_{16} to C_{36}; [f]Total n-Alkane: Sum of Odd and Even aliphatic hydrocarbons from C_{16} to C_{36}; [g]CPI: Carbon Preference Index, the ratio of Odd to Even carbon number; [h]Major Hydrocarbon: The Hydrocarbon which contains the majority of total n-alkane; and iACL: Average Carbon Chain Length which calculates as $[(25*C_{25})+(27*C_{27})+(29*C_{29})+(31*C_{31})+(33*C_{33})]/(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})$.

Table 3. PAHs Composition for Surficial Sediment of Selected Major Rivers from East Coast of Peninsular Malaysia. See Table 3 for definition of

	Besut River				Terengganu River				Kelantan River					
	A(E§)	B	C	D(u±)	A(E)	B	C	D(u)	A(E)	B	C	D	E	F(u)
$\sum$PAHs (ng/g-dry)[a]	264.56	114.23	58.80	424.96	295.00	1689.94	520.53	395.19	546.30	651.46	1031.72	769.10	389.98	78.70
MP/P[b]	1.98	1.36	1.35	2.11	1.03	2.03	1.62	1.83	1.31	1.70	0.86	1.39	0.77	1.51
$\sum$L-PAHs (ng/g-dry)[c]	263.16	112.25	56.33	421.56	228.51	64.02	419.20	220.79	540.73	496.54	96.63	261.26	233.06	56.22
$\sum$H-PAHs (ng/g-dry)[d]	1.40	1.97	2.47	3.40	66.49	1625.93	101.33	174.40	5.57	154.91	935.09	507.84	156.93	22.48
L/H PAHs[e]	188.49	56.85	22.78	124.00	3.33	0.03	3.16	1.18	2.47	2.38	0.10	0.39	0.97	1.44

§Estuary. ±Upstream. [a]$\sum$PAHs=sum of concentrations of Phenanthrene, Anthracene, 3-Methylphenanthrene, 2-Methylanthracene, 9-Methylphenanthrene, 1-Methylphenanthrene, 2-Methylphenanthrene, 1-Methylphenanthrene, Fluoranthene, Pyrene, 1-Methylpyrene, Benzo[a]Anthracene, Chrysene, Benzo[a]acenaphthene, Benzo[k]flourenthene, Benzo[a]pyrene, Benzo[e]pyrene, Dibenzo (a, h) antharacene. [b]MP/P ratio=a ratio of sum of 3-methylphenanthrene+2-methylphenanthrene+9-methylphenanthrene+1-methylphenanthrene relative to phenanthrene concentrations. [c]$\sum$L-PAHs=sum of concentration of Phenanthrene to Pyrene. [d]$\sum$H-PAHs=sum of concentration of 1-Methylpyrene to Dibenzo (a,h) antharacene. [e]L/H PAHs=sum of concentration of Phenanthrene to Pyrene relative to sum of concentration of 1-Methylpyrene to Dibenzo (a,h) antharacene.
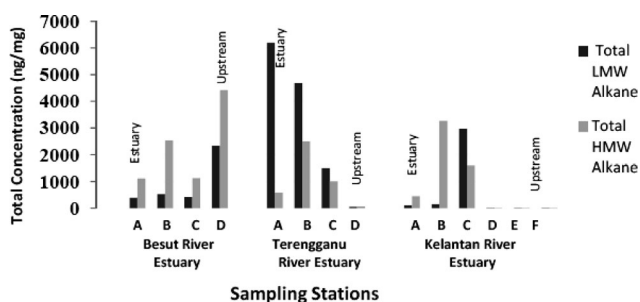
Fig. 2. Total LMW and HMW Alkane in Selected East Coast River Estuaries, Peninsular Malaysia. See Table 2 for definition of LMW and HMW Alkane.
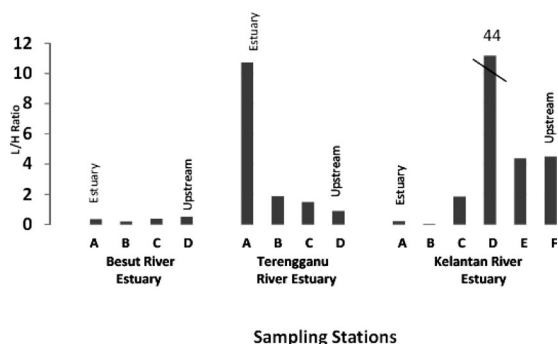
Fig. 3. Ratio of LMW over HMW Alkane in SelectedEast Coast River Estuaries, Peninsular Malaysia. See Table 2 for definition of L/H Akane.
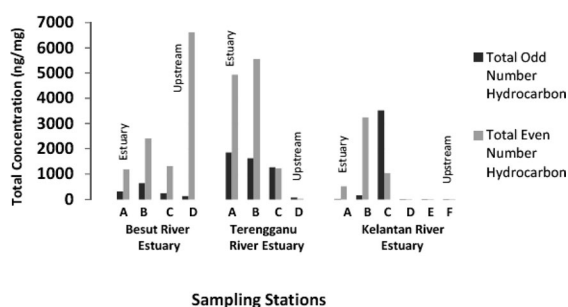
Fig. 4. Total Odd and Even Carbon Number Normal Alkane in Selected East Coast River Estuaries. See Table 2 for definition of Odd and Even Carbon Number Aliphatic Hydrocarbon.

