Faculty of Resource Science and Technology

Heavy Metals and Hydrocarbon Distribution Characteristics of Sediments from Batang Sadong of Samarahan Division, Sarawak, Malaysia

Omolayo Ajoke Omorinoye

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Heavy Metals and Hydrocarbon Distribution Characteristics of Sediments from Batang Sadong of Samarahan Division, Sarawak, Malaysia

Omolayo Ajoke Omorinoye

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Signature

Name: Omolayo Ajoke Omorinoye

Matric No.: 15010236

Faculty of Resource Sciences and Technology

Universiti Malaysia Sarawak

Date :

DEDICATION

To God Almighty for his mercies and love. To my loving husband and wonderful children. I would also like to dedicate this thesis to my parents and siblings for their love and encouragement.

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ABSTRACT

Sediments are useful tools in understanding the environmental processes. The physical and chemical characteristics of sediments are dependent on geology, hydrological factors, geochemical influences, human activities and others. Sadong River is a major river catchment in Sarawak and the characteristics of the river sediments can be influenced by natural and anthropogenic factors. The aim of this study was to describe the sedimentological features of the river, and also determine the spatial and vertical distribution of heavy metals as well as the hydrocarbons. The degree of contamination by heavy metals and hydrocarbon compounds in the sediments were assessed. The surface sediments and core sediments with depths between 25 – 45 cm from seven sampling locations along Batang Sadong of Samarahan Division, Sarawak have been studied. The surface and core sediments were subjected to sedimentological analysis to determine the grain size distribution, moisture content, total organic matter (TOM) and ash content. Geochemical analyses were also conducted to determine the heavy metal and hydrocarbon contents in sediments. Heavy metals were extracted by wet digestion using a mixture of HNO_3:HCl (3:1; v/v) and then analysed using atomic absorption spectrophotometer (AAS). Concentration of the eight (8) heavy metals and three (3) major metals in surface sediments were determined. The concentration of heavy metals in surface sediments were ranged 19.2 to 46.61 mg/kg (Zn), 3.45 to 12.30 mg/kg (Cu), 219.59 to 464.75 mg/kg (Mn), 1801.85 to 3447.62 mg/kg (Fe); 3.71 to 18.63 mg/kg (As) and 4.61 to 69.73 mg/kg (Pb). The geoaccumulation index (I_{geo}), contamination factor (CF) and enrichment factor (EF) showed that the surface sediments of Sadong River is unpolluted. Both principal component analysis (PCA) and cluster analysis (CA) showed the heavy metals were mainly derived from lithogenic sources with minimal

input from anthropogenic sources. The concentration of Fe in core sediments was consistent from the upper layer to lower layer for all cores. The concentration of Cu in core sediments was consistent for all samples except for Sungai Buloh (BS3). Distribution pattern of Ni, Zn and Mn varied from the upper to the lower layers of core with a fluctuated pattern. Both aliphatic and aromatic hydrocarbons in the surface and core sediments were analysed using Gas Chromatography-Mass Spectrometry (GC-MS). Domination of *n*-alkanes originated from vascular plants were observed with significance high molecular weight (HMW) *n*-alkanes with odd carbon numbers in the sediments. Data of average chain length (ACL) and carbon preference index (CPI) supported this finding as observed in Sadong Jaya (BS2) and Serian (BS7). Terrigenous aquatic ratio (TAR) showed the importance of terrestial plant over biogenic *n*-alkanes in the sediments. The LMW/HMW (value <1) showed domination of HMW *n*-alkanes in all sediment samples except for Sadong Jaya (BS2) sediment with a value 1.07. The presence of *n*-alkanes in the sediments of Sadong River may be associated with minimal petroleum input through direct deposition into the sediments or indirect ways by land runoff. Assessment of *n*-alkanes in the core sediment showed the hydrocarbons originated from terrestial vascular plants, phytoplankton, algae and petroleum. Sixteen (16) targeted PAHs have been detected in Sadong River sediments with the occurrence of pyrene and fluoranthene which indicated pyrolytic input. The distribution and environmental indices of heavy metals and hydrocarbons showed sediments of Sadong River are unpolluted with heavy metals and hydrocarbons which are derived mainly from natural and minimal input of anthropogenic sources.

Keywords: Batang Sadong, heavy metals, Gas Chromatography-Mass Spectrometry (GC-MS), hydrocarbons, principal component analysis (PCA)

Ciri-ciri Taburan Logam Berat dan Hidrokarbon dalam Enapan dari Batang Sadong di Bahagian Samarahan, Sarawak, Malaysia

ABSTRAK

Enapan merupakan petunjuk yang berguna untuk memahami proses yang berlaku di sekitaran. Ciri-ciri fizikal dan kimia enapan bergantung kepada geologi, hidrologi, pengaruh geokimia, aktiviti manusia dan sebagainya. Batang Sadong adalah salah satu tadahan sungai utama di Sarawak dan ciri-ciri enapan sungai boleh dipengaruhi oleh faktor semulajadi dan antropogenik. Kajian ini bertujuan untuk menerangkan ciri-ciri sedimentologi sungai dan juga menentukan taburan spatial dan vertikal logam berat dan hidrokarbon dalam enapan. Tahap pencemaran logam berat dan hidrokarbon dalam enapam telah dinilai. Enapan permukaan dan enapan teras dengan kedalaman antara 25-45 cm dari tujuh lokasi pensampelan di sepanjang Batang Sadong di Bahagian Samarahan, Sarawak telah dikaji. Analisis terhadap enapan dilakukan bagi menentukan taburan saiz bijian, kandungan kelembapan, jumlah bahan organik dan kandungan abu. Analisis geokimia dilakukan untuk menentukan kandungan logam berat dalam enapan serta analisis hidrokarbon. Logam berat diekstrak secara pencernaan basah menggunakan campuran asid HNO_3:HCl (3:1; isipadu/isipadu) dan seterusnya dianalisis menggunakan spektrofotometer serapan atom. Kepekatan lapan logam berat dan tiga logam utama dalam enapan permukaan telah ditentukan. Kepekatan logam berat dalam enapan permukaan adalah dalam julat 19.2- 46.61 mg/kg (Zn), 3.45-12.30 mg/kg (Cu), 219.59- 464.75 mg/kg (Mn), 1801.85- 3447.62 mg/kg (Fe); 3.71- 18.63 mg/kg (As) dan 4.61- 69.73 mg/kg (Pb). Indek penumpukan geo (I_{geo}), faktor pencemaran dan faktor perkayaan menunjukkan bahawa enapan permukaan Sungai Sadong tidak tercemar. Analisis komponen prinsipal dan analisis gugusan menunjukkan sebahagian besar logam berat adalah dari sumber litogenik dengan input minima dari sumber antropogenik. Kepekatan Fe dalam enapan teras adalah konsisten

dari lapisan permukaan ats ke lapisan bawah untuk semua enapan teras. Kepekatan Cu dalam enapan teras adalah konsisten pada semua enapan teras kecuali dari sampel Sungai Buluh (BS3). Taburan untuk Ni, Zn dan Mn adalah turun naik secara rawak dari lapisan atas ke lapisan bawah teras. Kepekatan Pb dalam enapan teras adalah konsisten dari lapisan atas ke bawah untuk semua enapan teras kecuali sampel Sadong Jaya (BS2). Hidrokarbon alifatik dan aromatik dalam enapan permukaan dan teras telah dianalisis menggunakan Kromatografi Gas-Spektrometri Jisim (KG-SJ). Sebatian n-alkana dari tumbuhan vaskular adalah dominan dengan n-alkana berat molekul tinggi serta nombor karbon ganjil dicerapi dengan ketara dalam enapan. Data purata panjang rantai) dan indek pilihan karbon menunjukan n-alkana dari tumbuhan vaskular adalah dominan terutama sampel Sadong Jaya (BS2) dan Serian (BS7). Nisbah akuatik daratan menunjukkan kepentingan n-alkana dari tumbuhan darat berbanding yang berasal secara biogenik. Nisbah LMW/HMW (nilai <1) menunjukkan n-alkana HMW adalah dominan dalam semua sampel kecuali Sadong Jaya (BS2) dengan nilai 1.07. Kehadiran n-alkana dalam enapan Sungai Sadong menerima input minimum petroleum melalui pengendapan langsung atau secara tidak langsung melalui aliran dari daratan. Penilaian terhadap n-alkana dalam enapan teras menunjukkan hidrokarbon berasal dari tumbuhan vaskular, fitoplankton, rumpair dan petroleum. Enam belas (16) PAHs sasaran dikesan dalam enapan dari Sungai Sadong dengan kehadiran pirena dan fluorantena menunjukkan input pirolitik. Taburan dan indek sekitaran menunjukkan Sungai Sadong tidak tercemar dengan logam berat dan hidrokarbon yang berasal terutamanya dari sumber semulajadi dengan input antropogenik yang minimum.

Kata kunci: *Batang Sadong, logam berat, Kromatografi Gas-Spektrometri Jisim (KG-SJ), hidrokarbon, analisis komponen prinsipal (PCA)*

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
ACL	Average chain length
CA	Cluster analysis
CEFAS	Centre for Environment, Fisheries and Aquatic Science
CF	Contamination factor
CPI	Carbon preference index
DOSM	Department of Statistics Malaysia
EF	Enrichment factor
FRST	Faculty of Resource Science and Technology
GC-MS	Gas Chromatography-Mass spectrometry
GPS	Global positioning system
HMW	High molecular weight
I_{geo}	Geoaccumulation index
LOD	Limit of detection
LOL	Limit of linearity
LOQ	Limit of quantification
LMW	Low molecular weight
MH	Major hydrocarbon
OSPAR	Oslo/Paris convention for the protection of the marine environment of the North-East Atlantic
PAHs	Polycyclic aromatic hydrocarbons
PCA	Principal component analysis

RF	Response factor
TAR	Terrigenous aquatic ratio
TNA	Total normal alkanes
TOM	Total organic matter
UCM	Unresolved Complex Mixture
UNIMAS	Universiti Malaysia Sarawak
USEPA	United States Environmental Protection Agency

CHAPTER 1

INTRODUCTION

1.1 Study Background

Batang Sadong is one of the major rivers in Sarawak located at Asajaya District of Samarahan Division which covers a large area of approximately 4,000 km^2 and the length is approximately 40 km (Bryant, 2003). There has been much interest recently on the geochemical distribution, characteristics and fate of hydrocarbons and heavy metals in the fluvial environment (Boboye & Abumere, 2014; Dhivert et al., 2016; Bhuyan et al., 2017; Krika & Krika, 2017; Brewster et al., 2018). The consequences of population growth, agricultural activities, urbanization and the development of new economic and industrial zones have geochemical effects on rivers and other water bodies (Praveena et al., 2008; Harikumar et al., 2009; Mohiuddin et al., 2010; Tatone et al., 2016). Water environment are categorized as both surface and groundwater bodies. The surface water bodies include rivers, coastal waters, lakes and transitional waters (Maanan et al., 2015). The transitional waters are bodies of surface water at river mouths which are partially saline and often influenced by flows from freshwater. Transitional waters are estuaries, others are rias and coastal lagoons. Rivers can be influenced by direct inflows of surface and groundwater from the land, primarily from small catchments because large rivers discharge into sea via the estuaries. Two main effects of increase in population on the rivers are the increasing demand for water resources and increase in population leads to the increased discharges of sewage effluent to the rivers (Arnell et al., 2015). Rivers are also affected by land use and cover, increased urbanisation and use of biofuels affect river

recharge generation and flow regimes. The greatest effect of land use and the alteration of river flows is on water chemistry (Arnell et al., 2015). Rivers are vulnerable to environmental and ecological changes and continuous advancement and development often leads to several undesirable consequences (Sim et al., 2016). Tropical rivers are mostly characterized with moderately high weathering rates due to elevated water temperature and higher extent of regular floods.

Sediment is defined as layers of relatively finely divided particles found in rivers, streams, lakes, bays, estuaries, oceans and reservoirs. Sediments are generally made up of mixtures containing fine to medium and coarse grained particles. River sediment particles are composed of clay, silt, sand together with organic matter. Sediment concentration and characteristics are the key physical properties of a water body, others are chemical and biological properties in the ecosystems (Arnell et al., 2015; Dalu et al., 2018). Chemical characteristics of a river are subject to the parent constituents disintegrated in the water or accumulated in the sediments. The geochemistry of river sediments is related to several factors such as bedrock geology, climate, topography, drift cover, diverse land use and other human activities (Praveena et al., 2008; Sundararajan et al., 2009; Sundararajan & Natesan, 2010; Yan et al., 2016). Weathering processes release the dissolved and suspended loads in large portion of the significant rivers of the world. Chemical weathering of rocks and soils is part of the essential processes in the geochemical cycling of metals in rivers. Residual products from mechanical and chemical weathering are carried by wind, rivers, streams and ocean as suspended load with a diameter in few microns and the coarser fraction representing the bed load. The metal contents of river are normally controlled by the geology of the area, biological processes and anthropogenic activities (Adekola & Eletta, 2007). Surface sediment is commonly

utilized as indicator for heavy metal and hydrocarbon contamination, while bottom sediments can also give a more profound understanding into the long-term contamination level of river.

The concentrations of chemical species are identified with variances in the mineralogical arrays, the occurrence and examination of sedimentary structures can be utilized to show the accumulation history of terrestrially derived materials and helps to understand the natural effect in river water. River sedimentation can be an active, dynamic process whereby the possibility of industrial effluent contamination is hosted by sediments which are often recycled in the river system, new sediments are transported into the river, while some are moved by river tidal action and river current. Changes that occur in river flow regimes can possibly influence erosion patterns and deposition of sediments inside the estuary and river channels. It is believed that pollutants can cause extensive harm to marine life, human wellbeing and natural resources (Sakari et al., 2008a; Sagheer, 2013).

The source and distribution of hydrocarbon vary in river via terrestial vascular plant wax or marine macroalgae and/or phytoplankton. Others include fluvial input, atmospheric discharge and agricultural runoff (Masood et al., 2016). Aliphatic and polycyclic aromatic hydrocarbons (PAHs) found in river sediments are generally as a result of lateral and atmospheric transportation. Low Molecular Weight (LMW) PAHs are more bioavailable but are less harmful and poisonous, moreover high molecular weights PAHs are less bioavailable but are more carcinogenic and toxic (Sakari et al., 2008b; Sakari et al., 2012).

Hence, this study was focused on the geochemical behaviour of sediments of the Sadong River catchment of Samarahan, Sarawak, Malaysia. This study has been

concentrated on the spatial and vertical distribution of heavy metals and hydrocarbons as well as their environmental consequences.

1.2 Problem Statement

The distribution of heavy metals and hydrocarbon compounds in rivers has recently gained a lot of interest from different scholars in developed countries and developing countries like Malaysia. This is due to the effects of increasing population, chemical weathering of bedrocks, run off from river banks, disposal of industrial and municipal wastes as well as application of pesticides on farmlands. River sediment is a great adsorptive sink for heavy metals and hydrocarbons and the high concentration in sediments can lead to high accumulation in living organisms through the food chain because of their non-degradable nature. The persistence and toxicity of these heavy metals and hydrocarbon compounds can cause health and environmental problems to human and animals. Besides the accumulation into the food chain, heavy metals and hydrocarbons that seep into sediments can contaminate underground water such as boreholes and water wells, as well as harm the consumers of that water. This research entails the heavy metal and hydrocarbon distribution characterisation of sediments from Sadong River, the previous studies in the study area focused on the heavy metals of some rivers in Sarawak (Sim et al., 2016; Chai et al., 2018) and West Malaysia (Abdullah et al., 2015; Elias et al., 2018; Sukri et al., 2018) as well as the peat dome in the Samarahan Division of Sarawak, Malaysia (Zulkifley et al., 2016).

Sadong River is one largest river in Sarawak and land cover and land use change in the study area have enhanced the mobility and accumulation of heavy metals and hydrocarbons in this river. This study provides a baseline data regarding heavy metals and

hydrocarbons composition together with their anthropogenic effects on the river. Seven important locations were investigated in this study. These locations were chosen based on their peculiar environmental, physical, geographical characteristics and the locations are from the upstream to the downstream of the river.

Study of heavy metals and hydrocarbons in both surface and core sediments have been carried out to determine the spatial and vertical distribution of heavy metals and hydrocarbons to provide information of contamination posed by heavy metals and hydrocarbons by indices of contamination. The heavy metal and hydrocarbon contamination in river sediments has become significant because of the integration of toxic heavy metal and hydrocarbons in the food chain which may be harmful to aquatic biota and human consumers thereby making the investigation of heavy metals and hydrocarbons in sediment of a great significance (Yan et al., 2016; Parween et al., 2017; Patel et al., 2018). The frequency of natural and anthropogenic activities and the discharge of heavy metals and hydrocarbons into rivers can make contamination ubiquitous in the river (Shen et al., 2019). The dissolved heavy metals in river can also play a vital role for natural purification of river (Nargis et al., 2018). This study was conducted in order to measure the concentration levels of the selected heavy metals and hydrocarbon compounds in Sadong River sediment and to evaluate the pollution status of river sediment based on geoaccumulation index (Igeo) and enrichment factor (EF). Therefore, it is essential to determine the concentration, distribution, effects and sources of heavy metals and hydrocarbons in Sadong River to protect human wellbeing and the preservation of the natural environment.

1.3 Objectives of the Study

The main objective of this study was to generate a baseline data in respect of the geochemical characterization of sediments of the Sadong River. This work was aimed to identify the geochemistry of sediments at major catchments and to understand the causes of geochemical fluctuations. The determination of the distribution of heavy metals and hydrocarbons in sediments of Sadong River and evaluation of their concentrations with possible contamination levels. Consequently, delineating the effects of natural controls and collective anthropogenic impacts on the river basin.

Therefore, the objectives of this study were to:

a) characterize the sedimentological features of the river sediment,

b) determine and quantify the spatial and vertical distributions of heavy metals, aliphatic hydrocarbons and aromatic hydrocarbons in sediments,

c) assess the degree of contamination by heavy metals and hydrocarbon compounds in the sediments using indices of contamination and

d) delineate the relationship between geogenic and anthropogenic variables using statistical analysis.

1.4 Chapter Summary

This chapter has provided the general introduction about the occurrence of heavy metals and hydrocarbons in river sediments. It serves as an overview on the different factors that control sediment deposition, sediment dispersal and their geochemical characteristics. The objective of the research has been clearly stated in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Geological Setting of Batang Sadong Basin

The Batang Sadong Basin is part of the Borneo Basin of southeast Asia, it is surrounded by plate boundaries, arc systems and marginal ocean basins (Fuller et al., 1999; Nagarajan et al., 2014). The Batang Sadong Basin is dominated by Cretaceous Eocene age sediments and the sedimentary deposits comprise siliclastic rocks such as sandstone, shale and siltstone (Hutchinson, 2005; Nagarajan et al., 2014).

2.1.1 Batang Sadong Basin

Batang Sadong in Malay language, means Sadong River and this river covers an enormous region of the Samarahan Division, Sarawak, Malaysia. The land area covered by Batang Sadong is 4,000 km^2 situated between longitudes 1° 14' 0.012" and 1° 34' 0.012" North and latitudes 110° 38.09'.5" and 110° 45' 0" East. The size is 4.8 km wide and about 82.1 km long (Bryant, 2003). This river covers a huge region from Serian District to the Samarahan-Asajaya District of Sarawak and flows enormously through the Sadong Basin at the Southern part of Sarawak. The river is located in the northwestern part of Borneo Island and it serves as the principal source of water to encompassing community. The significant contribution of fresh water is received from the upland area, at sediments are transported at a few metres and then the river meanders towards the path flowing into the estuary and afterward discharges into the South China Sea.

The environment of the Sadong River has several economic activities such as farming, fishing, peat swamps, deserted coal mining site, boat docks and tourist spots. About 20 km upstream of this river, it bifurcates towards the east at Simunjan where coal has been mined in the 19th to 20th century around an isolated mountain (Bryant, 2003). In recent times, coastal and estuary pollution have become a global crisis in the natural ecosystem. There is a lot of activities around the banks of the river in some areas with the Sungai Buloh Bridge which is the longest bridge (1.48 km long) crossing the Sadong River is located in this study area. The river environment is greatly affected by increase in population, industrialization and urbanization (Babek et al., 2015; Dhivert et al., 2015).

Geochemical studies and fluvial geomorphology reveal that rivers are sensitive to climatic conditions, changes in sediment transport and delivery of sediments which are often more intense than changes in the hydrological system (Arnell et al., 2015; Syvitski et al., 2015). There has been an increased rate of soil disintegration and sediment delivery due to the recurrence of intense rainfall in Sadong River. The soils present in the study area are formed from weathered rocks and developed over time representing the mineral and elemental composition of the parent materials and minor alterations (Scott, 1985; Padmanabhan et al., 2013). It is proposed that on an annual basis, the suspended sediment load may have significantly increased after development began in the drainage basin (Staub et al., 2000; Staub & Esterle, 1993).

The vertical flux of particulate materials in aquatic ecosystems transport organic matters and chemical substances from surface layers to the bottom layers of river sediments. Sediments serve as traps and have been extensively for the determination of the downward flux of suspended particles and particles bound to metals in various river systems (Tatone et al., 2016).

2.1.2 Physiographic Setting of Sadong River

The Sadong River basin has experienced extensive change in land use from the twentieth century due to increase in population, expansion of agricultural activities and industrialization. It is characterised by a shallow, gentle and bioturbated to a deep, fast and turbid river system (Bryant, 2003).

Agriculture is one of the major activities in vicinity of Sadong River such as rice farming and oil palm plantation which can be observed in some localities near to this river. The environs of the Sadong River are known for agricultural and economic activities such as oil palm plantation, mangrove swamps, fishing, tourism spots and peat swamps. This may lead to a non-point source of pollutants due to the use of pesticides because chemical compounds such as nutrients and salts can be localized depending on the volume and frequency of the use of pesticides.

2.1.3 Geomorphology of Sadong River Basin

Sarawak has an equatorial rainforest type of climate without distinct monsoon season. The Samarahan District has a generally flat topography with isolated hills in the floodplains of the Sadong River which makes them frequently inclined to high flooding. Rainfall leading to precipitation varies from around 3000 to more than 5500 mm annually (DOSM, 2012), thus the land is endowed with immense vegetative development, various perennial streams and large waterway. Over one-quarter of Sarawak as shown in Figure 2.1 is covered with alluvial coastal plains and low-lying peat swamps (Lim & Lye, 2003; Staub et al., 2007). The tropical vegetation provides biomass to accumulating sediments. The riparian vegetation which is composed of water-fed mangroves and Nypa covers the distal

region as shown in Table 2.1. The proximal area is comprised of dipterocarp forests and cultivated lands (Anderson, 1964;1983; Anderson & Muller, 1975; Esterle & Ferm, 1994).

Table 2.1: The geomorphology of Sarawak (Liechti et al., 1960; Tongkul, 1996)

Relief	Zones	Topographic features
Alluvial Coastal	Kuching, Sri Aman, Sarikei and Sibu	Peat soil, few drainage, mangrove, nypa and other swamp forest and tidal inundation
Mountainous	Northern Sarawak	Thick forest and very well dissected by fast flowing rivers with numerous rapids
Undulating Interior	East and Central Sarawak	Moderately rugged terrains dissected by fast flowing rivers bordering the interior mountainous region

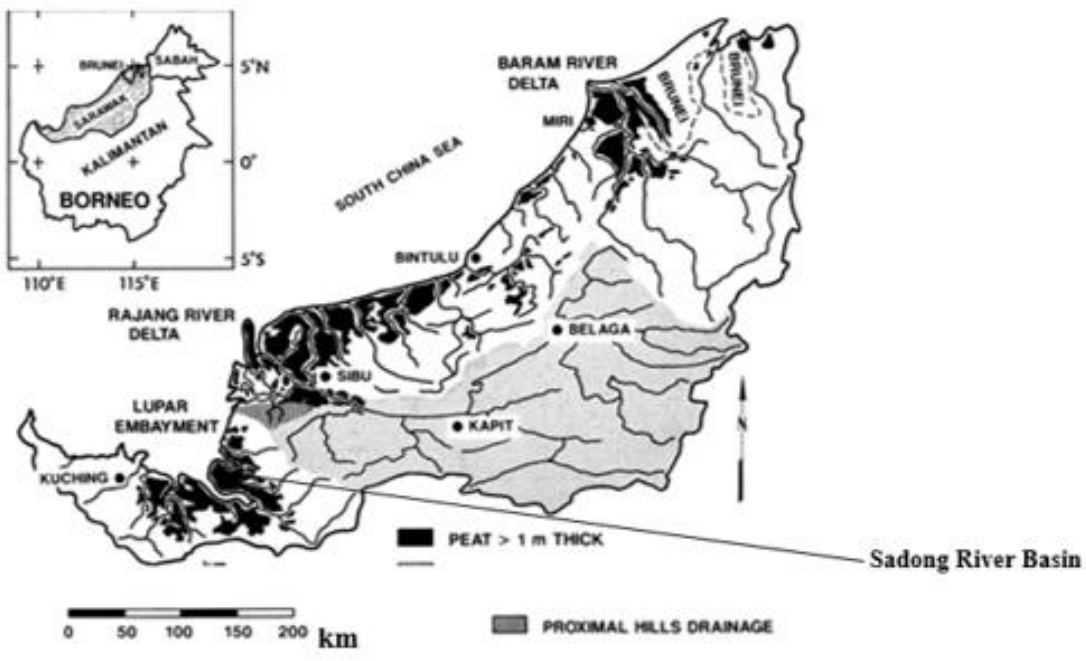


Figure 2.1: Map of Sarawak showing the Sadong River Basin (Staub et al., 2000)

Generally, the ground water level in the western part of the Samarahan-Asajaya area are about 0.2 - 0.5 m below ground surface, while the rivers have greater depths ranging from 0.5 - 2.0 m (Zulkifley et al., 2015). The surface of the river sediments near the shore are made up of woody materials such as tree logs, bark, broken branches and roots whereas the onshore top layer is composed of fine grained particles. The tidal currents and surface waves most often have an important role in sediment dispersal and deposition in the tide controlled systems (Harris et al., 1993) however, seasonal fluctuation in discharge is sometimes the most significant factor. Tides along the Sarawak coast are influenced by the shallowing and widening of the shelf (Staub et al., 2000).

The physical and chemical characteristics of river sediments of Sadong Basin are sometimes different from those of inland and peat soil. In places where seasonal discharge varies, processes in the estuary may dominate the delta plain up to year. The features of estuary maybe present in tide-dominated deltas and this process is common in regions where seasonal changes in river discharge is extremely high, mostly found in monsoon impacted Southeast part of Asia (Galloway, 1975; Staub et al., 2000).

2.1.4 Geological Aspects of Sadong River

The geology of the Sadong River basin is not complex, it is made of the basement rocks and sedimentary rocks. There is a mosaic of sedimentary rocks and volcanic rocks together with tertiary alluvial sediments (Hutchison, 2005). Sarawak host sedimentary deposits comprised mainly of siliciclastic rocks such as siltstone, sandstone and shale (Nagarajan et al., 2014). The structural development of the Borneo is believed to be formed by the tectonic collision of the northern Luconia microcontinental block into the Borneo Basement originating from the West which used to be part of the southern Sundaland

(Madon, 1999; Hutchison, 2005). The main constituents of most sediments are inorganic mineral materials, crustal rock like the basement rocks and sedimentary rocks are the primary sources of these mineral components. The rate of the rock weathering is strongly dependent on the stability and solubility of the constituent minerals (Andrews et al., 2013). There is an extensive peat/coal deposit and siliciclastic sediment dominated fluvial-deltaic system in the river basin since ancient times (Anderson, 1964; Cecil, 1990).

There are two types of sedimentary facies found in this study area which are the peat deposits and the floodplain deposits. The estuarine and deltaic sediments are overlain by these two sedimentary facies (Zulkifley et al., 2015). The geology of Sarawak is closely associated and linked to the tectonic development of the South China Sea Basin (Liechti et al., 1960; Rijks, 1981; Tongkul, 1996; Manoj et al., 2014). The basin is underlain by more than 12 km of carbonate and siliciclastic sediments which are Tertiary in age (Madon et al., 2013). It is divided into various stratigraphic provinces (Hutchison, 1996; Peng et al., 2004; Hutchinson, 2005).

Sarawak has four geological zones based on its historical development, these zones include Miri zone, Sibu zone, Kuching zone and West Borneo Basement (Hutchison, 1989). The Sadong River Basin lies within the Kuching zone.

a) The Miri zone is situated far north, dominated by shallow marine shelf sediments overlying older continental crust. It is represented by richly fossiliferous shallow marine limestone bodies. The boundary between the Miri zone and Sibu zone is Tatau-Mersing Line (Hutchison, 1989).

b) The Sibu zone is situated in the central part of Sarawak dominated by thick shale-sandstone turbidite sequences deposited above the oceanic crust. Uplift of the rocks occurred in Late to Middle Eocene (Hutchison, 2005). The oldest formation in the

Sibu zone is the Balaga Formation which is overlain by the Rajang group made up of deep marine turbidites. The boundary between the Sibu zone and Kuching zone is the Lupar Line.

c) The Kuching zone is situated at the southwestern part of Sarawak comprised of Jurassic to Cretaceous shelf deposits, related non-marine deposits and molasses on the edge of the West Borneo Basement Complex (Hutchison, 2005).

d) The West Borneo Basement is situated in the far south zone composed primarily of Carboniferous to Permian basement rocks intruded by Cretaceous and plutonic rocks (Madon 1999; Madon et al., 1999).

The major soil group in the study area is peat where the peat deposit within the study area were classified according to physical, chemical and physicochemical properties. Peat formation is primarily influenced by geological, climatic, environmental and biological factors and these processes are with respect to time. The continental crust was exposed to the atmosphere, making it vulnerable to physical, biological and chemical processes. These processes are important because physical, biological and chemical changes increase the surface area of rock and soil exposed to the various agents of chemical weathering (Staub & Esterle, 1993). Some of these reactions on rocks and soils are catalysed by bacteria called biological weathering. Most weathering reactions occur in soil organic matter which leads to the oxidation of soil organic matter causing acidity of natural waters. The peat deposit in this study area are fibric, hemic, hemic to sapric and sapric which have been identified according to their fiber content. They have different colours which include dark grey, grey, to dark brown colour with a distinctive odour (Zulkifley et al., 2016). The distribution of peat deposit in Sarawak is extensive covering about 1.66 million hectares (Anderson, 1983; Esterle & Ferm, 1994; Paramananthan, 2011). Generally,

peat deposits are commonly considered to be partially decayed biomass/organic matter. Tropical peats are usually composed of undecomposed and partially deteriorated logs, branches and/or twigs (Zulkifley et al., 2015).

The climate, landforms, local geology and hydrogeology create an anaerobic condition which are suitable for peat formation such as marsh, swamp, bog or mire. Sedimentary organic matter can originate near the site of deposition or at the site of deposition (autochthonous), organic matter can also be transported from another environment (allochthonous). These autochthonous inputs include the remains of phytoplankton and organisms that feed constantly or partially on phytoplankton (Killops & Killops, 2013). These phytoplankton (zooplankton and other microscopic organisms) live inside the water column and upper layers of river sediment. The allochthonous organic material are mostly derived from higher plants, usually transported by water from surrounding portion of land to the deposition site (Zulkifley et al., 2016).

2.1.5 Sedimentary Depositional Environment of Sadong River

Sediments accumulate in a wide variety of environments, both on the continents and in the oceans. It is believed that the distributary channels and rivers transport and deposit siliciclastic sediments originating from the upland drainage basins to delta, floodplain and coastal environments. However most of this sediment are delivered into the South China Sea (Staub & Esterle, 1993). The seasonal variation in release of sediment is the primary source of siliciclastic sediment dispersal in the Sadong river. During the dry season, the quantity of sediment transported to the delta plain originating from the drainage basin are stored on the delta plain with low to moderate discharge intervals. While during

wet season, the intervals of high discharge causes most of this sediment to be moved away from the shores (Staub et al., 2000).

Sadong River is characterized by the fluvial, shallow marine coastal plain and tidal flat depositional system. Coastal zones and estuaries are the fundamental channels between land (terrestial) and ocean (Masood et al., 2016). Estuaries are affected by influences of physical, chemical and biological processes trapping huge amount from natural and anthropogenic constituents (Liu et al., 2012a; 2012b; Shan et al., 2013). The organic matter derived from land can be transported to river systems by atmospheric deposition and river discharge (Keil et al., 1994; 1997; Masood et al., 2016).

2.1.5.1 Fluvial Environment

The primary route of sediment derived from weathering on the landmass reaching the ocean are through the rivers. River sediment includes dissolved material, colloids and particulate material (Staub et al., 1993). The vast majority of the sediments are transported to the ocean, while a specific lesser percentage is either deposited within the rivers transporting the sediments or interior drainage basins where the rivers end. The storage of the transported sediment is temporary because it is eventually remobilized in a later geologic cycle. The sediment is commonly stored for a long geological time about a huge number of years ranging between tens to millions of years and often sometimes billions of years. This duration is sufficient for the sediment to be deeply buried then lithified and may become metamorphosed.

Generally, rivers are enormously varied in size, dynamics and geometry, sediments and chemical characteristics (Lewis, 1984). Meandering rivers have simple description or characterization in respect to their physical features whereas braided rivers are much more

variable and complex. Straight rivers are not very common, most rivers are either meandering or braided, the former is evident in Sadong River. It is mainly a meandering river and its geomorphology is crucial to understand and interpret the characteristics of the sediments in this river. The meandering features show many similarity, which suggests that the sedimentological behaviour of this river is not complex. The geomorphology of the river is the array of overbank areas, channels and changes with time during gradual build-up of the floodplain. It was possible to study the sediment movement and deposition in the river as well as the vertical sequence of river sediments because of the gentle and distinct water-table (Omorinoye et al., 2019b).

Large rivers like Sadong River are fluvial rivers consisting of a floodplain composed of sediments which are formed by different processes as shown in Table 2.2. Its alluvial valley fill may become thicker with time. The two processes conducive for deposition of sediments in rivers are crustal subsidence and progradation. Progradation is a process where river flows to the land and sediment is delivered to the ocean, the mouth of this river build up towards the ocean. Due to the longitudinal profile of this river which is anchored by base level of the river at the mouth. The implication is that there was a slight uplifting in the deepest reach of this river, even up to a hundred meters of sediment. Moreover, crustal subsidence results to thick succession of the fluvial sediments to decline in the crust beneath the river. This progression along the river causes development of a little expansion of flow, lower velocity of flow and movement of sediment, leading to sediment storage along the river (Lewis, 1984). Whenever the sediment load that accumulates into a region of the river bed is higher than what is transported out, sediment is accumulated in that region and causes the build-up of bed thereby maintaining its longitudinal profile.

Table 2.2: Classification of the sedimentary depositional environments and sediment types (Galloway, 1975)

Environment	Transport processes	Depositional environments	Sediment types
Terrestrial Environments			
Alluvial	Gravity	Steep-sided valleys	Coarse angular fragments
Fluvial	Moving water	Streams	Gravel, sand, silt, and organic matter*
Marine Environments			
Deltaic	Moving water	Deltas	Sand, silt, clay, and organic matter*
Tidal	Tidal currents	Tidal flats	Silt, clay
Shallow water marine	Waves and tidal currents	Shelves and slopes, lagoons	Carbonates (in tropical climates); sand/silt/clay (elsewhere)
Deep water marine	Ocean currents	Deep-ocean abyssal plains	Clay, carbonate mud, silica mud

* Organic matter: only accumulates in swampy parts of these environments.

2.1.5.2 Floodplain Sediments

The flood plain deposits found in Sadong River basin are observed to be overlain by some peat deposits. This sediment consists of predominantly of clays, silts and minimal to abundant organic matter which is plant remains and are usually characterised by woody fragments. The floodplain sediments are closely overlain by the estuarine/deltaic sediments.

2.1.5.3 Tidal Flat Sediments

The siliciclastic sediments preserved in the delta plain are formed by the depositional process in the estuary that occurred during interval of dry season or reduced rainfall within April to November (Staub et al., 2000). This type of sediment occurred on open coasts with low relief, generally reduced energy and in likely protected regions of high-energy associated with estuaries. The necessary conditions for formation of tidal flats

include a viable tidal range and the absence of strong wave-induced currents. Animals and plants have an important role in tidal-flat environments. Plants and animals are mostly influential in sediment trapping, formation of faecal pellets with sediment particles, and generation of biogenic sedimentary structures due to the processes of feeding, habitat and movement.

Tidal flats that emerged from progradational conditions, as found in shallowing upward cycles in carbonates, are characterized by a succession of sediments fining-upward, comprised of coarse sediments at the base of the environment and progressively finer sediments toward the upper layer in a continuous vertical sequence. The sediments are usually deposited at further depths and are believed to be marine origin (Lam, 1988). This relationship is commonly reflected in reducing energy of a transition from subtidal to intertidal parts in the tidal flat environments.

Some sedimentary structures are peculiar of tidal flat environments such as thin lamination and desiccation cracks which are absent in this river and are commonly disrupted by bioturbation, microbial laminites and with or without fenestrae due to the exclusion of grazing shelled organism like snails in the tidal zone, microbial communities in this environment are allowed to flourish and form some intraclasts. Less than 0.1 % of the metals in the hydrological cycle are dissolved in the column of water and more than 99.9 % can be accumulated in river sediments and soils (Salomons, 1997).

2.1.5.4 Estuarine Sediments

Estuarine processes have a significant role in the distribution and fate of contaminants (Masood et al., 2016). These sediments are mainly clay minerals and organic matter. Fine grained clay minerals found in the estuary are the most abundant inorganic

colloids and particulate in river waters (Nagarajan et al., 2014). Estuaries have been filled with sediments from continental shelves for thousands of years. The gradients of chemical constituents in estuaries are very steep and localized to the earliest stage of mixing. However, unidirectional flow of rivers is replaced by reversing tidal flows in estuaries. Water velocity drops at high and low tides, thereby allowing a large amount of fine grained suspended sediments to sink and deposit. Estuaries are regarded as temporary features on the geological timescale. Estuaries are important traps for riverine particulate matter in recent time (Andrews et al., 2013). Sedimentation in estuaries is localized to region of low salinity by physical and chemical processes. The sediments are continuously re-suspended by tidal currents. The high concentration of particulate causes water turbidity leading to phytoplankton growth. Similar processes give rise to the concentration of sediments and particulate organic matter in estuaries.

During the residence time of estuarine sediments, the anthropogenic compounds derived from atmospheric and terrestial sources are subjected to biogeochemical processes that ultimately determined their dispersal and fate of the contaminants in the river (Masood et al., 2016) The nature of the organic component deposited in sediments is dependent on the kinds of living organisms contributing to the sediments (Killops & Killops, 2013). High primary productivity allows relatively larger amount of organic matter to reach and be incorporated into the sediments. This prevents them from being reworked or recycled within the water column. The water velocities are low enough in depositional environments are low enough for fine grained organic rich matter to accumulate instead of being washed away (Hart, 1995). The steady inputs of inorganic material are minimal thereby preventing the dilution of organic matter.

2.2 Sedimentological Characteristics of River Sediments

Sedimentology has become significant in environmental research particularly environmental pollution studies of rivers (Kashani et al., 2016). The past environmental processes as shown in Figure 2.2 can be combined with geochemical data on current conditions to predict possible future fluctuations. Frequent variation due to seasonal changes in river discharge is the primary control on siliclastic sediment dispersal pattern (Staub et al., 2000). This is useful in evaluating the impact of major processes on the transportation, accumulation, deposition, alteration of contaminants in fluvial and estuarine environment to create concise environmental management plans.

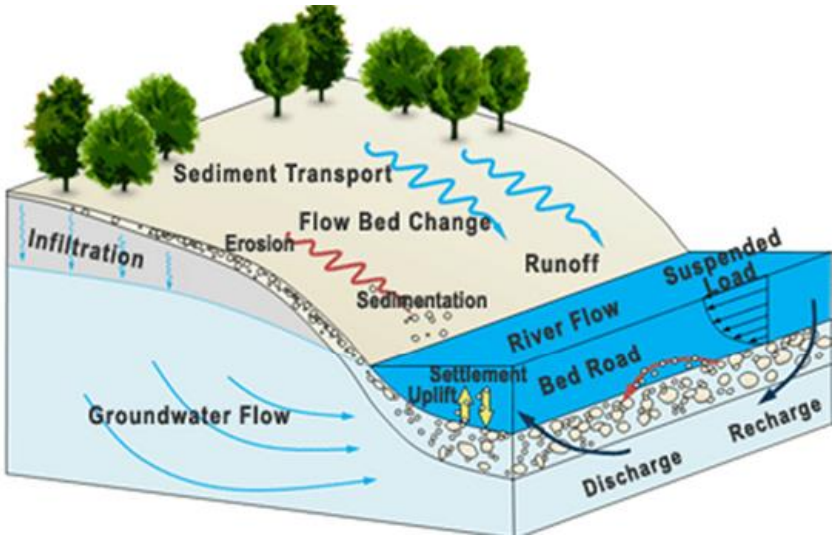


Figure 2.2: Sediment transport in a river system (Negrel and Petelet-Giraud, 2012)

Sediments in rivers and soils have a high storage capacity for contaminants because of their small surface area. Sediments are a mixture of several components comprised of different mineral species and organic debris (Abdullah et al., 2015). Therefore, both surface and core sediment samples are very valuable in geochemical

investigations of rivers. The surface sediments are uppermost layer of sediments in a river whereas the core sediments are layers of sediments from the topmost layer to the bottom depending on the length and diameter of the core are discrete vertical grab samples. The sediment core analysis is of great interest because the sediments at the bottom of rivers are the parent materials which have sank into the water body over time (Sundararajan & Srinivasalu, 2010).

Sediments are made up of mixtures containing fine, medium and coarse-grained sediment particles (Postma, 1960; Oyeyiola et al., 2011). These particles are composed of clay, silt, sand, mud and organic matter, the pore spaces may be filled with pure mineral element or plant and animal remains. Sediments act as traps and are important as sinks for heavy metals which are derived from a wide range of sources, the top samples between 0-5 cm are believed to represent recent input (Maanan, 2007; 2008).

Table 2.3: Particle size classification of sediments according to Folk (1957)

Nomenclature	Sediment Type	Particle Size
Gravel	Boulder	>256 mm
	Cobble	256-2 mm
	Pebble	64-2 mm
Sand	Sand	2-0.062 mm
Mud	Silt	0.062-0.0039 mm
	Clay	<0.0039 mm

Heavy metals usually have high concentrations at the surface and enriched in bottom sediments. Sediments are deposited by runoff by water, dissolved air, transfer of

glaciers from terrestrial environment and gradually form a bed of layers of sediments on the floor of a river, lake or ocean (Pekey, 2006; Maanan et al., 2013).

2.3 Geochemistry of Heavy Metals in River Sediments

Heavy metals are also known as trace elements which exist naturally in the ecosystem. The term heavy metals refer to any element with an atomic number of 21 or higher and these include transition metals, actinides, lanthanides and metalloids such as arsenic and antimony. Heavy metals have metallic properties which are mostly related to environmental pollutants that cause water, air, sediment and soil contamination (Maanan et al., 2015). Many heavy metals are toxic because toxic heavy metals are non-biodegradable. Nevertheless, there are some heavy metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe) and zinc (Zn) lack notable poisonous properties and are essential for metabolic functions of many living organisms (Karbassi & Amirnezhad, 2004; Chibunda et al., 2010). Geochemical studies of surface sediment and sediment from cores are useful in the evaluation of environmental pollution (Holm, 1988; Geetha et al., 2008; Al-Juboury, 2009; Chibunda, 2009; Ahmad et al., 2010) due to fluctuations in climatic conditions (Faganelli et al., 1987; Karbassi & Shankar 2005), accumulation and mobilization of heavy metals in the sediments of aquatic environment (Al-Masri et al., 2002).

The composition of sediments in the rivers can be influenced by the deposition of terrestrial materials due to erosion caused by the frequent rainfall. The contamination of river sediments by heavy metals has become a prevalent issue due to the increase in human population and agricultural activities (Yoo et al., 2013). River sediments can be polluted by heavy metals by human activities such as transportation (ships), economic activities (fishing, oil palm plantation and rice plantation) and sewage discharge into the river.

The physical and chemical characteristics of river sediments are distinct from those of inland soil (Walling et al., 2003). The soils present in this study area were formed from weathering of rocks and are developed over time representing the mineral constituent of the parent materials and minor alterations (Padmanabhan et al., 2013). River sediments have huge amount of fine grained particles such as clay, silt and high alkalinity values (Yoo et al., 2013). These unique features of river sediments directly affect the mobility of heavy metals in rivers. The vertical flux of particulate material in aquatic ecosystems transport organic matter and chemical substances from surface layers to the bottom layers of sediments. The major metals are stored in sediments and are usually retained in the sediments. Sediments serve as traps and can be used to determine the accumulation history of suspended and colloidal particles bound to metals in different river systems (Tatone et al., 2016).

Chemical properties of a river are influenced by dissolution of materials in the river, the heavy metals in sediments are influenced by factors such as bedrock geology, land use, drift cover, topography and climate (Praveena et al., 2008; Sundararajan & Natesan, 2010). Weathering processes initiated the dissolved and suspended loads in most of the major rivers of the world. Chemical weathering of rocks and soils is one of the essential process in the geochemical cycling of metals in rivers. The products from chemical and mechanical weathering are then carried via the rivers to the ocean as suspended load of fine grained sediments and the coarser fraction representing the bed load. The combination of organic matter in sediments with heavy metals form stable organo metallic complexes which are very stable and subsequently released into river sediments through several processes such as adsorption, ion exchange, complexation and mineral precipitation (Sundararajan & Srinivasalu, 2010).

Frequent floods, storms and forest fires could result in severe health effects because heavy metals are indestructible having toxic effects on living organisms when these heavy metals exceed the acceptable limit (Nobi et al., 2010). This river is biologically active and receives considerable amount of heavy metals input from municipal sources and agricultural activities. Sedimentation rate is gentle along many localities, the dynamic process in which the possibility of contamination is hosted by sediments which are often recycled in the river system. Fresh sediments are delivered into the rivers while others are moved away by river current and tidal action (Omorinoye et al., 2019b). Fluctuations in river flow regimes can influence erosion patterns and deposition of sediments within the river channels and estuaries. Pollutants can cause extensive harm to human health, aquatic life and natural resources (Sakari et al., 2008b; Sagheer, 2013;).

Sediments can accumulate and incorporate many metals into a body of natural water. Trace metals accumulate in the sediments and can be directly accessible to benthic fauna or discharged to the water column of the river through sediment suspension (Pekey et al., 2004). Sediments act as carriers and potential sources of pollution because heavy minerals are not permanently fixed by these sediments and heavy metals can be released back to the water column by fluctuations in environmental conditions. Due to their variable physical and chemical characteristics, sediments can be hosts, sinks and sources of contaminants in river basins (Rainey et al., 2003; Marchand et al., 2006; Priju & Narayana, 2007; Praveena et al., 2008; Sundararajan et al., 2009; Sundararajan & Natesan, 2010). It is believed that the fluvial geochemistry of world rivers in both geologically stable and tectonically dynamic systems is dominated by the instant weathering of inorganic and biogenic carbonates. The evaporation and the continuous disintegration of sedimentary aluminous silicate rocks, sandstones, shales and with minimal contributions from primary

basement formations influence river geochemistry (Meybeck, 1986; Berner & Berner, 1987). There is also a close relationship between weathering of rocks and salinity of water. Thus, the sampling and analyses of the sediments are useful in environmental monitoring (Mondal & Sharma, 2008).

The geochemical variations in rivers globally are significantly controlled by dissolved loads, trapped or suspended sediments and accumulated nutrients (Syvitski et al., 2005; Walling, 2006; Li et al., 2007). During sediment transport, the heavy metals experience various changes in their speciation due to dissolution, adsorption, precipitation and complexation processes (Akcay et al., 2003; Abdel-Ghani et al., 2007; Abdel-Ghani & Elchaghaby, 2007; Praveena et al., 2008; Harikumar et al., 2009; Mohiuddin et al., 2010; Tatone et al., 2016) which influence their behaviour and bioavailability. In the basin scale, spatial dispersals of the sedimentary contamination of metallic pollutants are to a great extent constrained by the settling capacity of 63 μm sized fine-grained sediments (Walling et al., 2003). However, before the increased population and rapid industrial development, Sadong river basin has provided an estimation of about 15 million tonnes (MT) of sediment annually to this river delta (Staub & Esterle 1994; Omorinoye et al., 2019b).

The heavy metals present in river are derived from multiple sources, such as lithological, atmospheric, anthropogenic and biological (Gupta et al., 2011). The distribution of heavy metals inside the diverse physicochemical phases found in river sediments provide an insight into their mobility, accumulation and fate within the environment. Distribution of metals (Cu, Al, As, Fe, Cd, Co, Cr, Pb, Ni and Zn) are often considered as markers for anthropogenic pollution (Maanan et al., 2014; Muralidharan & Ramasamy, 2014). Increased alkalinity and buffering limit of river sediments may require large amount of acids to extract heavy metals (Chand & Prasad, 2013).

2.3.1 Sources of Heavy Metals in River Sediments

Heavy metals can occur naturally in rivers and their concentration can be increased significantly in natural rivers due to industrial activities. Heavy metals may originate from both natural processes and anthropogenic activities. Table 2.4 listed several sources of heavy metals in the river sediments such as geological, biological, geochemical and human or anthropogenic sources. Common natural sources include geological weathering, wind-blown dusts, eroded soils and sediments which deposited large amounts of solid material into the river (Scott, 1985; Shen et al., 2019).

Apart from geological sources, living things assume a significant role in the exchange of gases inside the atmosphere and hydrosphere. Extreme processes such as climate change, environmental events such as storms, floods, avalanches, landslides, forest fires, earthquakes, volcanoes and tsunamis release enormous quantities of heavy metals. The anthropogenic activities are the major cause of heavy metal pollution in the river such as industrial discharges, vehicular exhaust, mining, atmospheric precipitation and agricultural cultivation (Keshavarzi et al., 2015; Liu et al., 2018). Heavy metals are derived from surface runoff from urban areas, agricultural runoff from farmland, groundwater dissolution from sediment, wastewater irrigation, excessive application of fertilizers and pesticides on farmlands, municipal and industrial wastes, mining, smelting and combustion of fossil fuels (Cengiz et al., 2017; Patel et al., 2018).

2.3.2 Heavy Metals in Malaysian River Sediments

Studies have been carried out on the heavy metals concentration in major rivers in Malaysia such as Kelantan River (Pooveneswary et al., 2020), Balok River in Pahang (Abdullah et al., 2015), Baleh River (Chai et al., 2018), Linggi River (Elias et al., 2018)

and Terengganu River (Sukri et al., 2018). These studies indicated occurrence of Cu, Ni and Zn which were derived from natural and anthropogenic sources. The average concentrations of Fe, Co, Cr, Cu, Mn, Ni, Zn, Cd and Pb in Balok River sediments were significantly higher compared to the background levels (Abdullah et al., 2015). Among the heavy metals determined in surface sediments of Pinang River, Cd, Cr, Zn and Pb concentrations were significantly elevated and might pose a threat to the aquatic ecosystem (Ong et al., 2016). The multivariate analysis indicated moderately to highly polluted levels of heavy metals in Pinang River, Penang Malaysia (Ong et al., 2016). The findings of the study of heavy metal contamination in sediments of Baleh River were low risk. The concentrations of heavy metals detected in Baleh River, Sarawak were within the permissible guidelines (Chai et al., 2018). The source analysis of Pb, Zn and Cu concentrations in sediments of Perak River were mainly due to natural sources while anthropogenic activities contributed to the higher concentration of Fe and Cd in surface sediments of Perak River (Salam et al., 2019). In Kelantan River, the overall concentrations of heavy metals sediments nearshore were high. The sediments of the nearshore of the river was extremely enriched with Cd, significant to very high enrichment for Pb, Moderate to significant enrichment for Mn, Cu, Zn, As and moderate to minimal enrichment for Ni and Cr (Pooveneswary et al., 2020).

Table 2.4: The sources and effects of some heavy metals found in natural water (Monisha et al., 2014)

Metal	Sources	Effects
Arsenic (As)	Natural: Weathering and volcanism Anthropogenic-Mining, chemical waste	Toxic and carcinogenic to human and animals
Cobalt (Co)	Natural: rocks, soil and plants Anthropogenic: combustion of fuel, Mining, industrial waste	Toxic to plants and algae at high levels
Copper (Cu)	Natural: dark leafy plants, shell fish Anthropogenic: Metal plating, electrical manufacturing, agro-chemicals, Mining, industrial waste	Toxic to plants and algae at high levels
Iron (Fe)	Natural: rocks, soils, leguminous plants Anthropogenic: Mining, Steel production, Fuels, industrial waste	Damage fixtures by staining, corrosion of water pipes
Lead (Pb)	Natural: Earth crust Anthropogenic: Metal plating, Mining, combustion of fuel, paints, batteries, industrial waste	Harmful to human and wildlife
Manganese (Mn)	Natural: microbial action Anthropogenic: Metal plating, Mining, industrial waste	Toxic to plants
Nickel (Ni)	Natural: Weathering, vegetation, wind-blown dust Anthropogenic: Metal plating, Mining, combustion of fuel, industrial waste	Toxic to plants and algae at high levels
Zinc (Zn)	Natural: Earth crust Anthropogenic: Metal extraction and production, Mining, industrial waste	Toxic to plants at high level

The water chemistry of river depends on weathering of mineral, precipitation, evaporation and crystallization processes (Gibbs, 1970). The product of different forms of weathering include river sediments or residue on land as soil (Singh et al., 2005). Chemical weathering occurs as a result of the physical erosion of rocks, transport in fluvial environment and sediment recycling (Nesbitt & Young, 1996). The mineralogical and chemical compositions of sediments provide information on their origins and can therefore be used to infer characteristics of sediments, sediment provenance, paleoclimate changes, weathering trends, sources of pollution in rivers, chemical speciation of their constituents and type of depositional environment (Nesbitt & Young, 1996; Calvert et al., 2001; Glasby et al., 2004; Naimo et al., 2005; Wei et al., 2006).

River water received its chemical load from these several sources (Huy et al., 1998). The dynamic nature of river causes rapid absorption of heavy metals by processes such as assimilation, dispersal, dilution, oxidation, degradation and sequestration into river sediments (Natesan & Seshan, 2010). Mobility of heavy metals in river sediments can be controlled by the large amounts of fine particles such as clay and silt. The complex diagenetic process can also influence the sedimentary heavy metals profiles where heavy metals combine with organic matter forming stable complexes. Silicates and carbonates are usually in high quantity in river sediments contributing to the increased alkalinity and buffering proportion of the sediments. In several cases, mobilization of heavy metals can occur after their deposition and then re-localized in the column of the sediment or diffused into the water column of the river.

Assessment of heavy metals in river sediments can be achieved by evaluating the heavy metals input from both natural and anthropogenic sources due to their accumulation in river sediments (Zourarah et al., 2007; 2009; Gupta et al., 2011; Kalloul et al., 2012).

The application of heavy metals as an indicator for river pollution was firmly recommended by international organizations such as United States Environmental Protection Agency (USEPA) and others (Maanan et al., 2015). Heavy metal characteristics are significant in understanding the chemical attributes of river sediments. The lithologic contribution of heavy metals is generally considered as a background value in river sediments (Forstener & Whittman, 1979; Walling, 2006), while the notable difference in concentration of a particular heavy metal in sediments is considered to point source such as industrial effluent, sewage discharges and others (Ratha & Sahu, 1994; Yan et al., 2016).

