UNIVERSITI PUTRA MALAYSIA

DISTRIBUTION AND SOURCES OF OIL POLLUTION USING TAR BALLS AS INDICATOR IN NORTHEAST SUMATRA, INDONESIA VIA FINGERPRINTING TECHNIQUES

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2009

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By

SOFIA ANITA

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

April 2009

“Yes, We are able to put together in perfect order the very tips of his fingers”

(Qur’an 75:3-4)

To my husband, son, father and mother, sisters who are to be patient for praying and waiting for me to complete my study

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirements for the degree of Doctor of Philosophy

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April 2009

Chairman : Associate Professor Mohamad Pauzi bin Zakaria, PhD

Faculty : Environmental Studies

Marine pollution due to oil spills in Northeast Sumatra, Indonesia had been started since Showa Maru spilled Middle East crude oil in 1975 and has become one of more severe environmental problem for this area and the Malacca Straits. The most polluted locations chosen were Aceh, North Sumatra, Riau and Riau Archipelago. This study presents fingerprinting and data interpretation used to characterize crude oils and tar balls in the Northeast Sumatra, Indonesia and a case study in of unknown spilled oil from Dumai coast. A variety of diagnostic ratios of molecular markers (i.e. n-alkanes, hopanes and polycyclic aromatic hydrocarbons; PAHs) were chosen to fingerprint them. The instrument used in this study was Gas Chromatography-Flame Ion Detector and Gas Chromatograph (GC) interfaced with Mass Selective Detector (MSD). Based on the objectives, the results reveal the following: (1) the origin of Minas, Duri, and Dumai crude oils is characterized by the diagnostic ratios of petroleum (i.e. unresolved complex

mixtures, Pr/Ph ratio, carbon preference index (CPI), Tm/Ts ratio, the source identifiers of C_{29}/C_{30} and ΣC_{31}-C_{35}/C_{30} ratio, MP/P ratio). The crudes were very likely due to the same basin, i.e., Central Sumatran Basin; (2) each tar ball has a different fingerprint and compound distribution. The tar balls found in Northeast Sumatra coasts are significantly different in the concentrations of PAHs. The ranges of polycyclic aromatic hydrocarbon levels (PAHs) vary from those low to very high petroleum contamination. Riau Archipelago coasts are found to be severe contaminated by PAHs originated from the spilled oil. The percentage of tar balls showed South East Asia Crude Oil, SEACO signature category to be 32%, Middle East Crude Oil, MECO 60%, and 8% from unknown sources (Bagan Siapi-Api and Batam tar balls). It is concluded that the sampling area in Northeast Sumatra might received spillage of waste petroleum product or used lubricating oil from multiple sources; (3) the spilled oil identified is the same as Dumai crude oil from Pertamina Refinery. The spills might be come from Pertamina Dumai refinery wash tank which took place in 2007.

Keywords: Fingerprinting, Oil spill, PAHs, n-Alkanes, Hopanes

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

TABURAN DAN SUMBER PENCEMARAN MINYAK MENGGUNAKAN BEBOLA TAR SEBAGAI PENENTU UKUR DI PANTAI TIMUR SUMATRA, INDONESIA MELALUI TEKNIK CAP JARI

Oleh

SOFIA ANITA

April 2009

Pengerusi : Prof. Madya Dr. Mohamad Pauzi bin Zakaria

Fakulti : Pengajian Alam Sekitar

Pencemaran laut yang berpunca dari tumpahan minyak telah bermula di Indonesia setelah tumpahnya minyak dari kapal tanker Showa Maru yang membawa minyak dari Negara Arab pada tahun 1975. Semenjak itu isu pencemaran ini menjadi salah satu masalah besar di kawasan persekitaran Indonesia dan juga Selat Malaka. Kawasan yang sangat tercemar telah dipilih iaitu Aceh, Sumatra Utara, Riau dan Kepulauan Riau untuk menentukan pencirian dan mengenal pasti sumber pencemaran tersebut. Kajian ini mengemukakan pencirian dan penggunaan teknik tafsiran data untuk mengenal pasti komposisi kimia dalam minyak mentah dan bebola tar di Pantai Timur Sumatra, Indonesia, dan sebuah kajian kes tentang tumpahan minyak yang terjadi di pantai Dumai. Pelbagai nisbah diagnostik penanda molekul (seperti, n-alkana, hopana, dan hidrokarbon polisiklik aromatik) telah digunakan dalam kajian ini. Instrumen yang digunakan dalam kajian ini ialah Gas Khromatografi yang digandingkan dengan Detektor Jisim terpilih dan Kromatografi Gas-Detektor Ion Nyalaan. Berazaskan

