

Characterization, Distribution, Sources and Origins of Aliphatic Hydrocarbons from Surface Sediment of Prai Strait, Penang, Malaysia: A Widespread Anthropogenic Input

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Abstract

Persistent organic pollutants such as petroleum hydrocarbons are one of the most serious and important class of pollutants that face to many countries including Malaysia. Aliphatic hydrocarbons contain straight chain alkane; derive from anthropogenic and natural sources to the marine environment. The multi-purpose strait of Prai is located in the Northwest of Peninsular Malaysia plays an important economic role in the Southeast Asia. Twenty surface sediment samples were collected using Eckman dredge to measure the concentration and determine the characterization, sources and origins of the aliphatic hydrocarbons in December 2006. Samples (top 4 cm) were extracted with Soxhlet, treated with activated copper and subjected to 2 steps column chromatography for purification and fractionation. Alkane fraction injected into Gas Chromatography–Flame Ionization Detector (GC-FID) for instrumental analysis. The results showed that total n-alkane concentrations are ranging from 512 to 10770 ng/mg d. w. Carbon Preferences Index (CPI) revealed an extreme widespread anthropogenic input and naturally derived (CPI= 0 to 4.88) hydrocarbons in the study area. The ratio of C_{31}/C_{19} indicated that natural hydrocarbons are generating from terrestrial vascular plants and transferring by rivers. The characteristics of Major Hydrocarbons provided evidences that oil and its derivatives either fresh or degraded are the major contributors of the pollution in the study area. Statistical approaches also confirmed that 85% of study area affected by oil sources of pollution. it is seen that aliphatic hydrocarbons mostly transfer by lateral input to the marine environment than atmospheric movements.

Keywords: aliphatic hydrocarbon; surface sediment; carbon preference index; Prai strait

1. Introduction

The end of World War II is the historical turning point of Penang (mainland and island) where she faced rapid development in urban and industries, especially in the past 30 years. Nowadays, Penang is a well known industrialized, shipping route, urbanized and tourism destination in the Southeast Asia. The term of development usually covers the usage of well known energy of oil. Oil includes variety of compounds and elements such as aliphatic hydrocarbons that is a potential for environmental hazard and impact for ecosystems and human life. Aliphatic hydrocarbons (n-alkane) consist of two different sources of anthropogenic and naturally derived compounds. The anthropogenic hydrocarbons come from human activities such as industries, urbanization, shipping, fishing and oil operations but natural hydrocarbons produce by organisms such as planktons, algae and bacteria or come from terrestrial plants. Anthropogenic hydrocarbons such as crude oil and its products that

have been recognized as important pollutants (Clark, 1992) appear in high concentration than biogenic source. Generally, non-polluted area demonstrates hydrocarbons concentration less than 10 ng/mg d. w. (UNEP, 1992).

Nature-derived hydrocarbons are controlled by the processes of biosynthetic or metabolic pathways that usually result in mixtures of compounds of limited complexity, which is due to structural specificity relations and specific biological functions (NAS, 1985). The n-alkane consist of odd and even carbon numbers ranging up to 64 carbons with no alkyl branch or substitutes. The “Odd” carbons come from the biogenic sources while “Even” carbon numbers are usually derive from the anthropogenic sources. In detail, n-C₁₅, n-C₁₇ and n-C₁₉ are produced by marine biogenic sources whereas C₂₅-C₃₃ hydrocarbons are produced from terrestrial vascular plants.

The n-alkane is one of the earlier molecular markers for identification of the hydrocarbon pollution and its sources. Farrington and Tripp (1977), reported

predominant of hydrocarbons in western North Atlantic surface sediment from land sources. The presence of these compounds in abyssal plain simply indicates the transport pathways of hydrocarbons to the marine environment. The hydrocarbon pollution also has potential to come through urbanized centers via urban storm water run-off (Robert *et al.*, 1985) as naturally derived n-alkane appears (Killops *et al.*, 1988).

Many ratios and indexes has been used to identify the sources of n-alkane in the environment such as Unresolved Complex Mixture (UCM), Carbon Preference Index (CPI), Major Hydrocarbon (MH), Average Carbon Chain (ACL) and C_{31}/C_{19} . The UCM is a complex mixture of hydrocarbon with branched and cyclic structures. The presence of UCM in chromatograms has been used as an indicator of the presence of petroleum hydrocarbons (Farrington and Quinn, 1973). Although most of the UCM are present in higher molecular weight range, they are also exist in low molecular weight range and can potentially be evaporated although the UCM can provide limited fingerprinting information (Revill *et al.*, 1992) but can indicate the biodegraded crude oil (Gough *et al.*, 1992). The CPI indicates the ratio of odd carbon numbers over even with different carbon groups. In the studies on marine sedimentary environment, the CPI is using frequently and been introduced by Farrington and Tripp (1977) and developed by others (Boehm and Requejo, 1986; Colombo *et al.*, 1989; Kennicutt *et al.*, 1987) that values from 3 to 6 is indicate terrestrial vascular plants and around unity shows petrogenic input (Boehm and Requejo, 1986; Colombo *et al.*, 1989) although Kennicutt *et al.*, (1987) believed the possibilities of marine micro organisms and/or recycled organic matter contribution for value of one. Biogenic-derived hydrocarbons appear with low concentrations mostly come from the riverine input and high level of hydrocarbons with anthropogenic source come through industrialized and urbanized area that confirms the petroleum pollution (Commendatore *et al.*, 2004). The ACL is an index to evaluate the predominant of odd carbon number in an environmental sample. Higher ACL values usually is consistent with higher plant input while lower numbers can be possibly due to pollution expose although it assumes to be constant among samples in specific location (Jeng, 2006). The ratio of C_{31}/C_{19} indicates the predominant of terrestrial and marine biogenic sources input in a sample, although was not fully applicable in this study.

Although, Malaysia is among the most important developing countries in the world but few studies have been addressing the hydrocarbon and petroleum pollution (Zakaria *et al.*, 2002; Sakari *et al.*, 2008). This study investigates the aliphatic hydrocarbons presence in the environment and surveys the possible

sources of exposure. This study is the first report in Penang areas to cover the following objectives; 1) to find the distribution and concentrations of natural and anthropogenic hydrocarbons in coastal zone of Prai Strait and 2) find out the possible sources and origins of petroleum hydrocarbon pollution in the study area.

