

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Fisheries Research Institute (FRI) Malaysia of Sarawak in collaboration with South East Asian Fisheries Center (SEAFDEC) and several universities in Malaysia have conducted a survey on demersal fish resources in Sarawak and Sabah waters. This study, off Sarawak, is a measurement of hydrocarbons and heavy metals in surface and core sediments of the South China Sea as the sea off Borneo is very deep and the sediment structure may be different. The flowing of large rivers from Borneo mainland into the sea might be affecting on continental shelf (Shazili et al., 1998). Hydrocarbons are naturally occurring compounds which are mainly found in the sedimentary organic matter from marine coastal areas. Particularly in recent decades, hydrocarbons distribution and composition are significantly affected by human activities. Hydrocarbons can be originated from assemblage of substances coming from biogenic, diagenetic, petrogenic, and pyrogenic sources (Gao and Chen, 2008).

Generally, aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) are the major components found in crude oil which are recognized as the main pollutants in marine sediments. Most of alkanes are posed to be narcotic and irritant while several PAHs show strong toxicity, carcinogenicity, teratogenicity and mutagenicity (Ruey-an and Yu, 2004). The existence of alkanes and PAHs in the marine environment may cause serious pollution to the water ecosystems and directly endanger the aquatic organisms (Zhang et al.,

2009). Sediments can act as sensitive indicators between natural and anthropogenic variables (Veerasingam et al., 2010). Hydrocarbons can be found in core sediments exhibit anthropogenic and natural inputs as well as metamorphism processes that occurred in the water column and during transportation and sedimentation (Wakeham and Farrington, 1990). Mille et al. (2007) stated that sediments are excellent sinks for contaminants such as hydrocarbons. This can occur when a large fraction of hydrocarbons with respective partitioning properties accumulates in underlying sediments and causing pollution (Colombo et al., 2005; Latimer and Quinn, 1996). These contaminants are usually more resistant toward biodegradation than other saturated biomarkers and likely to persist in atmospheric particulate matter, contaminated water, sediments and marine organisms (Guo et al., 2007). Furthermore, sediments are commonly used to identify and evaluate the major hydrocarbons sources and obtaining information of the events occurred in the water column (Lucia et al., 2010). Hence, the analysis of hydrocarbons in sediments provides valuable information regarding the history of persistent contamination and changes in chemical contamination.

In this study, the hydrocarbons compositions in surface and core sediment in selected stations at Sarawak's exclusive economic zone (EEZ) were determined. The study also aim to identify petroleum biomarkers such as hopane and sterane in surface sediments. The Gas Chromatography-Flame Ionization Detector (GC-FID) was used to analyze aliphatic and polyaromatic hydrocarbons quantitatively while Gas Chromatography-Mass Spectrometer (GC-MS) was used to determine petroleum biomarkers.

1.2 Problem Statement

The EEZ is a continental shelf that is known for the exploration activities and use of marine resources. Sarawak EEZ is located at South China Sea (SCS) area where the area is associated with oil and gas exploration activities and transportation of petroleum hydrocarbons. Understanding the sources of hydrocarbons in marine ecosystems is crucial because of their potential to exhibit toxicity, carcinogenicity and mutagenicity. Study regarding on distribution of hydrocarbons in sediments from Sarawak's EZZ is found to be limited. This study is purposely to establish concentrations of hydrocarbons, biomarker, composition and sources of hydrocarbons.

1.3 Objectives of the study

The objectives of this study were:

- a) to determine distributions of aliphatic hydrocarbons and PAHs in surface and core sediments from Sarawak's EZZ,
- b) to predict the sources of hydrocarbons in sediments of Sarawak EEZ by using several hydrocarbons biomarker indices and sediment quality guidelines (SQGs),

CHAPTER 2

LITERATURE REVIEWS

2.1 Exclusive Economic Zone of Malaysia

The South China Sea is a marginal sea located at the Southwest of the North Pacific and the largest sea in the Southeast Asia with a maximum depth more than 5,000 meters (Shaw, 1991). Malaysia is one of the countries that have a big influence on the sea claim instead of China, Philippine and Vietnam (Shaw, 1991). Malaysia's EEZ was declared by the government of Malaysia on 25 of April 1980 (Tunku Sofiah, 1996). This establishment of Malaysia's EEZ was in accordance to Exclusive Economic Zone Act, 1984. This proclamation is necessary in order to conserve, manage and develop the marine and estuarine fishing and fisher activities according to the Fisheries Act, 1985 (Jamil and Hadil, 2012). Malaysian EEZ include of 548,800 km², where 46% or approximately 250,000 km² of the combined EEZ of Sarawak, Sabah and the Federal Territory of Labuan (Jamil and Hadil, 2012). The EEZ of Sarawak is the largest which covered approximately 160,000 km². There are 270 million people population at coastal fringes of the South China Sea that contribute to anthropogenic impacts such as pollution and resources exploitation and expected to be huge (Morton and Blackmore, 2002).

2.2 The Concept of Exclusive Economic Zone (EEZ)

EEZ is a sea zone described by the United Nations Convention on the Law of the Sea (UNCLOS) where country or the state has special rights over the exploration and the use of marine sources (Patuzi, 2015). An EEZ of particular state comprises 200 nautical miles from its coast and shall not extend beyond 200 nautical miles from the baseline which comprise Exclusive Fishing Zone (EFZ). The main characteristic of the EEZ is the coastal State does not have sovereignty in its entire territorial but only have some rights such as exploration, exploitation, conservation and resource management (Patuzi, 2015). The UNCLOS grants coastal State rights to explore and exploit natural resources. The first concept of EEZ is the right and duties of the coastal State towards EEZ. One of the jurisdictions by the coastal State is on the rise and use of the artificial installations, research activities in the sea and environment protection (Juda, 1986). The second concept of EEZ is conservation of the living sources and non-living sources. The coastal State is responsible for the permission to catch the living sources in its exclusive zone. The conservation includes maintaining and restoring of harvested species at level which can produce maximum sustainable yield like economic need such as coastal fishing and non-living resources include minerals and hydrocarbons (Patuzi, 2015).

2.3 Hydrocarbons Studies in Malaysia

Concerns on the South China Sea such as living marine organisms and non-living resources has started approximately 33 years ago due to lacking of scientific information. Most hydrocarbons studies in Malaysia were mostly focused on rivers, estuaries and near shore areas but only several studies were conducted on offshore water. Several scientific expeditions such as Matahari Expeditions (1985–1989), SEAFDEC Expeditions and South China Sea Expeditions were carried out to cover important areas of the South China Sea including Malaysia EEZ. These expeditions provided the status on distribution of hydrocarbons in marine environment of Malaysia seas. Table 2.1 shows level of hydrocarbons in sediments from offshore water in Malaysia that surveyed by series of expeditions such as Matahari in year of 1985-1989 and SEAFDEC. Matahari Expeditions was carried out by several researchers from University Pertanian Malaysia (now called Universiti Putra Malaysia) and Kagoshima University collaborated to obtain scientific information on South China Sea. These collaborations were undertaken on board with research vessel, Kagoshima Maru and explored the South China Sea (Husain et al., 1998). This study has discovered high concentrations of hydrocarbons in sediment from offshore water of Terengganu EEZ ranged between 6.43-1332.13 mg/kg, Pahang EEZ ranged between 10.73-85.25 mg/kg, Sarawak EEZ ranged between 2.92-1153.53 mg/kg and Sabah EEZ ranged between 19.84-226.42 mg/kg. The areas which were found to have high hydrocarbons pollution are associated with oil platform traffic in EEZ. SEAFDEC expedition at offshore water off Eastern Peninsular Malaysia was conducted in 1996 showed low concentrations of hydrocarbons from surface sediments ranged between 0.06-1.36 mg/kg. The interest of study on hydrocarbons pollution in Malaysia was started when Law

et al. (1990) reported the bulk of petroleum contamination at Port Dickson in the Straits of Malacca (Sakari et al., 2012). Specific researches were then began in 1998 when scientists reported the level and sources of hydrocarbons such as aliphatic and PAHs in marine sediments and also in water, street dust, mussels and aerosol (Zakaria and Mahat, 2006; Zakaria et al., 2000). The significant conclusion of these studies is that the origin of hydrocarbons pollution derives from petrogenic sources (Zakaria et al., 2002). Since then there are more publication on on hydrocarbons study in Malaysia. Growing interest in hydrocarbons studies among researchers in Malaysia have provided informations on hydrocarbons status in rivers and coastal environment. Most of researchers have focused their studies on surface and core sediments because the sediment act as excellent sink for marine pollutants such as organic pollutants or hydrocarbons which can be a good indicator for environmental pollutions (Mille et al., 2007; Medeiros et al., 2005). Table 2.2 tabulats values of recent and past studies of hydrocarbons concentrations in coastal areas in Malaysia. Generally, high level of hydrocarbons was detected in the Straits of Malacca and the South China Sea Off Peninsular Malaysia. Yusoff et al. (2012) reported high concentration of hydrocarbons (35.6-144.1 mg/kg) in the surface sediments at Bako Bay of Kuching, Sarawak. This finding shows that the concentrations of hydrocarbons from the South China Sea off Kuching Division, Sarawak were found to be higher compare to other areas in the world (Yusoff et al., 2012). The South China Sea can be susceptible to hydrocarbons in sediments due to the huge amount of oily wastewater discharged via land activities by neighboring countries and also enormous number of ships that pass through this sea (Law and Hii, 2006). Bishop (1983) suggested safe level of hydrocarbons concentration in sediment should be below than 100 mg/kg. The sediments at Tuaran of Sabah were found to

be comparatively lower and uncontaminated compare to sediments from Kuching, the Strait of Malacca and the Johor Strait (see Table 2.2).

Table 2.1: Hydrocarbons concentrations in sediments from offshore water (South China Sea) surveyed during Matahari Expedition and SEAFDEC

Expeditions	Location	Concentration (mg/kg)	References
Matahari	Terengganu	6.43–1332.13	Law and Yusuf (1986)
	Pahang	10.73–85.26	Law and Mahmood (1987)
	Sarawak	2.92–1153.53	Law and Libi (1988)
	Sabah	19.84–226.42	Law (1990)
SEAFDEC	Eastern Peninsular Malaysia	0.06-1.36	Wongnapapan et al., (1999)

Table 2.2: Concentrations of petroleum hydrocarbons (mg/kg) in coastal sediments from several locations in in Malaysia.

Location	Sediment sample	Total hydrocarbon in sediment (mg/kg dw)	References
Papar to Tuaran, Sabah	Surface	0.24 – 20.65	Ali et al. (2015)
South China Sea off Kuching Division, Sarawak	Surface	35.6 – 1466.1	Yusoff et al. (2012)
Straits of Malacca	Surface	52.00 – 128.00	Zakaria et al. (2007)
Johor Strait, Johor	Surface and Core	117 - 4652	Sakari et al. (2011)
East Coast Malaysia	Surface	0.26-0.59	Elias et al. (2007)
Pulau Langkawi, Pulau Ketam, Tanjung Piai of Johor, Pulau Tioman and Kemaman	Surface	18.20 – 847.40	Abdullah (1997)
Terengganu	Surface	0.80 – 20.00	Tahir et al. (1997)
Port Dickson, Negeri Sembilan	Surface	21.73 – 74.50	Law et al. (1990)

2.4 Significant Study of Hydrocarbons in Marine Sediments of Malaysia

Malaysia is rich in biodiversity ranging from mangroves to coral reef and has more seas area including EEZ. Introduction of oil hydrocarbons into marine environment could affects via bioaccumulation on marine life such as fish, shellfish, mussels and other mammals (Ahmed et al., 2014). When small amount of petroleum hydrocarbons is introduced into marine environment, it may not pose immediate effects but would likely to pose side effect over long term of period (Adeniji et al., 2017). One of the biggest concerns when marine environment gets exposed with contaminated hydrocarbons is reduction of marine biodiversity. This happens when hydrocarbons pose detrimental effect on organisms that available in water surface, eggs or larvae of fishes, zooplankton and adult fishes to migrate and finally reduce the productivity of marine life (Mironov, 1968). Study conducted by Ahmed et al. (2014) found that fish samples from the Suez Gulf contained concentration of total alkanes was 987.439 ng/g in *Trachurus indicus* (horse mackerel), while in *Sepia officinalis* (Cuttle fish) contained 5007.2 ng/g total alkanes with relatively high amount of aromatic hydrocarbons. This result indicated that the contamination in fishes would likely to happen when fishes ingested contaminated materials and direct exposure of body with oil in water coloumn. Several studies on relation to hydrocarbons and fish have been conducted by several researchers (Ramalhosa et al., 2012; Dhanajayan and Muralidharan, 2012; Ramalhosa et al., 2009; Reynaud and Deschaux, 2006). Thus, hydrocarbons investigation in marine sediments is necessary because it provides status of petroleum contamination in the particular marine sediments (Floehr et al., 2015; Rahmanpoor et al., 2014; Chen et al., 2013). Continuous monitoring on hydrocarbons content in marine sediment could help to control

the concentrations of hydrocarbons in the range of baseline levels (Ahmed et al., 2014) and to protect marine life and human being (Chigor et al., 2013; Okoh et al., 2007).

This study of hydrocarbons in core sediments is important to record the accumulation history hydrocarbons in bottom sediments (Lorgeoux et al., 2016). Some quantitative monitoring studies on the level of hydrocarbons in sediment at coastal and developed areas have been conducted and the sources of hydrocarbons were predicted. Quantitative analysis of core sediments for the hydrocarbons content can be used to evaluate historical loadings of organic matter (Lorgeoux et al., 2016) and to provide specific data on temporal scale (Tao et al., 2012). Several studies on distribution of hydrocarbons in sediments have been conducted at the Johor Strait, Klang Estuary, Straits of Johor and Malacca by Sakari and co-workers (Sakari et al., 2012; 2011; 2010a; 2010b). These studies have reconstructed the accumulation history of hydrocarbons concentrations and predicted the sources of hydrocarbons in the sediments. Therefore, study on vertical distribution of hydrocarbons in sediments showed the accumulation history which can be used as references for future study or for comparison with the current status of hydrocarbons contaminations in sediment. Furthermore, study of hydrocarbons in sediments can provide information on the natural and anthropogenic input of organic matters by using several diagnostic characteristics such as unresolved complex mixture (UCM), carbon preference index of n-alkanes and also occurrence of hydrocarbon biomarkers such as hopane and sterane (Zegouagh et al., 1998). Identifying the sources of contaminants in marine aquatic environment can provide vital information on origin of anthropogenic sources of hydrocarbons so that the risk done by human anthropogenic activities on marine sediment environments can be clearly understood (Yunker et al., 2002).

2.5 Aliphatic Hydrocarbons

Aliphatic hydrocarbons can be found naturally in the form of linear, branched, cyclic, saturated and unsaturated. Aliphatic hydrocarbons may derive from several natural sources such as terrestrial plant waxes, marine phytoplankton and bacteria (Brassell et al., 1978) and they are also major components of petroleum products (Wang et al., 1999). The UCM of aliphatic hydrocarbons fractions are usually observed in marine sediments consisting of branched alicyclic hydrocarbons (Gough and Rowland, 1990), which have been proven to be toxic to sediment dwelling organisms (Scarlett et al., 2007). *n*-Alkanes with no alkyl group or substitutes comprise of odd and even carbon numbers which can be up to 64 carbons. The biogenic sources showed domination of odd numbered carbon while even carbon numbers are anthropogenic sources. Odd numbered carbons, *n*-C₁₅ to *n*-C₁₉ alkanes are originated from marine biogenic sources whereas to *n*-C₂₅ to *n*-C₃₃ hydrocarbons are originated from vascular plants (Sakari et al., 2008). The *n*-alkanes with less than *n*-C₂₀ originated from maritime low microscopic fish such as microorganisms and green growth (algae). *n*-Alkanes can be used as molecular markers to assess hydrocarbon contamination and to predict their sources (Duan et al., 2010).

2.5.1 Occurrence of Aliphatic Hydrocarbon in Marine Sediment

Aliphatic hydrocarbons in marine sediment can be originated from biogenic and anthropogenic sources. Aliphatic hydrocarbons are identified in the marine environment is often complex in composition because of the inputs from various sources. Petroleum contains complex hydrocarbons with a wide range of boiling points (NRC, 1985).

Anthropogenic hydrocarbons originated from human activities which incorporate industries, urbanization, delivering, angling and oil operations while common hydrocarbon can be originated from biogenic sources incorporate microbes, bugs, microscopic fishes, green growth microbes and terrestrial plants. Anthropogenic sources are also related to large petroleum oil spills or its derived from degradation products in marine environment (Commendatore et al., 2012).

Biogenic sources include biological process or in the early stages of diagenesis in recent marine sediment (Kennish, 1992). Phytoplankton is an important producer of natural matters in sea marine environment. Hydrocarbons are consisted in the lipid of algae which approximately 3-5% comprise of saturated and unsaturated hydrocarbons. Marine green algae consist of *n*-alkanes ranged between C₁₄ to C₃₂ where C₁₅ and C₁₇ are major *n*-alkanes in marine algae growth (Youngblood et al., 1977).

2.5.2 Source Identification of Hydrocarbons Using *n*-Alkane Molecular Marker

2.5.2.1 *n*-Alkanes Characteristics

Distribution of *n*-alkanes in oil sample can be used to predict the origin of the organic matter (Duan and Ma, 2001). Peters and Moldowan (1993) suggested that an increase in carbon number from *n*-C₁₅ to *n*-C₂₀ showed marine organic matters with biomass originated from algae and plankton. Guo and Fang (2012) reported that *n*-alkanes originated from small organisms such as algae, plankton and bacteria have short hydrocarbon chain with major peak at carbon number C₁₅, C₁₇ and C₁₉. Dominant of carbon number C₂₀ or C₂₁ indicates *n*-alkanes derived from the oil, automobile exhaust and fossil fuel combustion and with of

carbon number displayed in gas chromatogram peak do not shows odd even predominance (OEP) (Lu et al., 2002). Long carbon chains between C₂₇-C₃₃ are *n*- alkanes derived from terrestrial higher plants.

2.5.2.2 Carbon Preference Index (CPI)

Carbon Preference Index (CPI) is the predominant of odd carbon numbered over even carbon numbered of *n*-alkanes (Allan and Douglas, 1977). CPI is often used in marine sedimentary environment study (Sakari et al., 2012). Application of CPI was introduced by Farrington and Tripp (1977) and improved by others (Colombo et al., 1989; Kennicutt et al., 1987). CPI values in marine sediment samples are vary from different site to another and from sample to sample (Sakari et al., 2012). This due to the different inputs of terrestrial plants and marine biogenic origins (Jeng, 2006). Table 2.3 shows CPI values that accounted for biogenic and anthropogenic sourced of *n*-alkanes. Generally, sediments with *n*-alkanes derived from petroleum hydrocarbons origin possessed CPI less than 1 (Maioli et al., 2011; Petersen et al., 2007; Esemé et al., 2006; Harb et al., 2003; Jeng and Kao, 2002). CPI close to 1 is *n*-alkanes associated with marine animals or recycled organic matter. Hydrocarbons originated from vascular plant have CPI value more than 3 (Van Dongen et al., 2008; Bi et al., 2005).

Table 2.3: Respective inputs of *n*-Alkane based on CPI ratios.

CPI	Source of <i>n</i> -alkane	References
Between 5–10	<i>n</i> -Alkanes derived from land plant originating material.	(Commendatore et al., 2012; Kanzari et al., 2014)
Above 3	Biogenic input from vascular plant	(Kennicutt et al., 1987).
Below 1.0	Petrogenic inputs such as petroleum products.	(Pendoley, 1992)
Close to 1.0	Related to marine microorganisms and recycled organic matter.	(Kennicutt et al., 1987).

2.5.2.3 Major Hydrocarbons

Major hydrocarbon in *n*-alkanes profile is the highest *n*-alkane concentration that can be interpreted as evidence to identify the sources of pollution. The concentration of *n*-alkanes calculated from the peaks of gas chromatography provide enough information to conclude the sources of pollution (Colombo et al., 1989; Broman et al., 1987). Major hydrocarbons can distinguish the origin of *n*-alkane in sediment whether it is biogenic or petrogenic input. For instance, the carbon number indicates occurrence petroleum products in sediment is dominated by C₁₈ (Jacquot et al., 1999) while different species of algae have odd numbered carbons; C₁₅, C₁₇, C₁₉ and C₂₁ and vascular plants have number carbons of C₂₃, C₂₅, C₂₇, C₂₉, and C₃₁ (Simoneit, 1987; Blumer et al., 1971; Clark and Blumer 1967).

2.5.2.4 Low Molecular Weight to High Molecular Weight Ratio (LMW/HMW Ratio)

The molecular weight of aliphatic hydrocarbons can be used as a tool for identification hydrocarbons in the environment. Aliphatic hydrocarbons can be classified into low molecular weight (LMW) and high molecular weight. LMW hydrocarbons ranged between C₁₆ to C₂₆ while HMW hydrocarbons ranged between C₂₇ to C₃₆. The concentration ratio of LMW/HMW can used to trace the origin and sources of aliphatic hydrocarbons in marine sediment. LMW/HMW above 2 usually indicates fresh oil input or petroleum input (Commendatore et al., 2000). Ratio below 1 usually indicates for degraded crude oil (Wang et al., 2006).

2.4.2.5 Unresolved Complex Mixture (UCM)

The UCM normally appears in the GC chromatogram of aliphatic hydrocarbons fraction which is due to the petroleum contamination in water or sediment in environmental samples (Volkman et al., 1992). The occurrence of UCM in sediment implies the petrogenic input or biodegradation (Brassel and Englington, 1980). UCM appears in GC chromatograms peaks as the hump area or "envelop" between the solvent baseline and the curve defining the base of resolvable peaks.

2.5.2.6 Average Chain Length (ACL)

ACL is an important parameter in order to understand the effect of hydrocarbons input into the environment. ACL is defined as the weight average chain number of carbons

atom in higher plants which is ranged from C₂₅ to C₃₃. Jeng (2006) reported that ACL is not change under constant environment conditions. Petrogenic input into marine environment decrease ACL values. ACL usually compliments with other ratios and indices such as CPI, LMW/HMW and MH (Jeng, 2006).

2.5.2.7 Isoprenoids (Pristane to Phytane ratio, Pri/Phy)

Both pristane (2,6,10,14-tetramethyl pentadecane) and phytane (2,6,10,14-tetramethyl hexadecane) are originated from the phytol side chain of chlorophyll, either under reducing conditions (phytane) or oxidizing conditions (pristane) (Moustafa and Morsi, 2012). In extremely weathered crude oils, pristane and phytane are become dominantly saturated hydrocarbons components until they biodegraded (Moustafa et al., 2004). The ratio of Pristane/phytane is generally used to determine depositional environment (Peters et al., 2005). Ratio of Pristane/phytane ranged between 1-3 indicates for oxidizing depositional environments (Hunt, 1996) and also, ratio ranged for 1-6 indicated for biogenic hydrocarbons (Commendatore et al., 2000). Ratio that associates with petroleum input and highly reducing depositional environment is less than 1 (Broman et al., 1987).

2.6 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are organic compounds with fused aromatic rings. The physical and chemical characteristics of PAHs are depend on the number of aromatic rings attached and pattern of ring linkage. PAHs are lipophilic compounds in which their solubility and concentration are trivial in water (Nasr et al., 2010). PAH solubility in water decreases as the molecular weight increases (Nikolaou et al., 2009). Because of their hydrophobic properties, PAHs tend to settle out from water and finally accumulated at the bottom of sediment. PAHs in environment also act as an indicator of anthropogenic pollutant and presence of PAHs can be used to estimate overall environmental quality. Several factors such as the degree of toxicity, environmental and human health risk assessment and petroleum pollution are used to estimate environmental quality. (Bihari et al., 2006; Cachot et al., 2006; Requejo et al., 1996).

2.6.1 Sources of PAHs

Three main sources of PAHs in the environment are petrogenic, pyrogenic, and biogenic (Page et al., 1999; Neff, 1979). Petrogenic PAHs in the environment are released during burning of petroleum and coal at high temperature (100-300 °C) and high pressure (Boehm et al., 2002; Stout et al., 2001) and also formed during crude oil maturation. Petrogenic PAHs usually consisted of 2 and 3 rings PAH and their constituent homolog bunches display a prevalence of alkylated individuals to non-alkylated parent PAH. Petrogenic sources of PAHs can be derived from oil spills of fresh water, oceanic, storage tank leaks and accumulation of small releases of gasoline, motor oil, lubricating oil and

others related with transportation. Pyrogenic PAHs usually have 4-to 6-rings and formed during incomplete burning of fossil fuel or biomass at temperatures over than 500°C with absence of oxygen or low oxygen. The series of incomplete burning including combustion of motor fuel, wood, fireplaces and combustion of fuel oils in heating system. Next PAHs are also derived from biogenic process. For instance, certain plants and bacteria synthesized PAHs compounds during degradation of vegetative substances. Perylene is a natural PAHs compound that is produced via biological process.

2.6.2 Physical and Chemical Properties of PAHs

PAHs (also known as polynuclear aromatic hydrocarbons) are composed of two or more aromatic (benzene) rings which are fused together when a pair of carbon atoms is shared between them (Weast, 1968; Neff, 1979). The resulting structure is a molecule where all carbon and hydrogen atoms lie in one plane. Naphthalene with molecular weight of 128.16 g and chemical formula $C_{10}H_8$, formed from two benzene rings fused together, and the lowest molecular weight of all PAHs. The environmentally significant PAHs are those molecules which contain two (e.g., naphthalene) to seven benzene rings (e.g., coronene with a chemical formula $C_{24}H_{12}$ and molecular weight of 300.36 g). In this range, there is a large number of PAHs which differ in number of aromatic rings, position at which aromatic rings are fused to one another, and number, chemistry, and position of substituents on the basic ring system. Some general uses of PAHs in industries are shown in Table 2.4. Another PAHs compounds are contained in asphalt for road construction and roofing tar. Moreover, PAHs are used in electronic, plastics and liquid crystal industries. The physical and chemical characteristics of PAHs compounds depend on the number of aromatic rings attached and pattern of ring

linkage. PAHs have high melting and boiling points as shown in Table 2.5 due to low vapor pressure and aqueous solubility (Masih et al., 2012). Solubility of PAHs decreases as number of ring PAHs increases (Masih et al., 2010; Nikolaou et al., 2009). Nasr et al. (2010) reported that PAHs are lipophilic compounds in which their solubility and concentration are trivial in water. Because of hydrophobic properties of PAHs, they tend to settle out from water and accumulated at the bottom of sediment. This includes factors such as the degree of toxicity (Bihari et al., 2006; Cachot et al., 2006), petroleum pollution, environmental and human health risk assessments (Requejo et al., 1996). Physical and chemical characteristics of PAHs vary with molecular weight (see Table 2.5). PAHs are resistance to oxidation, reduction, and vapourization increases with increasing molecular weight (Masih et al., 2012).

Table 2.4: General use of PAHs in certain industries

PAHs	General use
Acenaphthene	Used for manufacturing of pigments, dyes, pharmaceuticals, plastics and pesticides.
Anthracene	Used as diluent for preservative of wood and manufacturing of dyes and pigments.
Fluoranthene	Used for manufacturing of dyes, pigments, and agrochemicals.
Fluorene	Used for manufacturing pesticides, pharmaceuticals, thermosets plastics, pigments and dyes.
Phenanthrene	Used for manufacturing of resins and pesticides.
Pyrene	Pigments synthesis.

Table 2.5: Physical and chemical properties of PAHs compounds

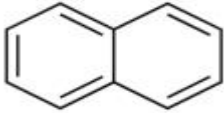
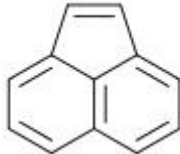
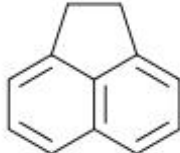
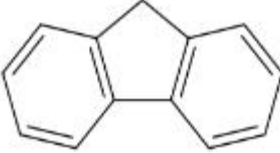

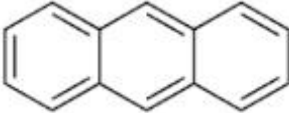
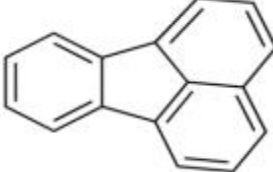
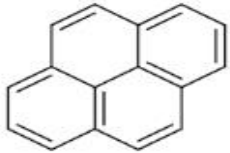
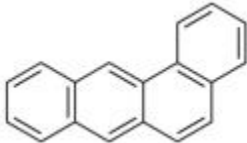
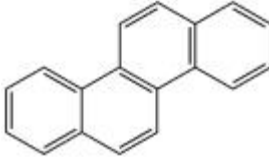
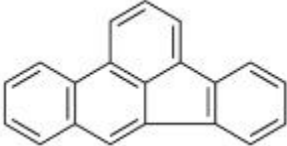
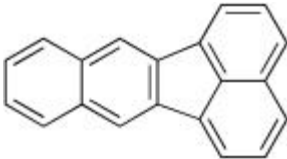
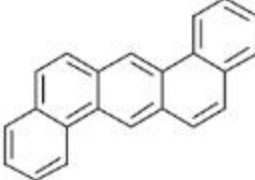

Name	Molecular Formula	Structure	Molecular Weight (g)	Boiling Point (°C)	Melting Point (°C)
Naphthalene	C ₁₀ H ₈		128.2	218	78.2
Acenaphthylene	C ₁₂ H ₈		152.2	280	91.8
Acenaphthene	C ₁₂ H ₁₀		154.2	279	93.4
Fluorene	C ₁₃ H ₁₀		166.2	295	116
Phenanthrene	C ₁₄ H ₁₀		178.2	332	101
Anthracene	C ₁₄ H ₁₀		178.2	340	45
Fluoranthene	C ₁₆ H ₁₀		202.3	375	110.8
Pyrene	C ₁₆ H ₁₀		202.1	404	148

Table 2.5 continued

Benzo(a)anthracene	$C_{18}H_{12}$		228.3	438	158
Chrysene	$C_{18}H_{12}$		228.3	448	254
Benzo(b)fluoranthene	$C_{20}H_{12}$		252.3	481	168
Benzo(k)fluoranthene	$C_{20}H_{12}$		252.3	480	217
Dibenz(a,h)anthracene	$C_{22}H_{14}$		278.3	524	262
Benzo(ghi)perylene	$C_{22}H_{12}$		276.4	545	278

2.6.3 Effects of PAHs Towards Organisms

PAHs are deposited into marine environment via atmospheric pathway derived from industrial emissions, combustions of engines and domestic heating systems. When molecular weight of PAHs increases, the carcinogenic effect also increases (Balcioglu, 2014). Several PAHs are known to be carcinogenic; benzo[a]anthracene, benzo[a]pyrene and dibenz[ah]anthracene (CCME, 2010; Armstrong et al., 2004; Bach et al., 2003). Lipophilic PAHs concentrations in sediments are commonly higher than in the water column. PAHs are also accumulated in marine life such as fish and shell fish which could lead to serious human health (Okay et al., 2003; Heintz et al., 2000; Carls et al., 1999; Takatsuki et al., 1985). PAHs are vital sources of pollution and might result in ecotoxicological effects that can occur at all stages of biological organization, from the molecular to the ecosystem stages (Fent, 2004; Wernersson et al., 2000). The toxicity of PAHs can be enhanced with presence of ultraviolet light instead of being affected by metabolisms and photo-oxidation. The degree of PAHs toxicity is from moderate to high acute toxicity toward aquatic life and bird (Peter, 2003). The adverse effects of PAHs towards these organisms are tumours, reproduction, development and immunity (ATSDR, 1995).

In human, PAHs effects will depend on the period of exposure and also depending on amount of concentrations of PAHs and route of exposure such as inhalation or skin contact. When PAHs is absorbed to the body, it will be metabolized by the liver and kidney and eliminated through feces and urine. The health problems that associated by PAHs exposure are lung cancer, low birth rates and decreased fecundity (AMAP, 1998). Exposure of high concentrations of PAHs resulted in symptoms such as nausea, vomiting, eye and skin irritation, convulsion and irritation (WHO, 2005). Long term exposure of PAHs could lead

to serious health problems such as liver damage, kidney problem, eye cataract and jaundice. Other sickness that resulted from long term exposure of PAHs are cancerous diseases such as skin, lung, bladder and gastro-intestinal. Specific PAHs compound, naphthalene, may cause breakdown of red blood cells when consumed in large amounts (SCF, 2002). Many people consumed PAHs from fish, shellfish and other marine products, these creatures exposed more PAHs with carcinogenic property. The World Health Organization (WHO) recommends that the intake of shellfish containing PAHs must not exceed 200 ppb (WHO, 1991). In Malaysia the study conducted by Nasher et al. (2016) on PAHs in sea bass (giant sea perch) showed that the mean concentration of 18 PAHs in the sea bass was 573.66 ± 47.56 ng/g dry weight and the calculated cancer risk for all 18 PAHs were 1.06×10^{-4} , 4.55×10^{-5} , and 3.69×10^{-6} . These results were within the ranged suggested by US EPA (10^{-6} to 10^{-4}). These results implied that consumption of sea bass does not pose significant pose exposure of PAHs towards Malaysians. The significant study of pollution in marine environment is a subject requiring more attention to handle. PAHs are known by their high toxicity, hydrophobicity and environmental stability which they can be transformed from marine life to final consumer the human body. Hence, their current concentrations in the marine environment should be studied and some efforts should be made to reduce or diminish them whenever possible.

CHAPTER 3

MATERIALS AND METHODS

3.1 Study Area and Field Sampling

Sediment samples were collected during the M.V. SEAFDEC 2, Cruise No.50-3/2015 expedition which is organised by Fisheries Research Institute Sarawak from 20th August to 5th October 2015. The surface marine sediments were collected using Smith McIntyre grab sampler, while core sediments were collected using gravity core sampler. The samples collected for hydrocarbons analysis were wrapped with aluminium foil. The samples were then stored frozen at -4 °C in the freezer before transported to the laboratory until further analysis. Figure 3.1 shows the study area and sampling locations for eleven surface sediments and three core sediments at Sarawak EEZ, while Table 3.1 lists the GPS position for all sampling sites.