daripada objektif, hasil kajian ini menunjukkan bahawa: (1) sumber asal minyak mentah dari Minas, Duri, dan Dumai ini dicirikan dengan menggunakan nisbah diagnostik petroleum (iaitu., UCM, nisbah Pr/Ph, CPI, Tm/Ts, pengenal pasti sumber C_{29}/C_{30} and ΣC_{31}-C_{35}/C_{30}, nisbah MP/P) adalah hampir sama; (2) setiap bebola tar mempunyai cap jari dan taburan sebatian yang berbeza. Pencemaran PAHs di Pantai Timur Sumatra adalah signifikan antara satu kawasan dengan yang lainnya. Julat pencemaran PAHs dari petroleum adalah pelbagai mulai dari julat rendah sehingga julat yang paling tinggi. Pantai Kepulauan Riau dikenalpasti sebagai pantai yang paling tercemar dengan PAHs yang berasal dari tumpahan minyak. Peratusan bebola tar menunjukkan tumpahan minyak yang berasal dari SEACO ialah 32%, MECO ialah 60%, dan 8% berasal dari jenis minyak mentah yang tidak dikenalpasti asal-usulnya (bebola tar yang berasal dari Bagan Siapi-Api and Batam). Simpulannya bahawa kawasan pensampelan di Pantai Timur Sumatra telah menerima limpahan kumbahan petroleum luaran atau minyak pelincir dari pelbagai sumber; (3) tumpahan minyak yang terjadi di Pantai Dumai dikenalpasti berasal dari minyak mentah Dumai yang dimiliki oleh Kilang Pertamina. Tumpahan ini kemungkinan berpunca daripada kerja-kerja mencuci tangki-tangki kilang Pertamina Dumai yang dilakukan pada tahun 2007.

Kata kunci: Cap jari, Tumpahan minyak, Hidrokarbon Polisiklik Aromatik, n-Alkana, Hopana

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I certify that a Thesis Examination Committee has met on 21 April 2009 to conduct the final examination of Sofia Anita on her thesis entitled "Distribution and Sources of Oil Pollution Using Tar Balls as Indicator in Northeast Sumatra, Indonesia Via Fingerprinting Techniques" in accordance with the Universities and University College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that student be awarded the Doctor of Philosophy.

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Date: 11 September 2009

DECLARATION

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

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SOFIA ANITA

Date: 21 April 2009

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LIST OF ABBREVIATIONS

An	Anthracene
Acenaph-d_{10}	Acenaphthene-deuterated-10
BaA	Benzo[a]Anthracene
BaPy	Benzo[a]Pyrene
BeAceph	Benzo[e]Acephenanthrene
BePy	Benzo[e]Pyrene
BkFluo	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
Σ C_{31}-C_{35}/C_{30}	Ratio of sum C_{31} homohopane to C_{35} homohopane relative to 17α,21β(H)-30-hopane
CPI	Carbon Preference Index
Db(a,h)A	Dibenzo[a,h]Anthracene
DBT	Dibenzothiophene
DCM	Dichloromethane
dry wt.	Dry weight
EI	Electron Impact
FID	Flame Ionization Detector
Fluo	Fluoanthene
GC-MS	Gas Chromatography-Mass Spectrometry
H/L PAH	Low Molecular Weight PAH/High Molecular Weight PAH

Hex	Hexane
IIS	Internal Injection Standard
LNG	Liquid Natural Gas
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-Methyl Pyrene
Napth-d_8	Napthalene-deuterated-8
Na_2SO_4	Sodium sulphate anhydrous
PAHs	Polycyclic Aromatic Hydrocarbons
Pery- d_{12}	Perylene-deuterated-12
PFTBA	Perfluorobutylamine
Phen	Phenanthrene
Phen-d_{10}	Phenanthrene-deuterated-10
ppm	part per-million
ppt	part per-trillion
Pr/Ph	Pristane/Phytane
Py	Pyrene
SEACO	South East Asian Crude Oil
SIS	Surrogate Internal Standard

tcf	Trillion cubic feet
Tm/Ts	17α-22,29,30-trisnorhopane/18α-22,29,30-trisnorhopane
UCM	Unresolved Complex Mixture
UPM	Universiti Putra Malaysia

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Oil pollution in marine environment originates from oil tanker disasters, offshore oil wells, harbors and marine terminals, and land sources. They are associated with the release of hydrocarbon in the oceans which can alter ecological process and result in long-term chronic impacts on the local environment. Oil spill can affect natural ecosystems and hence directly affect the livelihood of the population in the area such as fisheries coastal habitats, contaminate shellfish beds and coat recreational beaches. Sources of oil input to the marine environment are divided into 3 categories: land-based, sea-based, and natural sources. A major input is number of shipping spills (Wang et al, 2006). The spilled oil mixed with water to form an emulsion. The oil patches stretch and tear into smaller pieces called tar balls.

Several studies of oil pollution in term of tar balls have been done elsewhere. The fates and effects crude oils in the USA and Bermuda were discovered by Blumer et al (1973). Climate differences between Martha's Vineyard and Bermuda have only a minor effect on the degradation rate of weathering. At Bermuda, a physical disintegration of the weathering crust provides a larger surface area and responsible for some acceleration in evaporation rate. It also found that the microbial utilization of the n-alkanes and other physical and chemical changes involved in weathering