GEOLIPID HYDROCARBONS IN SURFACE SEDIMENTS
FROM THE COASTAL AREA OF RAJANG, SARIKEI

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Bachelor of Science with Honours
(Resource Chemistry)
2005
GEOLIPID HYDROCARBONS IN SURFACE SEDIMENTS
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The dissertation is submitted in partial fulfillment of the requirements for
the degree of Bachelor of Science with Honours
in Resource Chemistry

Faculty of Resource Science and Technology
UNIVERSITI MALAYSIA SARAWAK
APRIL 2005
DECLARATION

No portion of the work referred to this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

Fairous Binti Salleh

Program of Resource Chemistry

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ACKNOWLEDGEMENTS

ALHAMDULILLAH and most gratitude to Allah s.w.t for the strength and courage He gave to me throughout completing this project to success.

First and foremost, I would like to express my sincere appreciation to my supervisor, Assoc. Prof Dr. Zaini for his wise control, constant guidance, knowledgeable advices, constant encouragement and various logistic supports during completing this project. My special appreciation it also extended to Dr. Harwant Singh for his support, suggestions and comments of this project. A special thank to laboratory assistants, En Rajuna, En Jahina, Pn Dayang Fatmawati for their cooperation, technical support and help during this project.

A grateful thank to all postgraduate students, especially to Rabuyah Bt. Ni and my fellow friends, especially to Laurina Jacklyn Bt. Teo Choon Nee and Mohd Saiful Hazri B. Mat Yusof for their help, support and guidance during this project.

Last but not least, I would like to thanks to my mother, sisters and brother for their encouragement, support and understanding which is my inspiration throughout this project.
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ABSTRACT

The surface sediments collected from ten sampling sites located at the coastal area of Rajang, Sarawak. The samples were analyzed for aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) content by using high resolution capillary gas chromatography/flame ionization detector (GC/FID). The concentration of total aliphatic hydrocarbons (TAHs) and PAHs are in the range 25.4 μg/g to 457.8 μg/g (dry weight) and 1.32 μg/g to 50.40 μg/g (dry weight), respectively. The carbon preference index (CPI) together with other hydrocarbon biomarker indices showed that sediments located at the Rajang estuary and near to the coastal area were affected by high level of biogenic input. The sediments at deep water were considered to receive a mixture of both anthropogenic and biogenic inputs. Q-mode cluster analysis was performed to classify the sampling sites into groups according to their probable input sources. This results of this analysis showed that sediments located at the estuary and near to the coastal area were affected by high level of biogenic input. Combinations of both anthropogenic and biogenic input were observed for the sediments located at the deep sea water area. The distribution pattern of hydrocarbons in the sediments for this area is similar to distribution of hydrocarbons in petroleum product, organic matter and input from atmosphere.

Keywords: Surface sediments, aliphatic and aromatic hydrocarbons, GC/FID, anthropogenic and biogenic.
ABSTRAK

Enapan dari sepuluh lokasi pensampelan di kawasan pesisiran pantai Rajang telah dikaji. Sampel ini telah dianalisis bagi mengetahui kandungan hidrokarbon alifatik dan hidrokarbon aromatik polisiklik dengan menggunakan kromatografi gas/pengesan pengionan nyalaan (KG/PPN). Jumlah kepekulan hidrokarbon alifatik dan hidrokarbon aromatik polisiklik adalah dalam julat 25.4 µg/g hingga 457.8 µg/g and 1.32 µg/g hingga 50.40 µg/g berat kering, masing-masingnya. Indeks kecenderungan karbon (IKK) beserta dengan indek penanda biologi hidrokarbon lain menunjukkan enapan dari kawasan muara Rajang dan pesisiran pantai adalah dipengaruhi oleh tahap input biogenik yang tinggi. Enapan dari kawasan laut dalam adalah dianggap menerima campuran input antropogenik dan biogenik. Analisis kelompok Q-mode telah dilakukan bagi mengkelaskan kawasan pensampelan mengikuti sumber hidrokarbon. Hasil analisis menunjukkan bahawa enapan yang berada pada muara dan berhampiran dengan pantai adalah dipengaruhi oleh input biogenik yang tinggi. Gabungan input antropogenik dan biogenik telah dicerap pada enapan dari kawasan laut dalam. Corak taburan hidrokarbon dalam enapan dari kawasan ini adalah serupa dengan taburan hidrokarbon dalam produk petroleum, bahan organik dari input dari atmosfera.