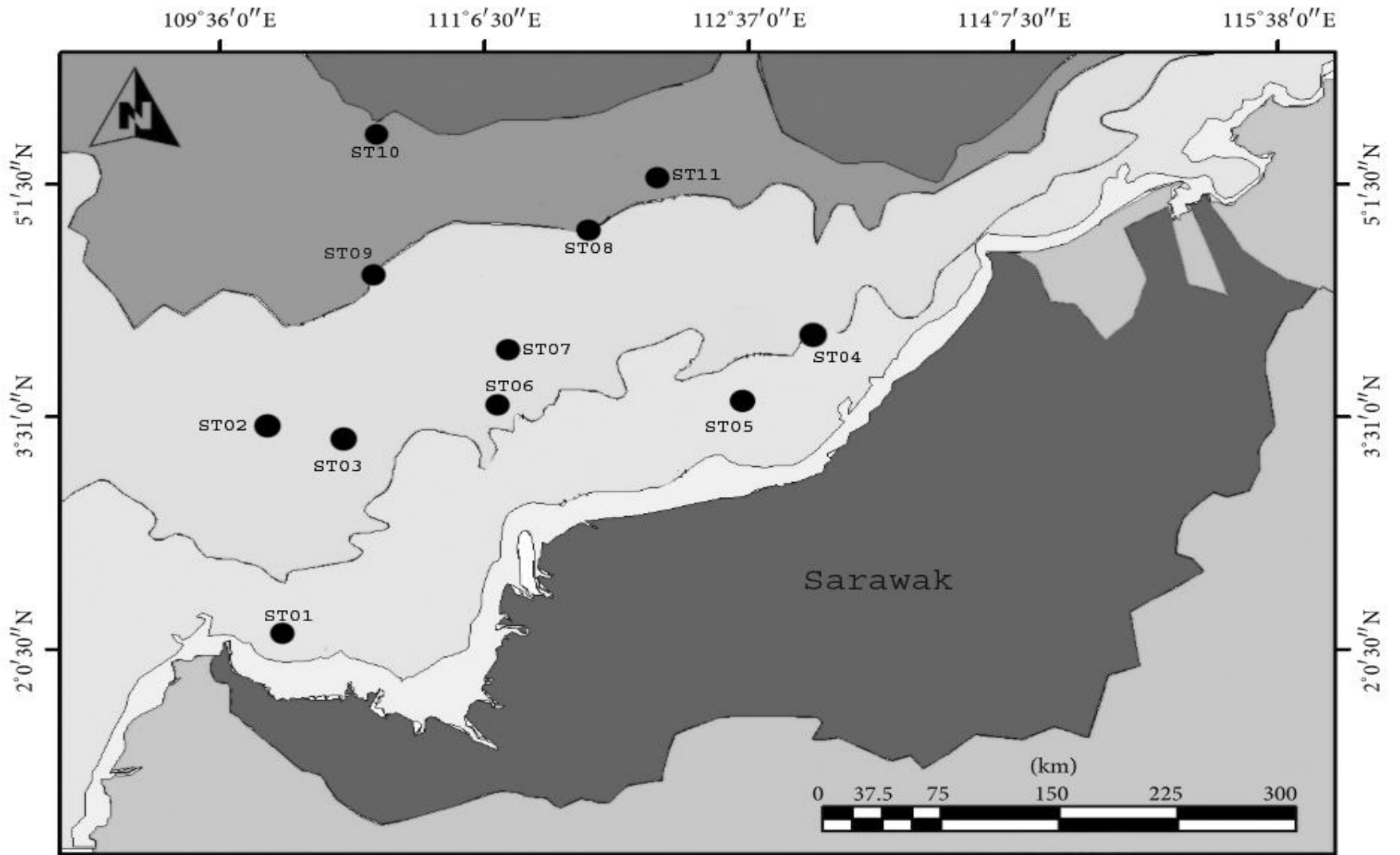


Figure 3.1: Sampling stations of surface and core sediments at Sarawak EEZ

Table 3.1: GPS reading and characteristics of sampling sites at Sarawak's EEZ

Sampling site	Surface sediment		Core sediment		Core Length (cm)	Water Depth (m)	Type of sediment	Date of sampling (2015)
	Latitude	Longitude	Latitude	Longitude				
ST01	02_17.95 N	109_52.09 E	02_17.95 N	109_52.09 E	12	37	Sand	2 October
ST02	03_31.80 N	109_56.14 E	03_31.80 N	109_56.14 E	12	75	Mud sand shell	5 October
ST03	03_20.25 N	110_20.50 E	03_20.25 N	110_20.50 E	12	70	Sand shell	3 October
ST04	4_01.95 N	113_02.02 E	-	-	-	45	Mud	22 August
ST05	3_37.62 N	112_32.45 E	-	-	-	47	Mud sand	26 August
ST06	3_36.97 N	111_12.36 E	-	-	-	62	Sand gravel	9 September
ST07	4_01.69 N	111_16.67 E	-	-	-	70	Mud	8 September
ST08	4_48.04 N	111_40.93 E	-	-	-	65	Mud	29 August
ST09	4_27.51 N	110_27.53 E	-	-	-	103	Mud	17 September
ST10	5_23.67 N	110_33.56 E	-	-	-	161	Mud sand	18 September
ST11	5_25.57N	111_58.85E	-	-	-	112	Mud sand	20 August

3.2 Proximate and Grain Size Analysis

3.2.1 Proximate Analysis

Total organic matter (TOM) was determined according to procedure described by Commendatore and Esteves (2004) with minor changes. Sediments were dried to a constant weight in an oven and the percentage of moisture was obtained using weight reduction that occurred. Exactly 2.0 g of sediment was weighted in silica dish and dried in an oven at 105 °C for 48 hours. The water content was calculated according to the following Equation 3.01:

$$\text{Moisture, \%} = [(A - B)/A] \times 100\% \quad \text{Equation 3.01}$$

where,

A = weight of sample used (grams),

B = weight of samples after heating (grams).

Ash content or inorganic matter was obtained by heating off organic matter at 450 °C in muffle furnace for 5 hours. Approximately 2.0 g of sediment sample was added in preheated crucible. Losses of ignition of the samples were obtained by measuring the crucible. The ignition loss at 450 °C was assumed as approximately the total organic matter (TOM) content in sediment sample. The ash content and TOM were calculated using Equations 3.02 and Equations 3.03.

$$\% \text{ Ash} = [(A-B)/C] \times 100\% \quad \text{Equation 3.02}$$

where,

A= weight of crucible + Ash (g),

B= weight of empty crucible (g), and

C= weight of sample (g)

$$\%TOM = [(A-B)/A] \times 100\%$$

Equation 3.03

where,

A= weight of sediment after heated at 105°C for 48 hours,

B= weight of sediment after heated at 550°C for 5 hours.

3.2.2 Grain Size Analysis

Prior for physical sieving, 30 g of wet sediment samples were dried in the oven at 105°C for 12 hours. Sediment samples were manually ground with mortar and pestle after the drying process. The samples were continued with sieve analysis, a procedure commonly used in sediment analysis to assess the particle size distribution of a granular material includes of sand (Sonaye & Baxi 2012). Sieving method involved a splitting process of sediment into several sediment fractions sizes (very Coarse, < 2 mm and < 1 mm, coarse sand: 500 µm, medium sand < 355 µm and silt and clay, < 50 µm). Sand fractions above > 50 µm were determined via dry sieving. Silt and clay fractions (< 50 µm) were determined via wet sieving using pipette method (Salem et al., 2014).

3.3 Determination of Hydrocarbons in Marine Sediment of Sarawak EEZ

3.3.1 Extraction and Fractionation of Hydrocarbons in Sediments

Extraction and fractionation of hydrocarbons in sediment were performed according to the procedure described by Yusoff et al. (2012). Briefly, approximately 10.0 g of wet sediment were placed in cellulose thimble and spiked with 50 μL of 50 $\mu\text{g/g}$ d_{10} -anthracene and 50 μL of 50 $\mu\text{g/g}$ n-eicosene. Both d_{10} -anthracene and n-eicosene serve as internal standards for aliphatic hydrocarbons and PAHs, respectively. A volume of 250 mL dichloromethane was used as an extracting solvent and approximately 0.1 g of anti-bumping was added in order to avoid the boiling liquid violently. The extraction process took 8 hours which equivalent to 16 extraction cycles. Subsequently, the extract was evaporated to 5 mL using a vacuum rotary evaporator. The crude extract is called geolipid. Geolipid was then isolated into two fractions on a silica gel (60 mesh) glass column chromatography (1.1 cm \times 50 cm) by eluting with appropriate solvent as described in Table 3.2.

Table 3.2: Fractionation of geolipid on silica gel column chromatography with respective eluting solvents

Silica Gel	Fraction	Eluting Solvent	Compound Separated
5% deactivated	A1	40 mL mixture of <i>n</i> -hexane to dichloromethane (3:1; v/v)	Mixture of aliphatic and PAHs
	A2	20 mL of mixture dichloromethane: Methanol (3:1; v/v)	Polar organic compounds
Fully activated	F1	20 mL of <i>n</i> -hexane	Aliphatic hydrocarbons
	F2	20 mL mixture of <i>n</i> -hexane to dichloromethane (3:1;v/v)	PAHs

Approximately 7.5 g of 5% of deactivated silica gel were mixed with *n*-hexane and packed into a glass column. Geolipid was placed at the top of the column and eluted using a mixture of 40 mL *n*-hexane:dichloromethane (3:1; v/v) and 20 mL of a mixture of dichloromethane:methanol (3:1; v/v) to obtain fractions A1 (hydrocarbons) and A2 (polar organic compounds), respectively. The A1 fraction which contained a mixture of aliphatic and aromatic hydrocarbons was then further fractionated on fully activated silica gel column chromatography into two fractions, that are F1 (aliphatic hydrocarbons) and F2 (PAHs). Fraction A1 was subsequently eluted using 20 mL of *n*-hexane followed by 20 mL mixture of *n*-hexane: dichloromethane (3:1; v/v) to obtain fractions F1 and F2, respectively. All fractions were then transferred into 5 mL vial and further evaporated to dryness using a gentle stream of nitrogen.

Both F1 and F2 fractions were subjected to desulphurization treatment on an activated copper column. Elemental sulphur can interfere the measurement of hydrocarbons in the GC analysis of aliphatic fraction (Stout and Wang, 2016). Approximately 3 g of activated copper (~ 40 mesh) were added into a glass column chromatography (1.1 cm i.d × 50 cm long). Both F1 and F2 fractions were eluted then separately using 20 mL of dichloromethane and the eluents were evaporated to dryness under a gentle stream of purified nitrogen.

3.3.2 Gas Chromatographic Analyses

Gas chromatography (GC) is a physical separation method in where volatile mixtures are separated. Two types of GC analyses were employed in this study; gas chromatography-mass spectrometer (GC-MS) and gas chromatography-flame ionization detector (GC-FID). Organic extracts were determined quantitatively and qualitatively by GC analyses.

3.3.2.1 Gas Chromatography-Flame Ionization Detector (GC-FID) Analysis

Both aliphatic hydrocarbons fractions (F1) (core sediments) and PAHs (F2) fractions (surface and core sediments) were analysed on Perkin Elmer Gas Chromatograph Model Clarus 680 equipped with flame ionization detector. The separation was carried out using HP-5 fused-silica capillary column (30 m×0.25 mm i.d ×0.25 µm film thicknesses) with nitrogen gas as the carrier gas with the injector and detector temperatures were programmed at 280 °C and 300 °C, respectively. The column temperature was initially set at 50 °C for 5 minutes, subsequently ramped to 320 °C at 6.5 °C/min and maintained at final temperature

for 10 minutes. Prior to GC-FID analysis, both F1 and F2 fractions were diluted with 100 μL dichloromethane. Exactly 1 μL of samples were injected into the column in split less injection mode.

3.3.2.2 Gas Chromatography-Mass Spectrometer (GC-MS) Analysis

GC-MS analysis was performed on a Shimadzu QP5000 GC-MS equipped with quadrupole mass analyser. The separation was carried out on the BPX-5 capillary column (30 m x 0.25 mm i.d x 0.25 μm film thickness) with helium gas as the carrier gas. Mass spectrum was recorded using linear scanning (m/z 45-450, cycle time of 1.0 second) and electron impact ionization (70 eV). The temperature program was set similar to GC-FID analysis. Aliphatic hydrocarbons (F1) of surface sediments of Sarawak EEZ were analysed with GC-MS. Post-run GC-MS data analysis on aliphatic hydrocarbons fraction was performed by selecting specific ions in full scan GC-MS data. This mass chromatographic analysis was carried by extracting m/z 191 and m/z 217 of full scan GC-MS data in order to identify terpanes and steranes, respectively.

3.3.3 Quantitative and Qualitative Analysis of *n*-alkanes and PAHs

3.3.3.1 Quantitative Analysis of *n*-Alkanes and PAHs

Response factors (RFs) is a response of the compound of interest relative to the internal standard calculated through external analysis of standard solutions. Determination of RFs of *n*-alkanes and isoprenoids were calculated relative to 50 $\mu\text{g/mL}$ of eicosene as

internal standard, while determination of RFs for PAHs were calculated relative to 50 µg/mL of d₁₀-anthracene as internal standard. RFs were carried out according to Equation 3.04 below:

$$\text{Response Factor (RF)} = (C_{\text{std}}/A_{\text{std}}) \times (A_{\text{is}}/ C_{\text{is}}) \quad \text{Equation 3.04}$$

where,

C_{std} - Concentration of standard,

A_{std} - Peak area of standard,

A_{is} - Peak area of internal standard,

C_{is} - Concentration of internal standard.

Concentrations of hydrocarbons in the sample were calculated using Equation 3.05 below.

$$\text{Concentration of analytes} = (C_{\text{is}}/A_{\text{is}}) \times A_{\text{x}} \times \text{RF}_{\text{x}} \quad \text{Equation 3.05}$$

where,

A_x - Peak area for analyte x,

C_{is} – Concentration of internal standard,

A_{is} - Peak area for internal standard,

RF_x - Response factor for analyte x.

3.3.3.2 Qualitative Analysis

Identification of peaks in chromatograms was made based on comparisons with mass spectra (MS) library in GC-MS data system and literature. Identification of hydrocarbons biomarkers were performed using mass chromatograms by selecting characteristic ions. Detection of the biomarkers for hopane and triterpene was carried out by monitoring m/z 191 and m/z 217, respectively (Zaghden et al., 2007).

3.3.4 Determination of Hydrocarbon Molecular Indices

Molecular *n*-alkane indices were determined based on the result of concentrations of specific compounds (Sakari et al., 2012). Several molecular *n*-alkanes indices were employed in this study; carbon preferences index (CPI), low molecular weight to high molecular weight of *n*-alkane (LMW/HMW), average chain length (AVC), terrigenous aquatic ratio (TAR), isoprenoid ratio and unresolved complex mixture (UCM).

3.3.4.1 Carbon Preferences Index (CPI)

CPI is calculated as the ratio of odd carbon numbered divided with even carbon numbered of *n*-alkanes (Allan and Douglas, 1977). CPI value is the primary indicator of biogenic or anthropogenic sources. The predominant of odd carbon numbered in sediment sample indicated for natural input while the predominant of even carbon numbered indicated for anthropogenic origin (Sakari et al., 2012). CPI is calculated using Equation 3.06.

$$\text{CPI} = \left[\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right] \times \frac{1}{2} \quad \text{Equation 3.06}$$

3.3.4.2 Average Chain Length (ACL)

The effects of hydrocarbons pollution in marine sediment can be further accessed by determining the ACL values. ACL Jeng (2006) reported that the effect of petrogenic sources will decrease the ACL values in the environment. Since ACL is defined as average weight of carbon atoms in *n*-alkanes of higher plant (C₂₅-C₃₃), Equation 3.07 below shows ACL being measured.

$$\text{ACL} = \frac{[25(nC_{25}) + 27(nC_{27}) + 29(nC_{29}) + 31(nC_{31}) + 33(nC_{33})]}{(nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33})} \quad \text{Equation 3.07}$$

3.3.4.3 Low Molecular Weight to High Molecular Weight Ratio (LMW/HMW)

The characteristic of hydrocarbons input in nature can be determined via ratio of LMW/HMW of *n*-alkanes. Ratio above 2 indicated for fresh oil input while around 1 indicated for for algae, plankton and petroleum, while sedimentary bacteria, seawater, marine animals (Sakari et al., 2012). The ratio is calculated using Equation 3.08 below.

$$\text{LMW/HMW} = \frac{C_{16} + C_{17} + C_{18} + C_{19} + C_{20} + C_{21} + C_{22} + C_{23} + C_{24} + C_{25} + C_{26}}{C_{27} + C_{28} + C_{29} + C_{30} + C_{31} + C_{32} + C_{33} + C_{34} + C_{35} + C_{36}} \quad \text{Equation 3.08}$$

3.3.4.4 Terrigenous Aquatic Ratio (TAR)

The terrigenous/aquatic ratio (TAR) can be used to evaluate the importance of terrigenous inputs against aquatic inputs (Mille et al., 2007). TAR is calculated as the ratio of the concentrations of long-chain *n*-alkanes to short-chain *n*-alkanes. TAR is calculated as shown in Equation 3.09 (Bourbonniere and Meyers, 1996).

$$\text{TAR} = \frac{C_{27} + C_{29} + C_{31}}{C_{15} + C_{17} + C_{19}} \quad \text{Equation 3.09}$$

3.3.4.5 Isoprenoid Ratios

Pristane to phytane (Pr/Phy) ratios were measured to determine sources of hydrocarbons (Commendatore et al., 2000). Pristine and phytane compounds were eluted closely with *n*-C₁₇ and *n*-C₁₈ into two pairs of characteristic peaks in chromatographic analysis. *n*-C₁₇/Pristane and *n*-C₁₈/Phytane indices (*n*-C₁₇/Pri, *n*-C₁₈/Phy) were measured to determine the presence of oil and the relative biodegradation of *n*-alkanes (Commendatore et al., 2000). Sources of hydrocarbons and relative biodegradation of oil indices based from isoprenoid ratios are calculated as shown in Equation 3.10, Equation 3.11 and Equation 3.12.

To calculate source of hydrocarbons from isoprenoid ratios,

$$\text{Isoprenoid ratio} = \frac{Pr}{Phy} \quad \text{Equation 3.10}$$

To calculate relative biodegradation of crude oil from isoprenoid ratios,

$$\text{Isoprenoid ratio} = \frac{n-C_{17}}{\text{Pristane}} \quad \text{Equation 3.11}$$

$$\text{Isoprenoid ratio} = \frac{n\text{-C18}}{\text{Phytane}}$$

Equation 3.12

3.3.4.6 Unresolved complex mixture (UCM)

Qualitative UCM was identified from GC-MS of aliphatic fraction of *n*-alkanes ranging from C₁₅ to C₃₂ that have both unimodal and bimodal patterns (Vaezzadeh et al., 2015). The characteristic of petroleum origin in gas chromatograms of aliphatic fractions were determined (Medeiros et al., 2005).

3.3.5 Environmental Evaluation Method of PAHs

3.3.5.1 Sediments Quality Guidelines (SQGs)

Long et al. (2006) reported that SQGs are very useful guideline for sediments assessments in marine environment. SQGs are divided into two target values; effects range low (ERL) and effects range median (ERM). Concentrations of individual PAH in studied sediments were compared with published ERL and ERM values (Zhang et al., 2016). Table 3.3 presents the toxicity guideline for individual PAH ranged for ERL and ERM.

Table 3.3: Toxicity guideline for individual PAH ranged for ERL and ERM

Compounds	SQGs ¹ (ng/g)	
	ERL	ERM
Naphthalene	160	2,100
Acenaphthylene	44	640
Acenaphthene	16	500
Fluorene	19	540
Phenanthrene	240	1,500
Anthracene	853	1,100
Fluoranthene	600	5,100
Pyrene	665	2,600
Benzo[a]anthracene	261	1,600
Chrysene	384	2,800
Benzo[b]fluoranthene	-	-
Benzo[k]-fluoranthene	-	-
Dibenz[a,h]anthracene	63.4	260
Benzo[ghi]perylene	-	-

Note: ¹SQGs values adopted from MacDonald et al. (1996) and Long et al. (1995)

3.5 Statistical Analysis

Software IBM SPSS version 22 was used to conduct statistical tests including correlation analysis, principal component analysis (PCA) and cluster analysis (CA). Data of hydrocarbons and proximate analysis were subjected to statistical analysis in order to determine any significant environmental variations.

3.5.1 Correlation Analysis

The strength of the relationship between variables (proximate analysis) can be measured through correlation coefficient. In correlation analysis, significant less than 0.05 ($p < 0.05$) indicated that there is less than a 5% that the relationship between variables occurred by chance.

3.5.2 Principal Component Analysis (PCA)

Concentrations of hydrocarbons together with molecular n-alkane indices, isomeric PAHs, proximate data, grain sizes data in surface sediments were analysed using PCA. The aim of using PCA on hydrocarbons in surface sediments was to determine The data in each sample were arranged in matrix after being standardized were subjected to PCA with varimax normalized rotation (Hu et al., 2009). The number of factors extracted from the variables was determined by a scree test, which retains only factors with eigenvalues that exceed one.

3.5.3 Cluster Analysis (CA)

For hydrocarbons study, the cluster analysis was conducted to determine the possible homogeneity between samples collected from several sites. CA for hydrocarbons were conducted with average and centroid linkages. The data presented in the form of dendrogram which was a tree diagram.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Grain Size Distribution and Proximate Data of Sediments

Major factors that affecting adsorption of hydrocarbons in sediment are total organic matter (TOM) and particle grain size (Keshavarzifard et al., 2017). Horowitz (1991) reported that sediments with high contain of coarse sand in sediment fraction and low TOM generally have lower pollutants concentrations than fine sediment fractions and high TOM. The distribution of particle sizes (weight and percentages) of surface sediments from Sarawak EEZ are shown in Table 4.1 and Table 4.2. The grain size of sediments was determined by using sieve with sizes 2 mm, 500 μm , 355 μm and 50 μm and referred as very course, coarse sand, medium sand and silt and clay, respectively. All sediments showed high percentages of silt and clay ranged between 59.9-93.6% and this indicated the sediments from Sarawak EEZ mainly composed of silt and clay. Amellal et al. (2011) stated that sediments were dominated with fine fraction (silt and clay) enables PAHs to have strong affinity and adsorption to small particles due to greater surface area to volume ratio. Percentage of sediment with very coarse size ranged between 4.0-9.7%. Coarse sand ranged between 4.2-16.4% and medium sand ranged 5.2-17.2% for all sediments. The increased of clay and silt fractions in surface sediments followed by a decrease of sand fractions.

The amount of total organic matter (TOM) in surface sediments of Sarawak EEZ ranged between 2.10-7.60% with the high TOM were detected in the surface sediments of ST05, ST09, ST01 (see Table 4.2). High amount of TOM could be derived from abundance

of organic matter that associated with decomposition of marine organisms and terrestrial input (Keshavarzifard et al., 2018). The significant correlation between TOM and silt and clay ($r= 0.77$) as shown in Table 4.3 indicated high proportion of organic matter in marine sediment of Sarawak EEZ. Moisture content in surface sediments of Sarawak EEZ ranged between 22.9-47.5%, while ash content ranged between 61.8-97.9%.

Table 4.1: Percentage of particle sizes for surface sediments of Sarawak EEZ

Percentage of particle sizes of surface sediments (%)				
Stations	Very coarse	Coarse sand	Medium sand	Silt and clay
ST01	4.0	4.2	16.0	59.9
ST02	4.8	6.5	9.8	62.8
ST03	4.5	6.7	16.2	80.7
ST04	9.3	9.5	12.8	76.7
ST05	4.9	4.7	5.2	93.6
ST06	5.8	4.4	7.9	89.2
ST07	9.7	8.7	17.2	88.7
ST08	7.7	13.3	7.8	71.1
ST09	6.5	16.0	9.2	68.0
ST10	7.1	16.4	9.4	66.1
ST11	7.6	10.6	7.8	79.3

Table 4.2: Proximate analysis of surface sediments of Sarawak's EEZ

Stations	Moisture Content (%)	TOM (%)	Ash Content (%)
ST01	38.17	6.56	66.23
ST02	35.63	5.25	63.60
ST03	33.78	5.82	65.72
ST04	34.46	5.11	64.35
ST05	47.51	7.60	61.85
ST06	22.99	1.50	75.86
ST07	32.29	4.10	64.94
ST08	47.40	4.57	95.43
ST09	37.70	7.02	92.98
ST10	28.23	2.10	97.90
ST11	45.15	5.32	94.68

Table 4.3: Correlation analysis of sediment fractions with TOM and Ash

	Sand	Silt and Clay	TOM	Ash
Sand	1			
Silt and Clay	0.423	1		
TOM	0.597	0.770	1	0.371
Ash	0.365	0.406	0.371	1

4.2 Aliphatic Hydrocarbons in Marine Sediments of Sarawak's EEZ

4.2.1 Aliphatic Hydrocarbons Standard

Identification of individual *n*-alkanes in F1 fraction in sediments from Sarawak's EEZ was carried out by comparing retention times of *n*-alkanes in the sample with a mixture of *n*-alkanes standard ranged between *n*-nonane (*n*-C₉) to *n*-tetracontane (*n*-C₄₀). A GC-MS chromatogram for a mixture of *n*-alkanes standard is shown in Figure 4.1 and the retention times of individual *n*-alkanes in a standard mixture are tabulated in Table 4.4.

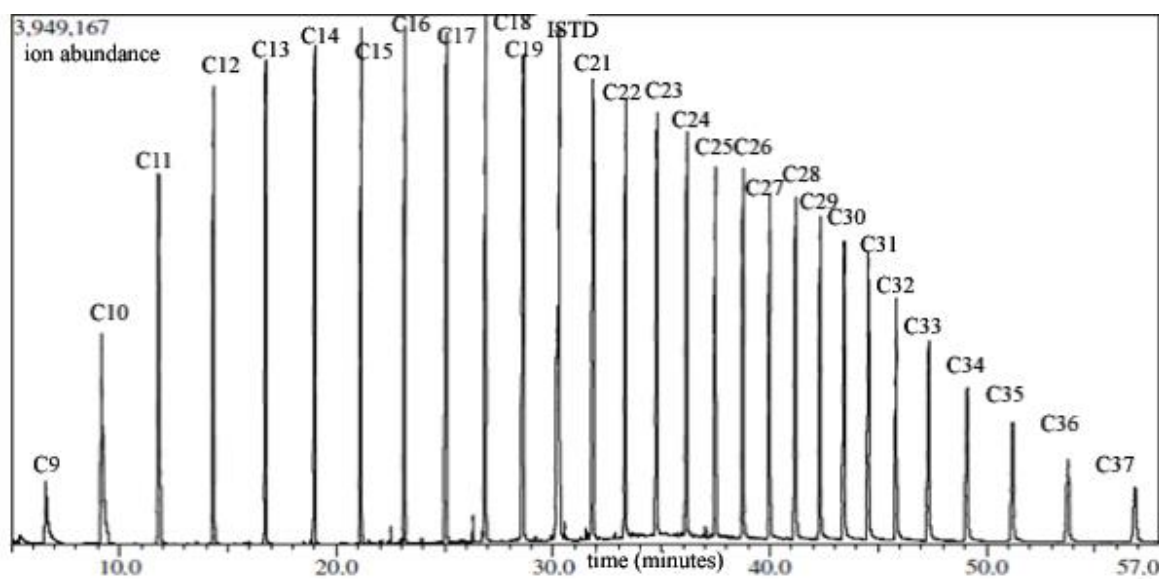


Figure 4.1: GC-MS chromatogram for mixture of standard mixture *n*-alkanes

Table 4.4: Retention times and response factors of n-alkanes and isoprenoids in a standard mixture

Compounds	Molecular formula	Retention Time	Relative Response Factor
<i>n</i> -Nonane	C ₉ H ₂₀	8.981	3.90
<i>n</i> -Decane	C ₁₀ H ₂₂	11.82	3.11
<i>n</i> -Undecane	C ₁₁ H ₂₄	14.401	1.63
<i>n</i> -Dodecane	C ₁₂ H ₂₆	16.749	1.67
<i>n</i> -Tridecane	C ₁₃ H ₂₈	18.900	1.54
<i>n</i> -Tetradecane	C ₁₄ H ₃₀	20.898	1.22
<i>n</i> -Pentadecane	C ₁₅ H ₃₂	22.765	1.01
<i>n</i> -Hexadecane	C ₁₆ H ₃₄	24.525	1.14
<i>n</i> -Heptadecane	C ₁₇ H ₃₆	26.189	1.28
<i>n</i> -Pristane	C ₁₉ H ₄₀	between C ₁₇ -C ₁₈	1.23
<i>n</i> -Octadecane	C ₁₈ H ₃₈	27.772	1.46
<i>n</i> -Phytane	C ₂₀ H ₄₂	between C ₁₈ -C ₁₉	1.25
<i>n</i> -Nonadecane	C ₁₉ H ₄₀	29.281	1.55
<i>n</i> -Eicosene- internal standard	C ₂₀ H ₄₀	30.706	0.72
<i>n</i> -Eicosane	C ₂₀ H ₄₂	30.786	1.05
<i>n</i> -Heneicosane	C ₂₁ H ₄₄	32.099	1.56
<i>n</i> -Docosane	C ₂₂ H ₄₆	33.42	1.11
<i>n</i> -Tricosane	C ₂₃ H ₄₈	34.686	1.48
<i>n</i> -Tetracosane	C ₂₄ H ₅₀	35.862	1.29
<i>n</i> -Pentacosane	C ₂₅ H ₅₂	37.067	1.41
<i>n</i> -Hexacosane	C ₂₆ H ₅₄	38.158	1.25
<i>n</i> -Heptacosane	C ₂₇ H ₅₆	39.267	1.31
<i>n</i> -Octacosane	C ₂₈ H ₅₈	40.311	1.28
<i>n</i> -Nonacosane	C ₂₉ H ₆₀	41.318	1.20
<i>n</i> -Eicontane	C ₃₀ H ₆₂	42.285	1.11
<i>n</i> -Henetricontane	C ₃₁ H ₆₄	43.218	1.00
<i>n</i> -Dotricontane	C ₃₂ H ₆₆	44.12	0.89
<i>n</i> -Tricontane	C ₃₃ H ₆₈	44.996	0.81
<i>n</i> -Tetratriacontane	C ₃₄ H ₇₀	45.844	0.65
<i>n</i> -Pentatriacontane	C ₃₅ H ₇₂	46.67	0.59
<i>n</i> -Hexatriacontane	C ₃₆ H ₇₄	47.553	0.44
<i>n</i> -Heptatriacontane	C ₃₇ H ₇₆	49.656	0.51

4.2.2 Aliphatic Hydrocarbons in Surface Sediments of Sarawak EEZ

Figures 4.2 to 4.5 show gas chromatograms of n-alkanes in surface sediment from Sarawak EEZ. The concentrations of n-alkanes (C₉-C₃₆) and isoprenoid hydrocarbons together with total aliphatic hydrocarbons (TAHs) in surface sediments of Sarawak EEZ are presented in Table 4.5. The TAHs in surface sediments of Sarawak EEZ ranged between 2.8-744.4 µg/g. The highest amount of TAH with 744.3 µg/g was recorded at ST02 (Kuching waters). High amount of hydrocarbons input in surface sediment of ST02 with absence of UCM might be due to anthropogenic activities. Low TAH (2.8 µg/g) was detected at ST01 (Kuching Waters) with the absence of UCM. Occurrence of bimodals UCM in the range of C₁₄-C₃₆ were observed for surface sediments of ST04, ST05, ST06, ST07, ST08, ST09, ST10 and ST11. Appearance of bimodals UCMs indicated the presence between of recent and old pollution (Azis et al., 2016) and this characteristic is usually attributed to hydrocarbons derived from petroleum (Medeiros et al., 2005). Aliphatic hydrocarbons in surface sediments of ST04, ST08, ST09, and ST11 are dominated by HMW hydrocarbons between C₂₇-C₃₆. Whereas, aliphatic hydrocarbons in surface sediments of ST05, ST06, ST07 and ST10 were dominated by LMW of C₁₆-C₂₆ hydrocarbons. Aliphatic hydrocarbons in surface sediments of ST01, ST02 and ST03 as shown in Figure 4.2 shared similar n-alkanes pattern with dominance of even numbered n-alkanes with major hydrocarbons at C₁₆, C₁₈ and C₂₂. Strong dominance of even number n-alkanes such as C₁₈ indicates the occurrence of petroleum pollution (Jacquot et al., 1999). Domination of LMW n-alkanes were observed in surface sediments of ST01, ST02 and ST03. The present of lighter n-alkanes indicated that the recent input of petrogenic hydrocarbons from fuel waste such as gasoline and diesel (Ines et al., 2013).

