Distribution and Sources of Aliphatic Hydrocarbons in Sediments from Sadong River, Sarawak, Malaysia

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Abstract

Twenty-one surface sediment samples collected from Sadong River, Sarawak were analysed for aliphatic hydrocarbons. These hydrocarbons were recovered from sediment by Soxhlet extraction and then analysed using gas chromatography equipped with mass spectrometer (GC-MS).

The sediments collected from Sadong River have high concentrations of total aliphatic hydrocarbons which ranged from 310.41 to 1296.43 μg/g. Evaluation of various n-alkane indices such carbon preference index (CPI: 1.32 to 1.98) and average chain length (ACL: 26.26-27.19) showed that there was a predominance of petrogenic sources of n-alkanes in the river and biogenic origin n-alkanes from vascular plants. The petrogenic source of n-alkanes are predominantly heavy and degraded oil with fresh oil inputs. It is believed that the hydrocarbons originated from both natural and anthropogenic sources. The hydrocarbons were mostly transferred by lateral input than atmospheric movements.

Keywords: Aliphatic hydrocarbon, carbon preference index (CPI), gas chromatography-mass spectrometer (GC-MS), Sadong River, Soxhlet extraction.

Introduction

The aquatic environment serves as an important sink for organic matter. The source and distribution of organic matter in the rivers are of great interest globally because they are primary indicators of current pollution levels. The major sources of hydrocarbon in sediments are natural sources and anthropogenic sources[1]. Sediment organic matter and hydrocarbon compounds may be derived from terrestial vascular plants and marine phytoplanktons[2,3]. The Sadong river covers a large area of the Kota Samarahan- Asajaya district. It receives a major freshwater input from upland towards Serian and it drains into main river channels and distributaries from the meandering along Satubong to the estuary finally into the ocean[4].

Petroleum hydrocarbons are widespread contaminants and may result to environmental problems when found in high concentration. Their effects may be toxic, mutagenic and carcinogenic as a result of their persistence and bioaccumulation[5]. Aliphatic hydrocarbons found in the environmental samples are usually as a result of direct and indirect discharges into rivers via lateral and atmospheric transportation[6]. Aliphatic hydrocarbons are ubiquitous sedimentary contaminants due to their tendency to accumulate in sediments[7].

The environs of the study area are characterized by extensive economic resources such as fishing, mangrove swamps, tourism spots and peat swamps. Many ratios and indexes have been used to identify the sources of *n*-alkane in the environment[6] such as carbon preference index (CPI), major hydrocarbon (MH), average carbon length (ACL) and ratio of low molecular weight to high molecular weight (LMW/HMW). The objective of this study is to investigate the spatial distribution of petroleum hydrocarbons and determine the possible sources of petroleum hydrocarbon pollution in sediments from Sadong River.

Material and Methods

A total of 21 surface sediments were collected in March 2017 and March 2018, these samples were collected from seven stations (Fig. 1). These samples were collected using a Wedepohl stainless steel grab sampler, transferred into aluminium foil and kept frozen until further analysis at -40^{o} C. All samples were analysed in the Gas Chromatography Laboratory, Faculty of Resource Science, Universiti Malaysia Sarawak. Sediments were allowed to thaw at room temperatures and 10 grams of sediment was weighed into cellulose thimbles. Before the extraction, sediments samples were spiked with internal standards of eicosene for aliphatic fractions. The sediments were subjected to Soxhlet extraction using 250 ml of dichloromethane (DCM).

The extracts were dried with rotary evaporator and nitrogen gas, they were fractionated on a silica gel column by elution with 30 ml of *n*-hexane for the *n*-alkanes, 20ml of hexane and DCM (3:1) and DCM[5]. Identification and quantification of the aliphatic compounds were carried out using Shimadzu QP2010 gas chromatograph-mass spectrometer fitted with a SGE BPX-5-fused silica capillary column. These *n*-alkane fractions were analysed using GC-MS at 50^{o}C for 5 minutes and increased to 300^{o}C at 10 minutes. The verification of peaks was based on the retention time compared to those of external standards.

