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UNIVERSITI PUTRA MALAYSIA

IDENTIFICATION OF SOURCES AND EXTENT OF WEATHERING OF TAR-BALLS FROM THE EASTERN SEABOARD OF PENINSULAR MALAYSIA USING HOPANES AND POLYCYCLIC AROMATIC HYDROCARBONS AS MOLECULAR MARKERS

KUHAN CHANDRU

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By

KUHAN CHANDRU

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

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DEDICATION

To my Appa and Amma, who is my daily reminder of all that is good in this world. Bless you

Abstract of thesis presented to the senate of Universiti Putra Malaysia in fulfillment of the requirement of the degree of Master of Science

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Chairman: Associate Professor Mohamad Pauzi Zakaria, PhD

Faculty: Environmental Studies

Oil pollution is considered to be one of the major contributors to marine pollution. The threat that oil pollution poses to the marine environment is extremely dangerous to its ecosystem. The South China Sea region is blessed with crude oil and has a proven oil reserves. Leaks and contaminations by oil fields are usually contributing factor to oil pollution in the region. However other major contributing factors like tanker accidents and ballast water is also substantial. Once oil is spilled to the ocean, the oil will go through many physical and biological processes like evaporation, emulsification, dissolution and microbial degradation; these initial processes will soon change the physical shape and chemical composition of the oil slick. Tar-balls are generated when emulsification occur on an oil slick, the very last stage of weathering. Tar-balls therefore are considered to be the remnants of an oil spill. These tar-balls will travel the oceans and end up on beaches. This study utilizes diagnostic ratios of n-alkanes, hopanes and polycyclic aromatic hydrocarbons (PAHs) to determine

the origins, distribution and weathering of tar-balls. Hopanes ratios (e.g. C_{29}/C_{30}, and $\Sigma C_{31}-C_{35}/C_{30}$ ratios) were used to identify the origin of tar-balls. The weathering effects were distinguished by using alkanes, namely the Unresolved Complex Mixture (UCM) and low molecular weight/ high molecular weight (L/H) ratios. Similarly, PAHs were also used for the determination of weathering processes undergone by the tar-balls. These diagnostic ratios gave a very strong indication on the origins of tar-balls in this study. For example, 16 out of 17 samples originate from South East Asian Crude Oil (SEACO) with one sample from Merang, Terengganu originating from the North Sea Oil (*Troll*). The TRME-2 sample may have come from a supertanker's ballast water discharge. The second possibility is that the source may have been transported via oceanography. The approaches applied in this study have given more insights on the behavior and weathering of the tar-balls in the marine environment.

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

PENGENALPASTIAN ASAL-USUL DAN LANJUTAN PROSES LULUHAWA BEBOLA TAR DARI PANTAI TIMUR SEMENANJUNG MANALYSIA DENGAN MENGGUNAKAN HOPANA DAN HIDROKARBON AROMATIK SEBAGAI PETANDA MOLEKULAR

Oleh

KUHAN CHANDRU

Oktober 2008

Pengerusi : Profesor Madya Mohamad Pauzi Zakaria

Fakulti : Pengajian Alam Sekitar

Pencemaran minyak merupakan salah satu penyumbang terbesar pencemaran laut. Kesan pencemaran minyak ini sangat berbahaya terhadap ekosistem. Kawasan Laut China Selatan merupakan salah satu kawasan yang tercemar akibat tumpahan minyak mentah. Kebocoran dan pencemaran daripada pelantar minyak merupakan antara faktor penyumbang kepada pencemaran minyak. Walau demikian, beberapa faktor lain seperti kelanggaran kapal tangki minyak dan air ballast dari kapal turut menyumbang kepada masalah ini. Sebaik sahaja tumpahan minyak terjadi, lapisan minyak ini akan melalui pelbagai proses fizikal dan proses biologi seperti penyejatan, emulsifikasi, dissolusi dan degradasi mikrobial. Proses-proses ini akan menyebabkan perubahan bentuk fizikal dan komposisi kimia pada lapisan minyak tersebut. Bebola tar terbentuk apabila proses emulsifikasi terjadi ke atas lapisan minyak iaitu proses yang terakhir luluhawa. Oleh itu, bebola tar telah dikenalpasti sebagai sisa baki selepas tumpahan minyak berlaku. Bebola tar-bebola tar ini