2. Material and Methods

2.1. Sampling

The location of the sampling stations is shown in Fig. 1 and explained in details in Table 1.

The Ekman dredge was used to provide the top 4 cm of sediments representing the modern input of hydrocarbon load. The samples placed into a stainless steel container with Teflon cap and shipped to the laboratory under dry ice condition and kept frozen in -20 °C prior to experiments. To prevent any contamination, the sampling equipments and experimental glassware were rinsed in soap solution, rinsing with tap and distilled water 6 times each and Methanol (MeOH), Acetone and distilled Hexane 3 times each, capped with Aluminum Foil (Al Foil) and dried 2 hours in specific oven in 64 °C and placed in clean shelves prior to use.

2.2. Chemicals

Authentic standards of aliphatic hydrocarbons including n-C16, C18, C20, C22, C24, C26, C28, C32 and C36 were purchased from Sigma Chemical Company, St. Louis, MO. A 100-200 (μm) mesh Silica Gel (F.C. 923) was applied for 2-steps of column chromatography, which baked at 200 °C for 12 h, cooled down in desiccators, deactivate with 5% distilled water (w/w) and filled with n-hexane for first step column chromatography. The second step the silica gel was baked in 380 °C for four hours and then continued at 200 °C for 4 h, and additional procedures was conducted as above. Organic solvents including n-Hexane, Dichloromethane (DCM) and Isooctane distilled in glass to take the final and pure isomers before use. Anhydrous Sodium Sulfate (Na_2SO_4) was baked in muffle furnace in 380 °C for 4 hours and keep in 120 °C oven and cooled down in desiccators prior to use.

2.3. Analytical procedures

The analytical procedures were described in detail by Sakari *et al.*, (2008). For dry weight determination sediment samples were weighed precisely (1 g) using analytical balance in 10 ml beaker and placed in the oven for 24 h in 63 °C, then re-weighed and baked

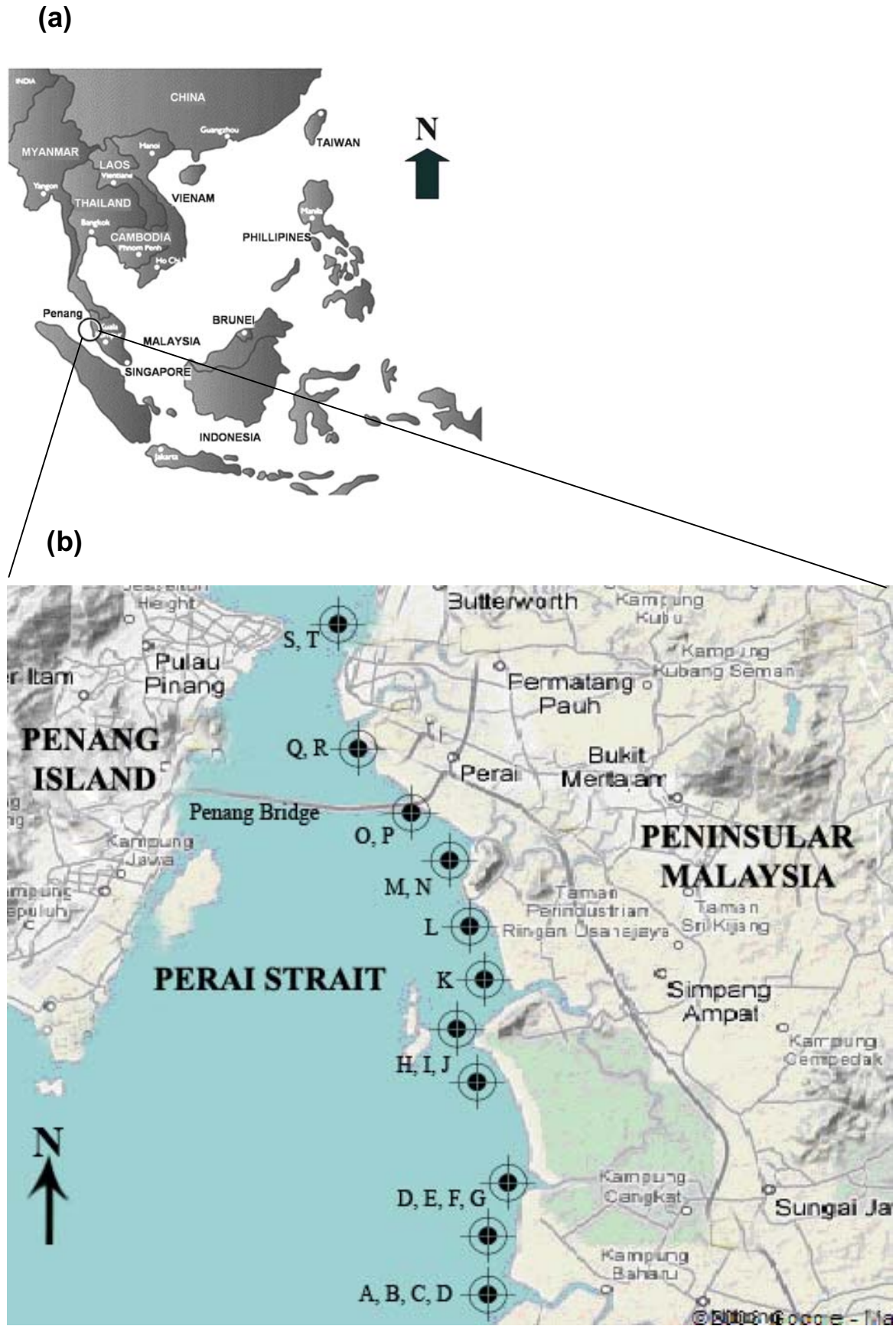


Figure 1. Map of the study area showing (a) Southeast Asia and Perai Strait (b) Map of Perai Strait and sampling stations.

