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Depositional History of Polycyclic Aromatic Hydrocarbons: Reconstruction of Petroleum Pollution Record in Peninsular Malaysia

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1. Introduction

In the last century, the world has experienced huge and various types of environmental threats. An important group of them is generated from the wide use of fossil fuel such as petroleum as the source of energy in industries, urban development and transportation. Hydrocarbons are the main constituents of fossil fuels thus petroleum hydrocarbons are possible and important source of pollution worldwide. Petroleum hydrocarbons enter the environment from accidental oil spill, natural leaks, industrial releases, vehicles or as by-products from commercial or domestic uses (Ou *et al.*, 2004). Hydrocarbons in petroleum include several types and categories of normal alkanes (saturated, n-alkane), unsaturated hydrocarbons, non-symmetric cyclic hydrocarbons (terpanes) and polycyclic aromatic hydrocarbons (PAHs). Predominance of these compounds in the environmental compartments or samples may indicate petroleum pollution. Petroleum hydrocarbon may disperse in the environment via atmospheric transportation and/or lateral transport. Petroleum contaminants are subject to several processes and changes after production or release such as degradation, photooxidation and decay. The trend over hydrocarbon changes in the environment depends on their chemical characteristics and depositional locations. Locations such as depository sediments under the sea bed surface usually keep hydrocarbon contents unchanged.

2. Polycyclic Aromatic Hydrocarbon (PAHs)

An important class of petroleum hydrocarbons is polycyclic aromatic hydrocarbons (PAHs). PAHs and their derivatives are ubiquitous in the environment such as air, water, soil, sediments and living organisms. PAHs are group of chemicals with more than 10,000 compounds that consist of two or more fused benzene rings (Fig. 1) in different arrangements (Blumer, 1976).
Among PAHs compounds, some have potential for being carcinogen, mutagen and disturbing human endocrine systems (Neff, 1979). Therefore they are categorized as environmental high priority contaminants. PAHs are lipophilic compounds consist of 2 to 7

benzene rings; the 2-4 rings are classified as Lower Molecular Weight (LMW) since 5-7 as Higher Molecular Weight (HMW). The LMW PAHs are more soluble in water and are acutely toxic to human and living organisms whereas HMW are highly soluble in lipid and more carcinogenic, mutagenic with more time period effects (Neff, 1979). The hydrophobic and lipophilic properties of some HMW PAHs make them relatively insoluble in water and tend to accumulate on surfaces or in non-polar matrices.
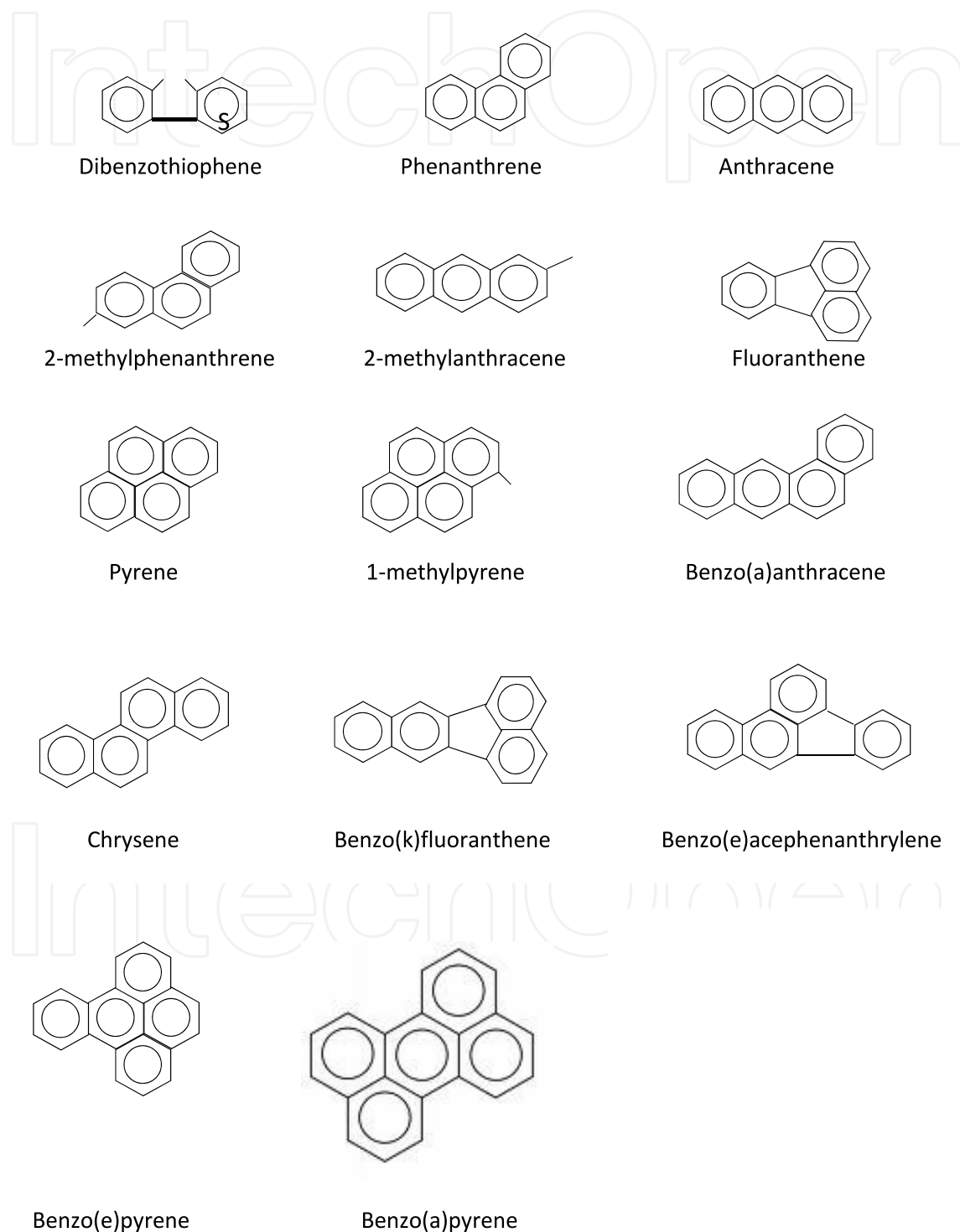

Fig. 1. Some of Polycyclic Aromatic Hydrocarbons Compounds.

The sorptive properties of PAHs are largely controlled by the organic particulate fraction of suspended and deposited sediments (Baker *et al.*, 1986). Particle bound PAHs have a short residence time in the water column before they are settled to the bottom sediments where they may be re-suspended, degraded or subjected to long-term retention. The extent of any release back to the water column depends on the degree of bioturbation, physical re-suspension and the physico-chemical properties of the compound (Wong *et al.*, 1995).

Concerns over PAHs compounds in the environment arise since they are persistent in the environment for a long period of time. PAHs are generated from anthropogenic source as well as nature. In the environment, natural products of PAHs are limited to few types such as Perylene, Phenantherene and Retene where there is no health effect on human and the environment (Neff, 1979).

Anthropogenic PAHs are widespread in the environment as pollutants produced from incomplete combustion of fossil fuel and biomass burning. Anthropogenic PAHs enter marine environment from two primary sources of Pyrogenic and Petrogenic. Pyrogenic source PAHs come from pyrolytic processes such as combustion of fossil fuel, urban and industrial activities, natural fire and biomass burning that produce high molecular weight and less or non-alkylated PAHs. Combusted PAHs after production attach into soot particles, move in far distances and get deposited on soil, terrestrial plants or surface layers of sediments at sea bottom. Some of pyrogenic products of PAHs such as fine particles from charcoals also are washed out from the place of production via sewage plants or precipitations to the marine environment.

Petrogenic sources of PAHs are mainly derived from the release of crude oil and petroleum products such as lubricating oil, diesel fuel, gasoline, asphalt and kerosene. This class of PAHs enters the environment via oil spill, tanker accident, routine tanker operation such as ballast water discharge and discharge from vehicle workshops (NAS, 2002).

3. Pentacyclic triterpanes

Major class of pentacyclic triterpanes, hopanes, is derived from precursor in bacterial membrane (microbial origins) of bacteriohopentetrol. Hopanes are the constituents of crude oil and some petroleum products. Hopanes are believed to be synthesized in the nature by cyclization of squalene precursor during the diagenesis (Fig. 2).
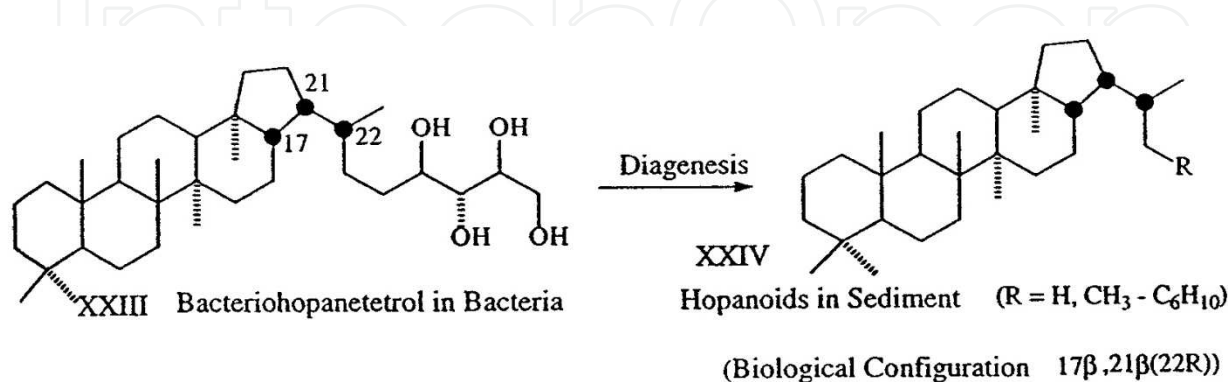

Fig. 2. Diagenesis process that converts bacteriohopentetrol in bacteria to $\beta\beta$ (22R) stereochemistry of hopane. This unstable configuration changes to more stable $\alpha\beta$ and $\beta\alpha$ hopane during the same process.

