

# Reconstruction of aliphatic hydrocarbons history and sources from sedimentary record of the Johor Strait, Malaysia

Mahyar SAKARI<sup>1\*</sup>, Mohamad Pauzi ZAKARIA<sup>2</sup>, Nordin Haji LAJIS<sup>3</sup>,  
Che Abd Rahim MOHAMED<sup>4</sup> and Mohd Harun ABDULLAH<sup>1</sup>

<sup>1</sup> Water Research Unit, School of Science and Technology, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia

\*E-mail: mahyar@ums.edu.my; mahyarsakari@gmail.com

<sup>2</sup> Laboratory of Environmental Forensics, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>3</sup> Department of Natural Products, Institute of Bioscience, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>4</sup> Marine Ecosystem Research Center (EKOMAR), Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

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**Abstract**—Hydrocarbon pollution is one of the most serious problems facing many developed and developing countries, including Malaysia. Aliphatic hydrocarbons comprising straight chain carbons are class of hydrocarbon pollution indices in the environment of anthropogenic and natural origins. To identify the historical trend of development, sediment samples were collected using a gravity corer from the narrow waterway of Johor Strait in the southern part of Peninsular Malaysia. The core samples were Soxhlet extracted, purified and fractionated using 2-step column chromatography followed by instrumental analysis with Gas Chromatograph Flame Ionization Detector. The results showed that the hydrocarbon contamination followed 4 distinct patterns. The pre-war period or at the onset of industrial development has seen a minimum input of alkanes. The World War II and postwar period (1945–1960) saw a decrease in hydrocarbon contamination because of the significant reduction in oil transportation. The third phase (1960–1990) saw a rapid increase in hydrocarbon input due to rapid economic development, industrialization and motorization and human population growth. The 4th phase (1990–present) saw a trend toward decreasing contamination due to strict environmental regulations (1990–2005). Surface aliphatic hydrocarbon concentration may have resulted from port operations, shipping activities and accidental spills. Total alkane concentration for the surface, middle and bottom core were 3180, 835 and 263  $\mu\text{g g}^{-1}$  dry weight, respectively. Fresh hydrocarbon input was inferred from the significant absence of pristane and phytane.

**Key words:** n-Alkane, petroleum hydrocarbon pollution, pollution history, Johor Strait, environmental regulations

## Introduction

Pollution from organic compounds of anthropogenic sources in aquatic environments has been an area of great concern (Baker 1980). Due to their high hydrophobic properties and relatively stable chemical structure, many organic pollutants have strong partitioning with particle surfaces and thus can be found at high concentration in contaminated coastal marine sediments (Karickhoff et al. 1979). Although organic pollutants are found in negligible concentration (ppb) even in pristine areas, some polluted sites nearby active ports, harbors and marinas show higher concentrations (ppt). Several molecular markers are used for source identification of hydrocarbon pollution (Zakaria et al. 2000, 2001, 2002, Sakari et al. 2008a, 2008b, Wang and Stout 2007, Chandru et al. 2008). Their unique structures provide very specific information on the origins of the compounds. Aliphatic hydrocar-

bons (n-alkanes) are a major component of petroleum pollution with elevated even carbon numbers. Odd carbon numbers, on the other hand, indicate natural input into the marine environment as well as into sediments. Application of n-alkane as a molecular marker to identify the sources of pollution usually provides different definitions, ratios and specific compound appearance.

Hydrocarbons usually come to the surface of marine sediments by biosynthesis and through anthropogenic and geochemical processes. In biosynthesis, living organisms produce hydrocarbon compounds. For example,  $\text{C}_{23}$ – $\text{C}_{33}$  n-alkanes are predominant in terrestrial plant detritus while  $\text{C}_{15}$ ,  $\text{C}_{17}$  and  $\text{C}_{19}$  (odd numbered n-alkanes) represent marine biogenic input. These odd-numbered n-alkanes do not usually appear in high concentrations in nature, but in petroleum the ratio of odd- to even-numbered carbons is 1:1 or near 1:1. Anthropogenic hydrocarbons arise through activities of man such as industries, urban activities and oil operations.

Geochemical processes are less well understood due to lack of study in this subject, but usually seepage processes will cause hydrocarbons in the sea surface sediment.

Malaysia is situated in the Southeast Asia (Fig. 1). Peninsular Malaysia is separated from Singapore by a narrow waterway, the Johor Strait. The Strait of Johor has been one of the busiest narrow waterways of Southeast Asia since the 15<sup>th</sup> century, with one of the oldest harbors and ports in the region.

In Malaysia, distribution and sources of hydrocarbon pollution vary from one location to another. For land-based sources, following rapid urban development and the establishment of several industrial zones, hydrocarbon pollution has been introduced via urban run-off and non-point source discharges such as used crankcase oil and industrial effluents. For sea-based sources, petroleum hydrocarbon pollution is released through oil tanker accidents and accidental spills in ports, harbors and marinas (Zakaria 2000). The current state of threats on the marine environment not only criticize the past but also warn of future scenarios ahead. Trends towards increasing development with alarming figures render a stark view of future environmental disasters.

In Malaysia, the study of hydrocarbon pollution started with the research of Law and Ravinthar (1989), who reported the bulk petroleum hydrocarbon pollution from one of heavy shipping location in the Straits of Malacca in Port Dickson. Specific compound analysis began in Malaysia in 1998 where scientists reported the levels and origins of aliphatic and polycyclic aromatic hydrocarbons (PAHs) in Malaysian marine sediment, water, mussels, aerosols, street dust (Zakaria et al. 2000, 2001, 2002, Zakaria and Mahat 2006). The most important conclusion of these studies is that the footprint of petroleum hydrocarbon pollution in Peninsular Malaysia comes from petrogenic sources (Zakaria et al. 2002), regardless of its history and coming trends.