thropogenic sources. The values of total odd to even carbon number concentrations are shown in Fig. 4. CPI values for all stations show no significant difference between stations (Fig. 5) where all but one station (Station C) was from anthropogenic input. In station E, the CPI value indicates that microorganisms, recycled organic matters and/or petroleum were the major source. This phenomenon was earlier suggested by (Farrington and Tripp 1977). Major aliphatic hydrocarbon for this river is range from C_{26} to C_{36} indicating in-
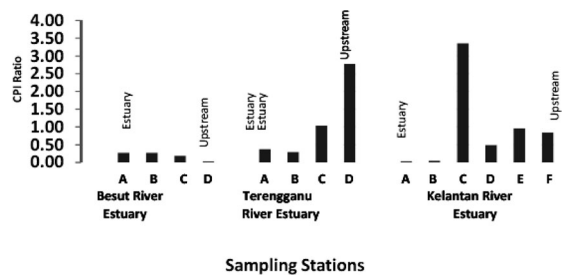
Fig. 5. Carbon Preference Index (CPI) in Selected East Coast River Estuaries, Peninsular Malaysia. See Table 2 for definition of CPI.
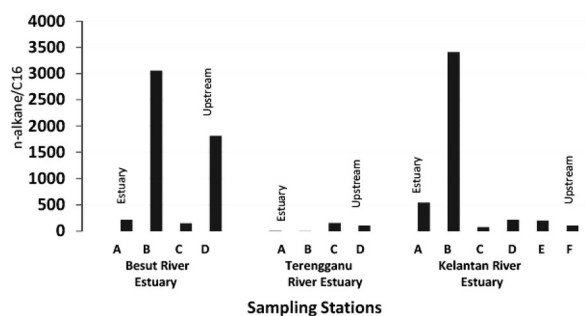
Fig. 6. Ratio of n-Alkane over C_{16} in Selected East Coast River Estuaries, Peninsular Malaysia.
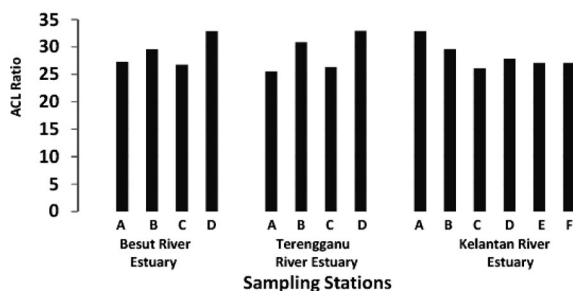
Fig. 7. Average Carbon Chain Lenght in Selected East Coast River Estuaries, Peninsular Malaysia. See Table 2 for definition of