Table 1. Sampling information

Stations	Geographical location		Date of Sampling	Depth (m)
A	N: 5° 10' 30''	E:100° 23' 48''	12/16/2006	2.5
B	N: 5° 10' 40''	E:100° 23' 49''	12/16/2006	3.0
C	N: 5° 10' 54''	E:100° 23' 48''	12/16/2006	2.8
D	N: 05° 11' 57''	E:100° 24' 03''	12/16/2006	3.8
E	N: 05° 12' 36''	E:100° 24' 00''	12/16/2006	2.4
F	N: 05° 12' 54''	E:100° 23' 59''	12/16/2006	3.2
G	N: 05° 13' 25''	E:100° 24' 00''	12/16/2006	3.1
H	N: 05° 14' 05''	E:100° 23' 36''	12/16/2006	4.0
I	N: 05° 15' 12''	E:100° 23' 48''	12/16/2006	4.5
J	N: 05° 16' 03''	E:100° 24' 12''	12/16/2006	4.4
K	N:05° 17' 10''	E:100° 24' 00''	12/16/2006	5.2
L	N: 05° 18' 18''	E:100° 23' 53''	12/16/2006	2.5
M	N: 05° 19' 09''	E:100° 23' 44''	12/16/2006	4.1
N	N: 05° 19' 45''	E:100° 23' 31''	12/16/2006	3.2
O (south of bridge)	N: 5° 20' 48''	E:100° 23' 31''	12/16/2006	3.7
P (north of bridge)	N: 05° 21' 16''	E:100° 22' 53''	12/16/2006	3.8
Q	N: 5° 21' 30''	E:100° 22' 48''	12/16/2006	4.3
R	N: 5° 21' 58''	E:100° 22' 26''	12/16/2006	2.2
S	N: 5° 22' 54''	E:100° 22' 14''	12/16/2006	2.1
T	N: 5° 24' 05''	E:100° 22' 13''	12/16/2006	3.1

again for 2 h more till the weight changes place less than 0.02 g. An aliquot of 5 g (dry weight basis) sediment samples was dried with enough Na_2SO_4 and transfer to the Cellulose thimble and placed in Soxhlet chamber. The Soxhlet extraction was conducted for 11 h using dichloromethane (DCM). Extracted materials were transferred into clean glassware for Na_2SO_4 treatment to remove the possible moisture and left to stand overnight. Activated copper was applied over night to remove elemental sulfur from extracted samples to prevent interferences in GC analysis. Then the volume of the extract was reduced to approximately 1 ml using rotary evaporator. The extract was ready for first step column chromatography (9 cm and 0.9 cm i.d. using 20 mL of 3:1 Hexane: DCM) to remove any compounds near the polarity of water. The extract from the first step was reduced to near dryness. The fractionation step was conducted using second step column chromatography (18 cm and 0.47 cm i.d. using 4 mL of hexane for n-alkane). The fraction volume was reduced using both rotary evaporator and nitrogen blow down and transferred to the 2 mL vial. The extract was fully dried using gentle nitrogen stream and 100 ml of isooctane was added prior to instrumental analyses.

2.4. Instrumental analysis

Normal and isoprenoid 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 maintained 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.

3. Results and Discussion

The results of this research for specific compounds n-alkane, total, LMW, HMW and ratios such as L/H, CPI and ACL are shown in Table 2.

As shown in Table 2, the concentration of n-alkane fluctuates among stations, the highest concentrations of n-alkane were observed in stations E and N, with total concentrations of 10770 and 10176 (ng/mg), respectively. The lowest concentrations were observed in Stations C and P with values of 421 and 512 (ng/

Table 2. Concentration of Aliphatic Hydrocarbons on Surface Sediments (ng/mg) and related ratios and indexes

Carbon numbers	Sampling Stations																			
	A south	B	C	D	E	F	G	H	I	J	K	L	M	N	O south of bridge	P north of bridge	Q	R	S	T north
16	0	0	0	0	0	0	341	0	1820	0	0	0	0	2972	0	0	1145	0	0	0
17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
18	355	851	0	0	166	202	423	0	0	854	0	0	795	2610	730	0	947	645	377	0
19	0	0	0	0	0	0	0	0	0	0	0	335	0	0	0	0	0	0	0	0
20	0	577	0	3675	833	238	287	0	0	595	0	0	785	2495	518	0	990	642	0	1166
21	7	14	0	0	0	75	0	0	0	0	0	0	43	9	0	0	19	0	0	0
22	8	23	0	2805	10	12	16	8	0	54	0	7	19	10	15	0	14	45	11	24
23	19	49	0	0	25	34	28	0	0	66	0	15	37	0	34	0	43	9	19	54
24	54	117	0	15	76	135	76	0	0	219	602	49	106	73	86	34	54	40	53	126
25	146	188	0	0	173	248	79	0	0	248	0	12	148	8	128	32	0	33	110	10
26	171	280	124	29	272	412	134	0	113	382	5	83	224	9	183	14	8	117	103	157
27	173	464	183	28	405	443	118	0	0	295	0	19	17	10	0	32	0	103	69	178
28	239	536	0	207	709	586	592	0	7	289	196	40	355	303	134	55	54	123	86	222
29	121	0	13	41	17	130	54	14	59	155	41	8	67	65	0	98	0	37	84	69
30	263	522	44	5	1191	805	439	28	101	176	279	304	570	340	89	19	277	92	105	302
31	27	12	16	36	0	0	0	0	47	23	0	11	31	30	8	55	0	8	17	7
32	83	315	16	0	1868	1255	852	514	85	293	448	348	947	306	66	19	289	54	21	243
33	36	86	18	0	82	99	43	33	0	77	2522	0	82	55	30	49	0	27	35	38
34	57	141	0	97	2425	1596	1180	51	79	140	663	260	1210	787	49	106	191	20	29	366
35	6	0	0	0	0	0	115	10	0	0	0	0	46	7	0	0	9	0	0	6
36	27	54	5	76	2417	1764	1128	373	66	432	748	214	1300	87	33	0	80	14	21	167
pristane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
phytane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
^a Total n-alkane	1792	4229	421	7013	10770	8033	5904	1021	2386	4299	5518	1705	6780	10176	2104	512	4120	2008	1140	3135
^b Total LMW Alkane	762	2098	124	6524	1555	1356	1383	8	1942	2417	608	501	2157	8186	1695	79	3220	1531	673	1537
^c Total HMW Alkane	1030	2131	297	490	9214	6677	4521	1013	444	1881	4910	1204	4623	1990	410	433	899	477	467	1598

Table 2. Concentration of Aliphatic Hydrocarbons on Surface Sediments (ng/mg) and related ratios and indexes (continued)

