CONCENTRATION OF SELECTED HYDROCARBON COMPOUNDS IN TROPICAL COASTAL WATERS OF SABAH.

KOGILA VANI ANNAMMALA

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Disahkan oleh;

Penulis : KOGILA VANI ANNAMMALA
Alamat:
515, Lorong Pipit Uban,
Taman Happy Garden
88450 Kota Kinabalu,
Sabah.

TANDATANGAN PUSTAKAWAN

Penyelia: Prof Dr Mohd Harun Abdullah

Penyelia bersama: Prof Dr Mazlin Mokhtar

Tarikh: 2008

Catatan: @ Tesis dimaksudkan SEBAGAI TESIS Ijazah Doktor falsafah dan Sarjana secara penyelidikan atau desertasi bagi pengajian secara kerja kursus dan penyelidikan, atau laporan Projek Sarjana Muda (LPSM)

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KOGILA VANI ANNAMMALA
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1. SUPERVISOR
(Prof Dr Mohd Harun Abdullah) ____________________

2. CO-SUPERVISOR
(Prof Dr Mazlin Mokhtar) ____________________

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ABSTRACT

CONCENTRATION OF SELECTED HYDROCARBON COMPOUNDS IN TROPICAL COASTAL WATERS OF SABAH

The main focus of this research is to provide a summary of the levels of contamination from oil and grease, 16 USEPA priority Polyaromatic hydrocarbons (PAHs) and 32 types of Volatile Organic Compounds (VOC) including Benzene, Ethylbenzene, Toluene and Total Xylenes (BTEX) compounds. Six sites were chosen and these sites includes three main small islands which known as the Tunku Abdul Rahman Park Islands namely Manukan, Mamutik and Sapi. Two other locations near shipping area which are Kota Kinabalu Port (also known as Jesselton Port) and two selected locations in Labuan Island. The level of oil and grease contamination are found to vary from 5.8 mg/L to 40.62 mg/L in December and 6.64 mg/L to 130.23 mg/L during February which is during low tide. The increase in contamination levels indicated the positive relation to tidal effect and boating activity near to the sampling location. While the Total PAHs in these small islands ranged from 0.55 µg/ml to 1.16 µg/ml, 0.46 µg/ml to 1.35 µg/ml in Labuan and 0.49 µg/ml to 0.53 µg/ml in Port Kota Kinabalu. Low levels of total PAHs were detected to be present in all study area during the observation period. Sediment samples did not contain high concentration of PAHs. It was noted that sandy nature of sediment at these islands may contribute to the low value of PAHs detected. The total VOCs in all sampled island showed almost similar level, ranged 3.72 to 8.33 µg/L, with non dominating compound to present. In Labuan the concentrations varied from 9.17 to 15.47 µg/L during December and 2.54 to 4.36 µg/L in February. Predominant compound detected was 2-Butanone also known as Methyl Ethyl Ketone (MEK) which is mainly used in paints and other coatings. It is also released to air by car and truck exhausts. This component was detected to be highly present in Kota Kinabalu Port which is by the main road heading towards the main city Kota Kinabalu. Apart from MEK, chloroform was also detected to be present. Concentration detected ranged from 8.80 to 12.23 µg/L for MEK and 28.73 to 32.5 µg/L respectively for chloroform in Port KK. Main contribution of the contaminant in the study area is directly linked to the activities in the research area which are boating and shipping activity.

Keywords: Oil and Grease, Polyaromatic Hydrocarbons (PAHs), Volatile Organic Compounds (VOCs), BTEX.