Results and Discussion

The total *n*-alkanes (TNA) concentrations in surface sediments along Sadong River are listed in table 2. The *n*-alkanes consist of odd and even carbon numbers with no alkyl branch or substitutes. The odd number carbons of aliphatic hydrocarbons were derived from biogenic sources while the even carbon numbers were usually derived from the anthropogenic sources. C_{25}-C_{33} hydrocarbons were produced from terrestial vascular plants[1]. The lower molecular weight hydrocarbons within range of C_{12} to C_{19} especially C_{17} have biogenic origin mainly from algae and cyanobacteria[8]. The *n*-alkane is one of the earlier molecular markers for the identification of the hydrocarbon pollution and its sources[6].

The total concentrations of C_9 to C_{33} ranged from 310.41 to 1296.43 μg/g in the sediments from Sadong River (Table 4). The highest TNA was found in SR3 followed by SR2 and SR5. The high concentration of TNA in SR3 was due to ferry service and proximity to agricultural discharges, this area is heavily loaded with suspended solids from terrestial runoff[2]. The source of *n*-alkanes in sediments was determined by using the molecular characteristic indicators of the compounds.

Generally, LMW *n*-alkanes indicate fresh oil inputs considering abundance of LMW *n*-alkanes in petroleum[3]. A ratio of LMW to HMW *n*-alkanes less than unity indicates higher heavy and degraded oil as well as biogenic inputs from vascular plants and aquatic fauna whereas the ratio ≥1 indicates a sign of fresh oil origin[1]. The stations were characterized with fresh oil origin.

The terrigenous aquatic ratio (TAR) which is the ratio of (C_{27}+C_{29}+C_{31}) over (C_{17}+C_{19}+C_{21}) was between 1-2 in all the stations with the exception of SR4 and SR7 which was higher than 2. Higher molecular weight *n*-alkanes within the range C_{20} to C_{33} with predominance of odd carbon atoms maximizing at C_{25} are indicators of higher plant wax.[9]

The carbon preference index (CPI) which is the ratio between odd numbered *n*-alkanes and even numbered *n*-alkanes was determined in this study. CPI is useful in understanding the sources of hydrocarbons in geological samples. Generally, *n*-alkanes with the CPI= 5 to 10 originated from land plant material and they show a predominance of carbon with odd number chains whereas the CPI value of human/anthropogenic origin is CPI=1. This value is also thought to indicate greater inputs from marine microorganisms and/or recycled organic matter. The CPI values of Sadong River ranged from 1.32 to 1.98. Low CPI values between 1-2 were observed in all surface sediments due to the mixed inputs from petroleum pollution and also organic matter from autochthonous, microorganisms and terrestrial higher plant detritus[3,5].



Fig. 1: Map showing sampling stations of the study area

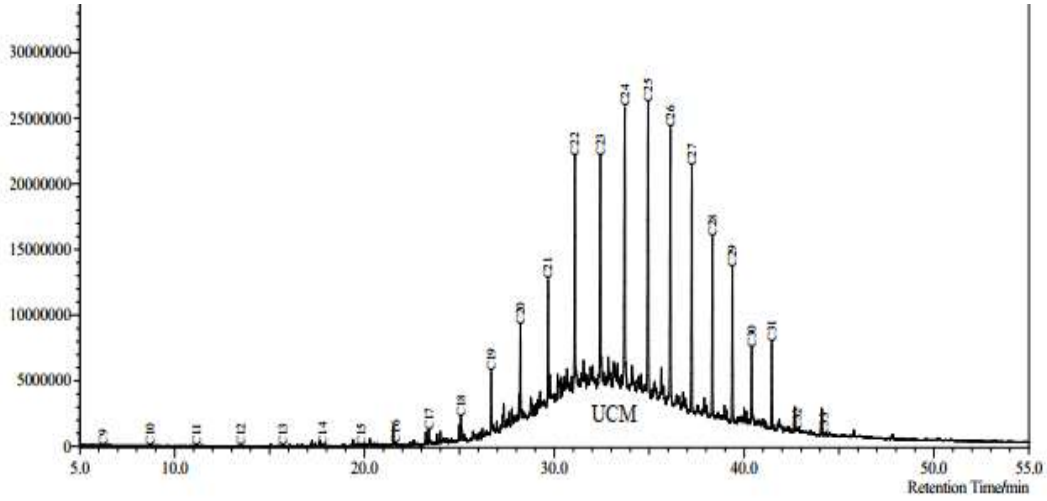


Figure 2: Gas chromatogram of aliphatic hydrocarbon in surface sediments from SR1