	Sampling Stations																T north				
	A south	B	C	D	E	F	G	H	I	J	K	L	M	N	O south of bridge	P north of bridge		Q	R	S	
^d LH ratio	0.74	0.98	0.42	13.32	0.17	0.20	0.31	0.01	4.37	1.28	0.12	0.42	0.47	4.11	4.14	0.18	3.58	3.21	1.44	0.96	
^e SUM (C23-C33)	522	799	231	105	702	953	322	47	115	864	2565	65	380	167	201	266	43	217	335	356	
^f SUM(C17,C19)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	334.64	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
^g Total Odd Number HC	535	812	231	105	702	1028	437	47	115	864	2575	400	469	183	201	266	71	217	335	362	
^h Total Even Number HC	1257	3417	190	6908	10068	7005	5467	975	2271	3435	2943	1305	6310	9993	1903	246	4049	1790	805	2773	
ⁱ CPI (25-33)	0.71	0.52	1.45	0.36	0.16	0.29	0.15	0.20	0.34	0.72	4.88	0.05	0.19	0.21	0.42	2.16	0.00	0.63	1.08	0.33	
^j Major Hydrocarbon	C18	C18	C27	C20	C34	C36	C34	C32	C16	C18	C33	C32	C36	C16	C18	C34	C16	C18	C18	C20	
^k n-Alkane/C16	NA	NA	NA	NA	NA	NA	17.32	NA	1.31	NA	NA	NA	NA	3.42	NA	NA	3.60	NA	NA	NA	
^l 1/CPI	2.35	4.21	0.82	656	14	6.81	12	20	19	3	1.14	3	13	54	9	0.92	57	8	2.41	7	
^m C31/C19	268	115	164	361	0.00	0.00	0.00	0.00	4666.51	2316.99	0.00	0.03	3092.18	2967.39	809.52	5511.60	0.00	769.79	1723.42	672.21	
ⁿ ACL	27.54	27.25	27.88	29.15	27.27	27.39	27.70	31.82	29.50	27.47	32.94	27.77	28.31	30.36	26.75	29.42	NA	27.97	27.71	28.23	
^o UNEP Guideline	lower	lower	lower	lower	higher	lower	lower	lower	lower	lower	lower	lower	lower	higher	lower	lower	lower	lower	lower	lower	lower

^a Sum of total aliphatic hydrocarbons range from C16 to C36; ^b Sum of aliphatic hydrocarbons range from C16 to C26; ^c Sum of aliphatic hydrocarbons range from C27 to C36; ^d The ratio of LMW over HMW ratio; ^e Sum of odd hydrocarbons range from C23 to C33; ^f Sum of C17 and C19; ^g Sum of Odd carbon numbers; ^h Sum of Even carbon numbers; ⁱ Carbon Preference Index, the ratio of average Odd to Even number carbons range from C25 to C33; ^j The hydrocarbon shows the highest concentration; ^k Ratio of total n-alkane over C16; ^l Ratio of unity over CPI; ^m Ratio of C31 over C19; ⁿ Average Carbon Chain value of odd carbon numbers from C25 to C33; ^o The concentration index limit of hydrocarbons (<10000 ng/g) in the environment.

mg), respectively. The average n-alkane concentration among stations calculated 4153 (ng/mg). The finding from this study is significantly higher than previously reported by other scientists around the world (Hostettler *et al.*, 1999; Tolosa *et al.*, 2004; Commendatore and Esteve, 2004 and Gao *et al.*, 2007) but consistent with findings from the east coast of Malaysia (Sakari *et al.*, 2008). As it is shown in Fig. 1, the location of Penang Bridge is located between stations "O" and "P" in the southern and northern part of the bridge, respectively.

The ratio of L/H n-alkane is an indicator of freshness of the released hydrocarbons in the environment and its sources. Predominant of lower molecular weight n-alkane exists in fresh oil while higher plants, marine animals and sedimentary bacteria show higher molecular weights more frequently. Likewise plankton sources, petroleum products also demonstrate equal lower and higher molecular weight n-alkane. Thus the ratio of L/H below the unity shows natural input from marine and terrestrial biogenic sources and around and above unity for petroleum (Commendatore *et al.*, 2000; Gearing *et al.*, 1976, Wang *et al.*, 2006). This is also confirmed that due to fast degradation of LMW n-alkane in crude oil or evaporation during distillation for petroleum products, the L/H ratio decrease significantly below the unity (Commendatore *et al.*, 2000; Stout *et al.*, 2002 and Wang and Fingas, 2005). The results from L/H ratio indicate that the study area receive fresh oil input in Stations D, I, J, N, O, Q, R and S; either from rivers discharge or by city drainage system and oil storage and transportation activities. It is seen that not only anthropogenic but also natural hydrocarbons discharges was release to the environment via rivers from the residential, industrial and agricultural activities in the watershed. This observation on petrogenic hydrocarbon in this study is consistent with report by Zakaria *et al.*, (2002). Depleted concentration of L/H indicates the lower concentration of LMW n-alkane where these are more bioavailable and fast degradable by chemical, physical and biological processes. Station T is revealed value around the unity which indicates the petroleum release into the environment (Gearing *et al.*, 1976). Station T is surrounded by oil storage facility in the north and marine transportation containers in the south therefore it is expected to release fresh oil into the study area. The rest of the stations are showing the values indicate a wide variety of hydrocarbon sources such as biogenic to petroleum input that is discussed in the following sections using combination of diagnostic ratios and matrix tables.

The short chain odd carbon numbers such as C₁₅, C₁₇, C₁₉ and C₂₁ produce by marine biogenic sources (Clark and Blumer, 1967; Blumer *et al.*, 1971) while

terrestrial and higher plants release longer odd carbon numbers range from C₂₅ to C₃₃ (Eglington *et al.*, 1962; Semoneit, 1978). The highest hydrocarbon proportion input from vascular plant that come from the watershed area were observed in stations K, P and C with 46.5, 52 and 55 percentage, respectively. Station "K" with the highest concentration of C₂₅-C₃₃ aliphatic hydrocarbon contributed more vascular plant input to the marine environment of the study area via river discharge. Stations D, N and Q were showed the lowest vascular plant concentration proportion (<2%) that also limited in total amounts of n-alkane input. Lack of marine biogenic sources in the study area is observed where almost all stations (except L) showed the value of zero. There are two possible interpretations for this phenomenon either the study area is highly polluted therefore less marine biogenic sources are available or it is subjected to rapid degradation after deposition (Prahl and Carpenter, 1984; Kvenvolden *et al.*, 1987). This is consistent with report from Johor Straits in Peninsular Malaysia (Sakari *et al.*, 2008; In press). Station L that is located away from rivers in shoreline is affected less by terrestrial input and maybe shows higher contribution of marine biogenic input.