ABSTRAK

Fokus utama penyelidikan ini adalah untuk mengkaji tahap pencemaran minyak dan gris, 16 komponen prioriti Poliaromatik Hidrokarbon (PAHs) yang tersenarai dalam panduan USEPA, 32 jenis komponen organik mudah meruap (Volatile Organic Compounds, (VOCs)) termasuk Benzene,Toulene, Etil-benzene dan jumlah Xylene (BTEX) di tiga pulau dikenali sebagai Taman Tunku Abdul Rahman; iaitu Pulau Manukan, Pulau Mamutik dan Pulau Sapi. Lokasi kajian turut meliputi Pelabuhan Kota Kinabalu yang juga dikenali sebagai Pelabuhan Jesselton, dan dua lokasi terpilih di Pulau Labuan. Kadar pencemaran minyak dan gris dalam julat 5.8 hingga 40.62 mg/L pada bulan Disember dan 6.64 hingga 130.23 mg/L pada bulan Febuari semasa air surut. Ini menunjukkan terdapat hubungan positif antara kadar pencemaran dengan kesan pasang surut air. Aktiviti yang dijalankan di kawasan kajian iaitu aktiviti bot laju saling berkait dengan tahap penceman minyak dan gris. Manakala pencemaran jumlah PAHs di pulau kecil adalah dalam julat 0.55 hingga 1.16 µg/ml, 0.46 hingga 1.35 µg/ml di pulau Labuan dan 0.49 hingga 0.53 µg/ml di Pelabuhan Kota Kinabalu. Kepekatan PAHs yang rendah telah dikesan sepanjang pemonitoran dijalankan. Jumlah VOCs di semua pulau kecil yang dikaji menunjukkan tahap kontaminasi dalam julat kepekatan yang hampir sama iaitu dari 3.72 hingga 8.33 µg/L. Tiada komponen VOCs yang dominan hadir. Di Pulau Labuan kadar kepekatan pencemaran VOCs varian dari 9.17 hingga 15.47 µg/L pada bulan Disember dan 2.54 hingga 4.36 µg/L di bulan Februari. Satu lagi komponen dominan yang turut dikesan adalah 2-Butanone juga dikenali sebagai Metil Etil Keton (MEK). Komponen ini banyak digunakan dalam cat dan penyalut cat, MEK juga dibebaskan ke atmosfera oleh ekzos kenderaan. Di Pelabuhan, Kloroform yang merupakan sejenis reagen dan pelarut merbahaya telah dikesan hadir dalam kepekatan yang tinggi. Julat antara 8.80 hingga 12.23 µg/L dan 28.73 hingga 32.5 µg/L dikesan bagi 2-Butanone dan Kloroform di Pelabuhan Kota Kinabalu. Penyumbang utama bahan pencemar di lokasi kajian adalah berkaitan dengan aktiviti kapal laut dan pengangkutan laut di lokasi kajian.

Kata kunci: Minyak dan Gris, Poliaromatik Hidrokarbon (PAHs), Bahan organik mudah meruap (VOCs), BTEX.

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ABBREVIATIONS

An	Anthracene
ASTDR	Agency for Toxic Substances and Disease Registry
BaA	Benzo [a] anthracene
BaP	Benzo [a] pyrene
BbF	Benzo [b] pyrene
BFB	Bromoflorobenzene
BkF	Benzo [k] Fluoranthene
BPE	Benzo [g,h,i] perylene
BTEX	Benzene, toluene, ethylbenzene, xylenes
CA	Chloroethane
CCCs	Calibration Check Compounds
CED	Council of the European Communities
Chr	Chrysene
CNS	Central Nervous System
DHHS	Department of Health and Human Services
DMBA	7,12-dimethlybenzanthracene
EtBENZ	Ethyl benzene
FDA	United States Food and Drug Administration
Flu	Fluranthene
FLU/PYR	Fluoranthene/pyrene
INWQS	Interim National Water Quality Standard
IMO	International Maritime Organization
IS	Internal Standards
LCS	Laboratory Control Standard
MCL	Maximum Contaminant Level
MEK	Methyl Ethyl Ketone
MPEC	The Marine Environmental Protection Committee
MS	Matrix spike
MSD	Matrix spike duplicate
PAH(s)	Poly aromatic hydrocarbon (s)
PAR	Precision and Recovery
Phe	Phenanthrane
PHE/ANT	Phenanthrene/anthracene
Py	Pyrene
QA	Quality Assurance
QC	Quality Control
SA	Spike added or concentration of the standard added
SC	Sample concentration (Pre-determined)
SPCCs	System Performance check Compounds
SR	Surrogate
SSC	Spiked sample concentration
TCE	1,1,2-trichloroethene
USEPA	United States Environmental Protection Agency
VOC(s)	Volatile organic compound(s)

CHAPTER 1

INTRODUCTION

In this chapter a series of topics were considered which deal with the background of the study, study problem, limitations of the study and the outflow of the thesis is presented.

1.1 Background of the Study

Coastal environment is a vast sparsely populated wilderness (Rovinsky *et al.,* 1995). These environments are susceptible to man-induced stresses, such as pollution and climate changes. Despite its daunting size, some regions are beginning to display signs of degradation. Decreasing plant biodiversity and increasing heavy metal contamination in soil, rivers and precipitation are some of the consequences of resource-exploitation (Walker *et al.,* 2006).