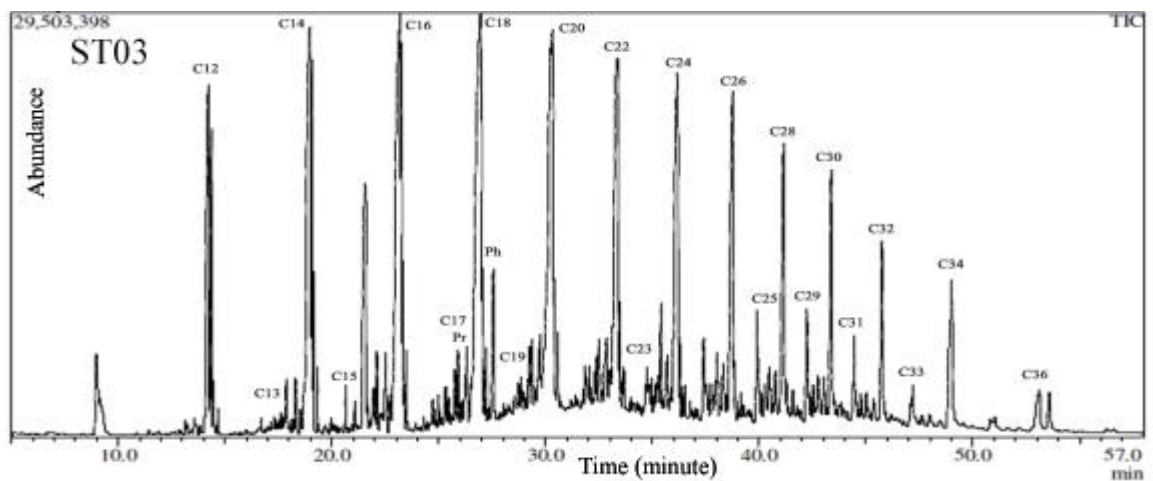
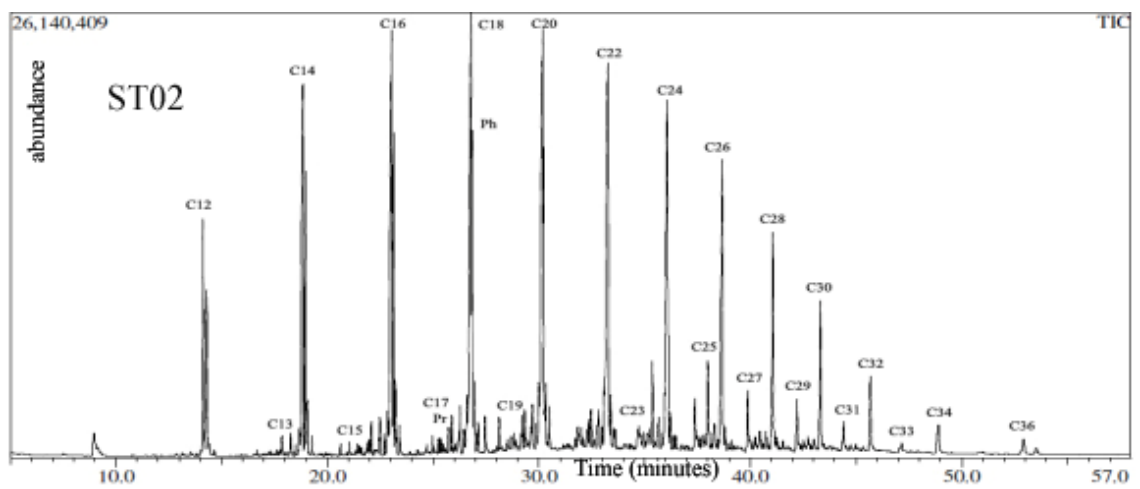
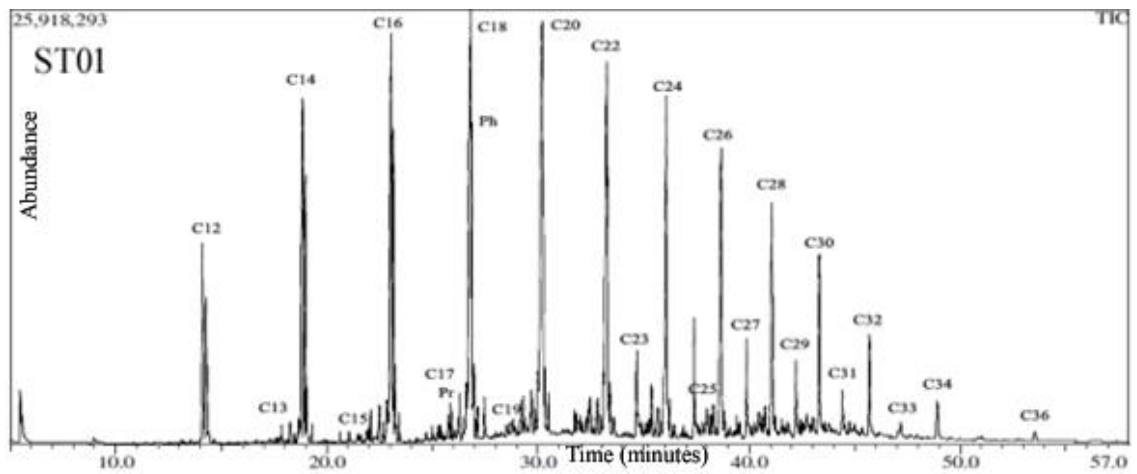


Figure 4.2: GC-MS chromatograms of aliphatic fraction in surface sediments of ST01, ST02 and ST03

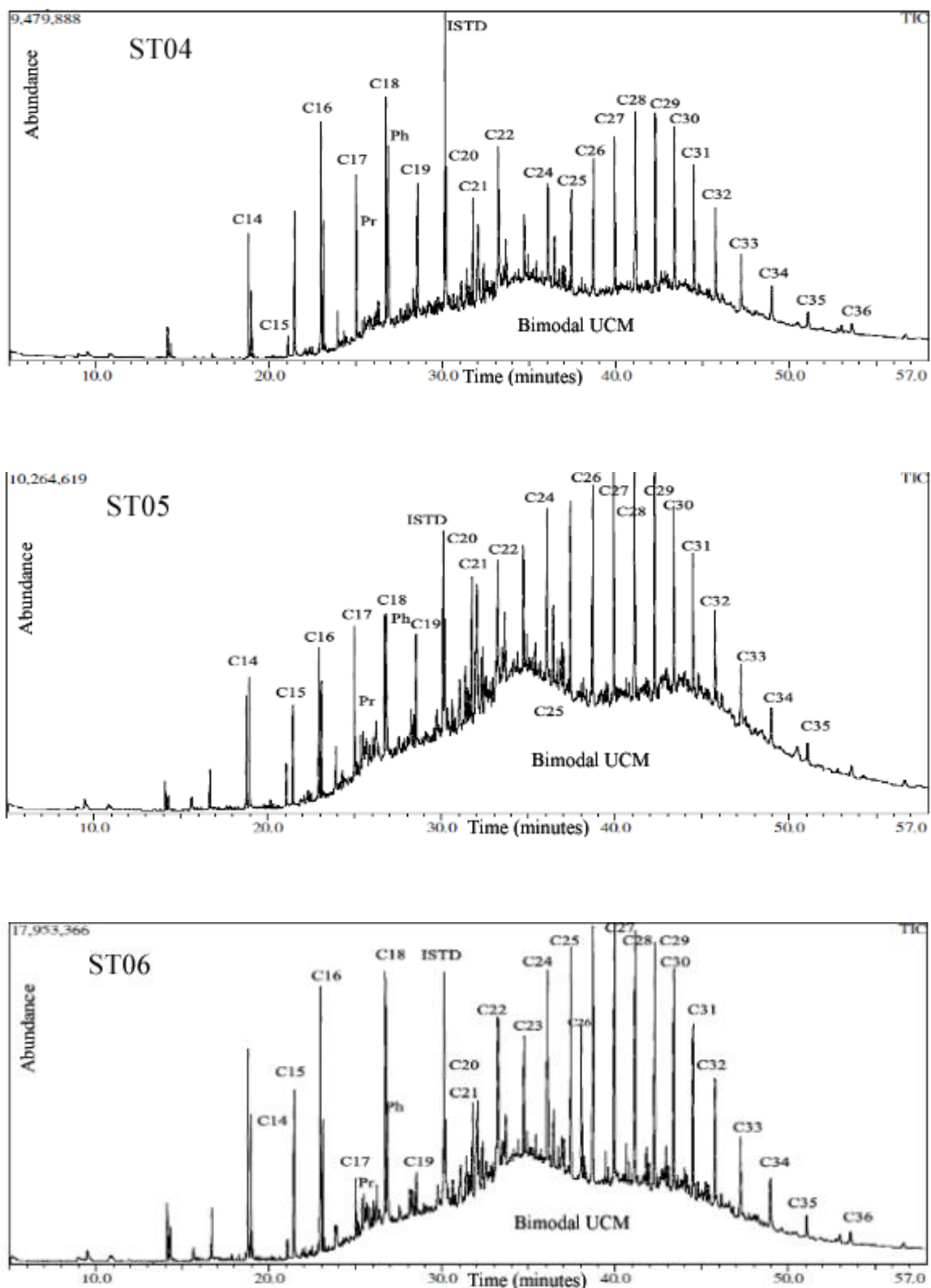


Figure 4.3: GC-MS chromatograms of aliphatic fraction in surface sediments of ST04, ST05 and ST06

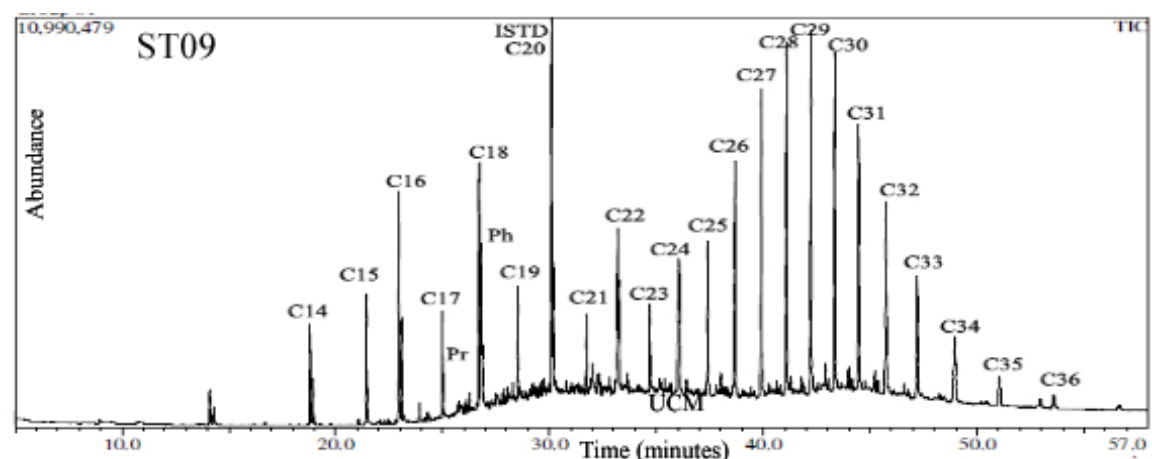
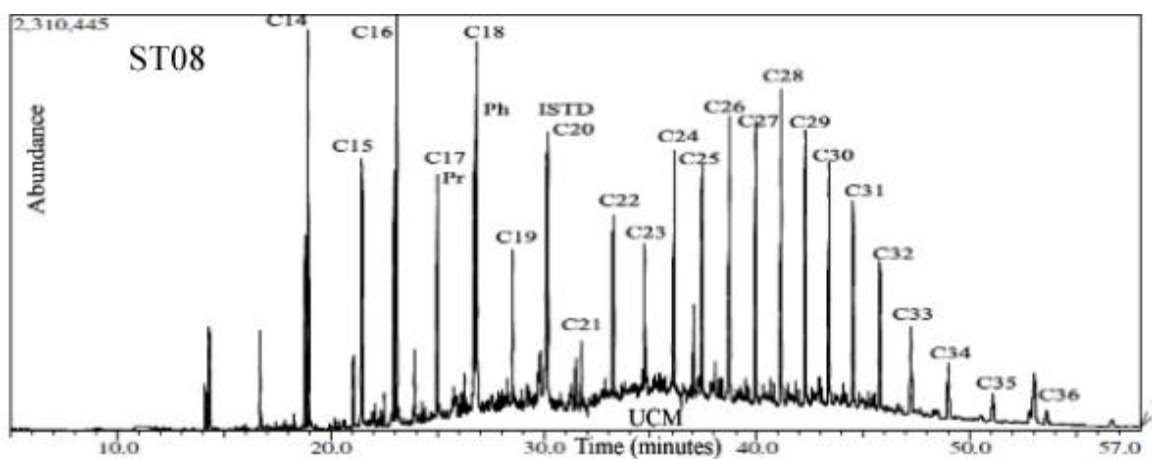
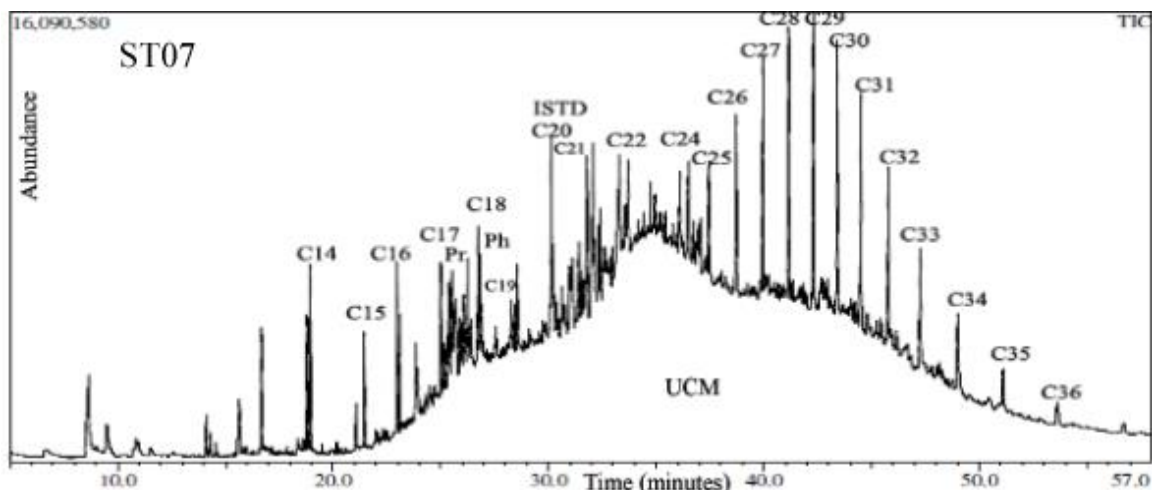


Figure 4.4: GC-MS chromatograms of aliphatic fraction in surface sediments of ST07, ST08 and ST09

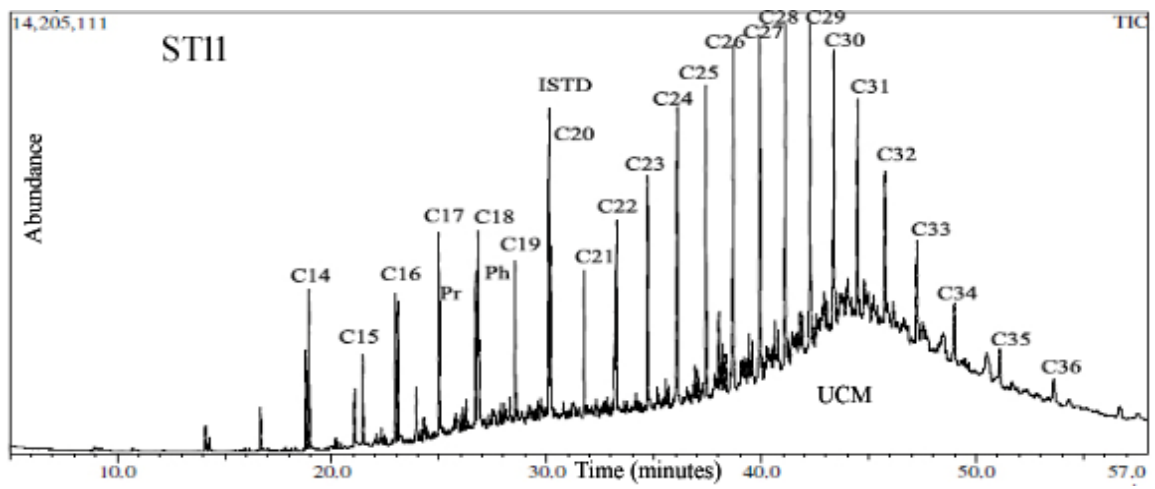
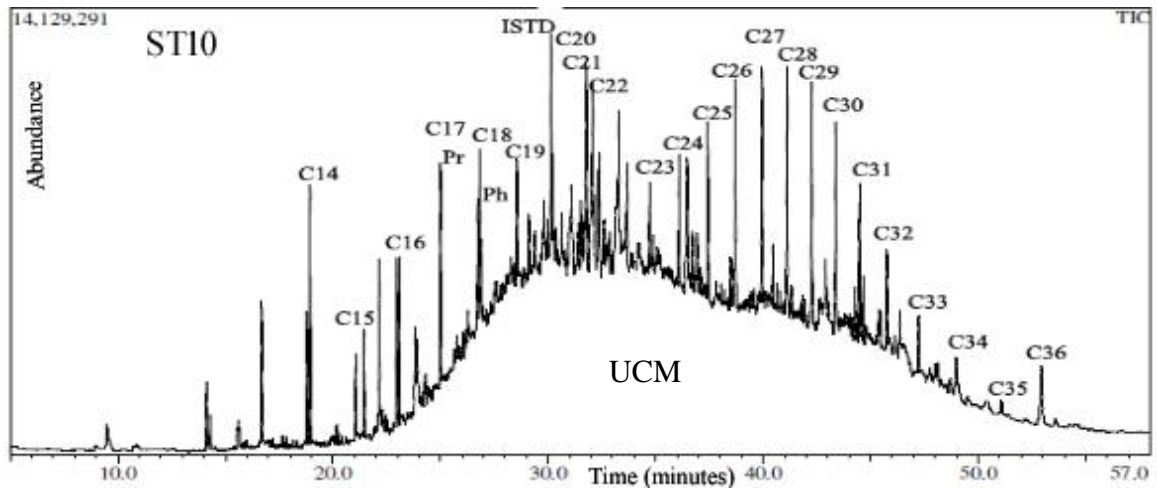


Figure 4.5: GC-MS chromatograms of aliphatic fraction in surface sediments of ST10 and ST11

Table 4.5: Concentration of aliphatic hydrocarbons ($\mu\text{g/g}$) in surface sediments from Sarawak's Exclusive Economic Zone

n-alkanes & isoprenoids	Concentration $\mu\text{g/g}$										
	ST01	ST02	ST03	ST04	ST05	ST06	ST07	ST08	ST09	ST10	ST11
Undecane C ₁₁	-	-	-	-	0.02	-	-	-	-	-	-
Dodacane C ₁₂	-	-	1.1	-	0.03	-	-	-	-	-	0.10
Tridecane C ₁₃	-	-	-	-	0.05	-	-	-	-	-	0.10
Tetradecane C ₁₄	0.10	19.7	0.8	0.01	0.01	-	0.03	-	0.1	0.03	0.01
Pentadecane C ₁₅	-	-	1.2	-	0.02	-	-	-	-	-	0.10
Hexadecane C ₁₆	0.20	38.5	10.1	0.01	0.1	-	0.04	-	0.20	0.10	0.04
Heptadecane C ₁₇	0.30	0.01	0.1	0.3	0.06	0.10	0.6	0.03	0.20	0.40	0.10
Pristane	0.30	0.02	0.01	0.1	0.1	0.2	0.10	0.10	0.30	0.40	0.08
Octadecane C ₁₈	0.30	126.7	3.7	0.2	0.2	0.3	0.50	0.10	0.30	0.20	0.20
Phytane	0.50	55.5	0.3	0.4	0.10	0.2	0.40	0.10	0.50	0.40	0.30
Nonadecane C ₁₉	-	2.8	0.04	0.3	1.6	0.01	0.40	1.7	-	0.50	0.60
Eicosane C ₂₀	0.30	204.9	14.5	1.0	0.70	0.02	0.90	1.6	0.30	0.60	0.20
Heneicosane C ₂₁	-	0.8	0.3	0.70	6.7	0.60	0.30	11.6	-	5.7	0.30
Docosane C ₂₂	0.60	130.8	8.5	0.20	2.9	0.30	0.90	7.1	0.6	3.2	0.30
Tricosane C ₂₃	-	0.7	0.10	0.20	2.2	0.10	0.80	2.5	0.01	0.10	0.60
Tetracosane C ₂₄	0.30	44.5	0.20	0.30	0.05	0.04	0.04	5.3	0.30	1.0	0.60
Pentacosane C ₂₅	0.01	59.8	0.04	0.40	0.10	0.90	0.02	7.0	0.01	0.70	0.80
Hexacosane C ₂₆	0.20	49.4	1.8	0.50	0.20	-	-	0.50	0.20	1.7	0.80
Heptacosane C ₂₇	-	0.9	0.02	0.50	0.20	-	0.05	9.4	0.01	1.9	0.90
Octacosane C ₂₈	0.10	23.3	0.80	0.60	0.90	1.0	0.10	11.6	0.10	1.9	0.80
Nonacosane C ₂₉	0.01	1.2	0.20	0.60	0.50	0.70	0.04	10.8	0.01	1.5	0.70
Eicontane C ₃₀	0.03	9.5	0.50	0.60	0.30	0.60	0.02	8.8	0.03	1.2	0.40
Henetricontane C ₃₁	0.01	1.2	0.10	0.70	0.30	-	0.10	0.50	0.01	0.10	0.30
Dotriconane C ₃₂	0.01	3.7	0.80	0.70	0.60	-	0.03	0.60	0.01	0.10	0.20
Triconane C ₃₃	-	0.50	0.10	0.80	0.20	0.01	0.05	0.60	-	0.20	0.10
Tetratricontane C ₃₄	0.04	1.4	5.9	0.70	0.04	-	0.04	2.1	0.04	0.20	0.90
Pentatriacontane C ₃₅	0.04	3.9	-	0.70	0.03	-	0.10	1.2	0.03	0.10	-
Hexatriacontane C ₃₆	0.03	23.1	1.2	0.02	0.02	0.10	0.10	0.70	0.02	3.8	-

Table 4.5 continue

Σ TAH	2.8	744.4	52.3	10.5	35.9	4.5	5.1	88.3	6.7	26.3	9.61
Σ LMW (C ₁₆ -C ₂₆)	2.49	450.9	33.5	4.49	15.1	2.76	4.53	37.6	2.14	14.7	4.28
Σ HMW (C ₂₇ -C ₃₆)	0.24	68.9	9.54	6.01	3.14	2.39	0.59	46.3	4.47	11.0	4.75

Note: Σ TAH- Total aliphatic hydrocarbons, Σ LMW- Total low molecular weight, Σ HMW- Total high molecular weight

4.2.3 Sources Identification of Aliphatic Hydrocarbons Using *n*-Alkanes Molecular Marker in Surface sediments of Sarawak EEZ.

Several hydrocarbon biomarkers indices were used to predict the sources of hydrocarbons in surface sediments of Sarawak EEZ. These include carbon preferences index (CPI), ratio LMW/HMW, average chain length (ACL), terrigenous/aquatic ratio (TAR), isoprenoid ratios and the occurrence of UCM. Table 4.6 tabulates the hydrocarbons biomarker indices for surface sediments from Sarawak EEZ, respectively.

Table 4.6: Molecular indices of *n*-alkanes from surface sediments from Sarawak EEZ

Station	Molecular Indices								
	TAH (ug/g)	CPI	ACL	LMW/ HMW	TAR	Pri/phy	Pri/C ₁₇	Phy/C ₁₈	MH
01	2.8	0.1	27.8	10.5	0.10	0.5	1.1	1.7	C ₂₂
02	744.4	0.1	28.7	9.5	1.17	n.d	0.8	0.4	C ₂₂
03	52.3	0.1	29.5	4.1	0.19	0.1	0.3	0.1	C ₁₆
04	10.5	1.5	29.6	0.7	3.0	0.2	0.2	2.4	C ₂₀
05	35.9	1.0	27.2	0.9	0.63	0.8	1.9	0.8	C ₂₁
06	4.5	0.8	26.8	0.9	7.21	0.9	2.3	0.6	C ₂₈
07	5.1	1.6	29.8	7.6	0.18	0.3	0.2	0.8	C ₂₀
08	88.3	1.7	27.4	0.9	11.7	0.6	2.1	1.1	C ₂₈
09	6.7	1.5	28.9	0.5	20.0	0.4	0.8	0.4	C ₂₉
10	26.3	1.3	26.4	1.3	3.95	0.1	0.1	1.6	C ₂₁
11	9.6	1.4	28.2	0.9	6.76	0.4	1.8	1.7	C ₃₅

Notes: Pri – pristane; phy - phytane

4.2.3.1 Carbon Preferences Index (CPI) and Ratios of Isoprenoid Hydrocarbons.

Low CPI with value 0.1 was recorded in surface sediments of ST01, ST02 and ST03, while the CPI values were 0.9 and 0.8 were recorded in surface sediments of ST05 and ST06, respectively. CPI values below 1 indicated for hydrocarbons derived from anthropogenic (generally petroleum) sources. CPI values significantly higher than 1 (1.0-1.7) as observed for hydrocarbons in surface sediments of ST04, ST07, ST08, ST09, ST10 and ST11 indicated terrigenous input (Commendatore et al., 2012). CPI values closed to 1 are typical of petroleum sources, recycled organic matters or marine animal input, while CPI values above 3.0 usually are related to high vascular plant (Tolosa et al., 2004; Ou et al., 2003).

In sedimentary environment, ratio of pristane/phytane above 1 reflects oxidizing sediment, whereas, pristane/phytane below 1 indicates highly reducing (anoxic) depositional environment. Ratios of C₁₇/pristane and C₁₈/phytane can be used to determine the source of n-alkanes. These ratios have been used as indicators of early effect of biodegradation of n-alkanes (Diez et al., 2007). Table 4.6 shows that all surface sediments of Sarawak EEZ have pristane/phytane < 1 which suggested petroleum inputs and reduced environment of sediments (Huang et al., 2017). Commendatore et al. (2012) have reported the ratios > 1 for both C₁₇/pristane and C₁₈/phytane indicated for recent petroleum input and slow degradation process. These have been observed in surface sediments of stations ST01 to ST11. However, surface sediment of ST08 has both C₁₇/pristane and C₁₈/phytane < 1 which indicated biodegradation process has been occurred.

4.2.3.2 Ratio of Low Molecular Weight to High Molecular Weight (LMW/HMW)

The oil characteristics in sediment can be determined by using the ratio of LMW/HMW where LMW/HMW > 2 indicates fresh oil input whereas LMW/HMW ratio < 1 stand for degraded oil or could be originated from organic material input, higher plants and sedimentary bacteria (Salem et al., 2014; Commendatore et al., 2000). Table 4.6 shows the ratios of LMW/HMW in surface sediments of Sarawak EEZ with fresh oil inputs were detected in surface sediments of ST01, ST02, ST03 and ST07 with LMW/HMW ratio ranged between 4.1-10.5. This fresh oil input could be originated from shipping activities and offshore oil explorations at the EEZ area.

Surface sediments at stations ST06 and ST10 showed LMW/HMW ~1, which indicated that n-alkanes were originated from both natural and petrogenic sources (Sakari et al., 2012). However, these values can be used as evidence for fresh oil input because surface sediments may subject for biodegradation in aerobic conditions and also contain high levels of odd-numbered carbon from the biogenic origin such as plankton (Gearing et al., 1976). The major hydrocarbon detected in surface sediment ST10 was C₂₁ with dominant even numbered carbon and CPI >1 which indicated the presence of aliphatic hydrocarbons derived from terrestrial plant. The ratios of LMW/HMW for surface sediments of ST04, ST05, ST08, ST09 and ST11 ranged 0.51-0.95 which represent degraded oil or n-alkane derived from biogenic sources such as sedimentary bacteria, plants and marine animal (Kanzari et al., 2012; Sakari et al., 2012)

4.2.3.3 Average Chain Length (ACL) and the Terrigenous/Aquatic Ratio (TAR)

The *n*-alkanes average chain length (ACL) is the weight-averaged number of carbon atoms for *n*-alkanes of the higher plant C₂₅-C₃₃. The amount of individual *n*-alkanes from higher plant sources increased with expanding carbon number in marine residue and this pattern is related to petrogenic hydrocarbons. The ACL would be diminished if petrogenic hydrocarbons were added to residue containing biogenic hydrocarbons (Jeng, 2006). Table 4.6 shows that the ACL of C₂₅-C₃₃ *n*-alkanes for surface sediments ranged from 27.4-29.8. Jeng (2006) reported the average ACL of plant wax in marine sediments was 30.0 ± 0.4 (range 29.1-30.3). Stations ST01, ST02, ST05, ST06, ST08, ST09, ST10, and ST11 showed the ACL value below the range indicated the hydrocarbons input towards sediments were believed from anthropogenic sources. Jeng (2006) reported that the ACL values for fossil fuels such as crude oils were 27.8, 27.9 and 28.4. Surface sediments from site ST03, ST04, ST07 the ACL values were 29.5, 29.6 and 29.8 respectively, which indicated the *n*-alkanes input from biogenic sources.

The terrigenous/aquatic ratio (TAR) can be used to evaluate the importance of terrigenous inputs against aquatic inputs (Mille et al., 2007). TAR is calculated as the ratio of the concentrations of long-chain *n*-alkanes to short-chain *n*-alkanes. Values of TAR ranged between 2.1 to 12.7 indicate the importance of terrigenous inputs. Increasing TAR leads to a decrease in the LMW/HMW ratio because of the increase in *n*-alkanes with HMW, such as C₂₅, C₂₇, C₂₉, and C₃₁. Overall, the *n*-alkanes between nC₁₆ and nC₃₆ were found in all surface sediments. Several stations have shown high TAR ranged 3.0-20.0 and low LMW/HMW ratio ranged 0.5-0.9 in sampling sites of ST04, ST06, ST08, ST09, ST10 and ST11. The presence of *n*-alkanes ranged between of C₁₆-C₂₀ was observed in surface sediments of stations ST04, ST06, ST08, ST09 and ST11 which

indicates for biogenic input of aquatic origin. Occurrence of high molecular weight of *n*-alkane in higher plants was also detected in surface sediments of ST04, ST06, ST08, ST09, ST10 and ST11 which were supported by TAR values 3.0, 7.21, 11.7, 20.0, 3.0 and 6.76. Low TAR values ranged from 0.10-1.17 were detected in surface sediments of ST01, ST02, ST03, ST05 and ST07 which indicated high input of LMW *n*-alkanes. Low TAR values in these sites may cause high LMW/HMW ratios ranged from 0.9-10.5. LMW of *n*-alkanes (C₁₆-C₂₆) were detected in all surface sediments. The presence of light hydrocarbons in surface sediment of ST01, ST02, ST03, ST05 and ST07 indicated the presence of oil product. The presence C₂₀ and C₂₄ of *n*-alkanes also confirmed the presence of petrogenic sources and supported by low CPI 0.1 in surface sediments of ST01, ST02 and ST03.

4.2.3.4 Unresolved Complex Mixture (UCM)

The presence UCM or hump in the GC chromatograms indicates the sign of petroleum input or the biodegraded of hydrocarbons (Mille et al., 2007; Frysiner et al., 2003). The biodegradation process in oil typically removed small alkanes (C₂ to C₁₂) and aromatics. This process continued, several major compounds disappear, and chromatographic baseline hump become more significant. Occurrence of unimodal and bimodal of UCM can be spotted in GC chromatograms. Although the UCM was not determined quantitatively but the appearance of UCM proved the presence of degraded oil in the sediment (Vaezzadeh et al., 2015). Figures 4.3 to 4.4 show that surface sediments of ST08, ST10 and ST11 have unimodal UCM detected from C₁₅ to C₃₅ which attributed to the presence of degraded of crude oil in sediment by microorganisms (Farrington and Tripp, 1977; Bouloubassi and Saliot, 1993). These confirmed ratios of

LMW/HMW surface sediments of < 1 in ST08 and ST11, respectively and LMW/HMW ~ 1 in surface sediment of station ST10 which also indicated for degraded oil. Gas chromatograms of aliphatic fraction of n-alkanes ranging from C₁₅ to C₃₂ have both unimodal and bimodal patterns characteristic of petroleum origin (Medeiros et al., 2005). Large bimodal UCM in gas chromatograms of aliphatic hydrocarbons were detected in surface sediments of ST04, ST05, ST06, ST07 and ST09. Table 4.7 shows ranged of carbon numbers for two humps in UCM bimodal pattern in gas chromatograms. The presence of UCM in gas chromatograms are supported by the ratio LMW/HMW of n-alkanes which proved that hydrocarbons in these sampling sites have undergone degradation process. The gas chromatograms in surface sediments of stations ST01, ST02 and ST03 did not showed the presence of UCM. The UCM hump is usually absence in fresh oil input of hydrocarbons (Vaezzadeh et al., 2015). This have been supported by the ratios of LMW/HMW in surface sediments of ST01, ST02 and ST03 showed the existence of fresh oil input and predominance of LMW n-alkanes.

Table 4.7: *n*-Alkanes ranged for bimodal in GC-FID chromatograms

Stations	UCM 1	UCM 2
ST04	C ₁₄ -C ₂₅	C ₂₆ -C ₃₅
ST05	C ₁₄ -C ₂₅	C ₂₆ -C ₃₅
ST06	C ₁₅ -C ₂₅	C ₂₆ -C ₃₅
ST07	C ₁₅ -C ₂₅	C ₂₆ -C ₃₅
ST09	C ₁₅ -C ₂₅	C ₂₆ -C ₃₅

4.2.4 Aliphatic Hydrocarbons in Core Sediments of Sarawak EEZ

Figure 4.6 shows typical gas chromatograms of aliphatic hydrocarbons in layer 2.5-3.0 cm of core sediments from ST01, ST02 and ST03 at Sarawak EEZ. Concentrations of n-alkanes and isoprenoid hydrocarbons in core sediments of ST01, ST02 and ST03 are shown in Appendices 1, 2 and 3, respectively. Total aliphatic hydrocarbons (TAHs) in core sediments of Sarawak EEZ varied from 7.00-324.4 $\mu\text{g/g}$. Elevated concentration of TAH in core sediments for all sampling sites could be originated from anthropogenic activities. TAH concentrations below 50 $\mu\text{g/g}$ are normally considered as uncontaminated (Zegouagh et al., 1998), while values above 100 $\mu\text{g/g}$ are remarked as contaminated and presence of petroleum biomarkers (Readman et al., 2002). Concentration of TAH in core sediment at ST01 was below 50 $\mu\text{g/g}$ from layer 5-7.5 to 10-12.5 cm, whereas TAH detected at the upper layers (0-2.5 cm and 2.5-5 cm) were 123.7 $\mu\text{g/g}$ and 56.1 $\mu\text{g/g}$, respectively. Aliphatic hydrocarbons in core sediment of ST01 were dominated by LMW with predominant of even numbered carbons (C_{16} , C_{20} , C_{22} , C_{26}) from layers 2.5 to 7.5 cm and C_{13} at layer 10.0-12.5 cm. TAH concentration in all layers of core sediment from ST02 was above 100 $\mu\text{g/g}$. The highest TAH concentration with 324.4 $\mu\text{g/g}$ was detected at the bottom layer (10-12.5 cm). High concentrations of TAH in this core sediment is followed by predominance of even numbered carbons such as C_{18} , C_{28} and C_{34} . All layers in core sediment at ST03 showed TAH concentrations below than 50 $\mu\text{g/g}$ with the highest concentration (46.6 $\mu\text{g/g}$) recorded at layer 5.0-7.5 cm. The predominant of even carbon numbered C_{18} , C_{26} and C_{28} was observed toward the bottom of core sediment except at the bottom of core (10.0-12.5 cm) with the predominant of odd numbered carbon, C_{29} .