Classification of hopanes is based on the degree of oil maturation from specific source rock. Hopane itself is not categorized as pollution however they are distributed in the environment with petroleum hydrocarbon pollution and consequently are ubiquitous. They resist degradation processes thus are persistent component in crude oil and petroleum products.Due to this, they are widely used as the sources identifier of oil pollution in the environment. They are relatively existed in small amounts (usually <1% by weight) among other hydrocarbons. Hopanes are commonly found in C_{29}-C_{35}, together with two C_{27} species called regular steranes.

Homohopanes are the name of hopane series which the number of carbon arises by 30. The hopanes are composed of three sterioisomeric series, namely 17α(H),21β(H)- Hopanes, 17β(H),21β(H)- Hopanes and 17β(H),21α(H)- Hopanes. Hopanes with αβ configuration range from C_{27} to C_{35} are characteristics of petroleum because of their greater thermodynamic stability compare to other epimeric (ββ and βα) series. In geologically mature samples, αβ epimeric isomers are greater predominant over βα isomer (moretane). However ββ-isomers are commonly found in living organisms. Ts (18α(H)-22,29,30-trisnorneohopane) and Tm (17α(H)-22,29,30-trisnorhopane) can be a sensitive indicator of thermal maturity when capering oil or sediment samples from the same source. In addition, Hopanes with predominance of 17α(H), 21β(H)- stereochemistry indicates a substantial contribution from petroleum pollution.

Hopane distributions are usually recorded using the m/z 191 in mass chromatograms. An unusually high proportion of the C_{29} hopane is often associated with oil derived from carbonate source rock oil which includes most of those from the Middle East. Those oils also show a slightly enhanced abundance of the C_{35} extended hopane compare with the C_{34} homohopane. In C_{31}-C_{35} hopanes the biologically conferred 22R configuration is preserved during the initial stages of diagenesis. Subsequent isomerization results in a final equilibrium mixture containing approximately equal amount of 22R and 22S isomers. Oleanane is another triterpanes commonly associated with oil derived predominantly from higher plant sources. In conclusion, pentacyclic triterpanes are useful biomarker to identify plant and petroleum input of PAHs into the aquatic environment as well as sediments (Wakeham *et al.*, 1980; Tan and Heit, 1981; Bouloubassi and Saliot, 1993; Yunker and McDonald, 1995; Chandru et al, 2008).

4. Source, distribution and fate of PAHs in aquatic environment

PAHs are released into the environment via natural and anthropogenic sources. Natural source includes oil seeps, volcanoes, grass fires, chlorophyllous and nonchlorophyllous (bacteria and fungi) plants. Anthropogenic sources of PAHs include discharge from routine oil transportation, oil spill, power plants based on fossil fuel consumption, biomass burning, pyrolysis of wood and internal combustion in industrial and vehicle engines.

PAHs enter into the marine environment usually by anthropogenic sources while natural sources have less contribution in this process. Among many possible sources for PAHs contamination in the marine environments; municipal and industrial wastes, city runoff, riverine discharge and atmospheric input have higher proportion.

Petrogenic and pyrogenic based PAHs usually show similar behaviors and fates after entering the environment. Pyrogenic PAHs that are produced via combustion processes have a high and strong affinity to airborne organic particles that may move in greater distances by wind and other atmospheric phenomena. PAHs associated with airborne

particles reach to the top layer of the water column in the marine environment, moving to the water column and the bottom of the sea where settles in the sediment. Petroleum and petroleum products which are originated from concentrated hydrocarbon sources enter the marine environment and subjects to dispersion, evaporations, settlement in the bottom on the sediments, weathering, chemical changes, sunlight effects (photooxidation) and microbial degradation (bacteria, yeast and fungi) in short and long term period (Neff, 1979). Petrogenic sources of PAHs on the sediment stick into the particles and consequently is subjected to different chemical and biological changes. Heavier and more complex compounds of crude oil and its products are more resistant to microbial degradation. Regardless of the origin of PAHs, in the marine environment, they adhere to the particles (clay, silt, organisms, detritus and microbes) and settle on the sediments, where a variety of microbes metabolize it into some simple and light compound structure. Accumulation and bioaccumulation of PAHs in the marine environment and organisms are inversely correlated to the potential and ability of hydrocarbons to metabolize them either chemically or biologically.

Finding the source of hydrocarbon pollution is a great concern for many scientists all around the world. Although the first track in this line had been started in 1970s, many researchers are currently try to identify the source of hydrocarbon pollution in the marine environment. In Southeast Asia, the pioneering studies on specific compound analysis have been started by intensive survey in the Straits of Malacca (Zakaria et al., 1999, 2000, 2001, 2002, 2006) and followed laterally in a study in Gulf of Thailand (Boonyatumanoond et al., 2006 and 2007).

In order to identify the sources of hydrocarbon pollution in the environment, there are many techniques such as use of isomer pair ratios (Yunker, 2002), individual compound ratios (Hase and Hites, 1976; Laflamme and Hites, 1978; Baumard et al., 1998; Zakaria et al., 2000) and biomarkers (Volkman et al., 1997; Zakaria et al., 2002 and Wang and Fingas, 2005).

Some molecular ratios of specific hydrocarbons were developed to distinguish differences between PAHs originating from various origins and sources. Among those, the ratio of Phenantherene/anthracene (Ph/An) and flouranthene/pyrene (Fl/Py) were widely used by scientists (Steinhauer and Boehm, 1992; Budzinski et al., 1997; Baumard et al., 1998, 1999). The ratio of F1/Py (fluoranthene/pyrene) has been used to identify fuel sources, showing values < 1.4 for coal combustion (Lee et al., 1977) and < 1.0 for wood (Lee et al., 1977; Knight et al., 1983). In sediments, value for this ratio was 1.3-1.7 at remote sites and < 1.0 near to urban centers (Gschwend and Hites, 1981; Helfrich and Armstrong, 1986). The phenanthrene/anthracene ratio also applies as an indicator for measuring the remoteness (>15) or vicinity (<10) of PAHs sources to urban areas (Zhang et al., 1993).

High-temperature processes such as combustion of organic matters generates PAHs characterized by low ratio of Ph/An (<10), whereas slow maturation during catagenesis, reach to higher values (Ph/An <15). Same trend observed in ratio of flouranthene/pyrene (Fl/Py), where values greater than 1 come from pyrogenic sources and less than unity is indicative of petroleum input. Another ratio which is summarized by Yunker et al., (2002) is Flu over Flu plus Pyr (Flu/(Flu+Pyr)) that is generally greater than 0.5 in grass, wood or coal combustion, and the petroleum boundary ratio appears closer to 0.40 than 0.50, whereas the Flu/(Flu+Pyr) ratios between 0.40 and 0.50 are more characteristic of liquid fossil fuel combustion. Above values were shown to be relatively less reliable in different geographical locations due to the various combustion material sources (Budzinski et al., 1997).

PAHs in the environment have definite behaviors which are controlled by several processes. Processes which can control the transport and degradation of PAHs in sediment include: 1) partition of the compounds between aqueous (pore-water) and particulate phase, 2) microbial degradation, 3) uptake, metabolisms and depuration of PAHs by the benthoses 4) photo-oxidation (surface sediment), chemical oxidation and 5) biosynthesis. Moreover the compounds specific selections for above mentioned processes are absolutely selective.

It is now well established that microbial degradation of PAH occurs primarily in the aerobic zone (Bauer and Capone, 1985) with highest rates occurring with low molecular weight homologues (Lee *et al.*, 1977; Gardner *et al.*, 1979; Readman *et al.*, 1982).

Consequently, any degradation should result in selective losses of, anthracene relative to benzo[a]pyrene, and so affect the ratio of residual PAH. Readman *et al.*, (1987) calculated that up to 80% of anthracene and 40% of benzo[a]pyrene could theoretically be degraded during the approximately 2 year particle/PAH passage through the aerobic layer at the laboratory condition (Table 1).

PAHs	Degradation Rate (10^{-3})	Half Life (years)	PAH Percentage Aerobically Degraded (2 years)
Anthracene	2.18	0.87	80
Fluoranthene	1.67	1.14	71
Benzo(a) Antheracene	1.17	1.63	57
Benzo(a)Pyrene	0.67	2.73	40

Table 1. Theorical impact of degradation on sedimentary PAHs (after Readman *et al.*, 1987).