As discussed earlier, the odd and even carbon numbers are leading the natural and anthropogenic input of the hydrocarbon load into the environment (Farrington and Tripp, 1977). Odd carbon numbers are usually appearing in lower concentrations than evens' (Matsumoto *et al.*, 1992; Harada *et al.*, 1995) especially near the developed area. Odd carbon numbers concentration in the study area showed that totally they are lower than evens'. Except station K that showed very close level as even carbon number the rest demonstrate significant differences. Although some of stations such as B, E, F and J are shown bigger values but comparing to the concentration of even carbon number of the same location is negligible. The ratio of CPI₍₂₅₋₃₃₎ as an index for odd and even carbon numbers was used very frequent by scientists (Bray and Evens, 1961; Eglington and Hamilton, 1967; Farrington and Tripp, 1977; Kennicutt *et al.*, 1987; Colombo *et al.*, 1989). In this study the CPI calculation was based on the following equation.

$$CPI_{25-33} = 0.5 * [(C_{25}-C_{33}) / (C_{24}-C_{32})] + [(C_{25}-C_{33}) / (C_{26}-C_{34})]$$

It is reported that CPI value close to one is sourced by recycled organic matters and/or marine micro organisms (Kennicutt *et al.*, 1987) as well as petroleum (Bray and Evens, 1961; Farrington and Tripp, 1977). Predominant of vascular plants input to the environment usually demonstrate the CPI values from 3 to 6 (Boehm and Requejo, 1986; Colombo *et al.*, 1989). In

this study the $CPI_{(25-33)}$ was shown that the natural input proportion is significantly lower than anthropogenic release (Fig. 2). Oil products usually reveal the same proportion of odd and even carbon numbers with minor changes of CPI around unity but when the natural inputs are predominant the values are getting higher. The reverse condition for anthropogenic release exists. Among stations, K and C are shown high CPI of 4.88 and 1.45, respectively, indicative of predominant of natural input mostly due to riverine input by Junjung and Jawi Rivers and Kerian Rivers, respectively but for the rest of the stations showed the numbers lower and around unity range from zero to 1.08 that represents the extremely anthropogenic inputs. From the base point of Penang Bridge (stations O and P), the CPI values changes in both sides irregularly indicate not constant and regular effects by Penang Bridge operation. This observation showed that a heavy vehicle traffic load over the Penang Bridge cannot severely affects the balance of n-alkane in the study area. This observation shows that atmospheric transport has less or no contribution to the n-alkane movement than lateral transport by rivers, drainage or direct oil release. It is observed that stations C and P demonstrate the lowest total n-alkane concentration therefore the value of CPI in mentioned stations are not contributed significantly by anthropogenic input due

to its geographical position or other physical phenomena. On the other hand the CPI from different locations and ecosystems could be varying. For instance, values from rivers and sea demonstrate different numbers (Jeng, 2006).

The carbon number of C_{31} is known to be an indication of land derived hydrocarbon while C_{19} presents the marine biogenic sources. The ratio of C_{31}/C_{19} use to identify the predominant of hydrocarbon input from land or sea basis. The value below 0.4 indicates the predominant of marine biogenic sources while numbers over 0.4 show land derived hydrocarbons (Moldowan *et al.*, 1985). In this study marine biogenic sources showed almost zero concentration while land derived was predominant. Although the ratio of C_{31}/C_{19} is not mathematically defined ($C_{19} = 0$), it is concluded that most of n-alkane are come from the land sources via river and drainage inputs. The only exception is station L which shows a defined number of 0.03 which is an indication of marine biogenic sources of hydrocarbon. This station showed the concentration of hydrocarbon below the half average of stations with CPI ratio less than unity and totally land derived hydrocarbon input.

The ACL shows the average chain length of hydrocarbons supposes to be constant in specific ecosystem while it receives hydrocarbons from the