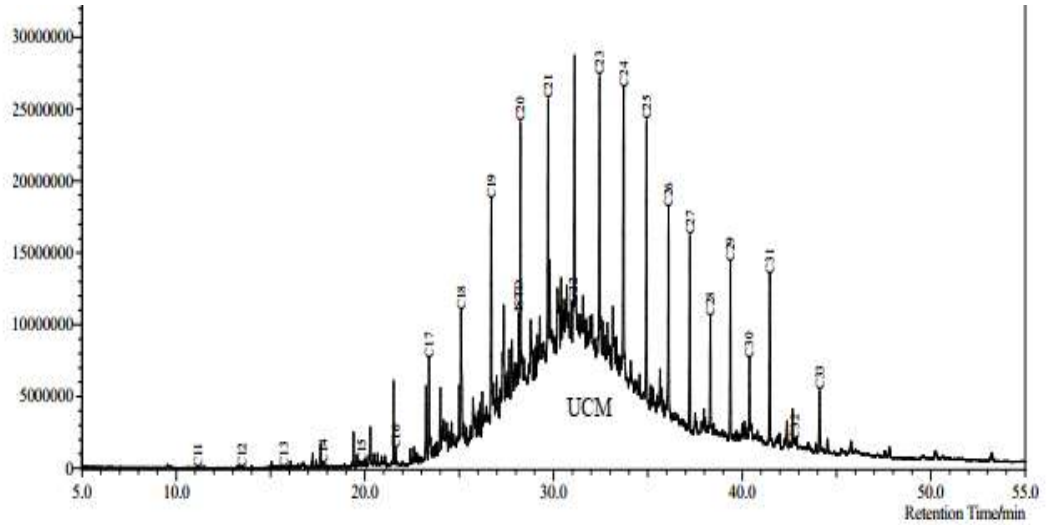


Figure 3: Gas chromatogram of aliphatic hydrocarbon in surface sediments from SR2

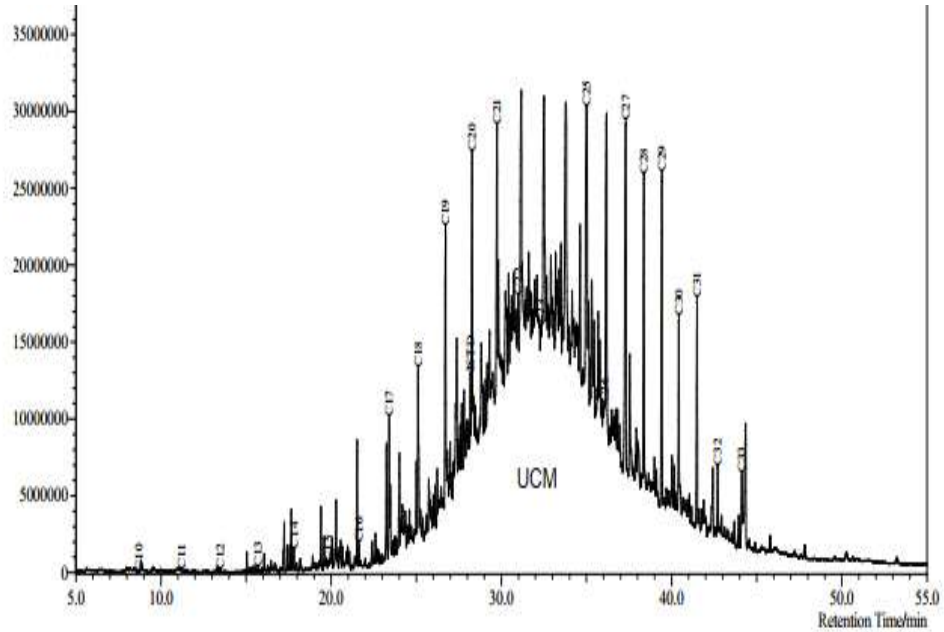


Figure 4: Gas chromatogram of aliphatic hydrocarbon in surface sediments from SR3

