DISTRIBUTIONS OF ALIPHATIC AND POLYCYCLIC AROMATIC HYDROCARBONS IN SURFACE SEDIMENTS FROM SARAWAK AND SANTUBONG RIVER, KUCHING

Abdul Hafidz Bin Yusoff

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DISTRIBUTIONS OF ALIPHATIC AND POLYCYCLIC AROMATIC HYDROCARBONS IN SURFACE SEDIMENTS FROM SARAWAK AND SANTUBONG RIVER, KUCHING

ABDUL HAFIDZ BIN YUSOFF

This project is submitted in partial fulfillment of the requirements for the degree of Bachelor of Science with Honors (Resource Chemistry Programme)

FACULTY OF RESOURCE SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SARAWAK
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DECLARATION

No portion of the work referred to in 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.

Abdul Hafiz Bin Yusoff
Resource Chemistry Programme
Department of Chemistry
Faculty of Resource Science and Technology
Universiti Malaysia Sarawak
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Distributions of Aliphatic and Polycyclic Aromatic Hydrocarbons in Surface Sediments from Sarawak and Santubong River, Kuching

Abdul Hafiz Bin Yusoff
Department of Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak

ABSTRACT

The surface sediments from ten sampling sites located along Sarawak and Santubong rivers, Kuching were analyzed for aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) content by using gas chromatography/flame ionization detector (GC/FID) equipped with DB-5 capillary column. The concentrations of total aliphatic hydrocarbons (TAHs) and total PAHs are in the range not detected to 83.63 μg/g (dry weight) and not detected to 11.25 μg/g (dry weight), respectively. Several molecular indices were used to predict the sources of hydrocarbons. CPI value and other molecular indices indicated that Sarawak and Santubong River are dominated by different sources of hydrocarbons. Majority of total extractable lipids (TELs) in sediments from Sarawak River are dominated by anthropogenic and petrogenic sources, while TELs in sediments from Santubong River are mix biogenic and anthropogenic sources. PCA analysis was performed to classify the sampling sites into groups according to their probable input sources. The results of this analysis showed that most of the sediments located along Sarawak River area were affected by high level of anthropogenic input. The sediments from Santubong River were considered to receive major biogenic inputs. Sediments from Santubong River also considered receiving pyrogenic input.

Key words: Surface sediments, aliphatic hydrocarbons, aromatic hydrocarbons, principle component analysis (PCA), petrogenic.
ABSTRAK

Kajian telah dilakukan terhadap enapan permukaan dari sepuluh lokasi pensampelan di sepanjang Sungai Sarawak dan Sungai Santubong, Kuching. Sampel enapan ini telah dianalisis bagi mengenalpasti kandungan hidrokarbon alifatik dan hidrokarbon aromatik polisiklik menggunakan kromatografi gas/pengesaan pengionan nyalaan (KG/PPN) dilengkahkan dengan turus DB-5. Jumlah kepekatan hidrokarbon alifatik dan hidrokarbon aromatik polisiklik adalah dalam julat tidak dikesan hingga 83.63 µg/g berat kering dan julat tidak dikesan hingga 11.25 µg/g berat kering, masing-masingnya. Analisis menggunakan analisis komponen prinsipal telah dilakukan bagi mengelaskan kawasan pensampelan mengikut sumber hidrokarbon. Hasil analisis statistik ini menunjukkan bahawa enapan dari Sungai Sarawak dipengaruhi oleh input antropogenik yang tinggi. Gabungan input antropogenik dan biogenik telah dicerap pada kebanyakan enapan dari Sungai Santubong. Enapan daripada Sungai Santubong juga menunjukkan pengaruh input pirogenik, manakala enapan dari Sungai Sarawak dipengaruhi oleh input petrogenik. Data indek kecenderungan karbon (IKK) dan indek penanda hidrokarbon juga menyokong hasil analisis ini.

