UNIVERSITI PUTRA MALAYSIA

HOPANES AND POLYAROMATIC HYDROCARBONS FROM 21 2T OIL AS MOLECULAR MARKERS FOR DETECTING THE SOURCES OF HYDROCARBON POLLUTION

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

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TO MY DEAREST FAMILY AND FRIENDS

Abstract of thesis presented to the Senate of University Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Faculty: Environmental Studies

Rapid growth of population, urbanization and industrialization in Malaysia led to sharp increase in numbers of motor vehicles. Therefore motor oils are potential land-based sources that contributed to hydrocarbon pollution in Malaysia. Two-cycle lubricating oil (2T oil) is a lubricating base oil specially used in two-stroke motorcycle engines. Lubricating base oils are complex mixtures of hydrocarbons. This study focused on alkanes, hopanes and PAHs in 2T oil due to their importance as molecular markers and their combination would be a powerful tool to distinguish input, sources and transport pathway of hydrocarbon pollution. The objective of this study is to analyze alkanes, hopanes and PAHs from 2T oil. Alkanes, hopanes and PAHs from 2T oil were used as molecular markers and were applied for detecting the sources of hydrocarbon pollution and the transport pathway of the 2T oil.

Three kinds of commonly use fresh 2T oil samples were purchased from local market. Used 2T oil sample was collected with pre-cleaned cotton buds from two-stroke motorcycles tail pipes at Central Parking of Universiti Putra Malaysia. The cotton buds were rinsed with 3:1 Hex/DCM. The extract was fractionated and analyzed for PAHs, Hopanes and alkanes by gas chromatography mass spectrometry (GC-MS). The result indicates that used 2T oil contained much higher concentration of PAHs than fresh 2T oil due to formation of PAHs in concentration during high temperature combustion in the engine (Rafael, 1989). Application of the source identifiers, UCM, Pr/Ph, CPI, C_{29}/C_{30}, ΣC_{31}-C_{35}/C_{30}, MP/P and H/L-PAH suggested that hydrocarbon from fresh and used 2T oil both were contributing to the street dust and air particulate in some level of contamination through the exhaust of two-stroke motorcycles. Combination of the alkanes, hopanes and PAHs fingerprints comparison among fresh and used 2T oil, river, inshore, offshore, street dust and air particulate showed that both hydrocarbons from fresh and used 2T oil were significant in coastal environment of Malaysia and they had been potentially transported via street dust and air particulate. PAHs from 2T oil might be discharged to river and inshore coastal zone of Malaysia through street dust and air particulate via lateral and vertical transportation.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

HOPANE DAN POLIAROMATIK HIDROKARBON DARIPADA MINYAK 2T SEBAGAI PENANDA-PENANDA MOLEKUL UNTUK PENGESANAN SUMBER PENCEMARAN HIDROKARBON

Oleh

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Pengerusi: **Profesor Madya Mohamad Pauzi bin Zakaria, PhD**

Fakulti: **Pengajian Alam Sekitar**

Perkembangan populasi, pembandaran dan pengindustrian yang pantas di Malaysia telah menyebabkan peningkatan dalam jumlah kenderaan yang pantas. Maka, minyak engin merupakan sumber daratan yang berpontensi menyumbangkan kepada pencemaran hidrokarbon di Malaysia. Minyak pelicin dua lejang (minyak 2T) ialah sejenis pelincir yang digunakan khasnya dalam enjin motosikal dua lejang. Minyak pelicin adalah campuran hidrokarbon yang rumit. Kajian ini memberi tumpuan atas alkane, hopane dan Polisiklik Aromatik Hidrokarbon (PAHs) dalam minyak 2T disebabkan mereka adalah penanda molekul yang penting dan kombinasi mereka akan menjadi sesuatu alat yang hebat untuk membezakan kemasukan, sumber dan perjalanan pencemaran hidrokarbon. Objektif kajian ini adalah untuk menganalisiskan alkane, hopane dan PAHs daripada minyak 2T. Alkane, hopane dan PAHs adalah digunakan sebagai penanda molekul untuk menentukan sumber pencemaran hidrokarbon.