At the same time, the anthracene/benzo[a]pyrene ratio would be expected to decrease from surface sediment around one third in the anaerobic sediments. Jones *et al.*, (1986), show that oil-derived aromatic hydrocarbons can be rapidly biodegraded in sediments, but combustion-derived aromatic hydrocarbons in the same sediments are relatively resistant to degradation. Similar anomalous behavior of PAH has also been reported by Farrington *et al.*, (1983) where it was suggested that petroleum-derived PAH are more available for uptake by mussels than are pyrogenic PAH. Another process that controls the characteristics and concentration of PAHs is the phenomenon of photo oxidation. Photooxidation is a process which starts from the beginning stage of PAHs production in surface layers of soil, sediment, water or during the transportation in the air. There are selective photooxidation for specific PAHs such as Benz[a]anthracene which is more labile to photooxidation than chrysene + triphenylene (Kamens *et al.*, 1986, 1988), therefore the benz[a]anthracene/(benz[a]anthracene + chrysene + triphenylene) ratio are supposed to be lower in summer than winter samples (Fernandez *et al.*, 2002). Benzo[a]pyrene is photochemically less stable than benzo[e]pyrene where light exposure transforms unstable BaP to more stable BeP (Nielsen, 1988). The indeno[1,2,3-cd]pyrene/(indeno[1,2,3-d]pyrene + benzo[ghi] perylene) ratio is a prior and more stable to photooxidation than the ratios discussed above. Therefore there is expectation for Southeast Asian countries environment to show less concentrations of the low stable PAHs due to heavy and continued sunshine. Interesting to know that PAHs are penetrating in sediment layers after the deposition,

where in upper layers of surface sediments PAHs are rich in 5-6 rings PAHs rather than 2-3 rings which migrate downward from upper to deeper layers due to integrity with fine particles and their physical migration with fine particles (Curtosi *et al.,* 2007).

Malaysia, which is located in Southeast Asia, has a unique tropical environment and climate. It is surrounded by the Straits of Malacca in the west and the South China Sea in the west of Peninsular Malaysia. The western part of peninsular Malaysia has been experiencing rapid development during the last half century. On the other hand, the strategic location of this country has made Malaysia as one of the busiest shipping route in the world due to huge petroleum demand from the Middle East to Japan and China (Fig. 3).
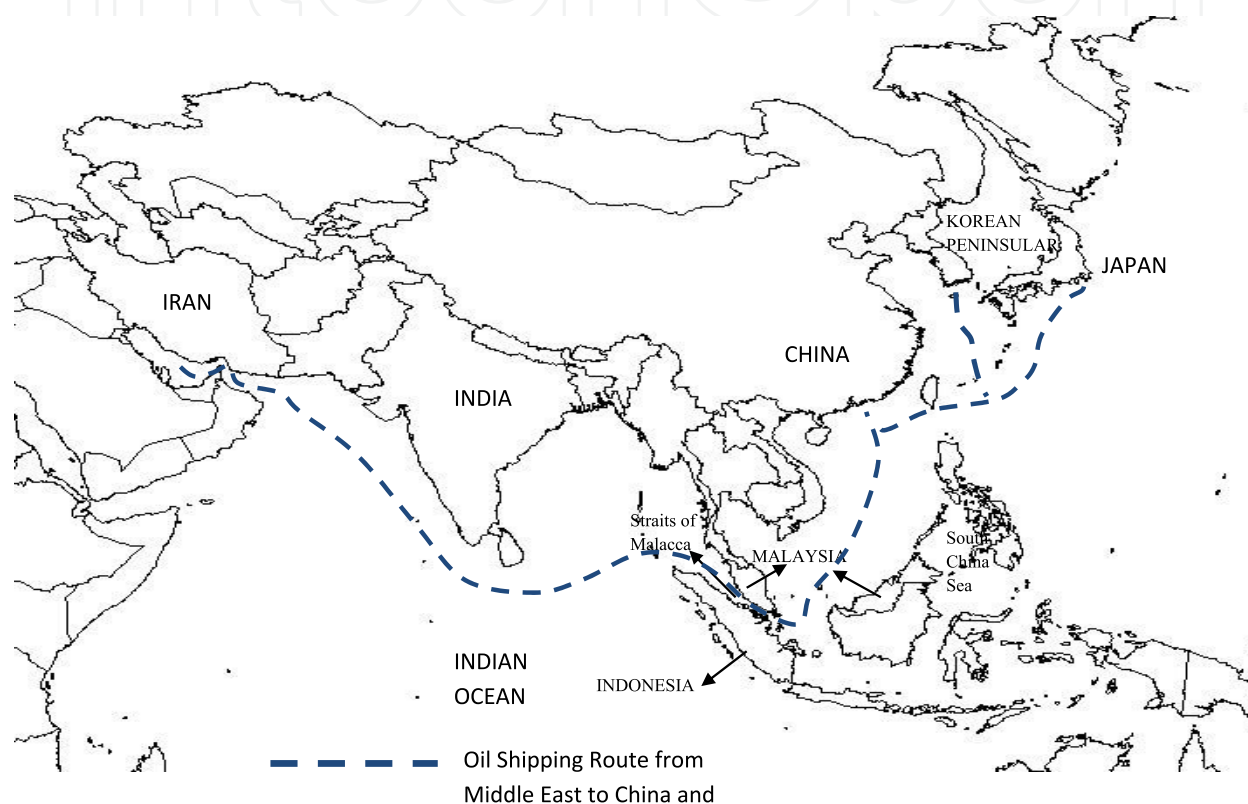

Fig. 3. Oil shipping route from the Middle East to the Far East via Straits of Malacca.

While Malaysia is experiencing extraordinary economic and population growth, it is also developing fast in industrialization, urbanization and motorization in last few decades. As a result of this development, the environment of this country is receiving more threats and hazards especially from the main source of energy which is petroleum. In Malaysia, the concentration and sources of hydrocarbon pollution vary according to locations. For instance, in western P. Malaysia, existence of rapid urban development and the establishment of several industrial areas, the hydrocarbon pollution is introduced throughout non-point and pointed sources. In the eastern P. Malaysia the pollution mostly comes from the urban area and less from industries, due to less industrial developments.

Besides that, Malaysian Marine Department reported 127 oil spill incidents since 1976 due to heavy oil tankers traffic in Straits of Malacca (Malaysian Marine Department, 2003). Zakaria and Takada (2003) believe that the Malaysian environment is under increasing threat of petroleum pollution; although this is not well-documented and recorded. To understand the

petroleum hydrocarbon pollution levels in the environment, scientists usually study different environmental samples such as water, sediment, bio-monitoring agents, particles and aerosols. In Malaysia, few researchers have studied petroleum hydrocarbon pollution and were used one or more types of above mentioned samples to demonstrate the status of hydrocarbon pollution in the country.

5. A brief on global historical records of PAHs

Studies on hydrocarbon pollution in historical trend were started alongside studies on recent and modern sediment hydrocarbon pollution. Among the first records, Hites *et al.*, (1977) studied PAHs concentration in Buzzards Bay, Massachusetts for the period from 1900 to 1970. Later on, Wakeham *et al.*, (1979) reported PAHs from sedimentary records of several lakes in Switzerland and Washington, indicative of high levels of PAHs pollution in modern input. In 1984, Prahl and Carpenter published data on PAHs and aliphatic hydrocarbons from Washington coastal sediments indicated that naturally derived aliphatic hydrocarbons are very frequent in ancient sediments while anthropogenic PAHs show high concentrations in recent deposited sediments. In Lake Michigan, the PAHs from sedimentary record reported by Christensen and Zhang (1993) showing a constant trend with fossil fuel consumption. Zhang *et al.*, (1993) reported PAHs maxima (maximum concentration) for early 1950s and 1985 for cores from Green Bay and Lake Michigan. Taylor and Lester (1995) reported significant decrease in PAHs concentrations since 1966 because of less coal combustion. This study is confirmed by Gevao *et al.*, (1997) where they reported PAHs sub-surface maxima in late 1960s and early 1970s from a small rural lake of Cambria, UK. This sub-surface maxima reported by Pereira *et al.*, (1999) from San Francisco Bay in California during 1950s.

There are many more studies on investigation of hydrocarbon pollution in sedimentary record. For instance, Hostettler *et al.*, (1998) studied the trace of biomarker profiles in San Francisco Bay dated sediments, showing anthropogenic input of hydrocarbons in recent decades depositions. Okuda *et al.*, (2002) reported high PAHs concentrations from Chidorigafuchi Moat, Japan, in 1960s. Furthermore, Yim *et al.*, (2005) reported high flux of PAHs in 1950s and 1980 from Masan Bay in Korea. Liu *et al.*, (2005) reported the PAHs fluxes from Pearl River Estuary, South China shows first sharp peak of PAHs levels in 1950s and consequently 1990s. Hartmann *et al.*, (2005) were reported depositional history of organic contaminants from Narragansett Bay, Rhode Island in the United States of America, showing highest PAHs fluxes in modern sediments from Apponaug Cove and sub-surface maxima in Seekonk River core sdiment.

There is an unpublished report of historical record of aliphatic and aromatic hydrocarbons in the straits of Malacca during 1980's by Law in a curtsey communication. Unfortunately, no more details are available since the scientist is deceased. In South East Asia the first available and published study pioneered by Boonyatumanond *et al.*, (2007) from Gulf of Thailand. In this report PAHs fluxes show high levels in 1950s and 1970s because of rapid increase in numbers of vehicles and their usage in Thailand. Also the molecular marker of Hopane shows high contribution of Petroleum and anthropogenic hydrocarbons in dated sediments from the studied area.