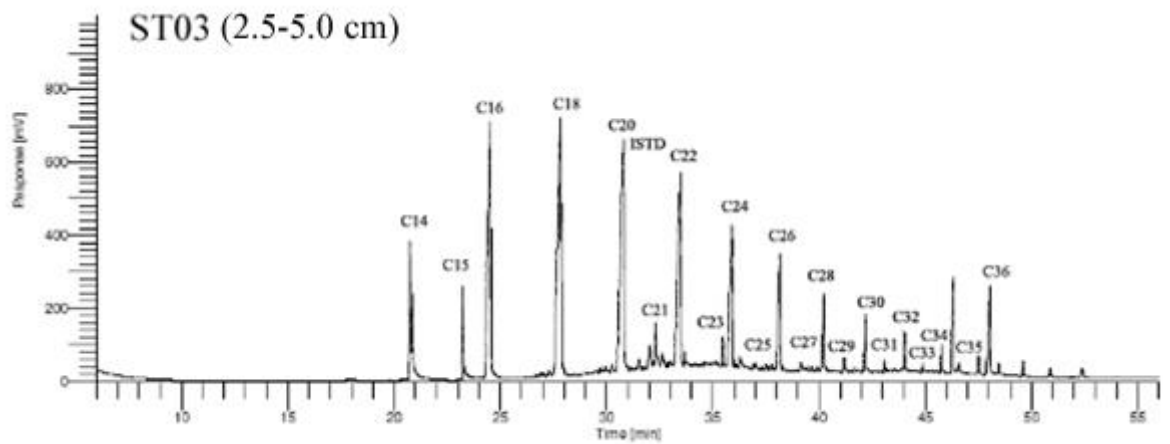
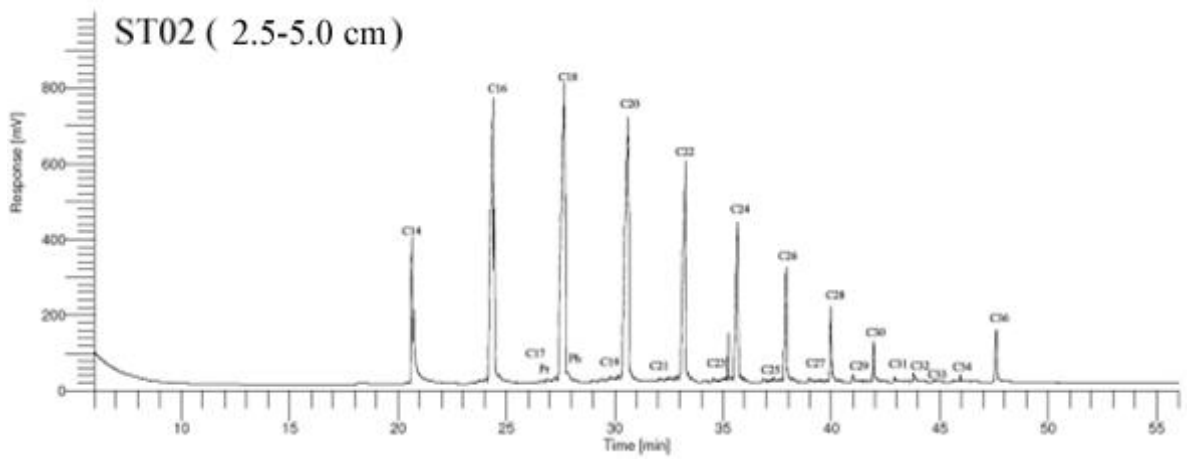
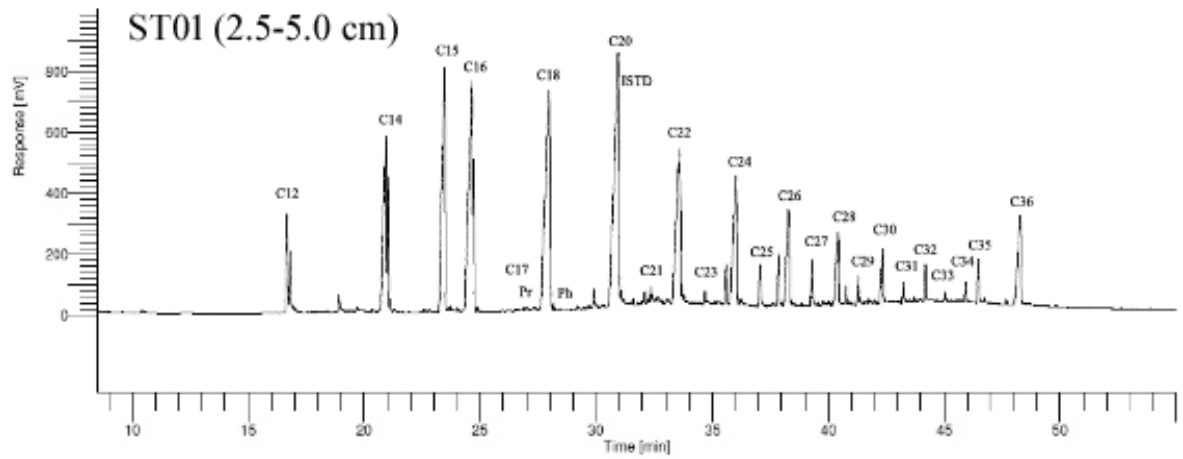


Figure 4.6: GC-FID chromatograms of aliphatic hydrocarbons in layer 2.5-5.0 cm in core sediments of ST01, ST02 and ST03

4.2.5 Sources Identification of Aliphatic Hydrocarbons Using *n*-Alkane Molecular Markers in Core Sediment of Sarawak EEZ

The sources of *n*-alkanes in core sediments of Sarawak EEZ were investigated by using several *n*-alkane molecular markers such as carbon preferences index (CPI), ratio of low molecular weight to high molecular weight (LMW/HMW) and ratios of isoprenoid hydrocarbons. Table 4.8 shows molecular *n*-alkane indices used for *n*-alkane investigation in core sediments of Sarawak EEZ.

4.2.5.1 Carbon Preferences Index (CPI) of *n*-alkane in Core Sediments

CPI values ranged from 0.17-1.1 were recorded in core sediment of ST01 as shown in Table 4.8, while vertical pattern of CPI is shown in Figure 4.7. The upper layers (0-2.5 cm to 5.0-7.5 cm) of core sediment of ST01 were believed to receive petrogenic inputs which were supported by appearance of even carbon numbered *n*-alkanes. The highest CPI values were recorded at the bottom layers (7.5-10.0 cm and 10.0- 12.5 cm) with CPI values of 1.0 and 1.1, respectively, indicating that source of hydrocarbons may have originated from marine microorganisms or recycled organic matter.

CPI values < 1 were constantly detected from above to the bottom of layers of core sediment of ST02 with the predominance of even numbered *n*-alkanes. The source of *n*-alkanes in core sediment of ST02 indicated a relatively higher proportion of *n*-alkanes from anthropogenic (mostly petroleum) sources. The CPI value in sediment core of ST03 varied from 0.1-1.56 (see Figure 4.7). The CPI value increase from upper to downcore of sediment. Low CPI values (0.1) were recorded in layers 0-2.5 cm to 2.5-5.0 cm with the domination

of even numbered carbon over the odd numbered carbon which indicated petrogenic sources. The CPI values were then increased from 1.1 to 1.56 from layer 5.0-7.5 cm to 10.5-12.5 cm which indicated the biogenic input. The presence of C₂₉, n-alkane, in the bottom layer indicated hydrocarbons derived from terrestrial plant. CPI higher than 1 was reported in coastal area of Delta Nigeria (Ekpo et al., 2012) and the source of hydrocarbons was linked to terrigenous/biogenic sedimentary sources.

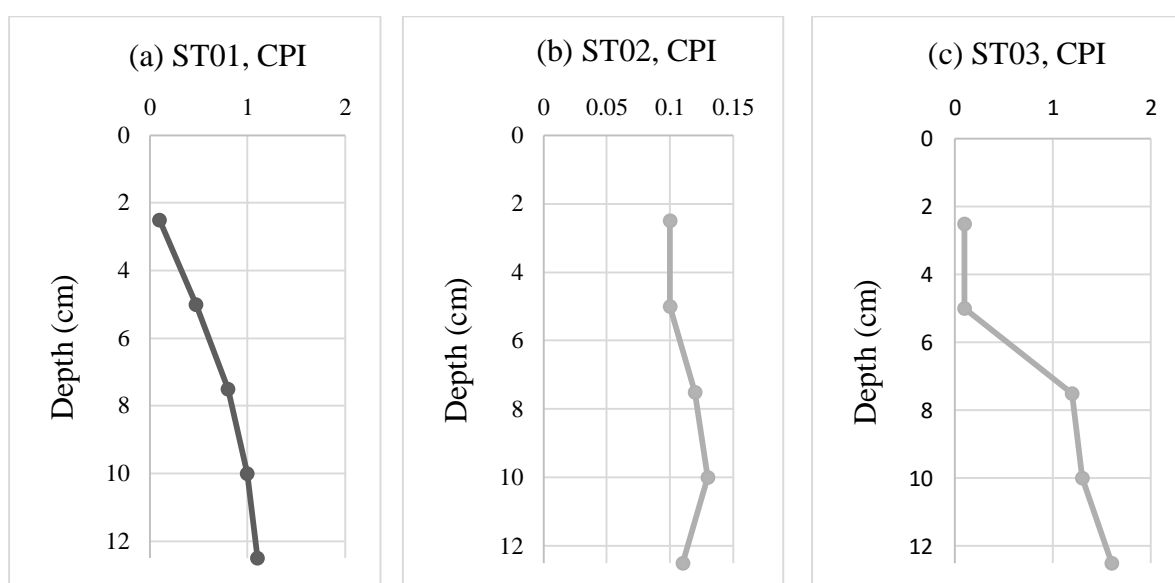


Figure 4.7: Vertical trend of CPI in core sediments of ST01, ST02 and ST03.

Table 4.8: Concentrations of TAH (ug/g) and molecular index of alkanes in each layers of core sediment from ST01, ST02 and ST03

Core Sediment	TAH (ug/g)	CPI	LMW/HMW	TAR	ACL	Pri/phy	C17/Pri	C ₁₈ /Phy	Major
ST01 (cm)									
0-2.5	123.7	0.3	3.8	36.7	19.1	-	1.5	0.8	C ₂₀
2.5-5.0	56.1	0.17	1.9	4.36	31.0	-	1.4	3.7	C ₃₄
5.0-7.5	7.0	0.4	1.0	3.81	27.4	0.1	0.2	0.6	C ₂₆
7.5-10.0	48.5	1.1	5.8	5.00	26.2	-	4.4	-	C ₁₆
10.0-12.5	9.45	1.0	1.4	2.69	26.1	0.5	0.6	1.0	C ₁₆
ST02 (cm)									
0-2.5	167.9	0.1	1.0	0.10	33.5	-	0.4	1.4	C ₃₄
2.5-5.0	122.6	0.1	1.4	0.37	29.6	-	-	9.6	C ₂₈
5.0-7.5	144.5	0.1	18.6	2.66	29.3	-	0.3	0.6	C ₁₈
7.5-10.0	204.3	0.1	0.4	1.74	29.9	2.2	1.1	40.9	C ₃₄
10.0-12.5	324.4	0.1	2.3	0.10	29.5	-	0.2	5.4	C ₁₈
ST03 (cm)									
0-2.5	8.05	0.1	5.7	7.19	28.6	0.01	1.2	8.5	C ₁₈
2.5-5.0	9.34	0.1	9.9	21.7	28.8	0.02	0.3	7.1	C ₁₈
5.0-7.5	46.6	1.1	0.6	89.51	28.4	-	-	0.2	C ₂₈
7.5-10.0	20.9	1.3	1.5	207.8	26.9	-	-	-	C ₂₆
10.0-12.5	35.5	1.6	0.3	103.9	27.9	-	-	-	C ₂₉

Notes: pri – pristane; phy - phytane

4.2.5.2 Ratio of Low Molecular Weight to High Molecular Weight (LMW/HMW) of *n*-alkanes in Core Sediments.

The vertical profiles for LMW/HMW ratios of *n*-alkanes in core sediments of ST01, ST02 and ST03 are shown in Figure 4.8. The fresh oil input was observed in core sediment at ST01, from upper layer toward down core of 0-2.5 cm, 2.5-5.0 cm and 5.0-7.5 cm with ratio of LMW/HMW 3.8, 2.0 and 2.5, respectively. Ratio LMW/HMW with value 1 at layers of 7.5-10.0 cm and 10.0-12.5 cm suggested two possible sources of *n*-alkanes. CPI values > 1 for both layers of 7.5-10.0 cm and 10.12.5 cm indicated biogenic input with major hydrocarbon in these layers 7.5-10.0 cm and 10.0-12.5 cm was C₁₆ with predominant of LMW *n*-alkanes thus the possible sources of *n*-alkanes in both layers can be petrogenic and plankton origins. Fresh oil inputs with LMW/HMW > 2, were observed at upper layers of 0-2.5 cm and 2.5-5.0 cm in core sediment of station ST03, whereas toward down core, layers from 5.0-7.5 cm to 10.0-12.5 cm, *n*-alkanes derived from biogenic sources as indicated by LMW/HMW ratio (0.3-1.5). This is supported by CPI >1 toward down core sediment of ST03.

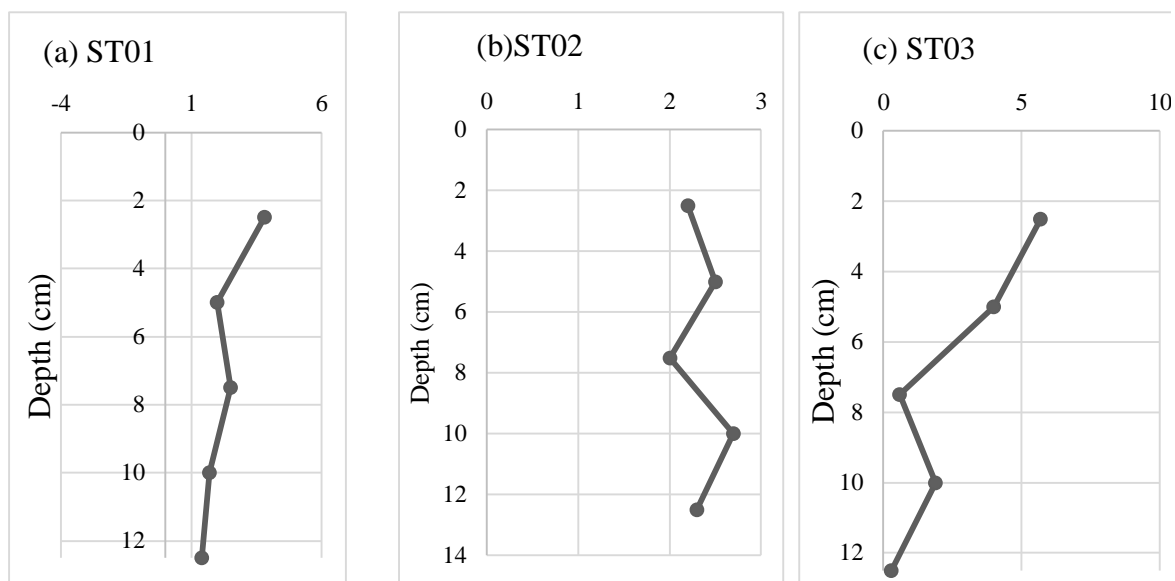


Figure 4.8: Vertical profile of LMW/HMW of *n*-alkanes in core sediments at ST01, ST02 and ST03

4.2.5.3 Ratios of Isoprenoid Hydrocarbons in Core Sediments

Due to low concentrations of pristane and phytane in the studied core sediments, only certain layers showed pristane/phytane ratios. Table 4.8 shows that ratios of pristane/phytane < 1 in core sediments of ST01 and ST03 which suggest a source of petroleum products (Medeiros et al., 2005). In core sediment of ST02, pristane/phytane ratios < 1 at layers 5.0-7.5 cm and 10.0-12.5 cm indicating for petroleum input except at 7.5-10.0 cm where pristane/phytane > 2 , the sources of hydrocarbons at this layer have received biogenic input. Figures 4.9 and 4.10 show vertical profiles of C_{17} /pristane and C_{18} /phytane, respectively.

The vertical profiles of C_{17} /pristane and C_{18} /phytane in core sediment of ST01 ranged 0.2-1.4.4 and 0.6-3.7, respectively. This indicated there was significant degradation process of *n*-alkanes have been occurred in this core sediment. Figure 4.9 shows vertical profile of

C_{17} /pristane values in ST02, the values were relatively low due to significant microbial degradation process. C_{18} /phytane ratios, above 1, were detected in layers 0-2.5 cm and 2.5-5.0 cm in core sediment of ST02 due to petroleum contribution. The ratios of C_{17} /pristane and C_{18} /phytane in core sediment of ST03 were considered high and the presence of fresh oil input at layer 0-2.5 cm and 2.5-5.0 cm due to slow degradation process occurred in this core sediments (Colombo et al., 1989).

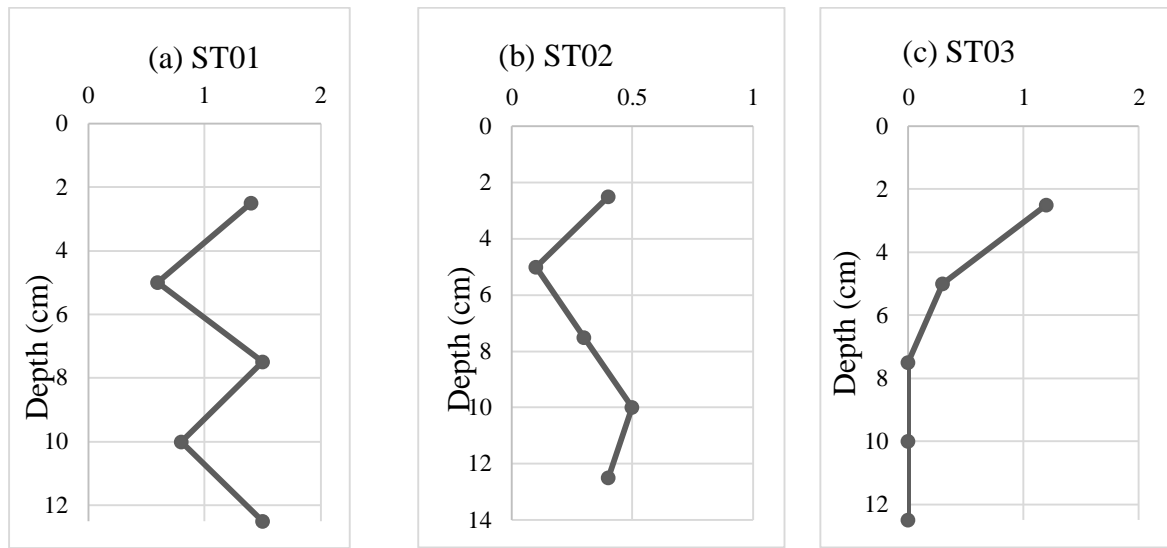


Figure 4.9: Vertical profile of C_{17} /pristane in core sediments of ST01, ST02 and ST03.

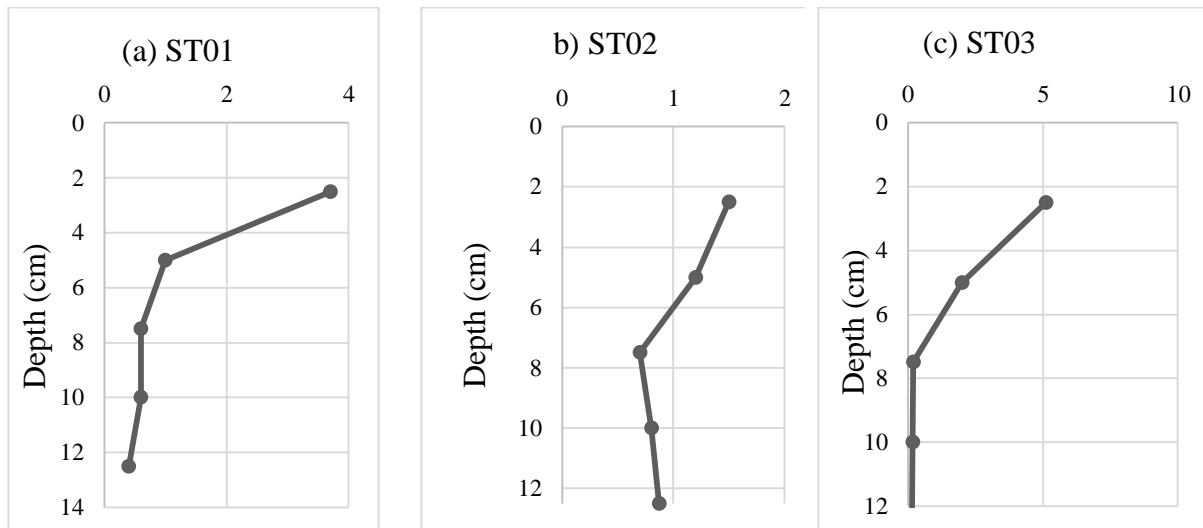


Figure 4.10: Vertical profile of C_{18} /phytane in core sediments of ST01, ST02 and ST03.

4.2.6 Aliphatic Hydrocarbon Biomarkers

Aliphatic hydrocarbons (F1 fractions) in surface sediments from Sarawak EEZ were analysed by GC-MS using full scan mode by monitoring ions between m/z 45 to 450. However, regular hydrocarbon biomarkers such as hopane and sterane can be seen in the gas chromatogram. Thus post-run data analysis was performed on GC-MS obtained by full scan mode using mass chromatogram analysis. Hopane and sterane were identified by extracting ions of m/z 191 and m/z 217, respectively. These biomarkers were detected between C_{24} - C_{36} n-alkanes and are usually masked hidden by the signal of n-alkanes and UCM. The structure of various hopanes and steranes can be achieved by pattern recognition of mass spectra, comparison of retention time with n-alkanes standard and available literature data for hopane and sterane fingerprints (Peters and Modowan, 1993).

4.2.6.1 Pentacyclic Triterpanes

Mass chromatograms of (m/z 191) for hopane were detected in all surface sediments of Sarawak EEZ. Figure 4.11 shows mass chromatograms of (m/z 191) in station ST06 of Sarawak EEZ. Terpane series such as tricyclic, tetracyclics, hopanes and other compounds are generally being used to detect oils and sources of rocks (Hunt, 1996). Mass chromatogram with m/z 191 was used to determine the presence of triterpane series in saturated hydrocarbons fraction in surface sediments. Mass chromatogram analysis showed the predominance of homohopanes between C_{31} to C_{35} with the homologs $> C_{30}$ present as the typically mature C-22 R/S pairs were detected in surface sediments. These homohopanes with the 22S and 22R configuration are derived from bacteriopolyhopanol of prokaryotic

cell membrane (Peters et al., 2005) and thermodynamically stable. The presence of trisnorneohopane (Ts) and trisnorhopane (Tm) were also observed in mass chromatograms; these compounds demonstrate mature crude oil and can be used to determine the origin of crude oil (Hu et al., 2009). The presence of hopanes series in the surface sediments have confirmed the petrogenic source and presence of mature oil (Gray and Becker, 2002).

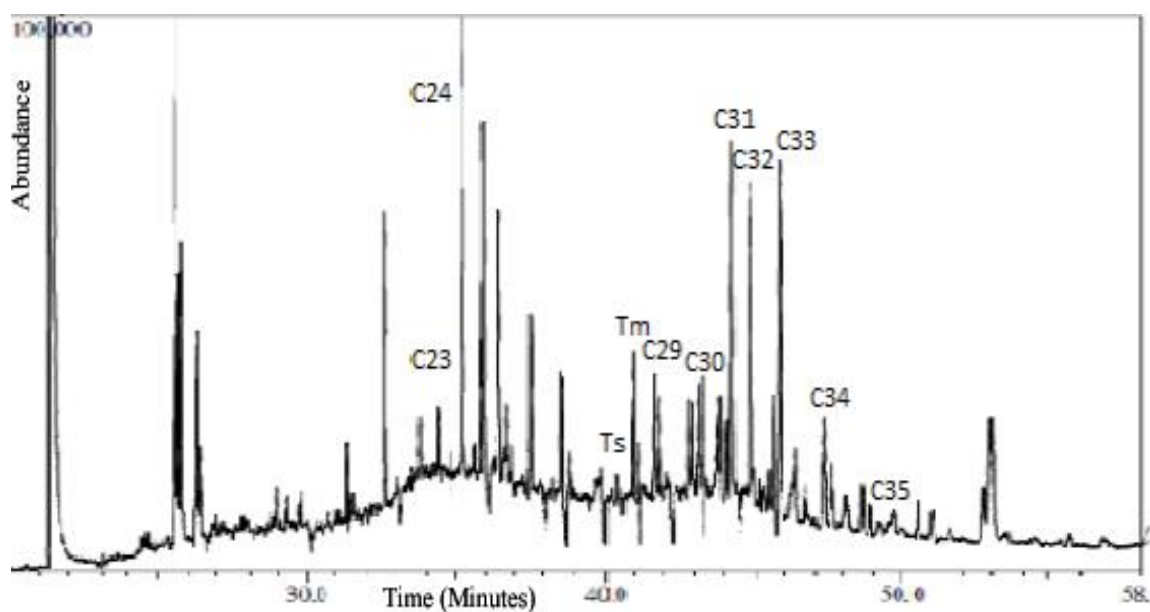


Figure 4.11: Mass chromatogram of hopane series (m/z 191) in aliphatic fractions from surface sediments in station ST06 of Sarawak EEZ

4.2.6.2 Sterane Fingerprinting

Steranes are not common content in gasoline or diesel fuels but can be introduced into the environment from petroleum or lubricating oils via emissions of vehicular engines (Abas and Simoneit, 1996). Mass chromatograms for steranes (m/z 217) in aliphatic fraction were detected in all surface sediments of Sarawak EEZ. Figure 4.12 shows mass chromatograms for steranes (m/z 217) of aliphatic hydrocarbons in station ST04. The

characteristic of 'V' shaped pattern indicated for C₂₇, C₂₈ and C₂₉ at retention times from 40-45 minutes (Wang et al., 2006). The mass chromatograms of steranes in surface sediments of Sarawak EEZ were characterized by predominance of C₂₇, C₂₈ and C₂₉ steranes with mainly the 5 α ,14 α ,17 β and minor 5 α ,14 α ,17 α configurations, both occurring as 20S and 20R epimers (Rushdi et al., 2017). This indicated oils from petroleum products were originated from a mixture of terrestrial and marine sources (Hunt, 1996).

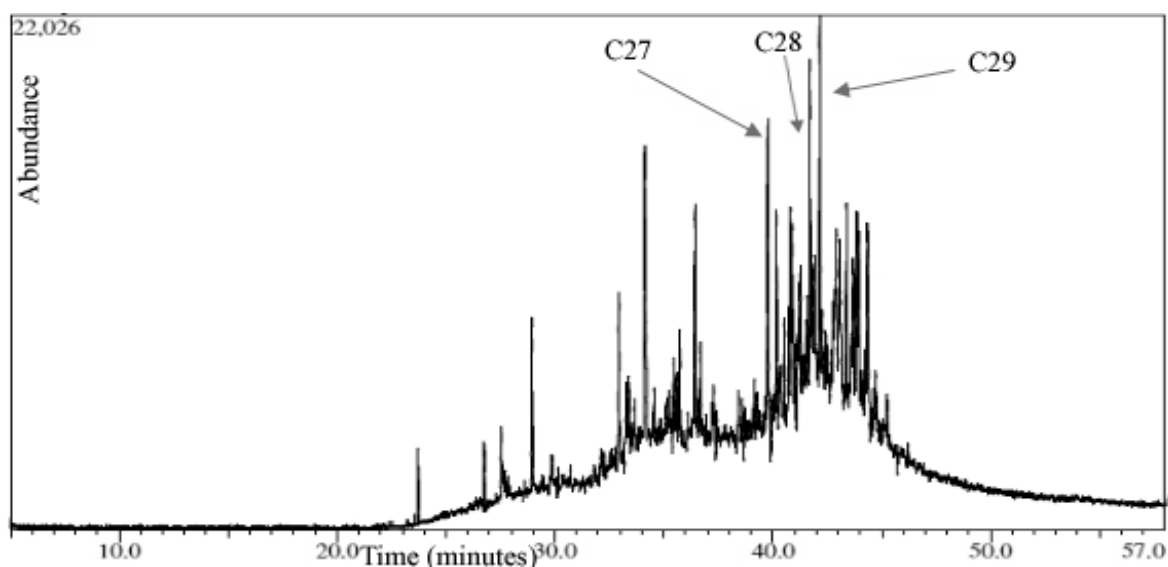


Figure 4.12: Mass chromatograms of steranes (m/z 217) in aliphatic fraction from surface sediments in station ST04 of Sarawak EEZ.

4.2.7 Summary on Aliphatic Hydrocarbons in Marine Sediments of Sarawak EEZ

The concentration of aliphatic hydrocarbons (C_{11} - C_{36}) in surface sediments of Sarawak EEZ ranged 2.8-744.4 $\mu\text{g/g}$. The highest concentration of TAH detected in this study at ST02 (Kuching Waters) (ST02) with 744.4 $\mu\text{g/g}$. The sources in marine sediment of Sarawak EEZ were also predicted using molecular-alkanes indices. Hopane and sterane fingerprints together with the presence of UCM confirmed the existence of petroleum contamination in surface sediments of Sarawak EEZ. Aliphatic hydrocarbons in core sediment of Sarawak EEZ ranged 7.0-123.7, 122.6-324.4 and 8.05-46.6 $\mu\text{g/g}$ at stations ST01, ST02 and ST03 respectively. ST02 has received more anthropogenic input from upper to down core of sediment. The anthropogenic sources of aliphatic hydrocarbon (AH) appeared in upper layers of core sediments at stations ST01 and ST03 but toward down core of sediments, the sources of AH were originated from biogenic sources such as sedimentary bacteria, animal marine and terrestrial input.

4.3 Polycyclic Aromatic Hydrocarbons (PAHs) in Marine Sediments of Sarawak's EEZ

4.3.1 Response Factor of Individual PAH in Standard Mixture

The retention times of standard PAHs have been used for qualitative and quantitative analysis of PAHs in sediments by using d_{10} -anthracene as an internal standard. Retention times of 14 mixtures of PAHs were used to compare PAHs components in surface and core sediments. Figure 4.13 shows a GC-FID chromatogram of standard mixture consist of 14 PAHs. Retention times and relative response factors for 14 PAHs are listed in Table 4.9.

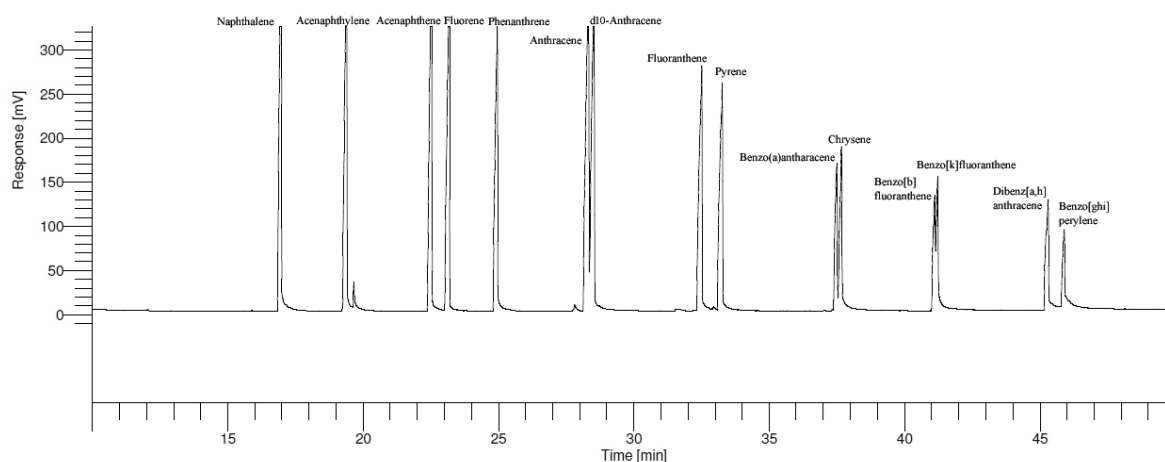


Figure 4.13: GC-FID chromatogram of 14 PAHs in standard mixture.

Table 4.9: Retention times and relative response factors for 14 PAHs standard using d₁₀ anthracene as internal standard.

PAH Compound	Retention time (min)	Relative Response factor
Naphthalene	16.97±0.011	1.12 ±0.16
Acenaphthylene	19.388±0.015	0.96 ±0.29
Acenaphthene	22.525±0.014	1.06 ±0.24
Fluorene	23.176±0.016	0.97 ±0.25
Phenanthrene	24.95±0.011	0.95 ±0.13
Anthracene	28.323±0.001	1.73 ±0.13
d ₁₀ -Anthracene (Internal standard)	28.53±0.002	1.00 ±0.00
Fluoranthene	32.505±0.010	1.53 ±0.14
Pyrene	33.227±0.036	1.59 ±0.13
Benzo(a)anthracene	37.495±0.015	1.15 ±0.44
Chrysene	37.669±0.059	1.33 ±0.26
Benzo[b]fluoranthene	41.11±0.001	1.09 ±0.31
Benzo[k]fluoranthene	41.223±0.088	0.84 ±0.22
Dibenz[a,h]anthracene	45.302±0.022	0.71 ±0.27
Benzo[ghi]perylene	45.894±0.120	1.25 ±0.19

4.3.2 Distribution of PAHs in Marine Surface Sediment

A total of 14 PAHs have been detected in surface sediment from Sarawak EEZ as shown in Figures 4.14-4.17. Total concentrations of PAHs ranged between 8.56-374.7 ng/g are tabulated in Table 4.10. The highest concentrations of PAHs was recorded in surface sediment of ST05 (374.7 ng/g) followed by ST06 (311.9 ng/g), ST02 (155.1 ng/g), ST09 (139.4 ng/g), ST04 (112.6 ng/g), ST03 (102.6 ng/g) and ST11 (106.8 ng/g). Low concentrations PAHs were detected in surface sediments of ST07, ST10 and ST01 with

concentrations 8.56, 38.6 and 46.5 ng/g respectively. Baumard et al. (1998) suggested that PAHs content in sediments can be divided into four degrees of pollution that are 0-100 ng/g as low polluted, 100-1000 ng/g as medium polluted, 1000-5000 ng/g as highly polluted, and > 5000 ng/g as most gravely polluted. Thus, surface sediments of ST05, ST06, ST02, ST09, ST04, ST03 and ST11 can be considered as moderately polluted, while ST01, ST07 and ST10 were considered as low polluted. The highest concentration of PAH was pyrene with concentrations 192.2 ng/g in surface sediment from ST05. The presence of pyrene and fluoranthene normally indicate pyrolytic input because these two PAHs are derived from condensation process of LMW PAHs at high temperature (Wang et al., 1999). Chrysene was detected in all surface sediments of Sarawak EEZ except at ST02 and ST05. Chrysene is also known as preserve biomarker in petroleum products and conservative due to its resistance towards weathering and bacterial degradation (Wang and Fingas, 2003).

Distribution of low and high molecular PAHs as reported by several reserchers (Sicre et al., 1987; Budzinski et al., 1997) can be used as a reliable tool to discriminate the petrogenic and pyrogenic origin of PAH. Concentrations of total HMW of PAHs ranged 7.33-336.7 ng/g with ST05 contained highest concentration of HMW PAHs (336.7 ng/g) followed by ST06, ST03 and ST09 with concnetrations of 310.1, 102.6 and 137.3 ng/g, respectively. Surface sediments from of stations ST02, ST04, ST07, ST10 and ST11 were below 100 ng/g. Sediments with dominant of heavier PAHs are associated with particulate matter (Abdel-Shafy and Mansour, 2016). Commendatore et al. (2012) reported that most of pyrogenic PAHs are introduced in marine environment through atmospheric transport and deposition. Total low molecular weights of PAHs ranged from 1.78-50.7 ng/g were detected in surface sediments of Sarawak EEZ. LMW of PAHs (38.6 ng/g) were dominant in ST01 over the HMW. Almost all LMW of PAHs components such as acenaphthylene,

acenaphthene, fluorene and anthracene were detected in ST01. These PAHs in surface sediment of ST02 contained highest concentration of LMW (50.7 ng/g) but low concentration of HMW PAHs. Unlike ST01, LMW of PAHs components in ST02 contained of acenaphthene, fluorene and anthracene that made up high Σ LMW. The surface sediments of stations, ST03, ST04, ST05, ST06, ST07, ST08, ST09, ST10 and ST11 reported less than 30 ng/g of Σ LMW.

The compositional patterns of unsubstituted PAHs in surface sediments from Sarawak EEZ are presented in Figure 4.18. PAHs of petrogenic origin are usually associated with 2- or 3-ring PAHs, while pyrogenic sourced PAHs associated with HMW of 4-6 ring PAHs (Zakaria et al., 2002; Neff, 1979). Figure 4.18 shows PAHs composition in surface sediments are mostly dominated by HMW PAHs with 6-64% 4-ring PAHs such as fluoranthene, pyrene, benzo[a]anthracene and chrysene, and 2-90% 5-ring PAHs such as benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene and benzo[ghi]perylene. Sediment tends to absorb more HMW PAHs compared to LMW PAHs because the latter is easily degraded (Wang et al., 2003; Jones et al., 1986). PAHs fraction in surface sediment of station ST01 is mostly dominated by 83% of 2 rings PAHs (naphthalene, acenaphthylene, acenaphthene and fluorene). Domination of 2- and 3-ring PAHs in sediments are the characteristic of petrogenic sources (Soliman et al., 2014). 3-ring PAHs such as phenanthrene, anthracene, fluoroanthene were dominant in surface sediment of ST02 (26%), ST04 (27%), ST05 (15%), ST07 (64%), ST09 (64%), ST10 (31%) and ST11 (25%). 6-ring PAHs such as benzo[ghi]perylene was minor composition of PAHs in surface sediment of ST06 (24%), ST09 (2%) and ST10 (4%).