Historical trends of polycyclic aromatic hydrocarbon pollutions in Peninsular Malaysia has been reported from Klang estuary (Sakari et al. 2010a), Straits of Johor (Sakari et al. 2010b) and Malacca (Sakari et al. 2011). In general, the results of these recent studies show a decreasing trend of hydrocarbon pollution in Peninsular Malaysia since its latest peaks during the rapid development of the country.

This study aims to provide the history of aliphatic hydrocarbon, concentrations and sources in the sedimentary records of the Johor Strait. The research focused on the determination of the chronology of sediment intervals throughout the core sample using <sup>210</sup>Pb and its decay trends for dating. The concentration of bulk and specific aliphatic hydrocarbons was achieved by gas chromatography via chromatogram peaks. Several identification tools were applied to determination hydrocarbon sources: average carbon chain length (ACL), ratio of higher to lower molecular weight (H/L), carbon preference index (CPI), major hydrocarbon

concentrations (MH) and ratios such as C<sub>31</sub>/C<sub>19</sub>.

To date, all studies in Malaysia have been focused on the current situation of petroleum hydrocarbon pollution; none have yet been conducted to investigate the historical trend of hydrocarbon pollution to determine the history of pollution in Peninsular Malaysia. This paper aims to reconstruct the historical profile of compound-specific aliphatic fractions of the organic compounds by analyzing the sedimentary core samples from the Johor Strait. This pioneering report identifies the input of petroleum compounds and other anthropogenic and natural sources of organic compounds, with their concentrations and origins in this region.

## Materials and Methods

### *Sample collection*

The core sample of sediment was collected from an inner location in the Johor Strait in September 2005 (Fig. 1) that would avoid collection from dredging sites. Although the Johor Strait has heavy port and shipping activities, vessels do not enter to the sampling location since the port is located in the outer part of the strait. At the sampling site boats and ferries use the water way for transportation to local and neighboring destinations.

As shown in the map, the waterway of the Johor Strait is narrow, reaching a width of less than a kilometer in some areas. Therefore, the sampling location is a quite isolated place where a bridge and the arched shape of the strait prevent huge water disturbances throughout the daily storm and seasonal monsoon. Meanwhile, bioturbation is found in the upper sedimentary layers where marine organisms live. This phenomenon significantly affects the aging process. Therefore, the top 5 cm of the sedimentary cores was excluded from examination of the aging processes. Samples were collected using stainless steel gravity corers (inner diameter (i.d.): 3 cm) which had been internally covered by compacted pre-cleaned plastic tube as to serve as a temporary sampling container prior to slicing. The depth of sampling was ~3 m and the resulting core measured 30 cm in length. The collected core was placed vertically in the sampling vessel and transferred immediately to the shore for slicing. On the shore, the core profile was sliced at 3-cm intervals using pre-cleaned stainless steel sheets from the top of collected sedimentary core; that each interval represents the specific time of sediment deposition and age. A 2-mm thickness from the outer part of each individual sliced sample was discarded to prevent cross contamination by the inner wall of the plastic tube container. Each interval was placed into the stainless steel container in a cooler box filled with gel ice, then transferred to the deep freezer in laboratory and stored at -18°C prior to analytical procedures. To prevent cross contamination, the sampling equipment and experimental glassware

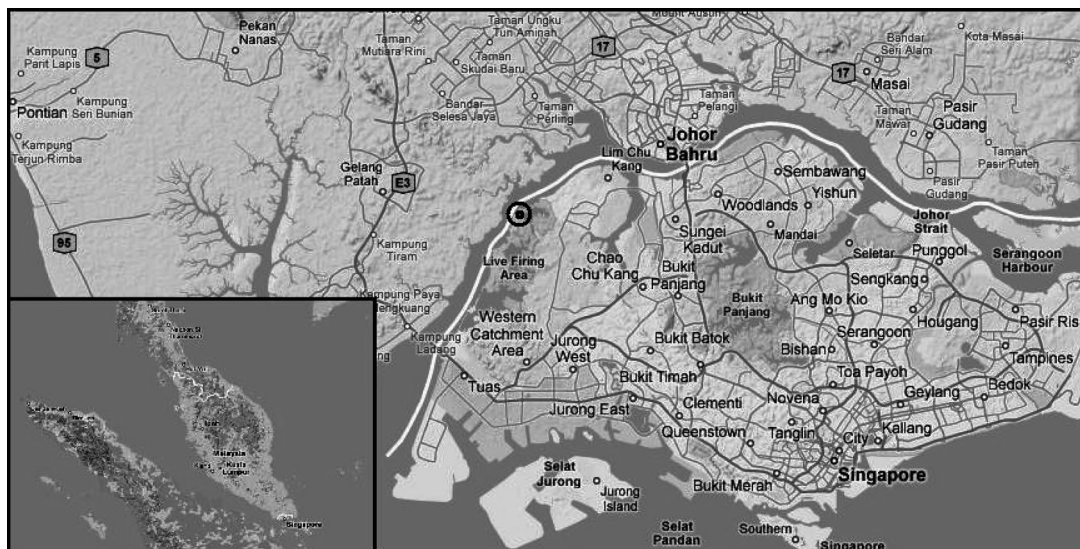


Fig. 1. Map of sampling station (black circle) in Johor Strait, Peninsular Malaysia (produced using free online Google Map service).

were immersed in soap solution and rinsed with tap and distilled water 6 times each and with methanol (MeOH), acetone and distilled hexane 3 times each, capped with aluminum foil and dried 2 h in the drying oven in 60°C and placed on clean shelves prior to use.

#### Preparation of chemicals

Authentic standards of n-C16, C18, C20, C22, C24, C26, C28, C32 and C36 were used. A 100–200 mesh silica gel (F.C. 923) was baked at 200°C for 12 h, then cooled in a desiccator, deactivated with 5% distilled water (w/w) and filled with n-hexane for the first step in column chromatography. For the second step, the silica gel was baked at 380°C for 4 h and then at 200°C for an additional 4 h, then cooled in a desiccator with added n-hexane. Organic solvents including n-hexane, dichloromethane (DCM) and isooctane were distilled in glass before use. Anhydride sodium sulfate was baked in a muffle furnace at 380°C for 4 h and kept in an oven at 120°C prior to further analysis.