significant input from the marine environment. Normal alkane over C_{16} ratio was found to be not less than 15 (83-3411) have also indicated that the sediment samples were not contaminated by petroleum input as suggested by Clark and Finley, 1973 (Fig. 6). Another interesting observation was that the ratio of C_{31}/C_{19} (0-11.78) showed that the hydrocarbons are mostly of terrestrial origin which was transported to the marine environment via rivers. This was consistent with a study conducted by Commendatore and Esteves, 2004. Average Carbon Chain Length (ACL) is very useful for identifications of environmental changes for a particular ecosystem. A constant value for ACL indicates little environmental changes are occurring in the system. Interestingly, the ACL value in this study showed wide range of values indicating broad range of terrestrial input from different ecosystems

into the river (Fig. 7). In summary, the distribution of alkane input into the river may have been influenced by natural and anthropogenic sources. However, urban runoffs may have a significant and anthropogenic for the hydrocarbon input for Station C.

PAH's Distribution and Characterization

PAHs concentrations range from 78 to 1031 ng/g (dry wt.) (Fig. 8). The lowest value of PAHs in Kelantan Rivers was in the upstream whereas higher concentrations were exhibited in the downstream. The relative abundance of methylphenantherenes to phenantherene (MP/P) is shown in Fig. 9 and Table 3. MP/P ratio is using to distinguish petrogenic and pyrogenic sources of PAHs. The values (0.77–1.83) generally indicate the contribution of mixture of pyrogenic and petrogenic sources. Zakaria et al., 2002 reported that the sedimentary environments of Malaysian rivers and estuaries had been severely affected by petrogenic input of PAHs. Boonyatumanond et al., 2006 also reported the same conditions from sediment samples collected from the Gulf of Thailand. Petroleum hydrocarbon pollutions in the marine environment undergo significant changes as a result of environmental degradation, weathering processes and diagenesis. For example, hydrocarbon compounds with lower molecular weight which is a major component in fresh and crude oil will deplete after depositional processes. The ratio of LMW to HMW PAHs (L/H-PAHs) is commonly used to recognize the freshness of the oil input to the marine sediment samples. In this study, L/H-PAHs range from 0.10 to 2.47 indicating very old oil input into the river. In summary, PAH's input into the Kelantan River is very minimal, Low MP/P ratio indicate that major input may have originated from long range atmospheric transport as suggested by Prahl and Carpenter, 1983.

In conclusion, alkanes and PAHs input are very low in Kelantan River. Low population density and less industrial activities along the river may have contributed to the low input hydrocarbon pollution. Kota Bharu town (Station C) showed a slight elevation of hydrocarbon input especially from urban runoffs and other unidentified multiple diffuse sources. In order to maintain pristine conditions of the river, long-term continous monitoring of hydrocarbon pollution for the river is recommended.