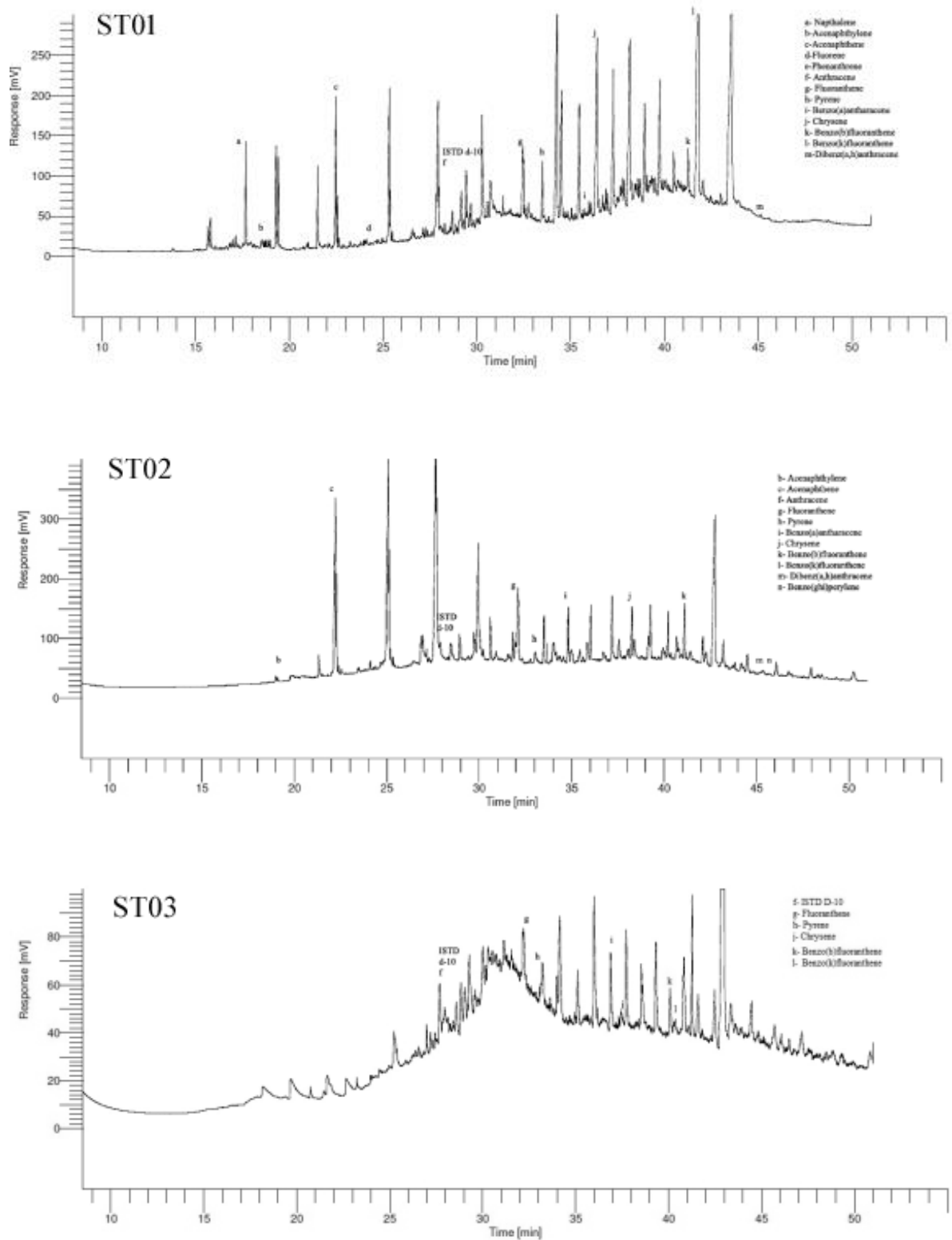


Figure 4.14: GC-FID chromatogram of PAHs in surface sediment at ST01, ST02 and ST03.

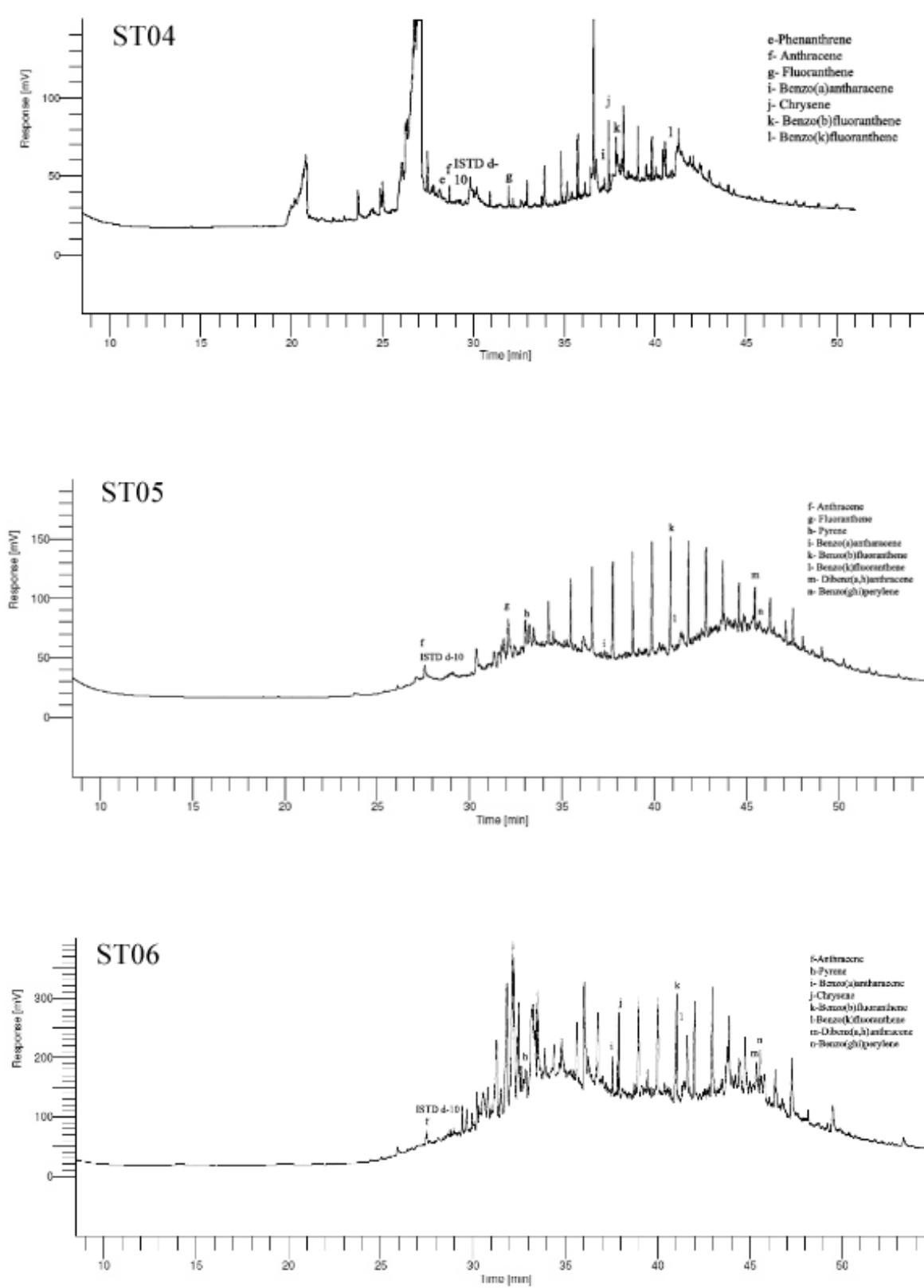


Figure 4.15: GC-FID chromatogram of PAHs in surface sediment at ST04, ST05 and ST06.

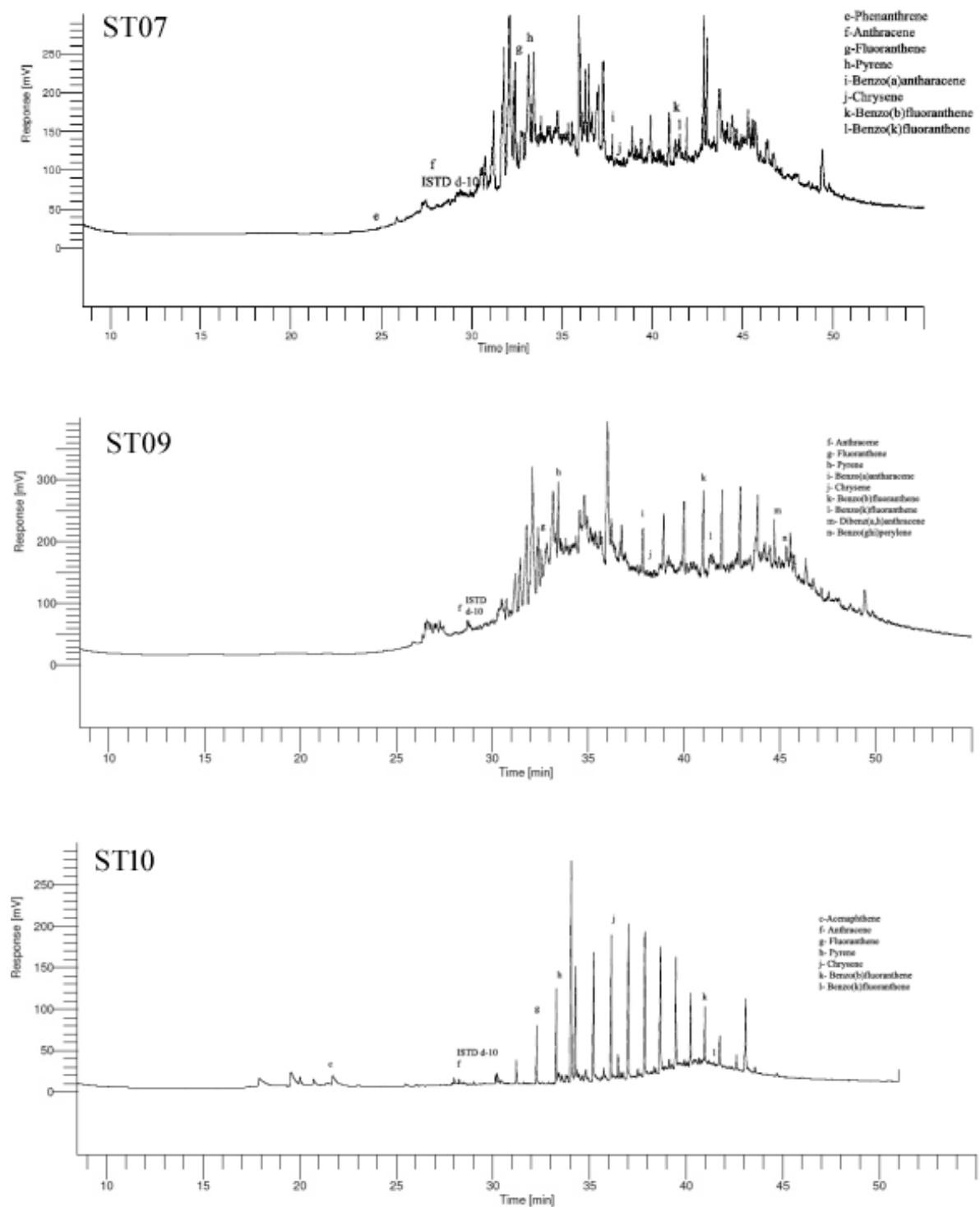


Figure 4.16: GC-FID chromatogram of PAHs in surface sediment at ST07, ST09 and ST10.

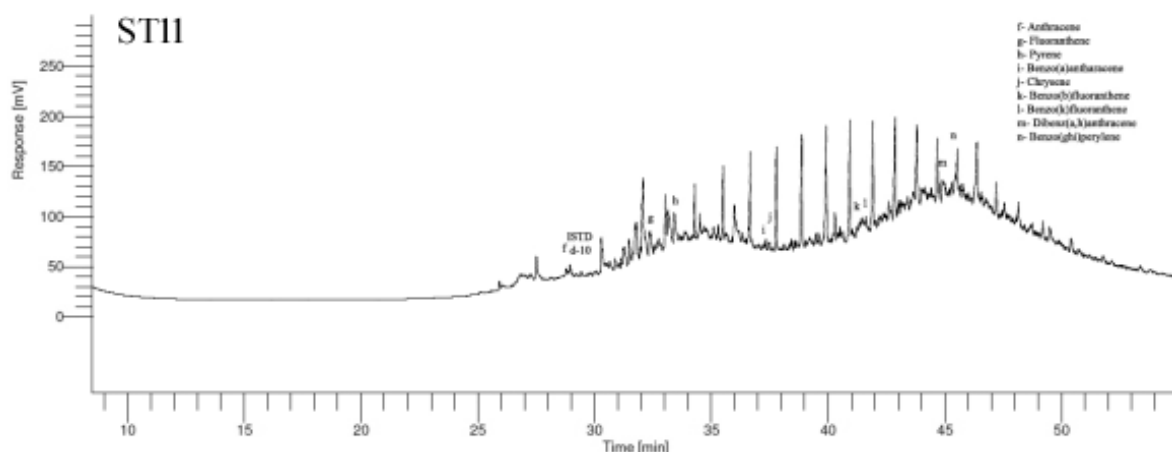


Figure 4.17: GC-FID chromatogram of PAHs in surface sediment at ST11.

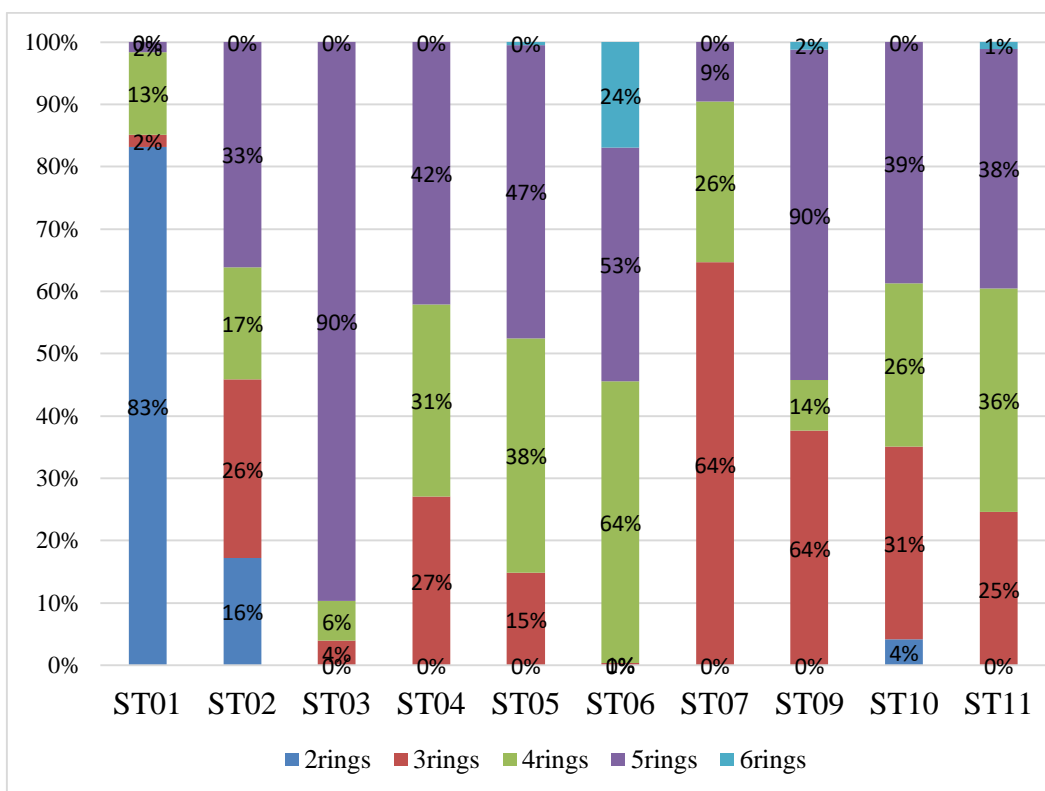


Figure 4.18: The percentage of compositional pattern for unsubstituted PAHs in surface sediments from Sarawak EEZ

Table 4.10: Individual concentration (ng/g) of PAHs in surface sediments from Sarawak EEZ

Compounds	Stations										
	01	02	03	04	05	06	07	08	09	10	11
Naphthalene	1.18	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Acenaphthylene	35.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Acenaphthene	1.14	5.48	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.59	n.d
Fluorene	1.1	19.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Phenanthrene	n.d	n.d	n.d	22.6	n.d	n.d	0.07	n.d	n.d	n.d	n.d
Anthracene	0.49	26	n.d	5.63	38.0	1.78	1.14	n.d	2.17	7.59	19.2
Fluoranthene	0.42	15.1	4.02	2.27	17.6	n.d	4.31	n.d	86.5	4.35	7.06
Pyrene	0.54	24.5	1.19	n.d	122.9	192.2	0.07	n.d	12.9	2.79	31.0
Benzo(a)anthracene	3.03	1.27	n.d	32.6	17.9	4.99	2.04	n.d	3.15	n.d	4.76
Chrysene	2.62	n.d	5.37	2.10	n.d	2.36	0.10	n.d	3.08	7.29	2.56
Benzo(b)fluoranthene	0.73	4.27	88.54	22.6	13.4	17.5	0.35	n.d	6.96	1.24	1.26
Benzo(k)fluoranthene	0	47.6	3.49	24.8	14.9	3.76	0.46	n.d	107.0	13.7	16.4
Dibenz(a,h)anthracene	n.d	n.d	n.d	n.d	148.2	144	n.d	n.d	11.1	n.d	23.4
Benzo(ghi)perylene	n.d	n.d	n.d	n.d	1.67	74.9	n.d	n.d	2.82	n.d	1.16
Σ PAHs (ng/g)	46.5	155.1	102.6	112.6	374.7	311.9	8.56	n.d	139.4	38.6	106.8
Σ LMW.PAHs (ng/g)	38.6	50.7	n.d	28.2	38.0	1.78	1.22	n.d	2.17	9.19	19.2
Σ HMW.PAHs (ng/g)	7.33	92.7	102.6	84.4	336.7	310.1	7.34	n.d	137.3	29.4	87.6

4.3.3 Possible Source of PAHs in Surface Sediment from Sarawak EEZ

PAHs associated with petrogenic input had LMW/HMW ratio > 1 , while pyrogenic sources had LMW/HMW < 1 (Liu et al., 2008; Soclo et al., 2000). Table 4.11 shows surface sediments of ST02, ST03, ST04, ST05, ST06, ST07, ST09, ST10 and ST11 have LMW/HMW ratio < 1 indicating that the PAHs input were derived from pyrogenic sources. Petrogenic sourced PAHs was detected in surface sediment of ST01 with LMW/HMW > 1 . Most of PAHs in marine sediments are originated from pyrogenic or petrogenic sources. Pyrogenic PAHs consisted with 4, 5 and 6 rings are formed during the incomplete combustion of coal, fossil fuels and carbons. However, petrogenic PAHs that consisted 2 and 3 rings PAHs are derived from crude oil and refined oil spillage (Soclo et al., 2000). Other significant PAHs ratios such as Phe/Ant, Flu/Pyr, Chr/BaA, Fluo/Fluo+Pyr and BaA/(BaA+Chr) were determined for surfaces sediment in all sampling sites. Phenanthrene is thermodynamically stable and its higher amount over anthracene indicates that the PAHs in sediment were mainly due to petrogenesis activities (Salem et al., 2014). Surface sediments of ST04 and ST07 showed Phe/Ant ratio 4.0 and 0.04, respectively. This ratio indicated for petrogenic PAHs source as reported by Salem et al. (2014). Flu/Pyr ratio < 1 indicates for petrogenic input such as oil spill and petroleum products inputs, while Flu/Pyr ratio > 1 indicates for pyrogenic such as fossil fuel combustion. Petrogenic input has been deposited in surface sediments of ST01, ST02, ST05 and ST11 with Flu/Pyr ratio 0.77, 0.63, 0.14 and 0.23 respectively. Pyrogenic input was detected in surface sediments of ST03, ST07, ST09, ST10 with ratios 3.3, 6.7 and 1.5, respectively. Ratio of fluo/fluo+pyr > 0.5 indicates for pyrolytic origin, while fluo/fluo+pyr < 0.5 indicates for petrogenic origin (Gogou et al., 1998; Budzinski et al., 1997). If the ratio of Flu/(Flu +Pyr) is between 0.4 to

0.5, PAHs are originated from the combustion of petroleum whereas if the ratio < 0.4 petroleum contamination is considered (Yunker et al., 2002). The surface sediments of ST02, ST05 and ST11 have Flu/(Flu +Pyr) ratio < 0.5 where the source of PAHs were associated with petrogenic, while the PAHs insurface sediments of ST03, ST04 and ST07 were pyrolytic origin.

Furthermore, Chr/BaA ratios in all surface sediments as shown in Table 4.11 were < 1 except ST01 which indicated pyrolytic sources (Soclo et al., 2000). BaA/(BaA+Chr) ratio > 0.35 demonstrates that sediments contain a significant proportion of combustion derived PAHs. However, BaA/(BaA+Chr) ratio of PAHs in all sediment samples were > 0.35 which clearly indicating the input of PAHs were originated from pyrogenic. Hence, the sources of PAHs in marine surface sediments were mixture of pyrolytic, petrogenic and pyrogenic.

Table 4.11: Sources of PAHs in marine surfaces sediment of Sarawak EZ based on isomeric pair ratio

Stations	LMW/HMW	Phe/Ant	Fluo/Pyr	Chr/BaA	Fluo/Fluo+Pyr	BaA/BaA+Chr
ST01	5.33	-	0.77	4.84	0.44	0.54
ST02	0.54	-	0.63	-	0.39	1.0
ST03	0.58	-	3.3	-	0.77	-
ST04	0.33	4.0	-	0.06	1.0	0.94
ST05	0.11	-	0.14	-	0.13	1.0
ST06	0.01	-	-	0.47	-	0.68
ST07	0.17	0.10	67	0.06	0.99	0.95
ST09	0.02	-	6.7	1.0	13.9	0.51
ST10	0.31	-	1.5	-	0.6	-
ST11	0.22	-	0.23	0.54	0.19	0.65

Note: Phe/Ant: Phenanthrene/Anthracene, Fluo/Pyr: Fluoranthene/Pyrene, Chr/BaA: Chrysene/Benzo(a)anthracene, Fluo/Fluo+Pyr: Fluoranthene/Fluoranthene+Pyrene, BaA/(BaA+Chr): Benzo(a)anthracene/Benzo(a)anthracene+Chrysen

4.3.4 Ecological Risk of PAHs in Surface Sediments of Sarawak EEZ

The United States numerical sediment quality guidelines (SQGs) were used to evaluate the environmental risks posed by PAHs in the sediments at the Sarawak EEZ. Two effects were used to assess the aquatic sediment, that were effects range low (ERL) and effects range moderate (ERM). The ERL is the adverse effects in a biological test data base that require 10% of test to show impacts in the aquatic system, while the ERM is the adverse effects at 50% of test (MacDonald et al., 2000; Long et al., 1995). ERL values are used to indicate possible adverse effects of biological on aquatic life, while ERM values proposed a high possibility of showing detrimental biological effects on aquatic life (Long et al., 1995; MacDonald et al., 2000). Table 4.12 shows the comparison of PAHs concentrations with sediment quality guidelines. The calculated concentrations of 14 PAHs in all surface sediments (242.9 ng/g) were below the ERL value of 4012 ng/g. Individual concentrations of PAHs did not exceeded ERL (see Table 4.12) except dibenz[a,h]anthracene compound. This maximum concentration of this compound has exceeded the ERL at ST05 which probably may cause occasional adverse biological effect. When concentrations of PAHs were below ERL, adverse effect such as toxicity could be less affected on the aquatic life (Baniemam et al., 2017; Jiao et al., 2012). The maximum concentrations of PAHs in surface sediments (799.5 ng/g) also did not exceed ERM values (22690 ng/g), thus there would be no adverse effects of PAHs toward aquatic organisms. If individual concentrations of PAHs exceeded the ERM, it indicates that biological effects would occur more often (Baniemam et al., 2017; Jiao et al., 2012). It can be concluded that according to US SQG the PAHs concentrations in surface sediment from Sarawak EEZ were unlikely to cause toxicity effects

towards marine organism's life. The significant study of adverse effects PAHs in aquatic organisms can be used as indicator of potential human health (Jiao et al., 2012).

Table 4.12: Sediment quality guidelines (SQGs) for PAHs in surface sediment of Sarawak EEZ

Compounds	Guideline		This Study	
	ERL	ERM	Average	Max
Naphthalene	160	2,100	1.18	1.18
Acenaphthylene	44	640	35.2	35.2
Acenaphthene	16	500	2.74	5.48
Fluorene	19	540	10.1	19.0
Phenanthrene	240	1,500	11.3	22.6
Anthracene	853	1,100	11.3	38.0
Fluoranthene	600	5,100	15.7	86.5
Pyrene	665	2,600	43.1	192.2
Benzo[a]anthracene	261	1,600	8.73	32.6
Chrysene	384	2,800	3.19	7.29
Benzo[b]fluoranthene	N/A	N/A	15.7	88.5
Benzo[k]-fluoranthene	N/A	N/A	15.1	47.6
Dibenz[a,h]anthracene	63.4	260	49.3	148.2
Benzo[ghi]perylene	N/A	N/A	20.1	74.9
Total	4012	22690	242.9	799.5

4.3.5 Distribution of Polycyclic Aromatic Hydrocarbons from Other Regions

Table 4.13 shows the comparison of PAHs studies in surface sediments from other areas. Concentrations of PAHs in surface sediments from other regions, in which the areas are associated with industrial, petroleum, fishing and tourism activities were reported in several studies. PAHs concentrations (8.56-374.7 ng/g) in surface sediments from Sarawak EEZ were lower than PAHs concentrations (2.6-1025.0 ng/g) in surface sediments from Qatar EEZ as reported by Soliman et al. (2014), coastal sediment of Klang Strait, Malaysia (100.3-3446.9 ng/g) reported by Sany et al. (2014) and offshore mouth area of the Volga, Russia (2.8-3258.0 ng/g) reported by Nemirovskaya et al. (2006). These areas are the major of petroleum activities such as oil and gas explorations and international shipping lanes. Concentrations of PAHs in surface sediments of this study also reported lower than other areas which known for economic activities such as fishing and shipping such as Sfax-Kerkennah channel (Tunisia, Southern Mediterranean Sea) PAHs concentrations ranged, 175-10769.0 ng/g, reported by Zaghdien et al. (2017), Red Sea, Egypt (0.74 - 456.91 ng/g) reported by Salem et al. (2014) and Langkawi island, Malaysia (869 -1637 ng/g) reported by Nasher et al. (2014). Sediment PAH concentrations ranged from 8.56 -374.7 ng/g in marine sediment of Sarawak EEZ were in the 'low-range' of concentrations compared to other available data for other areas. Results obtained from the present study provide a useful benchmark to evaluate PAH contamination levels in sediments both temporally and spatially within the Sarawak EEZ.

Table 4.13: Distribution of PAHs from Other Areas

Locations	PAHs concentration (ng/g)	Sources
Offshore Mouth Area of the Volga, Russia	2.8-3258.0	Nemirovskaya et al. (2006)
Exclusive economic zone (EEZ) of Qatar, Arabian Gulf	2.6-1025.0	Soliman et al. (2014)
Sfax-Kerkennah channel (Tunisia, Southern Mediterranean Sea)	175-10769.0	Zaghden et al. (2017)
Red Sea, Egypt	0.74–456.91	Salem et al. (2014)
Langkawi Island, Malaysia	869 - 1637	Nasher et al. (2013)
Coastal Sediment of Klang Strait, Malaysia	100.3 - 3446.9	Sany et al. (2014)
Kaohsiung Harbor of Taiwan	4425-51261	Dong et al. (2012)
Sarawak EEZ, Malaysia	8.56-374.7	This study

4.3.6 Distribution of PAHs in Core Sediments from Sarawak EEZ

The GC-FID chromatograms of PAHs in layer 2.5-5.0 cm of core sediments from ST01, ST02 and ST03 are shown in Figure 4.19. Concentrations of PAHs in core sediments of ST01, ST02 and ST03 ranged 13.6-92.5, 37.2-151.2 and 24.3-72.9 ng/g, respectively. Vertical profiles for concentration of PAHs in core sediments are shown in Figures 4.20. Core sediments at ST02 and ST03 are less polluted by PAHs (0-100 ng/g) except at layer 10-12.5 cm which was moderately polluted (100-1000 ng/g). Σ PAHs in core sediment of ST02 increased toward down core of sediment with layers of 0-2.5 until 5.0-7.5 cm were less polluted, while layers of 7.5-10.0 until 10.0-12.5 cm were layers of 7.5-10.0 until were moderately polluted.

The compositions of PAHs based on their ring size in core sediments are shown in Figures 4.21. PAHs with LMW (2-rings) were dominant for all layers in ST01 core sediment. LMW PAHs have higher solubility that makes them easily deposited in aquatic environment and more vulnerable towards environmental conditions such as long-distance transmission and evaporation (Zhao et al., 2017). The PAHs with 2-rings (naphthalene, acenaphthylene, acenaphthene and fluorene) accounted for 42% - 92% of Σ PAHs. The prevalence of 2-ring PAHs for all layers in core sediment are the characteristic unweathered PAHs (Stogiannidis and Laane, 2015). The 3-rings PAHs (phenanthrene, anthracene, fluoroanthene) accounted for 2%-5% of Σ PAHs. Although with minor percentages, 3-ring PAHs can be contributed to high Σ LMW PAHs. The 4-ring PAHs (fluoranthene, pyrene, benzo[a]anthracene and chrysene) accounted for 3%-13% of Σ PAHs, while 5-ring PAHs (benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene) accounted for 3%-25% of Σ PAHs. Dominant of LMW PAHs may be originated from local sources or recent input sources like

leakage of fuel and oil from shipping activities, sewage discharge and atmospheric deposition this because of properties. LMW PAHs are easily to degrade and evaporate faster than HMW PAHs (Hu et al., 2010; Zamora et al., 2002). In ST02, composition of the 2-ring PAHs accounted for 12%-77% of Σ PAHs in ST02 core sediment; 3-ring, 4-ring and 5-ring PAHs composed 14%, 5%-86% and 2%-86% of Σ PAHs, respectively. LMW PAHs were more abundant in layer 0-2.5 cm (58%), 2.5-5.0 cm (77%) and 7.5-10.0 cm (63%), while 4-ring PAHs (86%) were dominated in layer 5.0-7.5 cm and 5-ring PAHs (86%) in were dominated in layer 10.0-12.5 cm. HMW PAHs (4- and 5-ring) were abundantly found at the bottom layer 10-12.5 cm. The ST03 core sediment contained 2%-46% of 2-ring PAHs, 1%-4% of 3-ring PAHs, 13%-96% of 4-ring PAHs, 5%-59% of 5-ring PAHs and 2%-5% of 6-ring PAHs. The dominant of 4-ring PAHs was observed at upper layer (0-2.5 cm) until at the bottom layer (10.0-12.5 cm), while percentage compositions of 2- and 3-ring PAHs decreased toward down core sediment. HMW PAHs, such as benzo[a]anthracene, chrysene, pyrene, and benzo[ghi]perylene, were minor content in refined petroleum products (Wang et al., 2001) and are usually present in significant quantity only in HMW fractions such as asphalt (Readman et al., 2002) and possibly bitumen or coal.

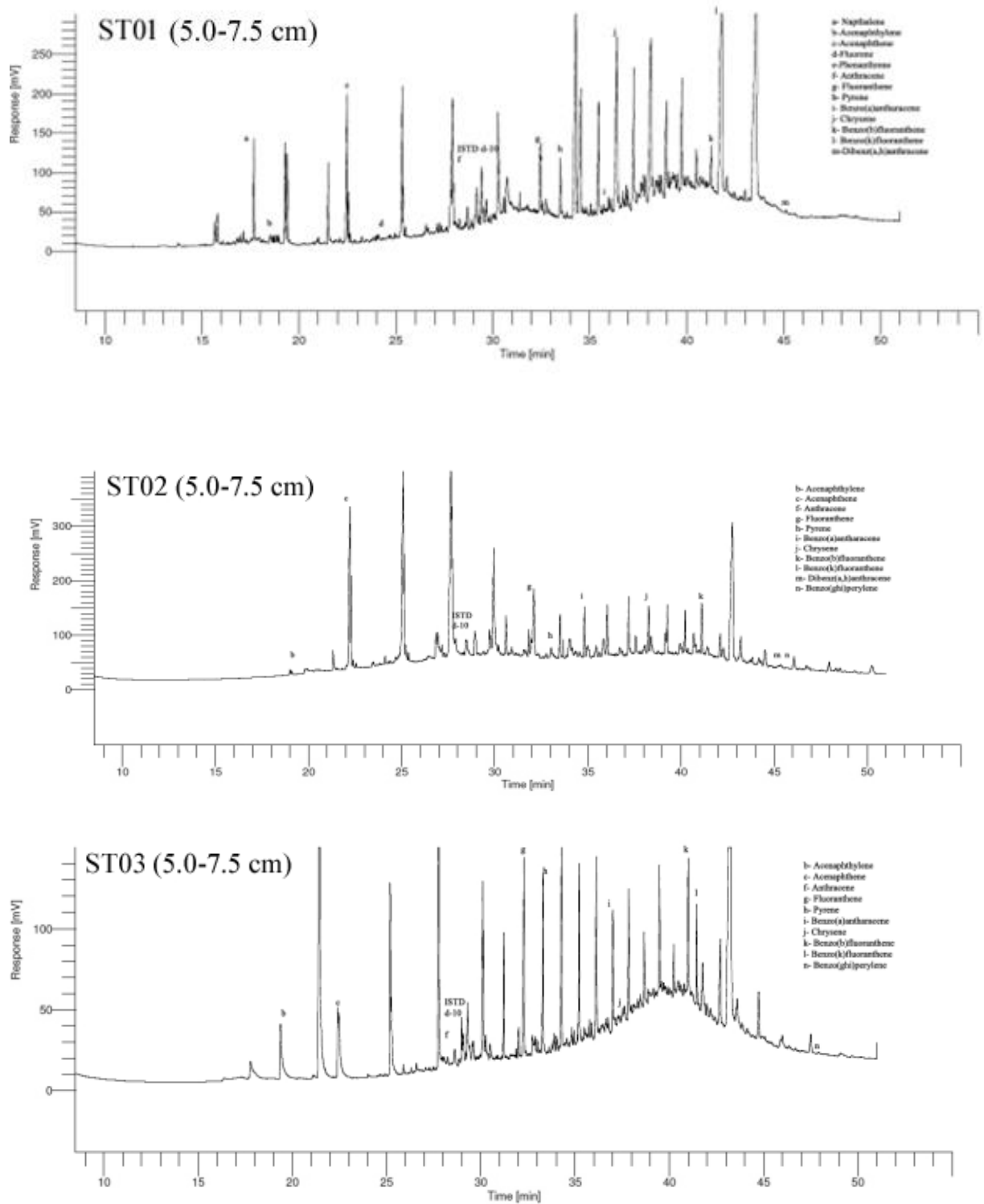


Figure 4.19: GC-FID chromatogram off PAH in layer 2.5-5.0 cm of core sediments from ST01, ST02 and ST03 of Sarawak EEZ.