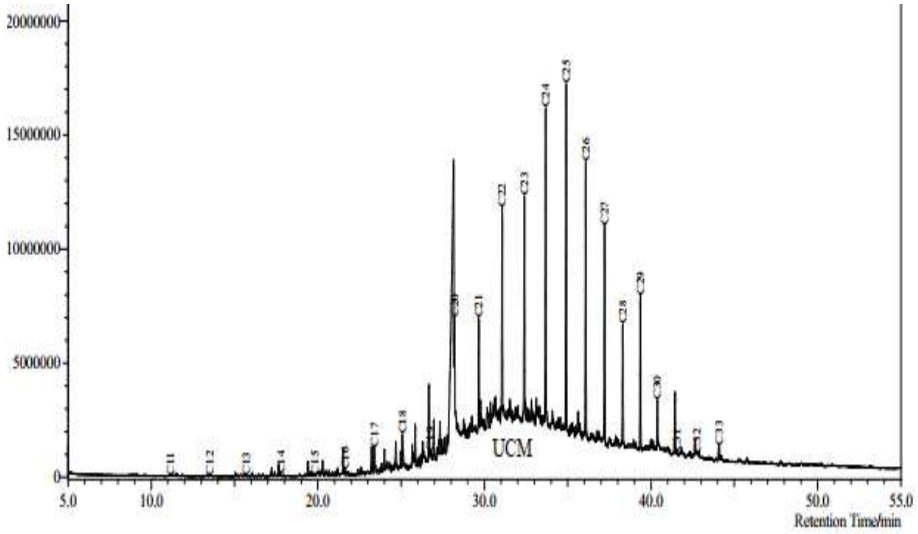


Figure 5: Gas chromatogram of aliphatic hydrocarbon in surface sediments from SR4

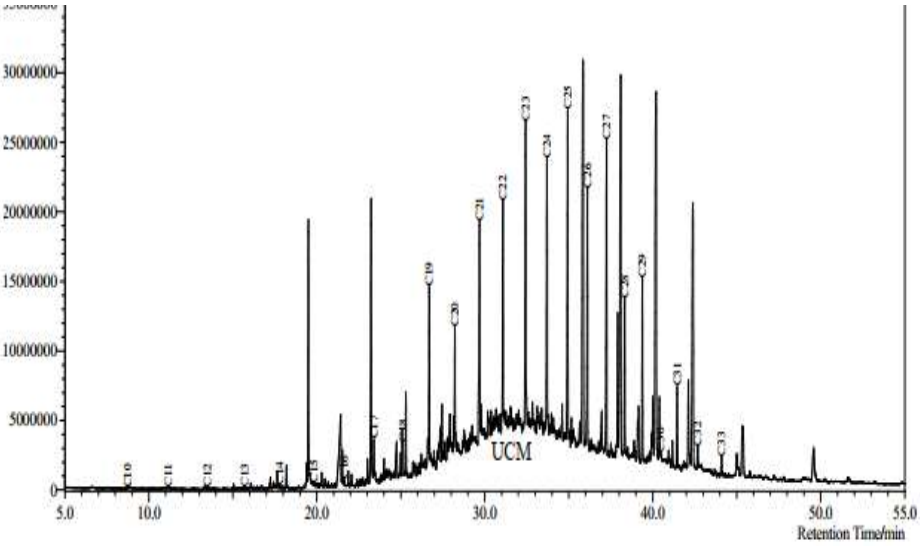


Figure 6: Gas chromatogram of aliphatic hydrocarbon in surface sediments from SR5

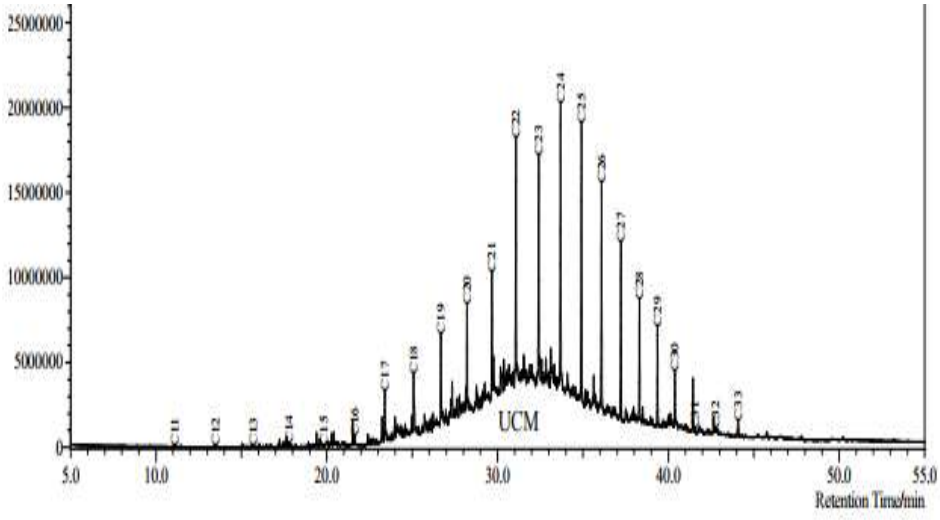


Figure 7: Gas chromatogram of aliphatic hydrocarbon in surface sediments from SR6