2.3.3 Ecotoxicological Aspects of Heavy Metals

Heavy metals can be harmful and carcinogenic to plants and animals and other living organisms (MacCarthy et al., 1991; Clement et al., 1995; Liu et al., 2018). The non-biodegradable and poisonous nature of many heavy metals are of substantial concern in the river system (Nair & Sujatha, 2013; Ferati et al., 2015; Guan et al., 2018). Heavy metals tend to remain stable in the environment for over a long period of time and create concerns due to their toxic and ubiquitous nature in the river environment (Kara et al., 2015). Heavy metals are known to threaten human lives when consumed or inhaled above acceptable limits and can lead to environmental deterioration. Contamination of heavy metals are often localized as opposed to widespread (Andrews et al., 2013). The concentration of detritus constituents is reflected in the major elements or major oxide geochemistry and the study of trace element indicated ferruginous nature of some elements in some rivers (Sundararajan & Srinivasalu, 2010; Kasilingam et al., 2016). Heavy metals have significant environmental risk due to their wide variety of sources, non-biodegradable attributes, ubiquity and accumulative characteristics. Heavy metals derived from surface runoff,

dissolution of sediments by groundwater, atmospheric depositions and anthropogenic sources such as agricultural runoff, wastewater irrigation, excessive application of fertilizers and pesticide on farmlands, municipal and industrial wastes, mining, smelting, traffic emission and burning of fossil fuels have been reported (Cengiz et al., 2017; Ke et al., 2017).

2.3.4 Environmental Pollution Indices

The study of heavy metal accumulation and deposition is of increasing interest because of the awareness that heavy metals present in river sediments may have negative consequences on human health and on the environment (Likuku et al., 2013). The composition of river sediments is influenced by the deposition of terrestrial materials due to erosion due to the frequent rainfall in the study area. Contamination of sediments by heavy metals is a prevalent issue due to increased human population and agricultural activities (Tatone et al., 2016). Heavy metals are also discharged into rivers by activities such as sewage discharge, wind-blown dust, eroded soils, flooding, municipal waste, vehicular emissions, ships, leakage of metallic storage tanks, mechanized farming and others (Kara et al., 2015). The primary pathways of heavy metals partitioning include adsorption, atmospheric deposition, complexation, precipitation and biological uptake (Scott, 1985; Sany et al., 2013).

2.3.4.1 Estimation of the Background and Baseline Concentrations

A number of diverse reference materials such as Fe, Al, Mn and others as well as enrichment calculation methods have been used by several researchers to assess the impact of heavy metal pollution on river sediments (Muller, 1969; Hakanson, 1980; Salomons &

Forstner, 1984). The initial crucial step in assessing the impact of sediment pollution and the level of contamination in a given area is to establish a reference background or baseline sample of known metal composition. Table 2.5 shows the metal concentrations in average continental shale and average continental crust. In earlier environmental work, a typical technique for comparing sediment metal concentrations with pre-civilization background levels was to compare the present day metal levels with their concentrations in standard earth materials such as average shale (Turekian & Wedepohl, 1961) or average crustal values (Taylor, 1986). The geochemical metals found in sediments are from anthropogenic sources and natural flux of elements in the catchment areas of the river basin. Metal ions may exist in diverse forms. Variables which control the form of the metal ion are the extent of complexation and the oxidation state (Mohiuddin et al., 2010).

Table 2.5: Selected metal concentrations in average continental shale and average continental crust

Metal	Average continental shale[a]	Average continental crust[b]
Cd	0.2	0.1
Cu	45.0	25.0
Pb	20.0	14.8
Zn	95.0	65.0

[a] Turekian and Wedepohl (1961)
[b] Wedepohl (1995)

2.3.4.2 Methods for Estimating Pollutant Impact

The common approach for the estimation of the anthropogenic impact on sediments is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels (Abrahim & Parker, 2008). The EF method normalises the measured heavy metal content with respect to a sample reference metal such as Fe or Al, these two metals act as a representative for the clay content (Ravichandran et al., 1995). One of the commonly used methods to distinguish the fraction of metals or enrichment is by normalization with respect to Fe, Mn and Al (Kemp et al., 1976; Loring, 1978; Van Metre & Callender, 1997). However, Fe or Al is widely used as a normalizer because it also compensates for variations in the grain size and composition. Al and Fe represents the quality of alumino-silicates which is the most significant agent for adsorbed metals in the aquatic environments. The variability of the normalized concentrations is expressed as EF, which is the ratio of the concentration of the metal in the sediment sample to the metal concentration corresponding to the pre-industrial period. EF is a useful tool for determining the degree of anthropogenic heavy metal pollution. The EF is calculated using the relationship as shown in Equation 2.1:

$$EF = (HM/RE)_{sample}/(HM/RE)_{Background/upper\ crust} \qquad \text{Equation 2.1}$$

where HM = heavy metal; RE – Reference element.

The reference element may be Al, Fe, Mn or Co (Abrahim & Parker, 2008) divided by the sediments continental crustal values (Taylor & McLennan, 1995). Fe usually has a relatively high natural concentration and is therefore not expected to be substantially enriched from anthropogenic sources in sediments (Niencheski et al., 1994). An EF around

1.0 indicates that the sediment originates predominantly from lithogenous material, whereas an EF much greater than 1.0 indicates that the element is of anthropogenic origin (Szefer et al., 1996). Aluminium (Al) is used as the reference element for geochemical normalization for the following reasons: Al and Fe are associated with fine solid surfaces with its geochemistry similar to that of many trace metals and its natural concentration tends to be uniform. The local geochemical backgrounds calculated from the value at down-core are used as background data. EF values will be interpreted as suggested by Sakan et al. (2009), where: EF<1 indicates no enrichment; 1<EF<3 is minor enrichment; 3<EF<5 is moderate enrichment; 5<EF<10 is moderately severe enrichment; 10<EF<25 is severe enrichment; 25<EF<50 is very severe enrichment; and EF > 50 is extremely severe enrichment.

The determination of the degree of pollution by a given heavy metal requires that the pollutant metal concentration be compared with an unpolluted reference material (geochemical background). Such reference material should be an unpolluted or pristine substance that is comparable with the studied samples (Maanan et al., 2015). Normalization with Fe values for all the heavy elements can be calculated. The geoaccumulation index (Igeo) is determined to ascertain the extent of pollution in sediments (Hahladakis et al., 2013; Obaidy et al., 2014).

Table 2.6 shows the Igeo of heavy metals in sediments. The equation below showed that Cn is the concentration of the metal in sediment and Bn is the geochemical background value as shown in Equation 2.2. The constant value 1.5 is the background matrix correlation factor as a result of the lithological variations (Muller, 1969).

$$I_{geo} = \log_2(Cn/1.5*Bn) \qquad \text{Equation 2.2}$$

Table 2.6: Geoaccumulation index (I_{geo}) of heavy metal concentration in sediments (Muller, 1969)

I_{geo}	Class	Pollution Intensity
0	0	Background concentration
0-1	1	Unpolluted
1-2	2	Moderate to Unpolluted
2-3	3	Moderately polluted
3-4	4	Moderately to highly polluted
4-5	5	High polluted
>5	6	Very highly polluted

The contamination factor (CF) is also used to evaluate the environmental risk. It is estimated by dividing the concentration of metals by the background value or baseline value as shown in Equation 2.3.

$$CF = C_{heavy\ metal} / C_{background} \quad \text{Equation 2.3}$$

where C is concentration

The pollution load index (PLI) is used to assess the extent of pollution of metals in sediments. It is calculated as a root of product of CF. The PLI value of > 1 is polluted whereas < 1 indicates no pollution. It can be calculated using the Equation 2.4.

$$PLI = \sqrt[n]{CF1*CF2*CF3*CF4*\ldots\ldots CFn} \text{ or}$$

$$PLI = (CF1*CF2*CF3*CF4*CF5\ldots\ldots)^{1/n} \quad \text{Equation 2.4}$$

where CF is contamination factor and n is number of heavy metals

2.4 Geochemistry of Hydrocarbons in River Sediments

Petroleum hydrocarbons comprised of a wide variety of chemicals with diverse origins (Zaghden et al., 2005; Zhang et al., 2018a). Petroleum pollution has been of great concern for a long time because several components in petroleum that have been proven to have mutagenic and carcinogenic impacts on living organisms (Vaezzadeh et al., 2015). The global increasing use of fuel such as petrol and diesel as well as accidental oil spills are the main contributors to the release of petroleum into the environment (Singh et al., 2012; Keshavarzifard et al., 2018).

2.4.1 Hydrocarbon Biomarkers as Tool for River Sediments Assessment

Sediments are the final sinks of hydrocarbons because hydrocarbons bind quickly to particulate materials in rivers. Hydrocarbons present in the environment are mainly from two primary sources which are naturally derived hydrocarbons and anthropogenic hydrocarbons. Two classes of hydrocarbons have been reported in the fluvial environment in Malaysia are aliphatic hydrocarbons and polycylic aromatic hydrocarbons (Zakaria et al., 2002; Sakari et al., 2008b; Tahir et al., 2015; Keshavarzifard et al., 2018). Naturally derived hydrocarbons are influenced by various biosynthetic processes or metabolic pathways resulting in the development of some other complex biological structures in the river. Significant sources of organic compounds such as terpenes, organic acids and aldehydes is forest. Peat, damp soils, marshes and/or rice paddies are dominated by microbiological environments which serves as food for man and animals are sources of organic compound (Andrews et al., 2013).

Anthropogenic hydrocarbons are mainly derived from human activities such as industrialization, urbanization and application of chemical fertilizers on farmlands. The chemical composition of petroleum product is complex and changes may occur over time after it has been discharged into the environment (Hatzinger & Alexander, 1997). Total petroleum hydrocarbon (TPH) is the total concentration of the hydrocarbons extracted and measured by different gas chromatography method. TPH is mostly referred to as hydrocarbon oil, mineral oil, extractable hydrocarbon and grease (Duan et al., 2019).

2.4.2 Aliphatic Hydrocarbon in River Sediments

Aliphatic hydrocarbons commonly referred to as *n*-alkane consist of a straight chain of carbon and hydrogen with no alkyl branch or substitutes. Aliphatic hydrocarbons occur naturally as linear, branched, cyclic, saturated and unsaturated. These straight chain hydrocarbons consist of odd and even carbon numbers ranging from C_4 to C_{64} with no alkyl groups (Ibadov & Suleymanov, 2015). The simplest form of alkane is methane, others include branched alkanes, isoprenoids and cycloalkanes. The straight chain molecules are commonly referred to as normal alkanes (*n*-alkanes) while the branched molecules are called iso-alkanes. *n*-Alkanes can be used as molecular markers to assess hydrocarbon contamination and to predict their sources (Duan et al., 2010).

2.4.2.1 Sources of Aliphatic Hydrocarbon

The naturally derived hydrocarbon is either biogenic or geogenic. Geogenic hydrocarbons are primarily from weathered organic rocks such as shale, limestone, and peat while the biogenic sources are mainly from marine organisms and terrestrial vascular plants (Sakari et al., 2008b; Liu et al., 2012b; Tahir et al., 2015). The sediments with aliphatic

hydrocarbons are derived naturally by organisms such as planktons, algae and bacteria or come from terrestrial plants. Anthropogenic sources of hydrocarbons are derived from human activities such as industrial activity, urbanization and oil spillage (Commendatore & Esteves, 2004; Duan et al., 2019). The sources of aliphatic hydrocarbon can be evaluated using the LMW/HMW ratio, unresolved complex mixture (UCM) and carbon preference index (CPI) which is the ratio of the odd carbon numbers and the even carbon groups (Commendatore & Esteves, 2004; Sakari et al., 2008a; Vaezzadeh et al., 2015).

2.4.2.2 *n*-Alkanes Based Biomarker Indices

Hydrocarbon biomarkers are organic compounds found in the environment with structures suggesting an unambiguous connection or link with known contemporary natural products. These specific indicator compounds which are found in extracts of geological and environmental sample such as sediment can be utilized for genetic source correlations (Yusoff et al., 2012). Hydrocarbons derived from biogenic sources appear with low concentrations in river sediments, while high level of concentration in hydrocarbon compounds are attributed to be of anthropogenic source which often lead to petroleum pollution. Several indices have been used to distinguish the origin of *n*-alkanes in the river such as LMW/HMW, CPI, the occurrence of UCM and ACL. Distribution of aliphatic hydrocarbons in sediment samples including isoprenoids such as pristane and phytane have been utilized to predict the possible source of organic matter in sediments, whereby pristane and phytane are utilized based on ratios either isoprenoid to isoprenoid like ratio of pristane to phytane or isoprenoid to *n*-alkanes (Sakari et al., 2008b; Sakari et al., 2012; Duan et al., 2019).

2.4.2.2.1 Carbon Preference Index (CPI)

The CPI is the ratio of odd and even carbon numbers with various carbon groups. CPI within the ranges C_{15}-C_{20} and C_{25}-C_{33} (CPI_{15-20} and CPI_{25-33}) are used to further identify sources of aliphatic hydrocarbons. $CPI_{15-20} > 1$ indicates planktonic origin; < 1 indicates bacterial sources and -1 indicates petrogenic inputs (Liu et al., 2012b). $CPI_{25-33} > 3$ indicates terrestial higher plants sources; - 1 indicates petroleum sources (Zahgden et al., 2017). The values from 3 to 6 is indicative of terrestrial vascular plants, while values 1-3 represent the petrogenetic input (see Table 2.7). It is also believed that the possibilities of marine micro-organisms and/or recycled organic matter as well as petroleum give a value of ≤ 1 (Yusoff et al., 2012; Ali et al., 2015; Duan et al., 2019).

Table 2.7: Source of *n*-alkanes based on CPI values (Commendatore *et al.*, 2012)

CPI Value	Source of *n*-alkane
-1	Petroleum sources
≤1	Related to recycled organic matter and/or marine organisms
1-3	Related to marine micro-organisms and recycled organic matter
3-6	Biogenic input from vascular plants
6-10	Derived from terrestial/land plants

2.4.2.2.2 Ratio of Low Molecular Weight to High Molecular Weight

This ratio is an indicator of freshness of the released hydrocarbons in the environment and its sources (Sakari et al., 2008b; Zhang et al., 2018b). LMW hydrocarbons ranged between C_{10} to C_{23} while HMW hydrocarbons ranged between C_{24} to C_{33}. High concentration of LMW carbon indicates an anthropogenic origin while high concentration

of HMW indicates a biogenic origin. Thus, the ratio of LMW/HMW below 1 shows natural input from marine, terrestial and biogenic sources whereas the value above 1 indicates petroleum origin (Commendatore et al., 2000).

2.4.2.2.3 Average Chain Length (ACL)

The ACL is an index used to evaluate the predominant of odd carbon number in a river sediment sample. ACL is an important parameter used to understand the source of hydrocarbons in the environment. It is defined as the weight average chain number of carbons atom in higher plants which is ranged from C_{25} to C_{33}. The higher ACL values are attributed to the higher plant input whereas the constant or lower values are believed to be caused by pollution (Zakaria et al., 2002; Silva et al., 2012).

2.4.2.2.4 Occurrence of Unresolved Complex Mixture (UCM)

The UCM is a complex mixture of hydrocarbon with branched and cyclic structures, the appearance of UCM in GC-MS chromatograms has been utilized as an indicator of the occurrence of petroleum hydrocarbons (Sakari et al., 2008a; Wang et al., 2015). UCM suggests biodegraded crude oil and usually occur in higher molecular weight range but can also exist in low molecular weight range. The UCM usually exists in the range of carbon number of 16-34 indicates oil pollution (Yusoff et al., 2012).

2.4.2.2.5 Isoprenoids

Isoprenoids such as pristane and phytane can also be useful in source identification of hydrocarbons in sediments (Vaezzadeh et al., 2015). Pristane is a natural terpenoid alkane primarily derived from shark liver oil and fishes. It can be derived from phytane by

loss of its C_{16} terminal methyl group. Pristane is a norterpene with a long-chain. Phytane is the isoprenoid formed from when phytol loses its hydroxyl group. The loss of one carbon atom by phytol yields pristane. Pristane and phytane can be originated from oxidation and reduction of phytol side chain of chlorophyll (Vaezzadeh et al., 2015). Abundance of phytane indicate bacterial activity in a reducing environment and the ratio of pristane/phytane < 1 is an indication of anoxic environment, while the ratio > 1 represents oxic environment. High ratios of pristane/phytane are attributed to biogenic sources such as bituminous coals and vascular plant origin (Duan et al., 2019).

2.4.3 Polycyclic Aromatic Hydrocarbons in River Sediments

Polycyclic aromatic hydrocarbons (PAHs) are hydrocarbons that have at least two fused benzene rings. PAHs are compounds formed through incomplete combustion and pyrolysis of organic matter (Kanzari et al., 2014). Figure 2.3 shows PAHs have at least two single or fused aromatic rings with a pair of carbon atoms shared between rings in their molecules. One of the simplest PAH is naphthalene. The presence of PAHs in the river environment occurs by atmospheric deposition, forest fires, vehicular emissions, industrial combustion of fossil fuel, riverine input and oil spillage (Mumtaz & George, 1995; Neff et al., 2005; Tahir et al., 2015). The general properties of PAHs are high boiling and melting points, low solubility in water and having firm affinity for organic matter which makes them accumulate in fine grained sediments compared to coarser sediments or sediments in the dissolved state (McElroy et al., 1989).

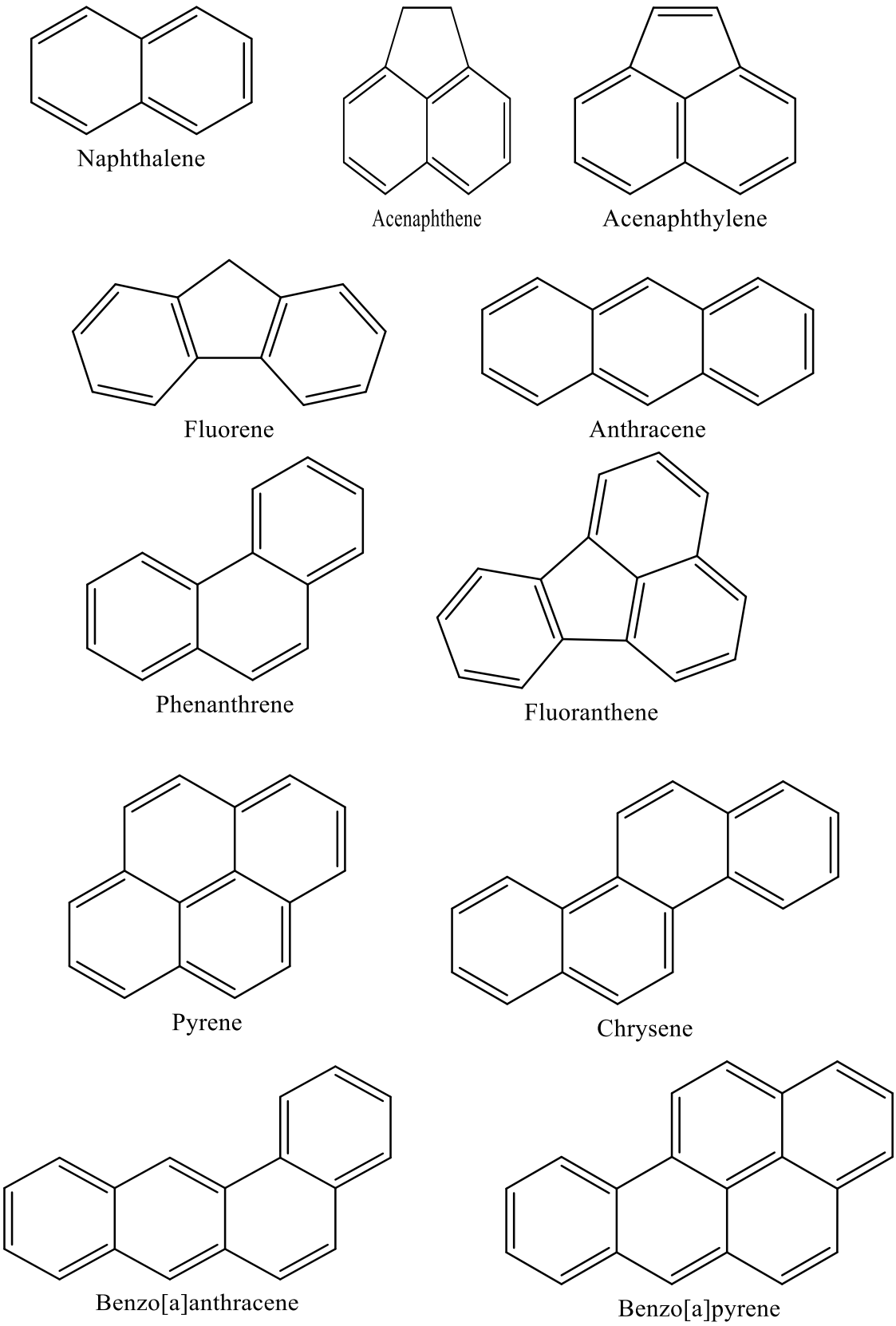
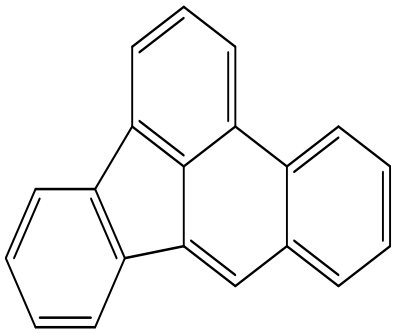
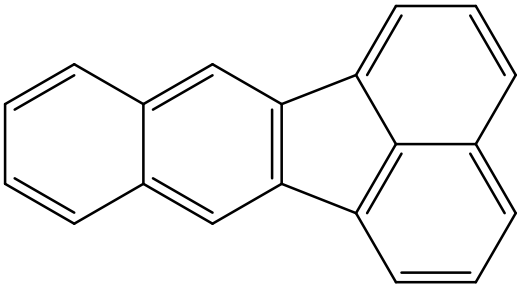


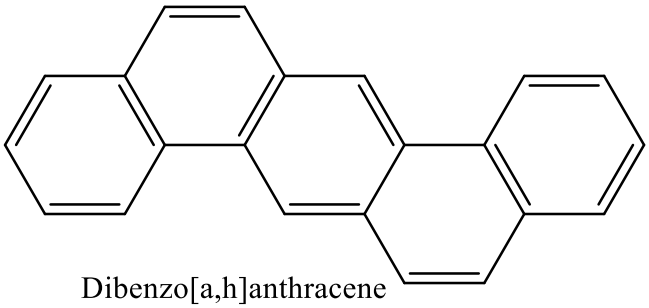
Figure 2.3: Structures of the priority PAH compounds



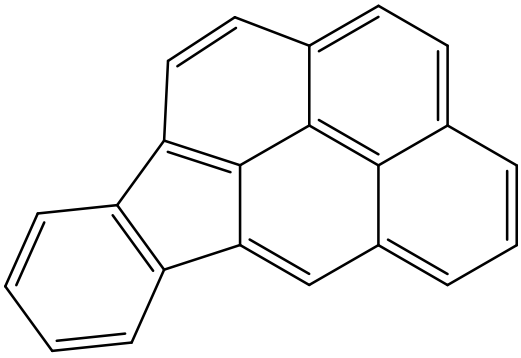
Benzo[b]fluoranthene



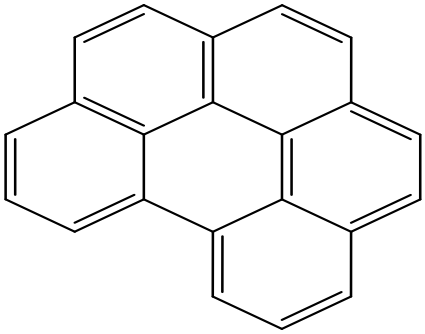
Benzo[k]fluoranthene



Dibenzo[a,h]anthracene



Indeno[1,2,3-c,d]pyrene



Benzo[g,h,i]perylene

Figure 2.3 continued

2.4.3.1 Sources of Polycyclic Aromatic Hydrocarbon

The source and distribution of PAHs in river sediments are of great interest globally because it is key indicator for current pollution levels and productivity in the coastal water and ocean. PAHs are usually various aromatic hydrocarbons which contain

several fused benzenoid rings. PAHs include phenanthrene, anthracene, fluoranthene, pyrene etc. PAHs are derived from natural sources and anthropogenic sources and thereafter transported to the riverine and coastal environments (Killops & Killops, 1993; 2013). The natural sources of hydrocarbons are from terrestial (vascular) plants wax or marine macroalgae and/or phytoplankton (Commendatore et al., 2000; Commendatore and Esteves, 2004). PAHs can be derived from two kinds of anthropogenic sources which are the petrogenic and pyrogenic sources. Higher plant lignins are the fundamental source of aromatic compounds in contemporary sediments.

The petrogenic sources include crude and refined petroleum which are brought into the aquatic environments through oil spills, discharge from oil tanker operations, municipal and urban runoff. These can be due to leakages of crankcase oil from inadequately maintained automobiles as well as illegal dumping of waste crankcase oil (Zakaria et al., 2002; Isobe et al., 2007). These sources have accounted for a broad contribution of petrogenetic PAHs into the South east Asian coastal area. Pyrogenic PAHs originated from the combustion of fossil fuel and biomass are discharged into the environment as fumes and soot particles. Several studies have shown that petroleum is the principal source of hydrocarbons in river sediments and coastal waters (Sakari et al., 2008a; Tahir et al., 2011; Keshavarzifard et al., 2014; 2015; Vaezzadeh et al., 2015).

The source of sedimentary PAHs can be inferred from the sum of methylphenanthrenes to phenanthrene (MP/P) which shows either it is petrogenic or pyrogenic (Zakaria et al., 2002). Biogenic PAHs in Malaysia such as perylene are mainly formed during early diagenesis. PAHs concentration are affected by dilution caused by frequent rainfall and sediment transport. Alkyl PAHs which are formed by low-temperature diagenesis has been reported in some industrialized nations (Wang et al., 2018). The PAHs

derived from combustion are transported in the atmosphere for a long distance and can serve as background values (Masood et al., 2016).

2.4.3.2 Polycyclic Aromatic Hydrocarbons Pollution

Generally, organic contaminants are compounds with a carbon structure/skeleton, usually associated with atoms of hydrogen, nitrogen, oxygen, phosphorus and sulphur. These atoms form an integral part of the molecule, alternatively may be present in functional groups. The presence of hydrocarbons does not necessarily indicate that pollution has occurred because these compounds could be originated from natural sources. The various structural forms of organic molecules such as saturated chains, unsaturated chains and rings result in a diverse range of organic contaminants (Andrews et al., 2004). The chemical composition of petroleum products is complex and may be altered over time after the release or discharge into the river (Zakaria et al., 2002; Tahir et al., 2015). Organic compounds interact with sediments by adsorption (surface phenomenon) and entrapment within sediment particle. They can be released from sediment particles rapidly or slowly. Petroleum groups include different categories of hydrocarbons such as saturated hydrocarbons, aromatics and polars/resins. The non-extractable residue is bound to the sediment matrix following an extraction process.

The increase of petroleum hydrocarbon concentration in the fluvial environment can cause negative impact on the river. Organic contaminants are transported into river and interact with sediments, mineral fractions and organic matter (Andrews et al., 2013). These organic pollutants can either persist or dissipate. Compounds persist when they have low solubility, low volatility and a molecular structure that resists degradation. Moreover, if compounds are highly volatile, highly soluble or are easily degraded, the hydrocarbon

compounds are easily destroyed or lost to other environments. The concentrations of petroleum products due to industrial and urban sources at the West Coast of Malaysia was reported to be significantly higher compared to the concentrations of petroleum products on the east coast (Zakaria et al., 2001). Some pollutants were transported from stationary sources such as industries, motor vehicles, open burning and municipal discharges. Other sources of hydrocarbon pollutants include urban and agricultural runoff as well as various sources that release toxins into the atmosphere. The presence and distribution of PAHs in fluvial sediments in South East Asia is rapid due to frequent rainfalls and erosion (Raza et al., 2013).

The source of PAHs in Malaysia is biogenic and anthropogenic with both sources having different characteristics. Anthropogenic materials are transported to the river via fluvial runoff and atmospheric discharges, which can be stored in sediments and dispersed by ocean currents. The occurrence of PAHs in sediments is an issue of concern due to their carcinogenic and mutagenic properties in humans. In a project by the National Waste Minimization Programme in U.S.A. conducted by United States Environmental Protection Agency (USEPA, 2002, 2008, 2014), twenty- eight (28) PAHs were identified as carcinogenic pollutants. PAHs which consist of fused benzene rings are hydrophobic in nature with very low water solubility and high octanol water partition coefficient. PAHs are ubiquitous contaminants that can be found in a broad framework of matrices such as air, fly ash, food, sediments, soil water, crude oil and petrochemicals (Youngblood & Blumer, 1975; Neff, 1979). Hence, PAHs tend to adsorb firmly to organic matter in sediments making them susceptible to biological and chemical degradation. Degradation of organic contaminants in sediments occur typically by either chemical or biological pathways. The

processes of biodegradation and transformation can significantly alter the hydrocarbon compound toxicity, mobility and affinity for sediment matrix (Andrews et al., 2013).

PAHs give cause for concern in many developing countries because some have toxic, poisonous and carcinogenic properties (Lehr & Jerina, 1977). Low molecular weight two- and three-ringed PAHs have an intense acute toxicity, whereas four- to six-ringed PAHs tend to show a more prominent carcinogenicity. PAHs show little reactivity after deposition with their presence in the river environment. Due to a variety of anthropogenic and biogenic activities with incomplete combustion and pyrolysis of fossil fuels serving as the primary source in rivers (McCready et al., 2000). The pyrolitic input is further enhanced by PAHs derived from grass and forest fires. In some places there may likewise be a petrogenic contribution of PAHs to estuarine sediments from coal, crude oil and different refinery products (Kanzari et al., 2014). The anthropogenic sources are typically from runoff, industrial and sewage discharges, spillage, shipping activities and others. These sources can be in some cases be natural with respect to occurrence of oil seepage from rocks at great depth.

Natural petrogenic PAHs in sediments can be originated from the diagenesis of common precursors such as terpenes, pigments and steroids. The ubiquity of PAHs and tainting of sediments from old pristine regions have been reported in places like the Beaufort and Barents seas of the arctic (Yunker et al., 1996). More than hundred PAHs exist in the environment but the United States Environmental Protection Agency (USEPA) has identified only sixteen as priority pollutants in recent times and these are most frequently monitored for regulatory purposes. The dispersal and ratios of some of these such as phenanthrene:anthracene and fluoranthene:pyrene can provide information on the possible sources of anthropogenic PAHs contamination (Readman et al., 2002).

PAHs are extremely non-polar and hydrophobic. PAHs tend to partition tightly into sediment organic matter leaving low concentrations of PAH in equilibrium with the other surrounding aqueous phase. PAHs concentrations fixed in the pore waters of sediment cores are very much lower than the concentration predicted by equilibrium partitioning models because of the presence of soot particles in some areas (Bucheli & Gustafsson, 2000). The sediment soot particles increase the partition of PAH into the particulate phase because they are generated concurrently with PAHs during incomplete combustion processes. This impacts the bioavailability of PAHs as these can be degraded into dissolved species by micro-organisms. Levels of organic compounds in both sediment and water samples and organotin concentrations were reported by Centre for Environment, Fisheries and Aquaculture Science (CEFAS, 1998) and Oslo/Paris Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR, 2000). These studies suggested that, as common with other contaminants, organotins are effectively scavenged from water by suspended particulate matter and then deposited in estuaries including docks and marinas where there is accretion of fine grained particles (Liu et al., 2012a).

Organic pollutants often accumulate in the bottom sediments. Estuaries and coastal channels between land and sea, trap large quantities of natural and anthropogenic organic matter via the interactions of a series of chemical, physical and biological processes (Liu et al., 2012a; Masood et al., 2016). Most studies on PAHs in sediments are dependent on the determination of a certain number of individual PAHs mostly between 9 and 28 (Readman et al., 2002) and the use of the 15 or 16 USEPA priority PAHs has been universally adopted for contaminated land and river assessment. These PAHs are highly hydrophobic and tend to absorb firmly to the organic content of sediments (Dean & Xiong, 2000) as opposed to associate with the more hydrophilic mineral constituents.

2.4.3.3 Formation of Polycyclic Aromatic Hydrocarbons

There are two primary mechanisms for the formation of PAHs namely: pyrolysis and pyrosynthesis which are responsible for the formation of PAHs in the environment. Pyrolysis is the combustion of organic compounds and materials such as crude oil at high temperatures to form small unstable fragments. While pyrosynthesis also involves the formation of PAH at higher temperatures (>500^{o}C) from carbon-hydrogen and carbon-carbon bond that are broken forming free radicals (Bastami et al., 2014).

2.4.3.4 Classes of Polycyclic Aromatic Hydrocarbons

There are two classes of PAHs: LMW PAHS and HMW PAHs. LMW PAHs consist of simple forms such as naphthalene, acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene and tend to be made up of two or three benzenoid ring core structure. Whereas, HMW PAHs are made up of four or more benzoid rings such as fluoranthene, pyrene, benzo(a)pyrene and benzofluoranthenes.

PAHs can be further classified as pyrogenic, petrogenic or biogenic/diagenetic. Pyrogenic PAHs are the result of incomplete combustion of coal, wood, petrochemicals and other organic materials at high temperatures over a short period of time. Due to this formation process, pyrogenic PAHs tend to have a source signature that contains predominantly HMW PAHs and parent PAH analytes (Zhang et al., 2019a). However, petrogenic PAHs are the result of a long application of low heat over millions of years. Primary sources of petrogenic PAH source primarily consist of LMW PAHs with little or no HMW PAHs. Biogenic PAHs are produced by biological reaction and degradation of organisms known as diagenesis (Bastami et al., 2014). A common example of biogenic PAH is perylene, it is a five-ringed PAH compound found in high concentrations in early

stages of degradation in terrestial soils, river and lake sediments as well as anoxic marine environments and swamps (Liu et al., 2012a).

2.5.1 Diagnostic Ratios of Polycyclic Aromatic Hydrocarbons (PAHs)

Identification of the potential sources of PAHs is critical to understand their fate in the river. Therefore, diagnostic ratios indicator or PAH molecular marker which is based on PAH concentration can be utilized to distinguish between combustion and petroleum sources of PAHs (Yunker et al., 2002; Zhang et al., 2019b). This technique of identification is limited to specific PAHs with identical molecular masses and similar environmental fate (Gilbert et al., 2006) so as to negate the distinctions in PAH physicochemical properties such as water solubility and volatility. The typical diagnostic ratios and reported values for particular processes are shown in Table 2.8.

Table 2.8: Typical diagnostic indicators using PAHs ratios

PAH ratios	Value Range	Source	References
Anthracene/(anthracene+phenanthrene)	< 0.1	Petrogenic	Yunker et al. (2002); Gilbert et al. (2006)
	>0.1	Pyrogenic	
Fluoranthene/(fluoranthene+pyrene)	<0.4	Petrogenic	Wang et al. (2010a); Tobiszewski et al. (2012)
	0.4-0.5	Fossil fuel combustion	
	> 0.5	Grass, wood. Coal combustion	
Benzo[a]Anthracene/ (Benzo[a]Anthracene+Chrysene)	<0.2	Petrogenic	Soclo et al. (2000); Yunker et al. (2002)
	0.2 - 0.35	Petrogenic or Pyrogenic	
	>0.35	Pyrogenic	
Indeno[1,2,3-c,d]Pyrene/ (Indeno[1,2,3-c,d]Pyrene+ Benzo[ghi]Perylene)	<0.2	Petrogenic	Yunker et al. (2002)
	0.2 - 0.5	Petroleum combustion	

2.5.2 Chapter Summary

This chapter has summarized the geological setting of Batang Sadong and geochemical characteristics of sediments in world rivers. The chemical properties of a river are influenced by the dissolution of materials on land and river, heavy metals are influenced by factors such as bedrock lithology, land use, topography and climatic factors. The geochemistry of heavy metals in some rivers in Malaysia were reported. Ecotoxicological aspects of heavy metals in river sediments using Igeo, EF and CF are important in environmental studies. The heavy metals and hydrocarbons in river sediments from Malaysia were derived from natural sources and anthropogenic sources. The different hydrocarbon biomarkers and their characteristics such as CPI, ACL and LMW/HMW have been used to determine the source of hydrocarbon in river sediments. This research entails the heavy metal and hydrocarbon characteristics of sediments from Sadong River.

CHAPTER 3

MATERIALS AND METHODS

3.1 Study Area and Sampling Locations

The sample collection was carried out between March 2017 to March 2018 in the northeast monsoon season. Study area is extensive with large land mass from the downstream to upstream. Sediments were collected from Sadong River at seven sampling locations which include upstream, midstream and downstream of the river as shown in Figure 3.1. The locality and Global Positioning System (GPS) reading for sampling sites are described in Table 3.1. The gravity corer tube length was 100 cm and the core size diameter was 5 cm. The sediment cores taken were ranged from 25 cm - 45 cm. Discrete samples were taken at each location. Three surface samples with triplicates and core samples were taken per station.

Table 3.1: Sampling stations and their coordinates at Sadong River

Stations	GPS Reading	Locality	Major Activities	Core Depth (cm)
BS1	N01^{0}33'03.2" E110^{0}45'56.4"	Sebangan	Farming and Fishing	45
BS2	N01^{0}30'51.0" E110^{0}44'24.6"	Sadong Jaya	Fishing, paddy rice farming	30
BS3	N01^{0}27'19.4" E110^{0}41'08.1"	Sungai Buloh	Farming and Fishing	25
BS4	N01^{0}14'49.3" E110^{0}41'06.6"	Simunjan	Fishing	25
BS5	N01^{0}14'38.5" E110^{0}40'42.5"	Gedong	Residential area (potential tourist attraction)	25
BS6	N01^{0}14'42.1" E110^{0}38'09.5"	Sebemban	Farming, Oil palm plantation	30
BS7	N01^{0}09'36.3" E110^{0}33'58.0"	Serian	Municipal area	45

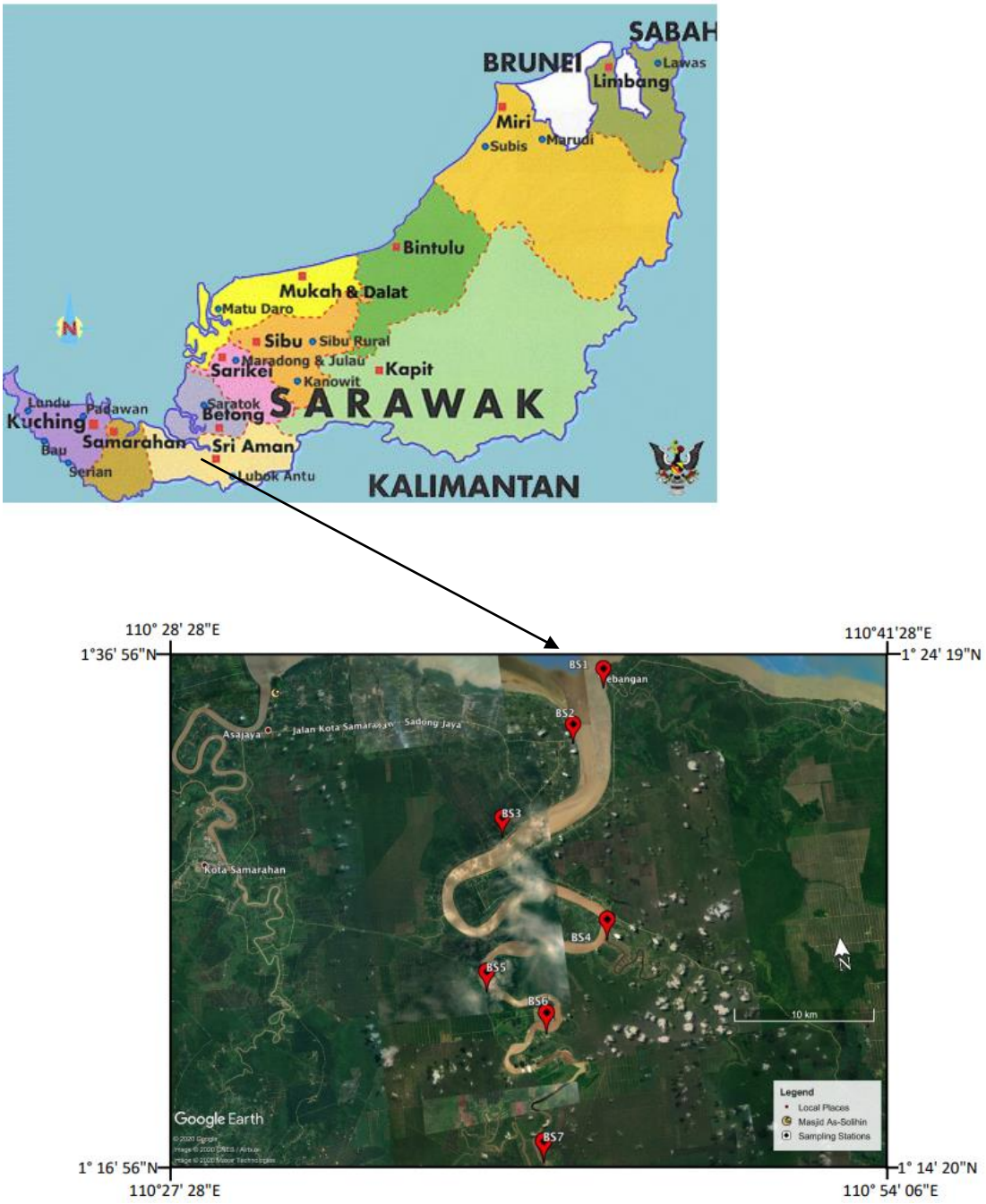


Figure 3.1: The sampling sites at Sadong River (Modified from Google map)

3.2 Sediments Collection and Preservation

A total of forty-two representative of undisturbed surface sediments were collected using a Wildco stainless steel grab sampler (see Figure 3.2) at seven sampling stations. A total of six core sediments were also collected from six stations using a gravity corer as shown in Figure 3.3. The corer tube length was about 100 cm and core tube size (diameter) was 5 cm. The core sediment was sliced into 2.5 cm interval. The 2.5 cm interval was to complement visual, textural description and deposition of sediments The sediments were then placed in plastic bags for heavy metals analysis, while the samples for hydrocarbon analysis were wrapped with aluminium foil. All the samples were labelled with location code, date of sampling and depth of core sediment samples stored in a cooler box during transportation.

Figure 3.2: Grab sampler for surface sediment collection

Figure 3.3: Gravity corer for core sediments collection

3.3 Sample Preparation and Procedure

The physical descriptions of the sediment such as the colour, particle shape, length of core were recorded. The colour of sediment was described based on sediment colour charts (Hossain et al., 2014). The particle shape was determined using hand magnifying lens. The purpose of these parameters were to describe the physical characteristics of the sediment. The separation of coarse material, homogenization and drying, which is the first crucial step of sediment analysis was done. Sediments were homogenized using a clean dry, ceramic mortar and pestle (Abdullah et al., 2015). Each surface and core sediment layer was allowed to dry for 72 hours. Dry sieving for particle size analysis were carried out to collect the <63 μm fine fraction and the coarse fraction containing insignificant quantities of plant remains (Ong et al., 2016). This was carried out in order to analyze sediment samples of same size.

3.4 Sedimentological Studies

The sedimentology of sediments was evaluated by determining the grain size, texture and total organic matter (TOM) according to Hahladakis et al. (2013). The sediments were air dried, finely powdered and used to analyze several parameters as described below.

3.4.1 Particle Size Analysis

Particle size analysis was carried out for the surface subsamples using a set of sieves ranged from 250 μm to 63 μm (Hahladakis et al., 2013). The sediments were air dried at room temperature for 72 hours. The samples were disaggregated using a mortar and pestle. The samples were then sieved through 63 μm stainless steel mesh sieve to remove materials such shells, leaves and twigs. The sizes were determined based < 2 μm, 2-63 μm and > 63 μm collected in each sieve.

3.4.2 Moisture Content, Total Organic Matter and Ash Content

All sediments were dried in a furnace at 105 ^{o}C for 16 hours in order to determine the moisture content according to ASTM D2974 (Hahladakis et al., 2013). Sediments were dried to a constant weight in an oven and the percentage of moisture was determined using weight reduction using Equation 3.1. The ash content was determined by heating in the furnace at 550 ^{o}C for five hours and calculated using Equation 3.2. TOM was calculated according to ASTM D2974 method using Equation 3.3 (Hahladakis et al., 2013).

$$\text{Moisture } \% = [(W_1 - W_2)/W_1] * 100 \qquad \text{Equation 3.1}$$

where, W_1= weight of sediment before heating (g); W_2= weight of sediment (g) after heating at 105 ^oC

Ash content % = $[W_3/W_2]$* 100 Equation 3.2

where, W_2 - weight of oven dried sediment at 105 ^oC (g); W_3 - weight of sediment (g) at 550 ^oC

Total organic matter % = 100 - % ash content Equation 3.3

3.5 Analysis of Heavy Metals in Sediments

The heavy metals in both surface and core sediments were determined using the atomic absorption spectrophotometer (AAS). The procedure prior to instrumental analysis include sample preparation, sample digestion using acids and method validation.

3.5.1 Sample Preparation

The sediments were air dried at room temperature for 72 hours and then pulverised into powder form using a mortar and pestle. All geochemical analyses were carried out on the < 63 µm fraction.

3.5.2 Extraction of Heavy Metals from Sediment Matrices

Extraction of heavy metals from sediments was carried out according to procedure described by Sim et al. (2016). 1 g of sample was placed in a crucible with a mixture of concentrated HNO_3 and HCl (3:1; v/v). A mixture was heated to near dryness using a hot plate and allowed to cool before filtration. The sediment samples were filtered through 0.45 µm Whattman filter paper. The filtrate was then transferred into a 100 mL volumetric flask

and made up to the mark with deionized water. All samples were digested in triplicates and the solution was poured into plastic bottles for heavy analysis using AAS at Faculty of Resource Science and Technology (FRST), UNIMAS. The concentration of metal in sediment were reported in dry weight basis.

3.5.3 Atomic Absorption Spectrophotometer (AAS) Analysis

The sample solutions were analysed for heavy metal content using Thermo Fisher Scientific AAS model iCE 3000 Series. Acetylene, nitrous oxide and compressed air were used for burning because these gases have a specific flow rate based on the element of interest. The heavy metals analyzed were Cu, Pb, Zn, Fe, Ni, Mn, As, Cd together with three major metals such as Mg, K and Na. The flame atomic absorption was used to analyze Cu, Pb, Zn, Fe, Ni, Mn, As, Cd, Mg, K and Na. Sample solution and purified acetylene gas and air generated from the air compressor were mixed together in the mixing chamber and channeled to the burner head for atomization (burning). Concentration of the respective heavy metals was determined using calibration curve plotted using a series of standards and blank. A linear calibration graph of absorption versus concentration was plotted using standard solution. Hollow cathode lamp is made of the metal to be analysed, the anode is made of Tungsten with a particular current for optimal performance. Deuterium lamp was used to calibrate the wavelength for background purposes. Standard solutions were prepared by using 1% HNO_3 and deionized water with the concentrations of standard solutions are shown in Table 3.2. The metal concentrations were calculated from the calibration curve. The calculated concentration was achieved by multiplying measured value by 0.1 L/0.001 kg and reported in mg/kg. The method was validated using Certified Reference Material

(CRM) 142Q, sewage sludge amended soil standardized by Community Bureau of Reference (BCR) (Asare et al., 2019).

Table 3.2: Concentration of metals in standard solutions for AAS calibration

Metal	Concentration (mg/kg)		
Cu	1.0	3.0	5.0
Pb	1.0	3.0	5.0
Ni	1.0	3.0	5.0
Zn	0.3	0.5	1.0
Cd	0.5	1.0	1.5
Fe	1.0	3.0	5.0
Mn	1.0	2.0	3.0
As	3.0	6.0	10.0
Mg	1.0	2.0	3.0
K	1.0	2.0	3.0
Na	1.0	2.0	3.0

3.5.4. Validation of AAS Analysis

Validation of AAS analytical method is the process of assessing the suitability of the methodology selected to provide useful geochemical data. The data obtained are useful in evaluating the uncertainty associated with measurements. This has been achieved by determining the concentrations of heavy metals and major metals in reference material (RM) and standard solution (SS).

3.5.4.1 Limit of Detection

The limit of detection (LOD) is defined as the lowest concentration or amount of analyte that can be determined from the blank sample using equation 3.4. It can also be detected with a reasonable statistical certainty but not necessarily quantified under the stated

condition of the test. LOD was calculated based on 10 replicates of blank sample (Marin et al., 2011).

$LOD = 3*(S.D_{blank}/m)$ Equation 3.4

where $S.D_{blank}$ is the standard deviation for 10 replicates of blank sample; m is the sensitivity that can be obtained from the slope of the calibration graph.

3.5.4.2 Limit of Quantification

Limit of quantification (LOQ) is the lowest concentration or amount of analyte that can be quantitatively measured with an acceptable level of precision and accuracy under the stated condition of the test as shown in Equation 3.5.

$LOQ = 10*(S.D_{blank}/m)$ Equation 3.5

3.5.4.3 Limit of Linearity

Limit of linearity (LOL) is defined as the range of concentrations that an instrument gives a linear response. A steeper line with a large slope indicates an excellent sensitivity of the instrument. LOL is denoted from calibration curve equation. Dynamic range was also defined as the range of lower and higher values between LOQ and LOL.

3.6 Assessment of Sediment Contamination

The assessment of sediment contamination was calculated using Fe as reference in a normalized EF as shown in Equation 3.6 as recommended by Kemp et al. (1976).

$EF = (HM/RE)_{sample}/ (HM/RE)_{Background/upper\ crust}$ Equation 3.6

Where HM = heavy metal; RE - Reference metal

The index of geoaccumulation (Igeo) was used to estimate the degree of anthropogenic influence on heavy metal concentration in the sediments using Equation 3.7 as suggested by Muller (1969).

$$I_{geo} = \log_2 (C_n/1.5*B_n) \quad \text{Equation 3.7}$$

where C_n is the measured heavy metal concentration in the sediment sample; B_n is the geochemical background value in the earth's crust

The contamination factor (CF) was calculated by comparing the mean of heavy metal concentration with average shale concentration given by Equation 3.8 as recommended by Tomlinson et al. (1980).

$$CF = C_{heavy\ metal}/C_{background} \quad \text{Equation 3.8}$$

where C is concentration

3.7 Analysis of Hydrocarbons in Sediments

The targeted hydrocarbon components to be analyzed that were *n*-alkanes and aromatic hydrocarbons have been extracted using Soxhlet extractor, followed by column chromatography fractionation before analyzed on capillary GC-MS. The Soxhlet extraction technique capable to separate and isolate the geolipid from the mixture compounds and impurities. The geolipid was then fractionated on silica gel column chromatography to aliphatic hydrocarbon and aromatic hydrocarbon fractions, respectively.

3.7.1 The Extraction of Sediment

Extraction of sediment was carried out following the procedure as outlined by Vaezzadeh et al. (2015a). 10 g of sediment was placed in a cellulose thimble and spiked with 50 µL each of the individual internal standards *n*-eicosene and d_{10}-anthracene with a concentration of 50 µg/g in separate solution. The sample was then Soxhlet extracted using 250 mL of dichloromethane for 8 hours on FAVORIT MS-EAM heating mantle. The extract was evaporated to nearly dryness using a Heidolph Laborota 4000 efficient vacuum rotary evaporator. When solvent was nearly dried up, the round bottom flask was removed and solvent was then transferred into 5 mL vial. It was further dried by blowing gently with prepurified nitrogen gas. This dried crude extract is called geolipid (Vaezzadeh et al., 2015a).

3.7.2 Fractionation of Geolipids

The geolipid was separated into two fractions on a glass column chromatography (1.1 cm × 25 cm) packed with 4 g of silica gel purchased from Merck with mesh size of 0.040-0.063 mm. The geolipid extract was placed on the top of silica gel and eluted with 20 mL of *n*-hexane. The chromatographic column was prepared by plugging a piece of glass wool into a long bodied burette. The silica gel slurry was mixed with 15 mL of *n*-hexane. The contents were swirled and the silica slurry was poured into the column slowly with 5 mL of *n*-hexane was added to rinse the wall of the burette. The meniscus of the solvent was not allowed to fall below the surface of the column. The column was eluted with 20 ml hexane to collect a mixture of aliphatic and PAHs, respectively. The solvent is removed using a vacuum rotary evaporator and dried by blowing gently with prepurified nitrogen gas. The column was eluted with 20 mL of hexane for *n*-alkanes and 20 mL mixture of *n*-hexane

and dichloromethane (3:1, v/v). The solution was ready for GC-MS analysis (Vaezzadeh et al., 2015a).

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

Concentrations of *n*-alkanes and PAHs in sediments were determined using a Shimadzu Gas Chromatography-Mass Spectrometer (GC-MS) model QP 2010. Chromatographic separation was achieved by a BPX-5 of non-polar capillary column (30 m×0.25 mm i.d., 0.25 μm film thickness) equipped with a splitless injector and quadrapole mass analyzer. Helium was used as the carrier gas (1 mL/min). Samples were injected in the splitless mode with both temperatures of an injector and detector were 280 °C, respectively. Oven temperature was programmed from 50°C, held for 2 minutes and ramped to final temperature at 300°C at 4.5°C/ min. Final temperature was held for 10 minutes. The aliphatic and PAHs fractions were diluted with 100 μL of *n*-hexane and dichloromethane, respectively. Exactly 1 μL of samples were injected into the column. Concentration of *n*-alkanes were determined according to their peak area (Vaezzadeh et al. 2015a).

3.7.4 Identification and Quantification of Hydrocarbon Compounds

The quantity of individual hydrocarbon was calculated using the response factor (RF) the component of interest relative to the internal standard calculated from the concentration of the standard solutions as shown in Equation 3.9 (Yusoff et al., 2012).

$$RF = (C_{std}/A_{std}) * (A_{is}/C_{is}) \quad \text{Equation 3.9}$$

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

while, the concentrations of individual hydrocarbon in the sample were calculated using Equation 3.10

Concentration of analyte = (Cis/Ais) * A_x* RF_x Equation 3.10

where, C_{is} – Concentration of internal standard; A_{is} – Peak Area for analyte x; A_x – Peak area for internal standard; RF_x – Response factor for analyte x.

3.7.5 Diagnostic Indices Based on Aliphatic Hydrocarbons

Several diagnostic indices were used to identify the sources of *n*-alkanes in the environment such as CPI, MH, ACL, terrigenous aquatic ratio (TAR) and UCM (Vaezzadeh et al., 2015a).