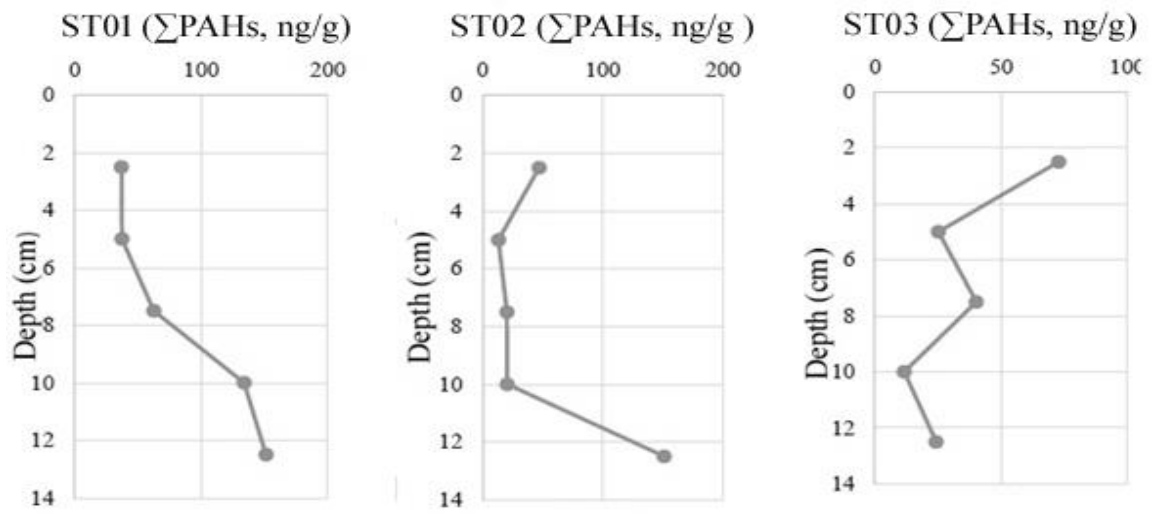


Figure 4.20: Vertical profile Σ PAHs in core sediments of ST01, ST02 and ST03

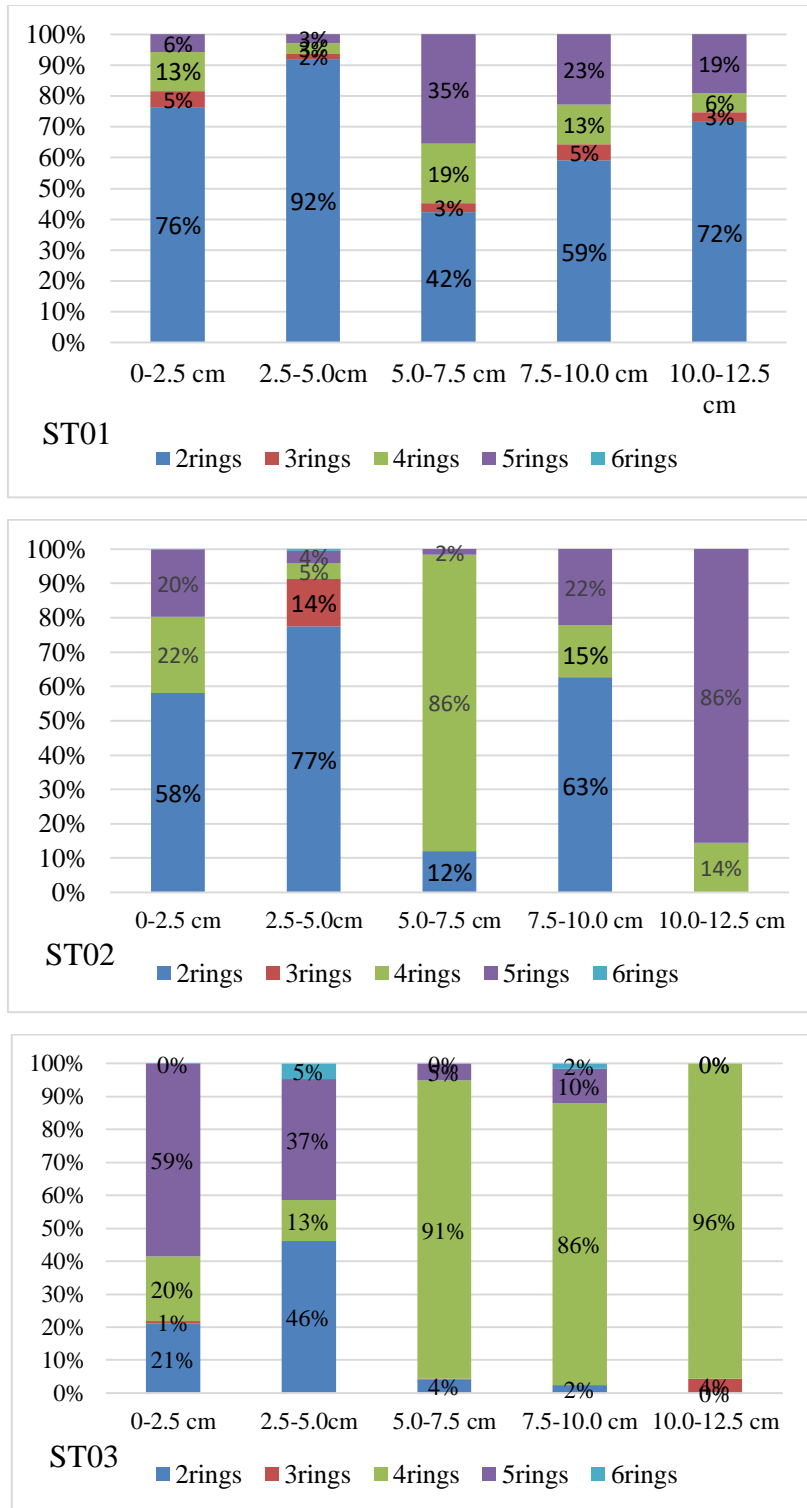


Figure 4.21: Percentage (%) composition of PAHs based on ring number in core sediments of ST01, ST02 and ST03

4.3.7 Possible Source of PAHs in Core Sediment from Sarawak EEZ

Vertical trend of LMW/HMW PAHs are shown in Figure 4.22. Appendix 4 shows isomeric PAHs ratios in core sediments of Sarawak EEZ. LMW/HMW PAHs ranged 0.90-5.74 in core sediment of ST01 indicated the primary source of PAHs was petrogenic. All layers showed association with petrogenic origin except layer of 5.0-7.5 cm which showed pyrogenic origin (LMW/HMW <1). LMW/HMW PAHs in core sediment from ST02 ranged 0.16-2.16 indicated a mixture of petrogenic and pyrogenic input. Petrogenic inputs were detected in layers 0-2.5, 5.0-7.5 and 7.5-10.0 cm. Pyrogenic inputs were observed at layers 5.0-7.5 cm and 10.0-12.5 cm which due to the dominant of 4-rings and 5-rings PAHs in layers 5.0-7.5 cm and 10.0-12.5 cm, respectively. the fluctuated ratios of LMW/HMW in core sediment ST02 indicated for a mixed sourced of PAHs although some post-depositional alterations within the sediment cannot be ruled out (Peter, 1999). Upper layers in core sediment ST02 showed petrogenic sourced of PAHs as indicated by LMW/HMW ratio >1. The dominant of LMW of PAHs in upper layers is might due to their exposure to petrogenic sources and/or to pyrogenic sources with low temperature fuel sources (Yan et al., 2009). Downcore of sediment ST02 was dominated by pyrogenic sourced of PAHs. This could be explained by the depositional character of PAHs compounds in core sediment. HMW of PAHs (4-6 rings) tend to deposit fast toward down core of sediment due to low solubility in water and this explained that the source of PAHs in bottom of the layers was pyrogenic due to dominant of HMW PAHs compounds. All layers in core sediment of ST03 showed LMW/HMW PAHs < 1 indicated pyrogenic origin. HMW PAHs with 4, 5 and 6-rings PAHs were found to be dominant in this core sediment and primary source of PAHs in this core sediment was pyrogenic source.

Vertical trend of isomeric ratios PAHs, Anth/(Anth+Phe), for all core sediments are shown in Figures 4.23. The ratios of Anth/Anth+Phe in core sediment from ST01 indicated for pyrogenic sources. This suggests the source of PAHs in core sediment of ST01 were mixture of petrogenic and pyrogenic as agreed by ratio of LMW/HMW PAHs earlier. Anth/(Anth+Phe) ratios in core sediment ST02 show pyrogenic source at layers 0-2.5 cm and 7.5-10.0 cm with ratios 0.87 and 1.00, respectively. None of anthracene and phenantrene was detected in other layers. In core sediment of station ST03, Anth/(Anth+Phe) ratios 1.00 for both layers; 0-2.5 cm and 5.0-7.0 cm which indicated for pyrogenic source. Thus, core sediments of stations ST01, ST02 and ST03 were mixed of pyrogenic sources according to Anth/(Anth+Phe) ratios.

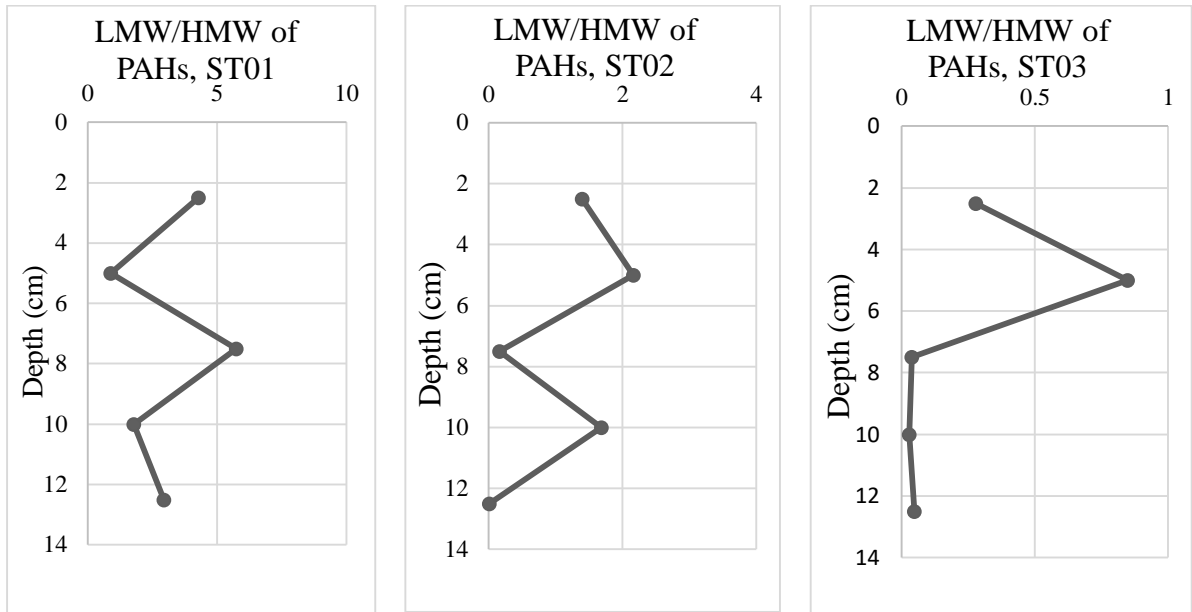


Figure 4.22: Vertical trend for LMW/HMW PAHs in core sediment ST01, ST02 and ST03

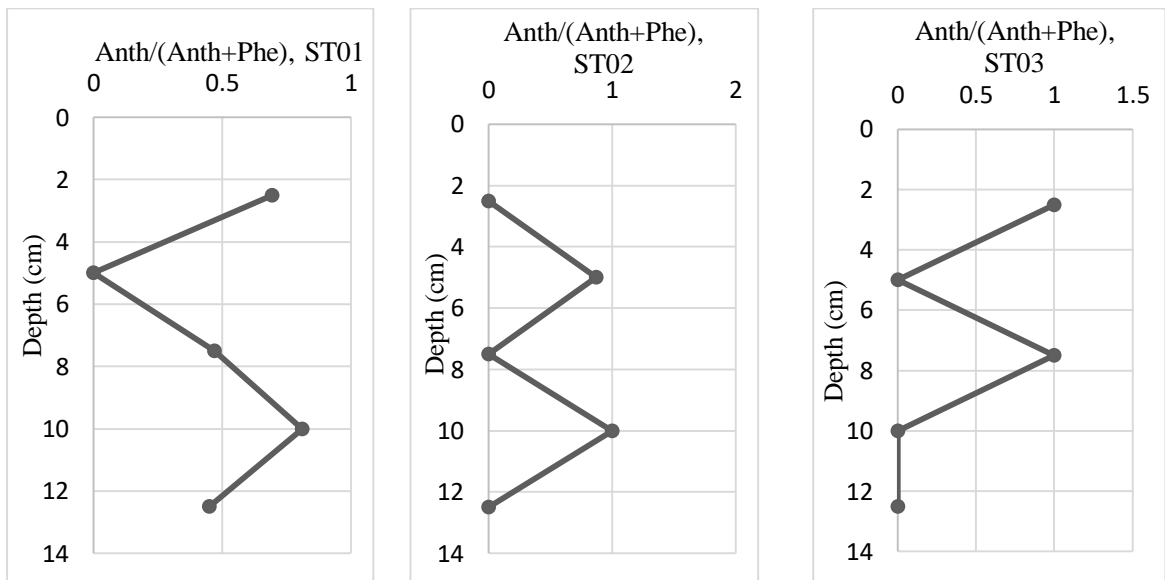


Figure 4.23: Vertical trend for Anth/(Anth+Phe) ratios in core sediment ST01, ST02 and ST03

Vertical trend for Fluo/(Fluo+Pyr) ratios are shown in Figures 4.24. Fluo/(Fluo+Pyr) ranged 0.16-0.74 in core sediment ST01. PAHs originated from combustion of liquid fossil fuels (petrogenic) were detected at 0-2.5 cm with ratio 0.49. While PAHs associated with pyrogenic source was detected at 5.0-7.5 cm with ratio 0.16 while at layers 7.5-10.0 to 10.0-12.5 cm, PAHs were originated from combustion of kerosene, grass, wood and coal (pyrolytic). In core sediment ST02, Fluo/(Fluo+Pyr) ratios were only detected at layers 0-2.5 and 2.5-5.0 cm with ratios 0.02 and 0.83 respectively. Pyrogenic origin was associated in layer 0-2.5 cm while PAHs in 2.5-5.0 cm derived from combustion of grass, wood and coal. Fluo/(Fluo+Pyr) ratios ranged from 0.37-0.81 were detected in ST03. PAHs associated with combustion from kerosene, wood, coal and grass was detected in layer 0-2.5 cm and 10.0-12.5 cm with ratio 0.81 and 0.61, respectively. PAHs in layer 2.5-5.0 cm and 5.0-7.5 cm was derived from pyrogenic input with ratios 0.37 and 0.39, respectively.

Vertical trend for BaA/(BaA+Chr) ratios in core sediments are shown in Figure 4.25. Diagnostic ratios of BaA/(BaA + Chry) ranged 0.21-0.48 in core sediment ST01. PAHs originated from pyrogenic source were detected at layers 0-2.5 cm, 2.5-5.0 cm and 10.0-12.5 cm with ratios 0.47, 0.48 and 0.61, respectively. PAHs derived from both mixed sources (petroleum or combustion) were detected at 5.0-7.5 cm and 10.0-12.5 cm with ratios 0.21 and 0.27 respectively (Christensen and Bzdusek, 2005). While in core sediment ST02, BaA/(BaA + Chry) ratios ranged 0.04-1.00. Layers 0-2.5 cm, 2.5-5.0 cm and 5.0-7.5 cm confirmed petrogenic PAHs source with ratios 0.10, 0.06 and 0.04 respectively (Ratios BaA/BaA + Chry < 0.2) while in layer 7.5-10.0 cm PAHs was derived from pyrogenic with ratio higher than 0.35. At the bottom core, 10.0-12.5 cm, the ratio BaA/(BaA + Chry) was between 0.20-0.35 thus PAHs was derived from mixed

sources. In core sediment from ST03, BaA/(BaA + Chry) ratios, 0.33, 0.32 and 0.13 at layers, 0-2.5 cm, 2.5-5.0 cm and 5.0-7.5 cm respectively, showed petrogenic sourced of PAHs while at bottom of core, 10.0-12.5 cm, the ratio showed (1.00) for pyrogenic source of PAHs. This study showed that the mixed petrogenic–pyrogenic sources in core sediment of Sarawak EEZ as suggested by the isomeric ratios. In some cases, when PAHs ratios are overestimating the contribution of pyrogenic of PAHs in sediment samples due to co-occurrence of PAHs in in petrogenic and pyrogenic sources (Wagener et al., 2010).

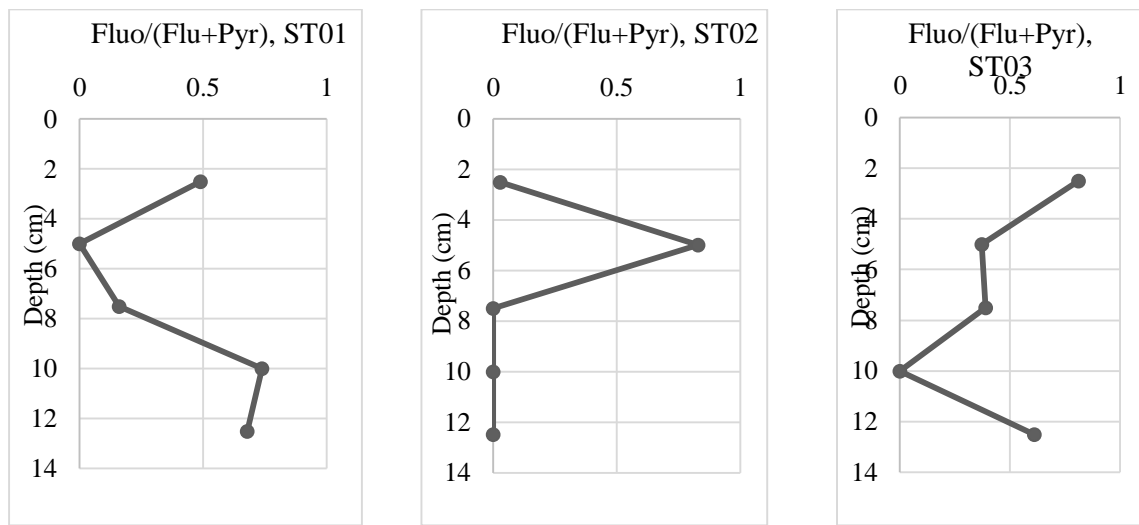


Figure 4.24: Vertical trend for Fluo/(Fluo+Pyr) ratios in core sediment ST01, ST02 and ST03

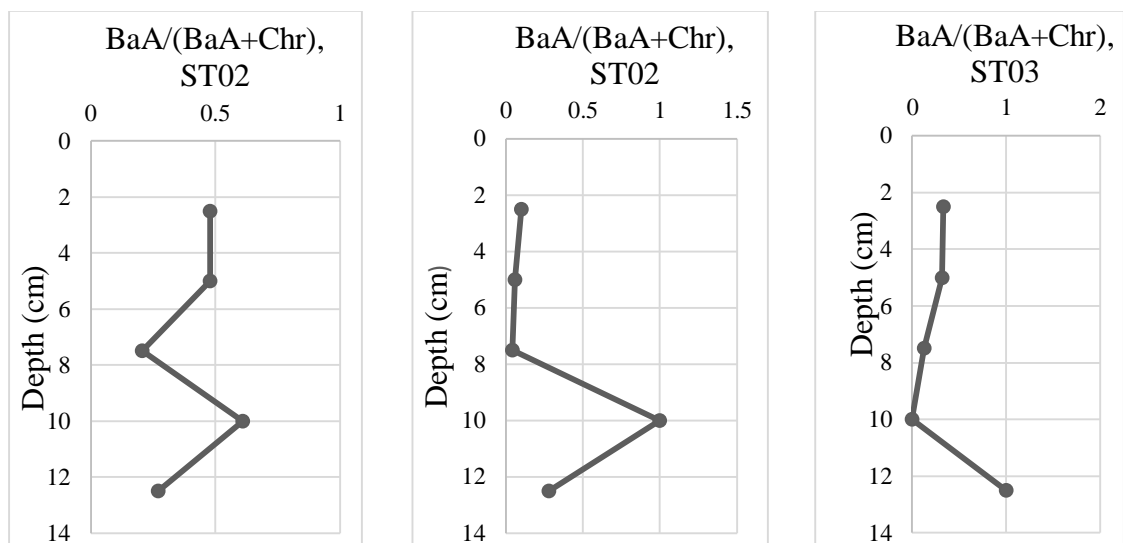


Figure 4.25: Vertical trend for BaA/(BaA+Chr) ratios in core sediments ST01, ST02 and ST03

4.3.8 Principal Component Analysis (PCA) on Hydrocarbons in Surface Sediment from Sarawak EEZ

The principal component analysis was conducted using IBM SPSS Statistic Version 22. 11 surface samples were analysed by factor analysis. The analysis included the concentration of TAH for every station, molecular n-alkane indices, PAHs, isomeric ratios of PAHs and proximate data. The eigenvalues of the extracted factor, the differences of eigenvalues among factors and the proportion of total sample variance explained by the factor are shown in Table 4.14. 23 variables were reduced into 4 new factors upon varimax rotation. The number of components were determined based on eigenvalues higher than 1 with amount of explained variance at least 70 to 80% of total variance.

Figure 4.26 shows PCA score plot described the relationship between the variables and Table 4.15 shows the loading variables of hydrocarbons which were presented with bold numbers. Factor 1 covers 23.2 %, Factor 2 covers 19.4 %, Factor 3 covers 14.5 % and Factor 4 covers 13.0 % of total variances. High loading variables were presented with bold numbers. Factor 1 explained the correlation between variables of LMW/HMW PAHs with Chr/BaA that related to sources of PAHs from Sarawak EEZ were mainly derived from combustion; pyrogenic and pyrolytic (Li et al., 2015). Factor 2 explained that \sum TAH showed correlation with both LMW and HMW of n-alkanes. Factor 3 explained \sum PAHs in surface sediments were correlated with HMW PAHs which were predominantly contributed by 4,5 and 6-rings PAHs. High rings of PAHs (4,5 and 6 rings) found in surface sediments were related to petroleum combustion and refined petroleum (Li et al., 2015). \sum PAHs also showed positive correlations with clay and silt. Factor 4 explained the correlation between Fluo/Pyr ratios

with sand. From the study Fluo/Pyr ratios in surface sediments indicated for petrogenic and pyrolytic that showed positive correlation with sand. LMW/HMW of n-alkane showed negative correlation with TAR, this inverse relationship showed that the influence of TAR values toward LMW/HMW ratios of n-alkane in surface sediments.

Table 4.14: Eigenvalues, percentage variance and total variance of hydrocarbons in surface sediments

Factor	Eigenvalues		
	Total	% of variance	% of total variance
1	5.3	23.3	23.3
2	4.4	19.4	42.6
3	3.3	14.5	57.2
4	3.0	13.0	70.2

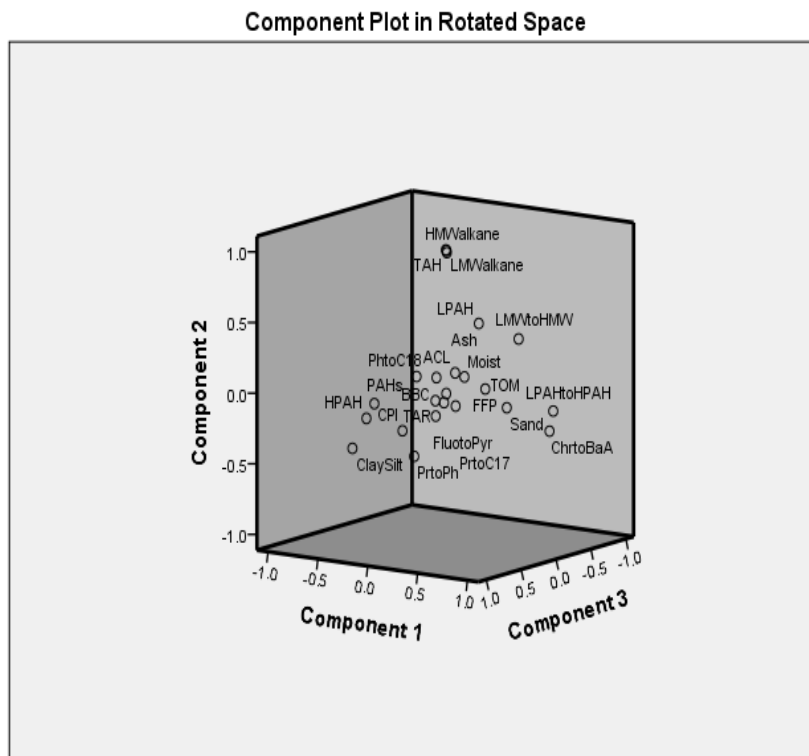


Figure 4.26: PCA score plot that accounting for 70% of total variance from hydrocarbons data in surface sediments

Table 4.15: PCA of hydrocarbons in surface sediments from Sarawak EEZ

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
Σ TAH	0.052	0.981	0.067	0.031
CPI	-0.598	-0.410	-0.241	-0.188
ACL	0.692	0.092	-0.063	0.472
LMW/HMW	0.055	0.396	-0.063	0.640
n-alkane				
TAR	-0.368	-0.194	-0.384	-0.619
Pristane/phytane	0.062	-0.412	0.535	-0.571
Pr/C17	-0.336	-0.194	-0.384	0.539
Ph/C18	-0.060	0.062	0.041	0.423
LMW n-alkane	0.062	0.977	0.072	0.054
HMW n-alkane	-0.108	0.911	-0.176	-0.155
Σ PAHs	-0.096	-0.005	0.879	-0.350
LPAH	0.576	0.553	0.343	-0.135
HPAH	-0.197	-0.124	0.849	-0.341
LMW/HMW PAHs	0.958	-0.104	-0.179	-0.26
Fluo/Pyr	-0.119	-0.227	-0.034	0.672
Chr/BaA	0.908	-0.253	-0.196	-0.145
Fluo/(Fluo+Pyr)	-0.107	-0.194	-0.301	-0.260
BaA/(BaA+Chry)	0.168	0.181	0.651	0.123
Sand	0.417	-0.150	-0.284	0.822
Clay and Silt	-0.392	-0.367	0.770	0.251
TOM	0.490	0.049	0.128	-0.182
Moisture	0.192	0.086	-0.001	-0.476
Ash	-0.435	-0.187	-0.635	-0.534
Eigenvalue	5.35	4.45	3.34	3.00
% of total variance	23.2	19.4	14.5	13.0
Cumulative% of variance	23.2	42.6	57.1	70.2

4.3.9 Cluster Analysis (CA) on Hydrocarbons in Surface Sediments of Sarawak EEZ

Figure 4.27 shows dendrogram of hierarchical cluster analysis on hydrocarbons in surface sediments and Table 4.16 shows the agglomeration schedule for hydrocarbons in studied surface sediments from Sarawak EEZ. Pearson correlation was used to determine the homogeneity of samples and then by the help of between groups linkage the dendrogram was constructed from these distances in order to visualize the similarities or dissimilarities of sampling locations. The first combined cluster appear in Figure 4.27 is Stage 2 which combined from cluster 5 (ST05) and cluster 11 (ST11) with coefficient value 0.878. this combination indicated for similar source of hydrocarbons derived from biogenic origin as indicated by $CPI > 1$, degraded oil as indicated by $LMW/HMW < 1$ in ST05 and ST11. Cluster 5 and 6 showed closed relationship with coefficient value of 1.000. this relationship showed that ST05 and ST06 have similar source of hydrocarbons which n-alkane derived from degraded oil as indicated by $LMW < 1$, both stations also dominated by HMW of PAHs (4-6 rings). Close relationship showed by cluster 9 and cluster 10 with coefficient value of 0.825. this relationship indicated the source of hydrocarbons in ST09 and ST10 were derived from biogenic source as indicated by $CPI > 1$ and high input of debris plant as indicated by $TAR > 1$ (). Close relationship showed by cluster 4 and cluster 7 with coefficient value of 0.797. ST04 and ST07 have similar source of hydrocarbons originated from biogenic source as indicated by $CPI > 1$ and PAHs dominated by HMW PAHs rings (4-6 rings). Another combined cluster is showed by cluster 1 and cluster 2 in stage 9 with coefficient value 0.501. This relationship suggested that hydrocarbons in surface sediment from ST01 and ST02 were originated from anthropogenic input as suggested by low $CPI < 1$ and presence of recent oil input as indicated by $LMW/HMW > 2$. Close relationship showed by cluster 1 and cluster 3 with coefficient value of 0.619. ST01 and ST03 showed close relationship due to source

of hydrocarbons originated from anthropogenic input as indicated by low CPI < 1 and presence of fresh oil input as indicated by LMW/HMW > 2.

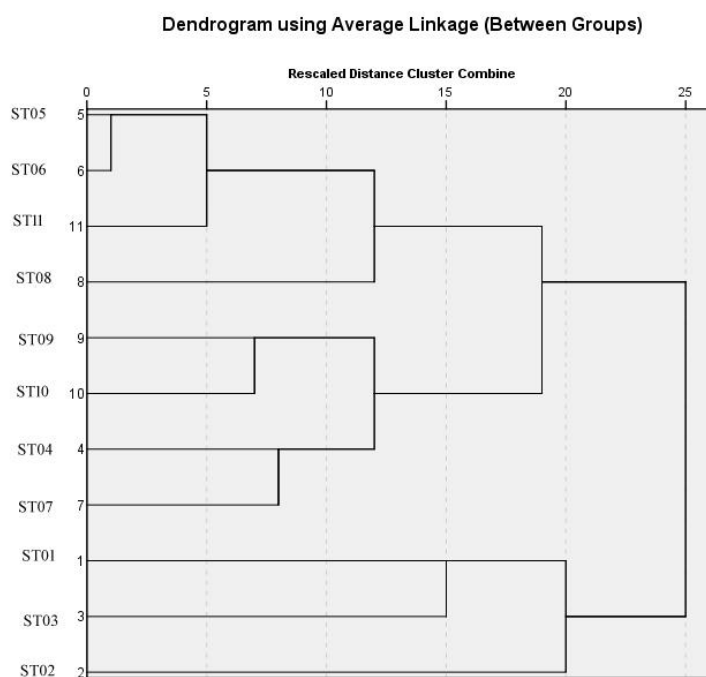


Figure 4.27: Hierarchical cluster analysis on hydrocarbons in surface sediments

Table 4.16: The agglomeration schedule for hydrocarbons in studied surface sediments from Sarawak EEZ

Stage	Cluster Combined		Coefficient	Stage Cluster First Appear		Next Stage
	Cluster 1	Cluster 2		Cluster 1	Cluster 2	
1	5	6	1.000	0	0	2
2	5	11	0.878	1	0	5
3	9	10	0.825	0	0	6
4	4	7	0.797	0	0	6
5	5	8	0.707	2	0	8
6	4	9	0.694	4	3	8
7	1	3	0.619	0	0	9
8	4	5	0.527	6	5	10
9	1	2	0.501	7	0	10
10	1	4	0.353	9	8	0

4.3.10 Summary on PAHs in Marine Sediments of Sarawak EEZ

The concentrations of PAHs in surface sediments of Sarawak EEZ ranged 8.56-374.7 ng/g. surfaces ediments of stations ST05, ST06, ST02, ST09, ST04, ST03 and ST11 were moderately polluted by PAHs, while PAHs in surface sediments of stations ST01, ST07 and ST10 were considered as not polluted. However, ecological risk using PAHs SQGs has shown that the concentrations of PAHs did not exceeded both ERL and ERM, thus there were no adverse effects or biological effects of PAHs in sediments toward marine life in Sarawak EEZ. PCA result has confirmed that the main source of PAHs in surface sediment from Sarawak EEZ was pyrogenic due to dominant of HMW PAHs in surface sediments. Positive correlation between HMW (4,5 and 6 ring) of PAHs with silt and clay in PCA indicated that strong relationship between PAHs with fine sediment fraction. Concentrations of Σ PAH in core sediment of ST01 ranged 13.6-92.5 ng/g. The dominant of LMW 2 rings PAHs were detected in all layers of core sediments which indicated by the presence of unweathered fresh petroleum input (petrogenic) in core sediment of ST01. Concentrations of PAHs in core sediment ST02 ranged 37.2-151.2 ng/g. LMW PAHs was dominantly in upper layers while HMW PAHs were mainly deposited at layers of down core sediment. The sources of PAHs in core sediment ST02 were derived from mixed of petrogenic and pyrogenic inputs with less pyrolytic inputs as indicated by isomeric ratios of PAH. PAHs concentrations in core sediment ST03 ranged 24.3-72.9 ng/g with dominant HMW PAHs at down core, while LMW compositions decreased toward down core of sediment. The main source of PAHs in core sediment ST03 was derived from combustion (pyrogenic), atmospheric depositions, as indicated by ratios isomeric ratios of PAHs.

CHAPTER 5

GENERAL CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The results of hydrocarbons study can be used as baseline data for current state of hydrocarbons in sediments of Sarawak EEZ, Malaysia. The concentrations of total AH in surface sediments of Sarawak EEZ are following the decreasing order ST02>ST08>ST03>ST05>ST10>ST04>ST11>ST09>ST07>ST06>ST01. Sampling sites of surface sediments at ST01, ST02 and ST03 which located near to Kuching waters were believed to receive fresh petrogenic input of AH. Whereas, sampling sites of surface sediments toward offshore water from ST04 to ST11, the sources of AH were originated from old petrogenic input with some contribution of biogenic compounds particularly from marine animal, sedimentary bacteria and recycled organic materials. Hopane and sterane fingerprinting together with the presence of UCM confirmed the existence of petroleum contaminations in surface sediments from Sarawak EEZ. In core sediment of ST02, the source of AH was mainly from anthropogenic inputs. Meanwhile in core sediment of ST01 and ST03, the anthropogenic sources of AH appeared in upper layers of core but toward down core of sediments, the sources of AH were originated from biogenic sources. The concentrations of total PAH in surface sediments of Sarawak EEZ are following the decreasing order; ST05>ST06>ST02>ST09>ST04>ST11>ST03>ST01>ST10>ST07. The main source of PAHs in surface sediments of Sarawak EEZ was believed from pyrogenic sources due to dominant of HMW PAHs. Sources of PAHs in core sediments at ST01, ST02

and ST03 of Sarawak EEZ were mainly influenced by compositions of LMW and HMW of PAHs. The main source of PAHs in core sediment of ST01 was derived from petrogenic PAHs, while in core sediment at ST02 PAHs originated from mixed petrogenic and pyrogenic inputs. In core sediment of ST03 the source of PAHs were believed from combustion of pyrogenic.