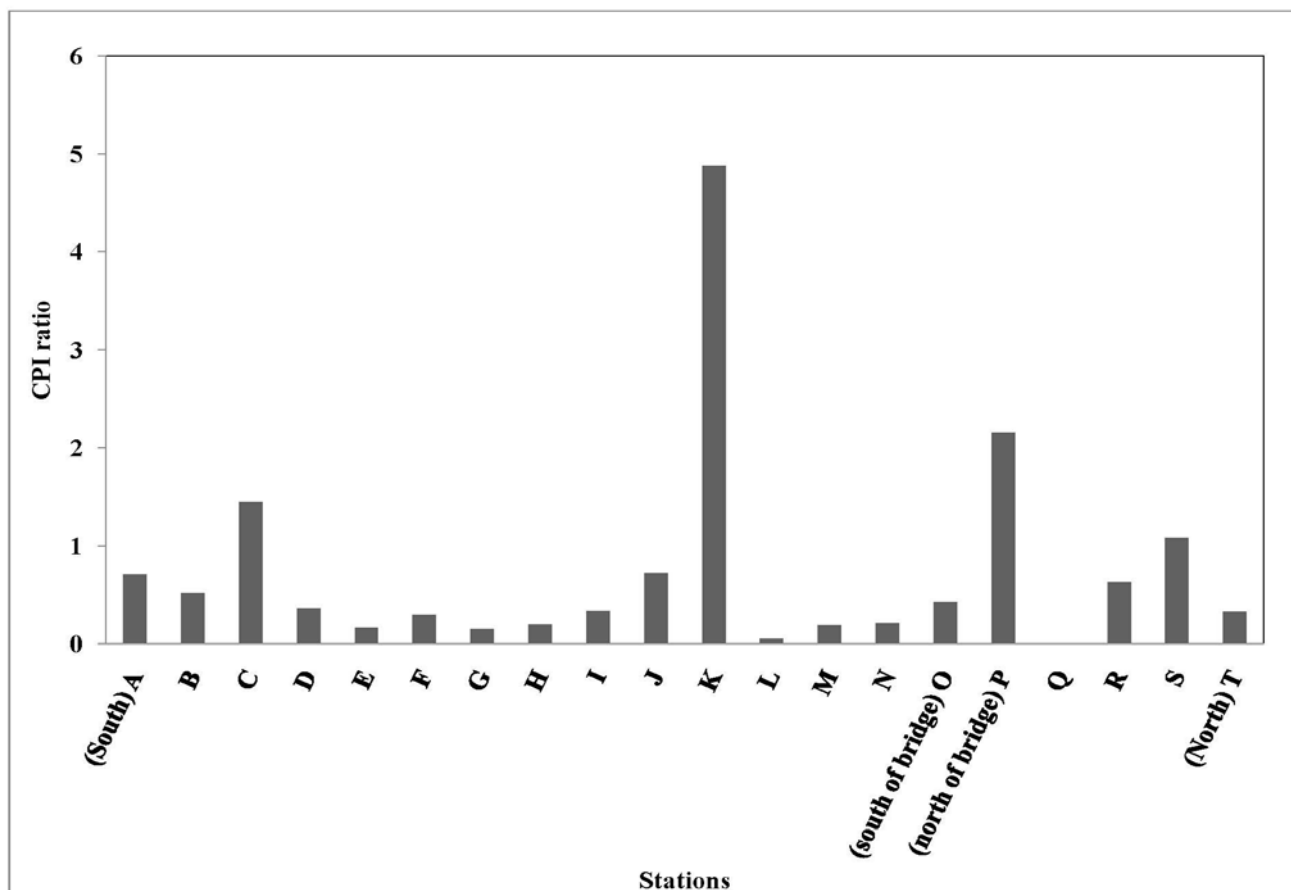


Figure 2. Carbon Preference Index (CPI) values among stations; Please see table 2 for definition of CPI.

same source. It describes the average number of carbon atoms per molecules based on the abundance of the odd carbon numbered higher plant n-alkane (Poynter and Eglington, 1990). This index value changes when the hydrocarbons with different ACL interfere to the total. In this case Jeng (2006) reported that petrogenic hydrocarbon decreases the ACL value to the lower numbers while non-affected area shows almost constant numbers. Constant ACL values reported from East Atlantic and crude oil samples (Rommerskirchen *et al.*, 2003) and Africa (Huang *et al.*, 2000). The ACL index in Prai Strait showed ranges from 26.75 to 32.94 which indicate 6.19 units of changes. This wide range of change in the study area shows the severe disturbances in the ecosystem due to heavy anthropogenic input where oil and its derivatives interfere to the ACL balance. It is also assumable that different rivers input carry out various ACL numbers to the stations (Cranwell, 1973) therefore it contribute to the total ACL numbers in each location. The highest and lowest ACL were observed from stations K and O (Station Q is excluded; ACL=0). So far station K showed the highest CPI (4.88) and high C_{25} - C_{33} (2565 ng/mg) odd hydrocarbon concentration. In Prai Strait the average ACL value calculated 28.55 and it is observed that 70% of stations are below the average level of this index. Jeng (2006) reported that the oil contamination with lower ACL values interfere with the normal ACL to the depleted values. Thus higher ACL seems to be totally natural while depleted levels show the anthropogenic input.

The highest concentration of n-alkane carbon number is defined as Major Hydrocarbon (MH) which contributes drastically in the total n-alkane (Broman *et al.*, 1987; Colombo *et al.*, 1989). It leads the total n-alkane to the specific direction of hydrocarbon load. This index is varying from one location to another. For instance, C_{21} which is usually predominant in marine biogenic sources was reported as the MH from Antarctica region (Harada *et al.*, 1995). In this study, it is found that except stations C and K which C_{27} and C_{33} are the most abundant hydrocarbons, the rest of stations are affected mostly by even carbon number such as C_{16} , C_{18} , C_{20} , C_{32} , C_{34} and C_{36} . The C_{16} , C_{18} and C_{20} present the oil input to the environment (Jacquot *et al.*, 1999; Broman *et al.*, 1987; Colombo *et al.*, 1989) which are abundant in 55% of stations such as A, B, D, I, J, N, O, Q, R, S and T. This observation in stations "O" can directly related to the Penang Bridge operation with oil leakage from the vehicles and flushing to the Prai Strait via daily heavy rain wash. Stations A and B are receiving the oil input from the watershed area via Kerian River and rest of stations can receive it likewise via rivers and drainage systems or oil operation activities. Station D, E, F and

G that show high to very high oil pollution receive the contaminants via Tengah River discharge and Sungai Jawi residential drainage. Junjung and Jawi Rivers discharge huge amount of water to the study area at stations H, I, J, and K that except K which shows higher plant input the rest of stations in this area indicate fresh, heavy and distilled oil. Station M and N showed high to very high anthropogenic hydrocarbon with the same sources as above that come from the busy city activities of Penang Area (mainland) from Juru River. Prai River also passes through heavy city activities and enters to the station S that showed low n-alkane concentration most probably due to high water volume and sluggish river flow. Stations R and T showed moderate oil input which is related to the adjacent oil activities by operation of oil storage tankers and marine shipping containers locations.

The information from MH is highly consistent (95%) with ratios of L/H and CPI. Where CPI and L/H showed petroleum sources of hydrocarbon input, the MH index definitely shows majority of C_{16} , C_{18} and C_{20} (Jacquot *et al.*, 1999; Broman *et al.*, 1987; Colombo *et al.*, 1989). In 2 stations of C and K that L/H and CPI showed biogenic input, consequently the MH appeared to be predominant by C_{27} and C_{33} . For the rest of the stations with L/H and CPI values below the unity the MHs are C_{32} , C_{34} and C_{36} . Degraded crude oil or heavy oil signature were concluded in stations A and B.

Chromatograms can reveal many characteristics of samples, whether it is degraded or still fresh (Farrington and Quinn, 1973). It is also indicate the presence petrogenic input or biodegradations (Brassel and Eglington, 1980). UCM also indicate the weathering condition of the environmental samples (Chandru *et al.*, 2008). The molecular weight and in sequence the boiling temperature of the natural and petroleum hydrocarbons are so different, therefore different UCM hump together with location of the UCM appearance occurs. In this study most of the UCM humps were appeared ranging from C_{20} to C_{32} . Fresh oil reveals no hump but degraded oil usually comes up with humps that show the biodegradation.