3.7.5.1 Carbon Preference Index (CPI) and Major Hydrocarbons (MH)

CPI was calculated as the ratio of odd carbon numbered (C_{25} to C_{33}) divided with even carbon numbered from C_{25} to C_{33} of *n*-alkanes using Equation 3.11 as used by Masood et al. (2016).

$$CPI = 0.5*[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})] + 0.5*[(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})] \quad \text{Equation 3.11}$$

3.7.5.2 Ratio of Low Molecular Weight (LMW) Alkanes to High Molecular weight (HMW) Alkanes

The ratio of low molecular weight hydrocarbon (LMW) to high molecular weight hydrocarbon (HMW) is determined using Equation 3.12. LMW hydrocarbons are ranged

between C_{10} to C_{23}, while HMW hydrocarbons are ranged between C_{24} to C_{33} (Sakari et al., 2008b).

$$LMW/HMW=(C_{16}+C_{17}+C_{18}+C_{19}+C_{20}+C_{21}+C_{22}+C_{23}+C_{24}+C_{25}+C_{26})/(C_{27}+C_{28}+C_{29}+C_{30}+C_{31}+C_{32}+C_{33})$$ Equation 3.12

3.7.5.3 Average Chain Length (ACL)

The ACL is defined as average weight of carbon atoms in *n*-alkanes of higher plant (C_{25}-C_{33}) as shown in Equation 3.13. The higher ACL values indicate the higher plant input whereas the lower value is believed to be caused by pollution (Zakaria et al., 2002).

$$ACL = [25(nC_{25})+27(nC_{27})+29(nC_{29})+ 31(nC_{31})+ 33(nC_{33})]/(nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33})$$ Equation 3.13

3.7.5.4 Terrigenous Aquatic Ratio (TAR)

The TAR can be used to evaluate the importance of terrigenous inputs against aquatic inputs (see Equation 3.14). It is the ratio of the concentrations of long chain alkanes to short-chain alkanes (Vaezzadeh et al., 2015a).

$$TAR = (C_{27}+C_{29}+C_{31})/(C_{17}+C_{19}+C_{21})$$ Equation 3.14

3.7.5.5 Unresolved Complex Mixture (UCM)

UCM can be identified in the aliphatic fraction and usually appeared as a hump in GC-MS chromatogram with either unimodal or bimodal patterns (Vaezzadeh et al., 2015a). UCM is an indication of hydrocarbon pollution by degraded oil.

3.7.5.6 Isoprenoids

Isoprenoids of pristane and phytane are useful for source identification of hydrocarbons in sediments. Pristane and phytane are resistant toward degradation compared to *n*-alkanes. The ratio of C_{17}-alkane/pristane and C_{18}-alkane/phytane less than one can be a sign of weathered oil. While, C_{17}-alkane/pristane with value >2 indicates phytoplankton origin of *n*-alkanes. The ratio of pristane/phytane higher than unity is a sign of petroleum source of hydrocarbons (Vaezzadeh et al., 2015a).

3.8 Statistical Analysis

All statistical analyses were carried out using the software IBM SPSS version 22. The one-way analysis of variance (ANOVA) was used to determine the statistically significant differences between the mean concentration values of heavy metals in surface sediment. Statistical analyses such as correlation analysis, principal component analysis (PCA) and cluster analysis (CA) were determined. The heavy metals data and hydrocarbons data of surface sediments were subjected to statistical analysis to assess the sources of these heavy metals. The main objective was to identify the sources of heavy metals and hydrocarbons in the river sediments and to understand the geochemical relationships between samples.

3.8.1 Correlation Analysis

Pearson correlation was carried out to determine the relationship between the heavy metals analyzed. The significance of the relationship between variables was measured from

the correlation coefficient. The correlation analysis was two-tailed as used by Shen et al. (2019).

3.8.2 Principal Component Analysis (PCA) and Cluster Analysis (CA)

The PCA was carried out to determine the possible sources of heavy metals and hydrocarbons. Both heavy metals and hydrocarbons data were subjected to PCA with varimax rotation. CA was carried out to determine the possible homogeneity between heavy metals. The CA was used in heavy metals investigation to infer the similarity or relationship among heavy metals and their origin (Shen et al., 2019).

3.9 Chapter Summary

The materials and methods have been explained in this chapter. It entails the sample collection and preparation, sedimentological studies, extraction of heavy metals and hydrocarbons from sediment matrices, assessment of sediment contamination and statistical analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Sedimentology of Sadong River

Table 4.1 shows the physical characteristics of the sediments of Sadong River. The sediments in depositional environments of the river systems can be classified into three main fractions which are clay (<2 µm), silt (2 µm - 63 µm) and the sand (>63 µm) as suggested by Keil et al. (1994). The sediments collected from Sadong River consist predominantly silts and clays with minor plant remains (Lam, 1988). Sadong River is an enormous river with varying dynamics and sediment geometry. The processes of sediment transport in Sadong River was mainly by runoff, erosion, infiltration, accumulation and deposition (Negrel & Petelet-Giraud, 2012). This may be due to the frequent rainfall in the area and the low lying topography in the vicinity of Sadong River.

Table 4.1: The physical characteristics of surface sediments from Sadong River, Sarawak

Stations	Location	Colour
BS1	Sebangan	grey to dark grey
BS2	Sadong Jaya	dark grey
BS3	Sungai Buloh	dark grey
BS4	Simunjan	grey to dark grey
BS5	Gedong	dark grey to black
BS6	Sebemban	dark grey to black
BS7	Serian	dark grey

4.1.1 Particle Size Analysis

The sediment of Sadong River is made up essentially of the 63 µm particle sized fractions. The particle size analysis helps to understand the sand silt clay ratios. This analysis is useful to differentiate metal partitioning between fine grained materials that transported in suspension and those transported as part of the bedload. Most top river sediment samples are silt, clay and sand (Sundararajan & Srinivasalu, 2010; Babek et al., 2015). Major factor that affect the adsorption of heavy metals and hydrocarbons in sediment is particle grain size (Keshavarzifard et al., 2017).

The particle size data showed the sedimentological behaviour of Sadong River is not complex. The fluvial environment, flood plain sediments and estuarine sediments of Sadong River have similar geometry. This may be attributed to the high amount of fine grained particles mostly derived from the sedimentary facies in the area. The fine grained sediments are mainly Cretaceous deposits and peat deposits (Nagarajan et al., 2014). There was no obvious sedimentary structure such as mudcrack and lamination in Sadong River.

The sediment texture of surface sediment reflected in the grain size distribution is important to understand the history of depositional environment (Kashani et al., 2016). In all the surface sediment samples except at Serian (BS7), silt and clay dominate over sand, indicative of relatively calm environment of deposition (Sundararajan & Natesan 2010). The grain size variability is inherent to fluvial sedimentation in the Sadong River system, these sediments are sorted based on particle size, organic content and pore water (Babek et al., 2015). The sediment grain size analysis of surface sediments from Kelantan River are mainly composed of silt and the sand content gradually decreased overall from the upstream to the downstream (Pooveneswary et al., 2020). This is similar to the sediment trend in surface

sediment of Sadong River with BS7 in the upstream comprised of high sand compared to other sampling stations of Sadong River.

Table 4.2: The particle size analysis of surface sediments from Sadong River, Sarawak

Stations	Particle size analysis (%)*			Type of sediment
	Clay < 2 µm	Silt 2 µm -63 µm	Sand > 63 µm	
BS1	11.5	85.7	2.8	Silt
BS2	15.8	72.3	11.9	Clayey silt
BS3	10.4	84.9	4.7	Silt
BS4	18.6	69.1	12.3	Clayey silt
BS5	22.9	70.5	6.6	Clayey silt
BS6	24.1	68.4	7.5	Clayey silt
BS7	10.3	23.9	65.8	Sandy silt

***-** Particle size analysis based on Dhivert et al. (2015)

4.1.2 Spatial Distribution of Moisture Content, Ash Content and Total Organic Matter

Figure 4.1 shows the moisture content in surface sediment has similar range for all sampling stations. The highest moisture content of 46.1% was recorded in Sebangan (BS1) sediment in the downstream of the Sadong River, while the lowest moisture content of 28.0% was recorded at Serian (BS7) sediment in the upstream of Sadong River. Organic matter is one of the important parameter that control heavy metal behaviour in the river sediments (Natesan & Seshan, 2010; Omorinoye et al., 2019a). The highest value for ash content was 96.3 % recorded in Serian (BS7) sediment and the lowest value was recorded in Sadong Jaya (BS2) and Sungai Buloh (BS3) sediments with 91.9% and 91.5%

respectively. The high ash content in Serian (BS7) sediments may be caused by the compaction of fine grained sediments (Arnell et al., 2015). In Figure 4.1, the error bars indicate the standard deviation while the letters a, b, c indicate significant difference in mean values in the seven stations. All surface sediments have moderate TOM. Sediments with high coarse sand fraction have low TOM and lower pollutant concentration whereas fine sediment fractions have moderate TOM. Sediments of Sadong River have high percentage of silt and clay which enable the sediments to have strong affinity and adsorption to heavy metals and hydrocarbon compounds due to greater surface area to volume ratio (Amellal et al., 2011). The TOM was highest in Sungai Buloh (BS3) and Sadong Jaya (BS2) with 8.5% and 8.0% respectively. The organic matter reported in the surface sediments of Perak River, Malaysia was ranged between 4.4-13.0% with sites S7, S8, and S9 (Salam et al., 2019) with the same range as Sadong river. The TOM reported in sediments from South Korea by Yoo et al. (2013) which are composed of fine grained sediment have similar range with sediments from Sadong River ranged 5.3-9.1%. TOM reported in surface sediments from Greece composed of fine grained sediments were between 4.19-7.87% (Hahladakis et al., 2013).

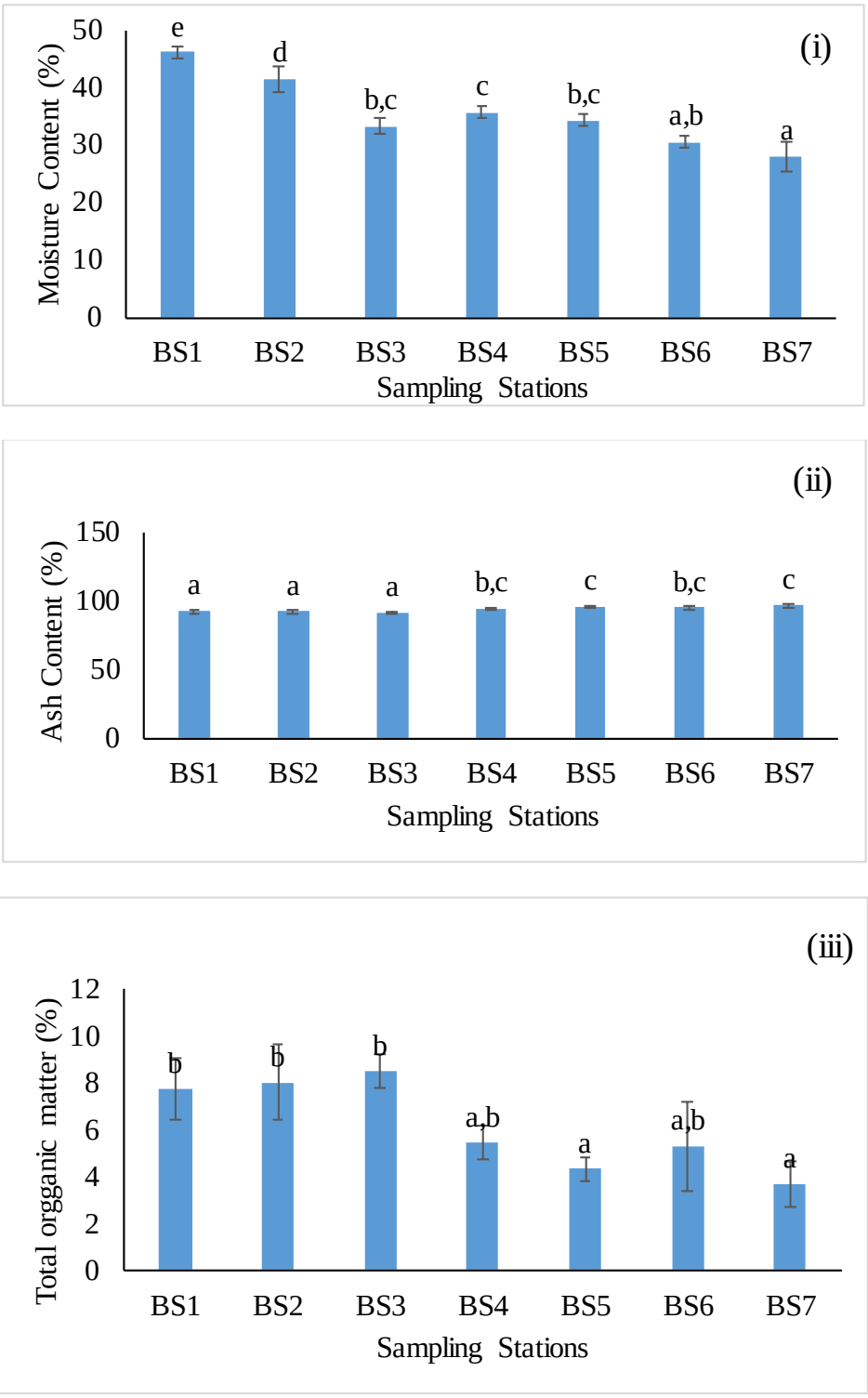


Figure 4.1: Spatial distribution of (i) moisture content (ii) ash content and (iii) total organic matter in surface sediments from Sadong River. The letters a, b, c indicate significant difference in mean values

4.1.3 Vertical Distribution of Moisture Content, Ash Content and Total Organic Matter (TOM)

Figure 4.2 shows the moisture content had consistent value in the top core samples and increased downwards to the middle layers and then varied considerably toward the bottom in all the sampling locations. The highest value for moisture content was 45.2 % at layer 0.0-2.5 cm in core sediments of Gedong (BS5). The top layer of BS5 had 45.0 % for layer 0.0-2.5 cm and 39.0 % for 2.5- 5.0 cm in the core sediments. The moisture content decreased at layer 7.5-10.0 cm with moisture content 38.3 %, and increased to 48.0 % respectively. High moisture content in the core sediments of Gedong (BS5) may be attributed to the silty clay sediments found in the area. Moisture content in core sediments of Sebangan (BS1) increased from the top layer to the lower of sediments with moisture content 47.1 % at upper layer 0-2.5 cm to 48.1 % at 7.5-10.0 cm layer and decreased at layer 22.5-25.0 cm to 39.1% and increased to 50.0 % at the 42.5-45.0 cm layer. The moisture content of sediment at Sadong Jaya (BS2) was consistent from the top layer to the lower layer of core sediments with 45.3 % at 0-2.5 cm layer, 42.3 % at the 15.0-17.5 cm layer and 38.3 % at the 27.5-30.0 cm which was the lowest layer. High moisture content were observed at deeper layers of core sediments of Sebangan (BS1) and Gedong (BS5) sediments which may be caused by the compaction of fine grained sediments.

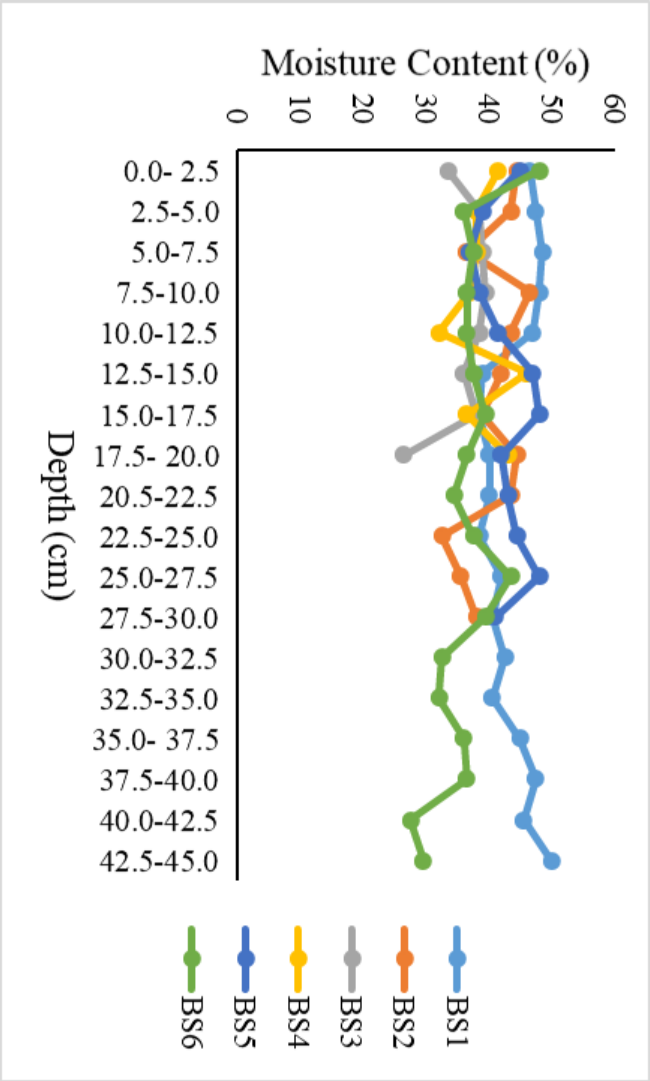


Figure 4.2: Vertical distribution of moisture content in core sediments from Sadong River

High ash content was recorded in BS5 sediment with 92.7% in layer 0.0-2.5 cm and 89.6 % at layer 12.5-15.0 cm. High ash content of 89.8 % were recorded in lower layer 17.5-20.0 cm at BS3. The ash content in the sediment from six sampling stations were consistent from the top layer toward the bottom layers as shown in Figure 4.3.

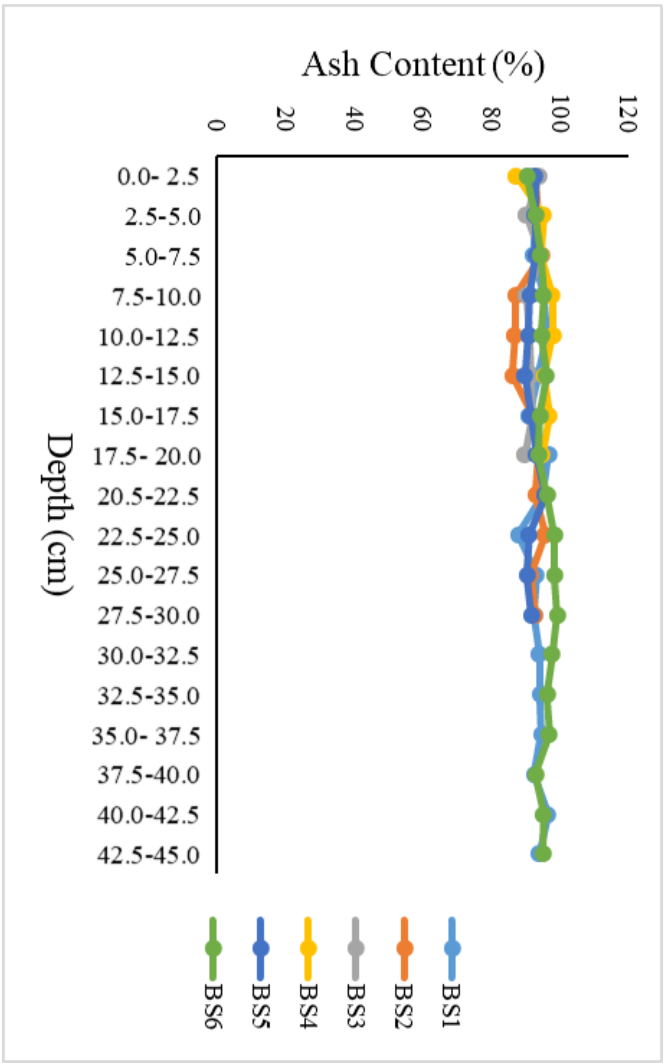


Figure 4.3: Vertical distribution of ash content in core sediments from Sadong River

The sediment of Sadong River was generally enriched by organic matter with the highest TOM was observed in core sediments of Sebemban (BS6) at 9.7%. at the upper layer 0.0-2.5 cm. The TOM varied considerably from the upper layer to the lower layer of core as shown in Figure 4.4. The TOM decreased from upper layer of core (0.0-2.5 cm) with TOM 9.7 % and decreased at the middle core from 10.0-12.5 cm to 20.5- 22.5 cm layer with TOM 5.5 % and 3.8 %, then increased towards the lower layer of core at 37.5- 40.0 cm and 42.5-45.0 cm had a TOM of 7.1 % and 5.0 %. Whereas the lowest value of TOM is

in BS3 sediment at 6.0 % at 0.0-2.5 cm and 8.9 % at the 10.0-12.5 cm layer. The mass of vegetation at the river banks may account for the amount of organic matter (Keil *et al.*, 1997). The mobility of heavy metal ions can be enhanced in the sediments enriched with organic matter.

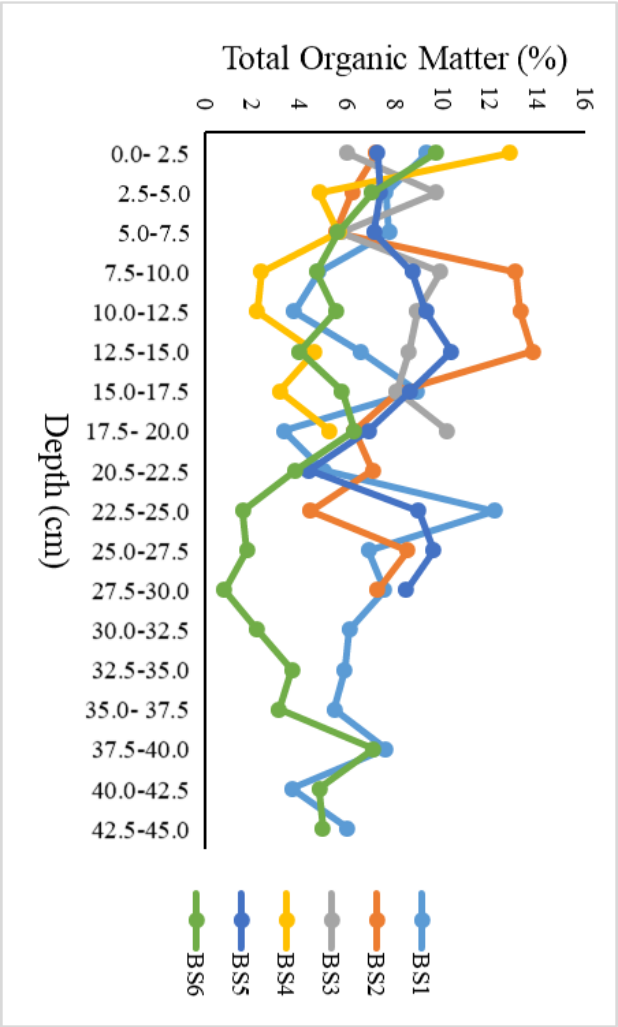


Figure 4.4: Vertical distribution of TOM in core sediments from Sadong River

Weathering and erosion of rocks or unconsolidated deposit released the sediment into the river environment. These sediments were then suspended, transported and deposited by water and other forms of sediment transport (Dhivert et al., 2016). The organic

matter can be derived from the decomposition of plants and animals as well as freshly deposited leaves, twigs, branches and others. Organic matter combined with heavy metals formed organo-metallic complexes which are stable and then released into river sediments (Sundararajan & Srinivasalu, 2010).

4.2 Validation of Analytical Methodology for Heavy Metal in Sediment samples

The calibration curves of the essential heavy metals and major metals as well as toxic heavy metals showed R^2 between 0.9969-0.9999. The results of validation are shown in Table 4.3. Calibration curves of metal standards were constructed for each heavy metal. A procedural blank was analysed periodically for each batch of samples. The LOD, LOQ and LOL for 11 metals analysed were then reported.

Table 4.3: Calibration parameters obtained from method validation for heavy metals and major metals in sediments using AAS

Metal	LOL (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)	Sensitivity (absorbance)	Dynamic Range	Regression (R^2)
Zn	0.95	0.08	0.27	0.20	0.27-0.95	0.9969
Cu	4.82	0.06	0.19	0.09	0.19-4.82	0.9982
Ni	4.74	0.06	0.19	0.10	0.19-4.74	0.9999
Fe	4.97	0.55	1.85	0.03	1.85-4.97	0.9968
Mn	2.95	0.38	1.26	0.16	1.26-2.95	0.9984
Mg	2.86	0.04	1.28	0.12	1.28-2.86	0.9986
Na	2.90	0.01	0.03	0.10	0.03-2.90	0.9986
K	2.90	0.02	0.01	0.04	0.01-2.90	0.9990
Pb	4.86	0.09	0.29	0.05	0.29-4.86	0.9980
As	9.88	0.03	0.08	0.01	0.08-9.88	0.9983
Cd	1.47	0.01	0.03	0.21	0.03-1.47	0.9990

Quantification of the analyzed metals was performed within the linear range of the calibration curves. The concentration ranges were within the concentration levels usually found in sediment samples. Calibration curves conformed to the concentration of standard solution for AAS calibration. The regression analysis and curves plotted from four points were achieved with the linearity ranges. Regression coefficients were higher than 0.99 for

all the metals analysed. LOD is the lowest concentration of the analyte that was distinguished from the blank sample. It was determined by a standard deviation and the values recorded showed the lowest concentration of the heavy metals and major metals. The analytical method was validated using CRM, sewage sludge amended soil standardized by BCR. The percentages of recoveries of the heavy metals were between 90% - 100% as shown in Table 4.4.

Table 4.4: Result of accuracy and precision analysis for CRM 142Q Sewage sludge amended soil, standardised by BCR (Asare et al., 2019)

Metals	Certified Value (mg/kg)	Analysed Value (mg/kg)	Recovery Value (%)
Cu	131±6.0	130.49±2.13	99.61
Zn	1047±18	1046.42±0.17	99.90
Ni	37.2±2.1	37.31±0.42	100.30
Pb	168±5.0	167.21±3.1	99.53
Cd	75.0±1.6	75.43±10.18	99.24
Fe	1061±17	1062.71±0.15	100.16
Mn	886±12	888.62±1.39	100.30
As	41±1.9	40.98±1.26	99.95

4.3 Distribution of Metals in the Sediments from Sadong River

The metals investigated in this study include the major metals, essential heavy metals and toxic heavy metals. Essential heavy metals include Zn, Cu, Ni, Fe and Mn, while the toxic heavy metals are Pb, Cd and As. The major metals are Mg, K and Na. Heavy metals

can be accumulated in river sediments and can be incorporated in several biological and chemical cycles affecting the water column and biota (Buhari & Ismail 2016).

4.3.1 Major Metals

Major metals in rivers can also be called bulk metals such as Mg, K and Na (Schroeder et al., 1969; Golasik et al., 2015; Qu et al., 2019). Major metals occurred as particulates, colloids and dissolved phases which can be easily absorbed to silica, clay and organic material. The adsorption process removes these metals from the river water and stored them in the sediment (Nduka & Orisakwe, 2011). Several factors such as alkanility, acidity (pH) and solubility product of essential metal can also control the concentration of these dissolved metals (Nair & Sujatha, 2013). Mg, Na and K are important dissolved constituents of natural river water and can be derived from terrestial sources (Kara et al., 2015).

Figure 4.5 shows the spatial distribution of Mg in surface sediments from Sadong River. Mg is often associated with the weathering of carbonates and carbonate minerals (Sukri et al., 2018). Lithology, climate, temperature, run off, relief and physical erosion have contributed the presence of Mg in all the sampling stations (Dalu et al., 2018). The highest concentration of Mg was detected in sediment from the midstream of the river at Sadong Jaya (BS2) with concentration 1860.15±3.26 mg/kg. There was an enrichment of Mg in the surface sediments at the midstream at Sadong Jaya (BS2) and Sungai Buloh (BS3). Lowest concentration was detected in sediments from the upstream in Serian (BS7) with concentration 383.23±29.71 mg/kg. The concentration of Mg reported in Terengganu River is 730.9 mg/kg (Sukri et al., 2018).

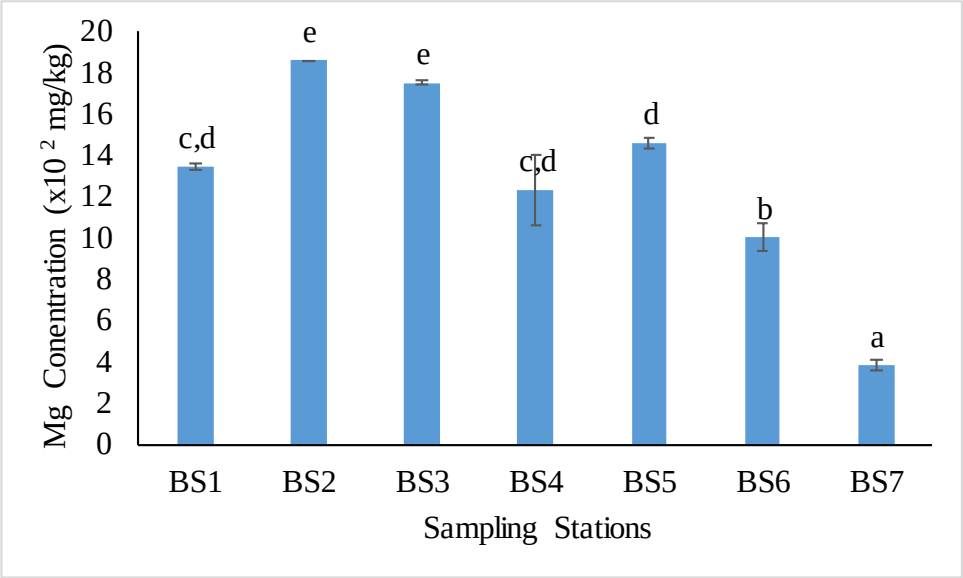


Figure 4.5: Spatial distribution of Mg in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

Certain factors affect the chemical composition of K such as grain size and sorting of minerals during the transportation of eroded sediments (Ge et al., 2019). The extent of the mobility of K is dependent on weathering and adsorption of dissolved K on clay minerals (Nesbitt & Young, 1996). The highest concentration of K as shown in Figure 4.6 in sediments is detected at Gedong (BS4) with concentration 1193.84±6.06 mg/kg. The surface sediments at the midstream and the downstream of the river have high concentration of K and concentration of K depleted at the upstream of the river. While the lowest concentration of K was detected in surface sediments of Serian (BS7) with concentration 318.81±70.09 mg/kg. The concentration of K reported in surface sediments from Terengganu River was 716.44 mg/kg (Sukri et al., 2018).

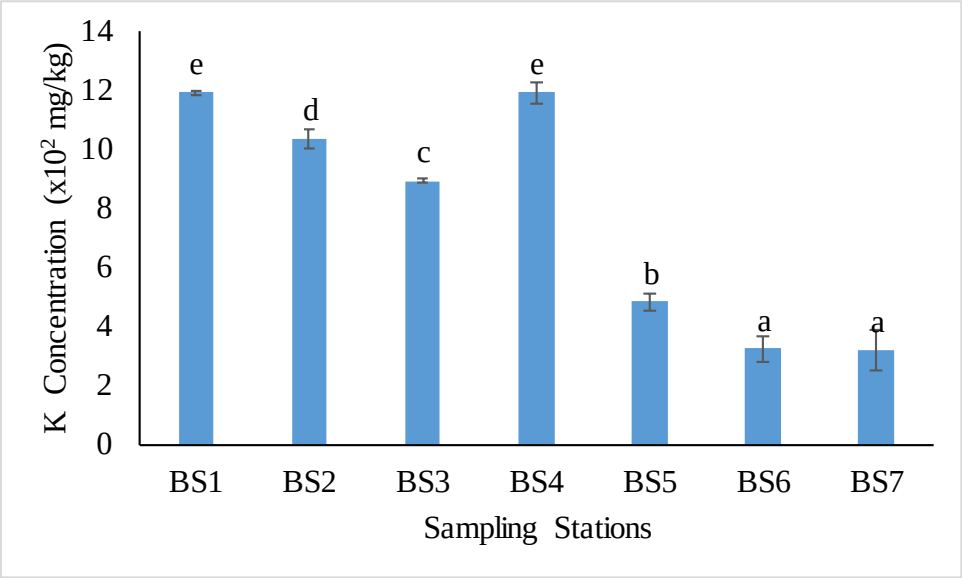


Figure 4.6: Spatial distribution of K in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

The spatial distribution of Na in surface sediments from Sadong River is shown in Figure 4.7. The contribution of Na from atmosphere is minimal suggested that Na in the river is originated from another source. Na could be derived from weathering of silicate minerals (Gupta et al., 2011). The highest concentration of Na was found in sediment from downstream of Sadong River at BS1 with concentration 1908.88±83.94 mg/kg. Concentration of Na in surface sediment increased steadily from the upstream towards the midstream to the downstream of Sadong River. The lowest concentration of Na was detected in BS7 sediment with value 35.11 ±7.97 mg/kg. The variation of Na concentration in the sediment at the upstream towards the midstream of the river indicated a depletion of dissolved ions during transportation and/or an addition of alkali from terrigenous sources.

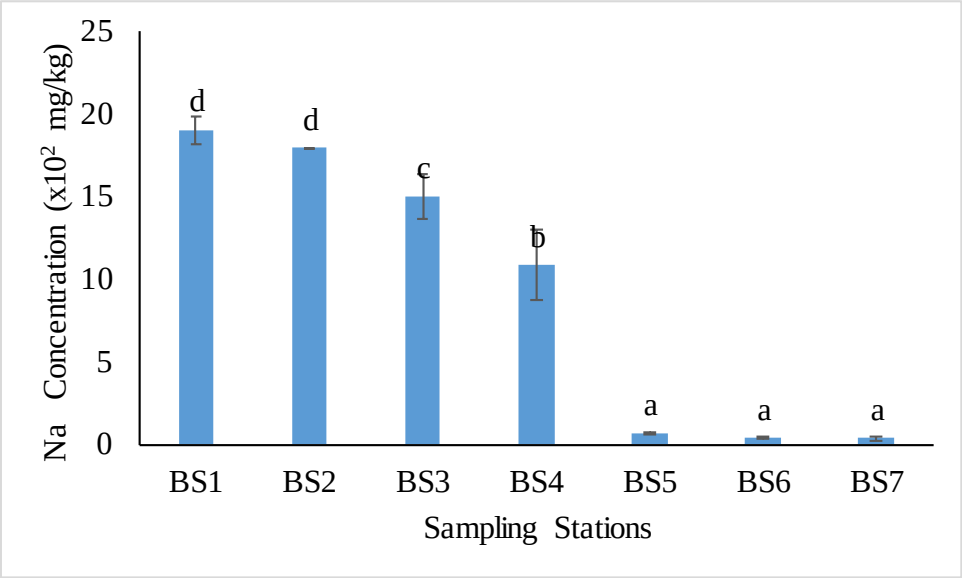


Figure 4.7: Spatial distribution of Na in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

The concentrations of Mg and K in surface sediments were recorded at exceptionally high in all sediments compared with Na with concentration ranged for Mg and K were 380.24±29.72 to 1857.16±3.26 and 319.01 mg/kg 70.10 to 1197.35±32.54 mg/kg, respectively. There was very low concentration of Na in surface sediments of Gedong (BS5), Sebemban (BS6) and Serian (BS7). The concentration of Mg, Na and K detected in surface sediments of Sadong River is lower compared to concentration of Mg (14,139±14,653 mg/kg), K (3,224±1,426 mg/kg) and Na (14,287±8,774 mg/kg) detected in surface sediments from Aliaga region, Turkey (Kara et al., 2015). The concentration of Mg reported in surface sediments from Selangor River Malaysia was 808.46 mg/kg (Othman et al., 2018) while the concentration of Mg and K ranged in Terengganu River in Malaysia between 202.0 to 2769.0 mg/kg and 63.36 to 1730.0 mg/kg respectively (Sukri et al., 2018).

4.3.2 Spatial Distribution of Heavy Metals in the Sediments from Sadong River

Assessment on spatial distribution of the heavy metals was carried out to understand the relationship between heavy metals concentration with sediment dispersal. Figures 4.8-4.14 show spatial distribution of heavy metals and major metals in the surface sediments from seven sampling sites of Sadong River, Samarahan. The river banks were visually homogenous having vegetation around the river banks and mostly composed of fine-grained sediments. Sebangan (BS1) and Sadong Jaya (BS2) are located at the downstream of Sadong River, while Sungai Buloh (BS3), Simunjan (BS4), Gedong (BS5) and Sebemban (BS6) are situated at the midstream of the river and Serian (BS7) is located at the upstream of the Sadong River.

4.3.2.1 Essential Heavy Metals

The essential heavy metals determined in sediments from Sadong River include Zn, Cu, Ni, Fe and Mn. The density of these of heavy metals is five times greater than water. These metals can be formed naturally from the terrestial environments and can be found in rocks, plants, soils and sediments (Emmanuel et al., 2018). Human and industrial activities can increase the concentration level of heavy metals in the river sediments and lead to environmental pollution (Tatone et al., 2016).

Figure 4.8 shows distribution of Zn in the surface sediments from Sadong River. The highest concentration of Zn in surface sediments of Sadong River is detected at Sebangan (BS1) with concentration 46.61±1.17 mg/kg. The concentration of Zn increased gradually from the upstream to downstream. The lowest concentration of Zn was detected in surface sediment of Simunjan (BS4) with concentration 19.29±2.09 mg/kg. Elemental Zn does not react with water molecules but the ion usually forms a protective water insoluble

zinc hydroxide (Guan et al., 2018). The concentration of Zn in the surface sediments of Sadong Jaya (BS2), Sungai Buloh (BS3) and Simunjan (BS4) were 31.24±2.34 mg/kg, 32.49±2.26 mg/kg and 19.29±2.09 mg/kg, respectively. The concentration of Zn in the surface sediments of Simunjan (BS4), Gedong (BS5) and Sebemban (BS6) were lower than 20 mg/kg whereas the concentration of Zn at Serian (BS7) was 21.76±3.78 mg/kg.

The discharge of Zn into Sadong River can be attributed to agricultural and fishing activities which might have contributed to the high concentration of Zn in surface sediment of Sebangan (BS1). The surface sediments of downstream of Sadong River is characterized with high concentration of Zn and moderate concentration of Zn at the midstream of the river. The higher concentration of Zn in the midstream and downstream of Sadong River may be due to point sources such as fungicide for paddy farmlands in the area or untreated sewage discharge (Patel et al., 2018). Concentration of Zn detected in surface sediments from Sadong River with concentration 46.61±1.17 mg/kg is lower than those reported in surface sediments of Port Klang, Selangor with concentration of 88.3±31.4 mg/kg (Sany et al., 2013). The concentration of Zn reported in surface sediments of Upper Loire France was 90.0 mg/kg (Dhivert *et al.*, 2015) and concentration of Zn in surface sediments of Uruguay River, Argentina was 84±7.6 mg/kg (Tatone et al., 2016). The concentration of Zn is surface sediments of Terengganu River, Malaysia was ranged between 2.05 to 31.30 mg/kg (Sukri et al., 2018). The mean concentration of Zn in surface sediments of Linggi River Malaysia was 103 mg/kg and were reported to originate industrial activities with higher concentrations at the downstream area of Linggi River (Elias et al., 2018). The highest concentration of Zn in Sadong River was reported in the surface sediments from downstream of Sadong River at BS1.

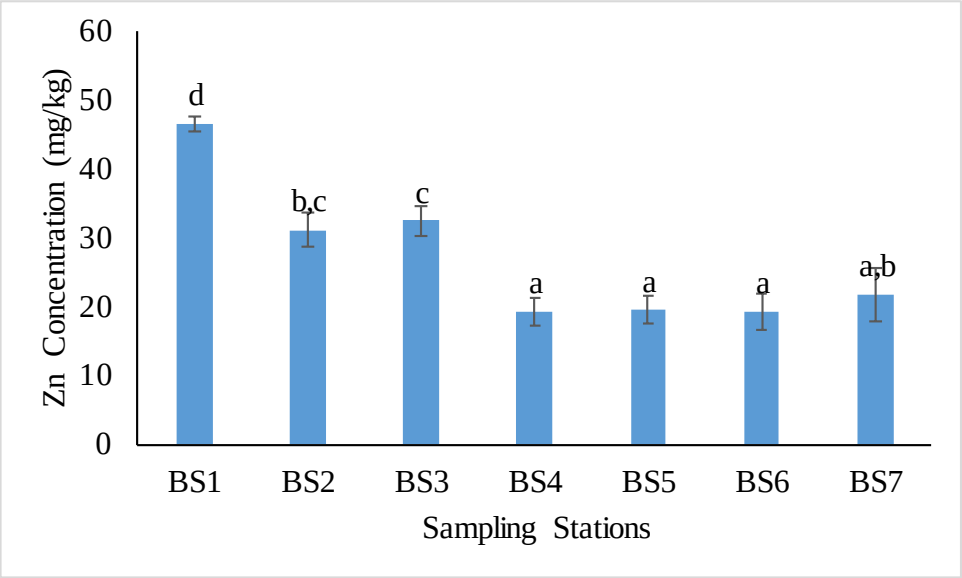


Figure 4.8: Spatial distribution of Zn in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

Cu is a naturally occurring element in the earth's crust and rivers. Cu is an essential nutrient for plants, fish, animals and human. The presence of Cu may be due to anthropogenic sources such as point and diffuse sources (Eucharia & Omparkash, 2016). The diffuse source is mainly contributed by agricultural activities that occur at the banks of the river. Cu occurred in river sediments as a versatile material which is recyclable, resistant to corrosion and durable (Parween et al., 2017). The spatial distribution of Cu in surface sediments of Sadong River is shown in Figure 4.9. The highest concentration of Cu was detected in surface sediment at Sebangan (BS1) with concentration 12.30±0.27 mg/kg in the downstream of Sadong River. High concentration of Cu detected in surface sediments of Sebangan (BS1) and Sebemban (BS6) may be contributed by agricultural and fishing activities. The lowest concentration of Cu was detected in the surface sediments at Serian (BS7) with concentration of 3.45±0.28 mg/kg.

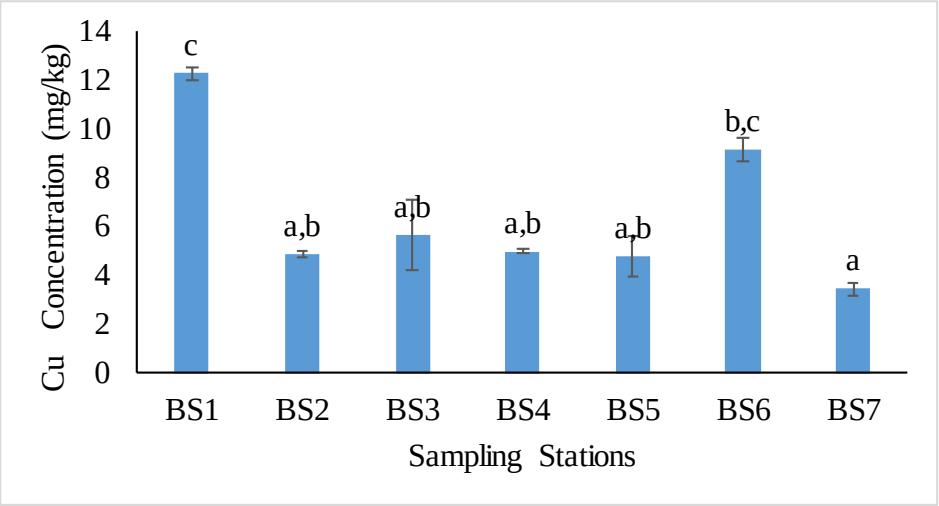


Figure 4.9: Spatial distribution of Cu in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

Concentration of Cu detected in surface sediments from Sadong River at 12.3±0.27 mg/kg is higher than that reported in surface sediments of Port Klang Selangor (Sany et al., 2013) with a concentration 5.29±1.50 mg/kg. Higher concentration of Cu in Sadong River was found in the estuary (BS1) due to fishing and agricultural activities in the area. Whereas the concentration of Cu in Upper Loire France was 21.3 mg/kg (Dhivert et al., 2015) and that of Uruguay River, Argentina was 56±6.9 mg/kg (Tatone *et al.*, 2016). These rivers are major river catchment in France and Argentina. The concentration of Cu reported in surface sediments of Linggi River, Malaysia was 14.6 mg/kg and Cu in Linggi River, Malaysia was derived from anthropogenic sources (Elias, 2018). The concentration of Cu reported in surface sediments from Terengganu River ranged between 0.38 mg/kg to 15.20 mg/kg and the accumulation of Cu was attributed to fishing and release of untreated discharge to the rivers (Sukri et al., 2018).

Ni is a ubiquitous trace metal that occur in sediments. It is mostly transported in the form of a precipitated coating on particles (Zhang et al., 2018). Figure 4.10 shows the spatial

distribution of Ni in sediments of seven sampling locations along Sadong River. The highest concentration of Ni was detected in surface sediments of Sungai Buloh (BS3) which is located at the midstream of Sadong River with concentration 12.05±1.10 mg/kg. The concentration of Ni is very low at Serian (BS7) which is located at the upstream of Sadong River. This may be due to dilution of river water and the influx of sediments in the area. The lowest concentration of Ni was detected in surface sediments of Simunjan (BS4) with concentration 1.73±0.12 mg/kg. High concentration of Ni in sediments at the downstream of Sadong River have may be due to influx of municipal waste or sewage and agricultural activities (Kasilingam et al., 2016). The occurrence of Ni in the surface sediments of Balok River was attributed to power plants and any combustion-related activities around Balok River (Abdullah et al., 2015). The concentration of Ni in surface sediments of Port Klang, Selangor was 3.0 mg/kg (Sany et al., 2013) and this concentration is lower compared to that detected in surface sediments of Sadong River with a concentration of 10.57±0.20 mg/kg. The concentration of Ni in surface sediments of Linggi River, Malaysia was ranged between 1.8 to 29.7 mg/kg.

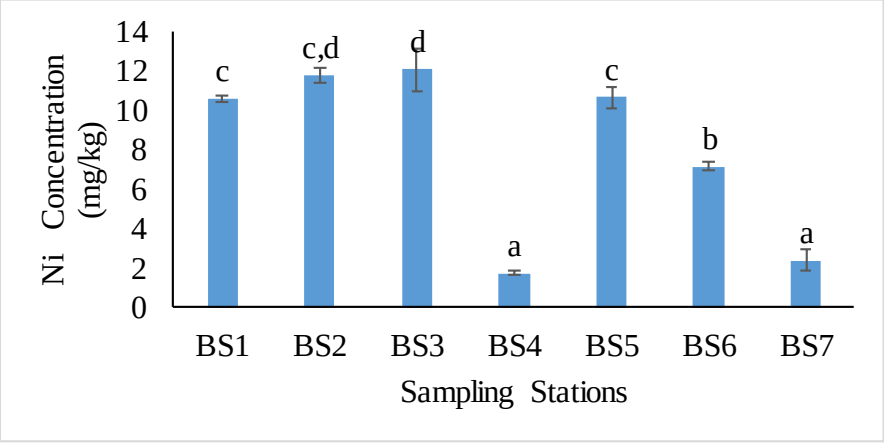


Figure 4.10: Spatial distribution of Ni in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

The spatial distribution of Fe in the surface sediments of seven sampling sites from Sadong River is shown in Figure 4.11. Fe was the most abundant heavy metal in surface sediments from Sadong River. The adsorption of Fe ions and complexes into sediments occurred as a result of ion exchange, hydrophobic interaction and surface complexation (Natesan & Seshan, 2010). The fine grained particles have a significant role in adsorption accumulation, desorption and exchange processes of the Fe ions in sediments (Sim et al., 2016; Amune et al., 2012). Highest concentration of Fe was detected in surface sediment from midstream of Sadong River at Sadong Jaya (BS2) with concentration of 3447.62±136.63 mg/kg. The concentration of Fe was depleted in the surface sediments at the downstream with lowest concentration was detected in sediment of Sebemban (BS6) with concentration 1445.37±522.44 mg/kg.

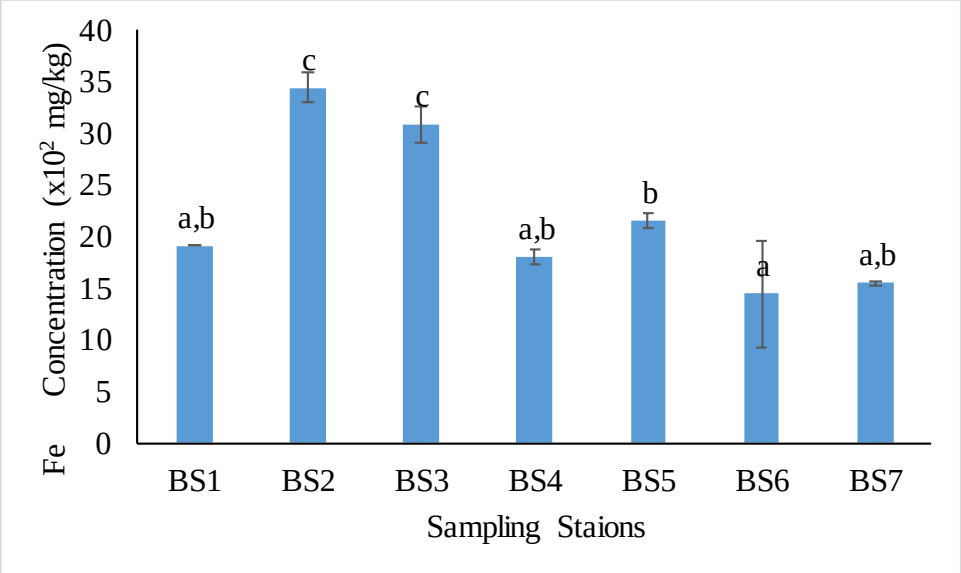


Figure 4.11: Spatial distribution of Fe in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

The occurrence of Mn in the river is contributed by natural processes and human activities (Babek et al., 2015; Kara et al., 2015). Atmospheric deposition and/or discharge of effluent may be responsible for the release of Mn into Sadong River. The highest concentration of Mn as shown in Figure 4.12 was detected in surface sediment of Sebangan (BS1) which is situated at the estuary with concentration of 464.75±17.82 mg/kg. The concentration of Mn is generally low in the surface sediments at the midstream of the Sadong River of Sungai Buloh (BS3) and Simunjan (BS4). The lowest concentration of Mn was detected in surface sediments at Serian (BS7) with concentration 188.65±4.31 mg/kg. Mn was transferred primarily by adsorption onto settling particles or by incorporation into biological phases by active uptake of organisms (Kara et al., 2015).

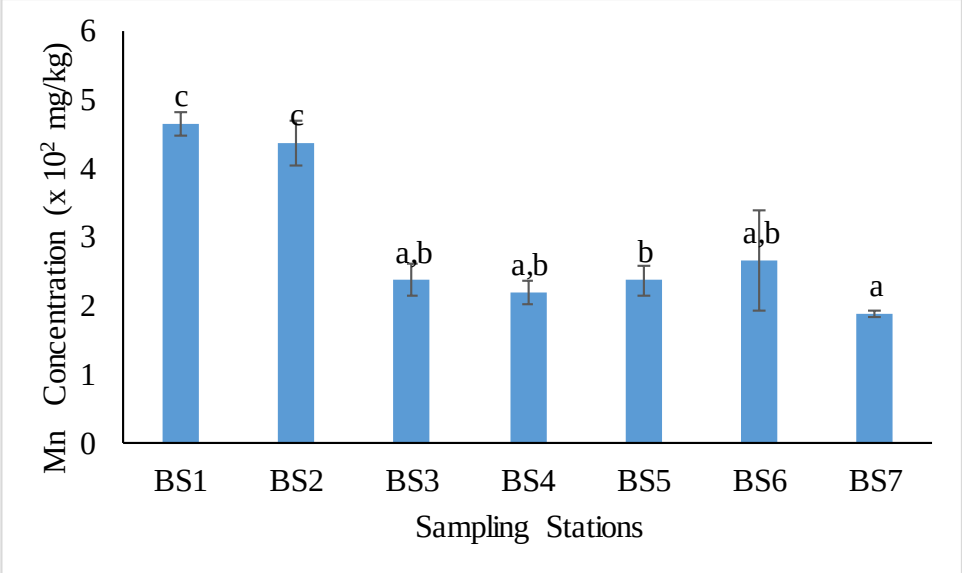


Figure 4.12: Spatial distribution of Mn in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

The high concentration of Fe in surface sediment was attributed to the fact that Fe is the most common metal found in nature and relatively abundant in the earth surface (Gupta

et al., 2011). Concentration of Fe can be influenced by the presence of dissolved rocks and organic matter. Fe and Mn have generally high concentration in tropical river due to the weather conditions caused by frequent rainfall (Aprile & Bouvy, 2010). The frequent rainfall is governed by the regime of the northeast and southwest monsoons (DOSM, 2012). The occurrence of Zn and Mn in surface sediments suggested that both heavy metals mainly originated from land based runoff and river discharges to Sadong River (Sany et al., 2013). The concentration of Fe detected in surface sediments from Sadong River with concentration 1913.42±3.71 mg/kg is lower than the concentration of Fe reported in surface sediments from Uruguay River, Argentina with concentration 48,969±7380 mg/kg (Tatone et al., 2016). Whereas the concentration of Fe reported in surface sediments from Balok River, Malaysia was 47028 mg/kg (Abdullah et al., 2015) and the concentration of Fe in surface sediments of Kepayang River, Malaysia was 14526.73 mg/kg attributed to tin mine effluent (Affandi et al., 2018) as shown in Table 4.5.

Table 4.5: The concentration level (mg/kg) of selected heavy metals in surface sediments of Sadong River with other rivers in Malaysia and in the world

	Heavy Metals				
	Cu	Fe	Mn	Ni	Zn
Balok River, Malaysia[a]	24.3	47028	155.9	16.0	159.4
Pinang River, Malaysia[b]	21.3	n.d	142	n.d	131.0
Linggi River, Malaysia[c]	14.6	n.d	n.d	10.3	103
Baleh River, Malaysia[d]	19.88±5.2	35495±573.73	446.97±10 0.82	n.d	54.97±6.30
Terengganu River, Malaysia[e]	5.33	n.d	15.95	n.d	12.56
Kepayang River, Malaysia[f]	94.48	14526.73	289.34	19.91	39.78
River Buriganga, Bangladesh[g]	14.07	n.d	37.58	6.39	36.73
Swarnamukhi River Basin, India[h]	108.3	23.296	38.8	6.0	40.93
Palk Strait, southeast coast of India[i]	69.1	55,680.3	661.4	27.9	244.2
Uruguay River, Argentina[j]	56± 6.9	48,969± 7380	1859± 233	16± 2.0	84± 7.6
Upper Loire River, France[k]	21.3	n.d	n.d	32.6	90.0
This study	12.3±0.27	1913.42±3.71	464.75±17.82	10.57±0.20	46.61±1.17

Notes:
n.d- not determined
[a]Abdullah et al. (2015), [b]Ong et al., (2016), [c]Elias et al. (2018), [d]Chai et al. (2018), [e]Sukri et al. (2018); [f]Affandi et al. (2018), [g]Nargis et al. (2019); [h]Patel et al. (2018), [i]Kasilingam et al. (2016), [j]Tatone et al. (2016), [k]Dhivert et al (2015)

4.3.2.2 Toxic Heavy Metals

The toxic heavy metals investigated in the study were Pb, As and Cd. The heavy metals are non-biodegradable and can be bioaccumulated (Shen *et al.*, 2019). The occurrence of Pb in sediments is important due to their environmental persistence, biogeochemical recycling and ecological impact (Ge et al., 2019). The spatial distribution of Pb in surface

sediments from Sadong River is shown in Figure 4.13. The highest concentration of Pb was detected in sediments at the upstream of Sadong River of Serian (BS7) with concentration of 15.48±0.61 mg/kg. This may be attributed to the activities in the vicinity of the river. Pb could be originated from atmospheric deposition via exhausts from vehicles passed through the Sungai Buloh bridge (BS3) (Liu et al., 2014; Patel et al., 2018). The concentration of Pb in surface sediment gradually decreased towards the midstream and then increased at the three stations at the downstream of the river. The lowest concentration of Pb was detected in surface sediments from the midstream of Sadong River at Simunjan (BS4) with concentration 4.61±0.42 mg/kg. Pb is a heavy metal related to pollution from industrial waste and runoff from human activities (Patel et al., 2018). Pb detected in surface sediments from Sadong River with concentration 11.24±0.51 mg/kg is lower compared to that reported in surface sediments from Uruguay River, Argentina with concentration 13±1.2 mg/kg (Tatone et al., 2016). Higher concentration of Pb reported in surface sediments of Balok River, Malaysia was 29.3 mg/kg (Abdullah et al. 2015) and in surface sediments of Klang Port of Selangor was 7.17±1.1 mg/kg (Sany et al., 2013).