#### N-alkane analysis

The analytical procedures follow those described by Zakaria et al. (2002) and Yim et al. (2005) and Sakari et al. (2008a, b). In brief, 1 g sediment samples were weighed in a 10 ml beaker on an analytical balance and placed in the oven for 24 h at 63°C, then re-weighed and heated again for a further 2 h and again re-weighed. If the differences between weighing were less than 0.02 g, the dryness percentage of the last reading was used as the basis for calculation. If not, heating continued for additional periods of 2 h until samples reached constant weight. A 5-gram (dw) sediment sample was dried with sufficient previously baked anhydrous Na<sub>2</sub>SO<sub>4</sub> and transferred to the cellulose thimble and put in the soxhlet chamber. Soxhlet extraction was carried out for 11 h using

DCM as extracting solvent due to its close polarity to the target compounds. Extracted materials were transferred to clean glassware for Na<sub>2</sub>SO<sub>4</sub> treatment to remove any possible water content overnight. Then the volume was decreased by about 1 ml using a rotary evaporator. As a clean-up procedure, the extract was transferred into the glass column (9 cm and 0.9 cm i.d.) using 20 ml 3 : 1 hexane : DCM for the first step of column chromatography to remove any compounds near the polarity of water and water itself. The volume from the first step was reduced to near dryness using a rotary evaporator and the content transferred to another glass column (18 cm and 0.47 cm i.d.) using 4 ml hexane for n-alkane) for the second step of column chromatography to fractionate the target compounds from the cleaned sample. The fraction's volume was reduced using a rotary evaporator and then transferred into a 2 ml vial. The content was dried gently in a nitrogen stream. Then 100 ml isooctane was added prior to instrumental analysis.

#### Instrumental analysis

Normal alkanes were analyzed using a Hewlett Packard 5980 gas chromatograph (GC) coupled with a 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 was used with helium as the carrier gas at 200 kPa. The injection port was maintained at 300°C and samples were injected with splitless mode, followed by a 1-minute purge after the injection. Column temperature was maintained at 70°C for 1 min, then increased by 30°C min<sup>-1</sup> to 150°C, then increased by 5°C min<sup>-1</sup> to 310°C and held for 10 min. The detector temperature remained at 310°C.

### *Analytical and instrumental procedure for determining age of the sediment core interval*

Age determination experiments followed the method described by Krishnaswamy et al. (1971) and Koide et al. (1972) with modification (Sakari et al. 2010a, b). In brief, samples were dried in an oven at 50°C overnight, sieved through a mesh of less than 250 µm mesh size and kept dry for analysis. Around 0.3 g of this sample was placed in a 50-ml beaker and 1 ml (25 ppm) PbSO<sub>4</sub> was added as carrier for <sup>210</sup>Pb extraction. Then 20 ml of HCl (8 M) was added to the sample, which was then left for 2 h on a hot plate at 60°C for digestion. Digested materials were filtered to separate undesired remaining solids using glass filter paper (47 mm i.d.). Digested liquid was left on the hot plate to dryness until a yellow-brown-colored paste remained. 30 ml HClO<sub>4</sub> was added to the paste and heated for ion-exchange resin column chromatography. For column chromatography 200 ml of HCl (1 M) was used to gradually dilute the samples in the column. Pb was separated in the column and collected in clean beaker, dried for a day on a hot plate to eliminate liquid till the sample became a white paste. 50 ml HNO<sub>3</sub> (1 M) was added to the remaining paste and left on a hotplate for 1–2 min, then cooled down at room temperature. Then a few drops of H<sub>2</sub>SO<sub>4</sub> were added to precipitate the Pb. The precipitated Pb (PbSO<sub>4</sub>) was left for 3 days in cool temperature at 4°C and filtered using glass paper filter (25 mm). Filtered materials were then subjected to β-spectrometry. Each sample was placed over the round plastic coin (Perspec™) and wrapped successively by Al-foil. Then the samples were sent to the Malaysian Institute of Nuclear Technology (MINT) in Bangi, Selangor. The β-emission of samples was measured in a β-spectrometer (Gross-Model: LB5100, Tennelec Inc.).

The sediment samples showed a general decreasing trend of <sup>210</sup>Pb activity with increasing depths. This decay zone was used to calculate the sedimentation rate via integrated line equation of <sup>210</sup>Pb activity versus depth (in cm). The water content of sediment decreased with increasing depth, while dry bulk density of sediment showed minimum changes over the decay zone. Some layers with higher and lower densities suggest the impact of land use changes of the Johor region over time that affects the sedimentation rate. Densities in the constant zone (deeper layers) were higher than those in the decay zone, indicating more compacted sediment and higher sedimentation rate in the former. These measurements could not be taken into account in the calculation of age, where the values of <sup>210</sup>Pb changed insignificantly. Therefore the average calculated sedimentation rate for the decay zone (0.2 cm y<sup>-1</sup>) was applied for the rest of the layer.

### *Quality control and quality assurance*

The quality of the results of the analytical procedures and instrumental analyses were ascertained by QC/QA procedures. Alkane standard was employed to identify peaks,

calculate concentration and recovery of the possible amount of the compounds' losses. Several fractions from empty laboratory glasses were analyzed as independent samples. Each batch of samples was accompanied by a procedure blank. During instrumental analysis, a purge (Capillary Column Solvent Wash) conducted after each batch of 8 samples. Besides the same quality control procedures these were applied for the chronology experiments, a bulk and standard samples with known β emission were run in the same conditions on the same instrument.