From the chromatograms, no pristane and phytane were found. The existence of pristane and phytane in the aliphatic hydrocarbon chromatograms is an indication for degradation of C_{17} and C_{18} . As it is clear no C_{17} almost reported from all stations and C_{18} were reported very frequently in this study. Absence of pristane and phytane in this research can conclude that the fresh input of hydrocarbons are exists.

Based on the above mentioned indications, it is concluded that Prai Strait receives low to very high range of hydrocarbon pollution from different sources. A combination of different applied ratios in this study

is shown in Table 3. In this matrix table, all of the possible interpretations of each diagnostic tool were placed. The summary of the table showed that usually hydrocarbons from natural input appear in low concentration as it is observed in stations C and P (NAS, 1985). The only exception in this research is for station K which high amount of natural input with the terrestrial higher plant hydrocarbon signature discharges via river input. Almost the rest of stations receive low to very high anthropogenic input to the study area. The summary of the matrix table demonstrate that fresh oil, petroleum distillate, degraded oil and heavy oil contribute to the pollution load of the study area (Table 3).

The predominant of hydrocarbon ranges from C_{16} to C_{20} were observed in all samples that represent fresh and distillate oil and C_{32} to C_{36} for samples those show degraded or heavy oil input. The ACL ratio has also indicated that heavier oil releases are consistent with higher ACL values. It is concluded that 85 percent

of the sampling stations receive oil derivatives in different forms which is an indication of a busy harbor (UNEP, 1995).

Statistical tool of scattered plot graph applied in this study showed that lower CPI and L/H are representing oil derivatives, petroleum distillate and degraded oil while higher L/H ratios in the same CPI values grouped for fresh oil. An increase in CPI in lower values of L/H also revealed terrestrial plant input in few studied station (Fig. 3).

The appearance of wide range anthropogenic input among stations was plotted in Fig. 3 for study area where the increase of CPI is not consistent with ACL raise. While there is no marine biogenic sources in the study area (severe absence of C_{17} and C_{19}), the natural hydrocarbon input is highly related to the terrestrial plants input. Hence, the linear regression of ACL and CPI appears close to the unity; but the results of this statistical test showed poor regression between these 2 factors ($R^2=0.08$) therefore it is concluded that the

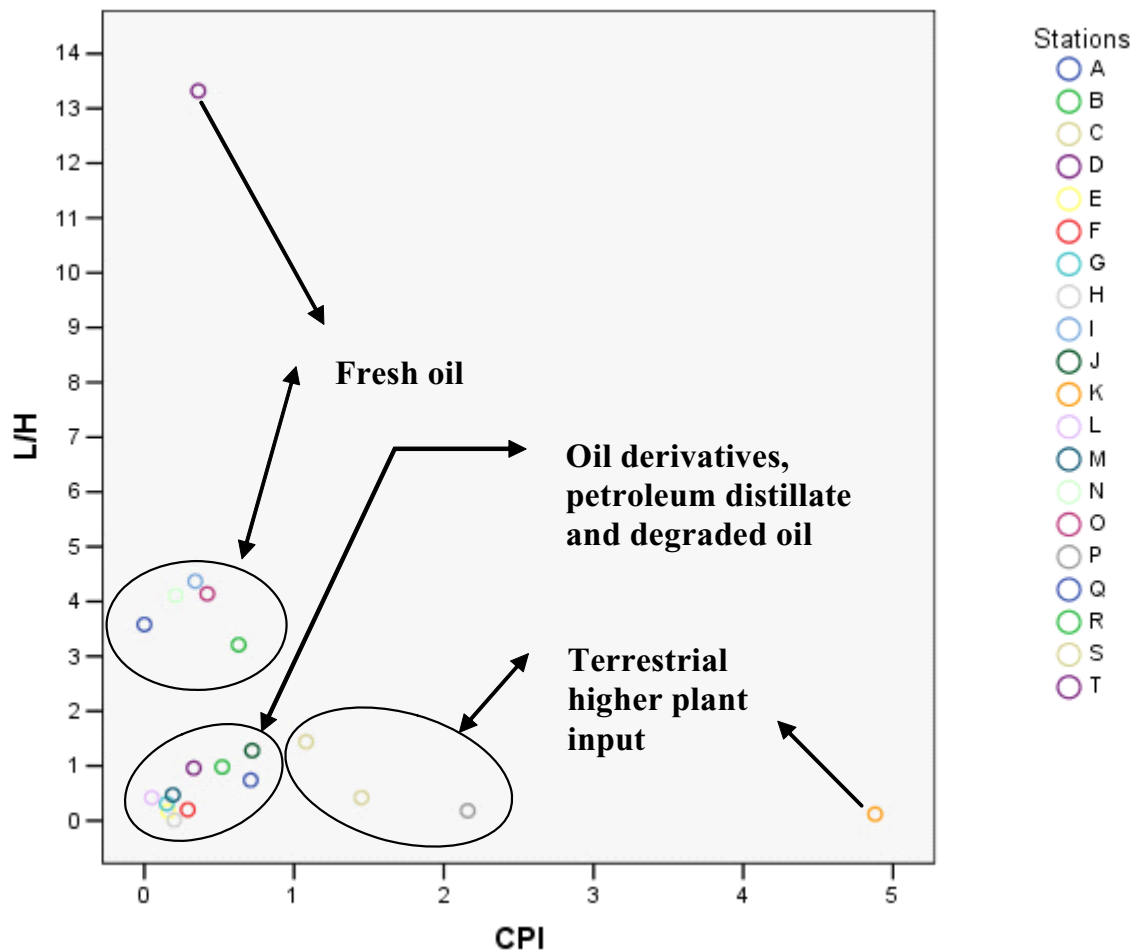


Figure 3. A scattered plot of two independent variables of CPI and L/H as source identification tool, Please see Table 2 for definition of CPI and L/H.