Kata Kunci: Enapan, hidrokarbon alifatik, hidrokarbon aromatik, analisis komponen prinsipal, petrogenik.
CHAPTER ONE
INTRODUCTION

1.1 Research Statements

There are two major rivers in Kuching City, namely Sarawak River and Santubong River. These rivers are opened to various ways for hydrocarbons enter it. Rapid industrialization, urbanizations and shipping activities along Sarawak River might be the major sources of hydrocarbon contaminants. Mangrove forest, especially Nypa palms can be found along Santubong River and might be the major sources of hydrocarbons along Santubong River. Therefore a continuous evaluation of contamination along Sarawak and Santubong River is essential in order to identify potential hotspot of high level contaminants, their geochemical fate and significance of land-based transportation of pollution to the river. The study of hydrocarbon in marine environment is great importance because these areas are biologically productive and received considerable pollutant input from land base sources. There also have been proven to be an efficient tool to identify environmental impacts (Fernandes et al., 1997). Furthermore, the determination of hydrocarbon contaminant is necessary in order to understand their distributions and fate in the marine environment (Said, 2005).

Hydrocarbon is one of the major groups of coastal and marine environmental contaminants. The presence of high concentrations of certain hydrocarbons in marine environment has an adverse effect and may cause toxicity on marine life (Long et al., 1998). Sediment is an integral component of aquatic ecosystem, providing habitat, feeding, spawning, and rearranging areas for many aquatic organisms. In aquatic systems,
sediment accumulates anthropogenic (man-made) chemicals and waste material, particularly persistent organic and inorganic chemicals. These accumulated chemicals are then reintroduced into waterways and have contributed to a variety of environmental problems (Ireland and Ho, 2005). Particles from pollutant will be deposited into the sediment and may accumulate over time. Because sediment comprises an important component of marine ecosystem providing habitat for wide range of marine organism, exposure to certain substances in sediments represents a potentially significant hazard to health of the organism (CCME, 2001). These kind of studies have provides a broader comprehension of overall health of aquatic environment (Sharma et al., 2000).

1.2 Objectives

The objectives of this project are to describe vertical and spatial distributions of aliphatic and polycyclic aromatic hydrocarbons in the sediments, and to assess the various origins of aliphatic and polycyclic aromatic hydrocarbons in surface sediments from Sarawak and Santubong River using hydrocarbon molecular indices. The other objectives is to carry out statistical analysis using principal component analysis (PCA) in order to trace the origin of organic matter in sediments.
CHAPTER TWO

LITERATURE REVIEW

2.1 Hydrocarbons in Sediments

Sediments contain deposited material consisting of organic matter in various stages of decomposition, particulate mineral water and organic material of biogenic origin (Salomons, 1995). Hydrocarbon are sequestered and preserved in sediment (Nishigima et al., 2001). Petroleum hydrocarbons are one of major ubiquitous group of coastal and marine environmental contaminants and derived from biogenic and anthropogenic sources (Preston and Merret, 1991).

Sediments have a number of features that make them less straightforward to manage than are soils (Apitz, 1998). Sediment grain size, organic matter content, and chemical composition of different kinds of sediment, as well as the amount and chemical properties of contaminants, influence the levels and extent of contamination in the environment (Leenheerer, 1991). Sediments in coastal areas are often integrators of contaminant input from multiple point or non-point sources within a watershed. This creates difficulties in tracking sources of contamination, and also can result in ubiquitous, regional "background" levels of anthropogenic contaminants that are difficult to separate from site-specific sources. For the same reason, sediments, much more often than soils, are impacted by multiple contaminants (or chemicals or constituents) making risk and difficult to manage. The hydrodynamics and geochemistry of sediment systems are also quite different than those of soil systems (Apitz, 1998).
In sediment, there are four major classes of hydrocarbon contaminant. N-alkanes (also called paraffins), cycloalkanes, alkenes and aromatic hydrocarbons. Aliphatic hydrocarbons consist of saturated normal alkanes from C2 to beyond C20 with smooth distribution between odd and even number of alkanes including isoprenoids. The most isoprenoid hydrocarbons are Pristane (C19) and Phytane (C20). Cycloalkanes (also called cycloparaffins) consist of minor constituent similar to isoprenoids and have specific plant (steranes, diterpanes, triterpanes) and animal precursor. Cycloalkanes serve as important molecular markers in oil spill and geochemical studies. Aromatic hydrocarbons contain one or more aromatic rings which are connected as fused rings (naphthalene) or line rings (biphenyl) and normally consist of unsaturated or parent aromatic structures and like structures with multiple alkyl substitution (Said, 2005).