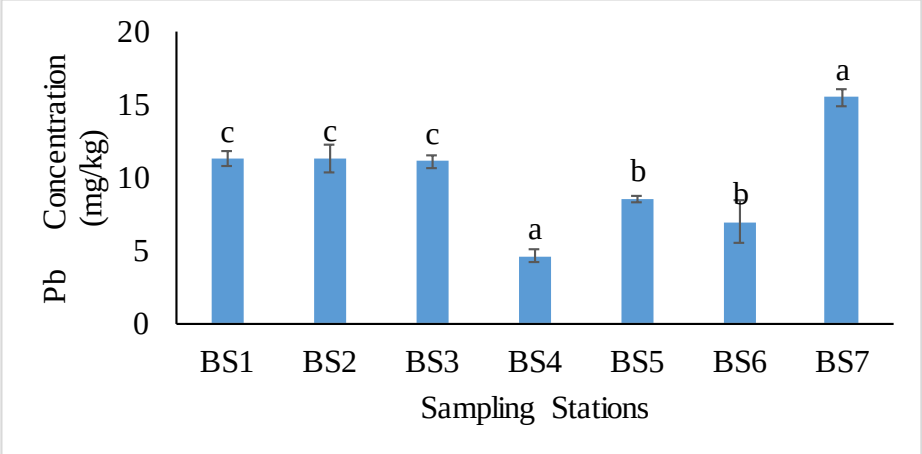


Figure 4.13: Spatial distribution of Pb in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

Figure 4.14 shows the spatial distribution of As in surface sediments from Sadong River. Highest concentration of As was detected in sediments from Sebangan (BS1) with a concentration of 18.63±0.21 mg/kg as shown in Figure 4.15. As was not detected in surface sediments of Simunjan (BS4), Gedong (BS5) and Sebemban (BS6) of Sadong River. As was detected in surface sediments of Sebangan (BS1), Sadong Jaya (BS2), Sungai Buloh (BS3) and Serian (BS7), these are the upstream and downstream of the Sadong River. The high concentration of As was detected in surface sediments at Sebangan (BS1) and Sadong Jaya (BS2) with concentrations of 18.63±0.21 mg/kg and 10.34±3.98 mg/kg respectively, recorded at the downstream and midstream. Sadong Jaya (BS2) and Sungai Buloh (BS3) are characterised by high vehicular movement and human activities. Arsenic may have originated from ship, fishing and boating activities in the study area. Arsenic is one of the most widely dispersed metalloid, though it can be found naturally in rock, soil, water and air (Sany et al., 2013).

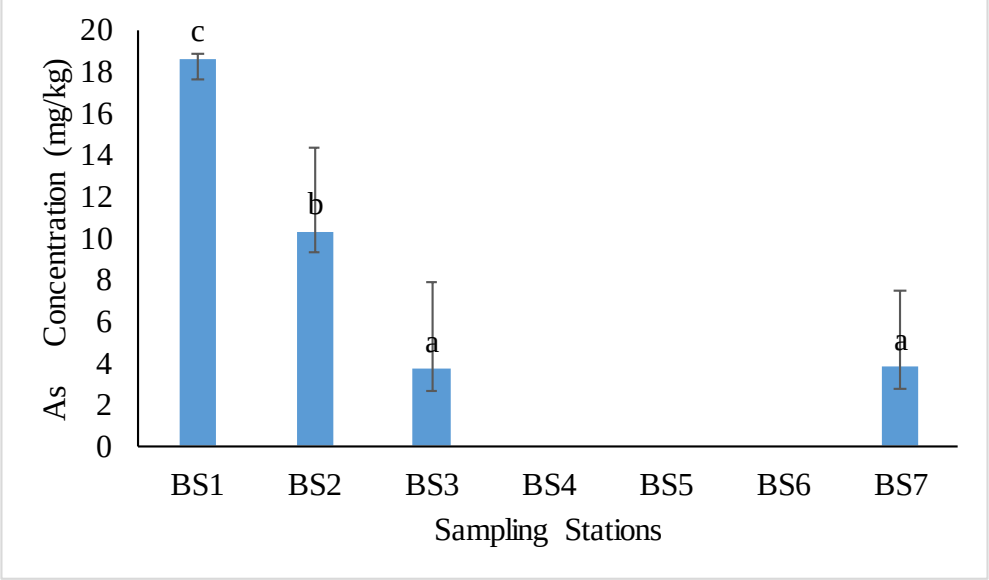


Figure 4.14: Spatial distribution of As in surface sediments from Sadong River (Error bar represents the standard deviation, Letters (a, b, c, d, e) indicate significant difference in mean values, Significant difference among stations in one way anova showed P value was <0.05)

Concentration of As in surface sediments from Sadong River were generally very low and As was not detected in three sampling locations namely Simunjan (BS4), Gedong (BS5) and Sebemban (BS6). Cd was also not detected in the surface sediments from Sadong River. The concentration of As in surface sediments of Sadong River was 9.72±2.95 mg/kg which is lower than the concentration of As reported in surface sediments at Linggi River, Malaysia which 36.0 mg/kg (Elias et al., 2018) as shown in Table 4.6.

Table 4.6: The comparison of the concentration level (mg/kg) of toxic heavy metals in surface sediments of Sadong River with other rivers

	Toxic heavy metals		
	Cd	Pb	As
Balok River, Malaysia[a]	0.5	29.3	n.d
Pinang River, Malaysia[b]	0.53	25.9	n.d
Kepayang River, Malaysia[c]	0.48	149.34	1038.10
Baleh River, Malaysia[d]	n.d	7.54±1.23	n.d
Linggi River, Malaysia[e]	0.29	30.0	36.0
Perak River, Malaysia[f]	2.94	28.86	n.d
Kelantan River, Malaysia[g]	3.66	50.89	12.21
River Buriganga, Bangladesh[h]	0.21	10.41	0.21
Swarnamukhi River Basin, India[i]	n.d	27.06	n.d
Uruguay River, Argentina[j]	n.d	13±1.2	
Upper Loire River, France[k]	0.4	37.0	n.d
This study	n.d	11.24±0.51	9.72±2.95

Notes:
n.d- not determined
[a]Abdullah et al. (2015), [b]Ong et al. (2016), [c]Affandi et al. (2018), [d]Chai et al. (2018), [e]Elias et al. (2018); [f]Salam et al. (2019), [g]Pooveneswary et al. (2020); [h]Nargis et al. (2019), [i]Patel et al. (2018), [j]Tatone et al. (2016), [k]Dhivert et al. (2015).

The surface sediments from Sebangan (BS1) contained high concentration of Zn, Cu, Mn and Na with concentration of 46.61±1.17, 12.30±0.27, 464.75±17.82 and 1911±81.01 mg/kg, respectively. Sampling sites of Sebangan (BS1), Sadong Jaya (BS2) and Sungai Buloh (BS3) are characterized with atmospheric deposition, movement of river water as well as tidal and seasonal currents. This may have caused temporal variation in mobility,

bioavailability and enrichment of heavy metals in the surface sediments. The surface sediments from Sebangan (BS1), Sadong Jaya (BS2) and Sungai Buloh (BS3) are characterized by high concentrations of heavy metals due to the increased human activities such as fishing and farming around the banks of the river and decreased dilution of river water (Seshan et al., 2010). Atmospheric deposition may be the main route for metals to accumulate in the sediments because a large amount of heavy metals can be transported for hundreds of miles from their place of origin (Sekabira et al., 2010).

There are high vehicular movement in the vicinity of Sadong Jaya (BS2) which may have led to the emission of heavy metals into the atmosphere and Sadong River (Manaf et al., 2009). The environs of Sadong Jaya (BS2), Sungai Buloh (BS3) and Simunjan (BS4) at Sadong River have boat docks and ferry service whereby some parts of the ship may have been corroded and released into the surface sediments. Several factors such as physicochemical parameters can control the rate of adsorption and desorption of Pb, Cd and As (Sany et al., 2013).

4.3.5 Environmental Assessment Based on Heavy Metals in Sediment

Table 4.7 shows the approach to establish a reference value by comparing the concentrations of the target metals in contaminated and uncontaminated sediments (Martin & Meybeck,1979; Salomon & Forstner, 1984). This can be done using sediment cores which showed the history of accumulation by comparing the pollutant concentrations in the upper layers of sediments with their pre-industrial concentration at the deeper layers of the same core (Faganelli et al., 1991; Siegel et al., 1994). The baseline concentration can also be established using the concentration of heavy metals at the deepest layers of sediment core (Abrahim & Parker, 2008).

Table 4.7: Background values of heavy metals

Cu	Ni	Zn	Fe	Mn	Cd	Pb	As	References
32	49	127	3600	-	0.20	16	-	a
1	-	10	-	6	-	0.2	-	b
32	49	127	-	-	0.20	16	-	c
32	-	127	300	750	0.3	16	10.0	d
32	49	127	35900	750	0.07	16	-	e

Note:
- = data not available
[a]Martin and Meybeck (1979), [b]World average (Turekian 1969), [c]Obaidy *et al.*, 2014, [d]Emmanuel *et al.* (2018), [e]This study

Heavy metals pollution can be assessed according to the degree of contamination (Krika & Krika, 2017; Shyamalendu et al., 2001). The degree of pollution in sediments of Sadong River has been assessed using several indices such as I_{geo}, EF and CF (Talbi & Kachi, 2019; Shen et al., 2019). The source of pollution was then determined by normalization of geo-accumulation values to the reference elements as shown in Table 4.8.

Table 4.8: I_{geo} of heavy metals in surface sediments of Sadong River

Station	Zn	Pb	Cu	Mn	Fe	Ni
BS1	-2.03	-1.09	-1.96	-1.28	-4.81	-2.80
BA2	-2.61	-1.09	-3.30	-1.37	-3.97	-2.64
BS3	-2.55	-1.12	-3.09	-2.25	-4.12	-2.61
BS4	-3.30	-2.38	-3.27	-2.36	-4.90	-5.41
BS5	-3.29	-1.49	-3.32	-2.24	-4.64	-2.79
BS6	-3.30	-1.78	-2.39	-2.09	-5.22	-3.36
BS7	-3.13	-0.63	-3.80	-2.58	-5.12	-4.93

The values of I_{geo} for all targeted heavy metals at all sampling stations were negative ($I_{geo}<0$). These results indicate that Sadong River is not polluted with the six heavy metals analyzed and can be grouped into Class 0 (Kara et al., 2015). The low I_{geo} may be attributed

to terrigenous influx from upstream of the river. The sources of heavy metals in the sediments of Sadong River can be considered natural which originated from the earth surface with small amount of anthropogenic and terrigenous input from the upstream of the river (Staub et al., 2000). The natural origin of heavy metals is due to weathering and erosion of rocks and soils (Cengiz et al., 2017), which can act as sensitive markers for any alterations in chemical compositions in sediments of Sadong River. The I_{geo} values for Zn, Pb, Mn and Fe in surface sediments from all sampling sites of Sadong River were < 1 indicating that the study area is unpolluted.

Table 4.9 shows the EFs of all heavy metals determined in surface sediment of Sadong River. Value of EF <3 was observed for Zn in surface sediments of Sadong Jaya (BS2), Sungai Buloh (BS3) and Gedong (BS5) indicated minor enrichment of Zn occurred. Moderate enrichment of Zn was observed in surface sediments of Simunjan (BS4), Sebemban (BS6) and Serian (BS7. Moderately severe enrichment of Zn was observed in surface sediments of Sebangan (BS1). Surface sediments from all the sampling sites of Sadong River have a moderately severe to severe enrichment of Pb in the sediments. An enrichment of Pb in surface sediment from Palk Strait in India has been reported by Kasilingam et al., (2016). Significant enrichment of Pb was observed in surface sediment of Serian (BS7), whereas surface sediment of Simunjan (BS4) showed a moderate enrichment of Pb. The EFs of Cu showed minor enrichment in sediments of Sadong Jaya (BS2), Sungai Buloh (BS3), Gedong (BS5) and Serian (BS7), whereas a moderate enrichment of Cu was observed in surface sediments of Simunjan (BS4) and moderately severe enrichment of Cu was observed in surface sediments of Sebangan (BS1) and Sebemban (BS6). These observations showed the river is unpolluted with all heavy metals analysed. The EF of Mn was highest in surface sediments of Sebangan (BS1), showing severe enrichment of Mn and

Sungai Buloh (BS3) had a moderate enrichment of Mn. Surface sediments from Simunjan (BS4), Gedong (BS5), Sebemban (BS6) and Serian (BS7) have a moderately severe enrichment of Mn. There was minor enrichment of Fe in surface sediments for all sampling sites with EFs value of 1. The EFs of Ni in the sediments at all sampling sites were less than 1 except for sediment of Sadong Jaya (BS2) which indicated a minor enrichment.

Table 4.9: EFs of heavy metals in surface sediments from Sadong River, Samarahan, Sarawak

Station	Zn	Pb	Cu	Mn	Fe	Ni
BS1	6.89	13.18	7.21	11.63	1.00	0.84
BS2	2.56	7.35	1.59	6.06	1.00	1.33
BS3	2.97	8.05	2.05	3.67	1.00	0.66
BS4	3.03	5.74	3.10	5.83	1.00	0.99
BS5	2.56	8.92	2.50	5.28	1.00	0.61
BS6	3.77	10.82	7.12	8.78	1.00	0.43
BS7	3.96	22.38	2.49	5.82	1.00	0.41

The CF for six heavy metals in surface sediments of Sadong River are shown in Table 4.10. CFs less than 1 indicate low degree of contamination (Natesan & Seshan 2010). Generally, all sediments were considered to be unpolluted. This showed that most of the contaminants in sediments of Sadong River originated from natural sources with low degree of contamination.

Table 4.10: CFs of selected heavy metals in surface sediments from Sadong River, Samarahan, Sarawak

Station	Zn	Pb	Mn	Fe	Ni	Cu
BS1	0.37	0.70	0.62	0.05	0.22	0.38
BS2	0.25	0.71	0.58	0.10	0.24	0.15
BS3	0.26	0.69	0.32	0.09	0.25	0.18
BS4	0.15	0.29	0.29	0.05	0.04	0.16
BS5	0.15	0.54	0.32	0.06	0.22	0.15
BS6	0.15	0.44	0.35	0.04	0.15	0.29
BS7	0.17	0.97	0.25	0.04	0.05	0.11

Low I_{geo} values for Pb were observed in surface sediment from Sadong River. Anthropogenic contribution of Pb in the surface sediments from gasoline residues may be responsible for Pb in sediment and urban refuse incineration can be source of the Pb in sediment (Nriagu & Pacyna, 1988). Midstream of Sadong River possess the strong water current and also the deepest water is usually found in the middle of the river. Midstream of river may possess strong current (Vuori, 1995) which may cause dilution of heavy metals in sediments. The concentration of heavy metals and several environmental indices have proven that the surface sediments from all sampling sites are unpolluted with heavy metals. The input of heavy metals in the sediments of Sadong River came from natural sources with minimal impact from anthropogenic activities.

4.3.6 Correlation Analysis

Correlation coefficient and inter elemental association can be evaluated using Pearson correlation coefficient (r) (Nargis et al., 2019). The results obtained from this analysis are presented in Table 4.11. The correlation coefficients between Zn with Mn (r = 0.7922), Fe with Ni (r = 0.6985), Zn with Cu (r = 0.6328) and Mn with Cu (r = 0.6079) showed the pair of metals were significantly correlated. Zn correlated with As (r = 0.943).

The correlation between Zn and As may suggest that these metas were derived similar sources which is anthropogenic. The correlation between As and Mn (r = 0.870) may suggest that these metals are from anthropogenic sources.

Table 4.11: Pearson correlation coefficient matrix for heavy metals in surface sediments from Sadong River, Samarahan, Sarawak

	Zn	Pb	Mn	Fe	Ni	Cu	As
Zn	1						
Pb	0.3805	1					
Mn	0.7922*	0.1934	1				
Fe	0.3605	0.1388	0.3907	1			
Ni	0.5651	0.1548	0.5755	0.6985	1		
Cu	0.6328	-0.1512	0.6079	-0.2623	0.3057	1	
As	0.943**	0.448	0.870*	0.245	0.424	0.0605	1

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

Zn shows positive correlation with Mn and Cu which implied that these heavy metals may have originated from the similar source. Fe showed a positive correlation with Ni, which are abundant in the sediments of Sadong River and these heavy metals are usually associated with basement rocks which were weathered and deposited in the river (Singh et al., 2002). The relationship between Zn and Cu showed these metals may have originated from the same anthropogenic sources such as untreated waste, municipal effluents and industrial activities. There was no effect due to tides and water currents at Gedong (BS5) and Sebemban (BS6), therefore the absorption of Pb by the surface sediments over a long period of time should be taken into consideration. Cu, Ni and Pb originated mostly from human activities such as discharge of municipal waste and sewage, burning of fuels as well as application of fertilizers and herbicides on farmland (Nair & Sujatha, 2013). The surface sediments from the seven sampling stations showed low ecological risk from heavy metals.

4.3.7 Principal Component Analysis (PCA) on Heavy Metals and Major Metals in Surface Sediment from Sadong River

The PCA was carried out to predict the possible sources of heavy metals in surface sediments of Sadong River. Table 4.12 showed three factors were extracted from the PCA using Varimax with Kaiser Normalization rotation method. PCA was carried out based on the concentration of the metals in sediment samples. PCA was applied to quantitatively evaluate the clustering behaviour of the metals. Factor 1 is made up of Cu, Zn, Mn, K, Na and As which are derived from mixture of sources. Factor 2 consists of Ni, Fe and Mg which are believed to be derived from natural sources. These metals were originated from weathering of parent materials (Ke et al., 2017). Factor 3 is made up of Pb which is believed to be derived from anthropogenic sources (Ashraf et al., 2018). Figure 4.15 depicts the component plot in rotated space for heavy metals in surface sediments from Sadong River. Factor 1 indicates the process of availability Cu, Zn, Mn, K, Na and As are from similar pathways in the river system. However, apart from natural weathering of minerals and rocks, direct discharge of domestic waste may be their source (Patel et al., 2018). Pb is often derived from atmospheric deposition (Liu et al., 2014). The presence of only Pb in Factor 3 may be attributed to atmospheric deposition via exhausts from automobiles because of the traffic around some localities around Sadong River.

Table 4.12: PCA analysis of heavy metals and major metals in surface sediments from Sadong River, Samarahan, Sarawak

Heavy Metals	Factor 1	Factor 2	Factor 3
Cu	**0.849**	-0.210	-0.203
Zn	**0.882**	0.346	0.244
Ni	0.306	**0.730**	0.186
Fe	-0.010	**0.978**	0.162
Mn	**0.825**	0.388	0.059
Pb	0.131	0.029	**0.976**
Mg	0.170	**0.921**	-0.288
K	**0.572**	0.505	-0.417
Na	**0.665**	0.651	-0.103
As	**0.912**	0.206	0.318

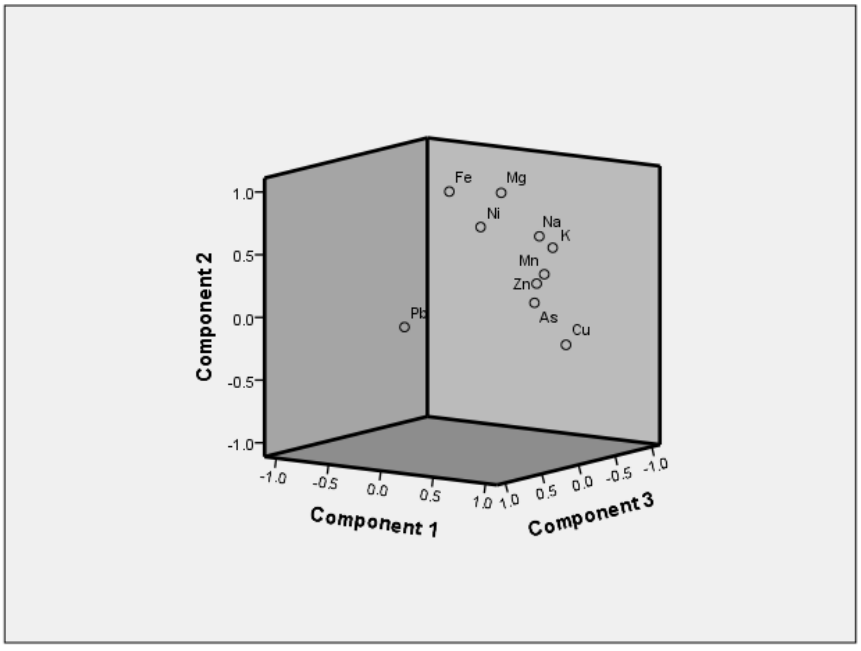


Figure 4.15: Component plot in rotated space of heavy metals and major metals in surface sediments from Sadong River, Samarahan, Sarawak

4.3.8 Cluster Analysis of Heavy Metals and Major Metals in Surface Sediments from Sadong River

Figure 4.16 shows the hierarchical Cluster Analysis for concentrations of heavy metals in surface sediments from Sadong River. A total of ten variables have been compared in order to evaluate the similarities (Ferati et al., 2015). The metals analysed were Cu, Ni, Zn, Fe, Mn, Pb, As, Mg, Na and K. Heavy metals such as Cu, Zn, Pb and As are clustered in Group 1. Group 2 consists of Mn, K and Na, while Group 3 consists of Mg and Fe. Group 1 indicates the heavy metals originated from anthropogenic sources, while Group 2 consists of heavy metals from mixed sources. Group 3 consists of heavy metals from natural sources. The major metals present in Group 2 and Group 3 are believed to be associated with weathering of rocks and soils in the study area (Ashraf et al., 2018). The presence of Cu, Ni, Zn, Pb and As in Group 1 are attributed to anthropogenic activities such as oil spillage, combustion of fuel, municipal waste, use of fertilizers and pesticides on farmland (Tatone et al., 2016; Patel et al., 2018).

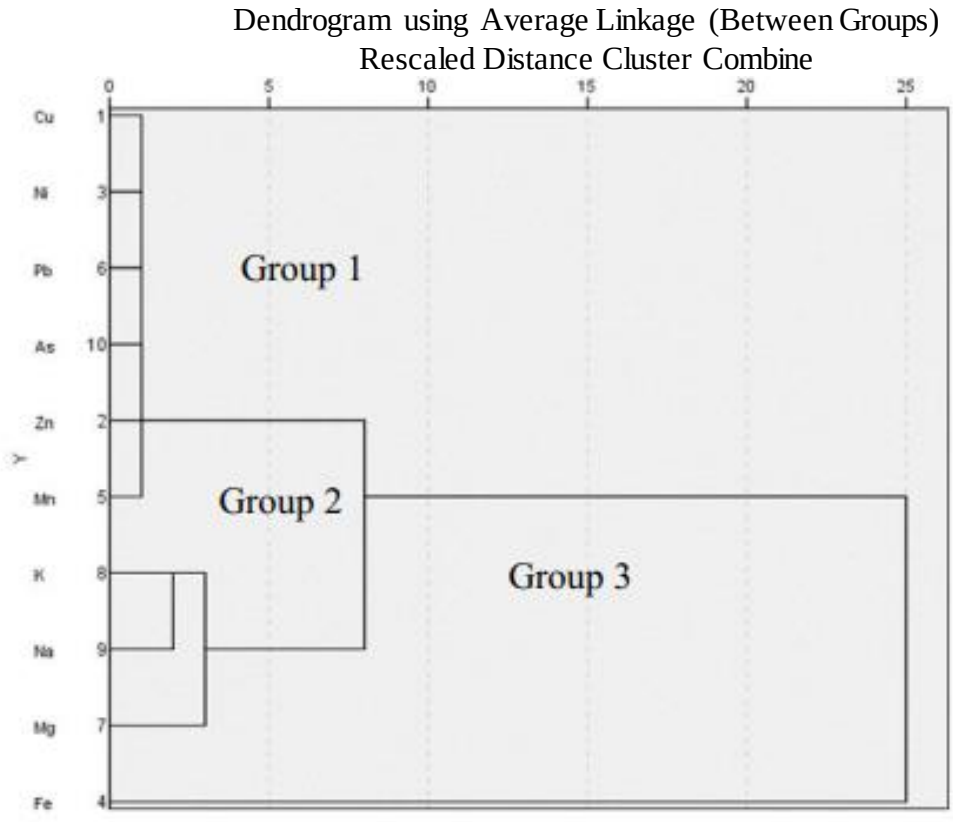


Figure 4.16: Heirarchical cluster analysis of heavy metals and major metals in surface sediments from Sadong River, Samarahan, Sarawak

4.4 Vertical Profile of Heavy Metals in Core Sediments from Sadong River

Vertical profile of essential heavy metals (Cu, Ni, Zn, Cd, Mn, Fe), major metals: (Mg, K, Na) and toxic metal (Pb, As and Cd) in core sediments from six sampling sites have been analysed. Distribution of heavy metals Ni and Zn in the core sediments from Sadong River varied from upper layer to lower layer of core sediment.

4.4.1 Essential Heavy Metals in Core Sediments from Sadong River

The essential heavy metals include Cu, Zn, Ni, Mn and Fe (Aghoghovwia *et al.*, 2018). Distribution of these metals in the core sediments from six sampling sites at Sadong

River are shown in Figures 4.17-4.21, respectively. The concentration of Cu in core sediments was consistent from upper layer to lower layer in all core sediments from Sadong River except in core sediment of Sungai Buloh (BS3). The concentration of Cu detected in Sungai Buloh (BS3) was 53 mg/kg at the upper layer (0.0-2.5 cm) and increased to 325 mg/kg at the 2.5-5.0 cm layer. The concentration of Cu decreased at layer 5.0-7.5 cm with concentration 185 mg/kg and then increased gradually at layers 7.5-10.0 cm, 10.0-12.5 cm to 12.5-15.0 cm with concentration of Cu at 221, 236, 325 mg/kg, respectively. This trend may be due to the accumulation of Cu into sediments periodically. There was a depletion of concentration of Cu at lower layer 22.5-25.0 cm with concentration 7 mg/kg.

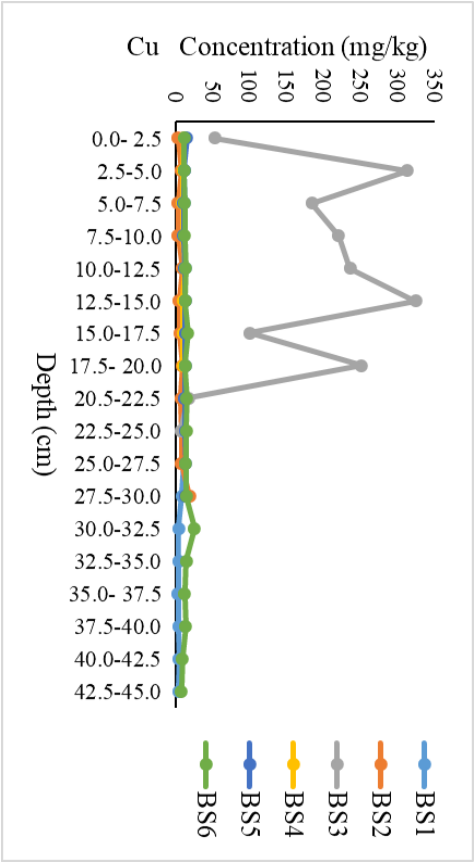


Figure 4.17: Vertical profile of Cu in core sediment from Sadong River

The vertical distribution of Ni in Sebangan (BS1) and Gedong (BS5) was consistent. Concentration of Ni in core sediments at upper layer 0.0 -2.5 cm from Sungai Buloh (BS3) was 43 mg/kg and decreased towards the middle core at layer 5.0 -7.5 cm and between 10.0 -12.5 cm to 15.0-17.5 cm with concentrations 16 mg/kg to 21 mg/kg, respectively. There was low concentration of Ni in the lower layer of core sediments at BS3 with concentration 13 mg/kg at 22.5 -25.0 cm as shown in Figure 4.18. The highest concentration of Ni was detected in core sediment at Sungai Buloh (BS3) with a concentration of 43 mg/kg at layer 0.0 -2.5 cm and 23 mg/kg at 7.5-10.0 cm layer. While the low concentration of Cu was detected in core sediments at Simunjan (BS4) with concentration of 7 mg/kg at layer 7.5-10.0 cm. Distribution of Ni in core sediment was consistent from upper layers to lower layers in all core samples, except core sediment of Sungai Buloh (BS3) with high concentration was observed at upper layer 0.0-2.5 cm of 43 mg/kg. Vertical concentration of Ni in core sediments of BS4 (Simunjan) was constant in the upper layer and then increased at the middle layer. It gradually decreased from layer 10.0-12.5 cm with a constant profile from layer 12.5-15.0 cm to 17.5-20.0 cm.

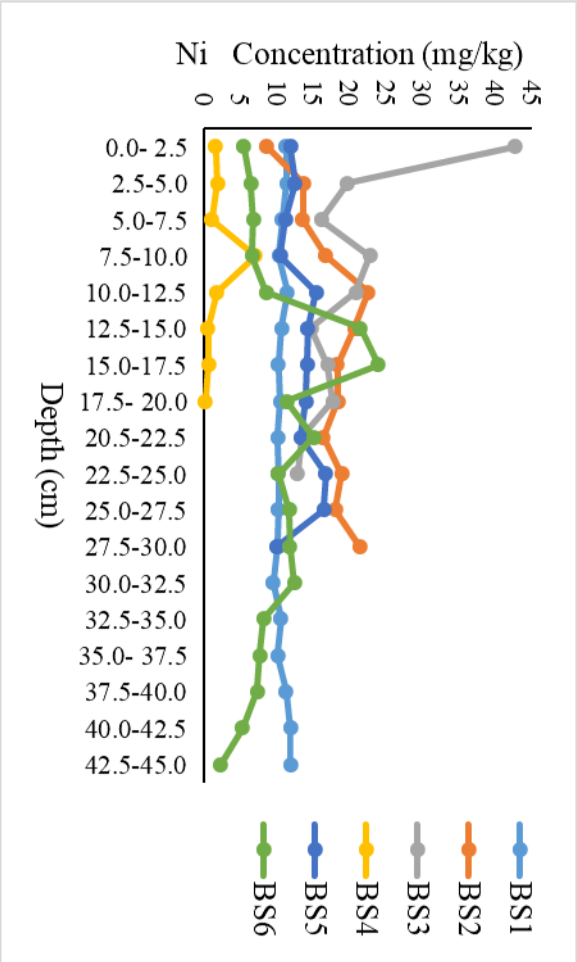


Figure 4.18: Vertical profile of Ni in core sediment from Sadong River

Concentration of Zn in core sediments at Sungai Buloh (BS3) and Gedong (BS5) were constant from the upper layer to the lower layer. The concentration of Zn in core sediments at Sebangan (BS1) slightly varied from upper layer to the lower layer of core. The upper layer at Simunjan (BS4) was constant and then increased at the middle layer of core, then gradually decreased towards lower layer. A fluctuated trend of Zn concentration was observed in core sediments from upper layer to the lower layer in Sebemban (BS6). Concentration of Zn detected in core sediment at Simunjan (BS4) was high with a concentration of 60 mg/kg depicting an increase of Zn from upper layer to the mid core and decreased towards the lower core at 17.5-20.0 cm with concentration 49 mg/kg. The high

concentration of Zn in core sediments from Sadong River was detected at Gedong (BS5) in lower layer 27.5-30.0 cm with concentration 40 mg/kg. The concentration of Zn in upper layer at BS2 increased from 23 mg/kg at 0.0-2.5 cm to 55 mg/kg at 2.5-5.0 cm layer. The concentration of Zn in middle layers of core between 12.5- 20.0 cm was 47, 44 and 47 mg/kg, respectively. Distribution pattern of Zn was varied from upper layer to lower layer of all core sediments as shown in Figure 4.19. The occurrence of Zn suggested that these heavy metals mainly originated from land based runoff and discharges to Sadong River. Zn has high affinity to humic substances that occured in organic matter (Nazeer et al., 2014).

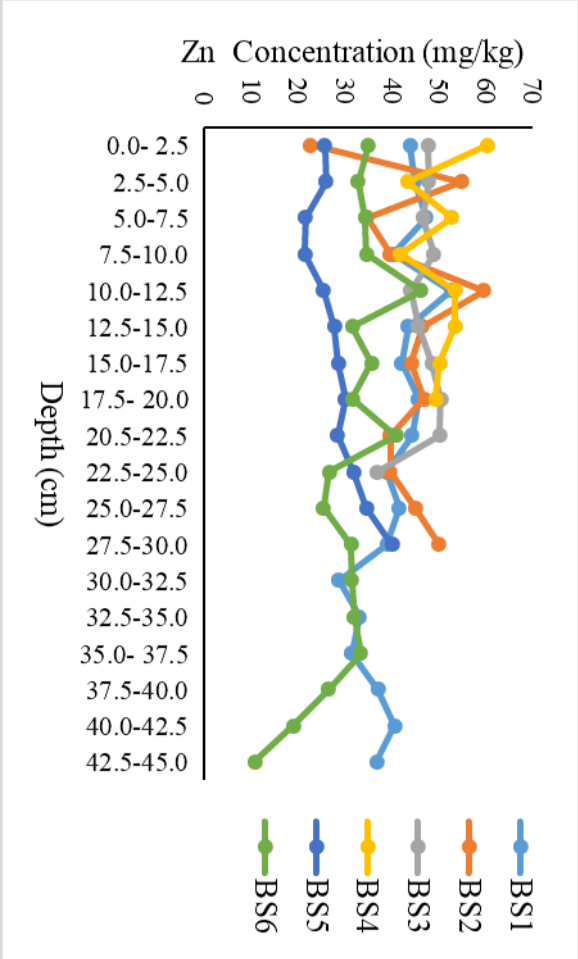


Figure 4.19: Vertical profile of Zn in core sediment from Sadong River

Distribution of Fe was constant from upper layer to lower layers for all sediments from Sadong River. There was a constant trend in core sediments from upper layer to lower layer. High concentration of Fe detected in the upper layer at 0.0-2.5 cm of Sungai Buloh (BS3) sediment with concentration of 4076 mg/kg and then decreased towards the middle layer of 10.0-12.5 cm and 17.5-20.0 cm with concentration 3956 mg/kg and 3959 mg/kg. Distribution pattern of Fe in sediments of Sadong Jaya (BS2) and Sungai Buloh (BS3) was constant from the upper layer of core to the lower layer of core. The concentration of Fe in core sediments at upper layer 0.0-2.5 cm was 1932 mg/kg, middle layer 7.5-10.0 cm had a concentration of 1896 mg/kg and lowest layer 17.5-20.0 cm was 1818 mg/kg at BS4 of Sadong River as shown in Figure 4.20. Concentrations of Fe in core sediments were noticed to be exceptionally high in all sediment samples. Fe is the most common metal found in nature and it is relatively abundant on the earth surface (Szefer et al., 1996). Fe originate mainly from natural sources and the accumulation of Fe in the core sediment is influenced by the presence of dissolved rocks and soils (Patel et al., 2018). The constant value of Fe concentration throughout the sediment cores may attributed to the grain sizes. The particle size of the sediments was small with low organic matter.

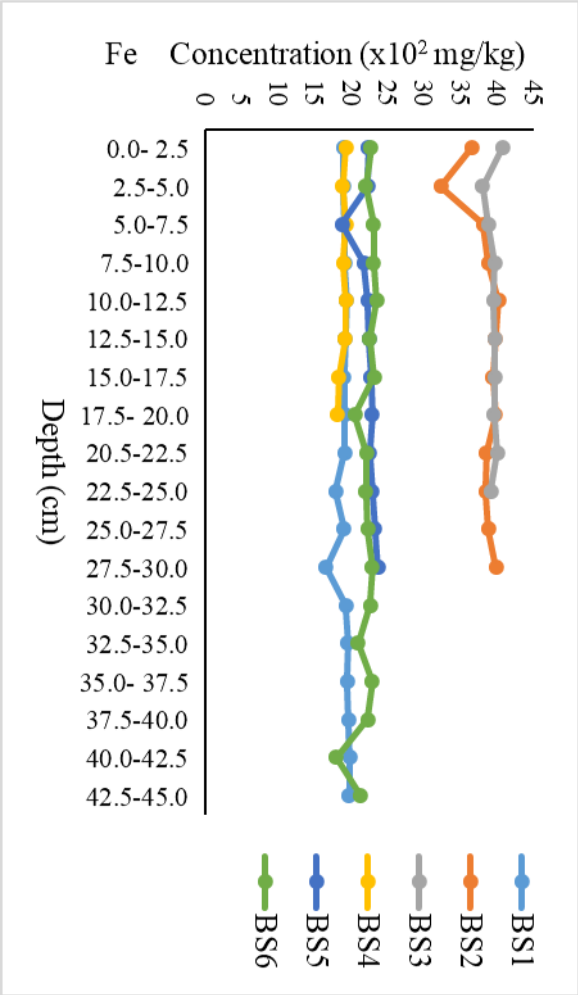


Figure 4.20: Vertical profile of Fe in core sediment from Sadong River

Concentration of Mn detected in core sediment at Sadong Jaya (BS2) was 314 mg/kg at the upper layer 0.0-2.5 cm and the middle layer at 10.0-12.5 cm had a concentration of 565 mg/kg. Lower layer at 27.5-30.0 cm of BS2 had 482 mg/kg as concentration of Mn. Low concentration of Mn was detected in the upper layer 0.0-2.5 cm of core sediment from Sadong River at 216 mg/kg but increased at layer 17.5-20.0 cm with concentration 305 mg/kg. Distribution pattern of Mn has a fluctuated trend with concentration varied from upper layer to lower layer of core in all stations as shown in Figure 4.21. The predominant process for heavy metals partitioning is adsorption because heavy metals have strong affinities between Fe as well as Mn and organic matter but a lesser extent to clay minerals

(Nobi et al., 2010). Determination of Mn in the core sediments is crucial in the assessment on anthropogenic input of heavy metals into river due to their long residence time hence can reflect the history of pollution in the river.

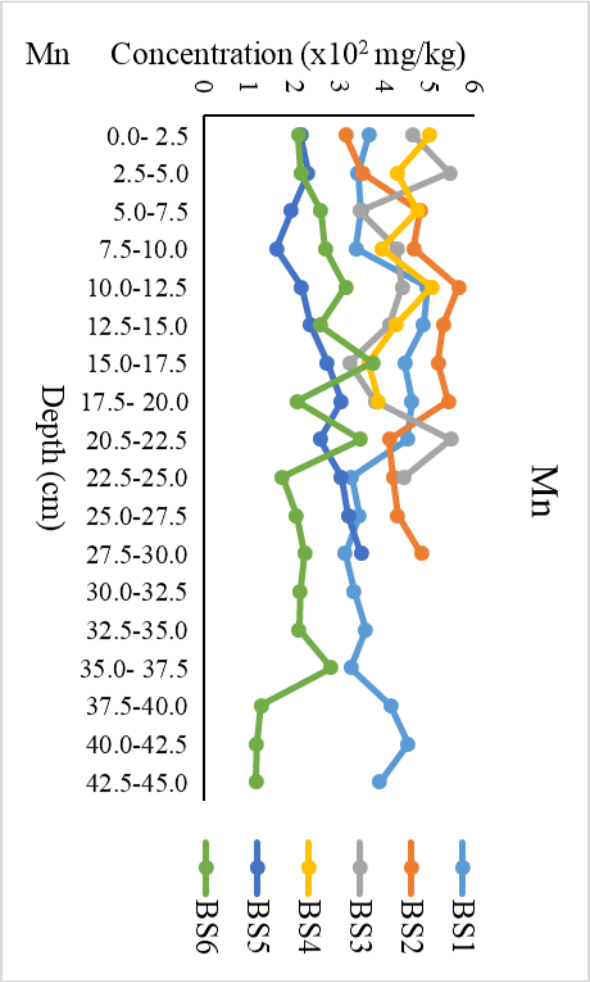


Figure 4.21: Vertical profile of Mn in core sediment from Sadong River

4.4.2 Toxic Heavy Metals in Core Sediments of Sadong River

The toxic heavy metals such as Cd and Pb were detected in the core sediments of Sadong River. Pb and Cd are non-biodegradable and can be bio-accumulated. As was not detected in all core samples from Sadong River. The concentrations of Cd detected in core sediments ranged between 0.01 mg/kg to 0.87 mg/kg. Cd was detected in core sediments at

the middle layer to the lower layer of Sadong Jaya (BS2). The concentration of Cd in the core sediments of BS2 increased from 0.03 to 0.38 in the layer of 15.0-17.0 cm to 27.5-30.0 cm layer. Cd was detected in all the layers of core from upper 0.0- 2.5 cm to lower layer 22.5-25.0 cm of core sediment of Sungai Buloh (BS3) but occurred at low concentration of Cd in core sediments of Sebangan (BS1), Simunjan (BS4), Gedong (BS5) and Sebemban (BS6). Concentration of Cd was 0.87 mg/kg in core sediment was detected in the middle layer of 12.5-15.0 cm and lower layer 20.5-22.5 cm of Sungai Buloh (BS3). The occurrence of Cd usually due to generation of sewage and agricultural activities which is the primary cause of high concentration of Cd in river sediments (Manaf et al., 2009). Phosphatic fertilizers contained high amount of Cd because it derived from the phosphatic rocks. The extensive use of phosphatic fertilizers in farmlands over the years has accumulated Cd in sediments resulted from higher overall movement and accumulation of Cd to the river sediments (Huang et al., 2018).

Figure 4.22 shows the vertical distribution of Pb in core sediments from Sadong River. The vertical trend of Pb detected in core sediments of Sadong Jaya (BS2) was a zig zag trend. Concentration of Pb detected in core sediment at upper layer 2.5-5.0 cm was 29 mg/kg in Sadong Jaya (BS2) of Sadong River and the middle layer at 12.5-15.0 cm had a concentration of 32 mg/kg. The lower layer at 27.5-30.0 cm of core sediment at BS2 with concentration of 11 mg/kg, which may be due to the accumulation of Pb from several human activities over a period of time. The upper layer concentration of Pb in core sediment detected at BS5 was 6 mg/kg at 0.0-2.5 cm and 2.5-5.0 cm. Distribution pattern of Pb in core sediments was consistent for all sampling sites except at BS2 with high concentration from upper layer at 2.5-5.0 cm with concentration 29 mg/kg and in the middle layer of core of

12.5-15.0 cm at 32 mg/kg while the lower layer at 27.5-30.0 cm had a concentration of 11 mg/kg. As was not detected in all core sediments collected from Sadong River.

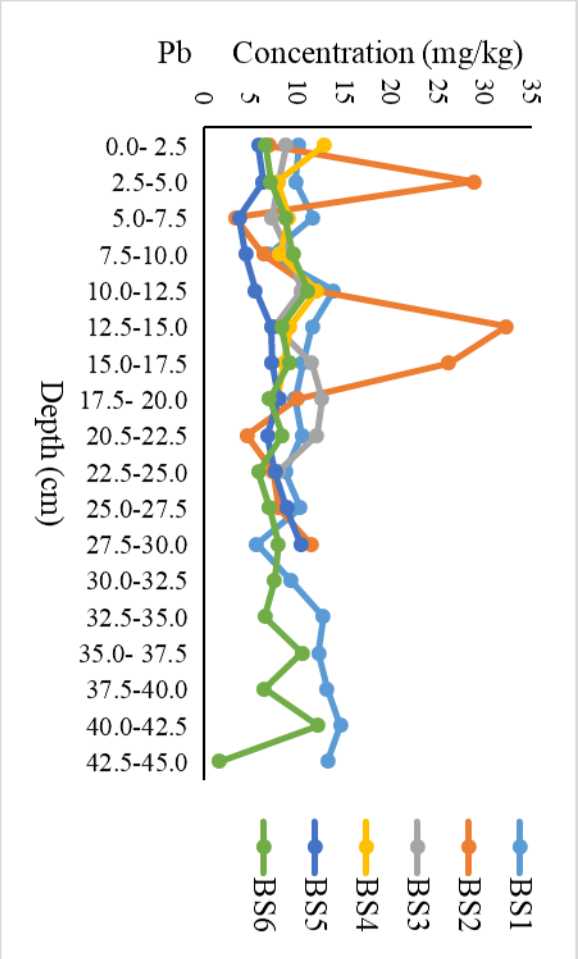


Figure 4.22: Vertical profile of Pb in core sediment from Sadong River

Six sampling sites at Sadong River are characterized by atmospheric deposition, movement of river water as well as tidal and seasonal currents with the exception of BS4 (Omorinoye et al., 2019b). This may have caused the temporal variation in bioavailability, mobility, accumulation history and enrichment of heavy metals in the sediments. The core sediments from three sampling sites: Sadong Jaya (BS2), Sungai Buloh (BS3) and Simunjan (BS4) are characterized by high concentration of heavy metals because of decreased mobility

and dilution. Atmospheric deposition can be the route for metals to accumulate in the sediments because a large amount of heavy metals can be transported until hundreds of miles away from their place or origin. There is high vehicular movement including ferry service in Sungai Buloh (BS3) can cause the emission of heavy metals into the atmosphere and river. The increasing population and agricultural activities of the locality had affected the chemical characteristics of the rivers as time passed.

Pb and Cd contents in core sediments originated from both natural and anthropogenic sources. The presence of Pb and Cd metals in river sediments are often associated with the release of sewage, municipal waste and fertilizers from farmlands (Tatone et al., 2016). Pb have high affinity for humic substances that occured in organic matter (Nazeer et al., 2014).

4.4.3 Major Metals in Core Sediments of Sadong River

Vertical profiles of major metals namely Mg, Na and K in core sediments from Sadong River is shown in Figures 4.23-4.25. The vertical trend of concentration of Mg from upper layer to lower layer of Sungai Buloh (BS3), Simunjan (BS4) and Gedong (BS5) is constant. The concentration of Mg varied from upper layer to lower layer in sediment cores at Sebangan (BS1) and Sadong Jaya (BS2). Concentration of Mg in core sediments of Sadong Jaya (BS2) increased in upper layer and then decreased in the middle layer to lower layer. The concentration of Mg in core sediment of BS2 was high in the upper layer 0.0-2.5 cm with concentration 1736 mg/kg and decreased at the middle layers between 10.0-12.5 cm to 15.0-17.5 cm with concentration below 212 mg/kg. There was an increase in the concentration of Mg in core sediments at lower layer 27.5-30.0 cm with concentration 1873 mg/kg at Sadong Jaya (BS2). Enrichment of Mg from upper layer to lower layer in core

sediments was observed at sampling sites of Sungai Buloh (BS3), Simunjan (BS4), Gedong (BS5) and Sebemban (BS6). The vertical trend of Mg in core sediments of Sebemban (BS6) was constant from upper layer to middle layer and fluctuated at the lower layer.

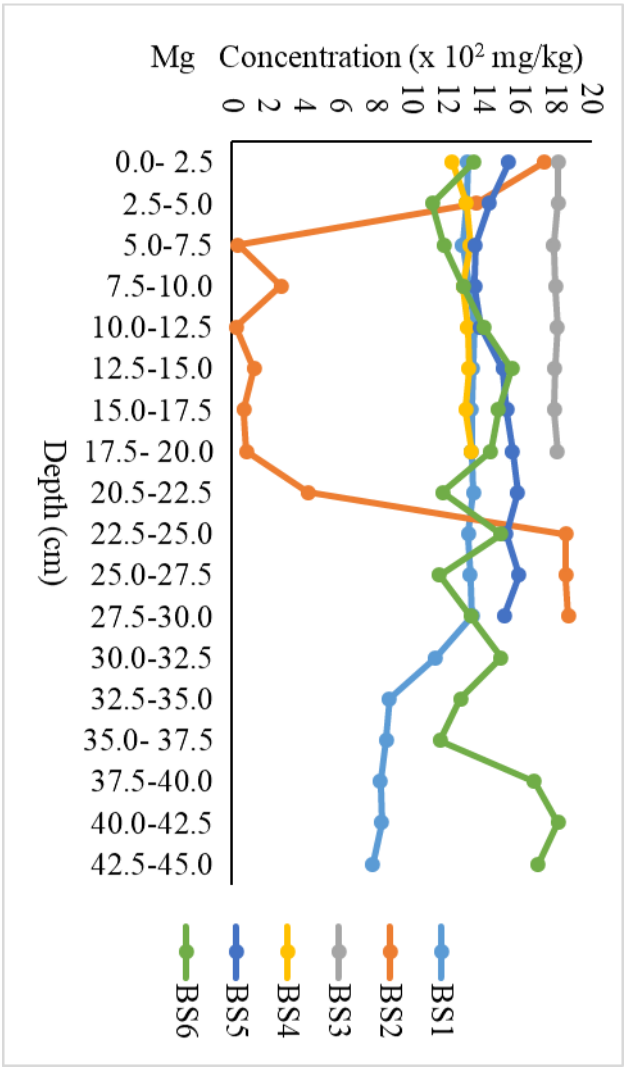


Figure 4.23: Vertical profile of Mg in core sediment from Sadong River

Concentration of K was higher in core sediments at sampling stations of Sebangan (BS1), Sadong Jaya (BS2), Sungai Buloh (BS3) and Simunjan (BS4) compared to the concentration in core sediments of Gedong (BS5) and Sebemban (BS6). Core sediment at Sebangan (BS1) have K concentration of 1310 mg/kg at layer of 0.0-2.5 cm and 781 mg/kg

at lower layer 781 µg/g. The concentration of K at Sadong Jaya (BS2) was 1736 µg/g in the 0.0-2.5 cm layer and 1873 mg/kg in the 27.5-30.0 cm layer. K was enriched in the core sediments of Sungai Buloh (BS3) at layers 0.0-2.5cm, 7.5-10.0 cm and 17.5-20.0 cm with concentration of 1295 mg/kg, 1311 µg/g and 1395 mg/kg, respectively. Core sediment of Simunjan (BS4) with concentration of 1162 mg/kg, 897 mg/kg and 1211 mg/kg in layers 0.0-2.5 cm. 7.5-10.0 cm and 17.5-20.0 cm respectively.

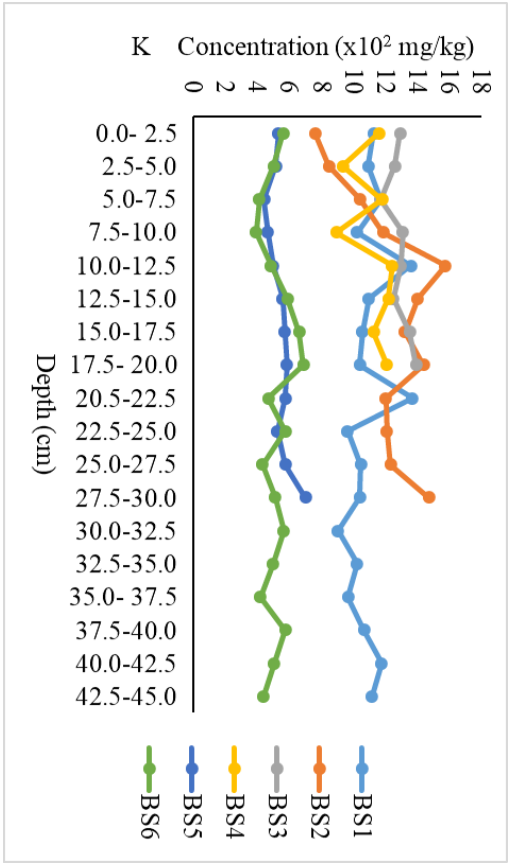


Figure 4.24: Vertical profile of K in core sediment from Sadong River

The concentration of Na in sediment at layers 0.0-2.5 cm, 20.5-22.5 cm and 42.5-45.0 cm at Sebangan (BS1) were 2060 mg/kg, 1946 mg/kg and 1936 mg/kg respectively. In Sungai Buloh (BS3), the upper layer of 0.0-2.5 cm with Na concentration of 1296 mg/kg and the middle layer of 10.0-12.5 cm with concentration 1239 mg/kg. Upper layer of core

sediments of layer 0.0-2.5 cm at BS5 had Na concentration of 276 mg/kg and lower layer of core sediments at 27.5-30.0 cm was 190 mg/kg. Na originate mainly from natural sources. Low concentration of Na was detected in the core sediments of upper layer 0.0-2.5 cm of Sebemban (BS6) with concentration 95 mg/kg which increased in the core sediments at the middle layer of 20.5-22.5 cm with concentration 339 mg/kg. The lower layer of core sediments at Sebemban (BS6) of layer 42.5-45.0 cm had a concentration of 120 mg/kg. Distribution pattern for concentration of Na was constant from upper layer to lower layer for sediments cores studied.

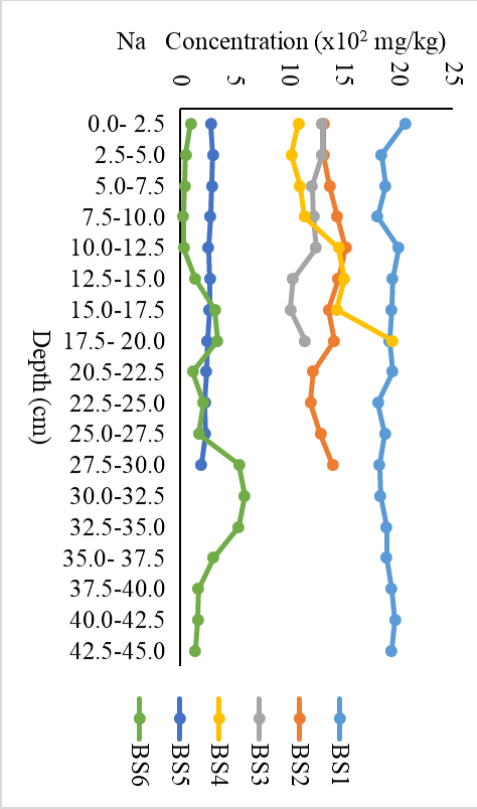


Figure 4.25: Vertical profile of Na in core sediment from Sadong River

4.5 Aliphatic Hydrocarbons

Aliphatic hydrocarbons ranged between of 9 to 33 carbon number are among the compounds commonly detected in the river sediments (Duan et al., 2019). The proportion of *n*-alkanes in the river can be as high as 35% of petroleum hydrocarbons (Vaezzadeh et al., 2015a). *n*-Alkanes are widespread and persistent compounds which occur in rivers from natural and anthropogenic sources.