The ratio of LMW(C_{10}-C_{23}) to HMW (C_{24}-C_{33}) *n*-alkanes in surface sediments of Sadong River ranged between 0.19-1.07. Generally, LMW *n*-alkanes indicate fresh oil inputs considering abundance of LMW *n*-alkanes in petroleum[3]. The ratios of LMW to HMW *n*-alkanes for all samples were less than unity except SR2 which indicates higher heavy and degraded oil as well as biogenic inputs from vascular plants and aquatic fauna.

The ratio of LMW/HMW was ≥1 which indicated a sign of fresh oil input observed at SR2 due to human activities in the area[1,10]. Active biodegradation of LMW *n*-alkanes in the sediments can be the reason behind the low values for the ratios of LMW to HMW *n*-alkanes in the sediments from several sampling sites[11].

The ACL of *n*-alkanes ranged between 26.26-27.19 in surface sediments of SR2 and SR3. This range may be a sign of petroleum inputs into these sampling sites. Generally, higher ACL is a sign of biogenic source of hydrocarbons whereas the lower values are attributed to anthropogenic inputs. Wider range of values has been reported in surface sediments from the Prai River in Malaysia with ACL values ranging between 26.75-32.94[1] while the ACL values for river sediments of north-eastern and North western Taiwan showed narrower range between 29.6-29.8 and 29.2-30.5 respectively[12].

MH can also be an indicator of hydrocarbon sources. Generally, a dominance of HMW over LMW *n*-alkanes was found in the sediment samples from Sadong River. Among LMW *n*-alkanes, a domination of odd carbon numbers was detected over even carbon numbers which showed biogenic sources over fresh inputs of petroleum[6]. MH for LMW *n*-alkanes was within C_{20}-C_{23} with C_{22} as the majority whereas MH for HMW *n*-alkanes was majorly C_{25}. The dominance of odd over even carbon numbers showed the higher inputs of *n*-alkanes with vascular plant origin.

Unresolved complex mixture (UCM) was detected in all surface sediments of Sadong River in varying extents. Figures 3-8 show the position of UCM in a typical chromatogram for *n*-alkanes in the sediments. The presence of UCM in the aliphatic fraction can be used to indicate the contribution of degraded oil in the environment[13]. UCM composed of acyclic or branched alkanes which are more resistant to biodegradation than *n*-alkanes, therefore, UCM occurred in the environment after *n*-alkanes degradation[14]. The presence of UCM can be an indication sign of weathered oil in the environment.[5]

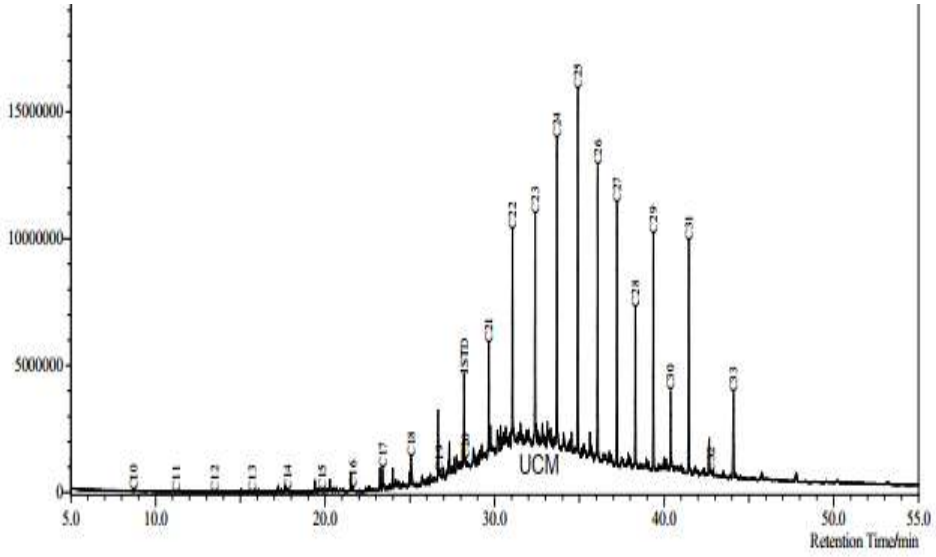


Figure 8: Gas chromatogram of aliphatic hydrocarbon in surface sediments from SR7