Kata Kunci: Enapan, hydrocarbon alifatik dan aromatik. KG/PPN, antropogenik dan biogenik.
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CHAPTER ONE
INTRODUCTION

1.1 Introduction

Marine coastal areas play an important role in the global carbon cycle either as sources of organic matter to the open ocean or as carbon sinks due to accumulation in sediments (Meybeck, 1982; Prahl et al., 1994). These areas are characterized by significant continental inputs which lead to increase of the marine productivity (Berger, 1989). In addition pollutants are often major components of the land-borne material introduced in coastal areas and have significant impact on coastal ecosystems and public health. Research on coastal environment has been thus recognized as critical for the understanding of the global carbon cycle and for achieving a sustainable management and ecosystem preservation.

Hydrocarbons occur in solid, liquid and gaseous states. Hydrocarbons are abundant components of the organic material in coastal zones and one major class of organic compounds. They enter into the marine of the environment by two path ways; there are aquatic and atmosphere, normally in form of dry and wet deposition. Other than that, the geographical setting also influences the abundance of hydrocarbons. (Prahl and Carpenter, 1984; Gagosian and Peltzer, 1986; Lipiatou and Albaiges, 1994).
Among hydrocarbons, the polycyclic aromatic hydrocarbons have received special attention since they have long been recognized as hazardous environmental chemicals (NAS, 1975), and are included priority pollutant list United States Environmental Protection Agency (USEPA) list. Besides anthropogenic sources, hydrocarbons also come from several natural ones, such as terrestrial plant waxes, marine phytoplankton and bacteria, biomass combustion and diagenetic transformation of biogenic precursors.

Their sources and physical and chemical properties largely control the transportation and fate of hydrocarbons in the marine environment. Biodegradation rates of PAHs in the marine environment can differ drastically (Mackay et al., 1992; Schwarzenbach et al., 1993).

1.2 Objectives

The objectives of this sediment analysis are as a tool for environmental monitoring of hydrocarbon contamination as a function of distance from the Kuala Rajang in Sarawak. This project was determined the factors that influence the concentration of abundances of hydrocarbon. Other than that this project was quantify the current levels of major, aliphatic and aromatic hydrocarbons along the Kuala Rajang River in Sarawak coastal zone. Other than that this project was determined their possible source using n-alkane distribution indices.
CHAPTER TWO

LITERATURE REVIEW

2.1 Hydrocarbons

The hydrocarbon background of the ocean bottom sediments is produced by a complex of genetically variable sources including biological (marine organisms, terrestrial plants and transformed products from the organic components, emanation (gaseous and hydrothermal plumes along faults, volcanic substances, oil seepage at the ocean bottom), anthropogenic come from the atmosphere or with river run-off and sheet wash as well as because of sea transport sources. Hydrocarbons are abundant components of the organic material in coastal zones and one major class of organic compounds. They enter into the marine of the environment by two path ways; there are aquatic and atmosphere, normally in form of dry and wet deposition. Other than that, the geographical setting also influences the abundance of hydrocarbons. (Prahl and Carpenter, 1984; Gagosian and Peltzer, 1986; Lipiatou and Albaiges, 1994).