### *Source identification indices*

Several source identification instruments were employed, including average carbon chain length (ACL), ratio of higher to lower molecular weight (H/L), carbon preference index (CPI), major hydrocarbon concentrations (MH) and ratios such as C<sub>31</sub>/C<sub>19</sub>. These were calculated using the results of the analysis of the concentration of specific compounds. The L/H is defined as the ratio of total lower molecular weight (C<sub>16</sub> to C<sub>26</sub>) over total higher molecular weight (C<sub>27</sub> to C<sub>36</sub>) alkane. While higher values indicate the freshness of the hydrocarbon input into the environment such as via fresh oil input, lower numbers indicate degraded and old input (Farrington and Tripp 1977, Commendatore et al. 2000).

ACL, or average carbon chain length, is another index which stands for is calculated as follows:

$$\text{ACL value} = \frac{[(25 \cdot C_{25}) + (27 \cdot C_{27}) + (29 \cdot C_{29}) + (31 \cdot C_{31}) + (33 \cdot C_{33})]}{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})}$$

This value should appear with limited changes within an environment and different in various ecosystem (Jeng 2006). Various values over time indicate changes in the ecosystem due to environmental disturbances.

Any types of pollutant such as petroleum are represented by higher concentrations of specific compound(s). Hence analyzing compounds provides evidence for source identification of environmental pollutants. Analysis of major hydrocarbon analysis indicates the alkane compound with the highest concentration among others (Broman et al. 1987, Colombo et al. 1989) and therefore indicates the highest contribution of a particular pollution type in environmental samples.

The sources of hydrocarbons are different in land and marine sources. Identification of origins of hydrocarbons which derive from either a terrestrial or a marine environment is determined by examination of the ratio of C<sub>31</sub> to C<sub>19</sub>, where C<sub>31</sub> represents terrestrial input while C<sub>19</sub> indicates sources from the marine environment (Farrington and Tripp 1977, Boehm and Requejo 1986). Hence higher values indicate higher terrestrial input and lower values indicate predominance of marine input.

The carbon preference index (CPI) is another source identifier (Farrington and Tripp 1977, Colombo et al. 1989,



Kennicutt et al. 1987). CPI calculates the ratio of odd to even carbon numbers. This value is the primary indicator of most natural or anthropogenic sources, where odd number carbons are predominant in natural input while anthropogenic sources such as petroleum are indicated by the predominance of even-numbered carbon. Therefore, the higher values of this ratio indicate natural input versus anthropogenic that appears with CPI values less than 1.

## Results

Values of n-alkane (total, even and odd carbon number), CPI, lower molecular weight n-alkane, higher molecular weight n-alkane, ACL, MH,  $C_{31}/C_{19}$  ratios and calculated age are summarized in Table 1.

As shown in this table, the total hydrocarbon concentrations varied from 117 to 4652  $\mu\text{g g}^{-1}$  dry weight. According to dating results and as indicated in Fig. 2, the minimum concentration of 117  $\mu\text{g g}^{-1}$  d.w. was observed during 1870–1885 while the maximum concentration of 4652  $\mu\text{g g}^{-1}$  was measured during the era of 1975–1990. While there were

several fluctuations in aliphatic hydrocarbon concentrations between 1885 and 1975, the trend generally increases. The contribution of odd-numbered carbon from biogenic sources and even-numbered carbon from anthropogenic sources were found to be significantly different in this study.

For instance, high concentrations of odd-numbered carbon appeared in old sediments while the predominance of even-numbered carbon was found to be very frequent in the last half century. Even-numbered aliphatic carbon compounds started increasing after 1915 when the oil exploration began in Malaysia. While levels of HMW aliphatic hydrocarbons increased significantly during the modern era (1990–2005), the LMW aliphatic hydrocarbons dropped around 50% in the same era. This change in LMW aliphatic hydrocarbons is consistent with that of the total level of aliphatic hydrocarbon. Basically, the total aliphatic hydrocarbon concentrations in the study period (1885–2005) showed very high consistency with those from anthropogenic sources for both HMW and LMW hydrocarbons. The marine input of hydrocarbons in this study revealed a minimal entry where  $C_{17}$  and  $C_{19}$  appeared in very low concentrations. Instead of marine input, terrestrial input peaked in early and modern

**Table 1.** Aliphatic hydrocarbon composition for sedimentary core from Johor Strait, Peninsular Malaysia.

Depth of Sediment Samples (cm)	0 to 3	3 to 6	6 to 9	9 to 12	12 to 15	15 to 18	18 to 21	21 to 24	24 to 27	27 to 30
$\Sigma$ n-Alkane <sup>a</sup> ( $\mu\text{g/g}$ )	3541	4652	1350	891	1489	744	218	200	117	473
$\Sigma$ LMW Alkane <sup>b</sup> ( $\mu\text{g/g}$ )	1910	4124	993	761	1221	733	90	59	0	124
$\Sigma$ HMW Alkane <sup>c</sup> ( $\mu\text{g/g}$ )	1631	528	357	130	267	12	128	140	117	349
L/H Alkane <sup>d</sup>	1.17	7.80	2.78	5.84	4.57	63.30	0.71	0.42	0.00	0.35
$\Sigma C_{23}\text{--}C_{33}$ <sup>e</sup> ( $\mu\text{g/g}$ )	458	239	237	101	115	0	162	127	98	379
$\Sigma C_{17}, C_{19}$ <sup>f</sup> ( $\mu\text{g/g}$ )	0	0	45	0	0	0	0	0	0	58
$\Sigma$ Odd Alkane <sup>g</sup> ( $\mu\text{g/g}$ )	458	267	299	120	149	0	162	152	117	437
$\Sigma$ Even Alkane <sup>h</sup> ( $\mu\text{g/g}$ )	3082	4385	1051	771	1339	744	56	48	0	36
CPI <sup>i</sup>	0.27	0.39	0.86	0.66	0.53	0.00	N/A	2.64	N/A	12.10
ACL <sup>j</sup>	29.13	26.01	28.50	28.82	26.94	N/A	28.06	30.53	30.19	29.06
Major Hydrocarbon <sup>k</sup>	C18, C20	C18, C20	C18, C20	C16	C16, C18, C20	C16, C18, C20	C27, C29, C31	C29, C31, C33	C29, C31, C33	C27, C29, C31
Age (Year)	1990–2005	1975–1990	1960–1975	1945–1960	1930–1945	1915–1930	1900–1915	1885–1900	1870–1885	1855–1870