Sebanyak tiga jenis sample minyak 2T mentah yang biasa diguna dibeli dari pasaran tempatan. Sample minyak 2T terpakai dikumpul dari paip belakang motosikal dua lejang dengan mengguna kapas yang bersih di tempat letak kereta utama Universiti Putra Malaysia (UPM). Kapas–kapas tersebut dibilas dengan 3:1 Hex/DCM. Ekstrak daripada bilasan tersebut dipisahkan dan dianalisis untuk PAHs, Hopane dan alkane dengan kromatografi gas spektrometri jisim (GC-MS). Keputusan kajian ini menunjukkan minyak 2T terpakai mengandungi kepekatan PAHs terlampau lebih jika berbanding dengan minyak 2T mentah. Ini disebabkan pembentukan PAHs dalam kepekatan semasa pembakaran pada suhu yang tinggi dalam enjin (Rafael 1989). Pemakaian penentu-sumber (UCM, Pr/Ph, CPI, C_{29}/C_{30}, ΣC_{31}-C_{35}/C_{30}, MP/P and H/L-PAH) jelas mencadangkan minyak 2T mentah dan terpakai telah menyumbangkan kepada abuk jalan dan zarah udara melalui eksos motosikal dua lejang pada garisan pencemaran yang tertentu. Kesemua perbandingan penanda alkanes, hopanes dan PAHs di antara minyak 2T mentah, minyak 2T terpakai, endapan sungai, pantai dalam dan luar Selat Melaka, abuk jalan dan zarah udara menunjukkan minyak 2T mentah dan terpakai berpontensi diangkut ke sediment Malaysia melalui abuk jalan dan zarah udara. Sumber PAHs dari minyak 2T kemungkinan discas ke dalam endapan sungai dan persekitaran pantai melalui perjalanan secara sisi dan menegak.

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LIST OF ABBREVIATION/GLOSSARY OF TERMS

An	Anthracene
Acenapth-d_{10}	Acenapthene-deuterated-10
BaA	Benzo[a]Anthracene
BaPy	Benzo[a] pyrene
BeAceph	Benzo[e] acephenantherene
BePy	Benzo[e]Pyrene
BkF	Benzo[k]Fluoranthene
Chry	Chrysene
Chry-d_{12}	Chrysene-deuterated-12
C_{29}/C_{30}	Ratio of 17α ,21β(H)-30-norhopane to 17α ,21β(H)-30-hopane
ΣC_{31}-C_{35}/C_{30}	Ratio of sum of C31 homohopane to C35 homohopane relative to 17α ,21β(H)-30-hopane
CPI	Carbon Preference Index
Cu	Copper
DBahA	Dibenzo[a,h] anthracene
DBT	Dibenzothiophene
DCM	Dichloromethane
Fluo	Fluoranthene
GC/MS	Gas Chromatography Mass Spectrometry
H/L-PAH	High Molecular Weigh PAH/Low Molecular Weight PAH
Hex	Hexane
HMW	High Molecular Weight
IIS	Internal Injection Standard
LABs	Linear Alkyl Benzenes
LMW	Low Molecular Weight
L/H-alkane	Low Molecular Weight Alkane/High Molecular Weight Alkane
MAn-2	2-methylAnthracene
MeOH	Methanol
MECO	Middle East Crude Oil

MP-1	1-methylphenanthrene
MP-2	2-methylphenanthrene
MP-3	3-methylphenanthrene
MP-9	9-methylphenanthrene
MP/P	Methylphenanthrene/Phenanthrene
MPy-1	1-methylPyrene
Napth-d_8	Napthalene-deuterated-8
Na_2SO_4	Sodium Sulphate Anhydrous
PAHs	Polycyclic Aromatic Hydrocarbons
Pery-d_{12}	Perylene-deuterated-12
Phe	Phenanthrene
Phe-d_{10}	Phenanthrene-deuterated-10
Pri	Pristane
Pr/Ph	Pristane/Phytane
Py	Pyrene
SEACO	South East Asian Crude Oil
SIS	Surrogate Internal Standard
T_m/T_s	17α-22, 29,30-trisnorhopane / 18α-22, 29,30-trisnorhopane
UCM	Unresolved Complex Mixture
UPM	Universiti Putra Malaysia
1,4-DCB-d_4	1,4-dichlorobenzene-deuterated-4
2T Oil	Two cycle Lubricating Oil

CHAPTER 1

INTRODUCTION

1.1 General introduction to hydrocarbon pollution

Nowadays, petroleum is a term used as common denotation for crude oil (mineral oil) and natural gas. Then petroleum also is a collective term for hydrocarbon whether solid, liquid or gaseous. Crude oil is a complex mixture of thousands of different chemical components, mainly organic compounds which usually made up about 95% of the crude oil. Before used as fuel or as raw material in the petrochemical industry, crude oil is refined into different fractions. At the refinery, crude oil is separated into light and heavy fractions such as natural gas, raw gasoline, intermediate distillates, heavy distillates and residues, which are then converted into various product, such as petrol, fuels, diesel oil, lubricating oil, waxes and asphalt.