Coastal sediment containing a mixture of natural and anthropogenic PAHs presents two important problems for assessing the fate and effect of PAHs in the environment (Wakeham *et al.* 1980). At first, anthropogenic PAHs should be evaluated by site-specific background of

the PAHs derived naturally to the studied area. Secondly, parent PAHs data, solely, does not deliver reliable information due to overlap of source composition. This paper investigates the reconstruction of PAHs history and hopanes in one of the highly developing country in tropical Asia that experiences the rapid industrialization, motorization and urbanization.

PAHs derive to the environment via natural and anthropogenic processes. Natural processes of PAHs production occur during diagenesis and microbial activities as well as natural seeps of hydrocarbons and forest fires. Anthropogenic PAHs productions were consistent entering to the environment since mankind used fire for any purposes. The most recent PAHs derive to the environment so called modern input, have been increased since industrial revolution, when man used fossil fuel in industrial wheels. Beginning of the 20th century was in conjunction with rapid increase in PAHs flow to the environment when oil production contributed in fast development of the globe. PAHs come from oil origin enter the environment via petroleum and petroleum products such as gasoline and lubricating oils and their combustion. Combustion derived PAHs are dominated by the un-substituted moieties, whereas PAHs in petroleum are dominated by the alkylated homolog (LaFlamme and Hites, 1978). Lower formation temperatures such as in the formation of petroleum during the diagenesis preserve a higher degree of alkylated compounds (Youngblood and Blumer, 1975). Alkylated and non-alkylated PAHs are the basic knowledge of source identification of hydrocarbon and petroleum pollution in the environment. The degree of alkylation and alkyl homologs existed in environmental samples provides information on the sources of pollution. Youngblood and Blumer (1975) have proposed natural combustion such as natural fires in the forest as primary source of PAHs in deep layers of long core sediments. This idea is criticized by Wakeham et al., (1979) where forest fire might have constant input to the marine environment. In addition to the recent arguments, PAHs from natural fire does not occur often, since forest fire in the environment is not a predominant event. The concentrations of PAHs in the core sediments do not always correspond the unity of sources and input. This is due to various sources and concentrations that possibly interfere in a single layer along sedimentary intervals. Complex mixtures of different sources usually demonstrate irregular ratios that interfere with the results of source identification. Due to the complexity of different PAHs sources, PAHs compound specific ratios are still the most valuable tool for determination of pollution origin (Yunker et al., 1999).

Applications of different ratios are based on molecular structure of specific PAHs compounds in the environment. Lower Molecular Weight (LMW) PAHs is categorized by 2-3 benzene rings while 4-7 rings are known as Higher Molecular Weight (HMW). Pyrogenic PAHs (combusted) are characterized by high abundance of HMW compounds (4-6 benzene rings) and un-substituted (parent) compounds, whereas petrogenic PAHs are dominated by alkyl substituted and abundance of LMW (2-3 benzene rings) PAHs (Garrigues et al., 1995; Budzenski et al., 1997). The ratio of LMW over HMW PAHs is often applied for source discrimination of PAHs in environmental studies. The ratio of LMW/HMW PAHs for values lower than unity indicates pyrogenic source while 2 to 6 is an indicative for petrogenic input into the marine environment. The relative ratio of Methylphenanthrenes over Phenanthrene (MP/P) is also frequently applied for source identification of PAHs. The MP/P is another valuable ratio, as discussed earlier, based on un-substituted moieties and alkylated homolog frequencies in the sample. The MP/P fluctuates among values such as

0.5-1 for combustion derived PAHs in the sediments and 2-6 in sediment dominate by fossil fuel direct release (Prahl and Carpenter, 1983; Garrigues *et al.,* 1995; Budzenski *et al.,* 1997). The MP/P ratio around 4.0 is reported to be derived from crankcase oil (Pruel and Quinn, 1988), close to 1.0 for street and urban dust samples (Takada *et al.,* 1990, 1991) and around 0.5 for atmospheric fallout (Takada *et al.,* 1991). This ratio is higher for coal combustion sources than petroleum (Lee *et al.,* 1977; Takada *et al.,* 1990, 1991).

Among other ratios, scientists use other permanent ratios such as the relevant concentrations of sum of methylfluoranthenes and methylpyrenes over fluoranthene (Youngblood and Blumer, 1975; Laflamme and Hites, 1978; Gustafson *et al.,* 1997). In this ratio, values above the unity (>1) indicate the petroleum sources of pollutions. In addition, the results of these two recent ratios (MP/P and (MFl+MPy)/Fl) are not necessarily same but in some studies deliver similar trends (Pereira *et al.,* 1999).

Some specific compounds are well known in their characteristics. Among those compounds, Benzo(*a*)pyrene are proven carcinogens material to living organisms (Neff, 1979). Characteristics of specific compound PAHs are derived in the environment are strongly associated with the origins. One of these ratios is benzo(ghi)perylene to indeno(1,2,3-cd)pyrene (B*ghi*P/IPy) where the high values come from the automotive exhaust particles (Marr *et al.,* 1999; Nielsen *et al.,* 1996 and Tuominen *et al.,* 1987).

Okuda *et al.,* (2002) reported specific compound PAHs from the core collected from Chidorigafuchi Moat in Japan. They showed that in surface sediments (0-8 cm) there are significant and high values of ratio of benzo(ghi)perylene to indeno(1,2,3-cd)pyrene than lower sections of the core, whereas the ratio showed a constant value around unity for depth below 20 cm and increasing for higher levels up to the sediments from the surface. This strongly suggests that since 1990 the PAHs are more influenced by automotive exhausts. This ratio shows a relatively high value in automotive exhaust particles as it is constant with the socio-economic condition of the study area.

Yim *et al.,* (2005) reported specific hydrocarbon compounds for source identification of the PAHs in a study conducted in Masan Bay, Korea. The ratio that used including Phenantherene/anthracene (Ph/An) and fluorenthene/pyrene (Fl/Py) indicates pyrolitic origins. In the ratio of Fl/Py, scientists reported lower values than those reported from same source of American and European coal. Although Budzinski *et al.,* (1997) showed this low value from coal sources of Australia (Fl/Py: 0.3-0.7).

The amounts of HMW and LMW PAHs in environmental samples are possibly indicative of pollution sources. For instance, coal usually produces high amounts of PAHs than other fuel materials such as petroleum and natural gas. The highest concentration of PAHs (maxima) in core samples collected from Masan Bay, Korea, indicates this issue, where the sharpest peak appeared from layers corresponds 1950s-1980s. During the above era the country was widely used coal for various energy purposes (Yim *et al.,* 2005). Although previous studies found PAHs maximum concentration (maxima) in the sedimentary environment during 1940-1950, as an indication of fuel type changes from coal to oil and gas. The fuel type changes usually reveal increase or decrease in the total concentration of PAHs in the environment (Gschwend and Hites, 1981; Bates *et al.,* 1984; Barrick and Prahl, 1987). Later on, in Masan Bay, Korea this pollution input trends have been decreasing due to Pollution Prevention Act established in 1963 and strong environmental control and monitoring conducted by local and national authorities (Yim, 2005).

Beside the PAHs analysis to determine the concentration and sources of pollution in the environment, there are other tools such as measurements of magnetic susceptibility. This is a fast and cost effective method based on the presence of magnetic-rich spherules that forms during the combustion processes by oxidation of pyrite to magnetic. This method successfully applied by Morris *et al.*, 1994 in Hamilton Harbour, Western Lake Ontario, Canada to compare the method efficiency with PAHs analysis, approve the pyrolytic sources of PAHs pollution in the studied area.

6. PAHs in depositional record, Malaysia

The depositional record of PAHs in peninsular Malaysia is studied during a 4 years scientific investigation. Eight sedimentary core samples were collected from 4 identical coastal areas. Each area represented a historical background of development and socio-economic events of peninsular Malaysia. They are consisted of Klang (Port and Offshore), Malacca (Near and Offshore), Johor (Near and Offshore) and Tebrau (No. 1 and 2). Thus there were 2 core samples taken from each location mainly from near shore and offshore locations to evaluate the distance factor effect of distribution and concentration of PAHs compounds in the environment (Fig. 4).
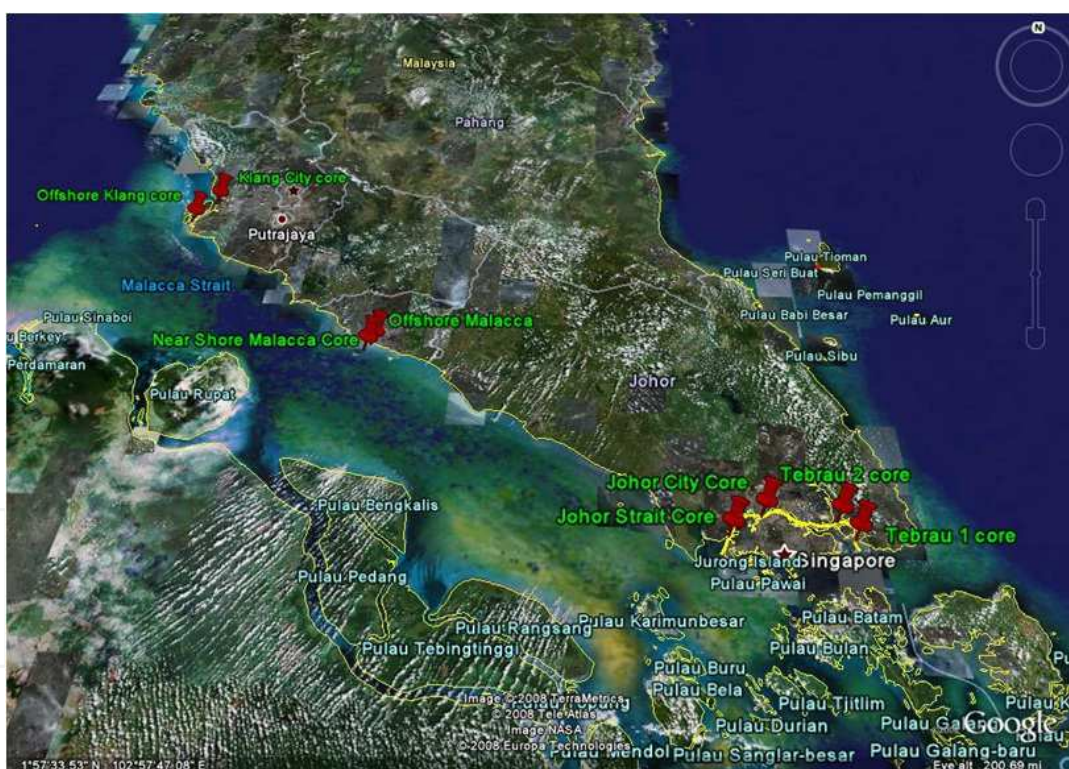