<sup>a</sup> Total n-Alkane: Sum of aliphatic hydrocarbons from  $C_{16}$  to  $C_{36}$

<sup>b</sup>  $\Sigma$ LMW Alkane: Sum of  $C_{16}$  to  $C_{26}$  aliphatic hydrocarbons

<sup>c</sup> Total HMW Alkane: Sum of  $C_{27}$  to  $C_{36}$  aliphatic hydrocarbons

<sup>d</sup> Ratio of LMW to HMW: Ratio of Low Molecular Weight aliphatic hydrocarbon to High Molecular Weight

<sup>e</sup>  $\Sigma C_{23}\text{--}C_{33}$ : Sum of odd carbon number alkane from  $C_{23}$  to  $C_{33}$

<sup>f</sup>  $\Sigma C_{17}, C_{19}$ : Sum of  $C_{17}$  and  $C_{19}$

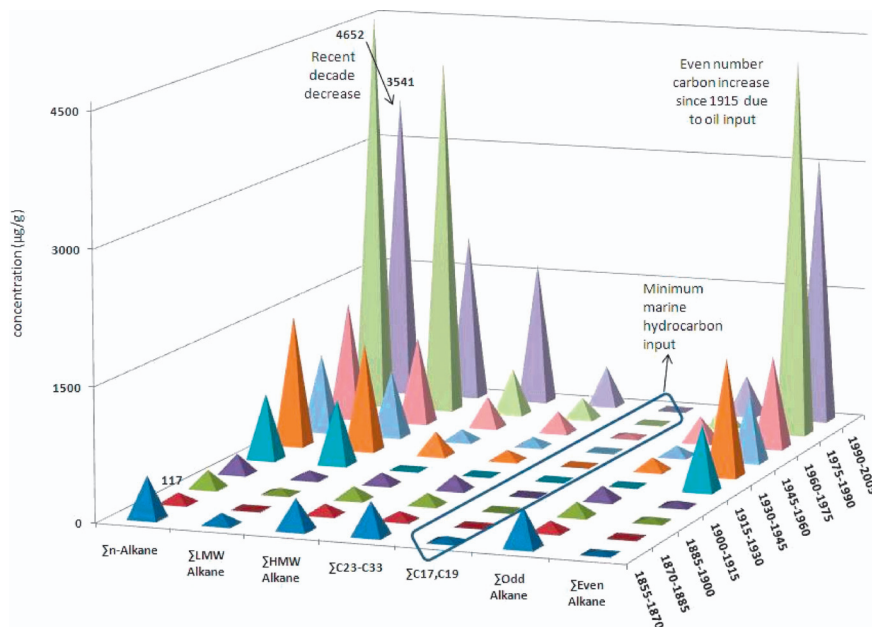
<sup>g</sup>  $\Sigma$ Odd Number Hydrocarbon: Sum of natural origin hydrocarbon from  $C_{17}$  to  $C_{35}$

<sup>h</sup>  $\Sigma$ Even Number Hydrocarbon: Sum of anthropogenic origin hydrocarbon from  $C_{16}$  to  $C_{36}$

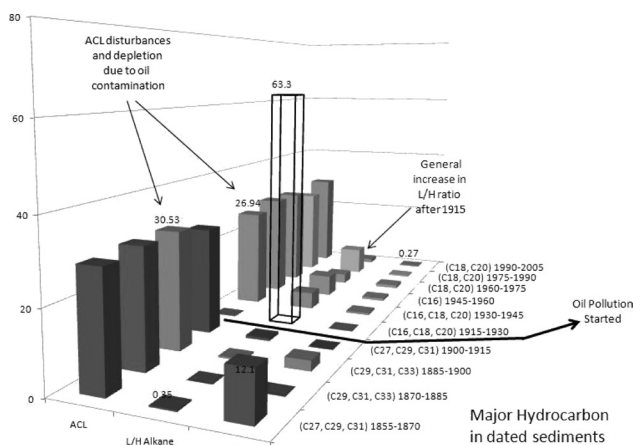
<sup>i</sup> CPI: Carbon Preference Index, the ratio of Odd to Even carbon number

<sup>j</sup> ACL: Average Carbon Chain Length which calculates as  $[(25 \cdot C_{25}) + (27 \cdot C_{27}) + (29 \cdot C_{29}) + (31 \cdot C_{31}) + (33 \cdot C_{33})] / (C_{25} + C_{27} + C_{29} + C_{31} + C_{33})$

<sup>k</sup> Major Hydrocarbon: The Hydrocarbon that contains the majority of total n-alkane.



**Fig. 2.** Historical trend of n-alkane in the study area: total n-alkane, low molecular weight (LMW), high molecular weight (HMW), terrestrial input, marine input, natural (odd carbon number), anthropogenic (even carbon number). See Table 1 for definition of terms.



**Fig. 3.** ACL, L/H and CPI ratios in dated core sediment from Johor Strait, Peninsular Malaysia. See Table 1 for definition of terms.

eras during 1855–1870 and 1990–2005, respectively. However, a steady increase has been appearing since 1930. An interesting observation from the timeline of this study is that early aliphatic input is highly correlated to the odd-numbered carbons with terrestrial origins. Since then, especially after 1915, the total aliphatic hydrocarbons are closely controlled by even-numbered carbon with a predominance of LMW and therefore a lower contribution of terrestrial input. The L/H ratio was found to fluctuate, ranging from the minimum level of 0.35 in 1855–1875 to the maximum of 63.3 during 1915–1930. However, excluding the highest value, there is a trend for the ratio to increase, with a sudden drop in the modern input.