### 2.2 Occurrence of Aliphatic Hydrocarbons in Marine Environment

There are two important sources of aliphatic hydrocarbons that are biogenic and anthropogenic. In the coastal marine environment, aliphatic hydrocarbons are sequestered and preserved in sediments. Characterizations and differentiation of aliphatic hydrocarbons from various sources is an essential part of any hydrocarbon studies. (Nishigima et al., 2001).

Biogenic sources are generated either by biological processes or in the early stages of diagenesis in recent marine sediment. Biological sources include terrestrial plants, phytoplankton, animals, bacteria, microalgae and macroalgae. Among biogenic aliphatic
hydrocarbon, n-alkanes are the most predominant group, and have been identified in many species of plants and animals (Nishigima et al., 2001).

Aliphatic hydrocarbons from biogenic sources show high predominance of the odd carbon number n-alkanes. Biogenic hydrocarbons are also often noted by the presence of single isoprenoid, usually pristane. The ratio of pristane to phytane is usually much greater than one in biogenic sources. Terrestrial and marine organisms synthesize n-alkane (C_{16} to C_{34}) where chains with odd carbon numbers are predominant. N-alkanes from terrigenous plant are characterized by odd carbon number predominant alkanes in the C_{23}-C_{35} region (Volkman et al., 1992). Marine phytoplankton synthesize n-alkanes with odd carbon number which are lower than n-C_{23}, normally n-C_{15}, n-C_{17} and n-C_{19} (Blumer et al., 1971).

Some of the aliphatic hydrocarbons enter the marine environment via several pathways such as direct pipeline discharge from coastal communities and dumping from ships (Kim et al., 1999). These sources of aliphatic hydrocarbon which includes industrials and domestic wastes, emissions from the transportation, storage, processing and combustion of fossil fuels are called anthropogenic sources (Doskey, 2000). Municipal, agricultural and industrial waste (sewage) can be categorized as land based pollution contributors, which are discharged directly into the sea or enter the coastal waters through the rivers. Waste water which are not treated can enter water bodies indirectly and through diffuse sources such as waters from parking lots, agricultural land, households and remote watersheds receiving waste water product from atmosphere (Welsh, 1992).
Oil spills are one of the major contributors of aliphatic hydrocarbons to the marine environment. Recent estimates show that one third of oil pollution of the world's oceans is caused by activities involving oil transportation. Oil spills from tankers originates either by tanker accident and/or normal tanker operations such as tank cleaning and ballast water discharge (Said, 2005). In the oil, aliphatic hydrocarbons show no predominance of odd or even carbon number (UNEP, 1991). Odd carbon numbered N-alkanes show a distribution pattern which are much abundant than even carbon-numbered alkanes in the range of n-C11 to n-C33, resulting in unusually high carbon preference index (CPI) value. CPI values for oil around 1. CPI is the sum of the odd carbon-numbered n-alkanes to the sum of even carbon-numbered (Bennece et al., 1996).

2.3 Occurrence of Polycyclic Aromatic (PAHs) Hydrocarbons in Marine Environment

NRC (1983) state that PAHs in coastal sediment occur is due to both natural and anthropogenic source. Forest-fires, natural petroleum seeps and post depositional transformation of biogenic precursors such as pigments and steroids are the natural sources of PAHs (Wakeham et al., 1980), whereas anthropogenic sources of PAHs include the combustion of fossils fuels, gasification and liquefaction processes of coal and production of coke, carbon black, coal tar pitch, asphalt and petroleum cracking (McCready et al., 2000).