4.5.1 *n*-Alkanes Standard

A GC-MS chromatogram of *n*-alkanes standard ranged between C_9 to C_{33} is shown in Figure 4.26. Identification of *n*-alkanes was performed according to the retention time of the *n*-alkanes standard that was analyzed prior to the analysis of sediment samples. The RF of *n*-alkanes were calculated relative to 50 µg/g of *n*-eicosene ($C_{20}H_{40}$) as internal standard. RF was then used to quantify individual *n*-alkanes in the sample as shown in Table 4.13. Quantification was carried out for *n*-alkanes in the range between *n*-C_9 and *n*-C_{33} including isoprenoid hydrocarbons that are pristane and phytane.

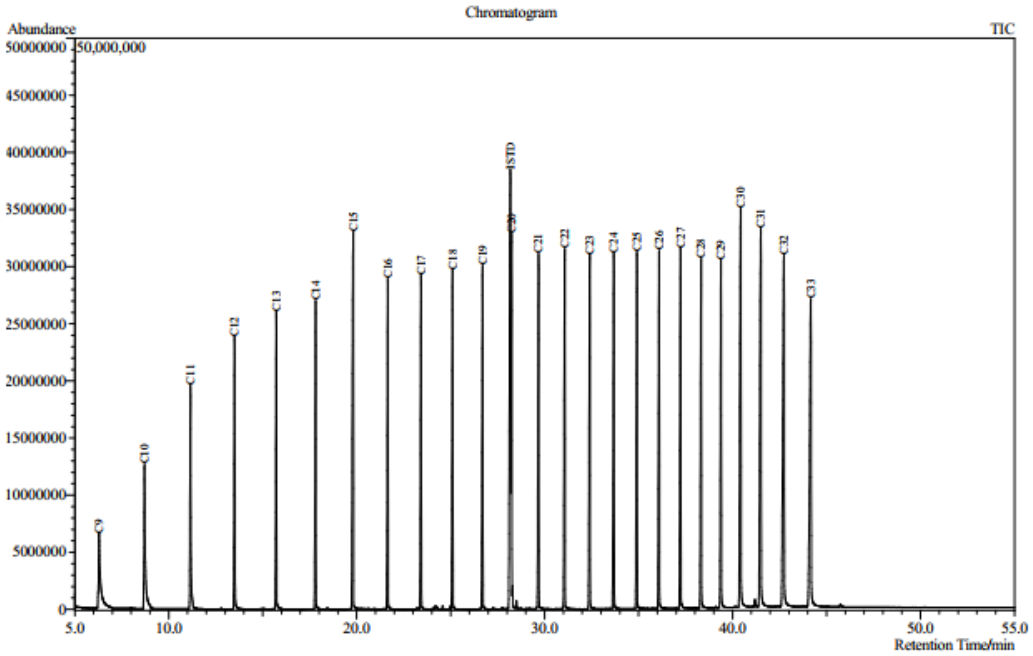


Figure 4.26: A GC-MS chromatogram of *n*-alkanes standard ranged between *n*-nonane (C_9H_{20}) to *n*-tritriacontane ($C_{33}H_{68}$)

Table 4.13: Retention times and RFs of *n*-alkanes in standard mixture

Compounds	Molecular Formular	Retention Time	Response Factor
Nonane	C_9H_{20}	6.29±0.17	3.76±0.23
Decane	$C_{10}H_{22}$	8.71±0.15	2.68±0.02
Undecane	$C_{11}H_{24}$	11.15±0.14	2.56±0.13
Dodecane	$C_{12}H_{26}$	13.50±0.14	2.26±0.10
Tridecane	$C_{13}H_{28}$	15.72±0.14	2.09±0.17
Tetradecane	$C_{14}H_{30}$	17.82±0.14	1.12±1.33
Pentadecane	$C_{15}H_{32}$	19.82±0.14	1.01±0.24
Hexadecane	$C_{16}H_{34}$	21.66±0.14	1.76±0.22
Heptadecane	$C_{17}H_{36}$	23.43±0.14	1.68±0.27
Pristane	$C_{19}H_{40}$	24.18±0.10	1.82±0.23
Octadecane	$C_{18}H_{38}$	25.10±0.14	1.63±0.33
Phytane	$C_{20}H_{42}$	26.25±0.14	1.60±0.21
Nonadecane	$C_{19}H_{40}$	26.70±0.14	1.60±0.28
Eicosene (ISTD)	$C_{20}H_{40}$	28.18±0.15	-
Eicosane	$C_{20}H_{42}$	28.25±0.15	3.57±2.36
Heneicosane	$C_{21}H_{44}$	29.68±0.14	1.65±0.11
Docosane	$C_{22}H_{46}$	31.07±0.15	1.71±0.00
Tricosane	$C_{23}H_{48}$	32.40±0.15	1.75±0.04
Tetracosane	$C_{24}H_{50}$	33.68±0.15	1.72±0.07
Pentacosane	$C_{25}H_{52}$	34.91±0.02	1.77±0.13
Hexacosane	$C_{26}H_{54}$	36.09±0.15	1.58±0.09
Heptacosane	$C_{27}H_{56}$	37.23±0.15	1.73±0.13
Octacosane	$C_{28}H_{58}$	38.33±0.15	1.81±0.17
Nonacosane	$C_{29}H_{60}$	39.39±0.15	1.85±0.19
Triacontane	$C_{30}H_{62}$	40.44±0.09	0.99±0.07
Untriacontane	$C_{31}H_{64}$	41.51±0.18	1.04±0.02
Dotriacontane	$C_{32}H_{66}$	42.73±0.21	1.09±0.13
Tritriacontane	$C_{33}H_{68}$	44.16±0.26	1.29±0.28

4.5.2 Spatial Distribution of Aliphatic Hydrocarbons in Sadong River Sediments

The *n*-alkanes are known as important component in total aliphatic fraction in geolipid from river sediments. The GC-MS chromatograms of *n*-alkanes in surface sediments from Sadong River are shown in Figures 4.27-4.30.

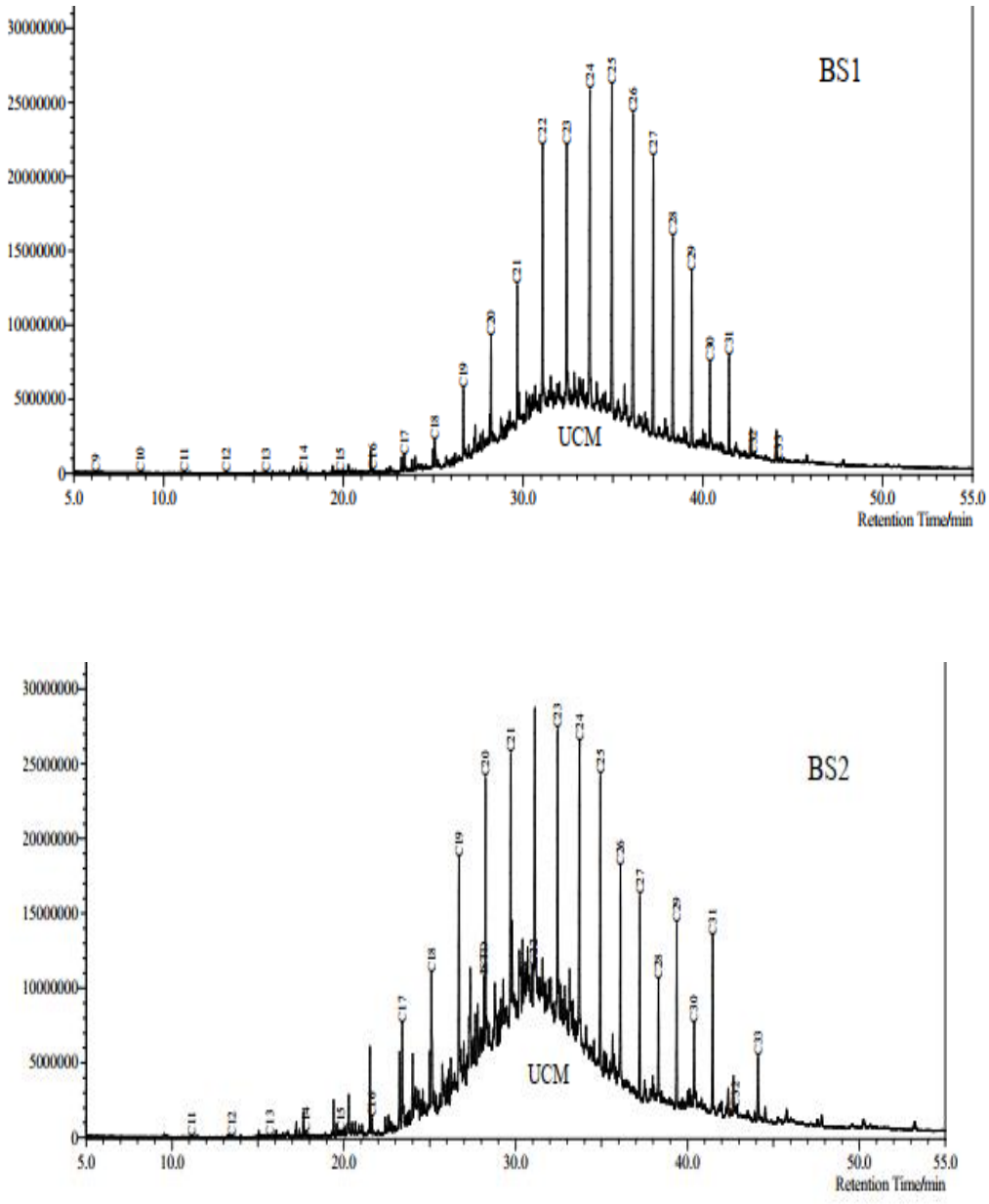


Figure 4.27: GC-MS chromatograms of aliphatic hydrocarbon fraction in surface sediments from BS1 and BS2

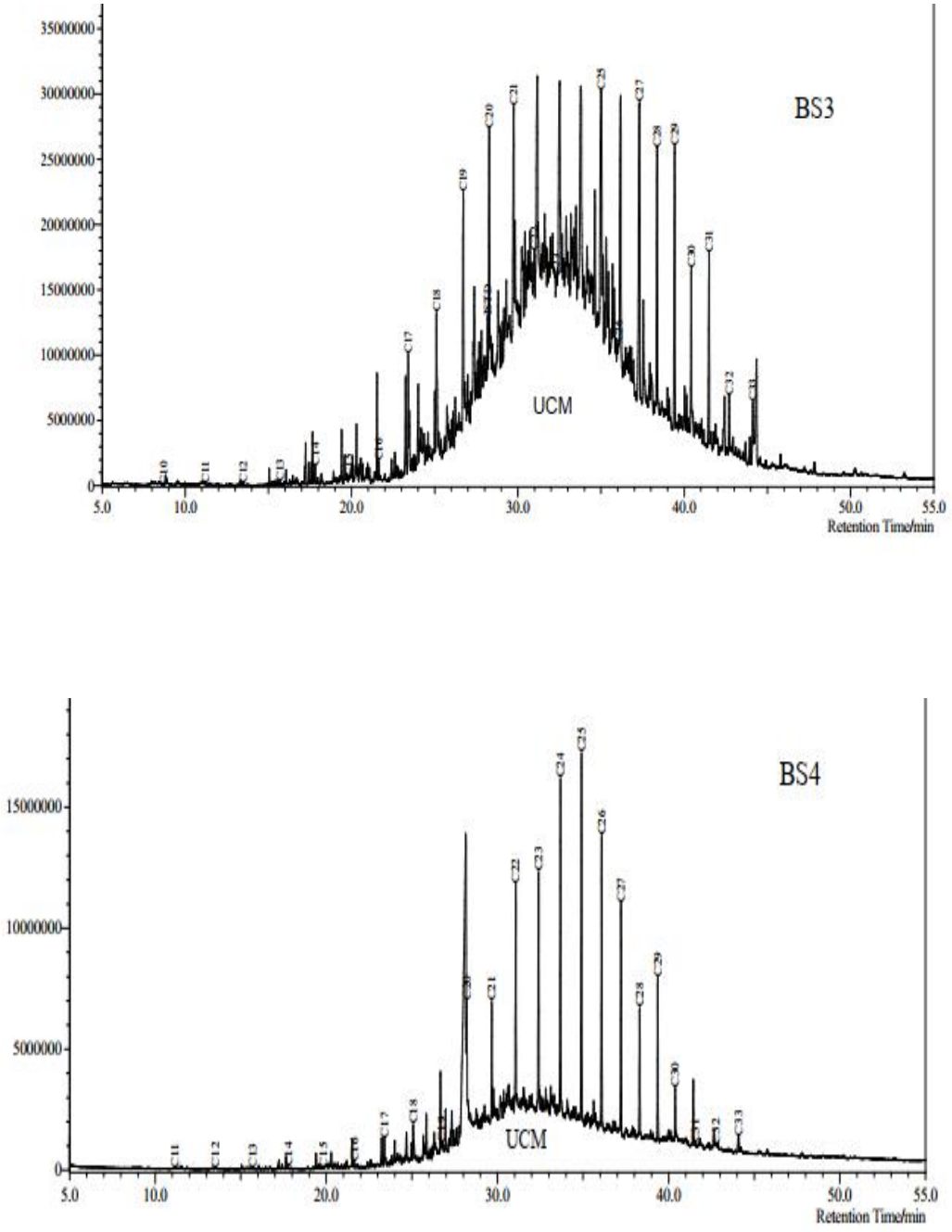


Figure 4.28: GC-MS chromatograms of aliphatic hydrocarbon fraction in surface sediments from BS3 and BS4

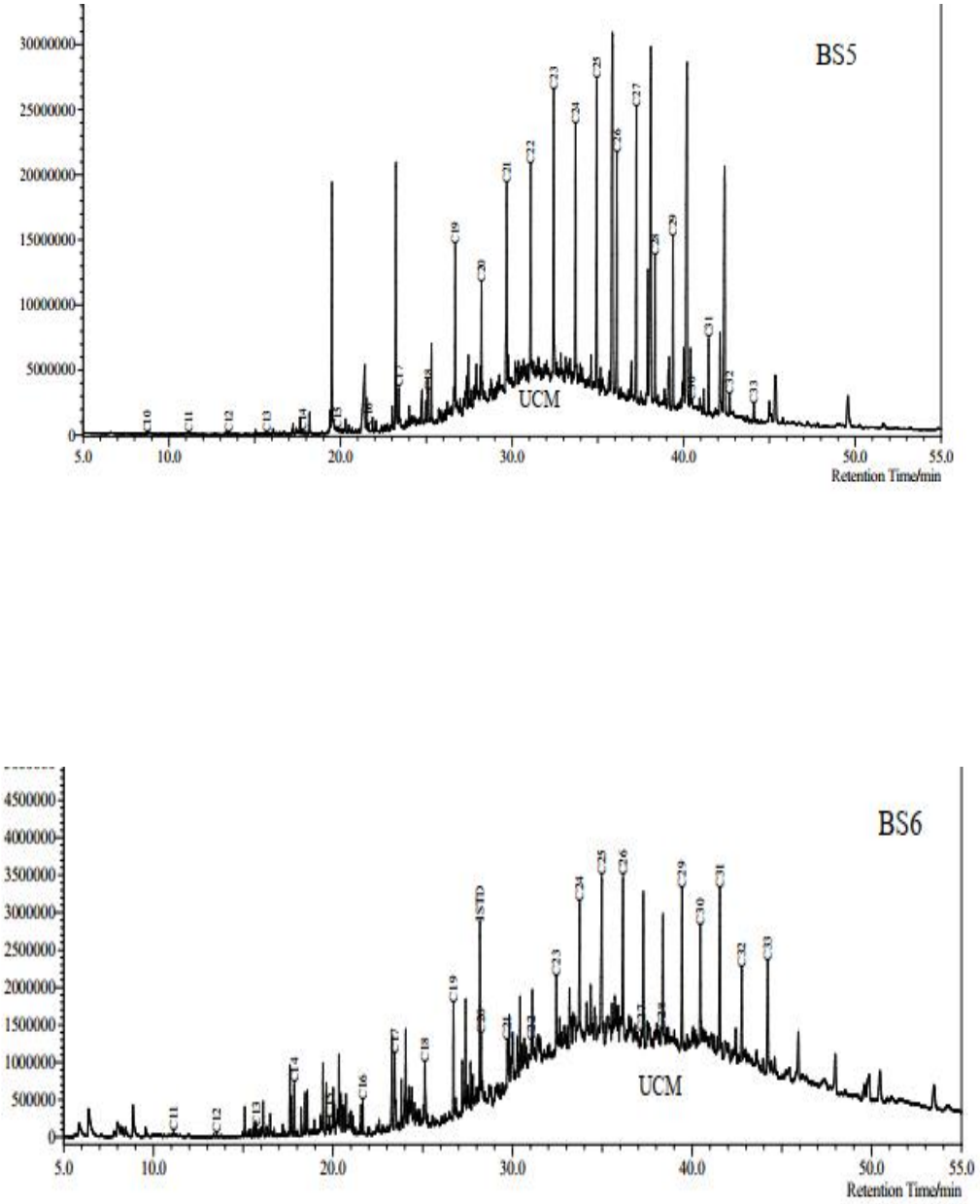


Figure 4.29: GC-MS chromatograms of aliphatic hydrocarbon fraction in surface sediments from BS5 and BS6

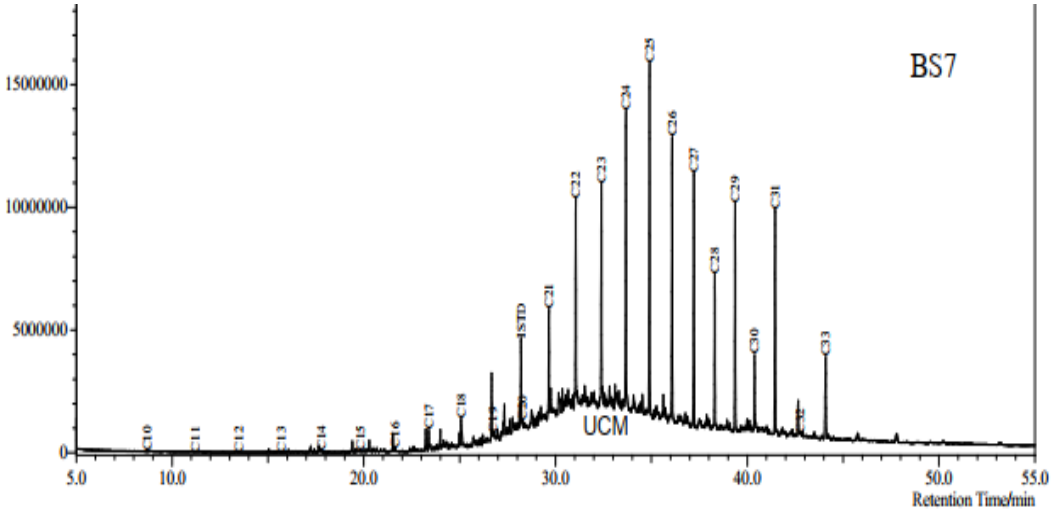


Figure 4.30: GC-MS chromatogram of aliphatic hydrocarbon fraction in surface sediments from BS7

4.5.3 Geochemical Assessment of *n*-alkanes in Surface Sediments

The occurrence of *n*-alkanes is often associated with petroleum contamination through direct deposition in the sediments or indirect ways such as land runoff. Although there might be contribution from natural sources such as terrestial vascular plants, organisms such as planktons, algae and bacteria as well as terrestial organic matter (Lima et al., 2012). The odd number carbons *n*-alkanes are derived from biogenic sources, while the even number carbon is usually derived from the anthropogenic sources. It is believed that *n*-alkanes originated from both natural sources mostly from vascular plants and anthropogenic sources (Li et al. 2015). The natural derived hydrocarbons are influenced by the biosynthetic processes or metabolic pathways (Sakari et al., 2008b; Zhang et al., 2019b). Concentration (μg/g) of *n*-alkanes in surface sediments from seven stations along Sadong River are shown in Table 4.14.

Table 4.14: Concentration (μg/g) of *n*-alkanes in surface sediments from Sadong River

n-alkanes	BS1	BS2	BS3	BS4	BS5	BS6	BS7
C_9	0.31	0.42	0.63	0.39	1.75	0.84	0.79
C_{10}	0.33	0.21	0.69	0.45	1.15	0.01	0.13
C_{11}	0.29	0.18	1.15	0.34	1.21	0.03	0.05
C_{12}	0.03	0.37	1.01	0.76	0.99	0.16	0.07
C_{13}	0.14	0.42	1.16	0.24	0.66	0.16	0.08
C_{14}	0.40	1.40	7.33	0.45	1.52	0.72	0.35
C_{15}	0.07	0.39	0.85	0.14	0.23	0.15	0.07
C_{16}	1.58	3.85	6.46	0.81	2.73	1.97	0.54
C_{17}	3.72	24.66	32.10	1.43	12.03	10.76	0.92
Pr	2.30	1.02	1.14	0.56	4.96	7.43	1.51
C_{18}	10.65	53.84	67.20	8.88	9.83	21.05	6.42
Ph	1.34	1.56	1.91	0.32	2.21	2.35	1.09
C_{19}	17.80	70.32	106.56	2.56	46.97	4.32	1.44
C_{20}	5.96	105.12	138.97	17.82	2.35	5.24	2.37
C_{21}	47.50	31.65	49.98	26.73	75.93	41.20	21.41
C_{22}	80.03	31.03	119.93	38.75	76.10	62.40	33.74
C_{23}	69.12	97.82	48.06	41.29	122.85	49.75	28.11
C_{24}	8.46	39.74	80.33	44.69	80.11	60.38	49.83
C_{25}	115.23	94.82	233.44	52.29	102.88	69.96	50.39
C_{26}	90.25	73.18	36.55	38.01	73.28	51.69	39.77
C_{27}	73.98	59.18	173.78	34.86	87.88	38.44	31.37
C_{28}	50.84	30.99	117.90	23.28	43.33	24.01	3.80
C_{29}	44.75	51.67	6.59	26.20	49.89	26.06	28.52
C_{30}	4.71	12.13	26.12	1.62	7.61	6.45	1.18
C_{31}	2.98	17.15	24.59	1.86	3.45	1.46	1.83
C_{32}	1.22	2.70	10.36	1.51	2.84	1.46	1.11
C_{33}	5.51	10.45	4.69	2.98	5.35	3.22	6.11

The *n*-alkanes in the surface sediments of Sadong River consist of odd and even carbon numbers with no alkyl branch or substitutes. Domination of odd carbons are derived from biogenic sources, while the even carbon numbers are usually derived from the anthropogenic sources. Hydrocarbons of C_{25}-C_{33} can be produced from terrestial vascular plants (Sakari et al., 2008a; Wang et al., 2018). The concentrations of TNA in surface sediments from seven locations along Sadong River in Table 4.15.

Table 4.15: Aliphatic hydrocarbon composition in surface sediments from Sadong River

	Stations						
	BS1	BS2	BS3	BS4	BS5	BS6	BS7
[a]TNA (μg/g)	635.89	813.70	1296.43	368.33	812.92	481.90	310.41
[b]LMW alkanes (μg/g)	237.63	421.27	581.45	140.65	354.56	197.93	95.71
[c]HMW alkanes(μg/g)	397.95	392.01	714.35	227.29	456.61	283.14	213.91
[d]L/H ratio	0.60	1.07	0.81	0.62	0.78	0.70	0.19
[e]CPI	1.60	1.71	1.98	1.46	1.58	1.32	1.91
[f]ACL	26.60	27.19	26.26	26.77	26.76	26.55	27.00
[g]TAR	1.76	1.01	1.09	2.05	1.05	1.17	2.60
[h] MH	C_{25}	C_{20}	C_{25}	C_{25}	C_{23}	C_{25}	C_{25}
C_{17}/Pr	1.62	24.18	28.16	2.55	2.43	1.45	0.61
C_{18}/Ph	7.95	34.51	35.18	27.75	4.45	8.96	5.89
Pr/Ph	1.72	0.65	0.60	1.75	2.24	3.16	1.39

[a] Sum of concentration of *n*-alkanes from C_9 to C_{33}
[b] Sum of low molecular weight *n*-alkanes from C_{10} to C_{23}
[c] Sum of high molecular weight from *n*-alkanes C_{24} to C_{33}
[d] Ratio of LMW alkanes to HMW alkanes
[e] $CPI = \frac{1}{2}\left(\frac{nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33}}{nC_{24}+nC_{26}+nC_{28}+nC_{30}+nC_{32}}+\frac{nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33}}{nC_{26}+nC_{28}+nC_{30}+nC_{32}}\right)$

[f] $ACL = \left(\frac{25(nC_{25})+27(nC_{27})+29(nC_{29})+31(nC_{31})+33(nC_{33})}{nC_{25}+nC_{27}+nC_{29}+nC_{31}+nC_{33}}\right)$
[g] $TAR = \frac{nC_{27}+nC_{29}+nC_{31}}{nC_{17}+nC_{19}+nC_{21}}$
[h] Major Hydrocarbon

The *n*-alkanes of C_{25}-C_{33} are produced from terrestial vascular plants (Sakari *et al.*, 2008a). While the LMW hydrocarbons ranged between of C_{10} to C_{23} particularly C_{17} have biogenic origin mainly from algae and cyanobacteria (Meyers, 2003). The *n*-alkane is one of the molecular markers for the assessment of the hydrocarbon pollution and its sources (Sakari et al., 2012; Ali et al., 2015). The TNA of C_9 to C_{33} in the sediments from Sadong River ranged between 310.41 to 1296.43 μg/g as shown in Table 4.15. The *n*-alkanes is one of the most abundant lipid molecules without functional groups, making them actively resistant to degradation and can be well preserved in river sediments (Mejanelle et al., 2017) as observed in Sadong River. Highest TNA was recorded in surface sediments of Sungai Buloh (BS3) followed by Sadong Jaya (BS2) and Sebemban (BS5). High concentration of

n-alkanes in surface sediments of Sungai Buloh was due to ferry service and proximity to agricultural discharges. This area is heavily loaded with suspended solids from terrestial runoff (Tahir et al., 2015). The sources of *n*-alkanes in sediments were determined by using the molecular characteristic indicators of the compounds. Generally, LMW *n*-alkanes indicate fresh oil inputs from various sources, considering abundance of LMW *n*-alkanes in petroleum (Commendatore et al., 2000). A ratio of LMW to HMW *n*-alkanes less than unity indicate higher heavy and degraded oil as well as biogenic inputs from vascular plants and aquatic fauna. The ratio LMW/HMW *n*-alkanes ≥1 indicates a sign of fresh oil origin (Sakari et al., 2008a). All sampling stations were characterized with fresh oil origin.

4.5.3.1 Ratio of LMW Alkanes to HMW Alkanes

The ratio of LMW (C_{10}-C_{23}) to HMW (C_{24}-C_{33}) *n*-alkanes in surface sediments of the Sadong River ranged between 0.19-1.07. Generally, LMW *n*-alkanes indicate fresh oil inputs due to the abundance of LMW *n*-alkanes in petroleum (Commendatore *et al.*, 2000). The ratios of LMW to HMW *n*-alkanes for all samples were less than 1, except at Sadong Jaya (BS2) which indicative of degraded oil as well as biogenic inputs from vascular plants and aquatic fauna. The ratio of LMW/HMW was ≥1 which indicated a sign of fresh oil input as observed at Sadong Jaya (BS2) due to human activities in the area (Wang et al., 2006; Sakari et al., 2008a; Wang et al., 2010a). The presence of lighter *n*-alkanes in the sediments from Sadong River indicated the recent input of petrogenic hydrocarbons from fuel waste such as diesel and gasoline (Ines et al., 2013). Active biodegradation of LMW *n*-alkanes in the sediments can be the cause of the low values for the ratios of LMW to HMW *n*-alkanes in the sediments from several sampling sites (Jeng & Huh, 2004).

4.5.3.2 Carbon Preference Index (CPI)

CPI is the ratio between odd numbered *n*-alkanes and even numbered *n*-alkanes and very useful in understanding the sources of hydrocarbons in the geological samples. Generally, *n*-alkanes with CPI ranged between 5 to 10 are originated from land based plant material and showed a predominance of carbon with odd number chains, whereas the CPI value of human/anthropogenic origin has CPI=1 (Zaghden *et al.*, 2017). This value is also believed to indicate higher inputs from marine microorganisms and/or recycled organic matter. The CPI values of surface sediments from Sadong River ranged from 1.32 to 1.98. Low CPI values between 1-2 were observed at all surface sediments which may due to the mixture of inputs from petroleum pollution and also organic matters from autochthonous, microorganisms and terrestrial higher plant detritus (Commendatore et al., 2000; Commendatore et al., 2012; Vaezzadeh et al., 2015a).

4.5.3.3 Average Chain Length

The ACL of *n*-alkanes in surface sediments of Sadong River ranged between 26.26-27.19 in surface sediments of BS2 and BS3. This range may be an indicator of petroleum inputs into these sampling sites (Vaezzadeh et al., 2017). Generally, elevated ACL is indicative of hydrocarbons from biogenic sources, whereas the lower values are attributed to anthropogenic inputs. Wider range of ACL values have been reported in surface sediments from the Prai River in Malaysia with ACL values ranged between 26.75-32.94 (Sakari et al., 2008a), while the ACL values for river sediments of north-eastern and northwestern Taiwan between 29.6-29.8 and 29.2-30.5, respectively (Jeng, 2006).

4.5.3.4 Unresolved Complex Mixture

UCM was detected in all surface sediments of Sadong River, in varying extents. Figures 4.27-4.30 show the position of UCM in a typical gas chromatogram for *n*-alkanes in the surface sediment. The concentration of UCM was not quantified, but the presence of UCM in the aliphatic fraction can be used to indicate the contribution of degraded oil in the environment (Simoneit, 2002). UCM composed of acyclic or branched alkanes which have more resistance to biodegradation compared to *n*-alkanes. Therefore, UCM occurred in the environment after degradation of *n*-alkanes (Hu et al., 2009). The presence of UCM can be an indication of weathered oil in the environment (Vaezzadeh et al., 2015a).

4.5.3.5 Terrigenous Aquatic Ratio

The terrigenous aquatic ratio (TAR) which is the ratio of (C_{27}+C_{29}+C_{31}) over (C_{17}+C_{19}+C_{21}) was between 1-2 in all sampling sites with the exception of Simunjan (BS4) and Serian (BS7) with the values higher than 2. High molecular weight *n*-alkanes within the range C_{20} to C_{33} with dominance of odd carbon atoms with maximum peak at C_{25} are derived from higher plant wax (Wang et al., 2010a; Wang et al., 2018).

4.5.3.6 Major Hydrocarbons

MH can also be used as an indicator of hydrocarbon sources. A dominance of HMW over LMW *n*-alkanes was detected in the sediment samples from Sadong River as shown in Table 4.16. Among LMW *n*-alkanes, a predominance of hydrocarbon with odd carbon numbers was detected over even carbon numbers which showed of biogenic sources over fresh inputs of petroleum (Sakari et al., 2008b). MH for LMW *n*-alkanes was ranged between C_{20}-C_{23} with C_{22} as the majority whereas MH for HMW *n*-alkanes was C_{25}. The dominance

of odd over even carbon numbers showed the higher inputs of *n*-alkanes with vascular plant origin as shown in Table 4.17.

Generally long chain *n*-alkanes (C_{26}-C_{33}) with a strong odd carbon dominance were derived from terrestial higher plants (Meyers, 2003; Duan et al., 2019). Short chain *n*-alkanes (C_{15}-C_{20}) with a strong odd or even carbon dominance are indicators of marine planktonic or bacterial origin (Meyers, 2003; Zech *et al.*, 2013). Middle chain *n*-alkanes (C_{21}-C_{25}) with odd carbon dominance are abundant in floating and submerged aquatic macrophytes (Kaiser & Arz, 2016).

4.5.3.7 Isoprenoids

The isoprenoids such as pristane and phytane are products of geologic alteration of phytol and are often used as good indicators of depositional environment and petroleum contamination (Monza et al., 2013). Pristane and phytane were detected in most of the surface sediments from Sadong River as shown in Tables 4.16 and 4.17. The ratio of pristane/phytane >1 is typical of uncontaminated sediments (Duan et al., 2019) as observed in surface sediments of Sebangan (BS1), Simunjan (BS4), Gedong (BS5), Sebemban (BS6) and Serian (BS7). However, low value of pristane/phytane ratios detected in BS2 and BS3 indicate petroleum contamination and an anaerobic reducing depositional environment.

Both ACL and CPI indicated the dominance of *n*-alkanes originating from vascular plants especially in surface sediments of Sadong Jaya (BS2) and Serian (BS7). TAR values showed the importance of terrestial plant over biogenic origin *n*-alkanes in the sediments. The LMW/HMW showed that the dominance of HMW *n*-alkanes in all sample stations with value <1 except for Sadong Jaya (BS2) with a value >1 which indicated that the petroleum has been released into the environment.

Table 4.16: Relative concentration (µg/g) in the surface sediments and indices of *n*-alkanes from different rivers around the world

n-Alkane Indices	Location				
	[a]Neuquen, Argentina	[b]Alagoas, Brazil	[c]Tyne, UK	[d]Taiwan, Taiwan	[e]Sadong, Malaysia
LMW/HMW	0.04-1.19	nd	nd	nd	0.60-1.07
Overall CPI	1.16-14.36	2.9-6.8	1.8-6.4	1.9-8.96	1.32-1.98
ACL	-	28.5-29.4	28.5-29.5	29.2-30.5	26.26-27.19
MH	C_{29}	C_{31} and C_{18}	C_{31}	C_{31}	$C_{20,}$ C_{23} and C_{25}
C_{17}/Pr	0.2-6.95	n.d	0.14-0.42	1.17-12.5	0.61-28.16
C_{18}/Pr	0.71-5.24	n.d	n.d	0.45-4.64	5.89-35.18
Pr/Ph	0.19-1.12	n.d	3.48-7.86	0.82-2.35	0.60-3.16
∑n-alkanes	410-54,050	3500-20,600	6500-26,600	1270-57,780	310-1296

[a]Monza et al. (2013); [b]Silva et al. (2012); [c]Ahad et al. (2011); [d]Jeng, (2006); [e]This study
n.d- not determined

Table 4.17: Relative concentration (µg/g) in the surface sediments and indices of *n*-alkanes from different rivers in Malaysia

n-Alkane Indices	Location		
	Penang[1]	Port Klang[2]	Sadong River[3]
LMW/HMW	0.01-13.32	0.15-1.26	0.60-1.07
Overall CPI	0.00-1.22	0.35-2.11	1.32-1.98
ACL	26.75-32.94	26.74	26.26-27.19
MH	C_{18} and C_{20}	C_{29}	$C_{20,}$ C_{23} and C_{25}
C_{17}/Pr	n.d	0.38-2.52	0.61-28.16
C_{18}/Pr	n.d	0.29-4.80	5.89-35.18
Pr/Ph	n.d	0.65-1.51	0.60-3.16
Total *n*-alkanes (TNA)	421,000-10,770,000	27,945-254,463	310-1296

n.d = not detected; [1]Sakari et al, (2008a); [2]Vaezzadeh et al. (2015); [3]This Study

4.6 Principal Component Analysis (PCA) of *n*-Alkanes in Surface Sediment from Sadong River

The PCA has been carried out to predict the sources of *n*-alkanes in surface sediments of Sadong River. Table 4.18 showed three factors were extracted from the PCA using Varimax with Kaiser Normalization rotation method. Factor 1 is made up of C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{18}, C_{19}, C_{20}, C_{25}, $C_{30,}$ C_{31} and C_{32} are derived from mixed sources. Factor 2 contained C_9, C_{10}, C_{11}, C_{12} and C_{24} are derived from natural sources. Factor 3 is made up of C_{23} C_{26} C_{29} and C_{33} are derived from higher plants and Factor 4 consist of C_{22}. Figure 4.31 depicts the component plot in rotated space for *n*-alkanes in surface sediments from Sadong River. The sources maybe petrogenic or pyrogenic sources. Factor 1 indicates the process of availability of *n*-alkanes were from similar pathways in the river system which include micro-organisms, algae and higher vascular plants. Direct discharge of domestic waste and oil spillage may be also responsible for their source (Zhang et al., 2019b).

Table 4.18: PCA analysis of *n*-alkanes in surface sediments from Sadong River using rotation method of Varimax with Kaiser normalization

	Component			
n-Alkanes	1	2	3	4
C_9	-.204	**.895**	.135	-.027
C_{10}	.147	**.848**	.193	.335
C_{11}	.409	**.773**	.045	.439
C_{12}	.421	**.773**	-.174	.130
C_{13}	**.790**	.523	-.099	.297
C_{14}	**.841**	.247	-.305	.365
C_{15}	**.940**	.213	-.193	.182
C_{16}	**.938**	.225	.031	.227
C_{17}	**.956**	.175	.083	.027
C_{18}	**.985**	-.071	-.022	-.017
C_{19}	**.938**	.265	.158	.147
C_{20}	**.989**	-.067	-.051	-.035
C_{21}	.071	.712	.413	.526
C_{22}	.441	.277	-.102	**.832**
C_{23}	.121	.517	**.833**	-.044
C_{24}	.340	**.805**	-.393	-.083
C_{25}	**.794**	.151	-.048	.580
C_{26}	-.146	-.103	**.952**	.237
C_{27}	.754	.303	-.047	.568
C_{28}	.737	.181	-.093	.642
C_{29}	-.305	.054	**.912**	-.263
C_{30}	**.931**	.173	-.085	.283
C_{31}	**.997**	.002	-.005	.044
C_{32}	**.846**	.260	-.293	.354
C_{33}	.440	-.206	**.661**	-.491

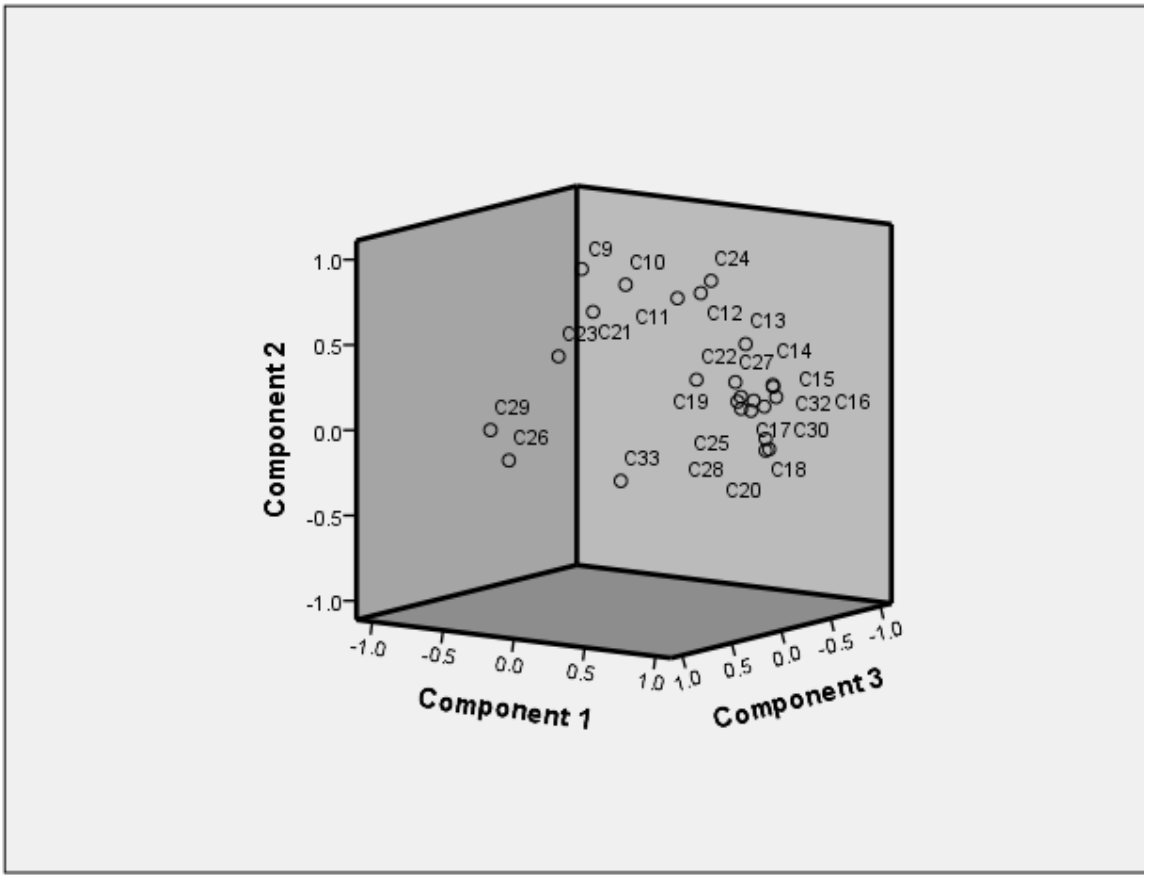


Figure 4.31: Component plot of surface sediments in rotated space of *n*-alkanes from Sadong River

4.7 Aliphatic Hydrocarbons in Core Sediments of Sadong River

Concentration of *n*-alkanes in the core sediments from Sadong River varied from upper layer to lower layer in Sebangan (BS1), Sadong Jaya (BS2) and Sebemban (BS6) core sediments as shown in Figures 4.32-4.34. The *n*-alkanes in the three sediment cores comprised of *n*-alkanes ranged between C_9-C_{33} with low concentration of C_9-C_{12}. The core sediments of Sebangan (BS1) was characterized with very low concentration of C_9-C_{12} at the upper layer to lower layer in all core sediments with the exception of layer 42.5-45.0 cm which had a concentration of C_9 at 0.84 µg/g, C_{10} was 1.08 ug/g, C_{11} was 0.27 µg/g C_{12} was 0.15 ug/g and C_{13} was 0.98 µg/g. All the layers of core sediments had a low concentration

of *n*-alkane C_9 with the exception of upper layer with concentration 1.19 μg/g, lower layer 40.0-42.5 cm with concentration 0.61 μg/g and 42.5-45.0 cm layer with concentration 0.84 μg/g. The middle layer of core sediments of Sadong River of Sebangan (BS1) at layers of 15.0-17.5 cm, 20.0-22.5 cm, 27.5-30.0 cm and 30.0-32.5 cm have a high concentration of *n*-alkanes C_{21}-C_{29}. The highest concentration of HMW *n*-alkane C_{26} was at layer 42.5-45.0 cm with concentration 103.66 μg/g.

The layers of the core sediments of Sadong Jaya (BS2) have low concentration of *n*-alkanes of C_9 to C_{13} except at layer 15.0-17.5 cm which had concentration of 3.93 μg/g, 7.28 μg/g and 0.48 μg/g for C_9, C_{10} and C_{11}, respectively. The highest concentration of *n*-alkanes was detected at layer 22.5-25.0 cm of C_{29}. There was an increase in the concentration of *n*- alkanes C_{21} to C_{25} in the layers of the core sediments. Whereas in the core sediments of Sebemban (BS6), the middle layer 20.0-22.5 cm had high concentration of *n*-alkanes C_{22} to C_{29} with concentration 47.17 μg/g and 55.53 μg/g. The increase of *n*-alkanes concentration of C_{20} to C_{24} with concentration 15.46 μg/g to 19.43 μg/g. The concentration was consistent at the lowest layer 40.0-42.5 and 42.5-45.0 cm

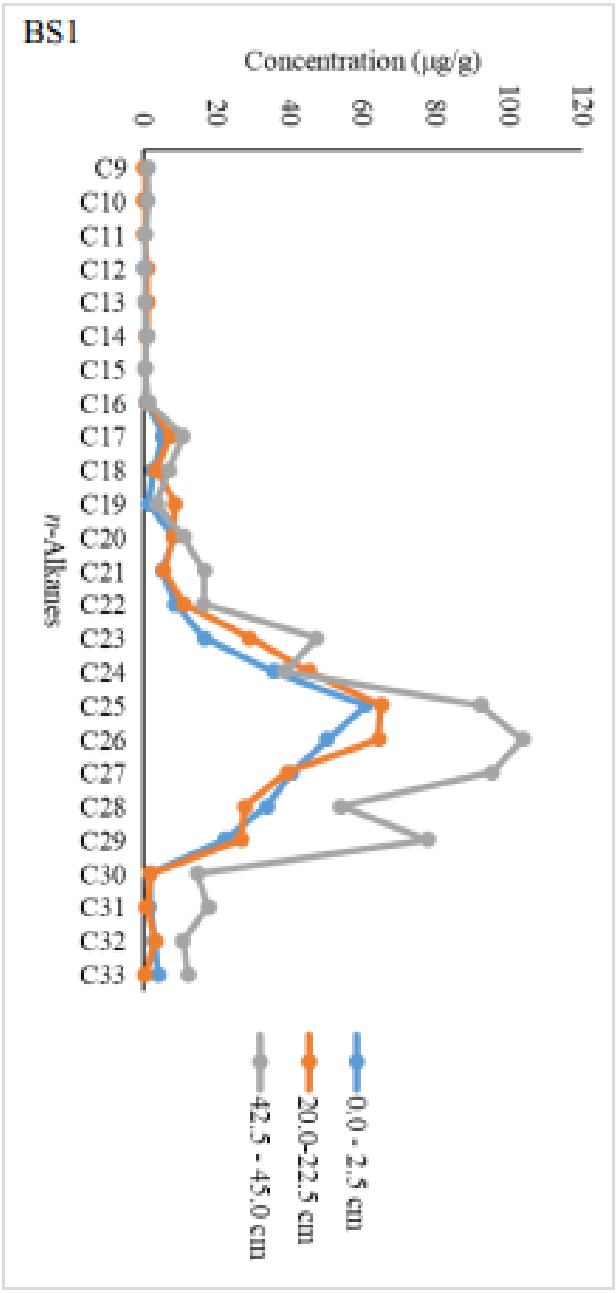


Figure 4.32: Variation of *n*-alkanes at upper layer, middle layer and lower layer in core sediments from BS1 of Sadong River

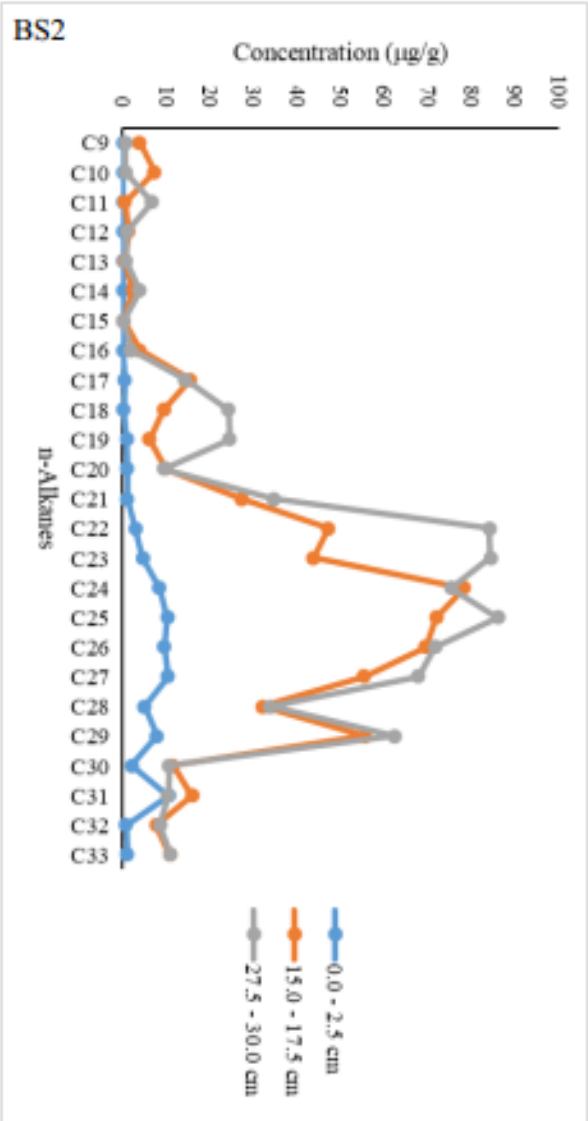


Figure 4.33: Variation of *n*-alkanes at upper layer, middle layer and lower layer in core sediments from BS2 of Sadong River

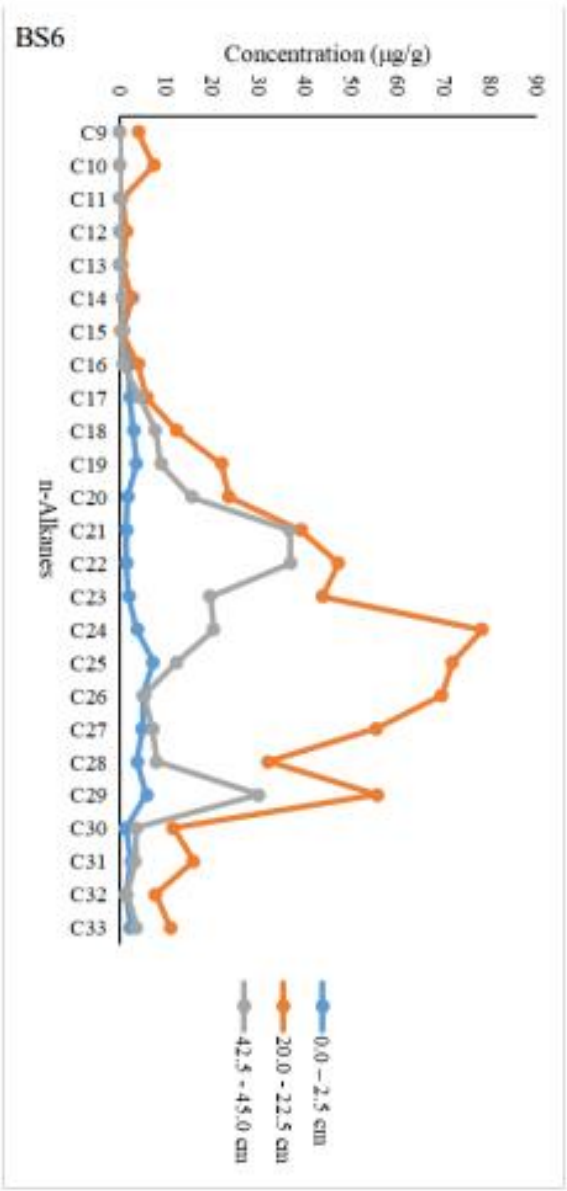


Figure 4.34: Variation of *n*-alkanes at upper layer, middle layer and lower layer in core sediments from BS6 of Sadong River

4.8 Diagnostic Indices of *n*-Alkanes in Core Sediments from Sadong River

Several diagnostic indices were used to determine the aliphatic hydrocarbons pollution in the core sediments from Sadong River. The diagnostic indices are TNA, CPI, ACL, LMW/HMW and MH. The ratio of LMW/HMW *n*-alkanes is an indicator of freshness of the released hydrocarbons in the river and its sources (Duan et al., 2019).

4.8.1 Total *n*-Alkanes and LMW/HMW

The *n*-alkanes was calculated in order to differentiate between natural and petrogenic aliphatic hydrocarbons. The TNA is the sum of the concentration of *n*-alkanes from C_9 to C_{33}. Figure 4.35 shows the vertical profile of TNA in the core sediments from Sadong River. The total *n*-alkanes recorded in core sediments from Sadong River was > 100 μg/g in all layers. The TNA in core sediments from Sadong River varied from upper layer to lower layers of core. The TNA in the layer of core sediments of Sebangan (BS1) at 0.0-2.5 cm, 20.0-22.5 cm and 42.5- 45.0 cm was 624 μg/g, 715 μg/g and 1274 μg/g respectively. This indicated the lowest layer at 42.5- 45.0 cm had a high TNA, TNA of the layer of core sediment of Sadong Jaya (BS2) from Sadong River at 2.5-5.0 cm, 15.0-17.5 cm and 27.5-30.0 cm was 569 μg/g, 646 μg/g and 799 μg/g respectively. The upper layer of core sediment at 0.0-2.5 cm was 88 μg/g with an increase deeper depth. High levels of *n*-alkanes in some layers of the core sediment of Sebangan (BS1) may be indicative of anthropogenic inputs of hydrocarbons due to the activities in the vicinity of Sadong River.

Upper layer at 0.0-2.5 cm of core sediments of Sebemban (BS6) was 137 μg/g, the middle layer at 20.0-22.5 cm was 1249 μg/g and lowest layer at 42.5-45.0 cm was 477 μg/g. It is suggested that some distinctive attributes of the ecosystem such as occurrence of vegetal

organic matter and detritus incorporated into the sediment which caused high deposition and accumulation of hydrocarbons (Vaezzadeh et al., 2015).

The ratios of LMW hydrocarbons ($<C_{24}$) relative to HMW *n*-alkane ($>C_{24}$) have been used to evaluate the relative contribution of the LMW and HMW hydrocarbons in Sadong River as shown in Figure 4.36. The odd number carbons of *n*-alkanes are derived from biogenic sources, while the even carbon number *n*-alkane are usually derived from anthropogenic sources (Aly Salem et al., 2014).

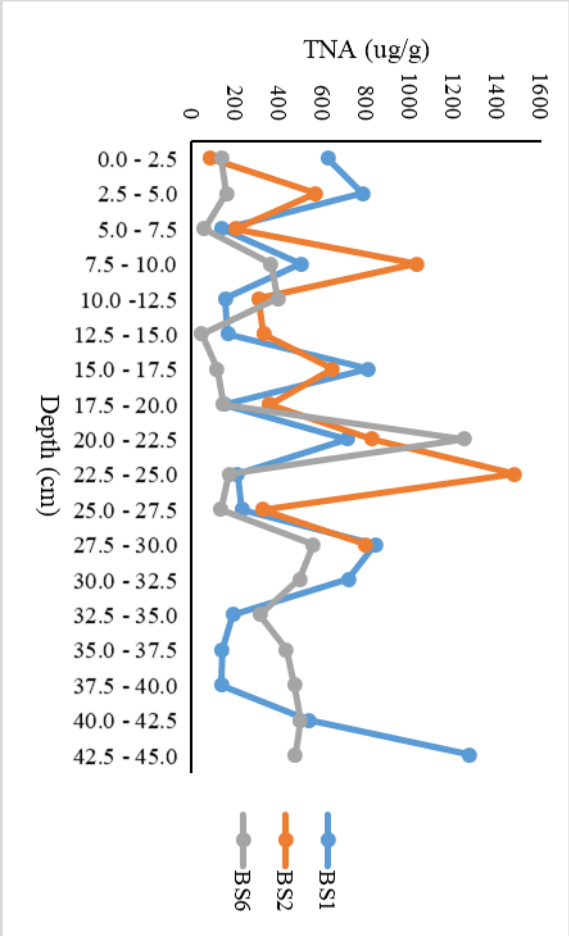


Figure 4.35: The vertical profile of TNA in core sediments from Sadong River

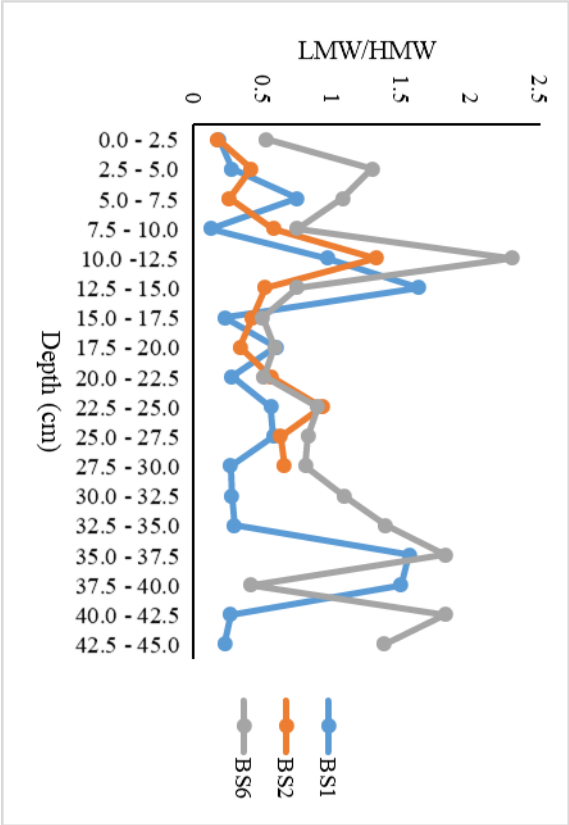


Figure 4.36: The vertical profile of LMW/HMW in core sediments from Sadong River

Elevated concentration of TNA in all core sediments may be due to the input from natural and anthropogenic activities. Concentrations of TNA below 50 µg/g is usually considered as uncontaminated (Zegouagh et al., 1998), while values above 100 µg/g are considered as contaminated and indicated the presence of petroleum biomarkers (Readman et al., 2002). The *n*-alkanes concentration in all layers were less than 100 µg/g except in core sediments at layer of 42.5-45.0 cm of Sebangan (BS1), layer 7.5-10.0 cm, 20.0-22.5 cm and 22.5-25.0 cm of Sadong Jaya (BS2). Thus, the value of TNA in all sediment cores indicate that they are slightly polluted with *n*-alkanes (Vaezzadeh et al., 2015).