5.2 Recommendations for Future Study

Based on this research, there are several recommendations are proposed. It is recommended to perform carbon (C^{14}) dating analysis of core sediment. In C^{14} dating of sediment, the date of deposition is associated with C^{14} age thus the accurate history of AHs and PAHs inputs in core sediments can be determined. The presence of hopanes and sterane of mass chromatograms in sediments should be determined by quantitatively. Quantitative analysis of aliphatic hydrocarbons biomarkers (hopanes and steranes) that require the use of internal standards of hopanes and steranes in order to obtain more information on the sources of hydrocarbons in sediments. To better understand past, present, and future distribution and accumulation of hydrocarbons, additional samplings of sediments are required in order to have wide range of hydrocarbons data in sediments of Sarawak EEZ. Future monitoring on hydrocarbons level in sediments of Sarawak EEZ should be considered. This is to ensure that the level concentrations of hydrocarbons remain at the safe level.

REFERENCES

- Abas, M.R.B., & Simoneit, B.R.T. (1996). Composition of extractable organic matter of air from Malaysia: Initial Study. *Atmospheric Environment*, 30(15), 2779-2793. doi: 10.1016/1352-2310(95)00336-3.
- Abdel-Shafy, H.I., & Mansour, M.S.M. (2016). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, 25(1), 107-123. doi: 10.1016/j.ejpe.2015.03.011.
- Abdullah, M.P. (1997). Hydrocarbon pollution in the sediment of some Malaysian coastal areas. *Environmental Monitoring and Assessment*, 44(1), 443-454.
- Adeniji, A.O., Okoh, O.O., & Okoh, A.I. (2017). Petroleum hydrocarbon profiles of water and sediment of Algoa Bay, Eastern Cape, South Africa. *International Journal of Environmental Research and Public Health*, 14(10), Article i.d: 1263, doi: 10.3390/ijerph14101263.
- Agency for Toxic Substances and Disease Registry (ATSDR). (1995). *Toxicological Profile for Polycyclic Aromatic Hydrocarbons*. Retrieved from: <https://www.atsdr.cdc.gov/toxprofiles/tp69.pdf>
- Ahmed, O.E., Ali, N.A., Mahmoud, S.A., & Doheim, M.M. (2014). Environmental assessment of contamination by petroleum hydrocarbons in the aquatic species of Suez Gulf. *International Journal of Modern Organic Chemistry*, 3(1), 1-17.
- Ali, S.A.M., Payus, C., & Ali, M.M. (2015). Surface sediment analysis on petroleum hydrocarbon and total organic carbon from coastal area of Papar to Tuaran, Sabah. *Malaysian Journal of Analytical Sciences*, 19(2), 318-324. Retrieved from: http://www.ukm.my/mjas/v19_n2/pdf/SitiAishah_19_2_5.pdf.
- Allan, J., & Douglas, A.G. (1977). Variations in the content and distribution of *n*-alkanes in a series of Carboniferous vitrinites and sporinites of bituminous rank. *Geochimica et Cosmochimica Acta*, 41(9), 1223-1230. doi: 10.1016/0016-7037(77)90068-0.

- Amellal, N., Portal, J. M., & Berthelin, J. (2001). Effect of soil structure on the bioavailability of polycyclic aromatic hydrocarbons within aggregates of a contaminated soil. *Applied Geochemistry*, *16*(14), 1611-1619. doi: 10.1016/S0883-2927(01)00034-8.
- Armstrong, B.G., Hutchinson, E., Unwin, J., & Fletcher, T. (2004). Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: A review and meta-analysis. *Environmental Health Perspectives*, *112*(9), 970-978. doi: 10.1289/ehp.6895.
- Arctic Monitoring and Assessment Program (AMAP). (1998). *The arctic monitoring and assessment program: arctic pollution issues: a state of the arctic environment reports*. Retrieved from: <https://www.amap.no/documents/doc/amap-assessment-report-arctic-pollution-issues/68>
- Azis, M.Y., Asia, L., Piram, A., Buchari, Doumenq, P., and Syakti, A.D. (2016). Aliphatics hydrocarbon content in surface sediment from Jakarta Bay, Indonesia. *Materials Science and Engineering*, *107*, 1-8. Article ID 012007. doi:10.1088/1757-899X/107/1/012007.
- Bach, P.B.M.D., Kelley, M.J., Tate, R.C., & McCrory, D.C. (2003). Screening for lung cancer: A review of the current literature. *Chest*, *123*(1), 72-82. Retrieved from: <https://www.ncbi.nlm.nih.gov/pubmed/12527566>.
- Balcioglu, E.B., Aksu, A., Balkis, N., & Ozturk, B. (2014). T-PAH contamination in Mediterranean mussels (*Mytilus galloprovincialis*, Lamarck, 1819) at various stations of the Turkish Straits system. *Marine Pollution Bulletin*, *88*(1-2), 344-346. doi: 10.1007/s12011-010-8721-2.
- Baniemam, M., Moradi, A.M., Bakhtiari, A.R., Fatemi, M.R., & Khanghah, K.E. (2017). Seasonal variation of polycyclic aromatic hydrocarbons in the surface sediments of the Southern Caspian Sea. *Marine Pollution Bulletin*, *117*(1-2), 478-485. doi: 10.1016/j.marpolbul.2017.01.027.
- Baumard, P., Budzinski, H., Michon, Q., Garrigues, P., Burgeot, T., & Bellocq, J. (1998). Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuarine, Coastal and Shelf Science*, *47*(1), 77-90. doi: 10.1006/ecss.1998.0337.

- Bi, X.H., Sheng, G.Y., Liu, X.H., Li, C., & Fu, J.M. (2005). Molecular and carbon and hydrogen isotopic composition of *n*-alkanes in plant leaf waxes. *Organic Geochemistry*, 36(10), 1405-1417. doi: 10.1016/j.orggeochem.2005.06.001.
- Bihari, N., Fafandel, M., Hamer, B., & Kralj-Bilen, B. (2006). PAH content, toxicity and genotoxicity of coastal marine sediments from the Rovinj Area, Northern Adriatic, Croatia. *Science of the Total Environment*, 366(2-3), 602-611. doi: 10.1016/j.scitotenv.2005.12.001.
- Bishop, P.L. (1983). *Marine Pollution and Its Control*. New York: McGraw-Hill Book Company, 357pp.
- Blumer, M., Guillard, R.R.L., & Chase, T. (1971). Hydrocarbons in marine phytoplankton. *Marine Biology*, 8(3), 183-189. doi: 10.1007/BF00355214.
- Boehm, P.D., Loreti, C.P., Rosenstein, A.B., & Rury, P.M. (2002). *A Guide to Polycyclic Aromatic Hydrocarbons for the Non-specialist*. Washington D.C: American Petroleum Institute.
- Boitsov, S., Petrova, V., Jensen, H.K.B., Kursheva, A., litvineko, I., & Klungsoyr, J. (2013). Sources of polycyclic aromatic hydrocarbons in marine sediments from southern and northern areas of the Norwegian continental shelf. *Marine Environmental Research*, 87-88, 73-84. doi: 10.1016/j.marenvres.2013.03.006.
- Bouloubassi, I., & Saliot, A. (1993). Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH). *Oceanologica Acta*, 16(2), 145-161. Retrived from: <http://archimer.ifremer.fr/doc/00099/21043/18669.pdf>.
- Bourbonniere, R.A., & Meyers, P.A. (1996). Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. *Limnology and Oceanography*, 41(2), 352-359. doi: 10.4319/lo.1996.41.2.0352.
- Brassell, S.C., Eglinton, G., Maxwell, J. R., & Philp, R.P. (1978). Natural background of alkanes in the aquatic environment. In: O. Hutzinger, I.H. Van Lelyveld & B.C.J Zoetman (Eds.). *Aquatic Pollutants: Transformation and Biological Effects*. Oxford: Pergamon Press, pp. 69-86.

- Broman, D., Colmsjo A., Ganning, B., Naf, C., Zebuhr, Y., & Ostman, C. (1987) Fingerprinting petroleum hydrocarbons in bottom sediment, plankton, and sediment trap collected seston. *Marine Pollution Bulletin*, 18(7), 380-388. doi: 10.1016/0025-326X(87)90317-1.
- Budzinski, H., Jones, I., Bellocq, J., Pierard, C., & Garrigues, P. (1997). Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde Estuary. *Marine Chemistry*, 58(1-2), 85-97. doi: 10.1016/S0304-4203(97)00028-5.
- Cachot, J., Geffard, O., Augagneur, S., Lacroix, S., Le Menach, K., Peluhet, L., Couteau, J., Denier, X., Devier, M. H., Pottier, D., & Budzinski, H. (2006). Evidence of genotoxicity related to high PAH content of sediments in the upper part of the Seine Estuary (Normandy, France). *Aquatic Toxicology*, 79(3), 257–267. doi: 10.1016/j.aquatox.2006.06.014.
- Canadian Council of Ministers of the Environment (CCME). (2010). *Canadian Soil Quality Guidelines for Potentially Carcinogenic and other PAHs: Scientific criteria document*. Retrieved from: <http://ceqg-rcqe.ccme.ca/download/en/320>.
- Carls, M.G., Rice, S.D., & Hose, J.E. (1999). Sensitivity of fish embryos to weathered crude oil: part 1. Low level exposure during incubation causes malformations and genetic damage in larval pacific herring (*Clupea Pallasii*). *Environmental Toxicology and Chemistry*, 18(3), 481-493. doi: 10.1002/etc.5620180317.
- Chen, C.F., Chen, C.W., Dong, C.D., & Kao, C.M. (2013). Assessment of toxicity of polycyclic aromatic hydrocarbons in sediments of Kaohsiung Harbor, Taiwan. *Science of the Total Environment*, 463-464, 1174-1181. doi: 10.1016/j.scitotenv.2012.06.101.
- Chigor, V.N., Sibanda, T., & Okoh, A.I. (2013). Variations in the physicochemical characteristics of the Buffalo River in the Eastern Cape Province of South Africa. *Environmental Monitoring and Assessment*, 185(10), 8733–8747. doi: 10.1007/s10661-013-3208-1.
- Christensen, E.R., & Bzdusek, P.A. (2005). PAHs in sediments of the Black River and the Ashtabula River, Ohio: source apportionment by factor analysis. *Water Research*, 39(4), 511-524. doi: 10.1016/j.watres.2004.11.016.

- Clark, R.C.J., & Blumer, M. (1967). Distribution of *n*-paraffins in marine organisms and sediments. *Limnology and Oceanography*, 12(1), 79-87. doi: 10.4319/lo.1967.12.1.0079.
- Colombo, J. C., Pelletier, E., Brochu, C., Khalil, M., & Catoggio, J. A.(1989). Determination of hydrocarbon sources using *n*-alkane and polyaromatic hydrocarbon distribution indexes. Case study: Rio de La Plata Estuary, Argentina. *Environmental Science and Technology*, 23(7), 888-894. doi: 10.1021/es00065a019.
- Colombo, J.C., Barreda, A., Bilosa, C., Cappelletti, N., Demichelis, S., Lombardi, P., Migoya, M.C., Skorupka, C., & Suárez, G. (2005). Oil spill in the Río de la Plata estuary, Argentina: 1. Biogeochemical assessment of waters, sediments, soils and biota. *Environmental Pollution*, 134(2), 277-289. doi: 10.1016/j.envpol.2004.02.032.
- Commendatore, M.G, Esteves, J.L., & Colombo, J.C. (2000). Hydrocarbons in coastal sediments of Patagonia, Argentina: Levels and probable sources. *Marine Pollution Bulletin*, 40(11), 989-998. doi: 10.1016/S0025-326X(00)00042-4.
- Commendatore, M.G., & Esteves, J.L. (2004). Natural and anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina). *Marine Pollution Bulletin*, 48(9-10), 910-918. doi: 10.1016/j.marpolbul.2003.11.015.
- Commendatore, M.G., Nievas, M.L., Amin, O., & Esteves, J.L. (2012). Sources and Distribution of aliphatic and polyaromatic hydrocarbons in coastal sediments from the Ushuaia Bay (Tierra del Fuego, Patagonia, Argentina). *Marine Environmental Research*, 74, 20-31. doi: 10.1016/j.marenvres.2011.11.010.
- Dhanajayan, V., & Muralidharan, S. (2012). Polycyclic aromatic hydrocarbons in various species of fishes from Mumbai Harbour, India, and their dietary intake concentration to human. *International Journal of Oceanography*, 2012, 1-6, Article ID 645178, doi:10.1155/2012/645178.
- Diez, S., Jover, E., Bayona, J.M., & Albaiges, J. (2007). Prestige oil spill: III. Fate of a heavy oil in the marine environment. *Environmental Science & Technology*, 41(9), 3075-3082. Retrieved from: <https://www.ncbi.nlm.nih.gov/pubmed/17539507>.

- Dong, C.D., Chen, C.F., and Chen, C.W. (2012). Determination of Polycyclic Aromatic Hydrocarbons in Industrial Harbor Sediments by GC-MS. *International Journal of Environmental Research and Public Health*, 9, 2175-2188. doi:10.3390/ijerph9062175.
- Duan, F., He, K., and Liu, X. (2010). Characteristics and source identification of fine particulate *n*-alkanes in Beijing, China. *Journal of Environmental Sciences*, 22(7): 998 -1005. doi: 10.1021/es0629559.
- Duan, Y., & Ma, L. H. (2001). Lipid geochemistry in a sediment core from Ruorgai Marsh deposit (Eastern Qinghai Tibet Plateau, China). *Organic Geochemistry*, 32(11), 1429-1442. doi: 10.1016/S0146-6380(01)00105-X.
- Ekpo, B.O., Fubara, E.P., Ekpa, O.D., & Marynowski, H.L. (2012). Determination of hydrocarbon sources using *n*-alkane and PAH distribution indices in sediments from coastal areas of Bonny River in Niger Delta, Nigeria. *ARPJ Journal of Earth Sciences*, 1(1), 9-20. Retrieved from: <https://scinapse.io/papers/2186993399>.
- El Nemr, A., & El-Said, G.F. (2012). Assessment of *n*-alkane and polycyclic aromatic hydrocarbons contaminated in the surface sediments of Egyptian Mediterranean coast. *Blue Biotechnology Journal*, 1(4), 557-580. doi: 10.1007/s10661-012-2889-1.
- Elias, M.S., Wood, A.K., Hashim, Z., Siong, W.B., Hamzah, M.S., Rahman, S.A., Salim, N.A.A., & Tablib, A. (2007). Polycyclic aromatic Hydrocarbon (PAH) contamination in the sediments of East Coast Peninsular Malaysia. *The Malaysian Journal of Analytical Sciences*, 11(1), 70-75.
- Eseme, E., Littke, R., & Agyingi, C.M. (2006). Geochemical characterization of a cretaceous black shale from the Mamfe Basin, Cameroon. *Petroleum Geoscience*, 12(1), 69-74. doi: 10.1144/1354-079304-668.
- Farrington, J.W., & Tripp, B.W. (1977). Hydrocarbons in Western North Atlantic surface sediments. *Geochimica et Cosmochimica Acta*, 41(11), 1627–1641. doi: 10.1016/0016-7037(77)90173-9.

- Fent, K. (2004). Ecotoxicological effects at contaminated sites. *Toxicology*, 205(3), 223-40. doi: 10.1016/j.tox.2004.06.060.
- Floehr, T., Scholz-Starke, B., Xiao, H., Koch, J., Wu, L., Hou, J., Wolf, A., Bergmann, A., Bluhm, K., Yuan, X., Nickoll, M.R., Schaffer, A., & Hollert, H. (2015). Yangtze Three Gorges Reservoir, China: A holistic assessment of organic pollution, mutagenic effects of sediments and genotoxic impacts on fish. *Journal of Environmental Sciences*, 38, 63-82. doi: 10.1016/j.jes.2015.07.013.
- Fryzinger, G.S., Gaines, R.B., Xu, L., & Reddy, C.M. (2003). Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environmental Science and Technology*, 37(8), 1653-1662. doi: 10.1021/es020742n.
- Gao, X., & Chen, S. (2008). Petroleum pollution in surface sediments of Daya Bay, South China, revealed by chemical fingerprinting of aliphatic and alicyclic hydrocarbons. *Estuarine, Coastal and Shelf Science*, 80(1), 95-102. doi: 10.1016/j.ecss.2008.07.010.
- Gearing, P., Gearing, J.N., Lytle, T.F., & Lytle, J. (1976). Hydrocarbons in 60 Northeast Gulf of Mexico Shelf sediment: A preliminary survey. *Geochimica et Cosmochimica Acta*, 40(19), 1005-1017. doi: 10.1016/0016-7037(76)90043-0.
- Gogou, A.I., Apostolaki, M., & Stephanou, E.G. (1998). Determination of organic molecular markers in marine aerosols and sediments: One-step flash chromatography compound class fractionation and capillary gas chromatographic analysis. *Journal of Chromatography A*, 799(1-2), 215-231. doi: 10.1016/S0021-9673(97)01106-0.
- Gough, M.A., & Rowland, S.J. (1990). Characterization of unresolved complex mixtures of hydrocarbons in petroleum. *Nature*, 344, 648-650. doi: 10.1038/344648a0.
- Gray, S.R., & Becker, N.S.C. (2002). Contaminant Flows in Urban Residential Water Systems. *Urban Water*, 4, 331-46. doi: 10.1016/S1462-0758(02)00033-X.
- Guo, J., & Fang, J. (2012). The distribution of n-alkanes and polycyclic aromatic hydrocarbons in water of Taihu Lake. *Procedia Environmental Sciences*, 12, 258-264. doi: 10.1016/j.proenv.2012.01.275.

- Guo, W., He, M., Yang, Z., Lin, C., Quan, X., & Wang, H. (2007). Distribution of polycyclic aromatic in water, suspended particulate matter and sediment from Daliao River watershed, China. *Chemosphere*, 68(1), 93-104. doi: 10.1016/j.chemosphere.2006.12.072.
- Habrink, P.L., Hein, S., Win, T., Bremser, W., & Nehls, I. (2010). Multi-residue analysis of PAH, PCB, and OCP optimized for organic matter of forest soil. *Journal of Soils and Sediments*, 10(8), 1487-1498. doi: 10.1007/s11368-010-0241-3.
- Harb, F.S.D., El Nady, M.M., & Basta, J.S. (2003). Oil: oil correlation for some oil fields in the north western part of the Western Desert, Egypt. *Petroleum Science and Technology*, 21(9-10), 1583-1600. doi: 10.1081/LFT-120023240.
- Heintz, R.A., Rice, S.D., Alex, C., Wertheimer, A.C., Bradshaw, R.F., Thrower, F.P., Joyce, J.E., & Short, J.W. (2000). Delayed effects on growth and marine survival of pink Salmon *Oncorhynchus Gorbuscha*, after exposure to crude oil during embryonic development. *Marine Ecology Progress Series*, 208, 205-216. doi: 10.3354/meps208205
- Horowitz, A.J. (1991). A primer on sediment-trace element chemistry [Adobe Digital Editions version]. doi: 10.3133/ofr9176.
- Hu, L., Guo, Z., Feng, J., Yang, Z., & Fang, M. (2009). Distributions and sources of bulk organic matter and aliphatic hydrocarbons in surface sediments of the Bohai Sea, China. *Marine Chemistry*, 113(3-4), 197-211. doi: 10.1016/j.marchem.2009.02.001.
- Hu, N., Shi, X.S., Liu, J., Huang, P., Liu, Y., & Liu, Y. (2010). Concentrations and possible sources of PAHs in sediments from Bohai Bay and adjacent shelf. *Environmental Earth Sciences*, 60(8), 1771-1782. doi: 10.1007/s12665-009-0313-0.
- Huang, X., Chen, S., Zeng, Z., Pu, X., & Hou, Q. (2017). Characteristics of hydrocarbons in sediment core samples from the Northern Okinawa Trough. *Marine Pollution Bulletin*, 115(1-2), 507-514. doi: 10.1016/j.marpolbul.2016.12.034.
- Hunt, J.H. (1996). *Petroleum Geochemistry and Geology*, 2nd edition. New York: W.H Freeman.
- Husain, M., Harith, M., Rosnan, Y., and Kassim, K.K.Y. (1998). Sedimentological characteristics of sediments of the South China Sea, Area II: Sarawak, Sabah and Brunei Darussalam Waters.

- Proceedings of 2nd Technical Seminar on Marine Fishery Resources Survey in the South China.* (pp. 95-110). Samutprakan, Thailand: Southeast Asian Fisheries Development Centre.
- Ines, Z., Amina, B., Mahmoud, R., & Dalila, S.M. (2013). Aliphatic and aromatic biomarkers for petroleum hydrocarbon monitoring in Khniss Tunisian-Coast, (Mediterranean Sea). *Procedia Environmental Sciences*, 18, 211-220. doi: 10.1016/j.proenv.2013.04.027.
- Jacquot, F., Le Dreau, Y., Doumenq, P., Munoz, D., Guiliano, M., Imbert, G., & Mille, G. (1999). The origins of hydrocarbons trapped in the Lake of Berre sediments. *Chemosphere*, 39(9), 1407-1419. doi:10.1016/S0045-6535(99)00043-0.
- Jamil, M., & Hadil, R. (2012). Deepwater (150-500m) demersal resources exploration in the Exclusive Economic Zone of Malaysia using beam trawl. *Malaysian Fisheries Journal*, 11, 42-79. Retrived from: <http://www.mycite.my/en/files/article/73305>.
- Jeng, W. (2006). Higher plant n-alkane average chain length as an indicator of petrogenic hydrocarbons contamination of the marine environment. *Marine Chemistry*, 102, 242-251. doi: 10.1016/j.marchem.2006.05.001.
- Jeng, W.L., & Kao, S.J. (2002). Lipids in suspended matter from the human-disturbed Lanyang River, Northeastern Taiwan. *Environmental Geology*, 43, 138-144. doi: 10.1007/s00254-002-0619-7.
- Jiao, W., Wang, T., Khim, J.S., Luo, W., Hu, W., Naile, J.E., Giesy, J.P., & Lu, Y. (2012). PAHs in surface sediments from coastal and estuarine areas of the Northern Bohai and Yellow Seas, China. *Environmental Geochemistry and Health*, 34(4), 445-456. doi: 10.1007/s10653-011-9445-8.
- Jones, D.M., Rowland, S.J., Douglas, A.G., & Howells, S. (1986). An examination of the fate of Nigerian crude oil in surface sediments of the Humber Estuary by gas chromatography and gas chromatography-mass spectrometry. *International Journal of Environmental Analytical Chemistry*, 24(3), 227-247. doi: 10.1080/03067318608076473.

- Juda, L. (1986). The Exclusive Economic Zone: Compatibility of national claims and the UN Convention of the Law of the Sea. *Ocean Development and International Law Journal*, 16, 1-58. doi: 10.1080/00908328609545784.
- Kanzari, F., Syakti, A.D., Asia, L., Malleret, L., Mille, G., Jamoussi, B., Abderrabba, M., & Doumenq, P. (2012). Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine and organophosphorus pesticides in surface sediments from Arc River and the Berre Lagoon, France. *Environmental Science and Pollution Research*, 19(2), 559-576. doi: 10.1007/s11356-011-0582-5.
- Kanzari, F., Syakti, A.D., Asia, L., Malleret, L., Piram, A., Mille, G., & Doumenq, P. (2014). Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and pesticides) in surface sediments of an industrialized urban river (Huveaune), France. *Science of The Total Environment*, 478, 141-151. doi: 10.1016/j.scitotenv.2014.01.065.
- Kennicutt II, M.C., Barker, C., Brooks, J.M., DeFreitas, D.A., & Zhu, G.H. (1987). Selected organic matter source indicators in the Orinoco, Nile and Changjiang deltas. *Organic Chemistry*, 11(1), 41-51. doi: 10.1016/0146-6380(87)90050-7.
- Kennish, M.J. (1992). *Ecology of Estuaries: Anthropogenic Effects*. Florida: CRC Press.
- Keshavarzifard, M., Moore, F., Keshavarzi, B., & Sharifi, R. (2017). Polycyclic aromatic hydrocarbons (PAHs) in sediment and sea urchin (*Echinometra mathaei*) from the intertidal ecosystem of the northern Persian Gulf: Distribution, sources, and bioavailability. *Marine Pollution Bulletin*, 123(1-2), 373-380. doi: 10.1016/j.marpolbul.2017.09.008.
- Keshavarzifard, M., Zakaria, M.P., Keshavarzifard, S., & Sharifi, R. (2018). Distributions, composition patterns, sources and potential toxicity of polycyclic aromatic hydrocarbons (PAHs) Pollution in Surface Sediments from the Kim Kim River and Segget River, Peninsula Malaysia. *Pertanika Journal of Science & Technology*, 26(1), 95-120. Retrived from: <https://www.researchgate.net/publication/320237295>.

- Latimer, J., & Quinn, J.G. (1996). Historical trends and current inputs of hydrophobic organic compounds in an urban estuary: the sedimentary record. *Environmental Science & Technology*, 30(2), 623-633. doi: 10.1021/es950367h.
- Law, A. T., and Yusuf, R. (1986). Hydrocarbon distribution in the South China Sea. In: A. K. M. Mohsin, M. Ibrahim, M. A., Ambak (Eds.), *Matahari Expedition 1985: A study on the offshore waters of the Malaysian EEZ*. (pp. 93-100). Universiti Pertanian Malaysia: Occasional Publication No. 3, Faculty of Fisheries and Marine Science.
- Law, A.T. (1990). Petroleum hydrocarbon distribution in the coastal waters off Sabah. In: A. K.M. Mohsin, M. Zaki, M. Said, M. I. H. Mohamed (Eds.). *Ekspedisi Matahari 1989: A Study on the Offshore Waters of the Malaysian EEZ*. (pp 57-64). Universiti Pertanian Malaysia: Occasional Publication No.9, Faculty of Fisheries and Marine Science.
- Law, A.T., & Hii, Y.S. (2006). Status, impacts and mitigation of hydrocarbon pollution in the Malaysian seas. *Aquatic Ecosystem Health & Management*, 9(2), 147-158. doi: 10.1080/14634980600701583.
- Law, A.T., and Libi, S.H. (1988). Petroleum hydrocarbon distribution in the coastal waters off Sarawak, In: A. K. M. Mohsin, M. Ibrahim (Eds.), *Matahari Expedition 1987: A Study on the offshore waters of the Malaysian EEZ*, (p 168). Universiti Pertanian Malaysia: Occasional Publication No. 8, Faculty of Fisheries and Marine Science.
- Law, A.T., & Mahmood, Z. (1987). Distribution of petroleum hydrocarbon in the South China Sea. In: A. K. M., Mohsin, M. A. Ambak, A. Ridzwan (Eds.), *Matahari Expedition 1986: A study on the offshore waters of the Malaysian EEZ*. (pp 53-60). Universiti Pertanian Malaysia: Occasional Publication No. 4, Faculty of Fisheries and Marine Science.
- Law, A.T., Ravinthar, V., and Yeong, C.H. (1990). Oil pollution in the coastal waters off Port Dickson, Straits of Malacca. *Pertanika*, 13(3), 381-387. Retrieved from: <http://psasir.upm.edu.my/id/eprint/2872/>.
- Li, J., Dong, H., Zhang, D., Han, B., Zhu, C., Liu, S., Liu, X., Ma, Q., & Li, X. (2015). Sources and ecological risk assessment of PAHs in surface sediments from Bohai Sea and Northern Part

- of the Yellow Sea, China. *Marine Pollution Bulletin*, 96(1-2), 485-490. doi: 10.1016/j.marpolbul.2015.05.002.
- Liu, Y., Chen, L., Jianfu, Z., Qinghui, H., Zhiliang, Z., & Hongwen, G. (2008). Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China. *Environmental Pollution*, 154(2), 298-305. doi: 10.1016/j.envpol.2007.10.020.
- Long, E.R., MacDonald, D.D., Smith, S.L., & Calder, F.D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management*, 19(1), 81-97. doi: 10.1007/BF02472006.
- Lorgeoux, C., Moilleron, R., Gasperi, J., Ayrault, S., Bonte, P., Lefevre, I., & Tassin, B. (2016). Temporal trends of persistent organic pollutants in dated sediment cores: chemical fingerprinting of the anthropogenic impacts in the Seine River basin, Paris. *Science of the Total Environment*, 541, 1355-1363. doi: 10.1016/j.scitotenv.2015.09.147.
- Lu, B., Pan, J.M., & Wang, Z.P. (2002). The composition indexes of *n*-alkanes in sediments and study on paleo environment in the Arctic. *Acta Oceanologica Sinica*, 24(6), 34-48. Retrieved from: <https://www.researchgate.net/publication/285702129>.
- Lucia, V., Angeles, M.F., J. Antonio, S., Jose, J.G., Jordi, P., & Joan, A. (2010). Sources and distribution of polycyclic aromatic hydrocarbons in sediments from the Spanish northern continental shelf. Assessment of spatial and temporal trends. *Environmental Pollution*, 158(5), 1551-1560. doi: doi.org/10.1016/j.envpol.2009.12.023.
- MacDonald, D.D., Carr, R.S., Calder, F.D., Long, E.R., & Ingersoll, C.G. (1996). Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology*, 5(4), 253-278. doi: 10.1007/BF00118995.
- MacDonald, D.D., Ingersoll, C.G., & Berger, T.A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology*, 39(1), 20-31. doi: 10.1007/s002440010075.

- Maioli, O.L.G., Rodrigues, K.C., Knoppers, B.A., and Azevedo, D.A. (2011). Distribution and sources of aliphatic and polycyclic aromatic hydrocarbons in suspended particulate matter in water from two Brazilian estuarine systems. *Continental Shelf Research*, 3(10), 1116-1127. doi: 10.1016/j.csr.2011.04.004.
- Masih, J., Masih, A., Kulshrestha, A., Singhvi, R., & Taneja, A. (2010). Characteristics of polycyclic aromatic hydrocarbons in indoor and outdoor atmosphere in the North Central Part of India. *Journal of Hazardous Materials*, 177(1-3), 190-198. doi: 10.1016/j.jhazmat.2009.12.017.
- Masih, J., Singhvi, R., Kumar, K., Jain, V.K., & Taneja, A. (2012). Seasonal variation and sources of polycyclic aromatic hydrocarbons (pahs) in indoor and outdoor air in a semi arid tract of Northern India. *Aerosol and Air Quality Research*, 12(4), 515-525. doi: 10.4209/aaqr.2011.11.0192.
- Medeiros, P.M., Bicego, M.C., Castelao, R.M., Del Rosso, C., Fillmann, G., & Zamboni, A.J. (2005). Natural and anthropogenic hydrocarbon input to sediments of Patos Lagoon Estuary, Brazil. *Environment International*, 31(1), 77-87. doi: 10.1016/j.envint.2004.07.001.
- Meyer, T., Lei, Y.D., & Wania, F. (2011). Transport of polycyclic aromatic hydrocarbons and pesticides during snowmelt within an urban watershed. *Water Research*, 45 (3): 1147-1156. doi: 10.1016/j.watres.2010.11.004.
- Mille, G., Asia, L., Guiliano, M., Malleret, L., & Doumenq, P. (2007). Hydrocarbons in coastal sediments from the Mediterranean Sea (Gulf of Fos area, France). *Marine Pollution Bulletin*, 54(5): 566-575. doi: 10.1016/j.marpolbul.2006.12.009.
- Mironov, O.G. (1968). Hydrocarbon pollution of the sea and its influence on marine organisms. *Helgoländer wissenschaftliche Meeresuntersuchungen*, 17(1-4), 335-339. doi: 10.1007/BF01611234.
- Moreau., R.A., Whitaker, B.D., & Kicks, K.B. (2002). Phytosterols, phytostanols and their conjugates in foods: Structural diversity, quantitative analysis, and health-promoting uses. *Progress in Lipid Research*, 41(6), 457-500. doi: 10.1016/S0163-7827(02)00006-1.

- Morton, B., & Balckmore, G. (2002). South China Sea. *Marine Pollution Bulletin*, 42(12), 1236-1263. doi: 10.1016/S0025-326X(01)00240-5.
- Moustafa, Y.M. (2004). Environmental assessment of petroleum contamination of Gamasa-Damiette Beaches. *Oriental Journal of chemistry*, 20(2), 219-226.
- Moustafa, Y.M., & Morsi, R.E. (2012). Biomarkers, Chromatography and Its Applications Sasikumar Dhanarasu, IntechOpen. doi: 10.5772/35750. Available from: [https://www.intechopen.com/books/chromatography and its applications/biomarker](https://www.intechopen.com/books/chromatography-and-its-applications/biomarker).
- Nasher, E., Heng, L.Y., Zakaria, Z., & Surif, S. (2016). Health risk assessment of polycyclic aromatic hydrocarbons through aquaculture fish consumption, Malaysia. *Journal Environmental Forensics*, 17(1), 97-106. doi: 10.1080/15275922.2015.1133733
- Nasher, E., Heng, L.Y., Zakaria, Z., and Surif, S. (2013). Assessing the Ecological Risk of Polycyclic Aromatic Hydrocarbons in Sediments at Langkawi Island, Malaysia. *The ScientificWorld Journal*, 2013, 1-13. Article ID 858309. doi: 10.1155/2013/858309.
- Nasr, I.N., Arief, M.H., Abdel-Aleem, A.H., and Malhat, F.M. (2010). Polycyclic aromatic hydrocarbons (PAHS) in aquatic environment at El Menofiya Governorate, Egypt. *Journal of Applied Sciences Research*, 6(1), 13-21. Retrived from: <https://www.researchgate.net/publication/228504877>.
- Neff, J. M. (1979). *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment, Sources, Fates, and Biological Effects*. London: Applied Science.
- Nikolaou, A., Kostopoulou, M., Lofrano, G., & Meric, S. (2009). Determination of PAHs in Marine Sediments: Analytical methods and Environmental Concerns. *Global NEST Journal*, 11(4), 391-405. doi: 10.30955/gnj.000662.
- Nemirovskaya, I.A., Brekhovskikh, V.F., and Kazmiruk, V.D. (2006). Aliphatic and Polyaromatic Hydrocarbons in Bottom Sediments of Offshore Mouth Area of the Volga. *Water Resources*, 33(3), 274-284. doi:10.1134/S009780780

- Odum, H.T. (2000). Back ground of published studies on lead and wetland. In: H.T *Odum (Ed.)*. *Heavy Metals in the Environment Using Wetlands for Their Removal*. New York: Lewis Publishers.
- Okay, O.S., Tolun, L., Telli-Karakoc, F., Tufekci, V., Tufekci, H., Olgun, A., & Morkoc, E. (2003) The changes of TPAH levels and health status of mussels in Izmit Bay (Turkey) after Marmara earthquake and subsequent refinery fire. *Environment International*, 28(8), 671-675. doi: 10.1016/S0160-4120(02)00109-5.
- Okoh, A.I., Odjadjare, E.E., Igbinsosa, E.O., & Osode, A.N. (2007). Wastewater treatment plants as a source of microbial pathogens in the receiving watershed. *African Journal of Biotechnology*, 6(25), 2932-2944. doi: 10.5897/AJB2007.000-2462..
- Ou, S.M., Zheng, J.H., Zheng, J.S., & Quinn, G.Q. (2003). Petroleum hydrocarbons and polycyclic aromatic hydrocarbons in surface sediments in Xiamen Harbour and Yuandang Lake. *Marine Environmental Science*, 22(4), 49-53. Retrived from: <https://europepmc.org/abstract/cba/552433>.
- Ou, S.M., Zheng, J.H., Zheng, J.S., Richardson, B.J., and Lam, P.K.S. (2004). Petroleum hydrocarbons and polycyclic aromatic hydrocarbons in the surficial sediments of Xiamen Harbour and Yuan Dan Lake, China. *Chemosphere*, 56(2), 107-112. doi: 10.1016/j.chemosphere.2004.02.022.
- Page, D.S., Boehm, P.D., Douglas, G.S., Bence, A.E., Burns, W.A., & Mankiewicz, P.J. (1999). Pyrogenic polycyclic aromatic hydrocarbons in sediments record past human activity: a case study in Prince William Sound, Alaska. *Marine Pollution Bulletin*, 38(4), 247-260. doi: 10.1016/S0025-326X(98)00142-8.
- Patuzi, D. (2015). The concept of the economic exclusive zone. *Academic Journal of Business, Administration, Law and Social Sciences*, 1(1), 149-159.
- Peter, H.A. (2003). *Petroleum and Individual Polycyclic Aromatic Hydrocarbon in Handbook of Ecotoxicology*. Boca Raton, Florida: Lewis Publishers.