Prodigious amount of crude oil are extracted from earth every year and moved across the oceans. It is estimated that about 0.1 % of the total oil extracted ends up in the marine systems each year, accidental spills are the most spectacular. Petroleum hydrocarbons also enter the coastal marine environment as exhaust particulates, fuel spills, urban runoffs contaminated with crankcase oil and the byproducts of biomass combustion (Thomas, 1984; Payal, 2002). The more volatile compounds evaporate and some are photo-oxidized. The less volatile compounds consist of poorly water soluble hydrocarbons, which ends up as weathered material and adsorb onto the coastal sediments (Karen, 1990).

Organization for Economic Co-operation and Development (OECD), estimates that there are greater than 110 000 manmade chemicals still in commercial use, with hundreds being added to the list each year (OECD, 1999; Tebutt, 1992). The major concerns are those compounds which are both toxic and stable in the environment with long term lethal combination. These problematic compounds include many pesticides, polychlorinated hydrocarbons, organic solvents and polyaromatic hydrocarbons (PAHs) (Chiou *et al.,* 1998).

According to the data provided by Malaysian Department of Environmental, Malaysia has a coastline measuring 4,675km, inclusive of Peninsular Malaysia and the States of Sabah and Sarawak, endowing more than 100 coastal islands whose marine environments are generally rich in natural resources. (www.doe.gov.my; Michael, 1991). Although Malaysia has taken substantial steps forward in recent years to ensure greater protection of its wildlife, endangered species and their habitat, much more can be done to further those environmental initiatives in the future. Malaysia continues to face considerable challenges in its attempt to balance its goals of increasing development and wealth with environmental protection. In addition many of the environmental challenges facing Malaysia are trans-boundary or global in nature including coastal marine resource depletion. With this respect, coastal marine water quality monitoring was started in 1978 for Peninsular Malaysia and 1985 in Sabah and Sarawak.

Monitoring has been identified as an effective way to provide early warning signs, identify harmful trends by determining a pollutants origin, pathway and destination. Monitoring marine coastal environmental pollution is a very vast topic to be covered. The main focus of this study is to provide a summary of the levels of oil and grease, Polycyclic Aromatic Hydrocarbons (PAHs), BTEX and 28 other common Volatile Organic Compounds (VOCs) found in the tropical coastal waters of Sabah, besides identifying its unanticipated impacts and an essential tool towards successful environmental auditing. Total of six sites were chosen for this study which includes three small islands in the Tunku Abdul Rahman Park namely; Manukan, Mamutik and Sapi Island, Kota Kinabalu main Port (also known as Jesselton Port) and two other selected locations in Labuan Island.

PAHs, VOCs have been reported to have implications for human and ecosystem health. Furthermore, analysis of spatial and temporal trends in this field are lacking specifically in Sabah coastal area (Soh & Abdullah, 2007). Thus the main focus of this study would be towards identifying the occurrence and source of pollutants of the mentioned parameters which will be elaborated in detail in the next part.

1.2 Theoretical Introduction on Monitored Parameters

Monitored parameters include physical and chemical characteristics of water. The three main parameters to be analyzed are oil and grease, PAHs, BTEX and 28 VOCs, besides in-situ readings such as temperature and pH.

1.2.1 Oil and grease

One of the most visible forms of ocean pollution is oil spill. Once in the marine environment it is dispersed across the ocean surface by wind, waves and currents as an oil slick (Ahmad Badri, 1987; APHA, 1985). Oil pollution causes extensive ecological and environmental damage. The toxic chemicals leach out from the oil and contaminate the surrounding water, poisoning sea life around and below. Park, (1997), mentioned that light oils can float freely on the ocean surface and be dispersed over a wide area whereas heavy oils form globules which sink to the bed and poisons plants and marine animals.

When an oil slick drifts or is blown towards the coast it can seriously pollute the shore, fouling beaches and affecting shore life (Basnyat *et al.,* 1999; Bannerman *et al.,* 1993). According to the Malaysian Interim Marine Water Quality Standard, Malaysia allows the concentration of oil and grease below 0.04 mg/L. While the ASEAN Marine water Quality criteria for oil and grease in the marine environment is 50 mg/L (www.doe.gov.my). Oil and grease contamination is a general analysis which includes detection of contaminant from hydrocarbon compound. Arising issues lately are related to petrogenic and pyrogenic contamination of PAHs.