Table 3. Matrix table of combination of n-Alkane ratios and indexes

Stations	A (South)	B	C	D	E	F	G	H	I	J	K	L	M	N	O South of the bridge	P North of the bridge	Q	R	S	T (North)	
^a Total n-alkane ng/mg	1792	4229	421	7013	10770	8033	5904	1021	2386	4299	5518	1705	6780	10176	2104	512	4120	2008	1140	3135	
^b L/H ratio	hp, ma, sb, ho dco, pd	pet, pl hp, ma, sb, ho dco, pd	hp, ma, sb, ho dco, pd	fo	hp, ma, sb, ho dco, pd	hp, ma, sb, ho dco, pd	hp, ma, sb, ho dco, pd	hp, ma, sb, ho dco, pd	fo	fo	fo	hp, ma, sb, ho dco, pd	hp, ma, sb, ho dco, pd	fo	fo	hp, ma, sb, ho dco, pd	fo	fo	fo	fo	pl, pet
^c C31/C19	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter	ter
^d CPI (25-33)	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth	anth
^e Major Hydrocarbon	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil	oil
^f ACL	ba	ba	ba	aa	ba	ba	ba	aa	aa	ba	aa	ba	a	aa	ba	aa	NA	ba	ba	ba	a
^g UNEP	Lower	lower	lower	lower	higher	lower	lower	lower	lower	lower	lower	lower	lower	higher	lower	lower	lower	lower	lower	lower	lower
^h UCM*	mod hump	mod hump	low hump	low hump	high hump	high hump	high hump	low hump	low hump	low hump	high hump	mod hump	high hump	mod hump	low hump	low hump	low hump	low hump	low hump	low hump	low hump
summary	mod dco, pd	mod pet hp sb	low hp sb	high heavy fo	very high dco, pd	high dco, pd	high dco, pd	mod ho, dco, pd	mod fo	mod fo	mod fo	high hp	mod fo	very high Heavy fo	mod fo	low hp	high fo	mod fo	mod fo	mod fo	mod oil

See Table 2 for definitions of “a” to “h”. hp, higher plant input; ma, marine animals input; sb, sedimentary bacteria; pet, petroleum; pl, plankton; fo, fresh oil; ho, heavy oil; dco, degraded crude oil; pd, petroleum distillate; ter, terrestrial; anth, anthropogenic; aa, above; nat, natural; average; a, average; mod, moderate.

*UCM classifications are based on observation of humps height and surface and are not calculated.

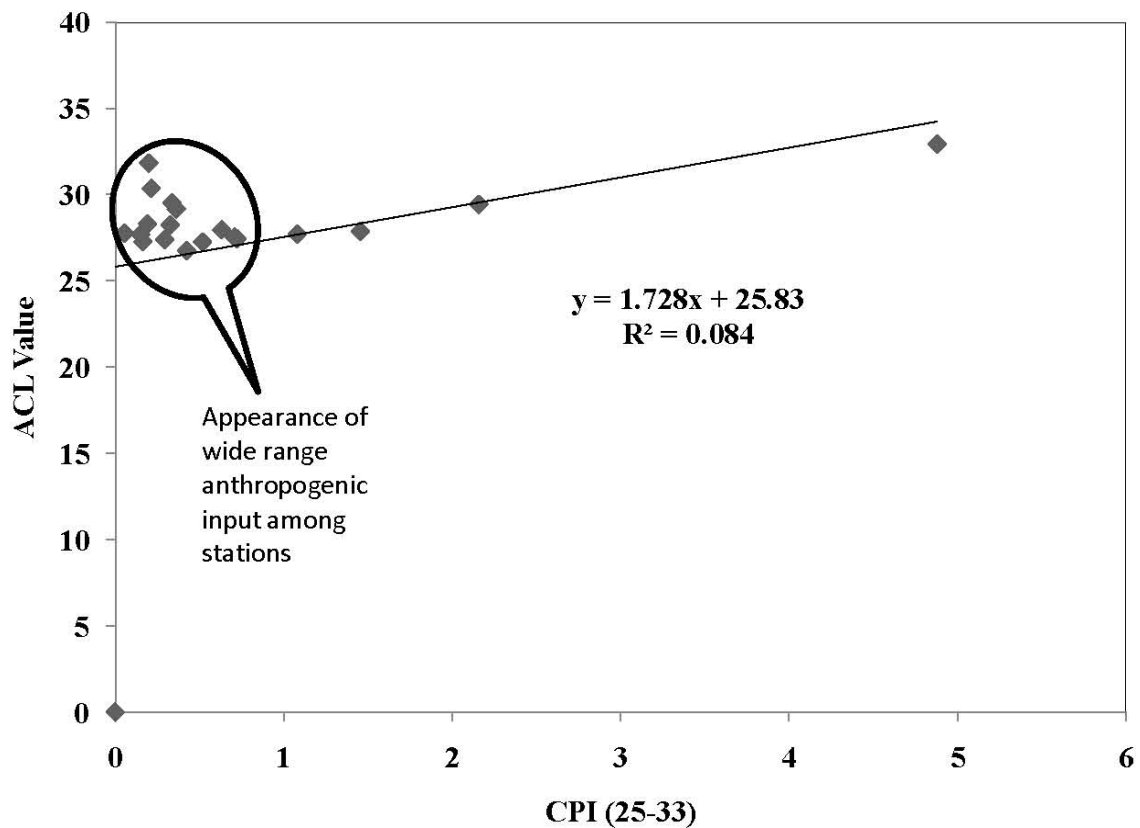


Figure 4. Linear regression analysis plot of CPI and ACL as dependent variables: Indication of anthropogenic input vs low biogenic release.

increase of CPI is not resulted as ACL raise (Fig. 4). The ACL values that normally raise with the increase of CPI from terrestrial input possibly affect by wide spread oil and its derivatives input to the study area therefore poor linear regression was observed in this study as it was stated before by Jeng (2006).

Penang Island and Prai Strait are important industrial and transportation hub in Malaysia and South-east Asia which play active role in Malaysian economy since independence in 1957 and especially in last three decades. High level of hydrocarbon pollution was apparently foreseeing in advance in this study area as a hypothesis where results of this study has approved the idea, accordingly. Although environmental evidences and incidents have been continuously demonstrating bright future for the environment in Peninsular Malaysia, it is expected that the governmental and non-governmental organizations conduct an integrated approach to monitor, control and reduce the pollution load in Peninsular Malaysia.

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