



UNIVERSITI PUTRA MALAYSIA

**CHARACTERIZATION, CONCENTRATION AND DEPOSITIONAL
HISTORY OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)
AND HOPANE FROM SELECTED LOCATIONS IN PENINSULAR
MALAYSIA**

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FPAS 2009 3



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HISTORY OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)
AND HOPANE FROM SELECTED LOCATIONS IN PENINSULAR
MALAYSIA**

By

MAHYAR SAKARI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
Malaysia, in Partial Fulfillment of the Requirement for the Degree of Doctor
of Philosophy**

January 2009



DEDICATION

To my wife, son and parents who have been supporting and encouraging me all along for my promotion in science.



ABSTRACT

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in partial fulfillment of the requirement of the degree of doctor of philosophy

CHARACTERIZATION, CONCENTRATION AND DEPOSITIONAL HISTORY OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND HOPANE FROM SELECTED LOCATIONS IN PENINSULAR MALAYSIA

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January 2009

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Faculty: Environmental Studies

Polycyclic aromatic hydrocarbons (PAHs) are one of the most important classes of pollutants in the marine environment that derive mostly from petroleum products. PAHs are ubiquitous compounds of concern due to its carcinogenic, mutagenic and toxic characteristics. Eight sedimentary cores were obtained from developed and developing areas around Peninsular Malaysia to investigate the historical profile of PAHs, their characteristics and its possible origins. Hopane composition and ratio were used as environmental forensic investigation biomarkers. The



results showed that the PAHs varied from below detection limit amounts in offshore and less developed areas to near 4500 ngg⁻¹ d. w. in developed and polluted locations. Most of the studied locations showed high contribution of PAHs from combusted fuel, coal, biomass and wood materials except for the southern part of Peninsular Malaysia which implied petroleum products release where shipping and marine transportation is active. The findings indicate pyrogenic and petrogenic PAHs comes from different intermediate materials such as asphalt, street dust, vehicular emission and crankcase oil with higher amounts near the city hinterland. Although there has been a decline of PAHs input into the marine environment in recent years, petroleum is shown to be a significant cause of marine pollution since the 1940's. Climatic conditions play a role such as heavy daily rainfall, high organic content and suspended particle, accelerated wash off of contaminated materials into the marine environment via lateral transport. Results of statistical tests of PAHs specific compound suggest that PAHs in the deeper cores are derived naturally from biogeochemical processes.



ABSTRAK

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENCIRIAN, KANDUNGAN DAN SEJARAH DEPOSISI HIDROKARBON AROMATIK POLISIKLIK (PAHS) DAN HOPANE DI BEBERAPA TEMPAT TERPILIH DI SEMENANJUNG MALAYSIA

Oleh

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Januari 2009

Pengerusi: Profesor Madya Mohamed Pauzi Zakaria, Ph.D.

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Hidrokarbon aromatik polisaiklik (PAH) merupakan salah satu klas terpenting bahan tercemar di dalam alam sekitar marin yang terhasil daripada petroleum. PAH adalah sebatian yang perlu dititikberatkan kerana ciri-cirinya yang karsinogen, mutagenik dan toksik. Sebanyak lapan teras sedimen telah diambil dari kawasan membangun dan sedang membangun di Semenanjung Malaysia untuk mengkaji profil sejarah PAH, ciri-cirinya dan asal usulnya. Komposisi hopane dan nisbah telah digunakan sebagai penanda-bio penyiasatan forensik persekitaran. Keputusan menunjukkan PAH berubah-ubah dari nilai di bawah had pengesanan di kawasan luar pantai dan kawasan kurang membangun hingga hampir 4500 ngg^{-1} berat kering di kawasan membangun dan tercemar.



Kebanyakan lokasi kajian menunjukkan penyumbang utama PAH adalah daripada bahan bakar, arang batu, biomas dan kayu-kayuan, kecuali bahagian selatan Semenanjung Malaysia yang menunjukkan hasil petroleum terbebas di mana kawasan tersebut aktif dengan aktiviti perkapalan dan pengangkutan marin. Hasil penemuan kajian menunjukkan pirogenik dan PAH petrogenik adalah berpunca dari bahan perantaraan yang berbeza seperti asfat, debu jalan, asap kenderaan dan tangki-tangki minyak yang terletak di sekitar bandar. Walaupun input PAH didapati menyusut pada tahun kebelakangan ini tetapi, petroleum menunjukkan punca pencemaran laut yang signifikan semenjak 1940 an lagi. Keadaan cuaca seperti hujan lebat seharian, kandungan organik tinggi dan partikel terampai memainkan peranan mempercepatkan pengaliran bahan-bahan tercemar ke dalam alam sekitar marin melalui pengangkutan menegak. Keputusan ujian statistik menunjukkan PAH di dalam teras sedimen terkedalam adalah dihasilkan secara semulajdi dari proses-proses biokimia.