Fig. 4. Map of sampling locations.

The study elucidated the "Distribution, Sources and Depositional History of PAHs and Hopanes in Selected Locations in Peninsular Malaysia" using chemical molecular markers such as PAHs and Pentacyclic Triterpanes (Hopane) in deposited sediments. The cores lengths were ranged from 21 to 56 cm. The ^{210}Pb was used to reconstruct the pollution history of collected cores, revealed a time period of 60 to 280 years in different cores. Table 2 shows the concentration of PAHs in the sedimentary core of the study areas.

The core that was collected from the Klang City station showed that since 1945, there was an increasing trend in total deposited PAHs (Sakari *et al.,* 2010a). The highest concentration of total PAHs was observed during the era of 1990 to 1998 (2442 ng/g d. w.) as a sub-surface maxima which is interestingly followed by minimum PAHs level of 33 (ng/g d. w.) for the era of 1999 to 2007. Although in lower layers, the total PAHs of 161 (ng/g d. w.) was reported from the period of 1954-1962. In all sedimentary layers and intervals, specific compounds such as BkF, BeP and BaP were the leading PAH among others. This trend of PAHs increase is highly correlated to population increase of surrounded area, increase in registered cars and economic data of the study area. The rapid and sudden drop of total PAHs was interpreted as a joint function of physical phenomena, as well as weather condition, improvements of vehicle engine performance and enforcement of law and legislations.

In Offshore Klang station, the results showed very much depleted concentrations compared to Klang City core. Except for the recent decades deposited sediments, that showed lower concentration usually the core revealed homogenized concentration of PAHs fluctuating from 20 to 32 (ng/g d. w.). It is reported that the highest level of 32 ng/g d.w. happened at the beginning of the 20th century. The PAHs input in this core was not correlated to any of above mentioned socio-economic data, indicative of constant input via atmospheric fallout, where the BkF and BeP were the leading compounds throughout the core intervals. In Offshore Klang core, again the signature of pyrogenic input of PAHs was observed as those MP/P and L/H ratios. For both cores of Klang area, it is found that pyrogenic input from vehicle's emission and asphalt are the main contributor of PAHs into the marine environment of this area, although none of hopane signatures showed definite sign of any specific oil sources mainly due to combustion effect of pyrogenic sources on molecular structure of hopane.

In Malacca, the first core was collected from the near shore location showed the highest concentration of total PAHs in the entire study areas. The highest concentration of total PAHs (4195 ng/g d. w.) was reported from 1977 to 1983 while the lowest were observed at the beginning of the 20th century (Sakari *et al.,* 2011). Interesting to see that very severe depletion of HMW exists in this core and in all layers. The predominant of compound in this core was shown to be Phenanthrene and most of the sediment intervals revealed pyrogenic sources with MP/P ratio below the unity.

Offshore Malacca core was shown lower concentration than near shore but still Phenanthrene and its derivatives are the main PAHs contributor to the total PAHs. The highest and lowest concentrations of PAHs were revealed during 1963 to 1969 and 1914 to 1920, respectively. The signature of PAHs likewise near shore station was shown pyrogenic. This is reconfirmed by MP/P values. Identification of the PAHs origin using hopane marker showed street and urban dusts of Malacca City as the main contributor as observed in near shore Malacca.

In Johor, the first core collected from a location near the city where the connecting bridge (causeway) commutes Malaysia to Singapore. In this location, along the core, the PAHs concentration has ranged from the minimum of 44 (ng/g d. w.) to the maximum concentration of 1129 (ng/g d. w.). The highest concentration of PAHs was observed during the era from 1922 to 1969. Moreover, the lowest concentration observed in recent deposited sediments (Sakari *et al.,* 2011b). The PAHs signature showed a mixture of pyrogenic and petrogenic input where most modern input showed more combusted materials than old sediments with pyrogenic signature. This statement is evidenced by MP/P and LMW/HMW ratios. The leading PAHs compounds along core intervals were BeP, BkF and Phe and its alkyl substitutes.

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Klang City Core

Concentration (ng/g d.w.)

Sediment age (year)*	1945-1953	1954-1962	1963-1971	1972-1980	1981-1989	1990-1998	1999-2007
[a]Total PAHs (ng/g d.w.)	488.99	161.35	238.11	1032.52	1572.97	2422.93	33.85
[b]L/H PAHs	0.55	0.60	0.56	0.75	0.35	0.45	0.92
[c]MP/P	0.63	1.11	0.92	0.66	0.83	0.83	1.11
[d]TOC mg/g	61.23	51.40	51.37	55.93	59.45	71.04	64.96

Offshore Klang Core

Concentration (ng/g d.w.)

Sediment age (year)	1910-1916	1917-1923	1924-1930	1931-1937	1938-1944	1945-1951	1952-1958	1959-1965	1966-1972	1973-1979	1980-1986	1987-1993	1994-2000	2001-2007
[a]Total PAHs (ng/g d.w.)	29.92	32.05	10.34	24.66	23.29	24.05	20.04	11.21	12.67	7.31	20.10	9.54	15.42	11.91
[b]L/H PAHs	0.55	0.82	0.49	0.49	0.36	0.96	0.41	0.34	0.38	0.34	1.26	0.34	0.99	0.40
[c]MP/P	0.23	0.24	0.22	0.22	0.34	0.46	0.32	0.59	0.37	0.52	0.51	0.54	0.64	0.83
[d]TOC mg/g	69.09	85.67	85.15	65.21	77.23	72.13	45.60	61.23	51.40	51.37	55.98	59.45	71.04	64.96

Near Shore Malacca

Concentration (ng/g d.w.)

Sediment age (year)	1879-1885	1886-1892	1893-1899	1900-1906	1907-1913	1914-1920	1921-1927	1928-1934	1935-1941	1942-1948	1949-1955	1956-1962	1963-1969	1970-1976	1977-1983	1984-1990	1991-1997	1998-2005
[a]Total PAHs (ng/g d.w.)	378.02	358.08	402.13	275.10	508.48	431.91	603.70	266.29	967.16	910.25	176.61	3111.47	4447.14	999.16	4195.07	2660.95	335.36	451.87
[b]L/H PAHs	96.84	23.31	126.59	39.66	22.75	12.93	22.87	8.98	29.36	26.70	174.55	144.23	195.50	204.02	122.70	505.00	24.16	20.22
[c]MP/P	0.78	1.26	3.17	0.77	0.84	0.76	0.88	1.09	2.39	1.03	0.72	0.80	0.71	1.31	0.93	0.86	3.19	8.58
[d]TOC mg/g	124.20	117.00	126.90	117.30	113.40	135.30	129.80	149.70	143.50	145.00	137.00	143.90	148.90	143.40	134.40	147.60	133.70	137.20

Offshore Malacca Core

Concentration (ng/g d.w.)