This trend for CPI ratio showed different values where a

higher number (12.1) was observed during 1855–1875 and has been declining towards 0.27 in modern input. The ACL ratio also fluctuated, with a smooth decline since 1885. The highest value was observed during 1885–1900, while during 1930–1945 it decreased to the minimum level of 26.94. However, no ACL value was reported for 1915–1930 due to mathematical error, a decreasing trend over the timeline is observable (Fig. 3).

The contributions of major hydrocarbons in the chromatogram traces vary in different stages and study periods. During 1855–1915 the majority of hydrocarbons are odd-numbered carbons, including  $C_{27}$ ,  $C_{29}$ ,  $C_{31}$  and  $C_{33}$ , but from 1915 to 2005 the major hydrocarbons were constantly  $C_{16}$ ,  $C_{18}$  and  $C_{20}$ .

## Discussion

### Source identification of hydrocarbons using n-alkane as molecular marker

The concentrations of n-alkane in this research vary from 117–4652  $\mu\text{g g}^{-1}$  (d.w.) over time (Table 1). During the early eras of sediment deposition, the levels were low and comprise virtually completely odd-numbered carbon, which is not pollution. During the era of 1960–1990 the concentrations of aliphatic hydrocarbons increased to the highest levels found in this study (4652  $\mu\text{g g}^{-1}$  d.w.), highly dependent on anthropogenic input. A similar observation was reported previously by Harada et al. (1995) from Antarctica and Sakari et al. (2010a) from Port Klang in Strait of Malacca. From 1885 till 1960, although the total n-alkane fluctuates between 200

to  $1489 \mu\text{g g}^{-1}$  (d.w.), comparing these numbers with global standards that have been introduced by United Nation Environment Program (UNEP, 1992, 1995) shows that except for the period of 1855–1885 which showed lack of or negligible pollution ( $<10 \mu\text{g g}^{-1}$  d.w.) for some periods (1885–1960), our results show the expected conditions for harbors and ports in the world ( $10\text{--}1000 \mu\text{g g}^{-1}$  d.w.; UNEP 1992). This is consistent with a report from Matsumoto et al. (1992) from Antarctica. The highest level of pollution appeared during 1960–2005 at higher than normal concentrations, indicating a need for strict environmental management in the studied area.

#### *Major hydrocarbons in sedimentary core*

The peaks of specific compounds from the chromatogram trace the n-alkane in the environmental samples, providing enough evidence to conclude the sources of pollution. Major hydrocarbons (MH) that indicate the highest n-alkane concentration (Broman et al. 1987, Colombo et al. 1989) can be used as an evidence to identify the sources of pollution. This index represents crude oil (with a dominance of  $C_{18}$ ), different types of algae ( $C_{15}$ ,  $C_{17}$ ,  $C_{19}$  and  $C_{21}$ ) and vascular land plants ( $C_{23}$ ,  $C_{25}$ ,  $C_{27}$ ,  $C_{29}$  and  $C_{31}$ ). In this study, odd- and even-numbered carbon hydrocarbon concentrations and types vary from one layer sample to another. For example, during 1855 to 1915 the majority of hydrocarbons came from terrestrial and marine biogenic sources while after this period the presence of these compounds diminished and gave way to anthropogenic aliphatic hydrocarbons with predominance of even-numbered carbon n-alkane.

The increasing rate of even-numbered carbon n-alkane in this study represents the increase of anthropogenic input to the marine sedimentary environment of the Johor Straits. In another study conducted by Harada et al. (1995), the hydrocarbon content from marine sedimentary core in Antarctica is characterized by a dominance of  $C_{21}$  concentration, which diminished with increase in depth. Short chain odd-numbered carbon n-alkane is produced by marine microorganisms such as phytoplankton and zooplankton (Blumer et al. 1971, Clark and Blumer 1967), and it is very normal that in the marine environment of Antarctica there should be high levels of these organisms. In the Johor Straits only very negligible levels of short chain odd-numbered carbon, indicating the weakness of marine biogenic sources of hydrocarbons. Also, short chain n-alkane is subject to degradation in the water column and aerobic upper layers in the sedimentary environment (Prahl and Carpenter 1984). Therefore we can conclude that the depleted levels of short chain odd-numbered carbon n-alkane can be related to degradation during the depositional period of sedimentation. This finding is also consistent with Kvenvolden et al. (1987), who found the same trend to a decline of marine biogenic sources from the sediment of offshore regions in Antarctica. Matsumoto et al.

(1992) in another study near the research site used by Harada et al. (1995) reported a different trend toward short chain odd-numbered carbon n-alkane, indicating lower concentrations of natural aliphatic hydrocarbons than of anthropogenic ones.

While marine organisms, including phytoplankton and zooplankton, produce short chain n-alkane with odd-numbered carbon such as  $C_{15}$  and  $C_{17}$  (Blumer et al. 1971, Clark and Blumer 1967), higher terrestrial plants contain long chain odd-numbered carbon ranging from  $C_{25}$  to  $C_{33}$  (Eglington et al. 1962, Simoneit 1978). Predominance of long chain odd-numbered carbon such as  $C_{27}$  to  $C_{33}$  in Johor sediment during 1855–1915 and a much reduced contribution of these compounds for the last 90 years indicate mass environmental change in the marine environment in the study region (Jeng 2006). This study, like results from Harada et al. (1995), significantly shows the role of terrestrial input as the major source of biogenic hydrocarbon to the environment in tropical zones.

In a few studies of hydrocarbons in core sediments, sometimes the trend from marine biogenic sources is reversing. For example, Hostettler et al. (1999) have found that the short chain n-alkane (marine biogenic sources) is increasing throughout the surface indicating more productivity of the marine environment in recent years.