In the last few decades, the molecular compositions of aliphatic hydrocarbons particularly their isoprenoid structures have received a wide acceptances for the identification of both biological and oil sources of aliphatic hydrocarbons. For instance, it has been shown that terrestrial plants, plankton and microorganisms vary in aliphatic composition and also in relation to the difference between even and odd alkanes in aliphatic structures (Bray and Evans, 1961; Clark and Blumer, 1967s et al.; Blumer et al., 1971; Youngblood et al.,
Petroleum aliphatic hydrocarbons are unlike those of biological origin although the separate structure fragments form a repetitive sequence in both hydrocarbon associations (Tissot and Welte, 1978). There are 2 sources of aliphatic hydrocarbons formation in the coastal and estuarine zone are anthropogenic sources and biogenic sources. Biogenic sediment is formed by living organisms animal or plant, biogases burning and digenetic processes. Diagenesis is all the changes that take place in sediment at low temperature and pressure after deposition. With increasing temperature and pressure, diagenesis grades into metamorphism. Diagenetic processes such as compaction, dissolution, cementation, replacement and recrystallization are the means by which unconsolidated, loose sediment is turned into a sedimentary rock, sandstone and coal (Selley, 1988).

Aliphatic hydrocarbon is formed by biochemical processes which occurred to the terrestrial plants and also marine organisms. This hydrocarbon biosynthesis will be released to environment through metabolisms activities and organisms. Petroleum aliphatic hydrocarbons are unlike those of biological origin although the structure fragments form a repetitive sequence in both hydrocarbon associations, which many researchers interpret as an evidence of the close origin of the two groups of aliphatics (Tissot and Welte, 1978).
2.3 Polycyclic Aromatic Hydrocarbon (PAH)

Polycyclic aromatic hydrocarbons (PAHs) can be used when identifying both anthropogenic and pyrogenic sources of hydrocarbons found at bottom sediments or other components of marine environment. PAHs' high indicative value is related to the relatively narrow range of their formation in comparison with the hydrocarbons of other classes. PAHs have become indicators not only of anthropogenic processes but also the natural processes of emanation impact of earth's crust bowels on sedimentary organic matter as well (Kawka and Simoneit, 1994; Pikovski et al., 1996; Simoneit, 1985, Simoneit and Fetzer, 1996).

Polycyclic aromatic hydrocarbons (PAHs) are known to enter aquatic environment through industrial discharges, petroleum spills, combustion of fossil fuels, automobile exhaust, and non-point sources such as urban runoff and atmospheric fall-out (Neff, 1979; Hoffman et al., 1984; Latimer et al., 1990, Simck et al., 1996).

Comparative study of hydrocarbons' geochemistry in the regions for obtaining indication criteria to identify the origin of hydrocarbon associations of marine environment. Such as research has been carried out by Wakeham (1996) who studied the distribution of aliphatics and PAHs in the Black Sea bottom sediments. The sea is known to under strong influence of anthropogenic pollution. Data on hydrocarbon molecular composition that hydrocarbons are transporting into sediments of shelf and abyss generally from
antropogenic and pyrogenic sources, and also from terrestrial plants whose fragments are moving into the sea with river run-off (Wakeham, 1996).

A large data body of hydrocarbon data in the Western Mediterranean sediments has been published during the last decade (Albaiges et al., 1984; Grimalt and Albaiges, 1987, 1990; Bouloubassi and Saliot, 1991, 1992; Bouloubassi et al., 1997; Lipiatou et al., 1997), there is a striking pouching of data for the Eastern Mediterranean. This research focuses on the determination of aliphatic and polyaromatic hydrocarbons in the sediment of Cretan Sea in Eastern Mediterranean.
CHAPTER THREE
MATERIALS AND METHODS

3.1 Sampling Location and Samples Collection

Core sediments were collected on the 4th September 2004 from ten sampling sites located at coastal area of Rajang from Paloh to Tanjung Jerijeh in Sarikei Divisions. These ten samples sampling sites are shown in Figure 1. The sediment samples were collected by using a gravity core sampler. The core sediments were collected to 15cm and then sliced vertically for every 5 cm depth. The samples were wrapped with aluminum foil, stored in clean plastic bags and transported in cooler box to the Unimas laboratory. Upon arrival at Unimas, the samples were stored in the cool room at -18°C until further analysis. Only the top 5cm of layers of the core samples (0 – 5 cm) were analyzed for this report.