Sediment age (year)	1886-1892	1893-1899	1900-1906	1907-1913	1914-1920	1921-1927	1928-1934	1935-1941	1942-1948	1949-1955	1959-1962	1963-1969	1970-1976	1977-1983	1984-1990	1991-1997	1998-2005
[a]Total PAHs (ng/g d.w.)	48.00	2.63	61.03	2.92	1.71	325.84	60.42	73.60	10.19	107.11	71.70	714.37	15.26	70.64	19.28	126.74	98.37
[b]L/H PAHs	3.96	NA	3.90	0.32	0.32	0.61	2.13	3.64	0.78	3.79	7.28	0.25	0.62	5.79	0.83	8.60	7.06
[c]MP/P	0.77	0.92	0.79	1.29	2.06	0.90	22.84	0.91	4.95	0.85	0.74	0.80	5.11	0.90	9.92	0.83	0.98
[d]TOC mg/g	143.30	144.60	139.80	137.90	154.20	149.90	141.00	66.90	138.50	136.10	105.60	141.30	129.20	159.60	172.60	156.10	184.10

Johor City Core						Concentration (ng/g d.w.)		
Sediment age (year)	1874-1885	1886-1897	1898-1909	1910-1921	1922-1933	1934-1945	1946-1957	1958-1969
aTotal PAHs (ng/g d.w.)	580.51	1005.40	648.67	478.73	1129.52	935.25	725.76	920.98
bL/H PAHs	0.95	0.15	1.93	0.60	4.27	0.60	0.44	0.54
cMP/P	2.45	2.39	2.41	1.93	1.87	1.66	1.61	1.04
dTOC mg/g	227.30	218.60	221.20	202.60	207.60	221.20	108.20	256.00

Offshore Johor Core						Concentration (ng/g d.w.)		
Sediment age (year)	1886-1895	1896-1905	1906-1915	1916-1925	1926-1935	1936-1945	1946-1955	1956-1965	1966-197
aTotal PAHs (ng/g d.w.)	304.64	321.69	92.06	68.58	411.00	363.70	521.15	215.28	286.63
bL/H PAHs	107.31	108.39	73.57	47.71	291.92	33.05	9.01	8.60	3.36
cMP/P	1.38	0.96	1.87	1.55	0.90	1.00	1.00	2.43	3.08
dTOC mg/g	77.90	82.10	153.50	53.40	50.30	55.40	44.80	51.70	45.40

Tebrau Core I						Concentration (ng/g d.w.)			
Sediment age (year)	1728-1847	1748-1767	1768-1787	1788-1807	1808-1827	1828-1847	1848-1867	1868-1887	1888-1907	1908-1927
aTotal PAHs (ng/g d.w.)	6.86	11.83	25.42	24.87	23.99	3.51	11.50	21.82	18.02	20.41
bL/H PAHs	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
cMP/P	0.29	2.00	0.95	0.95	0.99	0.00	0.72	0.90	0.76	0.87
dTOC mg/g	125.30	126.70	156.70	162.80	109.80	160.50	183.00	103.00	213.80	140.00

Tebrau Core II						Concentration (ng/g d.w.)		
Sediment age (year)	1862-1874	1875-1884	1886-1897	1898-1909	1910-1921	1922-1933	1934-1945	1946-1957	1958-196
aTotal PAHs (ng/g d.w.)	10.50	9.65	7.68	12.36	9.53	4.63	13.56	14.59	8.03
bL/H PAHs	6.16	23.23	NA	8.05	NA	NA	17.88	2.22	NA
cMP/P	0.86	0.92	1.00	0.80	0.51	0.93	0.89	0.59	0.85
dTOC mg/g	95.80	96.10	104.80	95.20	95.30	92.20	112.60	110.70	102.40

aTotal PAHs: sum of 18 PAHs ranging from Dibenzothiophene to Dibenzo (a,h) antharacene; bL/H PAHs: ratio
cMP/P: ratio of sum of 3-Methylphenanthrene, 2-Methylphenanthrene, 9-Methylphenanthrene and 1-Methylph
dTOC: Total Organic Carbon.

Table 2. The Concentrations of Polycyclic Aromatic Hydrocarbon (PAHs) and TOC and ratios of L/
collected from the study area.

The second core was collected from Johor strait. This core showed generally lower concentration than those observed in Johor City core. The highest concentration of PAHs (521 ng/g d. w.) observed soon after the WWII and during the independency. The main source of PAHs in this core showed petrogenic signature using MP/P and hopane ratio.

Tebrau Strait is the main gateway connecting Singapore and Malaysia to the waters of South China Sea. The cores from Tebrau Strait were collected from eastern part of Johor-Singapore waterway. The first core revealed the highest concentration during the modern era (1988-2005; 311 ng/g d. w.) and the lowest concentration during the ancient time (1827-1847; 3.51 ng/g d. w.). Since the study was not revealed significant HMW PAHs, the ratio of L/H was not mathematically available in this core however MP/P ratio showed pyrogenic input to the marine environment of the study area (Sakari, 2009).

The second core in Tebrau Strait likewise showed same increasing trend where the highest concentration observed in the recent deposited sediments. In general, the concentration in this core is lower than the first Tebrau core. The sources of PAHs again indicate that there is pyrogenic input received in this location where MP/P was shown values below the unity. The hopane ratio showed that mostly Southeast Asia Crude Oil is the main contributor of PAHs in these cores. This statement is confirmed by ratios such as C_{29}/C_{30} from the hopane compounds.

In conclusion, the concentration of PAHs and hopane in all cores showed that the increase in populations, number of cars, socio-economic indicators such as GDP and GNP, industries, urbanizations, oil production and transportation accelerate the pollution trend. The overall view of PAHs concentration showed that near shore locations demonstrate higher PAHs contribution than offshore stations.

The total concentration of PAHs in this study ranged from 1.7 to 4447 (ng/g d. w.) with a mean value of 381 (n=105). The results of all source identification tools have been shown that a range of highly pyrogenic to extremely petrogenic PAHs are existed in the study area where a zero value of other PAHs is observed in conjunction with a minimum Methyl Phenantherene concentration that possibly indicates negligible nature derived compounds. Total organic carbon (TOC) in this study were fluctuated from 44 to 256 (mg/g) with an average of 117 mg/g (n=105) that statistically showed to be in a very low to negative correlations with total PAHs. The source identification parameters that has applied in this research were ratios such as Ph/(Ph+An), Ph/An, Fluo/Pyr, Fluo/(Fluo+Pyr), BeP/(BeP+BaP), Phe/(Phe+An) and BaA/(BaA+Chry). The application of these ratios revealed vicinity of sources such as adjacent cities, vehicles and industries to the study areas. This study has concluded that these sources emit gasses and particle based materials that transfers via lateral movements by daily rain wash and flushing into the marine environment thru canals, rivers, and drainage and finally settle down to the estuaries and straits. It is also emphasized that shipping and oil transportation play an important role in releasing PAHs into the study areas where the daily heavy ocean going vessels transport goods and oil.

7. Sources and origins of PAHs in deposited environment

Several studies around the world were conducted to understand and determine the sources of hydrocarbon pollution in sedimentary cores. One of the most pioneering studies is conducted by Hites *et al.*, (1977), where three stages of hydrocarbon deposition were reported from 1850 till 1970 from the Buzzards Bay, Massachusetts. This report indicates the

sources that were almost constant from 1850 till 1900. The constant source of PAH pollution has been determined as combustion processes, regardless to its origin from natural or anthropogenic sides.

In the UK, Readman *et al.,* (1987) reported PAHs from Tamar Estuary, showing predominant of parent compound rather than alkyl homologues, a clear indication of pyrogenic input correlate with increased motor vehicle activity and road runoff. This is remarkable that compositional uniformity of PAHs throughout the polluted sedimentary core characterize biogeochemical transformation and exchange processes (sorption/leaching; microbial breakdown; photodegradation; etc). Thus it has been concluded that the majority of un-substitute PAHs comes from combusted fossil fuel and/or street dust. Rapid reduction in PAHs concentrations since 1940s may come due to fuel consumption changes from coal to petroleum (Gschwend and Hites, 1981; Bates *et al.,* 1984; Barrick and Prahl, 1987).

Industries are one of the most important contributors of PAHs input into the environment. Appearances of pollutions such as PAHs depends on the time and location of production and deposition. Martel *et al.,* (1987) reported considerable increase of PAHs concentration since 1930 from Saguenay Fjord, Quebec in Canada where two aluminum reduction plants increased the PAHs concentrations in the studied area. The above statement was approved after a couple of years by Cranwell and Koul, (1989) where anthropogenic PAH input that peaked 1900-1920 in Windermere North Basin is tentatively attributed to local industrial input. The decline in post-1975 flux values may result from replacement of coal as the source of energy by oil or gas however flux values remain ten times higher than in the pre-industrial age.

The sources of pollution are always not unique or with a same pattern. It can be a contribution of different sources such as natural and anthropogenic. Christensen and Zhang, (1993) identified a combination of sources including coal, petroleum and wood from four sediment cores collected in Lake Michigan for Source identification. In this study, the sedimentary record of PAHs high flux is reported with petroleum origins (oil and gas during 1985) but the high PAHs flux for 1950s was clarified when coal was used. As the background data, the concentration of PAHs was zero during 1900 for petroleum derived PAHs.

In another study Su *et al.,* (1998) analyzed 6 cores from Green Bay, Wisconsin in order to identify the PAHs concentration and sources. This study showed the same trend in source combinations for PAHs in the studied area. The total concentrations were reported from 0.46 to 8.04 ppm with combination of combustion sources from coal, wood and petroleum hydrocarbon.

Based on the regulations and the availability of different sources, in the energy markets, some of those are decreased in consumption or fully stopped. For instance, Taylor and Lester, (1995) showed that since 1966 that coal combustion had been banned; the coal derived PAHs has decreased and shifted to the oil and gas sources. Although the usage of coal is limited in many countries all around the world, there are still footprints of its application in many countries. For example, Liu *et al.,* 2005 reported 30% of coal combusted PAHs from air particles collected from Guangzhou, China atmospheric environment, due to wide use as energy source.

The historical profile of PAHs from the sedimentary cores collected from Lake Michigan, USA, showed the Wisconsin coal profile exhibit similar trends with peaks for 1946-1951 and 1968-1973, indicative of coal combustion source material (>36%) and petroleum sources (>76%) in various samples using Factor Analysis (FA) model (Rachdawong *et al.,* 1998).