Table 1
Sampling points and their coordinates

Sampling Station	Locations	Coordinates
SR1	Sebangan	N 01°33¹03.2[11] E110°45¹56.4[11]
SR2	Sadong Jaya	N 01°30¹51.0[11] E110°44¹24.6[11]
SR3	Sungai Buloh	N 01°27¹19.4[11] E110°41¹08.1[11]
SR4	Simunjan	N 01°24¹19.0[11] E110°40¹10.5[11]
SR5	Gedong	N 01°14¹38.5[11] E110°40¹42.5[11]
SR6	Sebemban	N 01°14¹42.1[11] E110°38¹09.5[11]
SR7	Serian	N 01°09¹36.3[11] E110°33¹58.0[11]

Table 2
Concentrations of aliphatic hydrocarbons (μg/g) in surface sediment from Sadong River

***n*-Alkanes**		**Stations**					
	SR1	**SR2**	**SR3**	**SR4**	**SR5**	**SR6**	**SR7**
C_9	0.31	0.42	0.63	0.39	1.75	0.84	0.79
C_{10}	0.33	0.21	0.69	0.45	1.15	0.01	0.13
C_{11}	0.29	0.18	1.15	0.34	1.21	0.03	0.05
C_{12}	0.03	0.37	1.01	0.76	0.99	0.16	0.07
C_{13}	0.14	0.42	1.16	0.24	0.66	0.16	0.08
C_{14}	0.40	1.40	7.33	0.45	1.52	0.72	0.35
C_{15}	0.07	0.39	0.85	0.14	0.23	0.15	0.07
C_{16}	1.58	3.85	6.46	0.81	2.73	1.97	0.54
C_{17}	3.72	24.66	32.10	1.43	12.03	10.76	0.92
C_{18}	10.65	53.84	67.20	8.88	9.83	21.05	6.42
C_{19}	17.80	70.32	106.56	2.56	46.97	4.32	1.44
C_{20}	5.96	105.12	138.97	17.82	2.35	5.24	2.37
C_{21}	47.50	31.65	49.98	26.73	75.93	41.20	21.41
C_{22}	80.03	31.03	119.93	38.75	76.10	62.40	33.74
C_{23}	69.12	97.82	48.06	41.29	122.85	49.75	28.11
C_{24}	8.46	39.74	80.33	44.69	80.11	60.38	49.83
C_{25}	115.23	94.82	233.44	52.29	102.88	69.96	50.39
C_{26}	90.25	73.18	36.55	38.01	73.28	51.69	39.77
C_{27}	73.98	59.18	173.78	34.86	87.88	38.44	31.37
C_{28}	50.84	30.99	117.90	23.28	43.33	24.01	3.80
C_{29}	44.75	51.67	6.59	26.20	49.89	26.06	28.52
C_{30}	4.71	12.13	26.12	1.62	7.61	6.45	1.18
C_{31}	2.98	17.15	24.59	1.86	3.45	1.46	1.83
C_{32}	1.22	2.70	10.36	1.51	2.84	1.46	1.11
C_{33}	5.51	10.45	4.69	2.98	5.35	3.22	6.11

Table 3
Aliphatic hydrocarbon composition and indices in surface sediments from Sadong River

			Stations				
	SR1	**SR2**	**SR3**	**SR4**	**SR5**	**SR6**	**SR7**
[a]Total *n*-alkanes (μg/g)	635.89	813.70	1296.43	368.33	812.92	481.90	310.41
[b]LMW *n*-alkanes (μg/g)	237.63	421.27	581.45	140.65	354.56	197.93	95.71
[c]HMW *n*-alkanes(μg/g)	397.95	392.01	714.35	227.29	456.61	283.14	213.91
[d]L/H ratio	0.60	1.07	0.81	0.62	0.78	0.70	0.19
[e]CPI	1.60	1.71	1.98	1.46	1.58	1.32	1.91
[f]ACL	26.60	27.19	26.26	26.77	26.76	26.55	27.00
[g]TAR	1.76	1.01	1.09	2.05	1.05	1.17	2.60
[h] MH	C_{25}	C_{20}	C_{25}	C_{25}	C_{23}	C_{25}	C_{25}