4.8.2 Carbon Preference Index (CPI) and Average Chain Length (ACL)

The CPI of *n*-alkanes has been used to differentiate between natural and petrogenic aliphatic hydrocarbons. The CPI of *n*-alkanes in the core sediments of Sadong River are presented in Figure 4.37. The CPI at Sebangan (BS1) for layers of 0.0-2.5 cm, 20.0-22.5 cm and 42.5-45.0 cm were 1.24, 1.14 and 1.47, respectively. The CPI values between 1 to 3 are related to marine micro-organisms and recycled organic matter (Tahir et al., 2015; Commendatore et al., 2012). The CPI for core sediments of Sadong Jaya (BS2) at layers 0-2.5 cm, 15.0-17.5 cm and 27.5-30.0 cm (BS2) were 1.93, 1.39 and 1.55, respectively. The CPI of core sediments at Sebemban (BS6) at layers 0.0-2.5 cm, 20.0-22.5 cm and 42.5-45.0 cm were 1.76, 1.39 and 2.29, respectively.

The vertical trend of CPI in core sediments of Sebangan (BS1), Sadong Jaya (BS2) and Sebemban (BS3) was zig-zag from upper layer to lower layer. Core sediments of Sebangan (BS1) and Sadong Jaya (BS2) showed a similar vertical trend for CPI as shown in Figure 4.37 as the CPI values increased gradually from uppermost surface and decreased in middle of core. In BS1, the CPI increased form middle towards the bottom of core with a sharp decrease in deepest having lowest CPI value of 0.34 in the 37.5-40.0 cm layer and the highest CPI of 5.53 in the middle core 25.0-27.5 cm layer. The relative high value is an indication of biogenic contributions. However, a significant decrease of CPI to 0.34 at layer 37.5-40.0 cm could be an indication of petrogenic contribution due to the fact that Sebangan which is the estuary and may be subjected to some of the anthropogenic activities in the area. The average CPI in Sadong Jaya (BS2) is greater than 1 with the exception of 7.5-10.0 cm layer and 12.5-15.0 cm layer having CPI values 0.95 and 0.97 respectively which indicated petrogenetic input from petroleum products.

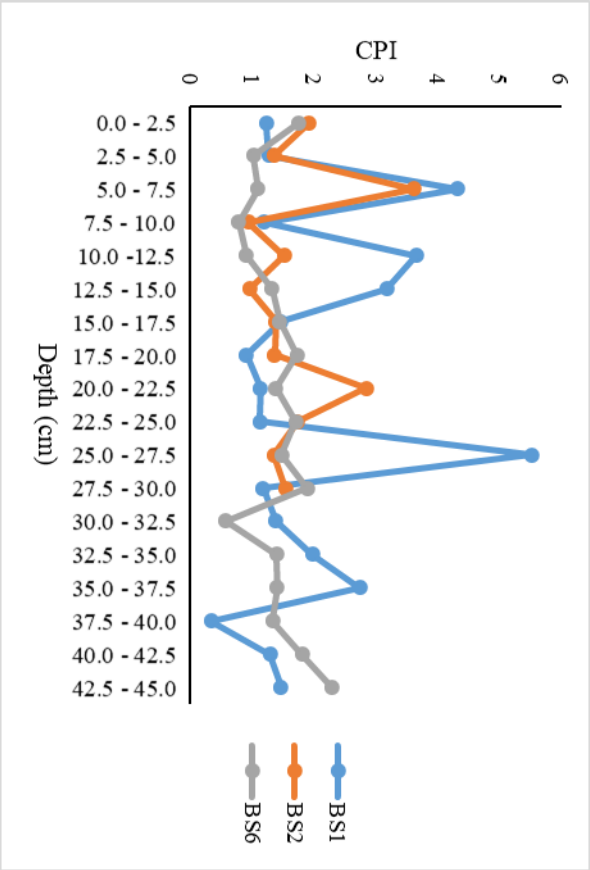


Figure 4.37: The vertical profile of CPI in core sediments from Sadong River

In Sebemban (BS6), the average CPI is between 1-2 which is related to marine micro-organisms and recycled organic matter. CPI value in 10.0-12.5 cm was 0.91 and 30.0-32.5 cm was 0.58, this attributed to petrogenetic input from petroleum products. High CPI value in BS6 was found in lowest layer 42.5-45.0 cm. Among all the core sediments from Sadong River, there is predominance of biogenic sources. Hence, a mixture of hydrocarbon sources is suggested which include petrogenic inputs, terrigenous sources, aquatic microorganisms and/or recycles organic matter (Duan et al., 2019).

Figure 4.38 shows the variation of ACL in core sediments from Sadong River. The trend of ACL in core sediments was zig zag from the upper layer to the lower layer of Sebangan (BS1), Sadong Jaya (BS2) and Sungai Buloh (BS3). The ACL of *n*-alkanes in core

sediments layers 0.0-2.5 cm, 20.0-22.5 cm and 42.5-45.0 cm respectively, of Sebangan (BS1) was 26.63, 26.45 and 27.39. The ACL values was observed to increase in the middle core and fluctuated towards the middle core with an increase at lower layer of core. Sadong Jaya (BS2) was characterised by an increase in the upper layer at 28.10 at 0.0-2.5 cm, a consistent pattern in the middle layer at 27.46 and an increase in the lower layer of core 22.5-25.0 cm and decreased to 27.25 at 27.5-30.0 cm. Sebemban (BS6) was characterised by a fairly consistent pattern form upper layer to bottom of core with upper layer 0.0-2.5 cm was 27.91, 20.0-22.5 cm was 27.46 and 42.5-45.0 cm was 28.24.

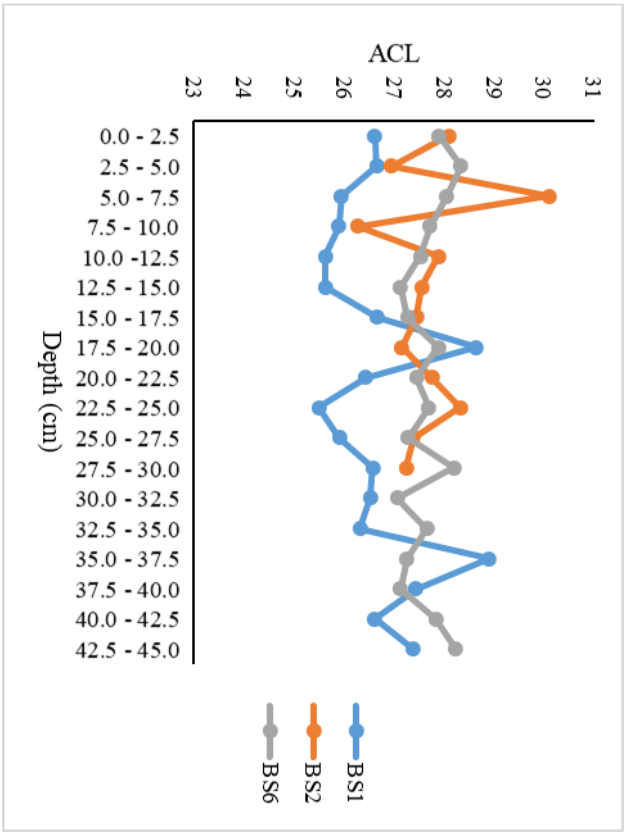


Figure 4.38: The vertical profile of ACL in core sediments from Sadong River

4.8.3 Major Hydrocarbon

Table 4.19 shows the MH for hydrocarbons in core sediments from Sadong River. The MH of hydrocarbons in sediments core of Sebangan (BS1) was C_{25} which represents terrestial sources with the exception of middle layer at depth 17.5-20.0 cm with C_{24} and layer 37.5-40.0 cm with C_{22} indicating marine sources. This showed that *n*-alkanes in core sediments of Sebangan (BS1) which is located at the estuary were contributed by a mixture of terrestial vascular plant, phytoplankton, algae and petroleum. Guo & Fang (2012) reported that *n*-alkanes originated from microorganisms such as algae, plankton and bacteria have short hydrocarbon chain with major hydrocarbons at C_{15}, C_{17} and C_{19}. Domination of C_{20} and C_{21} alkanes indicated *n*-alkanes derived from oil, automobile exhaust and fossil fuel combustion. The long chains *n*-alkanes between C_{25}-C_{33} are derived from terrestial higher plants.

Table 4.19: Major hydrocarbon (MH) in core sediments from Sadong River

	MH		
Depth	BS1	BS2	BS6
0.0-2.5	C_{25}	C_{31}	C_{25}
2.5-5.0	C_{25}	C_{22}	C_{14}
5.0-7.5	C_{25}	C_{33}	C_{20}
7.5-10.0	C_{25}	C_{26}	C_{24}
10.0-12.5	C_{25}	C_{22}	C_{21}
12.5-15.0	C_{25}	C_{26}	C_{9}
15.0-17.5	C_{25}	C_{24}	C_{25}
17.5-20.0	C_{24}	C_{25}	C_{25}
20.0-22.5	C_{25}	C_{27}	C_{24}
22.5-25.0	C_{25}	C_{20}	C_{20}
25.0-27.5	C_{25}	C_{24}	C_{20}
27.5-30.0	C_{25}	C_{25}	C_{29}
30.0-32.5	C_{25}	-	C_{28}
32.5-35.0	C_{25}	-	C_{21}
35.0-37.5	C_{29}	-	C_{21}
37.5-40.0	C_{22}	-	C_{26}
40.0-42.5	C_{25}	-	C_{22}
42.5-45.0	C_{26}	-	C_{22}

'-' - data not available

4.9 Polycyclic Aromatic Hydrocarbons (PAHs) in the Surface Sediments of Sadong River

A GC-MS chromatogram of a mixture of PAHs standard is shown in Figure 4.39. PAHs were identified according to their retention times, while RFs were also calculated for each PAH for quantification purpose. The retention times and RFs for PAHs standard are presented in Table 4.20.

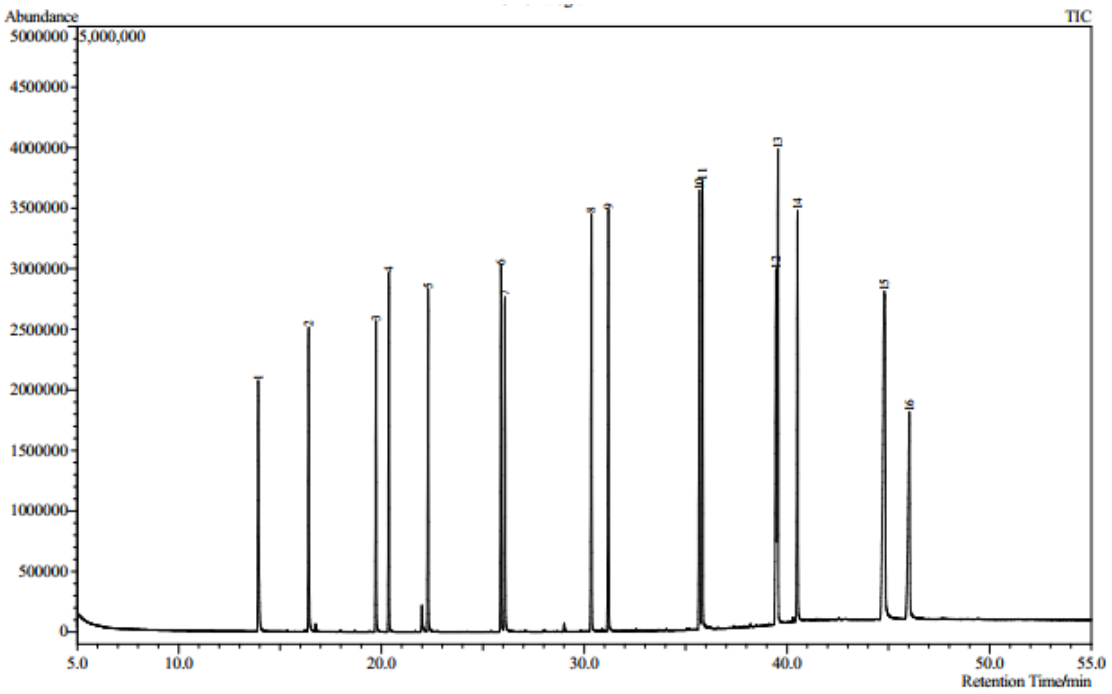


Figure 4.39: GC-MS chromatogram of a mixture of PAHs standard

Table 4.20: Retention times and RFs of individual PAHs standard analysed on GC-MS

PAHs	Short Form	Molecular Formula	Retention Time (Min)	Response Factor (RF)
Naphthalene	Nap	$C_{10}H_8$	13.93±0.01	1.13±0.15
Acenaphthylene	Acy	$C_{12}H_8$	16.42±0.01	0.36±0.08
Acenaphthene	Ace	$C_{12}H_{10}$	19.74±0.02	1.22±0.25
Flourene	Fluo	$C_{13}H_{10}$	20.37±0.01	0.83±0.18
Phenanthrene	Phe	$C_{14}H_{10}$	22.21±0.01	0.74±0.22
Anthracene	Ant	$C_{14}H_{10}$	24.71±2.07	0.92±0.13
Anthracene d_{10} (IS)	Ant	$C_{14}H_{10}$	26.03±0.11	
Fluoranthene	Flt	$C_{16}H_{10}$	28.94±2.47	1.44±0.15
Pyrene	Py	$C_{16}H_{10}$	30.93±0.49	1.52±0.13
Benzo[a]anthracene	BaA	$C_{18}H_{12}$	34.20±2.59	1.61±0.11
Chrysene	Chry	$C_{18}H_{12}$	35.80±0.09	1.01±0.27
Benzo[b]Fluoranthene	Bbf	$C_{20}H_{12}$	38.27±2.10	1.58±0.19
Benzo[k]Fluoranthene	Bkf	$C_{20}H_{12}$	39.54±0.06	1.98±0.31
Benzo[a]Pyrene	BaP	$C_{20}H_{12}$	40.14±0.50	0.98±0.50
Indeno[1,2,3-c,d]Pyrene	Ind	$C_{20}H_{12}$	41.95±2.45	1.26±0.08
Dibenzo[ah]anthracene	DBA	$C_{22}H_{14}$	44.85±0.04	1.48±0.37
Benzo[ghi]perylene	BgP	$C_{22}H_{12}$	46.06±0.04	1.09±0.12

4.9.1 Spatial distribution of PAHs in Surface Sediments of Sadong River

A total of 16 targeted PAHs have been detected in the surface sediments from Sadong River. The GC-MS chromatograms of individual PAHs in surface sediments for seven sampling sites are illustrated in Figures 4.40-4.43. The composition and distribution of individual PAH in surface sediments in each stations were varied from volatile LMW PAHs (i.e acenaphthylene and acenaphthene) in surface sediments of Sebemban (BS6) to the less volatile HMW PAHs (i.e fluoranthene and benzo[k]fluoranthene). Anthracene, pyrene and chrysene are dominant PAHs detected in the surface sediments of Gedong (BS5) from Sadong River (Omorinoye et al., 2019a).

The highest concentration of anthracene was detected in the surface sediment of Serian (BS7) with 59.05 μg/g, while the lowest concentration of anthracene was detected in surface sediments of Sebangan (BS1) with concentration of 4.75 μg/g. Concentration of pyrene was 11.88 μg/g in the surface sediments of Serian (BS7), while the lowest concentration of pyrene was detected in surface sediments of Sungai Buloh (BS3) with a value 1.11 μg/g. The occurrence of pyrene and fluoranthene in environment normally indicate pyrolytic input because these two PAHs are derived from the condensation of LMW PAHs at high temperature (Wang et al., 1999; Keshavarzifard et al., 2018). Chrysene has been detected in all surface sediments of Sadong River as shown Table 4.17 with low concentration of 0.59 μg/g of Sungai Buloh (BS3) and high concentration of 53.67 ug/g of surface sediment of Gedong (BS5). Chrysene is resistant to weathering and bacterial degradation (Wang & Fingas, 2003; Wang et al., 2015).

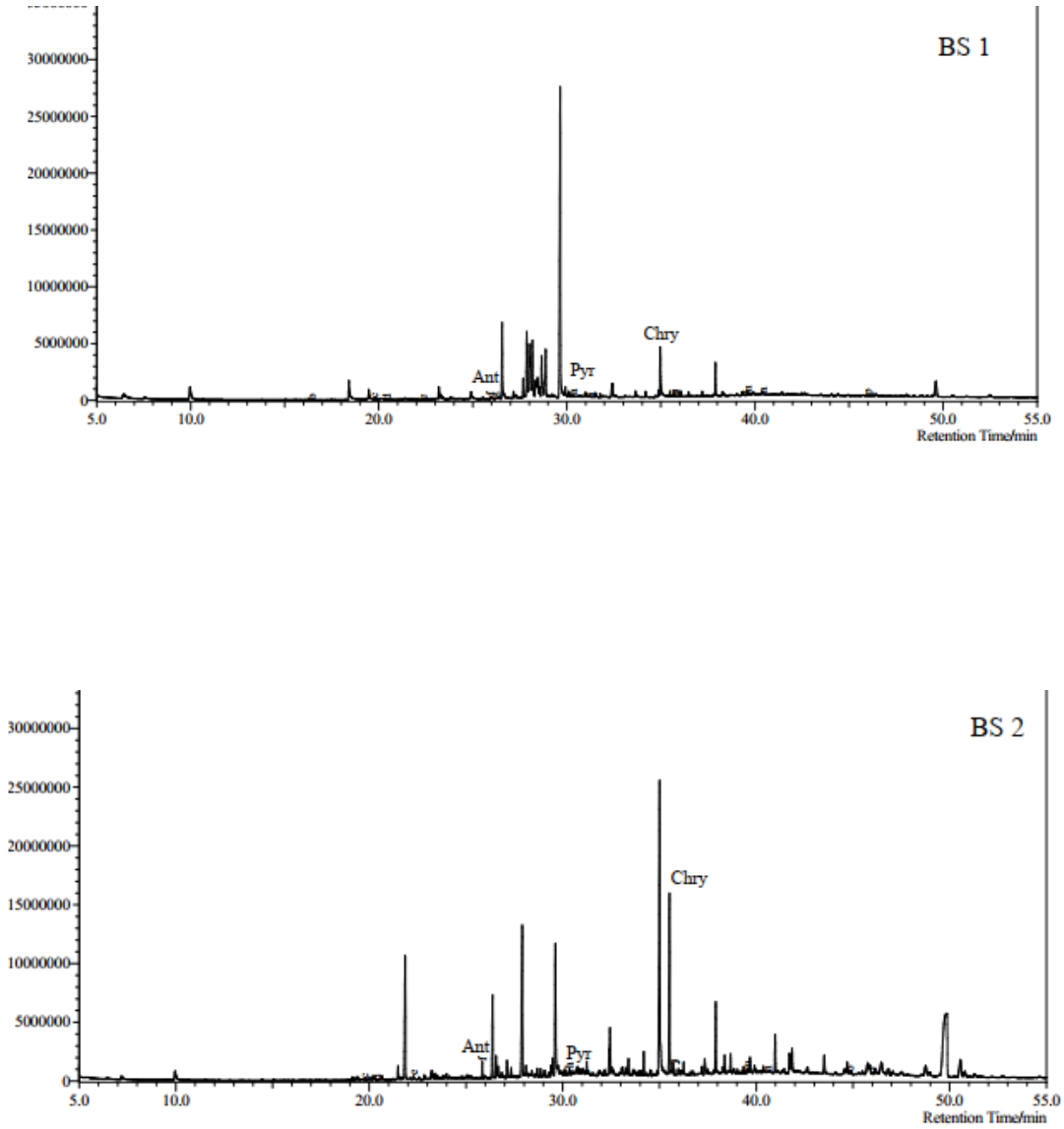


Figure 4.40: GC-MS chromatograms of PAHs in surface sediments from Sebangan (BS1) and Sadong Jaya (BS2)

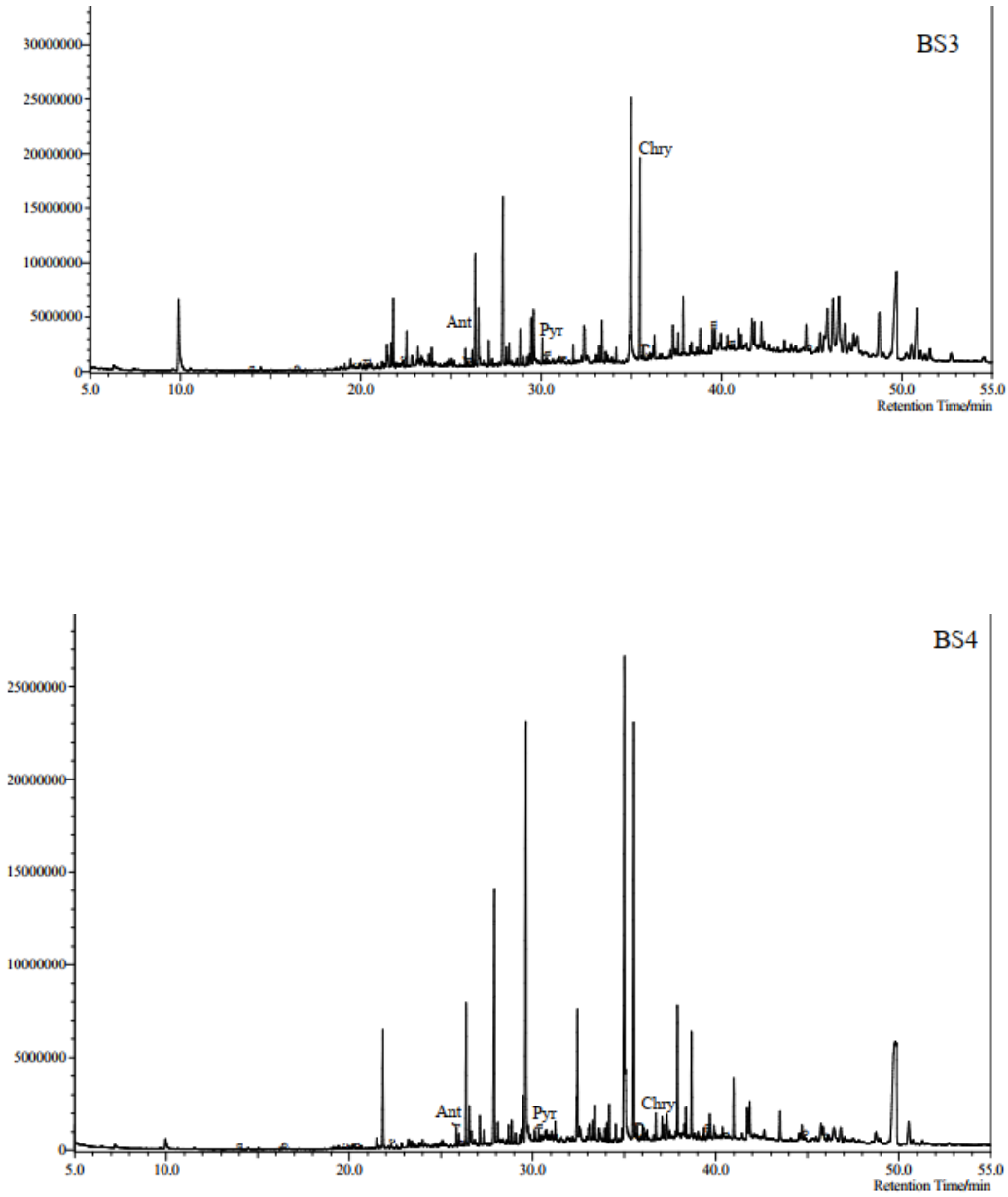


Figure 4.41: GC-MS chromatograms of PAHs in surface sediments from Sungai Buloh (BS3) and Simunjan (BS4)

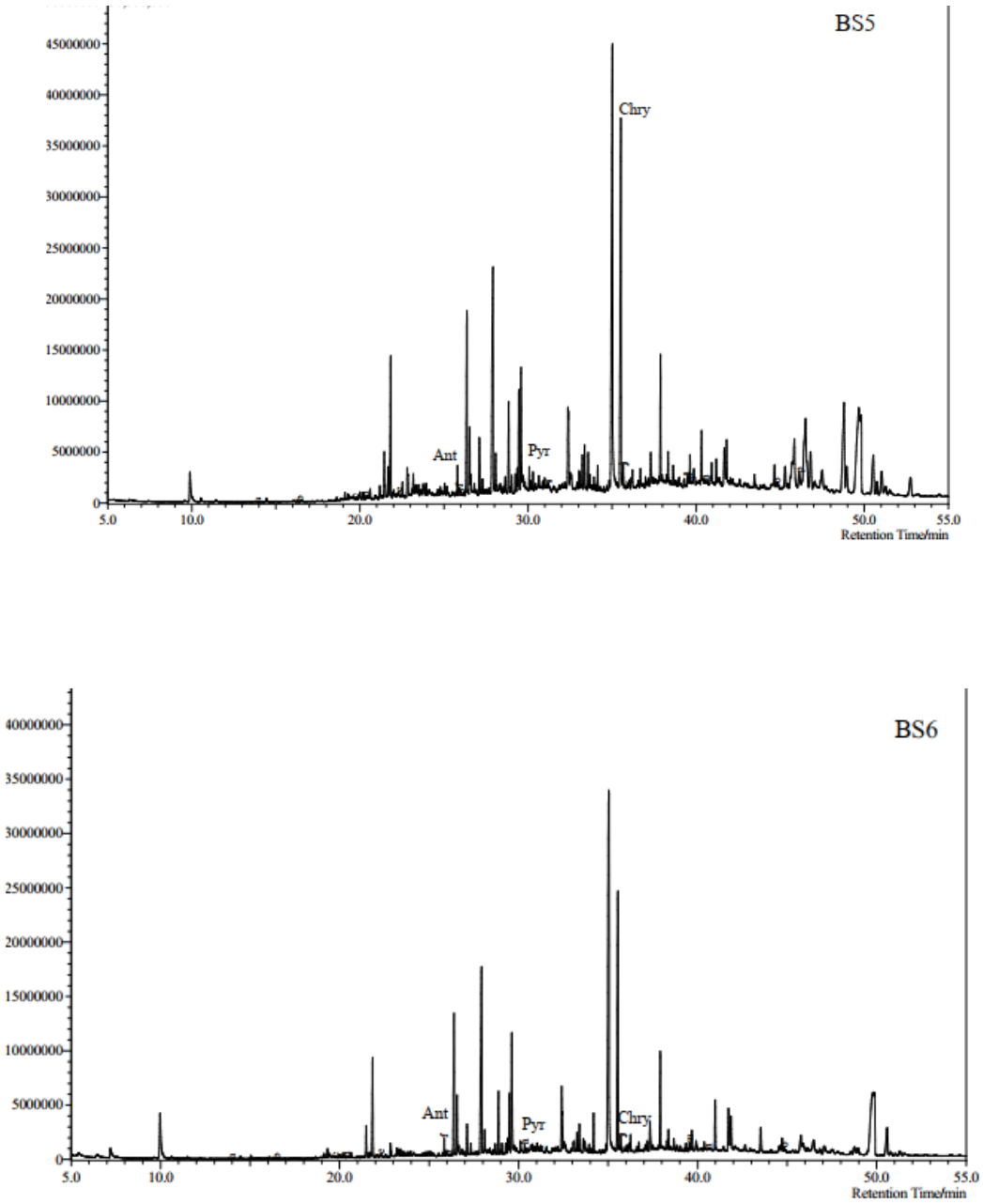


Figure 4.42: GC-MS chromatograms of PAHs in surface sediments from Gedong (BS5), and Sebemban (BS6)

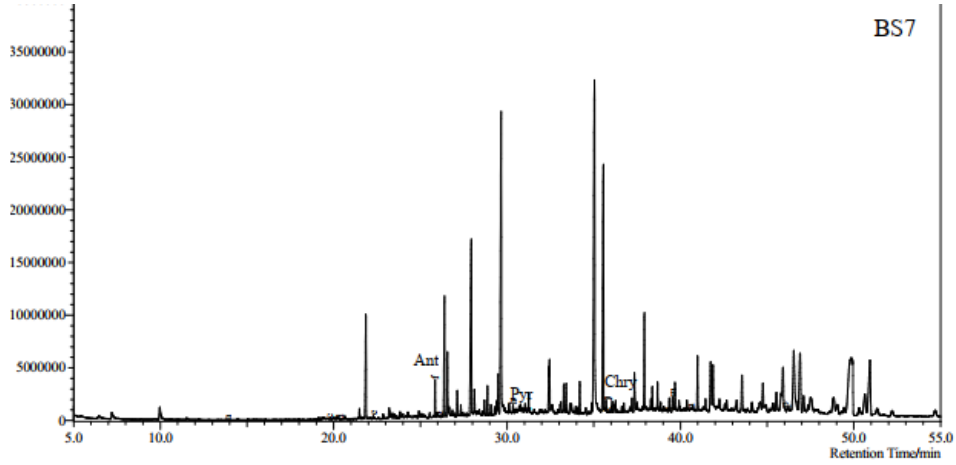


Figure 4.43: GC-MS chromatogram of PAHs in surface sediments from Serian (BS7)

High concentration of PAHs was detected in surface sediments of Serian (BS7) with 184.25 µg/g followed by sediments in Sebemban (BS6) with 123.45 µg/g, Gedong (BS5) with 108.43 µg/g, Sadong Jaya (BS2) with 79.22 µg/g and Simunjan (BS4) with 65.62 µg/g as shown in Table 4.21. Low concentration of PAHs was recorded in surface sediments of BS1 (18.21 µg/g) and BS3 (43.87 µg/g). Occurrence of PAHs in surface sediments at Sadong River suggested a low degree of pollution at the sampling sites of Sebangan (BS1), Sadong Jaya (BS2) and Sungai Buloh (BS3) whereas a medium pollution was observed at the sampling sites of the midstream of Sadong River at Gedong (BS5), Sebemban (BS6) and Serian (BS7) which is the upstream. Concentrations of total HMW PAHs in surface sediments from Sadong River ranged between 7.48-100 ug/g with Serian (BS7) having the highest concentration of HMW PAHs (100.05 µg/g) followed by Gedong (BS5) with 86.99 µg/g.

The composition and distribution of individual PAH in surface sediments at various sampling sites were dominated by different PAHs with more volatile LMW PAHs which include naphthalene, acenaphthylene and acenaphthene in surface sediments of Simunjan (BS4), Sebemban (BS6) and Serian (BS7) to the less volatile HMW PAHs such as

fluoranthene, pyrene, chrysene and benzo[k]fluoranthene in sediments of Gedong (BS5). The occurrence of the PAHs in sediments is likely due to contribution from multiple sources such as domestic waste, sewage discharge, oil spillage or leakages, urban runoff and atmospheric deposition (Aly Salem et al., 2014; Keshavarzifard et al., 2018)

Table 4.21: Concentration of PAHs (μg/g) in the surface sediment from Sadong River

PAH	BS1	BS2	BS3	BS4	BS5	BS6	BS7
Napthalene	0.02	0.03	0.03	0.17	0.02	0.24	0.51
Acenapthylene	0.19	0.87	0.25	0.29	0.21	1.62	0.03
Acenapthene	1.02	1.76	0.54	1.29	2.07	2.12	1.98
Fluorene	0.12	0.54	0.98	0.41	1.50	2.18	0.49
Phenanthrene	1.18	7.98	3.61	5.93	4.00	7.53	7.92
Anthracene	4.25	24.85	9.54	18.33	7.72	29.48	59.05
Fluoranthene	1.24	0.54	0.32	0.53	0.84	2.69	2.33
Pyrene	2.71	9.96	1.11	10.01	5.08	11.12	11.88
Benzo[a]anthracene	0.78	0.71	5.54	1.22	13.71	2.67	1.74
Chrysene	3.87	12.20	0.59	9.40	53.67	17.99	14.77
Benzo[b]fluoranthene	0.19	0.41	0.75	0.50	0.97	0.68	0.49
Benzo[k]fluoranthene	0.13	0.63	2.97	0.79	4.00	0.89	0.92
Benzo[a]Pyrene	0.67	8.91	0.53	8.25	1.29	15.13	27.66
Indeno[1,2,3-c,d]Pyrene	1.78	2.05	0.67	1.08	1.18	2.88	3.90
Dibenzo[ah]anthracene	0.04	4.83	0.53	4.61	1.10	21.57	45.07
Benzo[ghi]perylene	0.03	2.95	15.91	2.82	11.08	4.68	5.49
∑PAH (ug/g)	18.21	79.22	43.87	65.62	108.43	123.45	184.25
∑LMWPAH (ug/g)	9.38	43.33	16.50	34.79	17.64	50.81	81.18
∑HMWPAH (ug/g)	7.48	32.69	22.00	28.67	86.99	66.49	100.05
HMW/LMW	0.80	0.75	1.33	0.82	4.93	1.31	1.23
LMWHMW	1.25	1.33	0.75	1.21	0.20	0.76	0.81

4.9.1.1 Diagnostic Ratios of PAHs in Surface Sediments from Sadong River

Table 4.22 shows the diagnostic ratios of PAHs in the surface sediments. The PAHs in surface sediments from Sebangan (BS1), Sadong Jaya (BS2) and Simunjan (BS4) is pyrogenic with a LMW/HMW value <1 whereas Sungai Buloh (BS3), Gedong (BS5), Sebemban (BS6) and Serian (BS7) have LMW/HMW >1 in the surface sediments which infers petrogenic input contribution. The petrogenic PAHs are usually derived from crude and refined petroleum which are introduced to the river through accidental oil spills, municipal and urban run-off. While the pyrogenic PAHs are derived from the combustion of petroleum and biomass which are released into the river in the form of exhaust fumes and solid residues (Zakaria et al., 2002; Wang et al., 2015). LMW/HMW >1 and LMW/HMW < 1 indicate the petrogenic and pyrogenic contribution, respectively (Soclo *et al.*, 2000). PAHs with LMW/HMW > 1 was observed in the surface sediments of Sebangan (BS1), Sadong Jaya (BS2) and Simunjan (BS4), while LMW/HMW <1 have pyrogenic sources as observed in sediments of Sungai Buloh (BS3), Gedong (BS5), Sebemban (BS6) and Serian (BS7). The ratio of phenanthrene/anthracene < 1 in all surface sediments indicated petrogenic origin. The ratio of fluoranthene/pyrene <1 in all surface sediments indicated petrogenic origin. The ratio of chrysene/benzo[a]anthracene > 1 indicate petrogenic origin was observed for all surface sediments except Sungai Buloh (BS3) surface sediments which indicated pyrogenic origin. Ratio of fluoranthene/ (fluoranthene+pyrene) < 1 in all surface sediments indicated contribution from petrogenic source. The ratio of benzo[a]anthracene/ (benzo[a]anthracene+chrysene) < 1 in all surface sediments indicated petrogenic source. The ratio benzo[a]anthracene/(benzo[a]anthracene+chrysene) > 0.35 in surface sediments of Sungai Buloh (BS3) clearly indicated the pyrogenic input. Hence, the sources of PAHs in river sediments were petrogenic and pyrogenic.

Table 4.22: Diagnostic ratios of PAHs in surface sediments from Sadong River

PAH Ratios	BS1	BS2	BS3	BS4	BS5	BS6	BS7
Ant/(Ant+Phe)	0.78	0.76	0.73	0.76	0.66	0.80	0.88
Phe/Ant	0.28	0.32	0.38	0.32	0.52	0.26	0.13
Flu/Pyr	0.46	0.05	0.29	0.05	0.17	0.24	0.20
Chr/BaA	4.96	17.18	0.11	7.74	3.91	6.73	8.47
Flu/(Flu+Pyr)	0.31	0.05	0.22	0.05	0.14	0.19	0.16
BaA/ (BaA+Chr)	0.17	0.06	0.90	0.11	0.20	0.13	0.11
InP/(InP+BghiP)	0.99	0.41	0.04	0.28	0.10	0.38	0.42

Note: Ant/(Ant+Phe): Anthracene/(Anthracene+Phenanthrene), Phe/Ant: Phenanthrene/Anthracene, Flu/Pyr: Fluoranthene/Pyrene, Chr/BaA: Chrysene/Benzo(a)anthracene, Flu/(Flu+Pyr): Fluoranthene/(Fluoranthene+Pyrene), BaA/(BaA+Chr): Benzo(a)anthracene/Benzo(a)anthracene+Chrysene, Indeno[1,2,3-c,d]Pyrene/(Indeno[1,2,3-c,d]Pyrene+ Benzo[ghi]perylene)

4.9.2 Distribution of PAHs in Core Sediments from Sadong River

Vertical profile for the concentration of PAHs in core sediments are shown in Figures 4.44-4.46. Core sediments at Sadong Jaya (BS2) and Sebemban (BS6) are less polluted by PAHs with concentration ranged from 0-100 μg/g, whereas core sediments at Sebangan (BS1) was moderately polluted with PAHs with concentration of 100-1000 μg/g at layer 37.5-40 cm. According the Keshavarzifard et al. (2018), PAHs concentration in sediments ranged 0-100 μg/g are less polluted while PAHs concentration ranged 100-1000 μg/g are moderately polluted. The ∑PAHs in core sediments of Sebangan (BS1) increased from upper layer toward down layer of core whereas at Sadong Jaya (BS2) and Sebemban (BS6) varied from upper layer toward lower layer.

The vertical trend of phenanthrene, anthracene, fluoranthrene, pyrene, benzo[a]anthracene and chrysene fluctuated in all core sediments from Sadong River. Anthracene in sediments of Sebangan (BS1) was high at the upper layer 0.0-2.5 cm and decreased at the lower layer 42.5-45.0 cm. The concentration of anthracene was 73.38 μg/g at layer 25.0-27.5 cm and the low value 3.15 μg/g was observed at layer 5.0-7.5 cm. Pyrene was relatively high from upper layer to the lower layer with high value of 45.83 μg/g at 30.0-

32.5 cm layer and low value was 0.31 μg/g at 35.0-37.5 cm layer. Chrysene was highest in the 17.5cm-20.0cm layer with a value of 40.79 μg/g and the low concentration of 0.46 μg/g was observed at 35.0-37.5 layer. Anthracene was high from the upper layer to the lower layer in Sadong Jaya (BS2), high concentration of 67.91 μg/g was detected at layer 27.5-30.0 cm and the middle layer had a concentration of 5.90 μg/g at layer 12.5-15.0 cm. Pyrene was relatively high from upper layer to the lower layer with high concentration of 47.58 μg/g in sediments at layer 7.5-10.0 cm layer and low concentration of 8.09 μg/g was recorded in sediments at the top layer 0.0-2.5 cm. Chrysene was high in the sediment at layer 15.0-17.5 cm with a value of 79.11 μg/g and the low concentration of 1.48 μg/g at the top layer 0.0-2.5 cm.

Anthracene in Sebemban (BS6) was high from the middle layer 20.0-22.5 cm to the lowest layer 42.5-45.0 cm. High concentration of anthracene of 56.98 μg/g was detected in sediments at 10.0-12.5 cm layer and 79.30 μg/g at 20.0-22.5 cm and the low concentration of 2.15 μg/g was observed in sediments at upper layer 0.0-2.5 cm. Pyrene was relatively high from upper layer to the lower layer with concentration of 44.86 μg/g in sediments at 20.0-22.5 cm layer and low concentration of 1.15 μg/g in sediments at 17.5-20.0 cm layer. Chrysene had a high concentration in the sediments at 20.0 cm-22.5 cm layer with 79.11 μg/g and the low concentration of 0.03 μg/g was recorded at upper layer 0.0-2.5 cm.

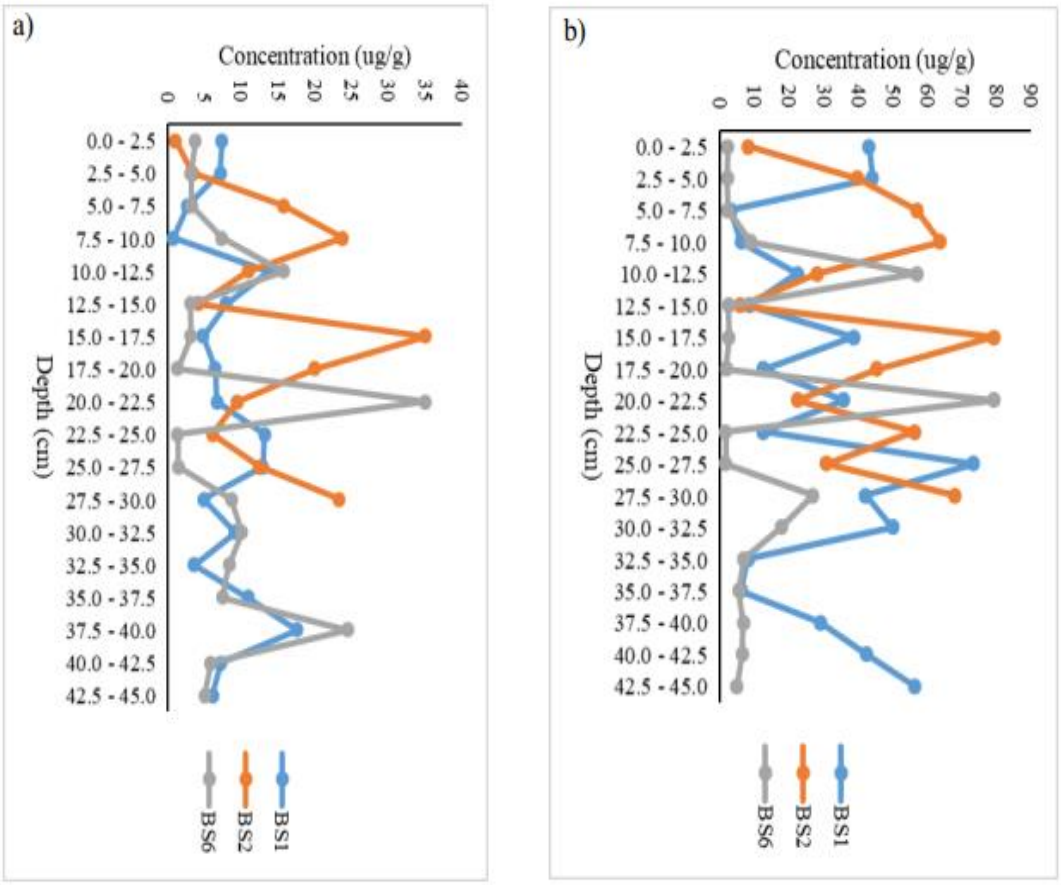


Figure 4.44: Vertical distribution of (a) phenanthrene and (b) anthracene in the core sediments from Sadong River

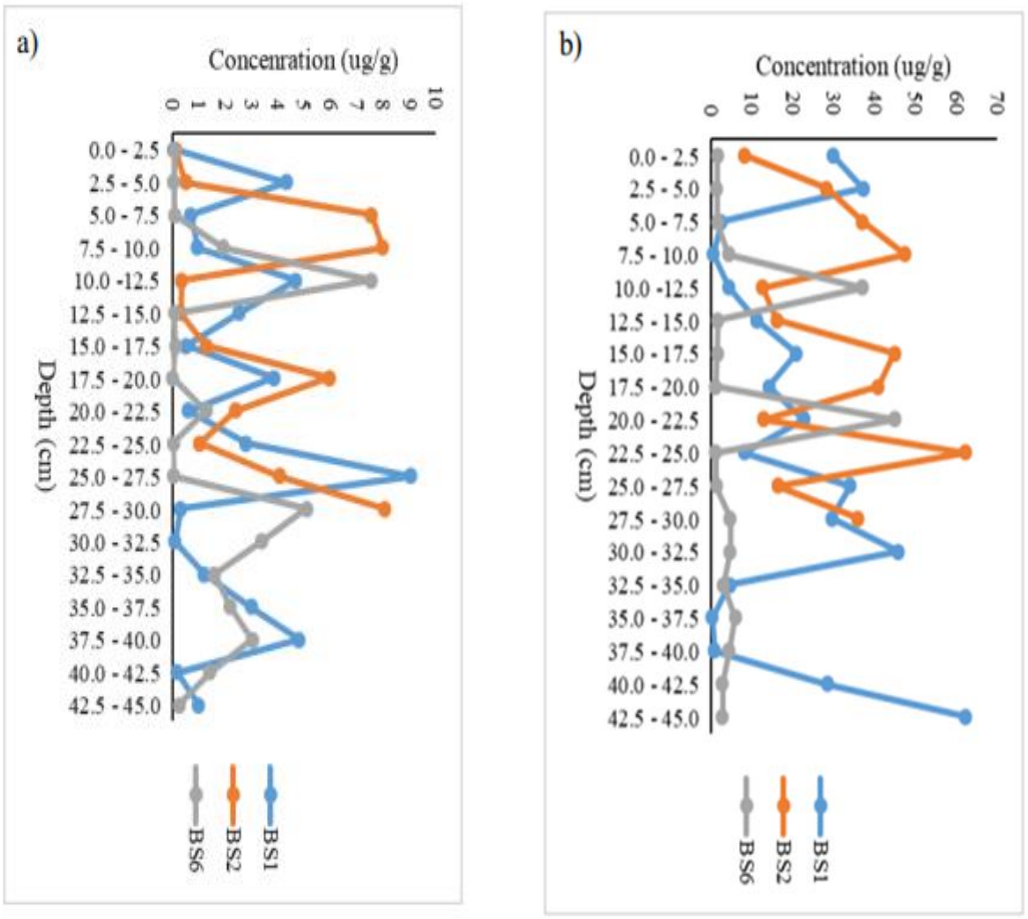


Figure 4.45: Vertical distribution of (a) fluoranthene and (b) pyrene in the core sediments from Sadong River

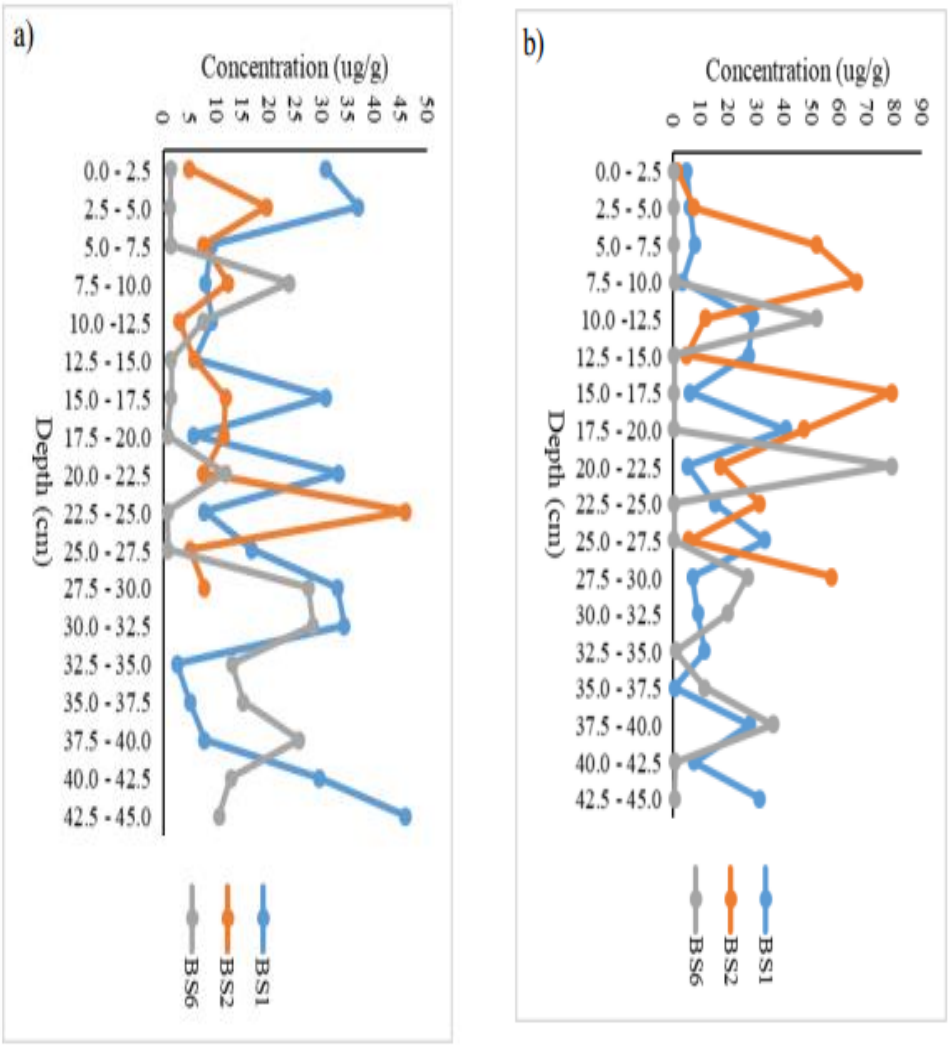


Figure 4.46: Vertical distribution of **(**a) benzo[a]anthracene and (b) chrysene in the core sediments from Sadong River

4.9.2.1 Possible Source of PAHs in Core Sediments from Sadong River

The vertical trend of PAHs in core sediments varied from upper layer to lower layer at Sebangan (BS1) with a zig zag pattern had concentration of benzo[a]pyrene 128 μg/g at 37.5-40.0 cm, while in Sadong Jaya (BS2) and Sebemban (BS6), the PAHs was < 100 μg/g from the upper layer to the lower layer. This indicated that the primary source of PAHs was petrogenic. LMW/HMW PAHs in sediments of Sebangan (BS1) was 0.14 μg/g in sediments at 35.0-37.5 cm layer and with the high LMW/HMW of 1.32 μg/g in sediments at 25.0-27.5 cm layer. The LMW/HMW PAHs in core sediments of Sadong Jaya (BS2) was 2.69 μg/g at 15.0-17.5 cm layer and low LMW/HMW of 0.71 μg/g was recorded at 12.5-15.0 cm. The upper layer 0.0-2.5 cm, layer 10.0-12.5 cm and lower layer 42.5-45.0 cm of Sebemban (BS6) had LMW/HMW of 0.57 μg/g, 0.64 μg/g and 0.16 μg/g, respectively. All layers in core sediments of Sebemban (BS6) indicated pyrogenic origin because LMW/HMW PAHs was < 1.

The use pesticides, herbicides and toxic chemicals as well as microbial pathogens may have contributed to the occurrence of PAHs in river sediments (Isobe et al., 2007; Vaezzadeh et al., 2015b; Keshavarzifard et al., 2018). The decrease of PAHs concentration at the upper layers toward the middle layers of the core sediment could be attributed to dilution of PAH compounds as a consequence of river flushing (Shaw et al., 2004). The composition and distribution of individual PAH in core sediments showed different stations were characterized with different compounds from more volatile LMW PAHs like acenaphthylene and acenaphthene to the less volatile HMW PAHs like fluoranthene and benzo[k]flouranthene (Zhang et al., 2019a). The 4-ring PAHs as well as 5 and 6-ring have been detected in abundance in most of the sediment samples. In addition, 2-ring PAHS have low concentration in the core sediments from all sampling sites of Sadong River. The

multiple sources of PAH in the river include domestic waste, sewage discharge, oil spillage, urban runoff and atmospheric deposition (Keshavarzifard et al., 2018). The inconsistencies of PAH composition pattern in the cores from upper layer to lower layer at Sebangan (BS1), Sadong Jaya (BS2) and Sebemban (BS3) may be due to differences in additional input sources such as severe to moderate temperature combustion processes and various fossil materials (Zhou & Maskaoui, 2003).

The higher concentration of HMW PAHs compared to LMW PAHs which is usually associated with pyrogenic origins is observed in this study. LMW PAHs are generally originated from petrogenic sources, while those of HMW are originated from pyrolytic sources (Mirza et al., 2014). The vertical profile of selected diagnostic ratios of PAHs in the core sediments from Sadong River are shown in Figures 4.47 and 4.48. The vertical trend of the diagnostic ratios was zigzag from the upper layer to lower layer of core sediments of Sebangan (BS1), Sadong Jaya (BS2) and Sebemban (BS6). The ratio of anthracene/ (anthracene+phenanthrene) in core sediments at BS1 of layers 0.0-2.5 cm, 20.0-22.5 cm and 42.5-45.0 cm were 0.85, 0.84 and 0.90 respectively this indicated a petrogenic origin. The ratio of anthracene/ (anthracene+phenanthrene) > 0.1 indicate petrogenic origin (Bastami et al., 2014). The fluoranthene/ (fluoranthene+pyrene) ratio in core sediments at BS2 was 0.01, 0.02 and 0.18 in layers 0.0-2.5 cm, 12.5-15.0 cm and 27.5-30.0 cm respectively indicating a petrogenic origin because the ratio was <0.5. The core sediments of Sebemban (BS6) at layers 0.0-2.5 cm, 20.0-22.5 cm and 42.5-45 cm had benzo[a]anthracene/(benzo[a]anthracene+chrysene) ratios of 0.98, 0.13 and 0.96, respectively. This indicated that the top layer (0.0-2.5 cm) and lowest layer (42.5-45.0 cm) were of pyrogenic origin, whereas the middle layer (20.0-22.5 cm) with ratio of 0.13 indicated a petrogenic origin because it is < 0.5 (Brewster et al., 2018).