Although the atmospheric environment distributes the PAHs in a homogenized concentrations, lateral transportation such as movements via rivers demonstrate irregular and high amounts of PAHs concentration in the environment. Witt and Trost, (1999) indicate significant contribution of river discharge of the petrogenic hydrocarbon to the sediment with predominant of higher molecular weight PAHs due to its stability in German coastal waters. The highest concentration of the PAHs occurred in recent sediments presented from 1 to 8 cm of surface, indicative of modern input. Petrogenic PAHs pollution which are mainly enter into the marine environment via lateral transport contribute to the pollution history of the world since past centuries. This petrogenic PAHs are abundant in riverine systems due to wash out phenomenon from the city run off. Liu *et al.*, (2000) reported the sources of PAHs from core collected in Yangtze Estuary, China; that mainly was petrogenic origin. However, PAHs concentration in sedimentary records may be affected due to physico-chemical conditions during sedimentation, the nature of inputs, biodegradation, and bioturbation (surface sediments).

As petrogenic PAHs affect the marine environment in short distances, the pyrogenic PAHs are subject to long range transportation via atmospheric movements (Prahl and Carpenter, 1983). This model of transport is able to influence remote and pristine areas. Rose and Rippey (2002) were reported low concentration in recent PAHs deposition via atmospheric movement into a remote lake in the north-west England. Specific compounds analysis for the definition of ratios tested for this study (phenantherene:anthracene and fluorenthene:pyrene) do not identify and clarify any specific reason while shows less urban discharges to the lake comparing to the era of pre-1830.

Natural disasters affect the concentration of the PAHs deposited in the marine environment. Flood as a natural disaster contributes in PAHs irregular concentrations where it washes out city surface to water bodies such as rivers and streams. Ikenaka *et al.*, (2005) reported the highest PAHs of core layers with multiple pyrogenic sources from Lake Suwa, Japan when the heavy rain and consequently flood had been historically consistent. Discharges from natural disasters and local input are characterized by irregular distributions of PAHs. Since PAHs enter locally in mass amounts distribute according to the physical and chemical properties of the destination points. In a study (Moriwaki et al, 2005) on historical trend of PAHs in reservoir sediment core of Osaka, Japan; however the sources of PAHs in the sedimentary record is found a combination of grass, wood and coal for pre-industrial era, for early 20th century and petroleum and its combusted derived materials in recent and mostly modern input.

As discussed earlier in previous sections, there are possibilities for natural inputs of PAHs entering into the enviroment. PAHs naturally derive from higher plant detritus and degradations products (Simoneit and Mazurek, 1982; Yunker and McDonald, 1995). Four and 5 benzene rings PAHs can be produced from microbial breakdown of plant wax and woody tissue. Prahl and Carpenter (1983) were reported natural sources of PAHs in Washington coastal sediments with a constant input of clay samples represents the era of Pleistocene. Quiroz *et al.*, (2005) reported 50 years of PAHs depositions into the Laja Lake from south central Chile, were showed relatively low PAHs concentration (226 to 620 ng/g d. w.) with mostly natural origins. One of the most important and mostly natural PAHs is Perylene. Perylene is 5 benzene rings PAHs which there are doubts in its origin. High temperature combustion of the internal engines produces perylene however other sources originate. This is strongly believed among scientist that perylene can produce naturally in the deep sediments via diagenesis. Interestingly, there are several reports that indicate the

high perylene concentration from surface sediments (Zakaria *et al.*, 2002; Tolosa *et al.*, 2004) and throughout the core (Barra *et al.*, 2006).

PAHs studies in core samples are subject to scientific debates. Core samples have different properties than surface sediments samples thus the fate of contaminants are various from surface. In surficial sediment, there are chemical, physical and biological properties which affect the targeted compounds in analytical analysis and interpretation of their data. In sediments collected from a core, there is no expectation of aerobic condition whereas the anoxic characteristics are notable for any possible chemical and biological changes. The profile of individual PAH concentrations with depth in sediment often reflect changes in source input over time rather than significant *in situ* biological degradation (Hites et el, 1977; Prahl and Carpenter, 1979). Although some organisms were capable to biosynthesize naturally the hydrocarbons (Graef and Diehl, 1966; Hancock *et al.*, 1970), other studies reveal the bioaccumulation effects of organisms in the core sediments (Hase and Hites, 1976). Moreover, some PAHs are generated by post-deposition transformations of biogenic precursors over a short period of time. This subject was confirmed for Perylene in research conducted by scientists (Aizenshtat, 1973; LaFlamme and Hites, 1978).

While aliphatic hydrocarbons are subjected to dissolution and microbial degradation, PAHs remain less or unchanged (Yunker *et al.*, 1999). Although Wakeham *et al.*, (1979) believe that lower molecular weight PAHs contribute in lower concentration in the total PAHs comparing high molecular weight in the core sediments. This interprets as a faster degradation of the PAHs that enter into the marine sediments. PAHs are always associated with organic carbon in sedimentary environment and are integrated with those values, but sometimes greater values of PAHs are not associated with TOC, indicative of soot particle existence in the sediments. For example Richardson Bay studies in the United States showed high values of PAHs with low values of TOC. This is an indicative of soot particle associated in the sediments come from the atmospheric transportations of combusted fossil fuel and organic contents that are less available in partitioned PAHs in the organic carbons (Pereira *et al.*, 1999). PAHs associated with soot particles are less biologically available for uptake than the PAHs derived from the petroleum and oil spill (Farrington *et al.*, 1983; Gustafson *et al.*, 1997). PAHs studies through the core samples are usually consistent with gradual and little changes either in concentration or in ratios in a normal condition but environmental disasters such as oil spills show significant changes. Therefore, core sections always do not show sudden changes in PAHs ratio values.

8. Application of biomarkers in petroleum pollution studies

The forensic chemistry techniques fingerprint pollutants in environmental samples. This technique is based on existence and abundance of the biomarkers. Terpanes are a group of biomarkers that are ubiquitous in the environment together with hydrocarbons. Pentacyclic triterpanes (hopanes) are the group of biomarkers that existed in crude oil and some petroleum products. As discussed earlier, hopane as a fingerprinting biomarker delivers from precursor of bacterial membrane (microbial origins) of bacteriohopentetrol (Fig. 2). The production of hopane in the nature is due to cyclization of bacteriohopanetetrol during the diagenesis. Basically, the stereochemistry of hopane makes them thermodynamically unstable (Peters and Moldowan, 1993). Hopanes in their biological origins present 17β(H), 21β(H) compounds that is known as biological stereochemistry.

Instability against temperature increase is due to their polar and non-polar ends. Upon change, they might convert from ββ to more stable configuration of αβ and βα structures. The αβ that is called hopane is predominantly available in crude oil and some petroleum products. Hopanes are relatively involatile, resist biodegradation, geologically mature and relatively stable in the environment (Simoneit et al., 1988) however there are chemical characteristics and properties among hopanes that compounds with higher number of carbon (*e.g.* C_{35}) shows bigger resistibility against biodegradation than lower numbered such as C_{31} (Frontera et al, 2002) (Fig. 5).
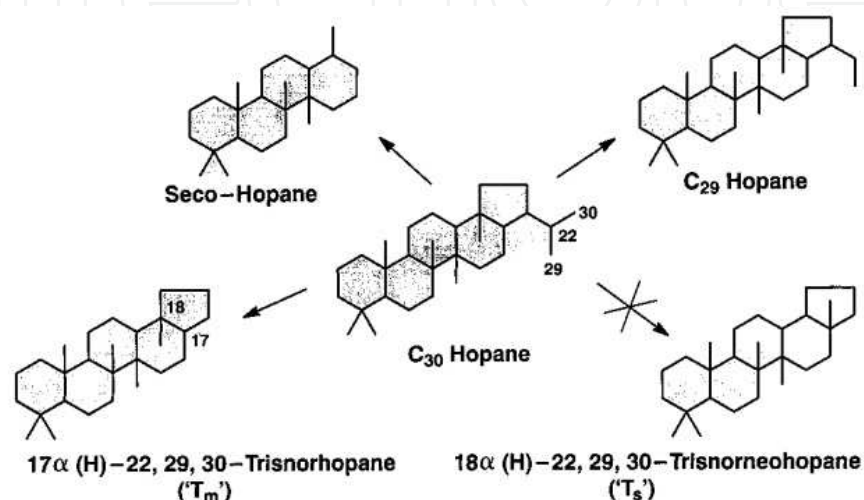
Fig. 5. Hopane chemical structures.

Homohopanes are the name of hopane series in which the number of carbon arises by thirty (n=30). The relatively more abundant homohopanes (C_{31}-C_{35}) are showed in less oil contaminated sites with significant loss of C_{30} (Colombo et al, 2005). In environmental samples from the biomass burning, hopane appears together with moretanes with abundance of C_{27} and C_{31} (Standley and Semoneit, 1987) that overlaps in common peaks (Omar et al., 2006).

Hopane is found in mineral oil and coal based fuel and lubricants (Kapalan et al, 2001). An unusually high proportion of the C_{29} hopane is often associated with oil derived from carbonate source rock oil which includes most of those from the Middle East however existence of oleanane is indicative of Southeast Asian oil.