akan melalui sepanjang laut dan akhirnya akan terdampar di persisiran pantai. Kajian ini mengaplikasi pendekatan diagnostic molekul terhadap bebola tar yang terdampar dengan menggunakan nisbah diagnostik alkana, hopana dan hidrokarbon polisiklik beraromatik (HPB) bagi menentukan asal, penyebaran dan proses luluhawa yang berlaku terhadap bebola tar. Nisbah hopana (contohnya C_{29}/C_{30}, dan nisbah $\Sigma C_{31} - C_{35}/C_{30}$) telah digunakan bagi mengenalpasti asal-usul bebola tar. Kesan proses luluhawa telah dikenalpasti dengan menggunakan penanda alkana. Kaedah yang digunakan ialah 'Unresolved Complex Mixture' (UCM) dan nisbah berat molekul; dari nisbah yang rendah dibahagi dengan nisbah yang tinggi (R/T). HAP turut digunakan dalam menentukan proses luluhawa yang berlaku ke atas bebola tar. Dalam kajian ini, pendekatan dari sudut nisbah diagnostic memberikan indikator yang kukuh tentang asal bebola tar. Sebagai contohnya, 16 daripada 17 sampel yang di analisi berasal daripada Minyak Mentah Asia Tenggara (MMAT). Hanya satu sampel daripada Merang Terengganu berasal daripada Minyak Laut Utara (*Troll*), Norway. Sampel TRME-2 mungkin berasal dari air ballast yang dikeluarkan oleh kapal tangki minyak. Keadaan ini juga mungkin terjadi kerana sumber asal tersebut telah dibawa arus melalui sepanjang laut . Pendekatan diagnostic yang telah digunakan dalam kajian ini sedikit sebanyak telah mendekatkan kita terhadap aktiviti bebola tar dalam sekitaran marin dan turut memberi penerangan terhadap proses luluhawa yang terjadi ke atas bebola tar.

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Most especially to my family and friends

And to the higher self, which made all things possible.

I certify that an Examination Committee has met on date of viva to conduct the final examination of Kuhan Chandru on his Master of Science thesis entitled "Identification of origins and the weathering extent of tar-balls using hopanes, alkanes and polycyclic aromatic hydrocarbons (PAHs) as fingerprinting molecular markers" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee Recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirements for the degree of Master of Science.

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DECLARATION

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

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KUHAN CHANDRU

Date

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVATIONS

GC-MS	Gas Chromatography Mass Spectrometry
GC-FID	Gas Chromatography Flame Ionization Detector
L/H	Lower Molecular Weight / Higher Molecular Weight
HMW	Higher Molecular Weight
IIS	Internal Injection Standard
LMW	Lower Molecular Weight
PAHs	Polycyclic Aromatic Hydrocarbons
Pery-d12	Perylene-d12
SIS	Surrogate Internal Standard
R.T	Retention Time

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The human population has hit a milestone of over 6.6 billion on July, 2007. In the East Asian region alone, the population had reached 1.9 billion, and is expected to reach 3 billion by 2015 (PEMSEA, 2003). The increase in population will only mean that the demand for energy will also rise. Currently, 90% of the world's total energy needs comes from fossil fuels with petroleum as a leading source (Griffin, 2007).

Oil pollution has been occurring in the marine environment for the past few decades, notably the Gulf War oil spill in 1991, regarded as the worst spill in history and most recently the *MT Hebei Spirit* oil spill in South Korea on December 2007.

The South China Sea is rich in natural resources such as oil and natural gas. The sea has oil reserves estimated at about 7.5 billion barrels, and oil production is currently around 1.3 million barrels per day (US.EIA, 1999). Despite the economic crisis of 1997 – 1999, the growing pace of Malaysia's economy as a developing nation has contributed many environmental problems. The discovery of petroleum in the east coast of Peninsular Malaysia during the 1950's has enriched its economy. Since then, oil pollution has persistently been affecting the marine environment in Malaysia (Law and Hii, 2006; Zakaria et al, 2000). The potential sources of oil pollution in the East Coast of Peninsular Malaysia is mainly attributed to oil fields in Terengganu as well as accidental spills from supertankers transporting oil from the Western hemisphere to the North East. Although the South China Sea is one of the most important routes for oil tankers, data on the origin of spills on beaches from the Eastern Seaboard of Peninsular Malaysia have not been well documented.

Crude oil originating from Northern Europe and the Middle East are mainly transported via the Straits of Malacca and South China Sea. The contribution of foreign vessels must never be underestimated. Over half of the world's merchant fleet sails through Malaysian waters making it one of the world's busiest international sea lanes. An average of more than 50,000 ships plies the Malaysian waters annually carrying about a quarter of the world's maritime trade, thus making the waters heavily trafficked and potentially accident prone. 39 oil spill incidents from tanker accidents have been documented from 1960 to 1993 in Malaysian and Singaporean waters (Welch, 1994).

Once spilled, oil in the marine environment undergoes various processes. The lower molecular weight (LMW) hydrocarbons will normally evaporate. The heavier compounds such as asphaltenes and resins will partially undergo deposition to the seafloor by gravitational force. The rest of the oil compounds remains on the sea surface and undergoes several physical, biological and chemical processes. These processes will interact along with environmental conditions to form a water-in-oil emulsion (Jordan and Payne, 1980). This emulsion may contain 70-80% water and forms a glue like mass, commonly known as ‘chocolate mousse' (Clark, 2002). After a long period, this mousse will disintegrate into smaller lumps and eventually be transported via sea currents to various places, usually stranding on the coastal beaches. Subsequently, the mousse will then be commonly referred as ‘tar-balls'. Stranded oil residues or tar-balls are generally described as spherical in shape, dark-colored pieces of oil. They can also be described as residue or lumps of oil weathered to a semi-solid or solid state and are usually sticky.