3.2 Extraction and Fractionation

The analyses of hydrocarbons in the coastal sediments were carried out according to the protocol as shown in Figure 2. The analyses of hydrocarbons in sediments were involved extractions, fractionations and instrumental analysis on GC/FID. Sample extraction procedure summarized below is based on method used by Zakaria (2000). Briefly, 10g of wet sediment were weighed in thimble and subsequently it were Sohxlet-extracted with 200ml dichloromethane (DCM),
Figure 1: Sampling sites at the coastal area of Rajang.
Wet sediments (~10 g) 
Soxhlet, 12-24 hours 
200ml dichloromethane 
Spiked with internal standard 
(50 µg/µL of octadecene and 
o-terphenyl)

Solvent Partitioning 
Rotary evaporate to yield geolipid 
Redissolved with 2 mL DCM 
Evaporated DCM and transferred to 
5mL vial 
Redissolved with 2 mL hexane

Column Chromatography

F1
Aliphatic hydrocarbons

Sulfur removal on 
Copper Column
ready for GC analysis

F2
PAHs

Sephadex Column 
Chromatography

F2S1
Non-PAHs
(Aromatic)

F2S2
PAHs 
ready for GC analysis

Figure 2: Extraction and Fractionation protocol for sediment samples from the coastal of Rajang.
for 24 hours. The total extractable lipid (TEL) was fractionated into five individual classes of organic on silica gel column chromatography by eluting with solvent and mixture of solvents as described in Table 1. However, only first and second fractions were considered in this project. The third to fifth fractions are kept in the vial for future analysis.

Activated copper column were used to remove elemental sulfur (S8) from the fractions F1 fraction (Blumer, 1957). The presence of appreciable quantities of S8 in some sediment samples interferes with accurate gravimetric determination of the total aliphatic hydrocarbon (TAH) content of the sample and GC/MS analysis of individual aliphatic hydrocarbons in the F1 fraction. Polycyclic aromatic hydrocarbons (PAHs) in F2 fraction was enriched on Sephadex LH-20. This enrichment separated the major non-PAH components in the F2 fraction such as polyunsaturated hydrocarbons (e.g. heneicosahexane, squalene) from the PAH (Giger and Blumer, 1974).

3.3 Gas chromatography/Flame Ionization Detector (GC/FID) Analysis

High resolution gas chromatography was conducted on Shimadzu 17A 5890 Series III gas chromatography equipment with fused silica column (25m ×0.3mm i.d ×025μm) film thickness and using Spilt/splitless capillary injection system and a flame ionization detector (FID). The samples were analyzed in the splitless mode using nitrogen as carrier gas at a rate of 1ml/min. The injector and detector temperatures will be maintained at 300°C and 300°C respectively. The initial temperature at 50°C and hold for 2 min,
increased to 300°C with rate 5°C/min and hold for 5 minutes. Helium will be carrier gas at a linear velocity of 39 cm/s at 280°C.

The PAH fractions were analyzed by a Hewlett Packard (HP) 5890A gas chromatography, equipped with a split/splitless capillary injection system and a flame ionization detector (FID). The samples were analyzed in the splitless mode using nitrogen as carrier gas at a rate of 1ml/min. The injector and detector temperatures will be maintained at 300°C and 300°C respectively. The initial temperature at 50°C and hold for 2 min, increased to 300°C with rate 5°C/min and hold for 5 minutes. Helium will be carrier gas at a linear velocity of 39 cm/s at 280°C.

Table 1: Fractions obtained for fractionation of crude extracts using different elution solvent system.

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<th>Solvent System</th>
<th>Class of Components</th>
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<tr>
<td>F1</td>
<td>40ml Hexane</td>
<td>Aliphatic Hydrocarbons</td>
</tr>
<tr>
<td>F2</td>
<td>10ml DCM: 30ml Hexane</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>F3</td>
<td>10ml DCM: 10ml Hexane 1ml EtOAc: 19ml Hexane</td>
<td>Alkenones, fatty acids</td>
</tr>
<tr>
<td>F4</td>
<td>4ml EtOAc: 36ml Hexane</td>
<td>Phthalanes</td>
</tr>
<tr>
<td>F5</td>
<td>7ml EtOAc: 33ml Hexane</td>
<td>Alcohol, sterol</td>
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