9. New dimension of biomarkers; A reliability test over hopane

PAHs and hopane compounds in the study area were identified by comparing chromatograms of samples and standard solutions in the GC-MS. Chromatograms were compared in their retention time, surface area and mass spectra. Some of samples from the core intervals in various locations presented an absence or irregularity of appearances of peaks (representing compounds) in the chromatograms. Since some of Hopane compounds were missing, the identification of sources was difficult. We noticed that hopanes with carbon numbers from 27 to 30 (single peaks) are the most missing or depleting compounds among others. However hopanes with carbon numbers from 31 to 35 that appears in twin peaks (S and R stereochemistry) are dominant showing an unchanged structure. In this

report, samples mostly from offshore locations such as Malacca and Klang showed this phenomenon. These samples are observed to be identical in their source and origin of production. They are highly pyrogenic appearing in extremely depleted MP/P and L/H ratios. Meantime, it is observed that hopane chromatograms appearing shorten or fade up in single peaks (C_{27}-C_{30}). Twin peaks however showed more resistance than single peaks, the depletion was also observed among them.

The scenarios are different among samples with petrogenic sources such as crankcase oil, spilled oil and lubricating oil. They show taller and sharper single peaks together with complete twin peaks representing C_{31} to C_{35}. We believe that the stereochemistry of twin peaks provides resistibility against temperature increase rather than single peaks. Thus, it is criticized that high temperature especially in combustion process of petroleum in internal engines may cause destruction on compound structure appear as demolished or depleted peaks in chromatograms (Peters et al 1992; Colombo et al, 2005). Hence, application of some compound and isomer pair ratios of hopane are failed to assist source identification of PAHs.

The correlation was applied for statistical comparison between MP/P and other ratios such as C_{31}-C_{35}/C_{30}, C_{29}/C_{30}, Tm/Ts and C_{31}-C_{35}/C_{29}. Increasing of hopane indices like C_{31}-C_{35}/C_{30} and C_{31}-C_{35}/C_{29} with depletion of MP/P (combusted) may suggest demolishing of chemical structures in C_{30}, C_{29} and MP compounds during the high temperature combustion (Peters et al, 1992).

Therefore in an environmental sample such as sediment, theoretically a decrease in MP/P values renders high temperature in combustion process. Here, the theory criticizes the possible changes on chemical structure of single peak hopane compounds with carbon numbers ranging from C_{27} to C_{30}.

A positive correlation were observed between Offshore locations such as Malacca and Klang together with near shore station such as Klang City demonstrate combustion of petroleum where several and average MP/P appear to be lower than unity. Here there are negative correlation between the MP/P and hopane indices of C_{31}-C_{35}/C_{30} and C_{31}-C_{35}/C_{29}. These correlation values indicate that combustion results lower values of either C_{29} or C_{30}. (Takada et al., 1990; Prahl and Carpenter, 1983; Pruel and Guinn, 1987; Garrigues et al., 1995).

10. Natural vs. anthropogenic PAHs

PAHs are known as anthropogenic and/or natural compounds, based on their sources of production (Simoneit and Mazurek, 1982; National Academy of Science, 2002). Natural process is called a procedure that bacterial and algae are involved. This process results in-situ production of PAHs that produce limited concentrations (Hites et al., 1977; Prahl and Carpenter, 1979). Anthropogenic processes usually produce greater concentration of PAH in the environment. They include combustion of organic matter such as plant and/or oil and direct release of oil and its derivatives into the environment (Neff, 1979). Thus natural in-situ PAH generation in sedimentary environment is negligible in the total concentration of anthropogenic amount. There are limited locations around the world that produce natural based PAHs. These reports are mostly from Brazilian tropical forest where scientists report appearance of Phenanthrene, Naphthalene and Perylene in remote and virgin locations (Wilcke et al, 2003, 2004).

Likewise reports from tropical forest of Brazil, we expect to have a natural contribution of some specific polycyclic aromatic hydrocarbons such as Phenanthrene and Perylene in Peninsular Malaysia. As it has been discussed earlier, it is too hard to differentiate specific compounds as background level from nature from those as anthropogenic input using ordinary instrumentations. The application of hopane assisted us to technically differentiate those natural from anthropogenic individual PAH. Dated sedimentary intervals along the core have shown deposited PAH in which represents an era before the oil exploration and usage contain limited but detectable concentrations of Phenanthrene. The same signature has been frequently found in dated ancient sediment from Malacca and Tebrau in which intervals represent an era of 17th century. This research expects a constant input of natural hydrocarbons into the study area.

11. High fluxes; Climate contribution to distribution of PAHs

Malaysia is located near the equator where the weather is characterized as hot and humid with constant daylight time of around 12 hours and heavy rainfall. This cause abundance of plants and thus increase in available organic matter in the environment. Daily heavy rainfall basically washes away organic material such as total organic carbon that is associated with PAHs from the city and land surface into the water. Since the media for PAHs transport is always available in the environment, it is expected to record the highest existed PAHs in the sedimentary environment.

Malaysia has been experiencing a rapid development in modernization, transport, urbanization and industries starting 1950's. Hence, it is hypothesized that due to the massive land development of the post-independence, the marine environment of Malaysia such as estuaries and coastal water should receive a considerable amount of TOC via rainfall and drainage runoff. Organic compounds including PAHs adhere to organic contents and are therefore able to travel over distances. In almost all stations of the study area, the concentrations of TOC were found to be very high as compared to other areas in the world.

There are basically four phases in cores from near shore stations namely pre-war (Pre-WWII), war-independency era, rapid development and finally modern input. The first phase belongs to era represents sediments with natural PAHs input or minimum anthropogenic input from pyrolysis of organic matters. The second phase intervals represent deposition during WWII and pre-independence. The third phase represents post-independence and rapid development (1956-1990) that shows the highest PAHs with oil signature. The last phase represents mostly sudden drop in PAHs in concentration however the sources are remained same as phase two and three (Fig. 6). The samples from the offshore unlikely have shown different results from the near shore cores. The Offshore cores are more erratic and expected to be derived presumably by the input from atmospheric movement. The results from the Offshore core show that MP/P ratios of 1 (in average) suggesting that the source of the PAHs were pyrogenic originated from street and urban dust and transported with atmospheric movements (Takada et al., 1990; 1991).

The near shore stations, the MP/P values indicated highly matched identified source comparing offshore cores. Since offshore PAHs are mainly derived by atmosphere, near shore locations receive via street run off, canals and drainage systems due to climate condition and rainfall.
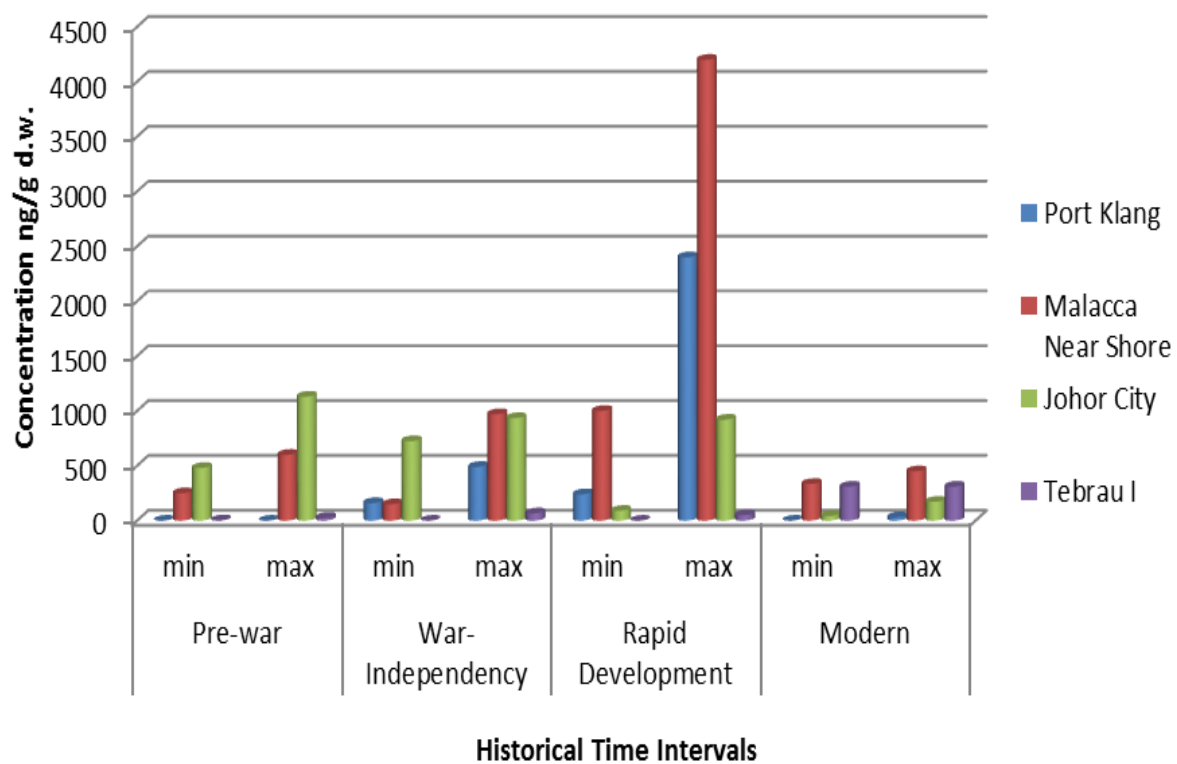
Fig. 6. The concentration of Polycyclic Aromatic Hydrocarbon (ng/g d.w.) during four identical time period in Malaysian history in selected study area.

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Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update

Edited by Dr. Tomasz Puzyn

Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

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