Predominance of even-numbered carbon around  $C_{18}$  usually indicates the presence of petroleum pollution (Jacquot et al. 1999). In this study it was found that especially in last 90 years the most hydrocarbon compounds have shifted noticeably from terrestrial (long chain odd-numbered carbon) to petroleum-based, with high predominance of even-numbered carbon around  $C_{18}$ . This phenomenon can be attributed to oil transportation and refinery activities during the studied eras in the research site which has ocean going shipping activities.

#### *LMW/HMW ratio*

Molecular weight and structure of n-alkane as a molecular marker in hydrocarbon studies in marine environment is useful tool for identification of the characteristics of hydrocarbon input to nature. One of the routine ways to classify the hydrocarbons in the class of aliphatic and aromatics is by their molecular weights. Aliphatic hydrocarbons can be divided into those with Low Molecular Weight (LMW) and those with High Molecular Weight (HMW). LMW aliphatic hydrocarbons cover hydrocarbons from  $C_{16}$  to  $C_{26}$  and HMW cover  $C_{27}$  to  $C_{36}$ . The ratio of LMW/HMW is used to identify the sources and origins of aliphatic hydrocarbons in the marine environment (Farrington and Tripp 1977). For example, fresh oil usually presents a LMW/HMW ratio of more than 2 (Commendatore et al. 2000). Although values around unity can represent petroleum existence, they also can come from plankton origins (Gearing et al. 1976). Gearing also believes

that values of more than one (less than 2) possibly come from higher plants, marine animals and sedimentary bacteria. While some bacteria introduce some aliphatic hydrocarbons into the marine environment, some others are able to degrade the LMW because structurally it is easy to degrade. Therefore, the LMW/HMW ratio in oil-contaminated samples can reach less than one (Commendatore et al. 2000) as well as heavier oil which has less LMW rather than HMW (Commendatore et al. 2000, Stout et al. 2002).

In this study multiple values of LMW/HMW were obtained for duration of the core age. For example, during 1930–1990 the presence of fresh oil input is very frequent (LMW/HMW ranging from 2.78–8.70), as also indicated by the (MH) index values (Fig. 1).

In the most recent period (1990–2005) these values changed to around unity (LMW/HMW~1.17), indicating both oil pollution and plankton origins. These values are not strong evidence for fresh oil input as they may be due partially to degradation in aerobic conditions of the near surface of the sediment and also to high levels of odd-numbered carbon in this period from the biogenic origins such as plankton (Gearing et al. 1976).

In the early sediment (1855–1915), the values of LMW/HMW (0.35–0.70) represent degraded oil, but historically there were no oil activities during that era, therefore it can be concluded that the ratio does not confirm oil pollution (Table 1). Another possibility is that significantly depleted levels of LMW and HMW are totally dependent on natural biogenic sources such as long chain odd-numbered carbon from terrestrial plant and leaf waxes (99% correlation between total HMW with natural input). Thus, a new approach in using LMW/HMW ratio for source identification would highly depend on the presence and normal distribution of LMW and HMW hydrocarbons in the studied samples. The data for the period of 1915–1930 the calculation is not applicable because the values are out of the normal distribution curve (LMW/HMW~63).

#### *Carbon Preference Index (CPI)*

The Carbon Preference Index (CPI) is one of the ratios used in the investigation of hydrocarbon studies using n-alkane as molecular marker. Generally, CPI indicates the ratio of odd-numbered carbon to even-numbered carbon. In studies on the marine sedimentary environment, the CPI is used frequently. It was introduced to these studies by Farrington and Tripp (1977) and developed by others (Boehm and Requejo 1986, Colombo et al. 1989, Kennicutt et al. 1987).

CPI, which is highly dependent on the presence of odd- and even-numbered carbon n-alkane in the marine sediment samples, varies from sample to sample and from one location to another. For example, values from 3 to 6 indicates terrestrial vascular plants and around unity for petrogenic sources, although Kennicutt et al. (1987) believe that the possibilities

of marine microorganisms and/or recycled organic matter account for the value of one.

The CPI that indicates the natural versus anthropogenic hydrocarbons in the environment was applied in this study. The harmony of CPI fluctuation in the investigated core also depleted as the investigation progressed higher to the upper levels of sediment, and the deposition during the last century indicates the transition from biogenic sources to anthropogenic ones. The period of 1855–1870 showed very high values of CPI (12.10) that indicates the biogenic input, while in the era of 1885–1900, the CPI declined to 2.64, indicating a decline in biogenic sources such as terrestrial vascular plants (Fig. 2). During the last century, this ratio significantly dropped in value and reached to below one (0.26–0.86). Although this ratio shows anthropogenic sources of hydrocarbon, the depleted levels indicated by the value below unity are concluded to be attributable to degradation, which is consistent with the LMW/HMW findings of this study.

Hostettler et al. (1999) in a study of core sediment from San Francisco Bay also found the same trend. They have reported that in the period pre-1952, the CPI ratios were very high, similar to our findings for 1855–1915. In another study in the western Sea of Okhotsk, Seki et al. (2006) reported average values of 5.5 for the studied area. Although findings of CPI values in these studies are usually taken to indicate biogenic sources, Jeng (2006), who believes that these values vary in marine and river ecosystems because of different input from both terrestrial vascular plants and marine biogenic sources, reported the CPI value of 1.7 from the marine sediment of Taiwan. The CPI in some locations is changing because of short term and sudden input of anthropogenic sources. For example, Harada et al. (1995) in their research in Lutzow-Holm Bay, Antarctica, found CPI value with biogenic sources in recently deposited sediments; in 1992, Matsumoto et al. reported different CPI (0.7–1.9), indicating some contribution of anthropogenic sources in the same location.