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APPROVAL

I certify that a Thesis Examination Committee has met on 5th January 2009 to conduct the final examination of Mahyar Sakari on his thesis entitled “CHARACTERIZATION, CONCENTRATION AND DEPOSITIONAL HISTORY OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND HOPANE FROM SELECTED LOCATIONS IN PENINSULAR MALAYSIA” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

MAHYAR SAKARI

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LIST OF ABBREVIATIONS

An	Antheracene
An-d10	Antheracene-d10
BaA	Benzo(a)antheracene
BaP	Benzo(a)pyrene
Benzo(e)Ace	Benzo(e)acephenanthrylene
BeP	Benzo(e)pyrene
BkF	Benzo(k)fluoranthene
Chry	Chrysene
Chry-d12	Chrysene-d12
DahA	Dibenzo(a,h)anthracene
DBT	Dibenzothiophene
DCM	Dichloromethane
Fluo	Fluoranthene
GC-MS	Gas Chromatography Mass Spectrometry
L/H PAHs	Lower Molecular Weight PAHs over Higher Molecular Weight PAHs
Hex	Hexane
HMW	Higher Molecular Weight
IIS	Internal Injection Standard
LMW	Lower Molecular Weight
2-MA	2-Methylantheracene
MeOH	Methanol
1-MP	1-Methylphenantherene



2-MP	2-Methylphenanthrene
3-MP	3-Methylphenanthrene
9-MP	9-Methylphenanthrene
MP	Sum of Methylphenanthrene
MP/P	Methylphenanthrene/Phenanthrene
1-MPyr	1-Methylpyrene
Naph-d8	Naphthalene-d8
P-terph-d14	P-terphenyl-d14
PAHs	Polycyclic Aromatic Hydrocarbons
Pery-d12	Perylene-d12
Phe	Phenanthrene
Pyr	Pyrene
SIS	Surrogate Internal Standard
Tm	17 α (H)-22,29,30-trisnorhopane
Ts	18 α (H)-22,29,30-trisnorneo-hopane



CHAPTER 1

INTRODUCTION

General introduction

In recent decades, there are increasing concerns for the environment. The environment of the world in the last century experienced huge and various types of threats and a part had already been lost due to increasing pressure from uncontrollable human use of the natural resources. A class of these threats is generated from the wide use of petroleum in industries, urban development and vehicles. Petroleum hydrocarbons come into the environment through accidents, spills or leaks, municipal, industrial releases and commercial or domestic uses (Ouedraogo *et al.*, 2004). Petroleum hydrocarbon pollution includes several types and categories such as normal alkanes (n-alkane) and polycyclic aromatic hydrocarbons (PAHs). Predominance of these compounds in the environment significantly reflect the existence of petroleum pollution, regardless of its sources and fate. Petroleum hydrocarbon as a source of pollution are generated from pure oil or from its usage, and dispersed to the environment via atmospheric transportation, urban runoff, oil spill, tanker accident and other possible ways. Petroleum contaminants are subject to several processes and changes after release from any sources in the marine environment.



Malaysia, which is located in Southeast Asia, has a unique tropical environment and climate. It is surrounded by the Straits of Malacca and the South China Sea in the western and eastern territories and it has been experiencing rapid development during the last half century (Fig. 1).

On the other hand, the strategic location of this country has made it as one of the busiest shipping route in the world due to huge petroleum demand from the Middle East to Japan and recently, China (Fig. 2).

While Malaysia is experiencing extraordinary economic and population growth, it is also developing fast in industrialization, urbanization and motorization in last few decades. As a result of this development, the environment of this country is receiving more threats and hazards especially from the main source of energy which is petroleum. In Malaysia, the concentration and sources of hydrocarbon pollution vary according to locations. For instance, in western P. Malaysia, existence of rapid urban development and the establishment of several industrial points, the hydrocarbon pollution is introduced through city run-off and non-point sources discharge as well as point sources such as factories and tanker accident.



Figure 1 Map of Malaysia in Southeast Asia