[a] Sum of concentration of *n*-alkanes from C_9 to C_{33}

[b] Sum of low molecular weight hydrocarbon from C_{10} to C_{23}

[c] Sum of high molecular weight from aliphatic hydrocarbons C_{24} to C_{33}

[d] Ratio of LMW alkanes to HMW alkanes

[e] Carbon Preference Index = $\frac{1}{2}\left(\frac{nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33}}{nC_{24}+nC_{26}+nC_{28}+nC_{30}+nC_{32}}+\frac{nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33}}{nC_{26}+nC_{28}+nC_{30}+nC_{32}+nC_{34}}\right)$

[f] Average Carbon Chain Length = $\left(\frac{25(nC_{25})+27(nC_{27})+29(nC_{29})+31(nC_{31})+33(nC_{33})}{nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33}}\right)$

[g] Terrigenous/Aquatic ratio = $\frac{nC_{27}+nC_{29}+nC_{31}}{nC_{17}+nC_{19}+nC_{21}}$

[h] Major Hydrocarbon

Table 4
Relative concentration (μg/g) and indices of *n*-alkanes in the sediments from different Rivers

***n*-Alkane Indices**	**Location**				
	a	**b**	**c**	**d**	**e**
	Neuquen, Argentina	**Alagoas, Brazil**	**Tyne, UK**	**Taiwan, Taiwan**	**Sadong, Malaysia**
LMW/HMW	0.04-1.19	nd	nd	nd	2.45-3.75
Overall CPI	1.16-14.36	2.9-6.8	1.8-6.4	1.9-8.96	1.32-1.98
ACL	-	28.5-29.4	28.5-29.5	29.2-30.5	26.26-27.19
MH	C_{29}	C_{31} and C_{18}	C_{31}	C_{31}	$C_{20,}$ C_{23} and C_{25}
C17/Pr	0.2-6.95	nd	0.14-0.42	1.17-12.5	nd
C18/Pr	0.71-5.24	nd	nd	0.45-4.64	nd
Pr/Ph	0.19-1.12	nd	3.48-7.86	0.82-2.35	nd
∑n-alkanes	410-54,050	3500-20,600	6500-26,600	1270-57,780	310-1296

[a]Monza et al[15]; [b]Silva et al[16]; [c]Ahad et al[17]; [d]Jeng[12]; [e]This study

Table 5
Relative concentration (μg/g) and indices of *n*-alkanes in the sediments from different Rivers in Malaysia

***n*-Alkane Indices**	**Location**		
	Penang[1]	**West Coast[2]**	**Sadong River[3]**
LMW/HMW	0.01-13.32	0.15-1.26	2.45-3.75
Overall CPI	0.00-1.22	0.35-2.11	1.32-1.98
ACL	26.75-32.94	26.74	26.26-27.19
MH	C_{18} and C_{20}	C_{29}	$C_{20,}$ C_{23} and C_{25}
C17/Pr	nd	0.38-2.52	nd
C18/Pr	nd	0.29-4.80	nd
Pr/Ph	nd	0.65-1.51	nd
Total *n*-alkanes (TNA)	421,000-10,770,000	27,945-254,463	310-1296

nd = not determined; [1]Sakari et al[1]; [2]Vaezzadeh et al[5]; [3]This Study

Conclusion

High concentrations of *n*-alkanes were detected in the sediments from Sadong River. The highest concentrations of *n*-alkanes were found in the midstream. Anthropogenic sources of *n*-alkanes in this location is majorly land-based especially from the activities around the banks of the river. Dominance of *n*-alkanes originating from vascular plants was observed with a significance of HMW *n*-alkanes with odd carbon numbers in the sediments. ACL and CPI indicated the dominance of *n*-alkanes originating from vascular plants especially in the locations.

TAR values showed the importance of terrestial plant over biogenic origin *n*-alkanes in the sediments. The LMW/HMW showed that the dominance of higher molecular weight *n*-alkane in all sample station with value <1 except for SR2 with a value >1 which indicates that the petroleum was released into the environment.