Besut River: The Alkanes Distribution and Characterization

Total aliphatic hydrocarbon concentrations ranged from 1507000 to 6743000 ng/g (dry Wt.) in Besut river estuary. There is no correlation between the sampling locations and the concentration of aliphatic hydrocarbons. Elevated concentrations of hydrocarbons were in the upstream stations while lower concentrations were found in the estuarine stations. Elevated concentrations of the hydrocarbons in the upstream could have been attributed to input from urban runoffs of Jerteh Town. However, the overall levels of hydrocarbons showed much lower values that had been previously reported from surficial sediment samples in industrialized location of Penang, Malaysia (Zakaria et al., unpublished information). LMW and HMW normal alkane which are used as a source identifier are shown Fig. 2. The ratios of LMW/HMW are below 1 indicating inputs from higher plant, sedimentary bacteria, and marine animals (Gearing et al. 1976) and degradation of light hydrocarbons (Commendatore 2000). The (CPI) shown in Fig. 4 and (Fig. 5), are almost equal for all stations and could be attributed anthropogenic input along the river. Major alkanes was found around C_{32} indicating higher plant input from the marine environment. Normal alkane over C_{16} ratio which more than 15 (i.e. 156-3054) indicated that the sediment samples are not contaminated by petroleum as suggested by Clark and Finley, 1973. The detail results are shown in Fig. 6. The results of C_{31}/C_{19} (0.13–2.85) ratio further evidence that the hydrocarbons input are of terrestrial origins as previously reported by Commendatore and Esteves, 2004. Average Carbon Chain Length (ACL) which is usually used for identifications of environmental condition changes showed fluctuating values throughout the river indicating wide range of terrestrial input from different multiple ecosystems within the watershed (Fig. 7). In summary, alkane input into the river was heavily influenced by urban runoffs. Stations further away from Jerteh Town, showed low input of alkane contamination.

PAH's Distribution and Characterization

PAHs concentrations range from 59 to 425 ng/g (dry Wt.) (Fig. 8). The lowest concentration of PAHs was in the middle section along the river. MP/P ratio in this river (1.35–2.11) indicates the most contribution were from the pyrogenic sources with the exception of petrogenic PAHs found in the estuary area. A relatively strong petrogenic signature may have been attributed to the boating and shipping activities in the Kuala Besut town which is located right at the mouth of the river estuary. Ecotourism and fish landing activities in the area have been steadily growing over the years which may further aggravate the localized hydrocarbon input. In contrast, a mixture of petrogenic and pyrogenic input were
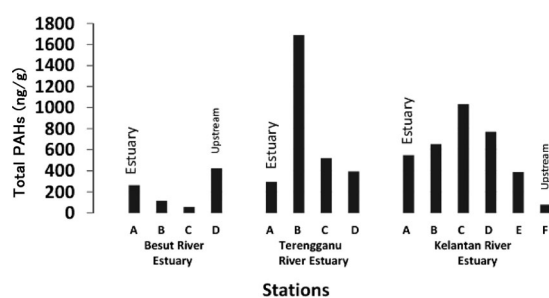

Fig. 8. Total PAHs in Major Rivers from East Coast of Peninsular Malaysia. See Table 3 for definition of Total PAHs.

found in the middle of the river as indicated by MP/P ratios of ~1.35 and 1.36). Even higher MP/P ratios of ~1.98 were found in upstream station just south of Jerteh Town. The contribution of urban runoffs of the town may have been the major factor for the petrogenic signature of the hydrocarbon input in the upstream portion of the river. Finally, L/H-PAHs ranging from 23 to 188 were found for the downstream stations providing further evidence that fresh oil input was the major source. In summary, PAH's input showed interesting pattern. The lower reaches of the river was influenced by perogenic input due to antropogenic activities. The middle section along the river however, was influenced by both petrogenic and petrogenic input from multiple difuse sources. However, the upstream, the hydrocarbon input was influenced by petrogenic signature from urban runoffs of Jerteh Town.

In conclusion, hydrocarbon pollution in Besut river is much lower than previous studies conducted by Zakaria et al., (2002). Possible petrogenic input from boating and ecotourism activities in the estuary of the river may be a cause for concern. Authorities should be seriously considered limiting the number of boats and fish landing activities in order to reduce hydrocarbon input into the river.