PAHs have different distribution patterns based on their sources. Due to the possible co-existence of several sources such as various pyrolytic sources, petrogenic
contamination, and early diagenesis, it is difficult to identify the origin of PAHs in sedimentary medium. Besides, physical-chemical properties of some PAHs such as chemical reactivity (photooxidation, oxidation), can contribute to such modification of the original distribution pattern of the emission sources (Butler and Crossley, 1981).

Said (2005) state that there are three major types of PAHs based on their origin including petrogenic PAHs, biogenic PAHs and pyrogenic PAHs. Petrogenic PAHs are related to unburned petroleum, including crude oil and its refined products. They are normally abundant in lower molecular weight range such as naphtanlenes, fluorenes, phenantrenes, dibenzothiophenes and chrysenes. Lower molecular weight PAH can more easily undergo weathering than higher molecular weight PAH, thereby after altering the original composition of PAHs.

Biogenic PAHs are generated by biological processes or by the early stages of diagenesis in marine sediments (e.g. chrysene and perylene- a 4-ring unsubstituted PAH). Chrysene is mainly derived from pentacyclic triterpenes such as α- and β-amyrins, which are major constituents of epicuticular waxes of terrestrial plants, by microbial degradation processes (Wakeham et al., 1980; Said, 2005).

Pyrogenic PAHs are generated by the recent organic material and combustions of fossils fuels such as coal and oil. Pyrogenic PAHs show distribution pattern dominated by the parent compounds of the 3-, 4-, and 5- rings PAHs where the most abundant compounds are usually fluoranthene and pyrene (Said, 2005).
PAHs in water tend to associate with particulate materials due to its low solubility and high octanol/water partition coefficient ($K_{ow}$). They are transported and accumulated with sediment, which can act as long term reservoir of hydrophobic contaminants, through the continuous settling of particulate material, flocs and fecal pellets (Bixian et al., 2001). Once deposited in the sediments, these compounds are less subjected to various transformation processes including chemical transformation, biological oxidation, photochemical degradation and thus tend to persist for longer periods and accumulated in high concentrations (GuzELia and de Paolis, 1994).

2.4 Molecular indices for Aliphatic Hydrocarbons.

Aliphatic hydrocarbon from anthropogenic and biogenic sources can be determined using different indices. The combination of different indices will provide a better comprehension for the hydrocarbon origin. Ratio of isoprenoid pristane and phytane (Pr/Ph) can be used as molecular indices to indicate the origin of hydrocarbon in sediments. In sediments uncontaminated with oil, the Pr/Ph ratio is higher than 1 usually between 3 and 5 (Steinhauer and Boehm, 1992).

The ratio between low molecular weight ($C_{13}$-$C_{20}$) over high molecular weight hydrocarbons are also used as molecular indices. Concentration ratio which show molecular weight less than or equal with $C_{20}$ indicate hydrocarbons from petroleum products, algae and plankton while molecular weight with $C_{21}$ indicates hydrocarbons from higher plants. (Colombo et al., 1989)
Odd to even ratio (odd/even) ratio of hydrocarbons can be used as plant waxes indicator in sediment. In plant waxes, odd chain alkanes are presented 8 to 10 times more abundant compared to even number while petroleum usually shows ratio of compounds with odd number of C atom to those with even number of C atom is close to 1 (Volkman et al., 1992).

Carbon Preference Index (CPI) is used in identifying plant wax contribution (biogenic) versus petroleum contamination (petrogenic). Natural sources or terrestrial sources are biogenic and the value is CPI > 1, while for anthropogenic sources, which indicates petroleum pollution, the value is CPI < 1 (Simoneit et al., 1991).

2.5 Molecular Indices for PAHs

Physico-chemical properties of PAHs are used as molecular indices to assess various origins of these pollutants (Saklo, 1986). It is possible to predict the relative importance of processes involved with generation of PAHs using these indices. There are four significant molecular markers used for this purposes: First, the ratio of phenanthrene over anthracene (phe/ant). Second, the ratio of fluoranthenes over pyrene (fluor/Pyr). Third, the ratio of benzo(a) anthracene and chrysene (B(a)A/Chry) and the last one is the ratio of low molecular weight (phe+Ant+Fluo+Pyr) over high molecular weight (B(a)A+Chry+B(b)F+B(k)F+Ind+DiBA+B(ghn) PAH, (LMW/HMW) (Budzinski et al., 1997).