- Peters, K.E., and Moldowan, J.M. (1993). *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Prentice Hall, 363pp.
- Peters, K.E., Walters, C.C., and Moldowan, J.N.(2005). *The Biomarker Guide*, 2nd edition. New York: Cambridge University Press.
- Petersen, H.I., Nytoft, H.P., Ratanasthien, B., and Foopatthanakamol, A. (2007). Oils from Cenozoic Rift-Basins in Central and Northern Thailand: Source and thermal maturity. *Journal of Petroleum Geology*, 30(1), 59-78.
- Rahmanpoor, S., Ghafourian, H., Hashtroudi, S.M., & Bastami, K.D. (2014). Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of the Hormuz Strait, Persian Gulf. *Marine Pollution Bulletin*, 78(1-2), 224–229. doi: 10.1016/j.marpolbul.2013.10.032.
- Ramalhosa, M.J., Paiga, P., Morais, S., Delerue-Matos, C., & Olivera, M.B. (2009). Analysis of polycyclic aromatic hydrocarbons in fish: evaluation of a quick, easy, cheap, effective, rugged, and safe extraction method. *Journal of Separation Science*, 32(20), 3529-3538. doi: 10.1002/jssc.200900351.
- Ramalhosa, M.J., Paiga, P., Morais, S., Sousa, A.M.M., Goncalves, M.P., Delerue-Matos, C., & Oliveira, M.B.P.P. (2012). Polycyclic aromatic hydrocarbons in fish: Optimisation and validation of microwave-assisted extraction. *Food Chemistry*, 135(1), 234-242. doi: 10.1016/j.foodchem.2012.04.078.
- Readman, J.W., Fillman, G., Tolosa, I., Bartocci, J., Villeneuve, J.P., Catinni, C. and Mee, L.D. (2002). Petroleum and PAH contamination of the Black Sea. *Marine Pollution Bulletin*, 44(1), 48-62. doi: 10.1016/S0025-326X(01)00189-8.
- Requejo, A.G., Sassen, R., McDonald, T., Denoux, G., Kennicutt II, M.C., & Brooks, J.M. (1996). Polynuclear aromatic hydrocarbons (PAH) as indicators of the source and maturity of marine crude oils. *Organic Geochemistry*, 24(10-11), 1017-1033. doi: 10.1016/S0146-6380(96)00079-4.

- Reynaud, S., & Deschaux, P. (2006). The effects of polycyclic aromatic hydrocarbons on the immune system of fish: a review. *Aquatic Toxicology (Amsterdam, Netherlands)*, 77(2), 229-238. doi: 10.1016/j.aquatox.2005.10.018.
- Ruey-an, D., and Yu, T.L. (2004). Characterization and distribution of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River, Taiwan. *Water Research*, 38(7), 1733-1744. doi: 10.1016/j.watres.2003.12.042.
- Rushdi, A.I., Al-Shaikh, I., El-Mubarak, A.H., Alnaimi, H.A.J.A, Al-Shamary, N., Hassan, H.M., & Assali, M.A. (2017). Characteristics and sources of anthropogenic and biogenic hydrocarbons in sediments from Tthe Coast of Qatar. *Marine Pollution Bulletin*, 124(1), 56-66. doi: 10.1016/j.marpolbul.2017.07.014.
- Sakari, M., Zakaria, M.P., Lajis N.H., Mohamed, C.A.R., & Abdullah, M.H. (2012). Reconstruction of aliphatic hydrocarbon history and sources from sedimentary record of the Johor Strait, Malaysia. *Coastal Marine*, 35(1), 142-152. Retrived from: <https://www.researchgate.net/publication/285310885>.
- Sakari, M., Zakaria, M.P., Lajis, N.H., Mohamed, C.A.R., Chandru, L., Shahpoury, P., Mokhtar, M., & Shahbazi, A. (2010b). Urban vs marine based oil production in the Strait of Johor, Malaysia: A century record. *Soil and Sediment Contamination: An International Journal*, 19(6), 644-666. doi: 10.1080/15320383.2010.515630.
- Sakari, M., Zakaria, M.P., Lajis, N.H., Mohamed, C.A.R., Chandru, L., Shahpoury, P., Shahbazi, A., & Anita, S. (2010a). Historical profiles of polycyclic aromatic hydrocarbons (PAHs), sources and origins in dated sediment Cores from Port Klang, Straits of Malacca, Malaysia. *Coastal Marine Science*, 34(1), 140-155. Retrived from: <https://www.researchgate.net/publication/277204030>.
- Sakari, M., Zakaria, M.P., Junos, M.B.M., Annuar, N.A, Yun, H.Y., Heng, Y.S., Zainuddin, S.M.H.S., & Chai, K.L. (2008). Spatial distribution of petroleum hydrocarbon in sediments of major rivers from East Coast of Peninsular Malaysia. *Coastal Marine Science*, 32(1), 9-18. Retrived from: <https://www.researchgate.net/publication/29778909>.

- Sakari, M., Zakaria, M.P., Mohamed, C.A.R., Lajis, N.H., Abdullah, M.H., & Shahbazi, A. (2011). Polycyclic aromatic hydrocarbons and hopane in Malacca coastal water: 130 years of evidence for their land-based sources. *Environmental Forensic*, 12(1), 63-78. doi: 10.1080/15275922.2010.547911.
- Salem, D.M.S.A., Morsy, F.A.E M., Nemr, A.E., El-Sikaily, A., & Khaled, A. (2014). The monitoring and risk assessment of aliphatic and aromatic hydrocarbons in sediments of the Red Sea, Egypt. *Egyptian Journal of Aquatic Research*, 40(4), 333-348. doi: 10.1016/j.ejar.2014.11.003.
- Sany, S.B.T., Hashim, R., Salleh, A., Rezayi, M., Mehdina, A., and Safari, O. (2014). Polycyclic Aromatic Hydrocarbons in Coastal Sediment of Klang Strait, Malaysia: Distribution Pattern, Risk Assessment and Sources. *PloS One*, 9(4), 1-14. doi: 10.1371/journal.pone.0094907.
- Scarlett, A.G., Galloway, T.S., & Rowland, S.J. (2007). Chronic toxicity of unresolved complex mixtures (UCM) of hydrocarbons in marine sediments. *Journal of Soils and Sediments*, 7(4), 200-206. doi: 10.1065/jss2007.06.232.
- Scientific Committee on Food (SCF). (2002). Polycyclic Aromatic Hydrocarbons - Occurrence in Foods, Dietary Exposure and Health Effects. Retrieved from: https://ec.europa.eu/food/sites/food/files/safety/docs/sci-com_scf_out154_en.pdf
- Shaw, P.T. (1991). The seasonal variation of the intrusion of the Philippine sea water into the South China Sea. *Journal of Geophysical Research*, 96(1), 821-827. doi: 10.1029/90JC02367.
- Shazili, N.A.M., Rashid, M.K.A., Husain, M.L.H., & Yaakob, R. (1998). Trace Metals in Surface Sediment of the South China Sea, Area II: Sarawak, Sabah and Brunei. *Proceedings of 2nd Technical Seminar on Marine Fishery Resources Survey in the South China*. (pp. 147-155). Samutprakan, Thailand: Southeast Asian Fisheries Development Centre.
- Shazili, N.A.M., Yunus, K., Ahmad, A.S., Abdullah, N., & Rashid, M.K.A. (2006). Heavy Metal pollution status in the Malaysian aquatic environment. *Aquatic Ecosystem Health & Management*, 9(2), 137-145. doi: 10.1080/14634980600724023.

- Shazili, N.A.M., Rashid, M.K.A., Husain, M.L., & Yaakob, R. (1998). Trace metals in surface sediment of the South China Sea Area II: Sarawak, Sabah and Brunei. *Proceedings of the Second Technical Seminar on Marine Fishery Resources Survey in the South China Sea Area II: Sarawak, Sabah and Brunei Darussalam*. (pp.146-155). Samutprakan, Thailand: Southeast Asian Fisheries Development Center.
- Shi, G.L., Feng, Y.C., Wu, J.H., Li, X., Wang, Y.Q., Xue, Y.H., & Zhu, T. (2009). Source Identification of Polycyclic Aromatic Hydrocarbons in Urban Particulate Matter of Tangshan, China. *Aerosol and Air Quality Research*, 9, 309-315.
- Sicre, M.A., Marty, J.C., Saliot, A., Aparicio, X., Grimalt, J., & Albaiges, J. (1987). Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: Occurrence and origin. *Atmospheric Environment*, 21(10), 2247–2259. doi: 10.1016/0004-6981(87)90356-8.
- Simoneit, B.R.T. (1987). The organic chemistry of marine sediment. In: J.P Riley & R. Chester, R. (Eds), *Chemical Oceanography* 7, London: Academic Press, pp. 233-311.
- Soclo, H., Garrigues, P.H., & Ewald, M. (2000). Origin of polycyclic aromatic hydrocarbons PAHs in coastal marine sediments: Case studies in Cotonou (Benin) and Aquitaine (France) areas. *Marine Pollution Bulletin*, 40(5), 387-396. doi: 10.1016/S0025-326X(99)00200-3.
- Soliman, Y.S., Al Ansari, E.M.S., & Wade, T.L. (2014). Concentration, composition and sources of PAHs in the coastal sediments of the Exclusive Economic Zone (EEZ) of Qatar, Arabian Gulf. *Marine Pollution Bulletin*, 85(2), 542-548. doi: 10.1016/j.marpolbul.2014.04.027.
- Stogiannidis, E., & Laane, R. (2015). Source characterization of polycyclic aromatic hydrocarbons by using their molecular indices: An overview of possibilities. *Reviews of Environmental Contamination and Toxicology*, 234, 49-133. doi: 10.1007/978-3-319-10638-0_2.
- Stout, S. and Wang, Z. (2016). *Standard Handbook Oil Spill Environmental Forensics*, 2nd edition. Singapore: Academic Press, 1142pp.

- Stout, S.A., Uhler, A.D., & McCarthy, K.J. (2001). A strategy and methodology for defensibly correlating spilled oil to source candidates. *Environmental Forensics*, 2(1), 87-98. doi: 10.1006/enfo.2001.0027.
- Tahir, N.M., Abdullah, A.R., & Shanmugam, S. (1997). Determination of total hydrocarbon concentration in coastal waters and sediments off the east coast of Peninsular Malaysia. *Environmental Geochemistry and Health*, 19(2), 67-71. doi: 10.1023/A:1018494204013.
- Takatsuki, K., Suzuki, S., Sato, N., & Ushizawa, I. (1985). Liquid chromatographic determination of polycyclic aromatic hydrocarbons in fish and shellfish. *Journal Association of Official Analytical Chemists*, 68(5), 945-949. Retrieved from: <https://www.ncbi.nlm.nih.gov/pubmed/4055642>.
- Tao, Y.Q., Xue, B., Yao, S.C., Deng, J.C., & Gui, Z.F. (2012). Triolein embedded cellulose acetate membrane as a tool to evaluate sequestration of PAHs in lake sediment core at large temporal scale. *Environmental Science and Technology*, 46(7), 3851-3858. doi: 10.1021/es203102b.
- Tolosa, I., de Mora S., Sheikholeslami M.R., Villeneuve, J.P., Bartocci, J., & Cattini, C. (2004). Aliphatic and aromatic hydrocarbons in coastal Caspian Sea sediments. *Marine Pollution Bulletin*, 48(1-2), 44-60. doi: 10.1016/S0025-326X(03)00255-8.
- Tsang, H.L., Wu, S.C., Leung, C.K., Tao, S., & Wong, M.H. (2011). Body burden of POPs of Hong Kong residents, based on human milk, maternal and cord serum. *Environment International*, 37(1), 142-151. doi: 10.1016/j.envint.2010.08.010.
- Tunku Sofiah, J. (1996). *Public International Law: A Malaysian Perspective, Volume II*. Kuala Lumpur: Pacifica Publications.
- Utoomprurkorn, W., & Snidvongs, A. (1999). Trace Metals Concentrations and Distributions in Sea Water of the South China Sea, Area II: Sabah, Sarawak and Brunei Darussalam. *Proceedings of 2nd Technical Seminar on Marine Fishery Resources Survey in the South China*. (pp. 131-145). Samutprakan, Thailand: Southeast Asian Fisheries Development Centre.

- Vaezzadeh, V., Zakaria, M.P., Tan, A.S.H., Ibrahim, Z.Z., Mustafa, S., Abootalebi-Jahromi, F., Masood, N., Magam, S.M., & Alkhadher, S.A.A. (2015). Forensic investigation of aliphatic hydrocarbons in the sediments from selected mangrove ecosystems in the West Coast of Peninsular Malaysia. *Marine Pollution Bulletin*, 100(1), 311-320. doi: 10.1016/j.marpolbul.2015.08.034.
- Van Dongen, B.E., Semiletov, I., Weijers, J.W.H., & Gustafsson, O.R. (2008). Contrasting lipid biomarker composition of terrestrial organic matter exported from across the Eurasian Arctic by the five Great Russian Arctic rivers. *Global Biogeochemical Cycles*, 22(1), 1-14. doi: 10.1029/2007GB002974.
- Veerasingam, S., Raja, P., Venkatachalapathy, R., Mohan, R., & Sutharsan, P. (2010). Distribution of petroleum hydrocarbon concentrations in coastal sediments along Tamil Nadu Coast, India. *Carpathian Journal of Earth and Environmental Sciences*, 5(2), 5-8. Retrived from: <https://www.researchgate.net/publication/215607776>.
- Volkman, J.K., Holdsworth, D.G., Neill, G.P., & Bavor Jr., H.J. (1992). Identification of natural, anthropogenic and petroleum hydrocarbons in aquatic sediments. *Science of the Total Environment*, 112(2-3), 203-219. doi: 10.1016/0048-9697(92)90188-X.
- Wagener, A., Hamacher, C., Farias, C., Godoy, J. M. & Scofield, A. (2010). Evaluation of tools to identify hydrocarbon sources in recent and historical sediments of a tropical bay. *Marine Chemistry*, 121(1-4), 67-79. doi: 10.1016/j.marchem.2.
- Wakeham, S.G., & Farrington J.W. (1980). Hydrocarbons in contemporary aquatic sediments. In: R.A Baker (Ed.). *Contaminants and sediments volume 1*. Michigan: Ann Arbor Science Publishers, pp. 3-32.
- Wang, X.C., Sun, S. Ma, H.Q., & Liu, Y. (2006). Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. *Marine Pollution Bulletin*, 52(2), 129-138. doi: 10.1016/j.marpolbul.2005.08.010.
- Wang, X.C., Zhang, Y.X., & Chen, R.F. (2001). Distribution and partitioning of polyaromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United

- States. *Marine Pollution Bulletin*, 42(11), 1139-1149. doi: 10.1016/S0025-326X(01)00129-1.
- Wang, Z., & Fingas, M.F. (2003). Development of oil hydrocarbon fingerprinting and identification Techniques. *Marine Pollution Bulletin*, 47(9-12), 423-452. doi: 10.1016/S0025-326X(03)00215-7.
- Wang, Z., & Stout, S.A. (2006). Oil spill environmental forensics: Fingerprinting and source identification. USA: Elsevier, pp. 505-536.
- Wang, Z., Fingas, M., & Page, D.S. (1999). Oil spill identification. *Journal of Chromatography A*, 843(1-2): 369-411. doi: 10.1016/S0021-9673(99)00120-X.
- Weast, R.C. (1968). *Handbook of Chemistry and Physics 1968-1969*. (49th ed.). United State of America: The Chemical Rubber Company.
- Wernersson, A.S, Dave, G., & Nilsson, E. (2000). Assessing Pollution and UV Enhanced Toxicity in Torsviken, Sweden, A Shallow Bay Exposed to Contaminated Dredged Harbour Sediment and Hazardous Waste Leachate. *Aquatic Ecosystem Health & Management*, 3(3), 301-316. doi: 10.1080/14634980008657029.
- Wongnapapan, P., Wattayakorn, G., and Snidvongs, A. (1999). Petroleum Hydrocarbon in Seawater and Some Sediments of the South China Sea, Area I: Gulf of Thailand and East Coast of Peninsular Malaysia. *Proceedings of 2nd Technical Seminar on Marine Fishery Resources Survey in the South China*. (pp. 105-110). Samutprakan, Thailand: Southeast Asian Fisheries Development Centre.
- World Health Organization (WHO). (1991). Evaluation of certain food and additives and contaminants, in: Thirty seventh report of the Joint Food and Agriculture Organization of the United Nations (FAO)/WHO Expert Committee on food Additives. Report No: 806. Retrieved from: http://apps.who.int/iris/bitstream/handle/10665/41790/WHO_TRS_815.pdf;jsessionid=B9E8C33CA79A2BE0BC42CCAB154F05A0?sequence=1

- World Health Organization (WHO). (2005). Summary and conclusions of the sixty-fourth meeting of the joint Food and Agriculture Organization of the United Nations (FAO) /WHO expert committee on food additives. Rome: World Health Organization Scientific Committee on Food. Report No: 928. Retrieved from: <http://www.fao.org/3/a-at877e.pdf>.
- Yan, W., Chi, J., Wang, Z., Huang, W., and Zhang, G. (2009). Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Daya Bay, South China. *Environmental Pollution*, 157(6), 1823-1830. doi: 10.1016/j.envpol.2009.01.023.
- Youngblood, W.W., Monaghan, P.H., & Schweisberger, R.T. (1977). Calculation of ages of hydrocarbons in oils: Physical chemistry applied to petroleum geochemistry; part 1. *American Association of Petroleum Geologists Bulletin*, 61(4): 573-600. Retrieved from: <https://www.osti.gov/biblio/7301578>.
- Yunker, M.B., Backus, S.M., Pannatier, E. G., Jeffries, D.S., & Macdonald, R.W. (2002). Sources and significance of alkane and pah hydrocarbons in Canadian Arctic Rivers. *Estuarine, Coastal and Shelf Science*, 55(1), 1-31. doi: 10.1006/ecss.2001.0880.
- Yunker, M. B., Macdonald, R. W., Brewer, R., Vingarzan, R., Mitchell, R.H., Goyette, D., & Sylvestre, S. (2002). PAHs in the Fraser Basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*, 33(4), 489-515. doi: 10.1016/S0146-6380(02)00002-5.
- Yusoff, H.B, Assim, Z.B., & Mohamad, S.B. (2009). *Vertical Profile of Heavy metals in Marine Core Sediments of Kuching Bay, Sarawak*. Malaysia: Perpustakaan Negara Malaysia. pp.175-183.
- Yusoff, H.B., Assim, Z.B., & Mohamad, S.B. (2012). Aliphatic hydrocarbons in surface sediments from South China Sea off Kuching Division, Sarawak. *The Malaysian Journal of Analytical Sciences*, 16(1), 1-11. Retrieved from: http://www.ukm.my/mjas/v16_n1/Hafidz.pdf
- Zaghden, H., Kallel, M., Elleuch, B., Oudot, J., & Saliot, A. (2007). Source and distribution of aliphatic and polycyclic aromatic hydrocarbons in sediments of Sfax, Tunisia, Mediterranean Sea. *Marine Chemistry*, 105(1-2), 70-89. doi: 10.1016/j.marchem.2006.12.016.

- Zaghden, H., Tedetti, M., Sayadi, S., Serbaji, M.M., Elluech, B., & Saliot, A. (2017). Origin and distribution of hydrocarbons and organic matter in the surficial sediments of the Sfax-Kerkennah channel (Tunisia, Southern Mediterranean Sea). *Marine Pollution Bulletin*, 117, 414-428. doi: 10.1016/j.marpolbul.2017.02.007.
- Zakaria, M.P., & Mahat, A.A. (2006). Distribution of Polycyclic Aromatic Hydrocarbon (PAHs) in sediments in The Langat estuary. *Costal Marine Science*, 30(1), 387-395. Retrived from: <https://www.researchgate.net/publication/29769986>.
- Zakaria, M.P., & Takada, H. (2007). Case study: Oil spills in the Strait of Malacca, Malaysia. In: Z. Wang & S.A. Stout (Eds.) *Oil Spill Environmental Forensics*. Elsevier, pp. 489-504.
- Zakaria, M.P., Horinouchi, A., Tsutsumi, S., Takada, H., Tanabe, S., & Ismail, A. (2000). Oil pollution in the Strait of Malacca, Malaysia: Application of molecular markers for source identification. *Environmental Science & Technology*, 34(7), 1189-1196. doi: 10.1021/es990950o.
- Zakaria, M.P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., & Kumata, H. (2002). Distribution of polycyclic aromatic hydrocarbons (Pahs) in rivers and estuaries in Malaysia: A Widespread input of petrogenic PAHs. *Environmental Science and Technology*, 36(9), 1907-1918. Retrived from: <https://www.ncbi.nlm.nih.gov/pubmed/12026970>.
- Zamora, M.J.V., Vega, M.E., & Celaya, V.J. (2002). PAHs composition of surface marine sediments: A comparison to potential local sources in Todos Santos Bay, BC, Mexico. *Chemosphere*, 46(3), 459-468. doi: 10.1016/S0045-6535(01)00069-8.
- Zegouagh, Y., Derenne, S., Largeau, C., Bardoux, G., & Mariotti, A. (1998). Organic matter sources and early diagenetic alterations in arctic surficial sediments (Lena River Delta and Laptev Sea, Eastern Siberia). II.: Molecular and isotopic studies of hydrocarbons. *Organic Geochemistry*, 28(9-10), 571-583. doi: 10.1016/S0146-6380(98)00020-5.
- Zegouagh, Y., Derenne, S., Largeau, C., Bardoux, G., & Mariotti, A. (1998). Organic matter sources and early Diagenetic alterations in Arctic surficial sediments (Lena River Delta and Laptev

- Sea, Eastern Siberia). II. Molecular and isotopic studies of hydrocarbons. *Organic Geochemistry*, 28(9-10), 571-583. doi: 10.1016/S0146-6380(98)00020-5.
- Zhang, D., Liu, J., Jiang, X., Cao, K., Yin, P., & Zhang, X. (2016). Distribution, sources and ecological risk assessment of PAHs in surface sediments from the Luan River Estuary, China. *Marine Pollution Bulletin*, 102(1), 223-229. doi: 10.1016/j.marpolbul.2015.10.043.
- Zhang, X., Ji, W., Kang, Z., Sun, D., Shan, W., & Na, R. (2009). Harmfulness of petroleum pollutants in water and its treating techniques. *Petrochemical Technology & Application*, 27(2), 181-186. Retrieved from: http://en.cnki.com.cn/Article_en/CJFDTotol-IZHM200902023.htm.
- Zhao, Z., Qin, Z., Cao, J., & Xia, L. (2017). Source and ecological risk characteristics of PAHs in sediments from Qinhuai River and Xuanwu Lake, Nanjing, China. *Journal of Chemistry*, 2017, 1-18. Article ID 3510796. doi.org/10.1155/2017/3510796.

APPENDICES

Appendix 1: Concentrations of *n*-alkanes ($\mu\text{g/g}$) in core sediment of ST01

Compounds	Layers (cm)				
	0-2.5	2.5-5.0	5.0-7.5	7.5-10.0	10.0-12.5
Undecane C ₁₁	n.d	n.d	n.d	n.d	n.d
Dodecane C ₁₂	n.d	n.d	n.d	3.34	n.d
Tridecane C ₁₃	53.8	n.d	0.11	n.d	n.d
Tetradecane C ₁₄	39.9	2.31	0.22	0.04	0.50
Pentadecane C ₁₅	n.d	0.01	n.d	0.07	0.01
Hexadecane C ₁₆	0.22	8.46	1.66	0.04	2.19
Heptadecane C ₁₇	0.52	0.01	0.002	0.01	0.01
Pristane	0.80	0.01	0.02	0.08	0.00
Octadecane C ₁₈	1.76	5.93	1.15	1.45	0.80
Phytane	1.75	2.81	0.02	0.88	0.61
Nonadecane C ₁₉	1.27	0.003	0.02	1.58	0.01
Eicosane C ₂₀	4.15	6.15	0.88	1.04	1.02
Heneicosane C ₂₁	0.68	0.02	n.d	0.24	0.04
Docosane C ₂₂	0.72	3.09	0.77	0.44	1.11
Tricosane C ₂₃	0.69	0.03	0.19	0.73	0.01
Tetracosane C ₂₄	2.44	3.42	0.07	2.66	0.94
Pentacosane C ₂₅	0.89	0.04	0.52	3.26	0.02
Hexacosane C ₂₆	1.87	4.10	0.39	11.9	0.76
Heptacosane C ₂₇	1.36	0.11	0.01	3.17	0.07
Octacosane C ₂₈	1.81	2.80	0.38	9.22	0.41
Nonacosane C ₂₉	1.66	0.16	0.02	1.60	0.06
Eicontane C ₃₀	1.58	1.98	0.02	5.10	0.37
Henetricontane					
C ₃₁	1.39	0.18	0.07	0.99	0.04
Dotricontane C ₃₂	1.83	0.89	0.02	2.25	0.20
Tricontane C ₃₃	0.90	0.56	0.04	0.57	0.13
Tetratricontane					
C ₃₄	0.81	10.6	0.02	0.74	0.55
Pentatriacontane					
C ₃₅	0.75	2.83	0.11	0.16	0.07
Hexatriacontane	n.d				
C ₃₆		0.23	0.28	0.22	0.09
Σ TAH (ng/g)	123.7	56.1	7.0	48.5	9.45

Appendix 2: Concentrations of *n*-alkanes (µg/g) in core sediment of ST02

Compounds	Layers (cm)				
	0-2.5	2.5-5.0	5.0-7.5	7.5-10.0	10.0-12.5
Undecane C ₁₁	n.d	n.d	n.d	n.d	n.d
Dodacane C ₁₂	n.d	n.d	1.95	2.89	4.69
Tridecane C ₁₃	n.d	n.d	0.06	n.d	n.d
Tetradecane C ₁₄	2.29	18.5	0.65	27.9	11.4
Pentadecane C ₁₅	n.d	n.d	0.02	0.02	13.6
Hexadecane C ₁₆	16.3	20.0	10.9	38.2	17.6
Heptadecane C ₁₇	0.01	n.d	0.28	0.32	0.05
Pristane	0.03	0.31	0.08	0.37	0.33
Octadecane C ₁₈	7.65	2.81	26.3	0.14	54.3
Phytane	5.52	27.1	42.6	5.96	10.1
Nonadecane C ₁₉	n.d	0.78	0.13	0.69	0.15
Eicosane C ₂₀	3.93	1.75	32.3	1.65	53.9
Heneicosane C ₂₁	0.01	0.22	0.95	0.32	0.26
Docosane C ₂₂	0.45	1.99	19.6	1.62	35.1
Tricosane C ₂₃	0.08	0.49	0.17	0.29	0.39
Tetracosane C ₂₄	24.7	2.66	0.82	1.36	20.6
Pentacosane C ₂₅	0.15	0.22	0.15	0.67	0.26
Hexacosane C ₂₆	0.36	2.56	0.17	0.82	11.9
Heptacosane C ₂₇	0.09	0.13	0.07	0.49	0.20
Octacosane C ₂₈	4.36	36.9	0.14	0.32	20.9
Nonacosane C ₂₉	0.18	0.15	0.07	0.94	0.48
Eicontane C ₃₀	3.08	0.29	0.05	19.8	10.2
Henetricontane					
C ₃₁	0.39	0.13	0.49	0.44	0.26
Dotricontane C ₃₂	2.77	0.14	0.43	7.81	3.85
Tricontane C ₃₃	2.94	0.36	0	1.64	0.45
Tetratricontane					
C ₃₄	32.3	4.80	0.25	46.4	39.8
Pentatriacontane					
C ₃₅	4.33	0.07	0	0.49	0.09
Hexatriacontane					
C ₃₆	4.80	0.04	5.71	42.7	13.3
Heptatriacontane		n.d	n.d	n.d	n.d
C ₃₇	10.0				
Octatriacontane		n.d	n.d	n.d	n.d
C ₃₈	12.9				
Nonatriacontane		n.d	n.d	n.d	n.d
C ₃₉	28.1				
ΣTAH	167.9	122.6	144.5	204.3	324.4

Appendix 3: Concentrations of *n*-alkanes ($\mu\text{g/g}$) in core sediment of ST03

Compounds	Layers (cm)				
	0-2.5	2.5-5.0	5.0-7.5	7.5-10.0	10.0-12.5
Undecane C ₁₁	n.d	n.d	n.d	n.d	n.d
Dodacane C ₁₂	n.d	0.01	0.11	n.d	n.d
Tridecane C ₁₃	n.d	n.d	n.d	n.d	0.18
Tetradecane C ₁₄	0.12	0.14	0.17	0.03	0.19
Pentadecane C ₁₅	0.001	n.d	n.d	n.d	n.d
Hexadecane C ₁₆	0.84	1.05	n.d	0.08	n.d
Heptadecane C ₁₇	0.005	0.001	1.71	n.d	n.d
Pristane	0.004	0.01	0.49	n.d	n.d
Octadecane C ₁₈	1.86	2.33	1.25	n.d	n.d
Phytane	0.22	0.33	0.14	0.88	0.37
Nonadecane C ₁₉	0.001	n.d	0.32	0.02	0.14
Eicosane C ₂₀	0.17	1.01	0.23	2.12	0.23
Heneicosane C ₂₁	0.14	0.02	1.31	0.04	0.36
Docosane C ₂₂	1.57	1.94	4.41	2.10	0.37
Tricosane C ₂₃	0.01	0.01	3.00	0.80	0.38
Tetracosane C ₂₄	0.94	0.74	5.98	2.67	1.15
Pentacosane C ₂₅	0.01	0.02	4.43	2.16	1.84
Hexacosane C ₂₆	0.56	0.87	6.33	3.02	3.32
Heptacosane C ₂₇	0.02	0.01	5.02	2.31	4.40
Octacosane C ₂₈	0.33	0.28	4.82	2.39	5.41
Nonacosane C ₂₉	n.d	0.02	3.37	1.61	6.23
Eicontane C ₃₀	0.09	0.26	1.88	0.14	5.77
Henetricontane					
C ₃₁	0.03	0.04	1.09	0.06	0.04
Dotricontane C ₃₂	0.04	0.01	0.28	0.01	0.27
Tricontane C ₃₃	n.d	n.d	n.d	0.02	0.21
Tetratricontane					
C ₃₄	0.07	0.03	0.29	0.01	0.07
Pentatriacontane			n.d		
C ₃₅	0.01	n.d		0.13	2.22
Hexatriacontane			n.d		
C ₃₆	0.42	0.17		0.31	0.07
TAH	8.05	9.34	46.6	20.9	35.5

Appendix 4: Concentration of PAHs in Core Sediments of Sarawak EEZ

Core Sediments Layers (cm)	Compounds														
	Nap	Acpy	Acp	Flu	Phe	Ant	Fluo	Pyr	BaA	Chr	B[b]F	B[k]F	Di[a,h] Ant	B[g] Pyr	∑PAHs
ST01															
0-2.5	6.89	20.2	1.12	0.55	0.35	0.8	0.8	0.82	1.5	1.64	1.87	0.32	-	-	37.1
2.5-5.0	11.6	19.7	-	-	0.62	-	-	-	0.57	0.61	0.52	0.42	-	-	37.4
5.0-7.5	1.24	17.4	5.19	0.89	0.87	0.73	1.29	6.31	0.77	2.93	2.26	16.7	1.71	-	62.7
7.5-10.0	0.76	47.4	23.9	1.43	1.21	5.21	2.77	1.01	7.45	4.78	25.8	2.47	-	-	134.1
10.0-12.5	-	57.6	43	0.92	2.4	1.94	2.16	0.99	1.55	4.18	0.88	24.4	1.52	-	151.4
ST02															
0-2.5	-	8.78	18.9	-	-	-	0.11	4.42	0.06	5.96	1.48	7.85	0.004	0.06	47.2
2.5-5.0	0.03	8.05	0.11	0.22	0.18	1.31	0.11	0.02	0.02	0.36	0.04	0.25	0.09	0.05	13.3
5.0-7.5	-	-	-	2.46	-	-	0.43	0	0.8	16.3	0.33	-	-	-	20.3
7.5-10.0	-	0.19	12.6	-	-	0.05	-	0.77	2.3	-	4.54	-	-	-	20.5
10.0-12.5	-	-	-	-	-	-	1.71	6.07	4.01	10.1	92.1	29.7	7.72	-	151.4
ST03															
0-2.5	-	8.01	7.32	-	-	0.68	9.21	2.14	0.96	1.92	38.9	3.81	-	0.03	72.9
2.5-5.0	-	6.75	4.87	-	-	-	1.02	1.75	0.12	0.26	6.92	1.41	0.92	1.18	25.2
5.0-7.5	-	1.68	-	-	0.06	-	9.56	13.4	1.69	11.8	1.62	0.39	-	-	40.2
7.5-10.0	-	-	0.28	-	-	-	-	-	-	9.9	0.81	0.17	0.21	0.19	11.6
10.0-12.5	-	-	-	-	-	1.07	-	2.21	1.39	19.4	-	-	-	-	24.3

Note: Nap- Naphthalene, Acpy-Acenaphthylene, Acp-Acenaphthene, Flu-Fluorene, Phe-Phenanthrene, Ant-Anthracene, Fluo-Fluoranthene, Pyr- Pyrene, B[a]A-Benzo[a]Anthracene, Chr- Chrysene, B[b]F-Benzo[b]Fluoranthene, B[k]K-Benzo(k)Fluoranthene, Di[a,h]Ant-Dibenz(a,h)Anthracene, B[ghi]P- Benzo(ghi)Perylene