Terengganu River: Alkane Distribution and Characterization

Total aliphatic hydrocarbon concentrations ranged from 109000 to 7168000 ng/g (dry wt.). There is no correlation between the sampling locations and the concentration of aliphatic hydrocarbons. The highest and lowest alkane concentrations are recorded in the middle of the river and upstream, respectively. Elevated concentrations of the hydrocarbons could be attributed to input from urban runoffs and shipping and boating activities in the area. However, the levels of hydrocarbons showed lower values that had been previously reported from surficial sediment samples in industrialized location of Penang, Malaysia (Zakaria et al. unpublished data). Low Molecular Weight (LMW) and High Molecular Weight (HMW) normal alkanes which are used as a source identifier is shown in Fig. 2. The ratio of low to high (L/H) molecular weight alkane which identifies the sources of pollution range from 0.91 to 10.73 in stations D and A, respectively. According to L/H ratio, the hydrocarbon input near the mouth of the river was indicative of fresh oil input. This fresh oil input could have been attributed to localized activities of boating, fishing and other recreational activities as well as sea-based input from offshore oil explorations and productions. The offshore oil could have been carried to the shore by Monsoon currents. Using the same ratio, however, other locations in the more upstream of the same river showed rather 'old' oil input and planktonic signatures. The 'old' oil input could have originated from depositional process from multiple diffuse sources along the river. The CPI ratio as

shown in Fig. 5 are almost equal in all stations except for Station D. Hydrocarbon sources in Station D indicates that of microorganisms and recycled organic matters as proposed by Farrington and Tripp, 1977. The CPI ratios for the rest of the stations showed hydrocarbons are of anthropogenic origins. This could be due to the input from urban runoffs of Kuala Terengganu city. Spatial distribution of the alkanes in the river range from C_{16} to C_{26} indicating oil input from the marine environments. Normal alkane over C_{16} ratio was found from 3 to 160 as shown in Fig. 6. Values above 15 are input from non-petroleum sources. The n-alkane to C_{16} ratios for Stations A and B showed readings lower than 15 indicating that the sediment samples are contaminated by petroleum as suggested by Clark and Finley, 1973. The results of C_{31}/C_{19} (0.09–138) ratio for most stations gave further evidence that the hydrocarbons input for the river are of terrestrial origins as previously reported by Commendatore and Esteves, 2004. The ACL values for the river showed fluctuating values throughout the river indicating wide range of terrestrial input from different multiple ecosystems within the watershed (Fig. 7)

In summary, alkane input into the Terengganu River was influenced by fresh oil input at the lower reaches of the estuary. The fresh oil input could be influenced by localized activities of boating, fishing and other recreational activities as well as sea-based input from offshore oil explorations and productions. In stations nearby the city, urban runoffs played a significant role to the hydrocarbon pollution input. In the upstream stations, major hydrocarbon input is characterized by natural sources including long range transport and biogenic sources. These sources made up to the background levels as depicted in the results of this study.

PAH's Distribution and Characterization

PAHs concentrations range from 295 to 1690 ng/g (dry wt.) as shown in Fig. 8. The lowest value of PAHs in Terengganu River was in the estuary. This scenario is consistent with the alkanes distribution as discussed earlier. MP/P ratio range from 1.03 to 2.03 indicative of mixture of pyrogenic and petrogenic sources. The petrogenic sources could have originated from fresh oil spill or input from offshore oil explorations and productions and urban runoffs whereas the pyrogenic sources have their origins traced to long range transport and other multiple difusse sources, The ratio of lower to higher molecular weight (L/H) PAHs were found to be fluctuated from 0.03 to 3.33 indicating 'old' oil input. The 'old' oil input could have originated from depositional process from multiple diffuse sources along the river.