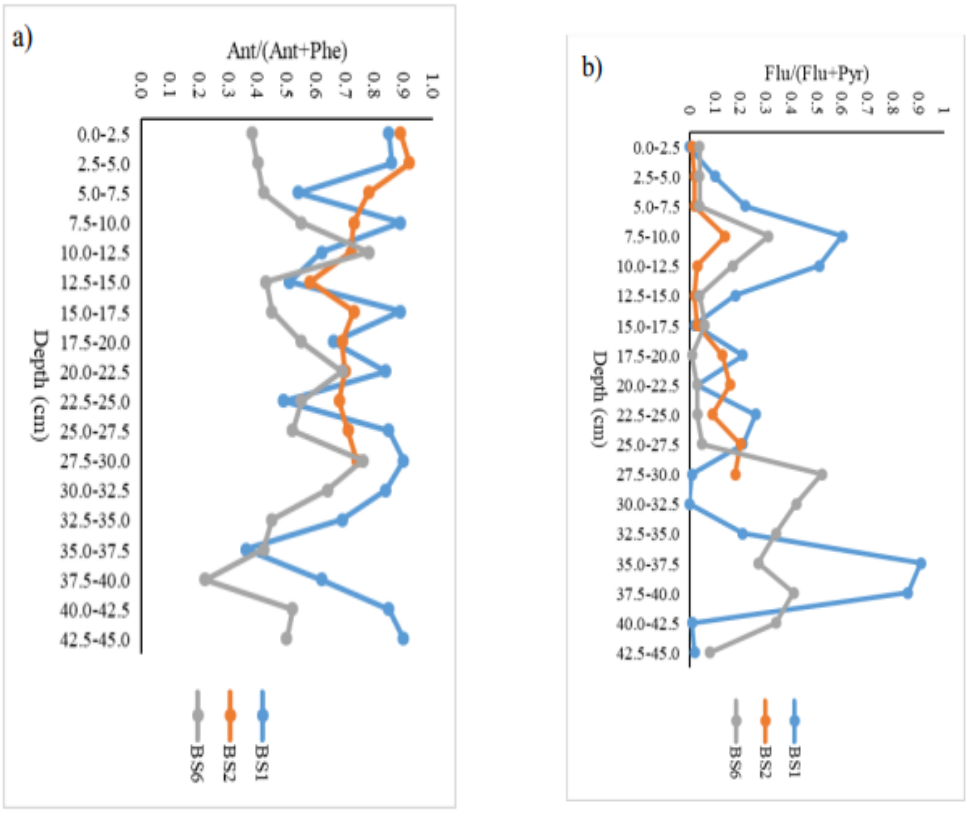


Figure 4.47: Vertical distribution of **(**a) anthracene/ (anthracene+phenanthrene) and (b) fluoranthene/ (fluoranthene+pyrene) in the core sediments from Sadong River

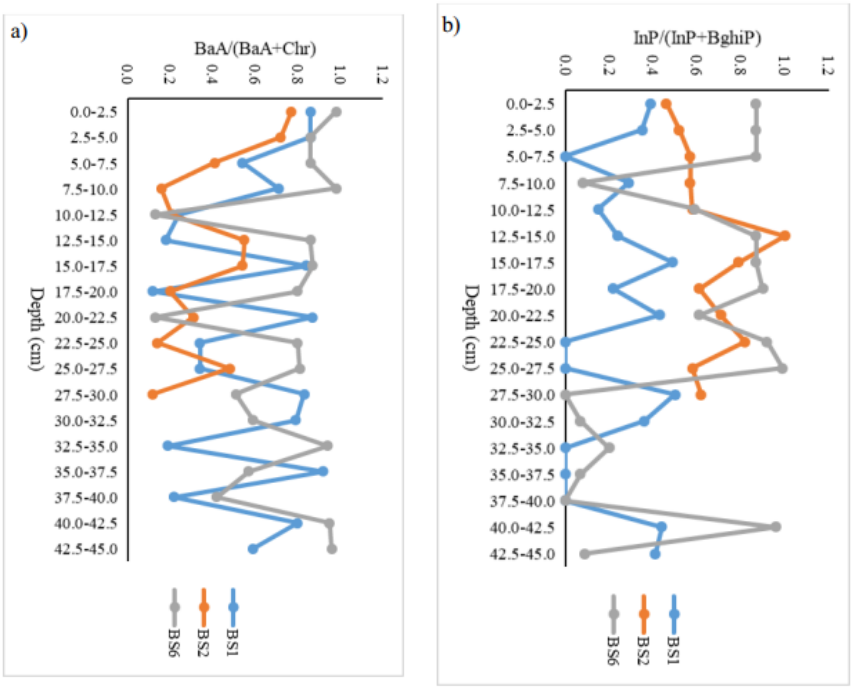


Figure 4.48: Vertical distribution of **(**a) benzo[a] anthracene/ (benzo[a] anthracene+chrysene) and (b) indeno[1,2,3-c,d]pyrene / (indeno[1,2,3-c,d]pyrene + benzo[ghi]perylene) in the core sediments from Sadong River

4.9.3 Chapter Summary

This chapter summarizes the geochemical characteristics of Sadong River. Targeted heavy metals detected in the sediments are Cu, Ni, Zn, Fe, Mn and the toxic heavy metals are Pb, Cd and As while the major metals are Mg, K and Na. The value of I_{geo} for Zn, Pb, Mn and Fe at all sampling sites were negative indicating the area is unpolluted. As was absent in the surface sediments at the midstream in Simunjan (BS4), Gedong (BS5) and Sebemban (BS6) of Sadong River. The concentration of heavy metals and several data obtained have proven that the sediments from all sampling stations were unpolluted with heavy metals. High concentration of Fe in the surface sediment are due to the detrital mineral grains transported from weathered parent material. The occurrence of Mg, K and Na suggests the domination of rock forming minerals such as K-feldspar and plagioclase

feldspar in the river sediments. Vertical distributions of heavy metals in core sediments from Sadong River, Samarahan were fairly consistent from the upper layer toward the lower layers for Cu, Ni, Pb, Zn, Cd, Fe and Mn. The concentration of Pb was higher in core sediments of Sadong Jaya (BS2) compared to other stations. All the heavy metals and major elements were reported in the core sediments and Cd was only detected in two cores from the midstream at Sadong Jaya (BS2) and Sungai Buloh (BS3), respectively. Heavy metals in the study area originated mainly from natural sources such as weathered rocks and soils with minimal impact of anthropogenic activities in the sediments of Sadong River. The major metals detected in the sediments from Sadong River include Mg, Na and K. The concentration of Na in surface sediments was low at the upstream in Serian (BS7) and the midstream at Gedong (BS5) and Sebemban (BS6).

PAHS such as naphthalene, acenaphthylene, acenaphthene and fluorene have low concentration in the core sediments from all stations of Sadong River. The ratios of phenanthrene/anthracene in sediment were < 1 for all sediment samples indicated petrogenic origin and the ratio of fluoranthene/pyrene <1 in all samples indicated petrogenic origin. The ratios of chrysene/benzo[a]Anthracene in sediments > 1 which is petrogenic origin in all sediment samples except Sungai Buloh (BS3) which indicated pyrogenic origin. The ratio of fluoranthene/ (fluoranthene+pyrene) < 1 in all sediment samples indicated petrogenic origin. PAH of benzo[a]Anthracene/ (benzo[a]anthracene+chrysene) was < 1 in all sampling stations which indicated petrogenetic origin, the benzo[a]anthracene/(benzo[a]anthracene+chrysene) ratio of PAHs was > 0.35 in BS3 which clearly indicated pyrogenic origin. Hence, the sources of PAHs in river sediments were petrogenic and pyrogenic. The multiple sources of PAH in Sadong River include domestic waste, sewage discharge, oil spillage, urban runoff and atmospheric deposition.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study gives an understanding on the sedimentological and geochemical characteristics of Sadong River. All sediments contained mostly of fine grained particles. The sediment particles are comprised of clay, silt, sand and organic matter. The river sediments were derived mainly from weathered rocks and soil which were transported and deposited by wind, water and human activities. Small percentage of sediments were derived from the atmosphere as dust particles. Organic matter was moderate in the surface sediments while the moisture content varied from upper layer to the lower layer in core sediments of Sadong River. The sedimentary sequence of the core sediments of Sadong River showed a fine particle-sized upward sequence in the sampling locations except for BS7 (Serian) where sediments were coarse grained. The increase in population and urbanization has impacted the study area as well causing varying geochemical characteristics of sediments. The concentration of heavy metals and several data obtained have proven that the sediments from all sampling stations were unpolluted with heavy metals. High concentration of Fe in the surface sediment are due to the detrital mineral grains transported from weathered parent material. The occurrence of Mg, K and Na suggests the domination of rock forming minerals such as K-feldspar and plagioclase feldspar in the river sediments.

Targeted essential heavy metals in the Sadong River include Cu, Ni, Zn, Fe and Mn while the toxic metals are Pb and As in surface and core sediments. Cd was detected in

the core sediments of only two stations. Ecotoxicological assessment showed that the essential heavy metals and toxic metals originated mainly from natural source with minimal impact of anthropogenic activities in the sediments. The statistical analysis showed that three factors were derived from PCA on distribution of the metals in surface sediments of Sadong River. The factor 1 comprised of Cu, Zn, Mn, K, Na and As which are derived from both natural sources and anthropogenic sources. Factor 2 contained Ni, Fe and Mg are originated from natural sources. Fe and Mg are mainly derived from weathering of siliciclastic rocks and soil in the study area. Factor 3 is made up of Pb which was derived mainly from anthropogenic sources such agricultural activities and boat docking around the banks of the river.

Concentration of *n*-alkanes detected in the surface sediments from Sadong River varied from the upstream to midstream of the Sadong River, the highest concentrations of *n*-alkanes have been detected in midstream of the river. Anthropogenic sources of *n*-alkanes in this river are land-based sources particularly from the activities around the banks of the river such as use of fertilizers and pesticides on oil palm plantation and rice paddies, exhaust fumes from boat docking as well as shipping. Domination of *n*-alkanes originating from vascular plants were observed with a significance of HMW *n*-alkanes with odd carbon numbers in the surface sediments.

The PCA was carried out to predict sources of *n*-alkanes in surface sediments of Sadong River. Three factors were extracted from the PCA using Varimax with Kaiser Normalization rotation method. Factor 1 comprises of C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{18}, C_{19}, C_{20}, C_{25}, $C_{30,}$ C_{31} and C_{32} which are derived from natural and anthropogenic sources. Factor 2 consists of C_9, C_{10}, C_{11}, C_{12} and C_{24} which are derived from natural sources. Factor 3 is made up of C_{23} C_{26} C_{29} and C_{33} which are derived from higher plants, while Factor 4 consists of

only C_{22}. The sources of *n*-alkanes are petrogenic or pyrogenic sources. Factor 1 indicated that the availability of *n*-alkanes was via similar pathways in the river system such as micro-organisms, algae and higher vascular plants. Anthropogenic sources include the direct discharge of domestic waste and oil spillage.

Various environmental assessments carried out suggesting the source of essential heavy metals in the sediments were from natural sources. The toxic heavy metals such as Pb, Cd and As were derived from human activities such as agricultural activities, urban waste and there may be seepages of corroded parts from ships in BS3 (Sungai Buloh). The hydrocarbons are mainly derived from natural sources such as terrestial vascular plants, algae and micro-organisms with minimal impact of anthropogenic activities. Sixteen targeted PAHs were detected in the surface and core sediments from Sadong River. The hydrocarbon compounds were derived from multiple sources. The Sadong River is believed to be unpolluted with heavy metals and hydrocarbons.

5.2 Recommendations for Future Study

Water samples and fish samples are required in order to have a wider range of heavy metals and hydrocarbons data for environmental studies of Sadong River. The effects of fluvial depositional environments on sediment archiving processes, aggradation rates and geochemical patterns should be considered. The study of the depositional environments showing the sedimentation rates and the age of sediments can be considered. Flood plain sediments of Sadong River can further be considered to understand the causes of fluctuation in geochemical characteristics of the Sadong River. Factors such as short term over bank floods, lateral transect of the river, exchanges between dissolved fractions and particulate

within the sedimentary column which are important factors controlling the fate of contaminants can be studied. The relationship between spatial fluctuation during high discharge events due to erosion intensity across the depositional environments especially the floodplain can be studied.

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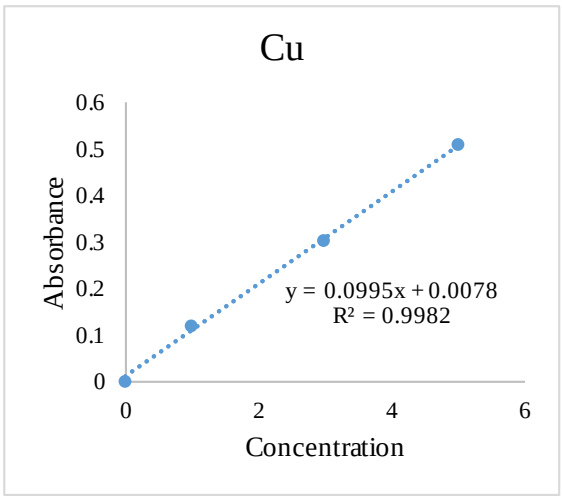
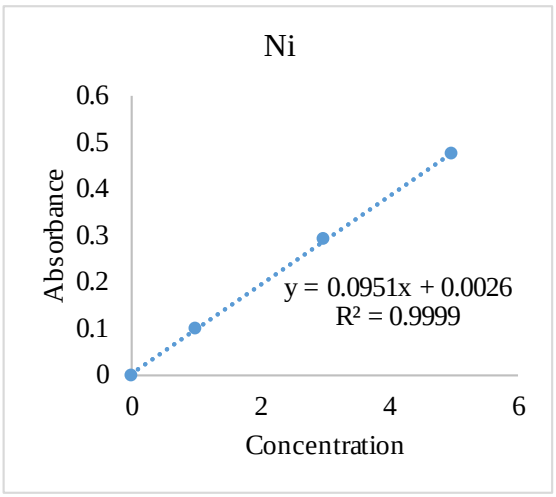
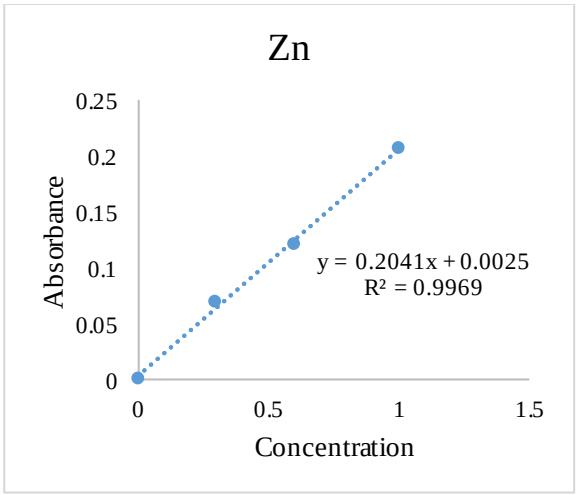
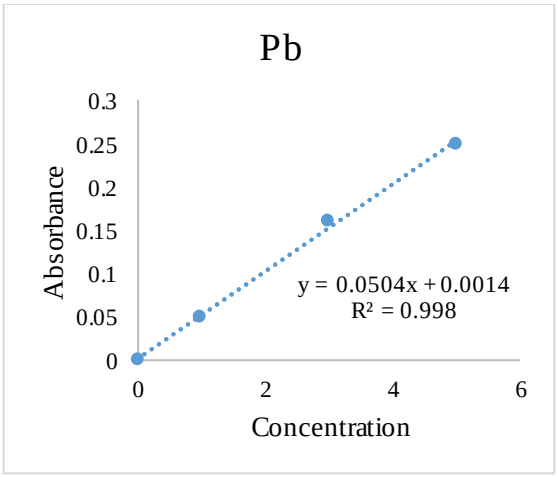
APPENDICES

Appendix 1: The calibration curve for standard of Cu, Ni, Zn and Pb analysed on AA**S**

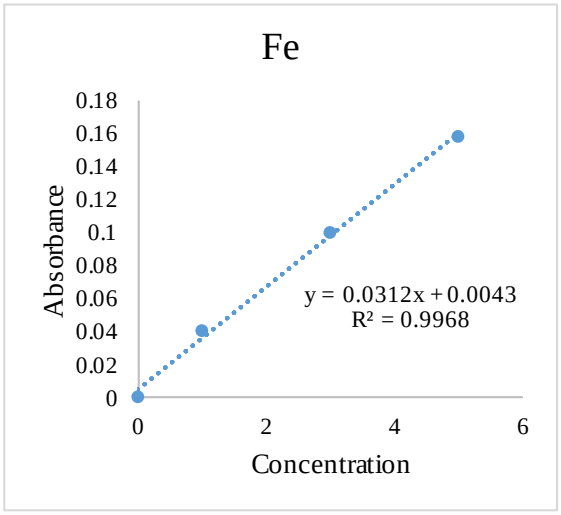


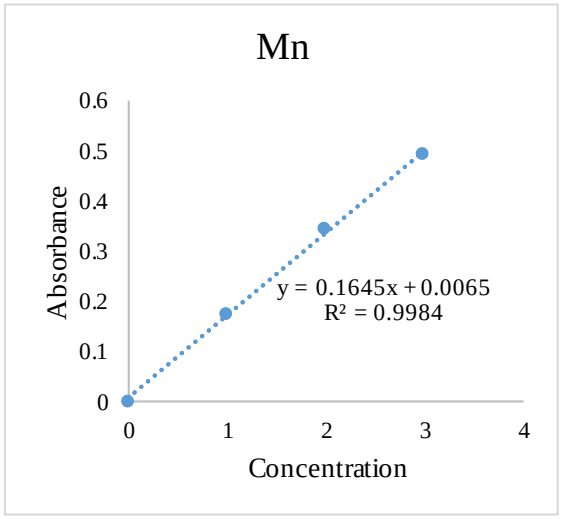


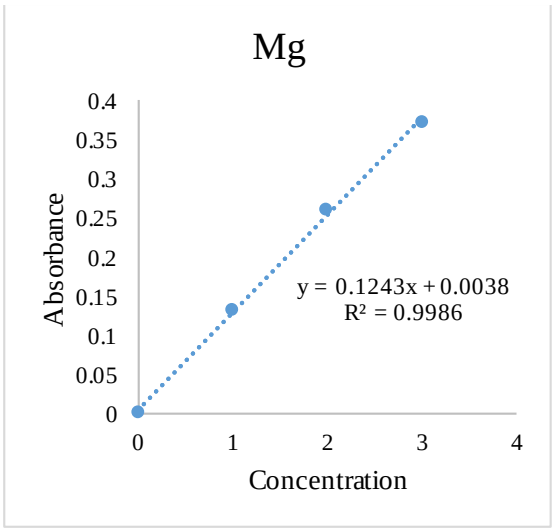


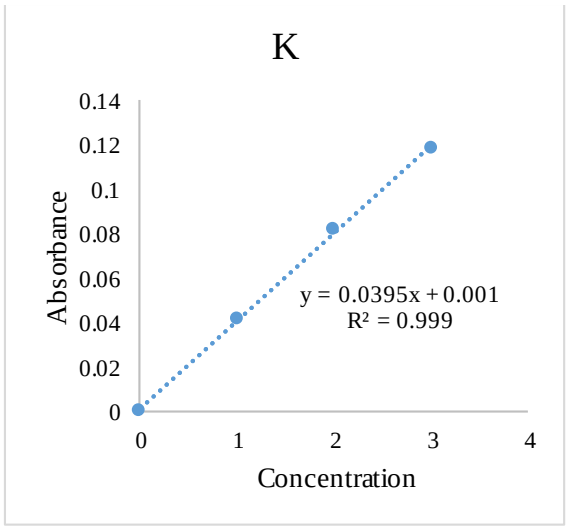


Appendix 2: The calibration curve for standard of Fe, Mn, Mg and K analysed on AAS

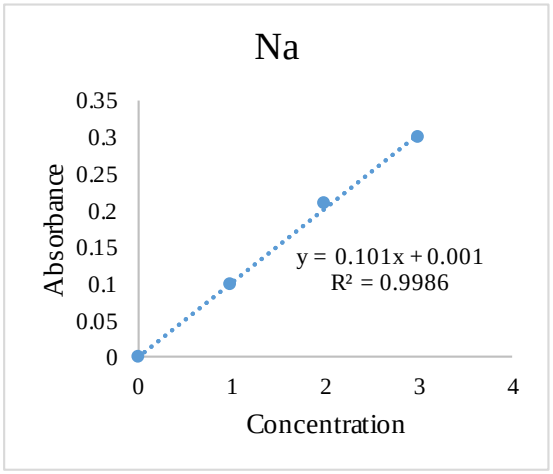


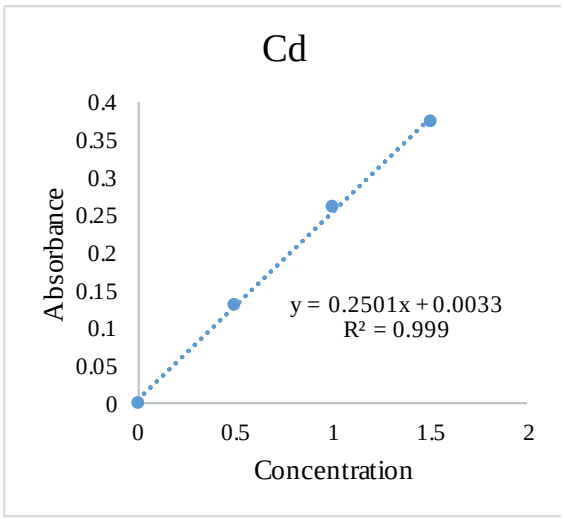


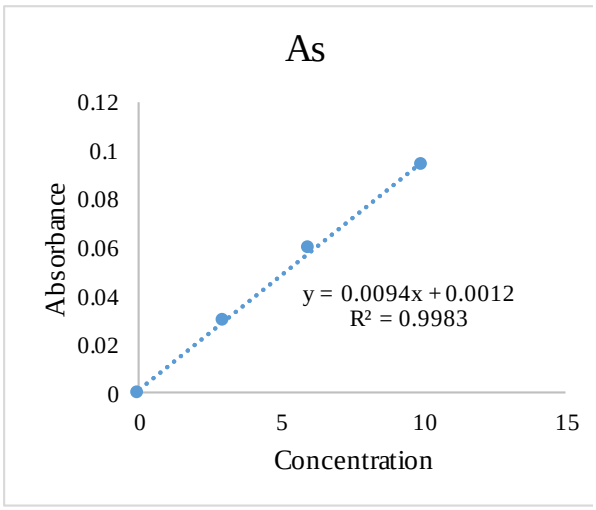




Appendix 3: The calibration curve for standard of Na, Cd and As analysed on AAS







Appendix 4: The vertical profile of mean concentration (mg/kg) of (a) Cu and (b) Ni in core sediments from Sadong River

(a) Cu

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	12	4	53	12	15	12
2.5-5.0	12	8	314	10	12	12
5.0-7.5	13	4	185	10	11	13
7.5-10.0	11	4	221	11	11	13
10.0-12.5	13	10	236	13	12	14
12.5-15.0	12	5	325	11	14	14
15.0-17.5	12	6	101	11	13	17
17.5- 20.0	12	10	252	11	13	14
20.5-22.5	12	8	18	-	13	16
22.5-25.0	11	9	7	-	13	15
25.0-27.5	12	9	-	-	14	14
27.5-30.0	9	19	-	-	14	15
30.0-32.5	5	-	-	-	-	26
32.5-35.0	5	-	-	-	-	15
35.0- 37.5	4	-	-	-	-	13
37.5-40.0	5	-	-	-	-	14
40.0-42.5	6	-	-	-	-	10
42.5-45.0	5	-	-	-	-	8
Mean	9	8	171	11	13	14
Maximum	13	19	325	13	15	26
Minimum	4	4	7	10	11	8

'-' – data not available

(b) Ni

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	11	9	43	2	12	6
2.5-5.0	11	14	20	2	13	7
5.0-7.5	11	14	16	1	11	7
7.5-10.0	10	17	23	7	11	7
10.0-12.5	12	23	21	2	15	9
12.5-15.0	11	21	15	1	14	22
15.0-17.5	10	18	17	1	14	24
17.5- 20.0	11	18	18	0	14	11
20.5-22.5	10	16	14	-	13	15
22.5-25.0	10	19	13	-	17	10
25.0-27.5	10	18	-	-	17	12
27.5-30.0	10	21	-	-	10	12
30.0-32.5	10	-	-	-	-	12
32.5-35.0	11	-	-	-	-	8
35.0- 37.5	10	-	-	-	-	8
37.5-40.0	11	-	-	-	-	7
40.0-42.5	12	-	-	-	-	5
42.5-45.0	12	-	-	-	-	2
Mean	11	17	20	2	13	10
Maximum	12	23	43	7	17	24
Minimum	10	9	13	0	10	2

'-' – data not available

Appendix 5: The vertical profile of mean concentration (mg/kg) of (a) Zn and (b) Fe in core sediments from Sadong River

(a) Zn

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	44	23	48	60	26	35
2.5-5.0	45	55	48	43	26	33
5.0-7.5	47	35	47	53	22	34
7.5-10.0	40	40	49	42	21	35
10.0-12.5	53	60	44	53	25	46
12.5-15.0	44	47	46	53	28	32
15.0-17.5	42	44	49	50	29	36
17.5- 20.0	46	47	50	49	30	32
20.5-22.5	44	40	50	-	28	41
22.5-25.0	39	40	37	-	32	27
25.0-27.5	42	45	-	-	35	25
27.5-30.0	39	50	-	-	40	31
30.0-32.5	29	-	-	-	-	31
32.5-35.0	33	-	-	-	-	32
35.0- 37.5	32	-	-	-	-	33
37.5-40.0	37	-	-	-	-	26
40.0-42.5	41	-	-	-	-	19
42.5-45.0	37	-	-	-	-	11
Mean	41	44	47	51	28	31
Maximum	53	60	50	60	40	46
Minimum	29	23	37	42	21	11

'-' – data not available

(b) Fe

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	1899	3658	4076	1932	2242	2277
2.5-5.0	1898	3237	3801	1891	2235	2202
5.0-7.5	1915	3811	3883	1933	1882	2312
7.5-10.0	1917	3882	3974	1896	2184	2308
10.0-12.5	1940	4026	3956	1934	2237	2354
12.5-15.0	1923	3982	3971	1925	2254	2258
15.0-17.5	1909	3948	3976	1839	2274	2321
17.5- 20.0	1914	3978	3959	1818	2294	2060
20.5-22.5	1916	3856	4008	-	2262	2214
22.5-25.0	1797	3846	3918	-	2294	2207
25.0-27.5	1910	3885	-	-	2329	2233
27.5-30.0	1658	3990	-	-	2372	2292
30.0-32.5	1938	-	-	-	-	2271
32.5-35.0	1963	-	-	-	-	2101
35.0- 37.5	1954	-	-	-	-	2293
37.5-40.0	1966	-	-	-	-	2231
40.0-42.5	1983	-	-	-	-	1799
42.5-45.0	1977	-	-	-	-	2136
Mean	1910	3842	3952	1896	2238	2215
Maximum	1983	4026	4076	1934	2372	2354
Minimum	1658	3237	3801	1818	1882	1799

'-' – data not available

Appendix 6: The vertical profile of mean concentration of Mn (mg/kg) in core sediments from Sadong River

Mn

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	366	314	464	501	216	209
2.5-5.0	343	352	545	428	231	215
5.0-7.5	349	479	346	474	193	260
7.5-10.0	338	465	429	395	162	270
10.0-12.5	496	565	440	506	216	314
12.5-15.0	487	531	411	426	237	258
15.0-17.5	445	520	324	366	273	375
17.5- 20.0	461	543	380	387	305	207
20.5-22.5	452	411	548	-	258	347
22.5-25.0	328	420	445	-	304	174
25.0-27.5	345	429	-	-	321	205
27.5-30.0	314	482	-	-	349	224
30.0-32.5	333	-	-	-	-	214
32.5-35.0	359	-	-	-	-	211
35.0- 37.5	326	-	-	-	-	281
37.5-40.0	414	-	-	-	-	127
40.0-42.5	454	-	-	-	-	117
42.5-45.0	390	-	-	-	-	116
Mean	389	459	433	435	255	229
Maximum	496	565	548	506	349	375
Minimum	314	314	324	366	162	116

'-' – data not available

Appendix 7: The vertical profile of mean concentration (mg/kg) of (a) Mg and (b) K in core sediments from Sadong River

(a) Mg

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	1310	1736	1818	1226	1492	1347
2.5-5.0	1305	1360	1815	1303	1434	1118
5.0-7.5	1280	-5	1790	1325	1356	1182
7.5-10.0	1318	212	1803	1284	1353	1289
10.0-12.5	1349	-20	1812	1312	1384	1401
12.5-15.0	1340	-57	1798	1317	1510	1561
15.0-17.5	1333	-49	1798	1301	1530	1483
17.5- 20.0	1333	68	1813	1332	1562	1440
20.5-22.5	1343	374	-	-	1591	1176
22.5-25.0	1314	1857	-	-	1526	1497
25.0-27.5	1325	1859	-	-	1600	1158
27.5-30.0	1336	1873	-	-	1517	1331
30.0-32.5	1132	-	-	-	-	1500
32.5-35.0	877	-	-	-	-	1273
35.0- 37.5	859	-	-	-	-	1160
37.5-40.0	827	-	-	-	-	1683
40.0-42.5	835	-	-	-	-	1814
42.5-45.0	781	-	-	-	-	1803
Mean	1178	767	1806	1300	1488	1401
Maximum	1349	1873	1818	1332	1600	1814
Minimum	781	-57	1790	1226	1353	1118

'-' – data not available

(b) K

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	1130	763	1295	1162	484	564
2.5-5.0	1097	849	1263	937	518	504
5.0-7.5	1175	1047	1171	1182	445	417
7.5-10.0	1027	1190	1311	897	467	396
10.0-12.5	1361	1576	1298	1245	503	487
12.5-15.0	1098	1403	1252	1221	560	593
15.0-17.5	1060	1324	1354	1131	575	663
17.5- 20.0	1044	1440	1395	1211	590	690
20.5-22.5	1371	1206	-	-	580	472
22.5-25.0	968	1212	-	-	528	577
25.0-27.5	1050	1235	-	-	579	437
27.5-30.0	1044	1473	-	-	704	514
30.0-32.5	908	-	-	-	-	569
32.5-35.0	1026	-	-	-	-	502
35.0- 37.5	969	-	-	-	-	422
37.5-40.0	1069	-	-	-	-	585
40.0-42.5	1178	-	-	-	-	550
42.5-45.0	1118	-	-	-	-	512
Mean	1094	1227	1292	1123	544	525
Maximum	1371	1576	1395	1245	704	690
Minimum	908	763	1171	897	445	396

'-' – data not available

Appendix 8: The vertical profile of mean concentration (mg/kg) of Na in core sediments from Sadong River

Na

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	2060	1309	1296	1086	276	95
2.5-5.0	1845	1308	1296	1021	293	48
5.0-7.5	1881	1367	1204	1100	284	37
7.5-10.0	1810	1435	1216	1140	274	22
10.0-12.5	2002	1512	1239	1454	256	27
12.5-15.0	1948	1444	1029	1501	267	135
15.0-17.5	1937	1388	1006	1433	261	314
17.5- 20.0	1916	1407	1074	1947	243	339
20.5-22.5	1946	1211	-	-	236	113
22.5-25.0	1814	1189	-	-	219	208
25.0-27.5	1875	1284	-	-	226	168
27.5-30.0	1826	1393	-	-	190	535
30.0-32.5	1835	-	-	-	-	587
32.5-35.0	1890	-	-	-	-	532
35.0- 37.5	1892	-	-	-	-	298
37.5-40.0	1939	-	-	-	-	164
40.0-42.5	1968	-	-	-	-	120
42.5-45.0	1936	-	-	-	-	148
Mean	1907	1354	1170	1335	252	216
Maximum	2060	1512	1296	1947	293	587
Minimum	1810	1189	1006	1021	190	22

'-' – data not available

Appendix 9: The vertical profile of mean concentration (mg/kg) of (a) Pb and (b) Cd in core sediments from Sadong River

(a) Pb

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	10	7	9	13	6	7
2.5-5.0	10	29	8	8	6	7
5.0-7.5	12	3	7	9	4	9
7.5-10.0	7	6	9	8	5	10
10.0-12.5	14	12	10	12	6	11
12.5-15.0	12	32	8	9	7	8
15.0-17.5	11	26	12	9	7	9
17.5- 20.0	10	10	13	8	8	7
20.5-22.5	11	5	12	-	7	8
22.5-25.0	9	7	8	-	8	6
25.0-27.5	10	8	-	-	9	7
27.5-30.0	6	11	-	-	10	8
30.0-32.5	9	-	-	-	-	8
32.5-35.0	13	-	-	-	-	7
35.0- 37.5	12	-	-	-	-	11
37.5-40.0	13	-	-	-	-	7
40.0-42.5	15	-	-	-	-	12
42.5-45.0	13	-	-	-	-	2
Mean	11	13	10	9	7	8
Maximum	15	32	13	13	10	12
Minimum	6	3	7	8	4	2

'-' – data not available

(b) Cd

Depth	BS1	BS2	BS3	BS4	BS5	BS6
0.0- 2.5	n.d	n.d	0.41	n.d	n.d	n.d
2.5-5.0	n.d	n.d	0.34	n.d	n.d	n.d
5.0-7.5	n.d	n.d	0.46	n.d	n.d	n.d
7.5-10.0	n.d	n.d	0.65	n.d	n.d	n.d
10.0-12.5	n.d	n.d	0.55	n.d	n.d	n.d
12.5-15.0	n.d	n.d	0.87	n.d	n.d	n.d
15.0-17.5	n.d	0.03	0.75	n.d	n.d	n.d
17.5- 20.0	n.d	0.21	0.74	n.d	n.d	n.d
20.5-22.5	n.d	0.23	0.87	n.d	n.d	n.d
22.5-25.0	n.d	0.30	0.79	n.d	n.d	n.d
25.0-27.5	n.d	0.25	n.d	n.d	n.d	n.d
27.5-30.0	n.d	0.38	n.d	n.d	n.d	n.d
30.0-32.5	n.d	n.d	n.d	n.d	n.d	n.d
32.5-35.0	n.d	n.d	n.d	n.d	n.d	n.d
35.0- 37.5	n.d	n.d	n.d	n.d	n.d	n.d
37.5-40.0	n.d	n.d	n.d	n.d	n.d	n.d
40.0-42.5	n.d	n.d	n.d	n.d	n.d	n.d
42.5-45.0	n.d	n.d	n.d	n.d	n.d	n.d
Mean	n.d	459	433	n.d	n.d	n.d
Maximum	n.d	565	548	n.d	n.d	n.d
Minimum	n.d	314	324	n.d	n.d	n.d

'n.d' – below detection limit

Appendix 10: Concentration (μg/g) of *n*-alkanes in the core sediments from Sebangan (BS1) of Sadong River

n-Alkanes	Depth (cm)																	
	0.0 - 2.5	2.5 - 5.0	5.0 - 7.5	7.5 - 10.0	10.0 - 12.5	12.5 - 15.0	15.0 - 17.5	17.5 - 20.0	20.0 - 22.5	22.5 - 25.0	25.0 - 27.5	27.5 - 30.0	30.0 - 32.5	32.5 - 35.0	35.0 - 37.5	37.5 - 40.0	40.0 - 42.5	42.5 - 45.0
C_{9}	1.19	0.00	0.01	0.01	0.01	0.01	0.00	0.11	n.d	0.03	0.01	n.d	n.d	0.00	0.07	n.d	0.61	0.84
C_{10}	0.03	0.66	n.d	0.01	0.01	0.01	1.32	n.d	n.d	0.01	n.d	n.d	0.89	n.d	0.01	n.d	n.d	1.08
C_{11}	0.11	2.10	0.01	0.01	0.02	n.d	0.00	0.01	n.d	n.d	0.01	n.d	n.d	n.d	0.01	n.d	n.d	0.27
C_{12}	0.05	0.61	0.01	0.01	0.02	n.d	0.00	0.01	0.83	0.07	0.02	0.73	0.51	n.d	n.d	n.d	0.76	0.15
C_{13}	0.16	0.76	0.03	0.03	0.03	n.d	0.78	0.04	0.88	0.16	0.04	0.22	0.45	n.d	0.02	0.14	0.17	0.25
C_{14}	0.51	0.56	0.01	0.04	0.71	0.01	0.86	0.13	0.78	0.00	0.03	2.48	2.33	0.50	0.81	0.35	0.63	0.98
C_{15}	0.10	0.20	0.04	0.03	0.04	0.03	0.28	0.04	0.17	0.10	0.04	0.30	0.18	0.21	0.04	0.07	0.15	0.12
C_{16}	0.77	0.95	0.16	0.15	0.20	0.27	1.27	0.17	1.02	0.29	0.13	7.23	1.05	0.35	0.34	0.42	0.72	1.27
C_{17}	5.21	7.47	1.63	0.75	1.55	1.70	9.53	1.06	7.18	2.92	0.94	2.72	6.86	1.63	3.23	2.02	6.25	10.81
C_{18}	2.57	2.94	1.12	0.93	2.23	3.83	4.18	1.78	3.26	1.75	1.62	3.90	3.29	0.49	2.46	2.03	2.43	6.88
C_{19}	1.35	9.15	1.43	1.33	1.19	3.75	1.96	1.67	8.64	1.43	1.96	9.06	1.58	0.43	2.35	1.34	7.72	3.59
C_{20}	8.11	13.07	3.72	3.35	4.09	8.87	8.05	3.50	8.02	3.95	6.27	13.25	11.34	1.24	5.63	4.09	8.02	10.94
C_{21}	5.03	10.04	5.81	6.68	8.22	12.98	6.41	5.18	5.64	8.72	8.77	8.06	6.14	4.34	7.49	8.77	6.95	16.48
C_{22}	8.57	12.76	6.01	8.05	7.99	5.53	10.34	5.86	10.89	9.55	9.39	14.83	18.58	5.41	7.59	9.79	8.06	16.35
C_{23}	16.61	23.61	4.08	6.35	5.94	7.19	29.05	3.65	28.98	4.94	7.94	25.89	24.09	4.50	4.61	5.26	13.85	47.30
C_{24}	35.62	49.98	4.67	47.44	6.55	5.70	45.31	31.66	45.18	6.90	8.43	55.61	43.16	4.11	4.05	6.06	29.51	38.65
C_{25}	60.63	67.56	18.38	57.73	18.34	14.40	82.71	0.46	64.98	26.25	37.32	71.49	72.84	22.57	1.30	2.38	46.03	92.10
C_{26}	50.34	65.17	1.06	50.65	1.78	1.00	69.29	0.73	64.27	14.32	2.17	70.85	53.88	12.89	0.98	9.60	45.14	103.66
C_{27}	40.64	51.07	1.31	39.11	2.01	1.44	53.43	0.30	39.20	2.15	2.65	55.91	42.91	10.55	0.66	0.85	37.28	95.35
C_{28}	33.74	29.08	1.63	12.50	1.20	1.64	30.53	1.01	27.81	7.84	2.65	39.34	31.99	5.34	1.40	1.18	21.68	54.08
C_{29}	22.18	28.93	2.31	1.39	1.32	1.12	35.09	3.29	26.67	0.39	8.25	27.93	23.30	7.51	10.66	0.54	19.90	77.57
C_{30}	1.66	1.69	0.88	0.94	0.72	0.63	2.06	0.46	1.82	1.00	0.91	1.68	1.38	0.22	0.86	0.78	1.16	14.63
C_{31}	1.51	1.17	0.62	0.32	0.45	0.36	1.41	0.30	0.75	0.53	0.43	1.08	4.53	0.14	0.66	0.57	0.45	17.72
C_{32}	2.98	2.66	0.38	0.11	0.56	0.57	1.01	0.40	3.12	0.42	0.62	0.37	0.28	0.48	0.63	0.36	1.39	10.83
C_{33}	3.84	3.41	0.87	0.38	0.27	0.19	5.43	0.08	0.28	0.77	0.52	2.73	2.08	0.34	0.98	0.61	1.94	12.08

n.d – not detected

Appendix 11: Concentration (μg/g) of *n*-alkanes in the core sediments from Sadong (BS2) of Sadong River

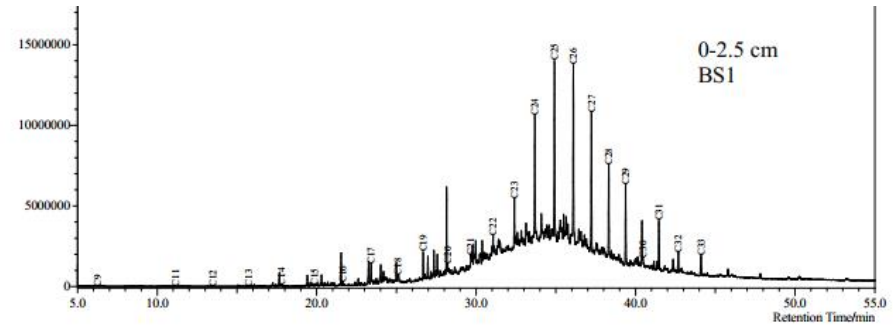
n- Alkanes	Depth (cm)											
	0.0 - 2.5	2.5 - 5.0	5.0 - 7.5	7.5 - 10.0	10.0 -12.5	12.5 - 15.0	15.0 - 17.5	17.5 - 20.0	20.0 - 22.5	22.5 - 25.0	25.0 - 27.5	27.5 - 30.0
C_{9}	0.08	0.06	0.08	0.02	0.03	0.45	3.93	0.10	0.98	1.38	0.38	0.63
C_{10}	0.10	0.21	0.07	0.01	0.01	1.61	7.28	0.03	0.47	0.80	0.10	0.67
C_{11}	0.10	0.09	0.01	0.03	0.02	0.04	0.48	0.01	0.21	0.37	0.01	6.76
C_{12}	0.05	0.01	0.05	0.02	0.01	0.65	1.41	0.04	0.09	0.10	0.08	0.89
C_{13}	0.03	0.06	0.02	0.01	0.03	0.15	0.50	0.10	0.31	0.17	0.22	0.79
C_{14}	0.05	0.33	0.04	5.51	3.44	0.08	2.40	0.78	1.57	0.34	22.80	3.91
C_{15}	0.02	0.08	0.01	2.62	2.45	0.40	0.26	0.07	0.42	0.09	0.07	0.16
C_{16}	0.09	1.07	0.10	4.40	15.39	0.55	3.89	0.77	4.09	1.35	1.22	1.89
C_{17}	0.52	1.69	0.53	36.60	12.33	10.86	15.47	1.02	24.52	54.37	6.27	14.30
C_{18}	0.28	6.61	1.44	26.69	18.78	0.46	9.36	6.36	41.21	16.81	9.75	24.23
C_{19}	0.98	8.50	1.06	47.82	23.21	12.54	6.19	1.39	46.87	21.86	2.14	24.59
C_{20}	1.07	6.95	7.36	56.11	21.62	5.55	9.87	9.18	48.79	354.64	12.47	9.39
C_{21}	1.02	6.33	3.90	64.70	18.54	14.50	27.27	13.87	26.30	10.83	14.50	34.63
C_{22}	2.98	91.01	6.44	53.60	33.17	21.35	47.17	23.84	30.59	41.87	22.14	84.14
C_{23}	4.56	18.97	11.81	32.75	20.33	31.15	43.75	21.94	33.59	40.05	29.37	84.37
C_{24}	8.44	46.39	10.72	40.07	21.78	19.82	78.38	35.60	13.34	7.49	36.24	75.41
C_{25}	10.27	72.57	13.95	138.41	18.92	40.03	71.95	47.81	76.89	67.00	32.95	86.06
C_{26}	9.54	67.63	8.92	146.89	14.38	41.06	69.59	42.15	38.77	57.67	30.07	71.62
C_{27}	10.39	56.70	14.27	97.44	18.14	10.08	55.44	34.68	116.71	98.06	28.13	67.86
C_{28}	5.06	29.70	8.94	92.56	13.41	19.57	32.06	26.12	33.33	80.87	15.74	33.89
C_{29}	7.87	38.19	16.29	15.65	20.12	23.05	55.53	29.88	99.33	133.17	26.87	62.35
C_{30}	2.04	8.89	3.04	13.71	5.07	17.08	11.48	4.21	21.20	36.97	5.85	10.68
C_{31}	10.59	3.91	3.98	11.94	7.27	9.02	15.94	1.91	21.92	37.29	3.32	10.43
C_{32}	0.80	6.49	0.60	7.63	4.08	6.02	7.66	2.35	18.50	33.66	6.52	8.50
C_{33}	1.14	7.60	44.93	1.75	5.00	8.02	10.85	7.95	21.24	34.93	6.39	10.95

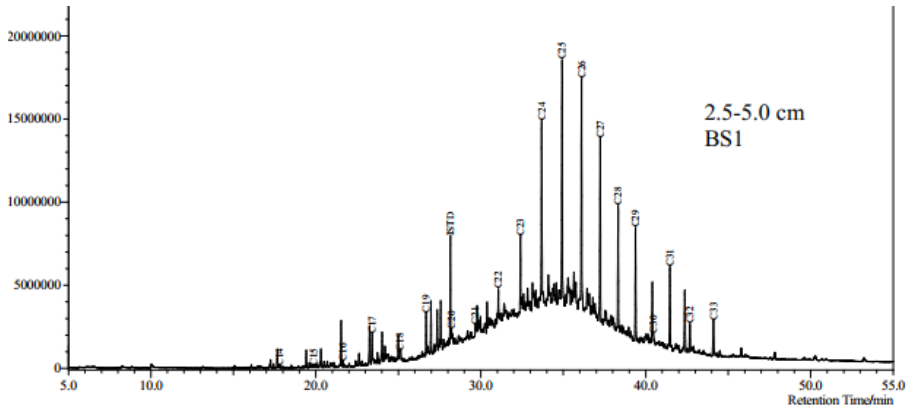
Appendix 12: Concentration (μg/g) of *n*-alkanes in the core sediments from Sebemban (BS6) of Sadong River

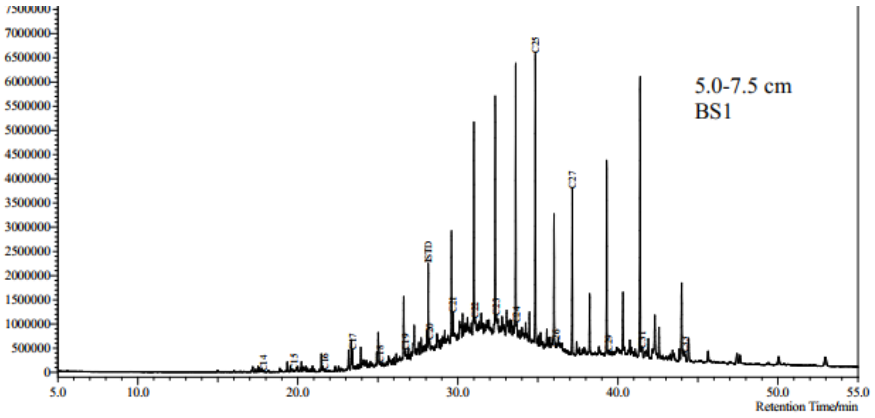
n-Alkanes	Depth (cm)																	
	0.0 – 2.5	2.5 - 5.0	5.0 - 7.5	7.5 - 10.0	10.0 - 12.5	12.5 - 15.0	15.0 - 17.5	17.5 - 20.0	20.0 - 22.5	22.5 - 25.0	25.0 - 27.5	27.5 - 30.0	30.0 - 32.5	32.5 - 35.0	35.0 - 37.5	37.5 - 40.0	40.0 - 42.5	42.5 - 45.0
C_{9}	n.d	n.d	n.d	n.d	1.27	3.33	n.d	n.d	3.93	n.d	0.00	0.35	0.31	0.04	0.04	n.d	0.02	0.02
C_{10}	n.d	n.d	n.d	0.19	0.38	0.46	4.00	n.d	7.28	n.d	3.42	0.90	0.42	0.01	0.06	n.d	0.01	0.01
C_{11}	n.d	n.d	n.d	0.04	0.13	n.d	n.d	n.d	0.48	n.d	n.d	0.09	0.14	0.02	0.30	0.02	0.04	0.03
C_{12}	n.d	n.d	n.d	0.02	0.01	n.d	n.d	n.d	1.41	n.d	n.d	0.06	0.01	0.01	0.01	0.01	0.03	0.01
C_{13}	n.d	3.58	n.d	0.21	0.19	0.51	1.07	1.73	0.50	n.d	n.d	0.22	0.23	0.08	0.10	0.01	0.15	0.13
C_{14}	2.66	8.17	1.16	0.02	n.d	0.33	0.93	3.25	2.40	1.74	0.87	0.04	0.34	0.04	0.03	0.03	0.41	0.42
C_{15}	0.62	0.92	0.07	0.16	2.50	0.08	0.28	0.76	0.19	0.51	0.27	0.61	0.50	0.06	0.03	0.06	0.33	0.33
C_{16}	1.84	3.70	1.50	0.28	0.69	0.21	1.34	0.61	3.89	0.45	1.24	0.80	0.52	0.39	1.13	0.29	2.22	0.66
C_{17}	2.09	2.91	0.20	0.61	1.47	0.18	1.74	2.49	5.76	2.19	1.68	1.08	0.98	0.92	1.67	0.63	3.19	4.34
C_{18}	2.88	5.64	0.14	3.34	8.82	0.29	1.07	3.45	12.33	1.08	1.04	5.78	5.93	5.85	9.97	3.24	13.87	7.72
C_{19}	3.54	4.91	0.28	4.50	9.71	0.24	1.44	4.30	21.91	1.55	1.36	7.24	7.33	6.87	11.21	7.16	13.28	8.80
C_{20}	1.69	2.84	3.54	9.79	30.43	0.45	0.56	1.92	23.55	20.23	12.43	11.74	19.44	13.58	16.74	9.73	17.09	15.46
C_{21}	1.34	3.18	0.20	18.15	33.34	0.19	0.77	1.47	39.19	3.82	0.68	30.04	30.21	24.63	39.30	4.53	40.00	36.66
C_{22}	1.34	3.91	0.74	20.25	30.84	0.16	0.94	1.53	47.17	1.72	0.65	35.07	31.99	20.25	29.31	31.64	41.31	36.81
C_{23}	1.86	2.21	0.17	14.25	10.87	0.24	2.07	2.06	43.75	1.83	1.93	25.31	24.29	10.25	21.38	8.82	21.50	19.43
C_{24}	3.71	2.46	0.50	57.30	17.83	0.72	4.19	3.96	78.38	6.15	3.98	27.06	28.42	15.73	20.68	21.51	20.92	20.24
C_{25}	7.16	5.16	0.70	7.22	9.30	0.96	6.75	7.67	71.95	7.03	6.46	18.64	18.24	9.90	15.78	32.09	11.82	12.26
C_{26}	4.93	6.30	0.68	3.98	4.44	0.79	6.00	5.13	69.59	5.42	5.60	10.09	7.76	4.13	4.68	32.15	5.27	5.19
C_{27}	4.79	1.49	1.21	5.08	3.43	0.54	4.75	4.99	55.44	6.02	4.61	7.95	6.28	5.93	6.66	24.36	7.54	7.09
C_{28}	3.70	4.61	0.61	8.78	7.67	0.47	3.29	3.91	32.06	3.43	3.22	13.40	35.40	6.28	6.86	16.13	7.40	7.98
C_{29}	5.72	4.82	1.26	5.59	4.01	0.58	3.97	6.26	55.53	5.29	3.91	50.01	4.40	8.36	5.67	17.24	22.12	30.06
C_{30}	1.21	2.08	1.77	2.33	2.99	0.13	0.63	1.71	11.48	1.05	0.59	6.89	2.37	2.70	3.44	2.77	2.97	3.40
C_{31}	2.41	2.26	0.31	1.80	2.11	0.16	1.29	2.58	15.94	2.18	1.23	4.28	3.08	2.06	2.52	5.51	1.98	3.30
C_{32}	1.29	1.27	0.10	1.74	2.16	0.07	0.49	1.28	7.66	0.70	0.44	4.45	3.33	2.08	2.53	1.50	2.49	1.50
C_{33}	2.27	2.14	0.27	2.00	2.24	0.07	0.89	2.27	10.85	1.72	0.85	3.78	3.02	2.34	3.13	3.14	1.66	3.51

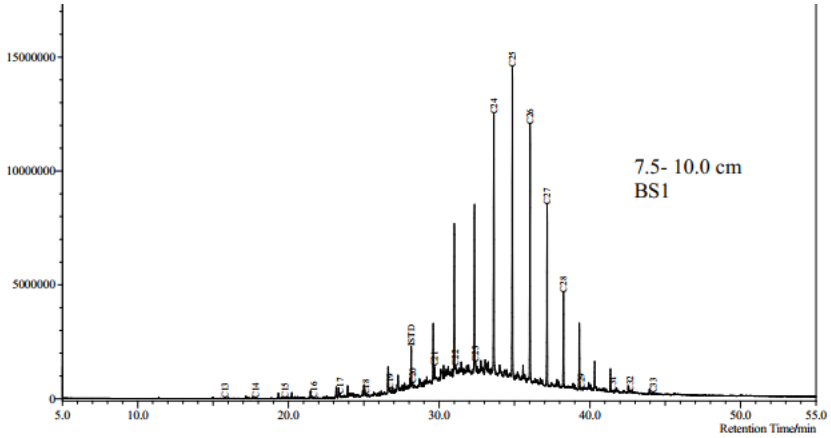
n.d – not detected

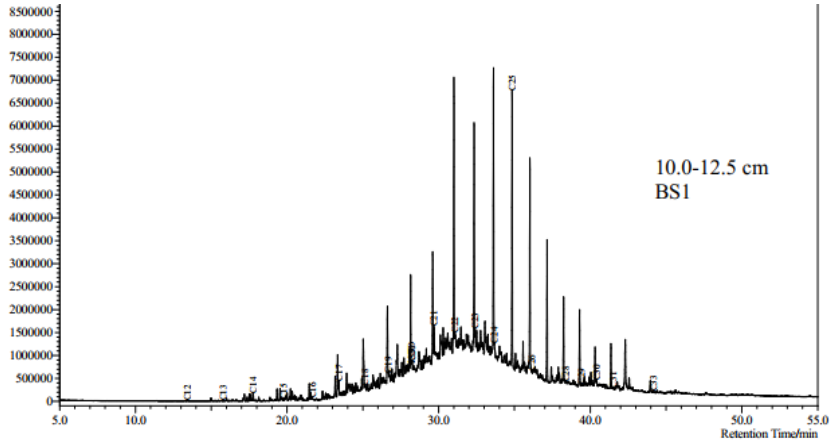
Appendix 13: GC chromatogram of aliphatic hydrocarbon fractions in core sediments from Sebangan at different depths