Oil, refined product and pyrogenic hydrocarbons are the most frequently discovered contaminants in the environment (Wang and Fingas, 2003). When crude oil or refined petroleum product are accidentally released to the environment, it will cause oil or hydrocarbon pollution in the environment. When petroleum hydrocarbons introduce to an ecosystem, they alter most of the ecological process and result in long-term chronic effects on marine organisms (Elizabeth, NST, 30 May 2004)).

Sources of oil input to the marine environment are often divided into natural, land-based and sea-based. Natural sources are sources come from natural seeps. Land-based sources are sources discharges of untreated or insufficiently treated of oil from coastal refineries, oil terminal, etc. While sea-based sources are sources comes from accidental oil spills, oil platforms (blowouts), pipelines, operational discharges of oil, dumping of oily waste, ship-related activities (i.e. motor boat with two-stroke engine), emission of gaseous hydrocarbons from tankers and pleasure craft, etc.

Accidental, operational discharge and spills of oil from ships, especially tankers, offshore platforms and pipelines, is the most obvious and visible cause of oil pollution of the marine environment. Table 1.1 shows the current oil spills accidents occurring in the world. Table 1.2 shows the current oil spills accidents occurring in the Straits of Malacca, Malaysia.

However, natural sources (large quantities) and land-based sources account for a large part of the total annual input of oil to the marine environment. An estimated 21 million barrels of oil run into the oceans each year from street run-off, effluent from factories and from ships flushing their tanks (Elizabeth, NST, May 30, 2004).

According to the recent report published in 2002 by National Research Council (NRC) of the U.S. National Academy of Sciences, the total average worldwide annual input of oils to the marine environment is about 1.3 million tones per year.

Table 1.1: Oil Spills Occurring in the World

Year	Name	Accident Place	Cause	Amount (Millions Gallons)
1967	Torrey Canyon	English Channel	Grounding	38.2
1972	Sea Star	Gulf of Oman	Collision	37.9
1977	Hawaiian Patriot	Pacific Ocean	Fire	31.2
1978	Amoco Cadiz	Brittany Coast, France	Grounding	68.7
1979	Ixtoc-1 Oil Well	Gulf of Mexico	Blowout	140
1979	Atlantic Empress	Trinidad and Tobago	Collision	42.7
1980	Well	Southeast of Tripoli	Operations	42.0
1980	Irenes Serenade	Greece	Grounding	36.6
1981	Storage Tanks	Shuaybah, Kuwait	Operation	31.2
1983	Castillo de Bellver	64km off Table Bay, South Africa	Fire	78.5
1989	Exxon Valdez	Prince William Sound, Alaska, USA	Human Error	11.0
1991	Terminals, Tankers, Pipelines, Persian Gulf	Kuwait & Arabian Gulf	Gulf War	240
1992	Oil Well Fergana Valley	Uzbekistan	Operations	88.0
1993	Braer	Shetland Island	Grounding	25.0
1994	Pipeline Kharyaga-Usinsk	Russia	Burst Pipe	30.7
1996	Sea Empress	Wales	Grounding	24.0
1999	Maltese Tanker Erika	South of Brest, France	Fierce Storm	2.8

Source: Oil Spill History (marinegroup.com), 2004

Table 1.2: Oil Spills Accidents Occurring in Strait of Malacca, Malaysia

Year	Name of Ships	Cause	Amount (tons)
1975	SHOW MARU	Grounding	400
1976	DEIGO SILANG	Collision	4000
1981	MT OCEAN TRESURE	Human Error	60
1986	BRIGHT DUKE	Collision	NA*
1993	NAGASAKI SPIRIT	Collision	13300
1997	ANTAI	Grounding	235

Source: Razif Ahmad (1995)
*NA – Not Available

The major categories of sources that contributed to the input are shown in Figure 1.1. It shows that natural seeps and discharge from consumption of oil (land-based source) contribute larger input (up to 80 %) of oil pollution to the worldwide seas. While, Figure 1.2 shows the relative contribution of different sources to the oil pollution in the South China Sea (GESAMP, 1993). 50% of the oil pollution contribution in South China Sea comes from land-based sources (municipal and industrial sources). Furthermore, it has been estimated that on global scale, up to 70% of pollution in the seas originated from land-based sources (UNEP, 1990).

Malaysia is geographically made up of two regions, West Malaysia (peninsular Malaysia) and East Malaysia (Sabah and Sarawak), which are separated by South China Sea. It occupies a total land area of approximately 332, 800 square km and total sea area of approximately 598,540 km (The World Factbook, 2004). Being located between longitude 1°- 7° North and latitude 100° - 120° East, Malaysia is influenced by the equatorial environment and is well outside volcanic, tornado and severe drought belts. Strategically, the country is centrally located to various international air and sea transport and communication routes. The strategic location as a major international shipping lane and the concentration of agriculture, industry and urbanization were predominate on the west coast of Peninsular Malaysia making the Straits of Malacca a great variety of environmental stresses.