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References

1. Sakari M., Zakaria M.P., Junos M.B.M., Annuar N.A., Yun H.Y., Heng Y.S., Syed Zainuddin S.M.H. and Chai K.L., Spatial distribution of petroleum hydrocarbon in sediments of major rivers from east coast of peninsular Malaysia, *Coastal Marine Science*, **32**, 9-18 **(2008a)**

2. Tahir N.M., Pang S.Y. and Simoneit B.R.T., Distribution and sources of lipid compound series in sediment cores of the southern South China Sea, *Environmental Science and Pollution Research*, **22(10),** 7557-7568 **(2015)**

3. Commendatore M.G., Nievas M.L., Amin O. and Esteves J.L., Sources and distribution of aliphatic and polyaromatic hydrocarbons in coastal sediments from the Ushuaia Bay (Tierra del Fuego, Patagonia, Argentina), *Marine Environmental Research*, **74**, 20-31 **(2012)**

4. Bryant W., Naturalist in the river: The life and early writings of Alfred Russel Wallace, New York, Universe Inc., 192 **(2003)**

5. Vaezzadeh V., Zakaria M.P., Shau-Hwai A.T., Ibrahim Z.Z., Mustafa S., Abootalebi-Jahromi F., Masood N., Magam S.M. and Alkhadher S.A.A., Forensic investigation of aliphatic hydrocarbons in the sediments from selected mangrove ecosystems in the west coast of Peninsular Malaysia, *Marine Pollution Bulletin*, **100(1)**, 311-320 **(2015)**

6. Sakari M., Zakaria M.P., Lajis N.H., Mohamed C.A.R., Bahry P.S., Anita S. and Chandru K., Characterization, distribution, sources and origins of aliphatic hydrocarbons from surface sediment of Prai Strait, Penang, Malaysia: A widespread anthropogenic input, *Environment Asia*, **2**, 1-14 **(2008b)**

7. Yusoff H.B., Assim Z.B. and Mohamad S.B., Aliphatic Hydrocarbons in surface sediments from south china sea off Kuching division, Sarawak, *The Malaysian Journal of Analytical Sciences*, **16(1),** 1-11 **(2012)**

8. Meyers P.A., Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes, *Organic Geochemistry*, **34**, 261-289 **(2003)**

9. Wang Y., Fang X., Zhang T., Li Y., Wu Y., He D. and Wang Y., Predominance of even carbon-numbered n-alkanes from lacustrine sediments in Linxia Basin, NE Tibetan Plateau: implications for climate change, *Applied Geochemistry*, **25**, 1478-1486 **(2010)**

10. Wang Z., Stout S.A. and Fingas M., Forensic fingerprinting of biomarkers for oil spill characterization and source identification, *Environmental Forensic*, **7**, 105-146 **(2006)**

11. Jeng W.L. and Huh C.A., Lipids in suspended matter and sediments from the East China Sea Shelf, *Organic Geochemistry*, **35**, 647-660 **(2004)**

12. Jeng W.L., Higher plant n-alkane average chain length as an indicator of petrogenic hydrocarbon contamination in marine sediments, *Marine Chemistry*, **102**, 242-251 **(2006)**

13. Simoneit B.R.T., Biomass burning- a review of organic tracers for smoke from incomplete combustion, *Applied Geochemistry*, **17**, 129-162 **(2002)**

14. Hu L., Guo Z., Feng J., Yang Z. and Fang M., Distributions and sources of bulk organic matter and aliphatic hydrocarbons in surface sediments of the Bohai Sea, China, *Marine Chemistry*, **113**, 197-211 **(2009)**

15. Monza L.B., Loewy R.M., Savini M.C. and Pechen de d'Angelo A.M., Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments from the Neuquen River, Argentine Patagonia, *Journal of Environmental Science and Health, Part A*, **48(4)**, 370-379 **(2013)**

16. Silva T.R., Lopes S.R.P., Sporl G., Knoppers B.A. and Azevedo D.A., Source characterization using molecular distribution and stable carbon isotopic composition of n-alkanes in sediment cores from the tropical Mundau-Manguaba estuarine-lagoon system, Brazil, *Organic Geochemistry*, **53**, 25-33 **(2012)**

17. Ahad J.M.E., Ganeshram R.S., Spencer R.G.M., Uher G., Gulliver P. and Bryant C.L., Evidence for anthropogenic 14C-enrichment in estuarine waters adjacent to the North Sea, *Geophysical Research Letters*, **33(8)**, 239-249 **(2006)**.

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