Phe/Ant ratio is used to differentiate PAHs of petrogenic origin from pyrogenic origin in the environment. Sediment with ratio of Phe/Ant greater than 10 were mainly petrogenic origin while ratio which are less than 10 are pyrolytic processes (Budzinski et
al., 1997). Petrogenic origin are generally characterized by high Phe/Ant ratio (normally >15) while those from pyrogenic origin are characterized by lower ratio of Phe/Ant (Benner et al., 1990).

Fluo/Pyr ratio used to determine PAHs from petrogenic sources and pyrolytic origin. Fluo/Pyr ratio less than 1 shows that PAHs are from petrogenic sources and values greater than 1 shows that PAHs are from pyrolytic origin. The ratio of benzo(a) anthracene and chrysene (B(a)A/Chry) suggested to trace PAHs from petrogenic and pyrolytic origin also. The B(a)A/Chry ratio less than 1 indicated pyrolytic origin while more than 1 indicated petrogenic origin. The ratio of LMW/HMW used based on fact that petrogenic origin are dominant by LMW while pyrolytic origin are dominant with HMW (Soci et al., 2000).

2.6 Effect of hydrocarbons in aquatic environments.

The effects of hydrocarbons on marine organisms depend on the concentration of the hydrocarbons, types of hydrocarbon, duration of contact with hydrocarbon and organisms sensitivity. Once marine organisms absorb a hydrocarbon compound, the compound may be metabolized, stored with possible elimination at a later time, or excreted unchanged. The hydrocarbons may enter the organisms in several ways, active uptake of dissolved or dispersed substances, by ingestion of petroleum-sorbed particles including live or dead organic matters and by drinking or gulping of water containing the chemicals, as in the case of fish (Said, 2005).
Hydrocarbons contaminants in sediment also have been implicated as the cause of the abnormal pathology observed in benthic and demersal organisms and the alterations in the structure of benthic invertebrate populations and communities. Aromatic hydrocarbons have been correlated with observations of live tumors, fin erosion and mortality on bottom-dwelling fish and invertebrates, as well as with the degradation of benthic community structure. Hydrocarbons can cause mortality and reductions in somatic growth rate and gonad production of sea urchins (Long and Chapman, 1985).

The toxic properties of petroleum hydrocarbons include a variety of mutagenic and carcinogenic responses, such as the disruption of DNA and the induction of tumors in mammals on exposure to nitro-aromatic polycyclic aromatic hydrocarbons (Preston and Merrot, 1991). The volatile hydrocarbons, thought comparatively toxic to marine organism, Volatile hydrocarbon evaporate relative quickly and hence serve little purpose as diagnostic aids. Polycyclic aromatic hydrocarbons (PAHs) includes compound that give toxicity (Crosby, 1998).

The U.S. Environmental Protection Agency has identified several PAHs as "priority pollutants" on the basis of their known or potential ability to cause cancer, mutations, or other genetic damage. By considering their carcinogenic and mutagenic properties, the US EPA has categorized 16 PAHs compounds as priority pollutants. The lower molecular weight PAHs such as naphthalenes, fluorenes, phenanthrenes and anthracenes have significant acute toxicity to aquatic organisms, whereas the high molecular weight PAHs from chrysenes to coronenes and benzo(b)fluoranthene and dibenzo(a,h)anthracene are not acutely toxic (Said, 2005).
CHAPTER THREE

MATERIALS AND METHODS

3.1 Sampling Area

The sediment samples were collected from Santubong River and Sarawak River. The sampling location for sediment is shown in Figure 1. The sediment samples were collected using a gravity core sampler and then sliced at 5 or 10 cm interval. However, only top layers (0-5) cm was considered in this study. The sediments were then wrapped with aluminum foil and stored in cooler box during the sampling. All the sediments were then stored in cold room until further analysis.

Figure 1: Location of ten sampling stations at Sarawak River and Santubong River, Kuching.