Malaysia is having a rapid social-economic growth in the last two decades to achieve a developed country by the year 2020. Therefore, urbanization, industrialization and population are increasing rapidly especially in the capital city

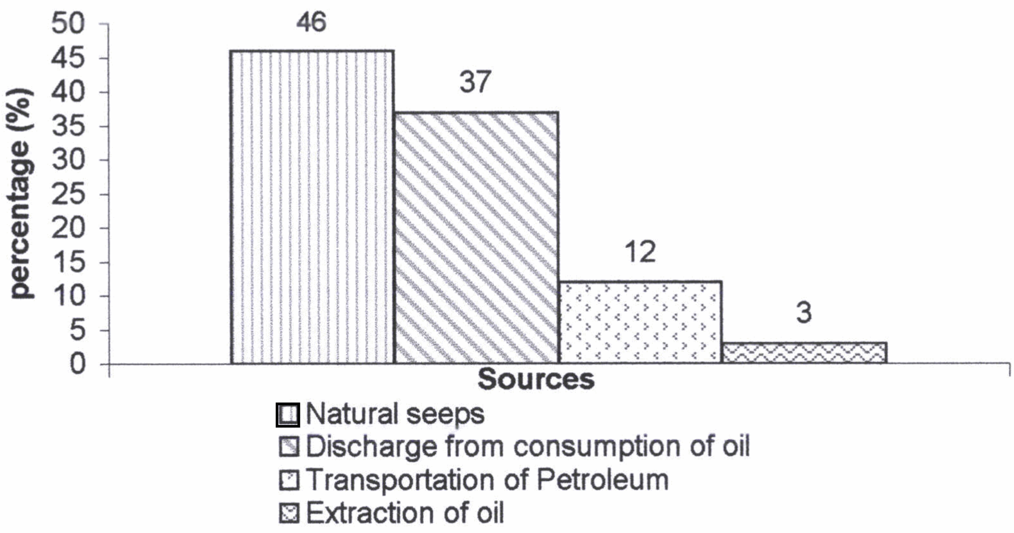

Figure 1.1 : The percentage of the main categories of sources contribute to the total worldwide annual released of petroleum about 1.3 million tones per year (NRC, 2002).

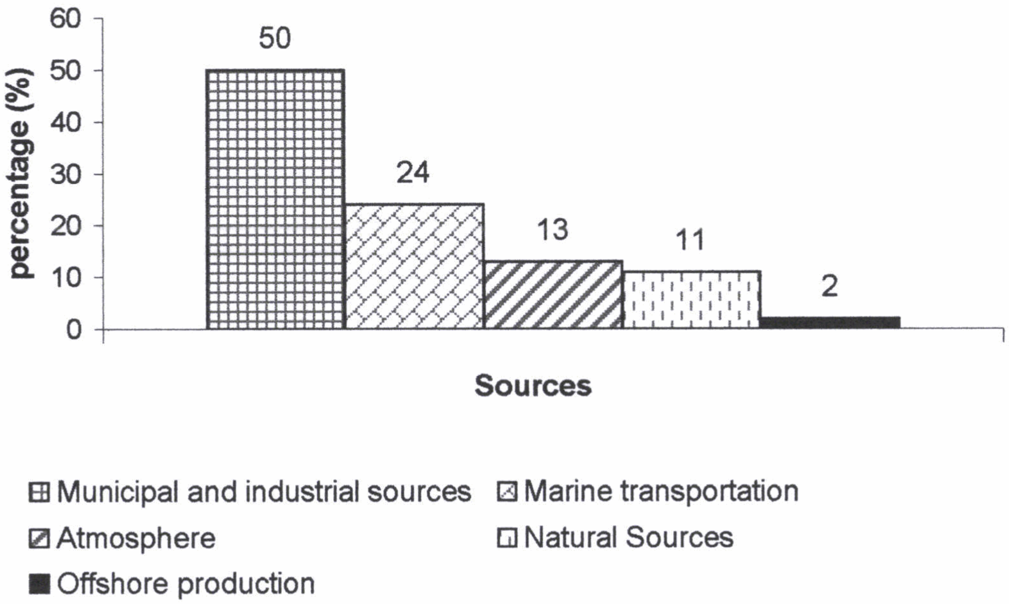

Figure 1.2: Contribution of different sources to oil pollution in the South China Sea (GESAMP, 1993)