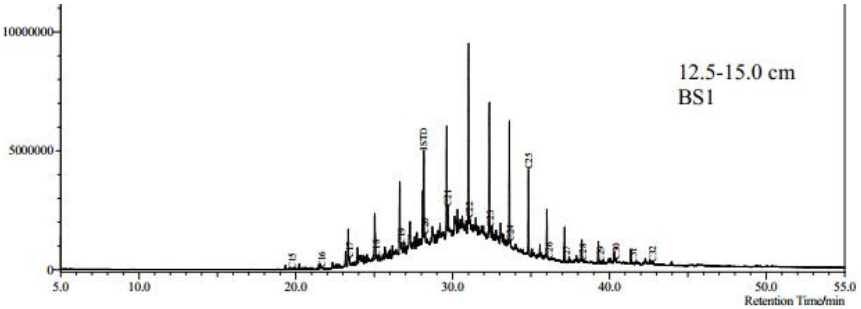


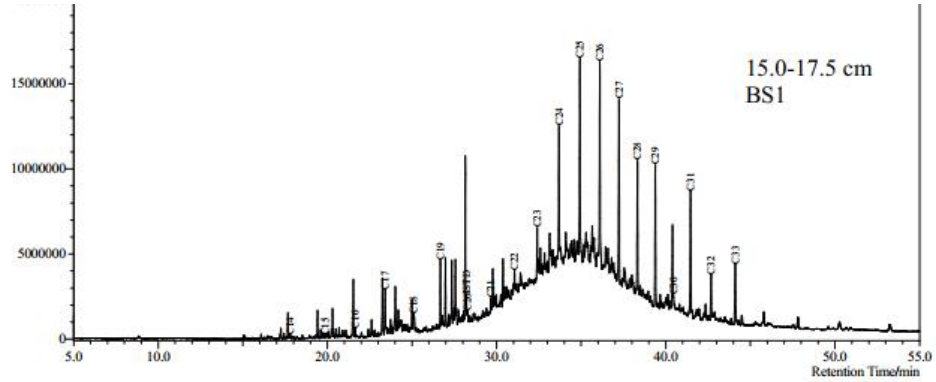


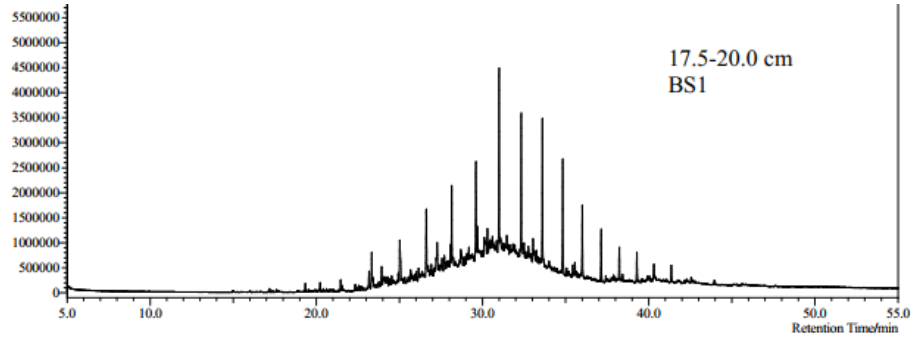


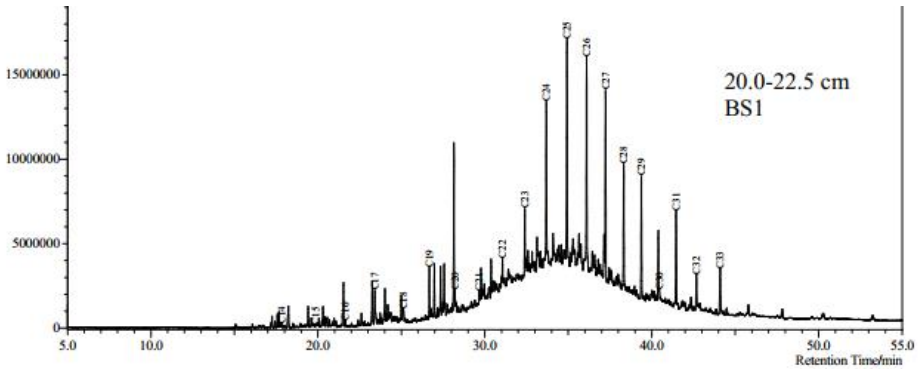

7.5- 10.0 cm
BS1
Retention Time/min

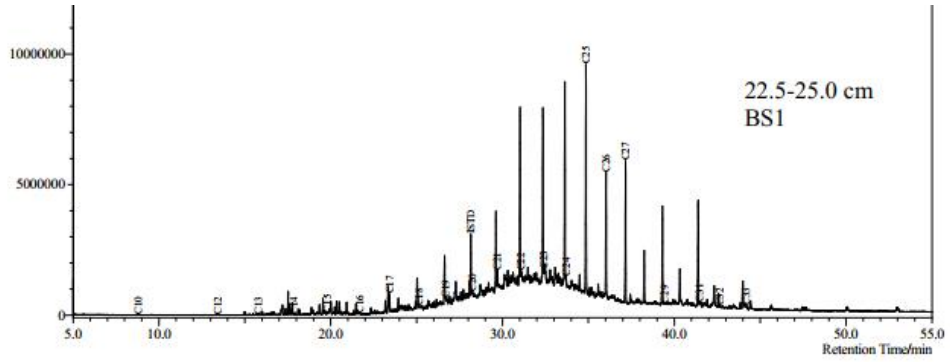

10.0-12.5 cm
BS1
Retention Time/min

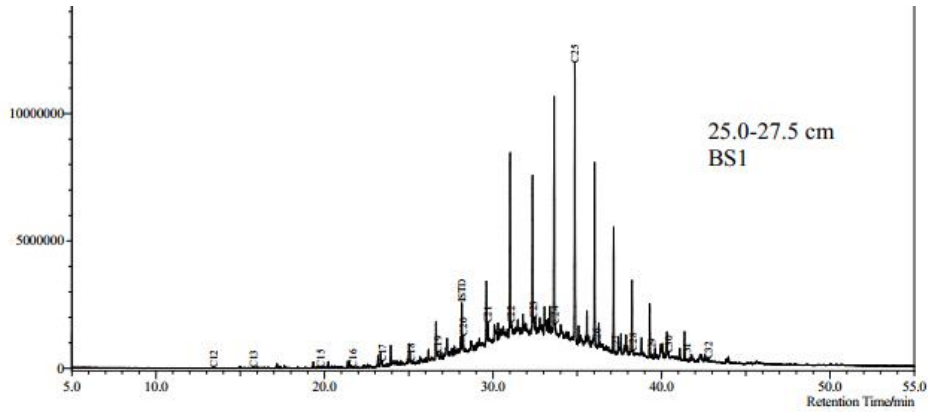

12.5-15.0 cm
BS1
Retention Time/min

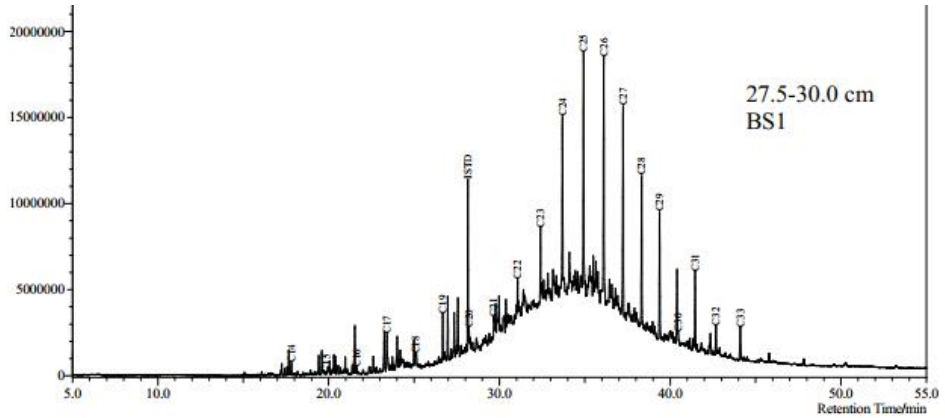

15.0-17.5 cm
BS1
Retention Time/min

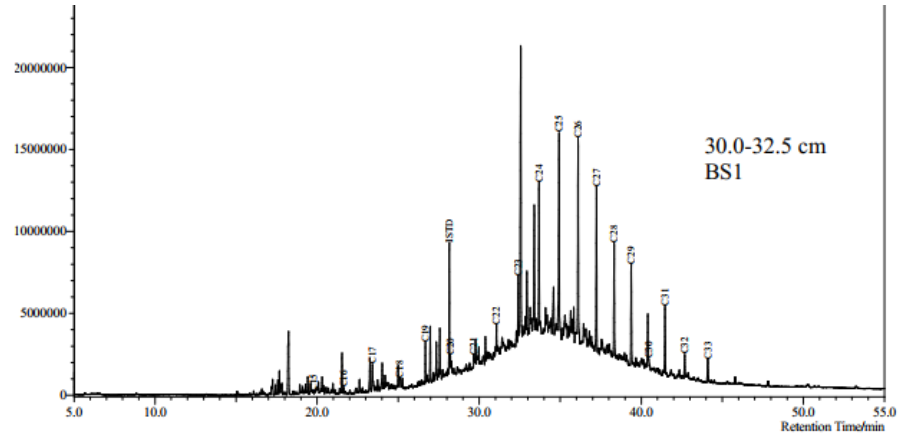

17.5-20.0 cm
BS1
Retention Time/min

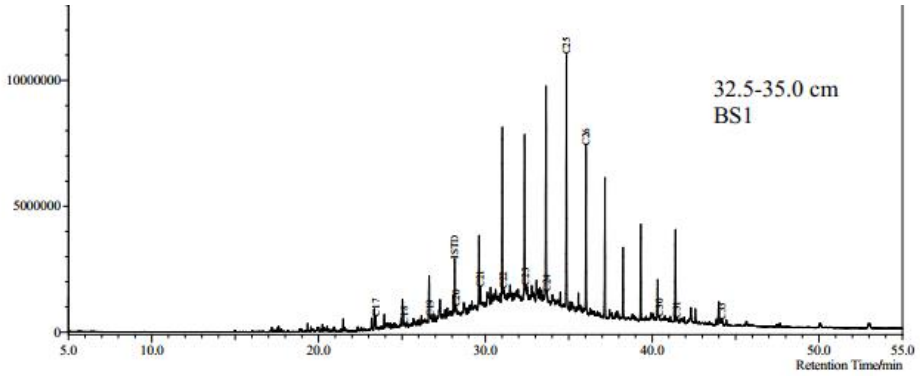

20.0-22.5 cm
BS1
Retention Time/min

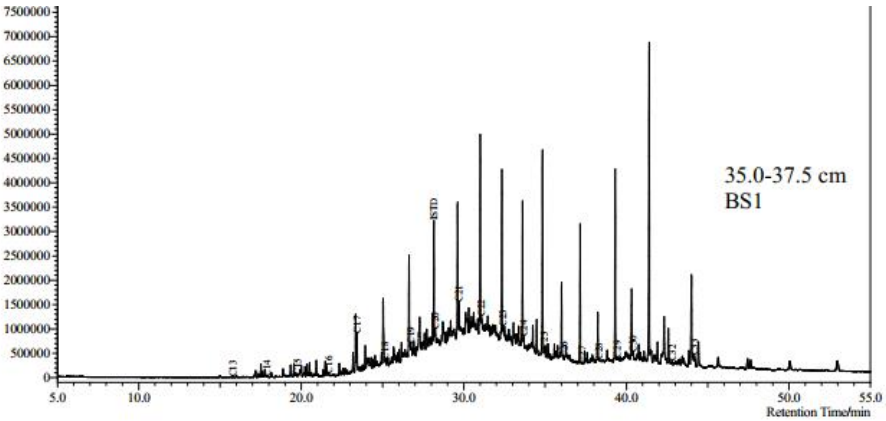

22.5-25.0 cm
BS1
Retention Time/min

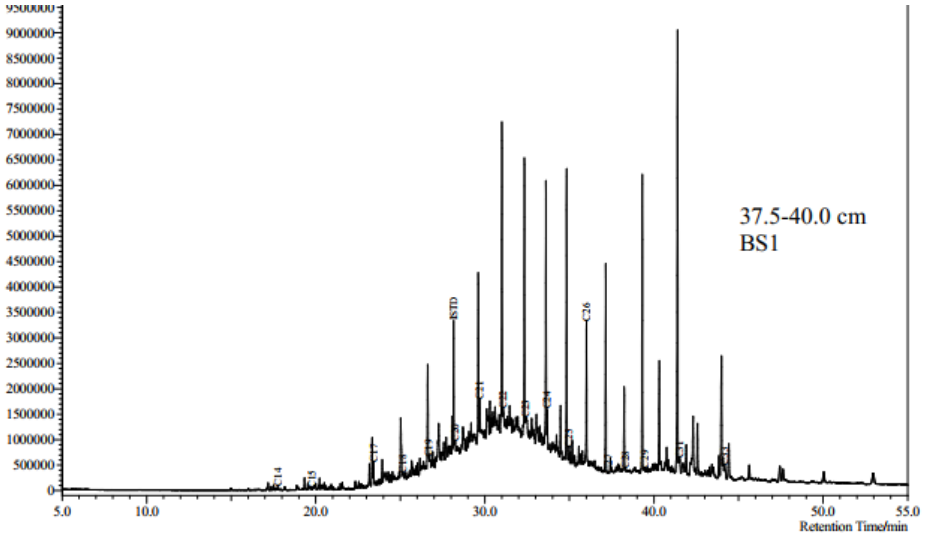

25.0-27.5 cm
BS1
Retention Time/min

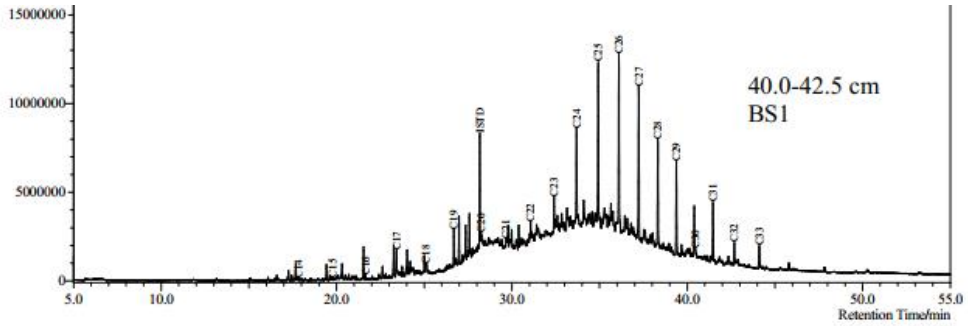

27.5-30.0 cm
BS1
Retention Time/min

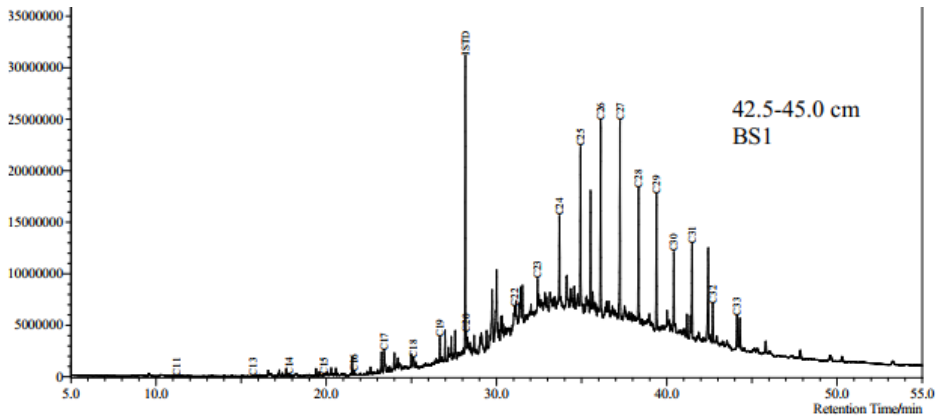

30.0-32.5 cm
BS1
Retention Time/min


32.5-35.0 cm
BS1
Retention Time/min

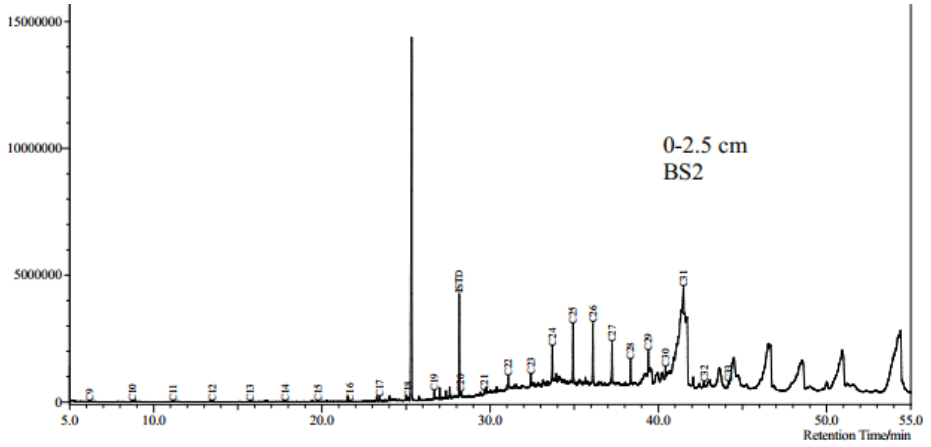

35.0-37.5 cm
BS1
Retention Time/min

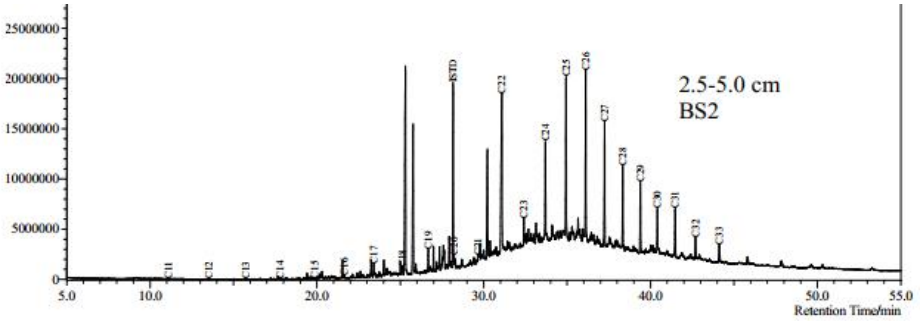

37.5-40.0 cm
BS1
Retention Time/min

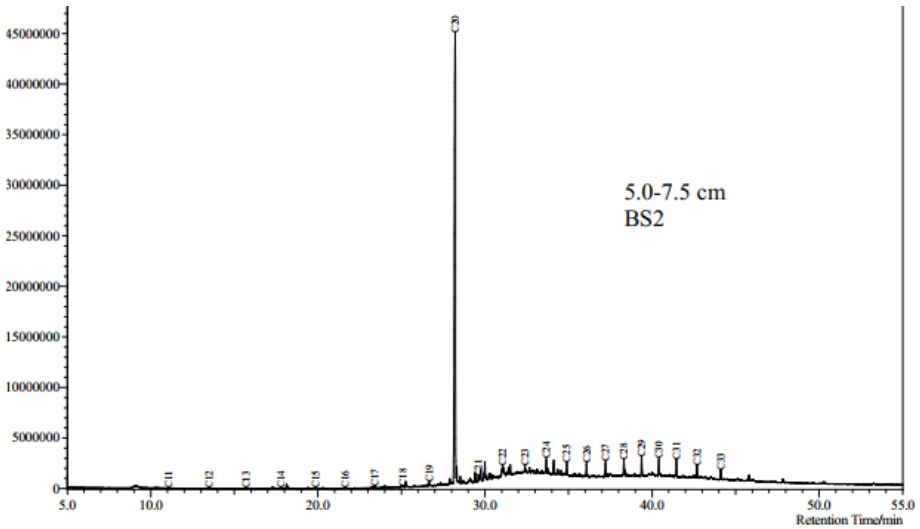

40.0-42.5 cm
BS1
Retention Time/min

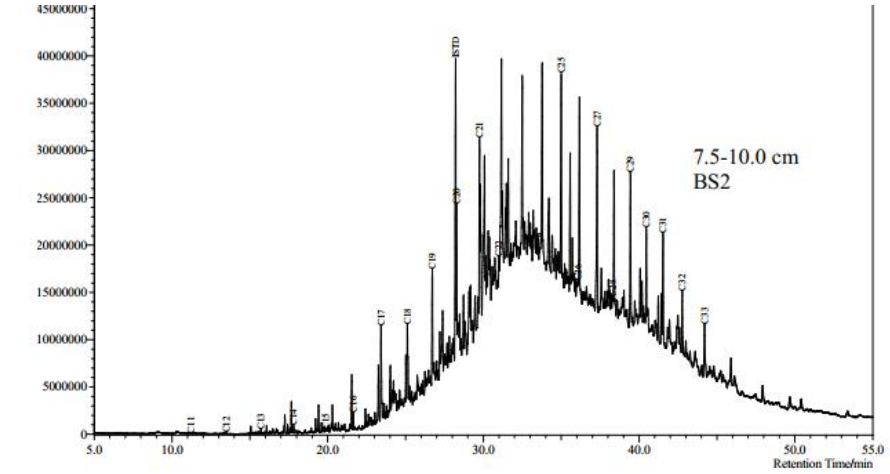

42.5-45.0 cm
BS1
Retention Time/min

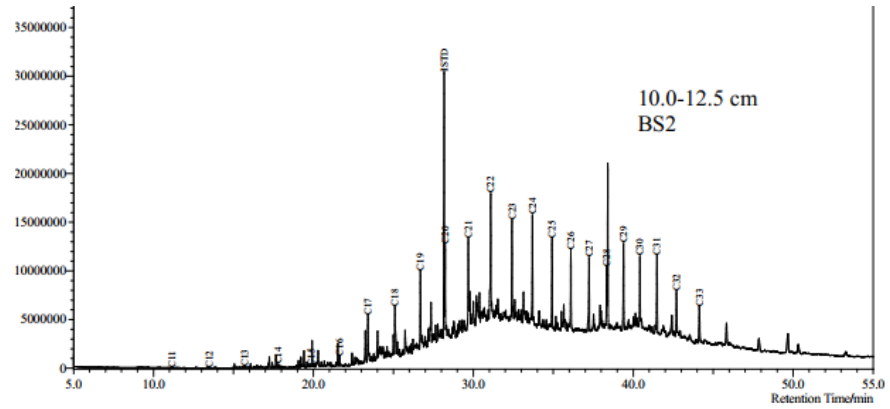
Appendix 14: GC chromatogram of aliphatic hydrocarbon fractions in core sediments from Sadong Jaya (BS2) at different depths

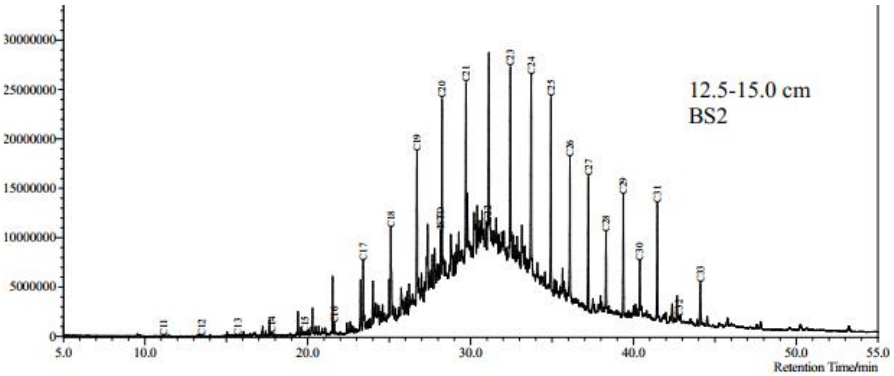


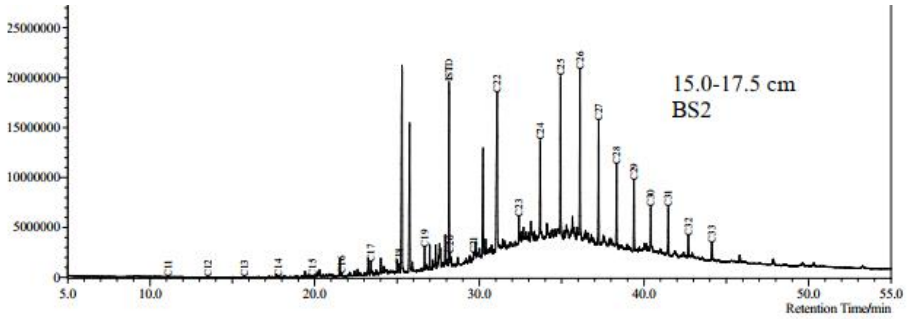


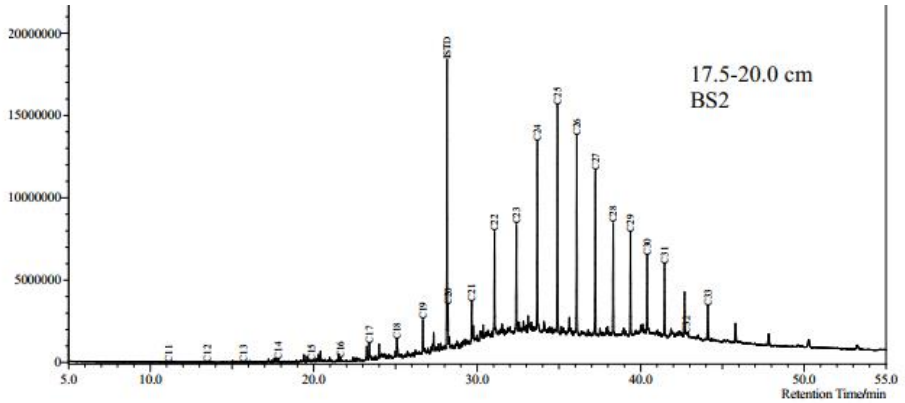


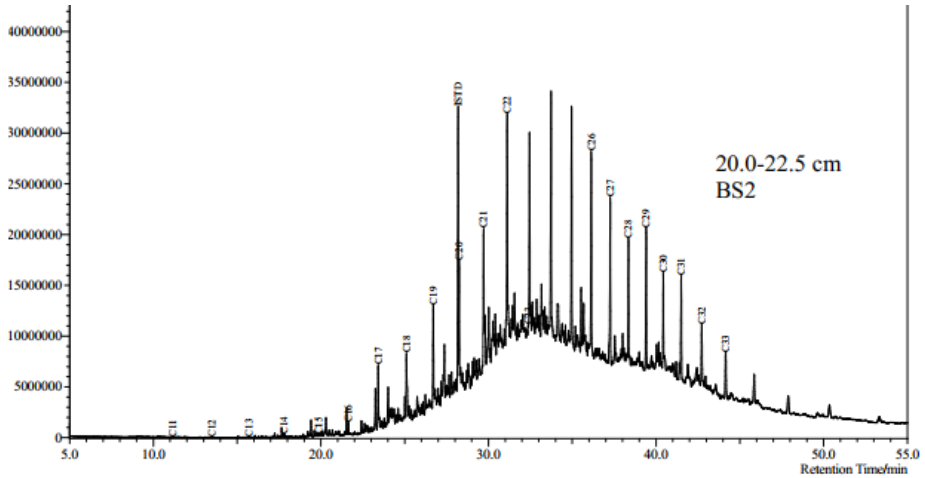

7.5-10.0 cm
BS2
Retention Time/min

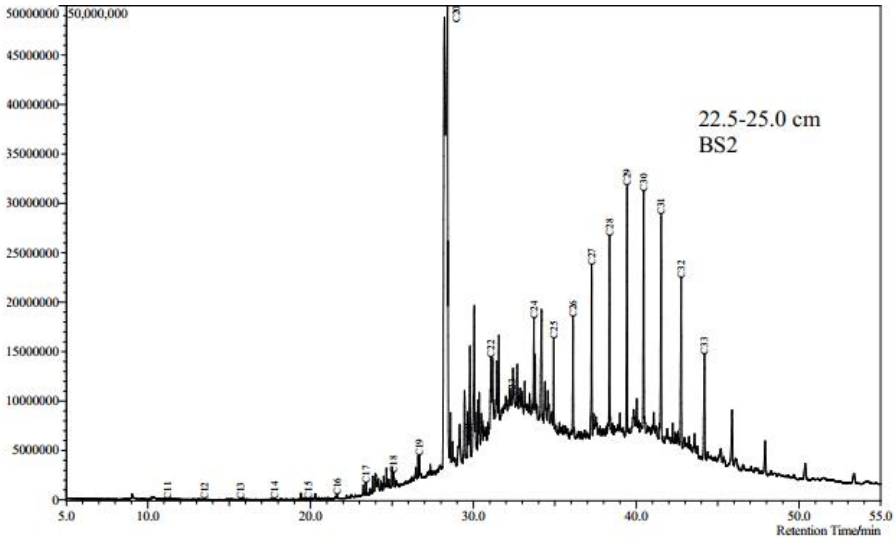

10.0-12.5 cm
BS2
Retention Time/min

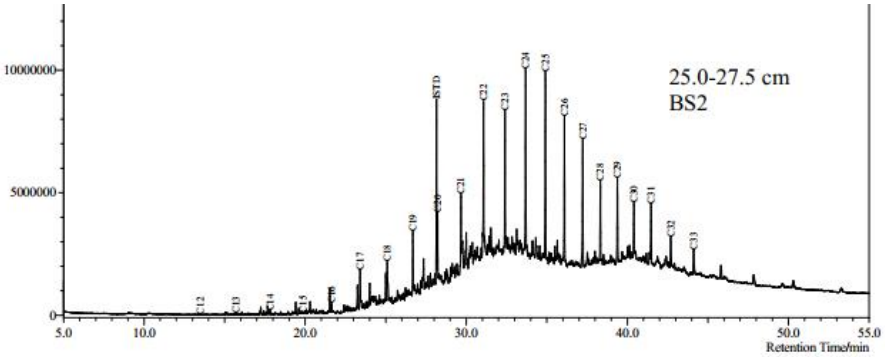

12.5-15.0 cm
BS2
Retention Time/min

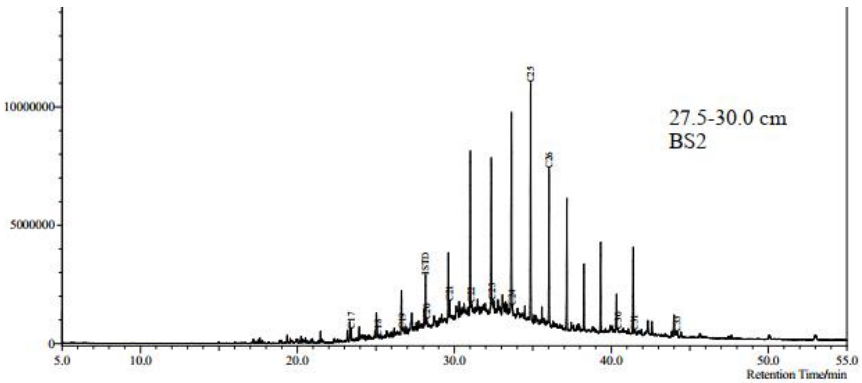

15.0-17.5 cm
BS2
Retention Time/min


17.5-20.0 cm
BS2
Retention Time/min

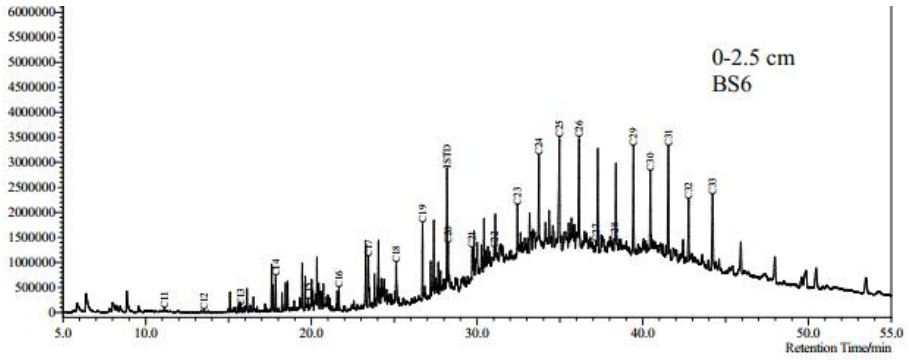

20.0-22.5 cm
BS2
Retention Time/min

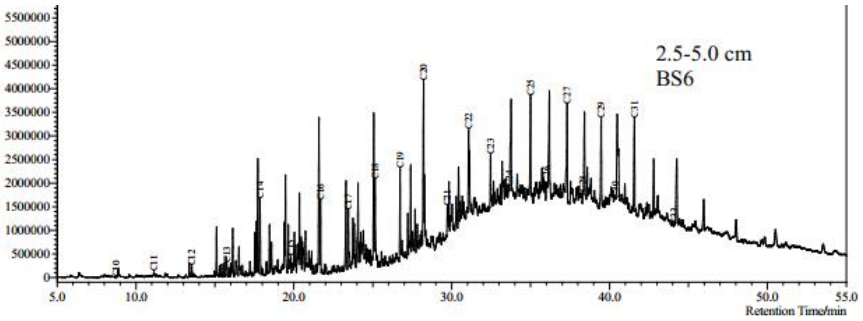

50,000,000
22.5-25.0 cm
BS2
Retention Time/min

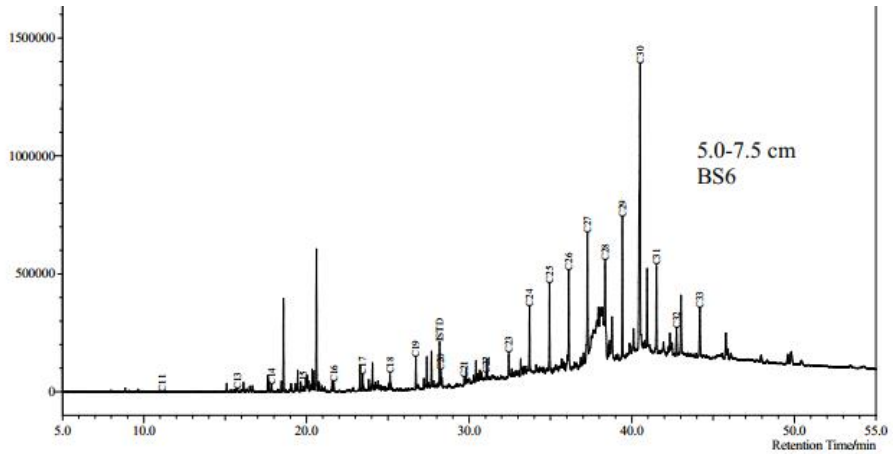

25.0-27.5 cm
BS2
Retention Time/min

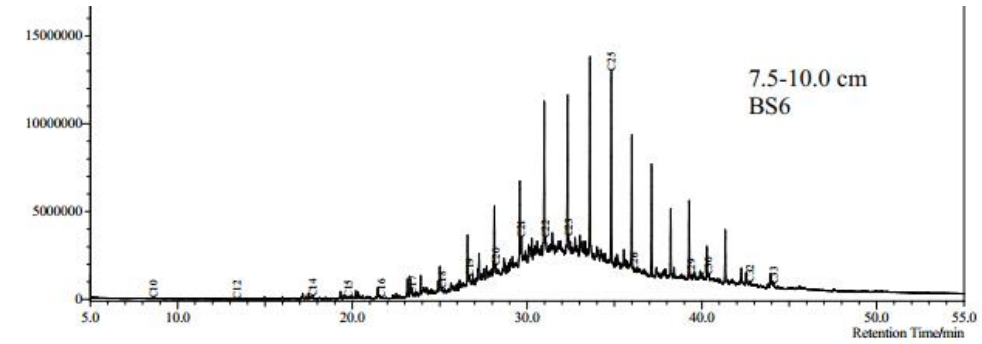

27.5-30.0 cm
BS2
Retention Time/min

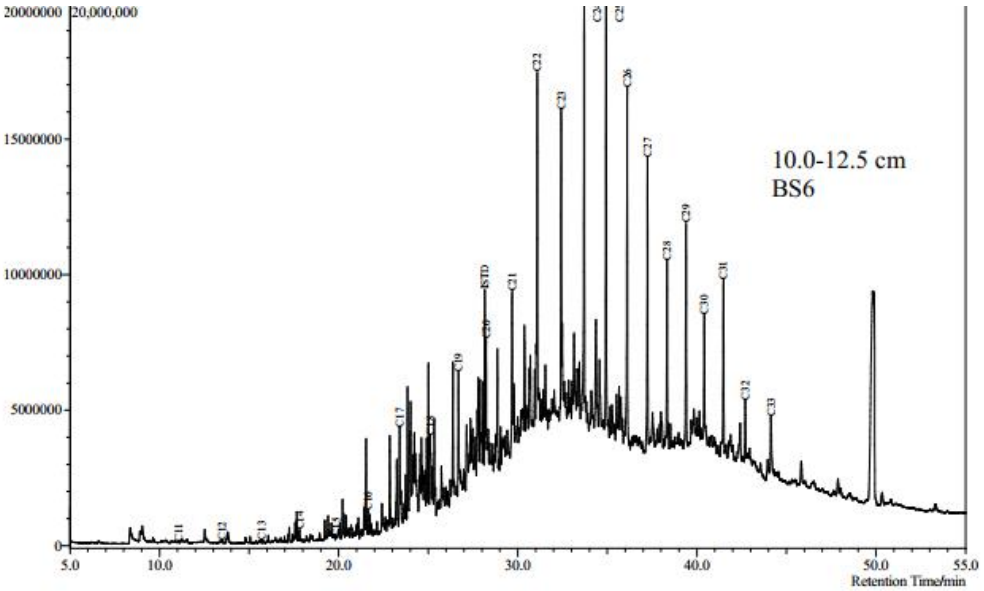
Appendix 15: GC chromatogram of aliphatic hydrocarbon fractions in core sediments from Sebemban (BS6) at different depths

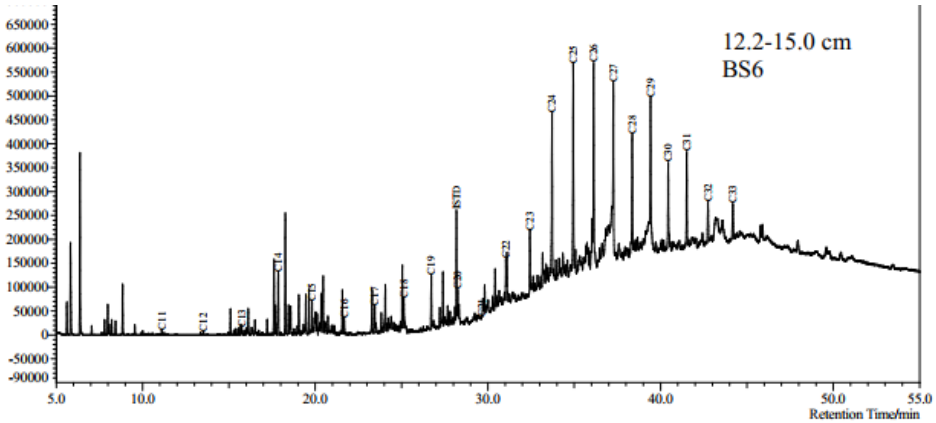


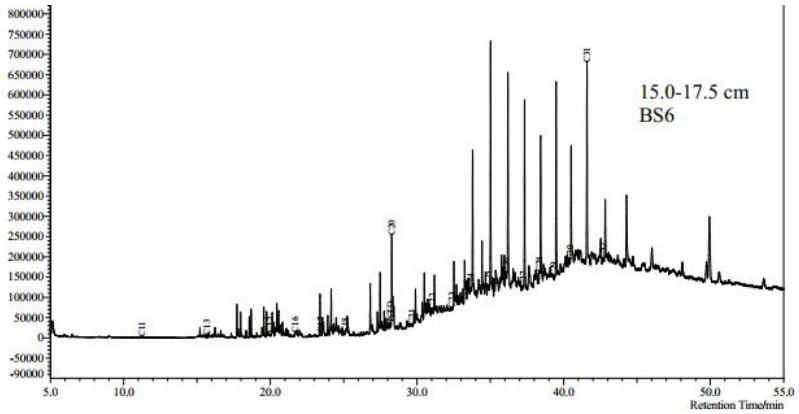


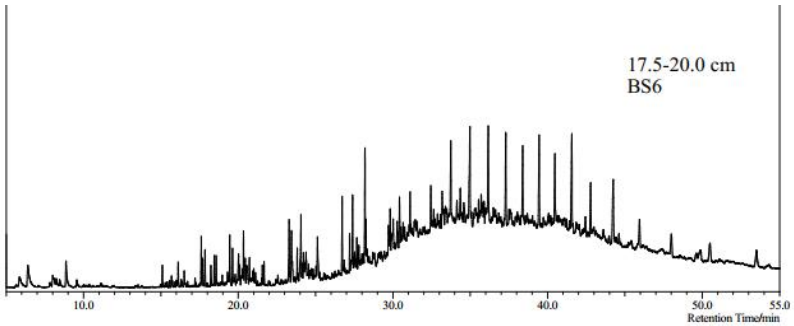


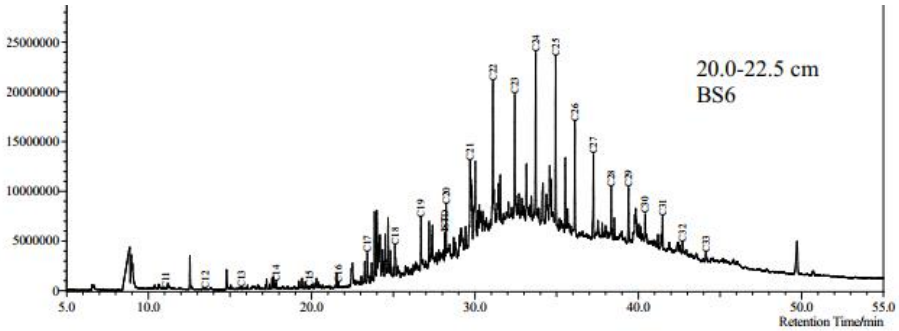

7.5-10.0 cm
BS6
Retention Time/min

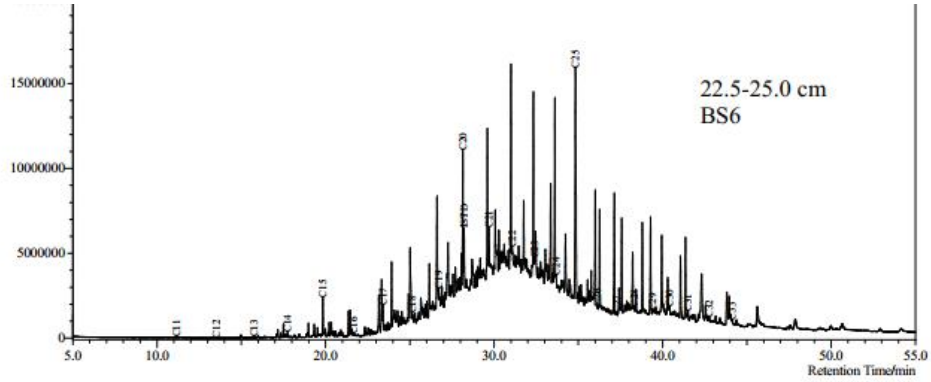

20,000,000
10.0-12.5 cm
BS6
Retention Time/min

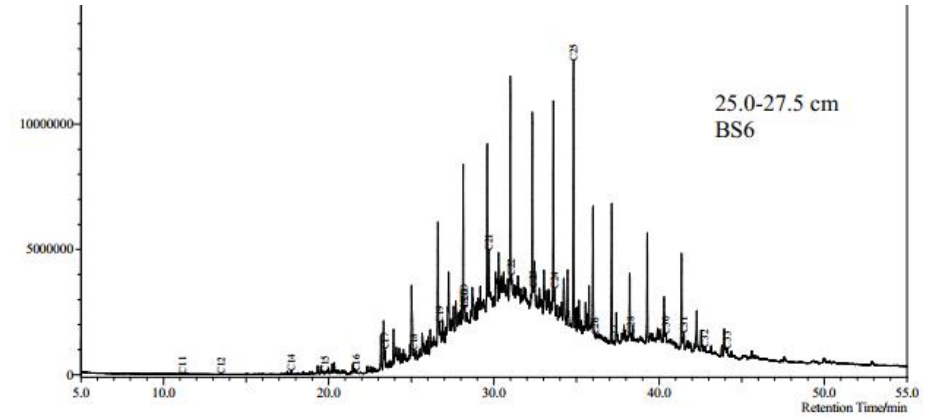

12.2-15.0 cm
BS6
Retention Time/min

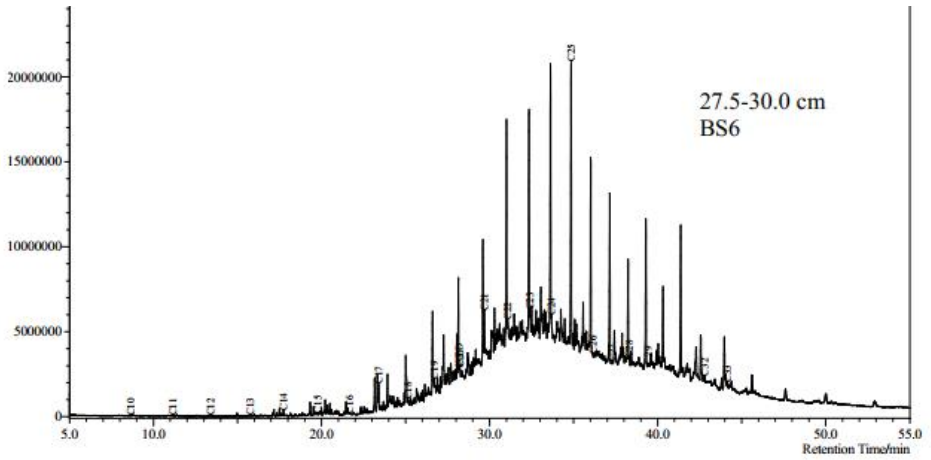

15.0-17.5 cm
BS6
Retention Time/min

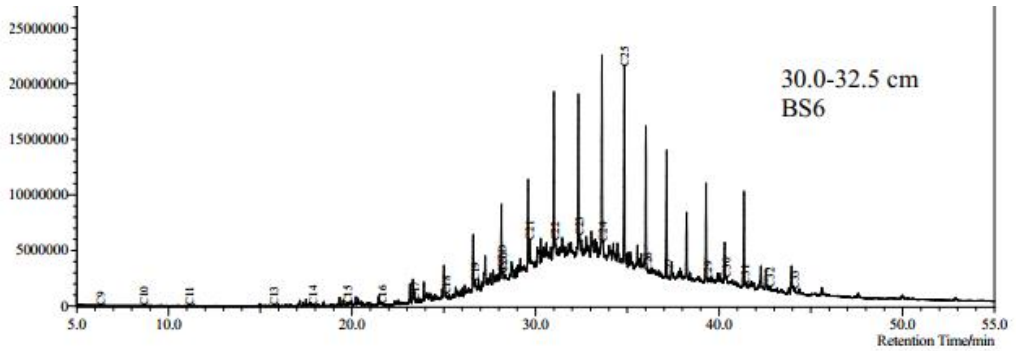

17.5-20.0 cm
BS6
Retention Time/min

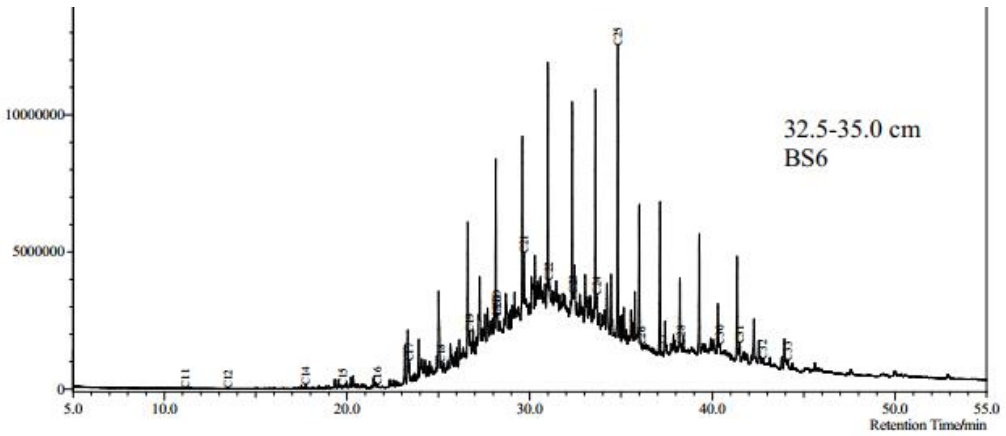

20.0-22.5 cm
BS6
Retention Time/min

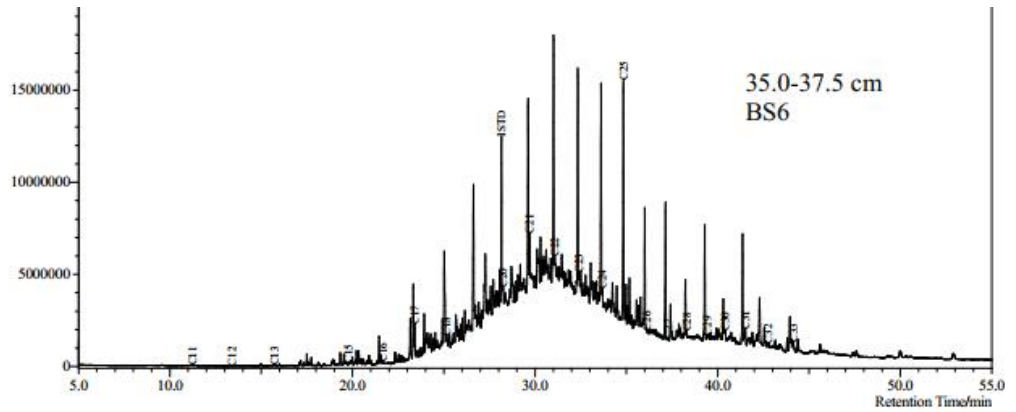

22.5-25.0 cm
BS6
15000000
10000000
5000000
0
5.0
10.0
20.0
30.0
40.0
50.0
55.0
Retention Time/min


25.0-27.5 cm
BS6
10000000
5000000
0
5.0
10.0
20.0
30.0
40.0
50.0
55.0
Retention Time/min


27.5-30.0 cm
BS6
20000000
15000000
10000000
5000000
0
5.0
10.0
20.0
30.0
40.0
50.0
55.0
Retention Time/min


30.0-32.5 cm
BS6
Retention Time/min


32.5-35.0 cm
BS6
Retention Time/min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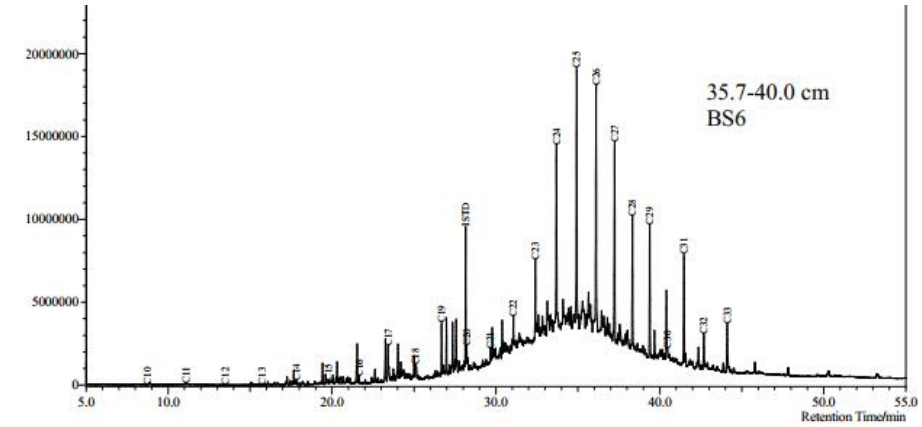
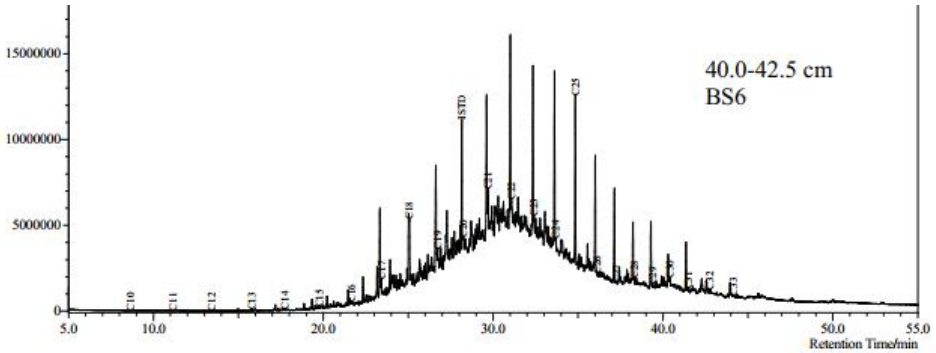
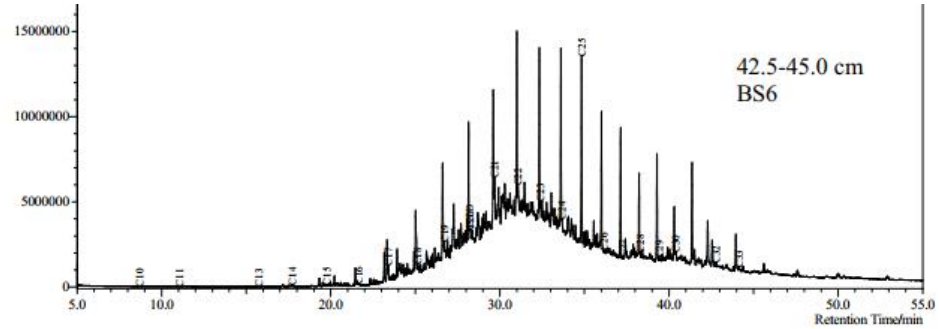
BS6
Retention Time/min


35.7-40.0 cm
BS6
Retention Time/min


40.0-42.5 cm
BS6
Retention Time/min


42.5-45.0 cm
BS6
Retention Time/min

Appendix 16: Publication

1. **Omorinoye, O.A**., Assim, Z.B., & Jusoh, I.B. (2020). Geochemistry of Elements in Sediments from Sadong River, Sarawak, Malaysia. Accepted for publication in *Asian Journal of Science and Technology*.

2. **Omorinoye, O.A**., Assim, Z.B., & Jusoh, I.B. (2020). Geomorphological and Sedimentological Features of River Sadong, Sarawak, Malaysia. Accepted for publication in *Indonesian Journal of Geosciences*.

3. **Omorinoye, O.A.,** Assim, Z.B., Jusoh, I.B., Bamigboye, O.S., & Alebiosu, M.T. (2019). Distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Sadong River Sarawak, Malaysia. *Asian Journal of Applied Science and Technology*, *3*(4), 57-66.

4. **Omorinoye, O.A**., Assim, Z.B., Jusoh, I.B, Durumin Iya, N.I., & Asare, E.A. (2019). Vertical profile of heavy metal concentration in sediments from Sadong River, Sarawak, Malaysia. *Indian Journal of Environmental Protection*, *39*(11), 971-978.

5. **Omorinoye, O.A**., Assim, Z.B., Jusoh, I.B, Durumin Iya, N.I., Bamigboye, O.S. & Asare, E.A. (2019). Distribution and sources of aliphatic hydrocarbons in sediments from Sadong River Sarawak, Malaysia. *Research Journal of Chemistry and Environment*, *24*(6), 70-77.

6. **Omorinoye, O.A**., Assim, Z.B., Jusoh, I.B, Durumin Iya, N.I., & Umaru, I.J. (2019). Review of the sedimentological and geochemical approaches for environmental assessment of River Sadong, Samarahan-Asajaya District Sarawak, Malaysia. *Nature Environment and Pollution Technology*, *18*(3), 815-823.