Total PAHs in this study show low to moderate levels as described by Baumard, 1998. One interesting observation could be made in that the concentrations of PAHs in the river are comparable with previous studies reported (for examples in Zakaria et al. (2002), Zakaria and Mahat (2006), Boonya-
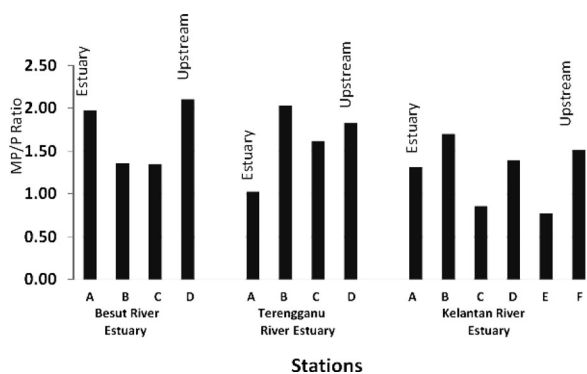
Fig. 9. MP/P Ratio in Major Rivers from East Coast of Peninsular Malaysia. See Table 3 for definition of MP/P Ratio.
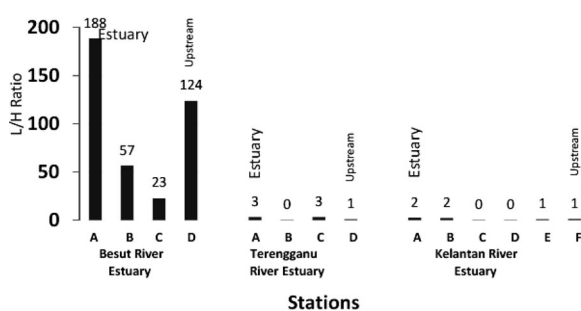

Fig. 10. L/H PAHs Ratio in Major Rivers from East Coast of Peninsular Malaysia. See Table 3 for definition of L/H PAHs Ratio.

tumanond et al. (2006) and Lukman et al. (2007). At the same time other studies had also showed that a few locations around the world, the hydrocarbon pollution is extremely high as reported in Marvin et al., 2000 from Hamilton Harbor in Canada; Oug et al., 1998 from Fjord Harbor study in Norway; and Shiaris and Jambard-Sweet 1986 in Boston Harbor. However, PAHs concentrations in this study is several magnitudes lower than that of the polluted harbors and estuaries in developed countries.

The levels of LMW PAHs shows strong positive correlation with the total PAHs ($r^2=0.80$). These numbers indicate that that the PAHs pollution in the river is controlled by petrogenic input or fresh oil input. Lower molecular weight PAHs are more bioavailable and therefore could pose significant human health implications. High molecular weight PAHs are less bioavailable but they are generally more toxic. High molecular weight (HMW) PAHs for this study are generally low hence it pose insignificant hazards to human health.

In conclusion, low to moderate hydrocarbon pollutions had been demonstrated for the three rivers investigated in this study. Petrogenic input are significant for areas close proximity to anthropogenic activities which include urban areas, boating activities and ecotourism activities. Generally, aliphatic hydrocarbon concentrations for the three rivers are low and of terrestrial and natural origins. Furthermore, the profile of the compound-specific PAHs in this study is much

lower than that of the previous studies for Gradual shift from petrogenic to pyrogenic PAHs was observed. More data have to be collected in the 3 rivers as part of the long term monitoring programs. Long term trends of hydrocarbon data are indispensable to predict hydrocarbon pollution to those rivers. Protection of these pristine and beautiful rivers is of prime necessity in order to preserve and protect the rich ecosystem.

Acknowledgement

References

Baumard, P., Budzinski, H., Garrigues, P., Sorbe, J. C., Burgeot, T. and Bellocq, J. 1998. Concentrations of PAHs (Polycyclic Aromatic Hydrocarbons) in various marine organisms in relation to those in sediments and to trophic level. Mar. Pollut. Bull. 36: 951–960.

Boonyatumanond R., Wattayakom, G., Togo A. and Takada, H. 2006. Distribution and origins of Polycyclic Aromatic Hydrocarbons in estuarine, rivers and marine sediments in Thailand. Mar. Pollut. Bull. 52: 942–956.

Chetwittayachan, T., Shimazaki, D. and Yamamoto, K. 2002. A comparison of temporal variation of particle-bond PAH concentration in different urban environments Tokyo, Japan and Bangkok Thailand. Atmos. Environ. 36: 2027–2037.

Clarck Jr., R. C., Finley, J. S. 1973. Techniques for analysis of paraffin hydrocarbons and for interpretation of data to asses oil spill effects in aquatic organisms. *In*: Proceedings of Joint Conference on prevention and Control of Oil Spills. pp. 161–172, American Petroleum Institute, Washington, DC.