Tar-ball comes from many petroleum sources; they are mostly derived from tanker washing and routine shipping operations (Clark, 2002). Operational losses of fossil fuel hydrocarbon from drilling, petroleum platforms and terminal or tanker derived oil spills is also a main contributor to their occurrence. This is a common phenomenon in areas where there is intense oil exploration and exploitation such as the South China Sea (Asuque, 1991).

The applications of molecular marker were initially used to correlate oil with each other and with their source rocks, thus improving the understanding of reservoir relationship, petroleum migration pathway, and possible new exploration ways in the oil and gas industry (Peters and Moldowan, 1993). However molecular markers application doesn't end there as it was soon introduced as a tool to monitor oil spills incidents and weathered oil residue (tar-balls). The molecular marker approaches have been applied to investigation on some oil spill incident (e.g., Barakat et al,1999; Bence et al, 1996; Boehm et al, 2001; Kvenvolden et al, 1993; Zakaria et al, 2000). Analysis and characteristics of stranded tar-balls are numerous (e.g. Thingstad and Pengerud, 1983; Kvenvolden et al,1993; Bae et al, 2003; Wang et al, 1995; Zakaria et al, 2000; Zakaria et al, 2001). In Malaysia few studies on tar-balls have been conducted notably by Zakaria et al (2001); Yong (2002), Johnson (2003) and lately Chandru (2005).

Tar-balls were used in this study because of their oil spill origins and its accessibility of sampling from beaches. This study uses tar-balls randomly collected from the east coast of Peninsular Malaysia facing South China Sea as a target location, because of the major petroleum activity in that region. The study discusses the origins of tar-ball collected from the East Coast of Peninsular Malaysia using hopanes as origin identifier. Alkanes, hopanes and PAHs were also used to co-respond the extent of weathering in the samples.

1.2 Significance of Study

Identifying spilled oil origins using tar balls and linking them to a known source is extremely important in settling questions of environmental impact and legal liabilities for both government agencies and the oil and gas industry.

1.3 Research Objectives

i) To identify the origins of tar-balls by using hopanes as a molecular marker

ii) To evaluate the weathering of tar-balls using alkanes and PAHs

CHAPTER 2

LITERATURE REVIEW

2.1 Malaysia

Malaysia is a nation known for its natural imputes and ethnic complexity. She consists of West Malaysia on the southern limb of the South East Asian mainland; and East Malaysia, comprising two states; Sabah and Sarawak on the island of Borneo. West Malaysia borders Thailand to the north. Northern and central West Malaysia is predominantly craggy while the eastern corner of the peninsular is characterized by broad river valleys and extensive coastal plains. The South China Sea, the Straits of Malacca and the narrow Tebrau straits enclose the landmass of Peninsular Malaysia.

2.2 East Coast of Peninsular Malaysia

The state of Kelantan, Terengganu, Pahang and Eastern Johor describes the constituent of the East Coast facing the South China Sea. Fishing, rice cultivation and also timber harvesting is part of the east coast economy. The expansion of offshore oil and gas production during the 1980s and 1990s has led to the development of onshore facilities such as refineries, pipelines, and shipping terminals most notably in state of Terengganu. Recently, natural gas was discovered in Kelantan, which is yet to be exploited.

2.3 Meteorology

The characteristic features of the climate of Malaysia are uniform temperature, high humidity and copious rainfall and they arise mainly from the maritime exposure of the country. The climate of the east of Peninsular Malaysia is controlled by seasonal monsoon winds.

Four seasons can be distinguished, namely, the southwest monsoon, northeast monsoon and two shorter inter-monsoon seasons (Malaysian Meteorology Service, 2003). The shorter inter-monsoon seasons last about four to seven weeks in April and October (Chua, 1984). Air mass descends over the cold Asian continent during winter raising the formation of a high atmospheric pressure system. At the same time, air mass rises over the warm Australian continent. A low atmospheric system is formed. These differences in the atmospheric pressure system in unison with Coriolis Effect generate a northeast wind in the gulf of Thailand and along the east coast of Peninsular Malaysia from November to March. This is generally known as the northeast monsoon (Saadon et al, 1999)

In the Northern summer, in the Asian continent, the reciprocal is true. A high and low atmospheric pressure system over Australia and the Asian continents respectively enhanced. As the consequence of this a southwest wind prevails over the Gulf of Thailand and Peninsular Malaysia from May to September. This is known as the southwest monsoonal period (Saadon et al, 1999). The east coast usually undergoes heavy rain falls and strong steady winds during