#### *Unresolved Complex Mixture (UCM)*

Chromatograms of n-alkane from GC analysis indicate the features of each sample, particularly whether it is degraded or still fresh. The presence of Unresolved Complex Mixture (UCM) is an indicator of petroleum in the samples which is under the weathering conditions. UCM is a baseline rise in the GC of total hydrocarbon, which indicates petroleum contamination in water or sediment in environmental samples (Volkman et al. 1992).

The molecular weight and the boiling temperature of the natural and petroleum hydrocarbons are so different, therefore the pattern for UCM changed from one sample to another. According to Brassel and Eglington (1980) the presence of UCM indicates petrogenic input or biodegradation. In this research, although there were no significant levels of



UCM in recently deposited sediments, indicating the relative freshness of the oil input, in old sediment there were elevated levels of UCM in the HMW area and possibly can mean significant degradation of terrestrial plants, which to our knowledge has not been reported elsewhere. Hostettler et al. (1999) in their study of San Francisco Bay show the trend towards increasing levels of UCM from deep to the surface sediments. This finding contrasts completely adverse with current research and can be attributed to better degradation processes in the modern input and recent era, maybe because of the better environmental conditions of the surface sediment such as aerobic condition and bio-exchange of the upper sediment layers and easy aeration. The absence of UCM in lower LMW range in this study shows the lack of bacterial degradation of natural organic matter such as algal detritus, as proposed by Venkatesan and Kaplan (1982).

#### *Dominance of environmental changes indicated by Average Chain Length (ACL)*

One of the important results from n-alkane investigation has been to understand the effect of pollution or any hydrocarbon input into the environment. Average chain length (ACL) is an important tool for these purposes. The n-alkane ACL is the weight average number of carbon atoms of the higher plants  $C_{25}$ – $C_{33}$  n-alkane. ACL under constant environmental conditions will not change (Jeng 2006). ACL varies from arid to humid ecosystems with varying types of vegetation. In the studied area, ACL values of this individual location changed, in line with historical trends. They ranged from 26.01 in the period 1975–1990 to 30.53 in the period 1870–1900, which shows an extraordinary fluctuation which is not regularly found in a single location, reflecting the environmental changes of the past one and half centuries in Johor (Fig. 2). This is consistent with our findings based on ratios and indices such as CPI, LMW/HMW and MH, indicating that petrogenic sources of pollution will depress ACL levels (Jeng 2006). According to Jeng (2006), in surficial sediment the range of ACL of a single sampling time showed limited change, varying little (29.2–30.5), while in different locations ACL shows various numbers and values. For example, in Africa (0–40°N) the values range between 28.3 and 29.9 (Huang et al. 2000). In the South East Atlantic (5–30°S) also the changes have been found to be very limited (29.9–30.8; Rommerskirchen et al. 2003). Not only do the virtually constant values of ACL in marine sediments from a specific location change little, but also there is very little variation from the values of different fossil fuels such as crude oil (values of 27.8, 27.9 and 28.4 for 3 different crude oils) (Jeng 2006). We conclude that with petrogenic input into the marine environment the ACL values are declining, which is a strong evidence for increasing petrogenic input into the Johor Strait over the last century.

In general, the pollution trend in this study showed start-

ing point of early 20<sup>th</sup> century while records of 19<sup>th</sup> century indicates no pollution scenarios. Moreover, specific compound analyses witness an early 20<sup>th</sup> century input of oil pollution in the study area where high  $C_{18}$  contents are observed. This evidence also shows high contribution of odd-numbered carbon in 19<sup>th</sup> century with degradation of short chain hydrocarbons (*i.e.*  $C_{15}$ ,  $C_{17}$ ,  $C_{19}$ ) from both terrestrial and marine environment entries. These are in agreement with findings of the ratio of LMW/HMW that approves again a high contribution of oil input since 1930. The presence of low values of CPI and ACL after 1952 have concluded oil pollution in the studied area however this value was very high during late 19<sup>th</sup> century indicating natural input to the studied area.

#### *Historical trend of pollution; predominance of petrogenic input*

Data on hydrocarbon contamination in the studied area can be grouped into 4 distinct patterns. The pre-war period or the period at the onset of industrial development saw a minimum input of hydrocarbon pollution. The World War II and postwar period (1945–1960) saw a decrease in hydrocarbon contamination because of the significant reduction in oil transportation (Table 1). The third phase (1960–1990) showed a rapid increase in hydrocarbon input due to rapid economic development, industrialization, and motorization and population growth. The 4th phase (1990–present) saw a trend toward decreasing contamination due to strict environmental regulations. Surficial aliphatic hydrocarbon concentration may have resulted from port operations, shipping activities and accidental spills.

The average total alkane concentration for the surface, middle and bottom levels of the core were 3180, 835 and  $263 \mu\text{g g}^{-1}$  dry weight, respectively. For the surface sediments, the findings was consistent with other studies (Zakaria et al. 2001, 2002 ) and was slightly elevated compared with previous studies done in more industrialized countries (Farrington and Tripp 1977, Boehm and Requejo 1986, Gearing et al. 1976, Harada et al. 1995, Hostettler et al. 1999, Jacquot et al. 1999, Kvenvolden et al. 1987, Matsumoto et al. 1992, Prahl and Carpenter 1984, Seki et al. 2006).

In conclusion, social and economic events have considerable impact on contaminant distribution and concentration in the environment. While our study showed a general increase in pollution input over time, there are also evidences from the recent hydrocarbon input (1990–2005) that indicate a decreasing trend of contamination input. Furthermore, this study showed that introduction of pollution-type alkane compounds is concomitant with gradual disappearance of natural ones. The Johor region marine ecosystem showed significant changes on its quality over time. Petrogenic input was predominant, especially in recent decades. This is consistent with research hypotheses that expect increasing trends of contamination over time due to rapid economic develop-

ments. Although the rate of increase of pollution has slowed in recent years, it is unlikely that the environmental regulations will be entirely effective where other factors such as the physico-chemical properties of environmental compartments would impede their effectiveness.

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