Commendatore, M. G., Esteves, J. I., Colombos, J. C. 2000. Hydrocarbons in coastal sediments of Patagonia, Argentina: levels and probable sources. Mar. Pollut. Bull. 40: 989–998.

Farrington, J. W., Tripp, B. W. 1977. Hydrocarbons in western North Atlantic surface sediments. Geochim. Cosmochim. Acta 41: 1627–1641.

Gearing, P., Gearing, J., Lytle, T. F., Lytle, J. 1976. Hydrocarbons in 60 Northeast Golf of Mexico shelf sediment: a preliminary survey. Geochim. Cosmochim. Acta 40: 1005–1017.

Lukman, M., Balzer, W. and Jose, C. 2006. Polycyclic Aromatic Hydrocarbon (PAHs) pollution in coastal sediment from Riau Province, Indonesia. Extended Abstract. Proceeding.

Marvin, C. H., McCarry, B. E., Vilella, J., Allan, M. and Bryant, D. W. 2000. Chemical and biological profiles of sediments as indicator of sources of genotoxic contamination in Hamilton Harbor. Part I: Analysis of Polycyclic Aromatic Hydrocarbons and Thia-arene compounds. Chemosph. 41: 979–988.

Neff, J. M. 1979. *Polycyclic Aromatic Hydrocarbon in the Aquatic Environment: Sources, Fates and Biological Effects*. Applied

Science Publishers, London.

Oug, E., Nes, K. and Rygg, B. 1998. Relationship between soft bottom macrofauna and Polycyclic Aromatic Hydrocarbons (PAHs) from smelter discharge in Norwegian fjord and coastal waters. Mar. Ecol. Prog. Ser. 173: 39–52.

Prahl, F. G. and Carpenter, R. 1983. Polycyclic aromatic hydrocarbon (PAH)-phase associations in Washington coastal sediment. Geochim. Cosmochim. Acta, Volume 47: 1013–1023.

Shiaris, M. P. and Jambard-Sweet, D. 1986. Polycyclic Aromatic Hydrocarbon in surficial sediments od Boston Harbor, Massachusetts, USA. Mar. Pollut. Bull. 17: 469–472.

Smith, D. J. T., Edelhauser, E. C. and Harrison, R. M. 1995. Polynuclear aromatic hydrocarbon concentration in road dust and soil samples collected in the united kingdom and Pakistan. Environ. Technol. 16: 45–53.

UNEP, 1995. Determination of petroleum hydrocarbons in sediments. Reference Methods For Marine Pollution Studies No. 72.

Yim, U. H., Hong, S. H., Shim, W. J., Oh, J. R. and Chang, M. 2005. Spatio-temporal distribution and characteristics of PAHs in sediments from Masan Bay, Korea. Mar. Pollut. Bull. 50: 319–326.

Zakaria M. P., Horinouchi A., Tsutsumi S., Takada H., Tanabe S. and Ismail A. 2000. Oil Pollution in the Strait of Malacca, Malaysia: Application of Molecular Markers for Source Identification. Environ. Sci. Technol. 34: 1189–1196.

Zakaria M. P., Okuda T. and Takada H. 2001. Polycyclic Aromatic Hydrocarbons (PAHs) and Hopanes in Stranded Tar-Balls on the Coasts of Peninsular Malaysia: Applications of Biomarkers for Identifying Sources of Oil Pollution. Mar. Pollut. Bull. 42: 1357–1366.

Zakaria M. P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kuono, E. and Kumata, H. 2002 Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Rivers and Estuaries in Malaysia: A Widespread Input of Petrogenic PAHs. Environ. Sci. Technol. 36: 1907–1918.

Zakaria M. P. and Mahat A. A. 2006. Distribution of Polycyclic Aromatic Hydrocarbons in the Langat estuary. Coastal Mar. Sci. 30: 387–395.