1.2.2 Polyaromatic Hydrocarbons (PAHs)

PAHs compounds are chemical compounds that consist of fused aromatic rings. This compound can originate from point source pollutants (eg; oil spill) and non point source (eg; atmospheric deposition). PAHs are considered as one of the most widespread organic compounds based pollutants. Focuses on existence of PAHs in the environment are increasing due to their widespread occurrence, mutagenic, carcinogenic and tetratogenic effects. The physical properties and chemical structures of the most common PAHs are presented in Figure 1.1

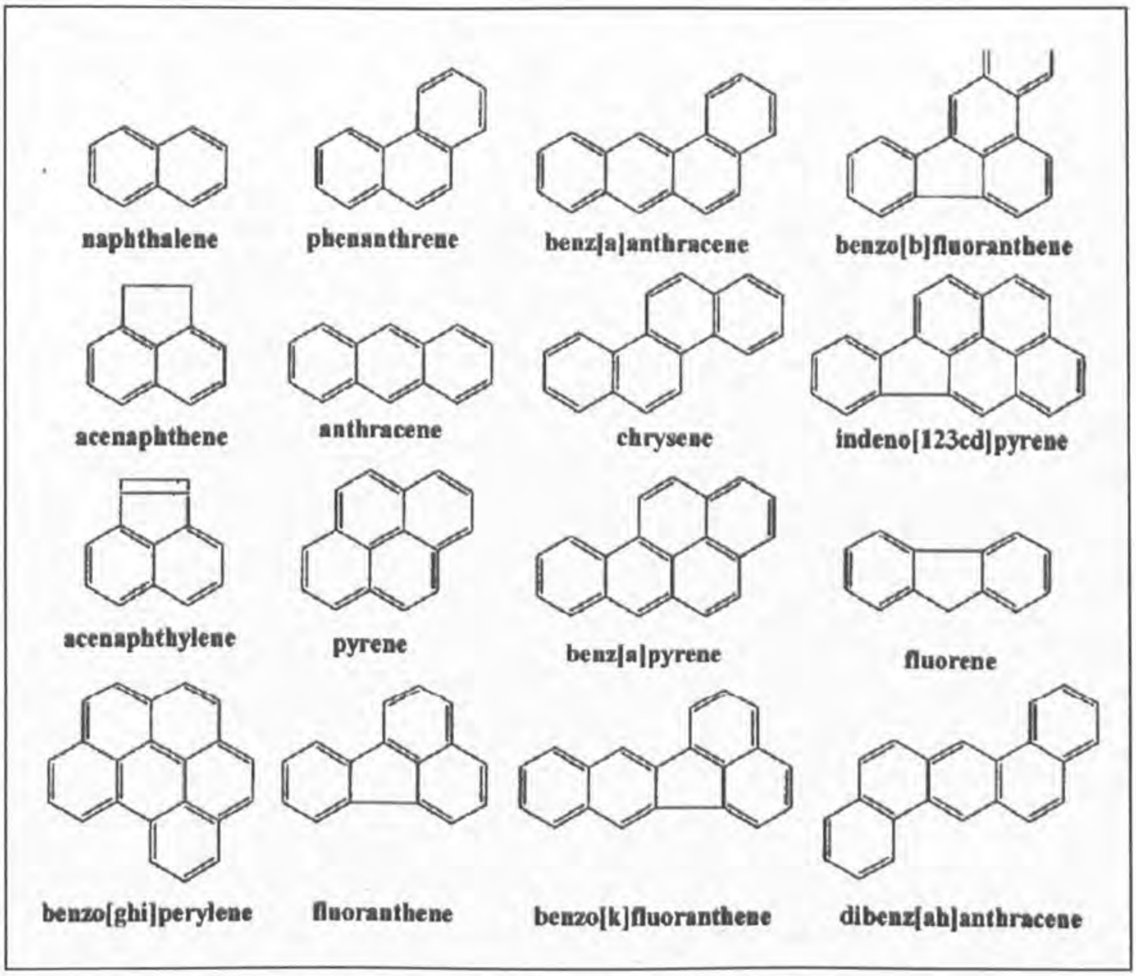

Figure 1.1: The chemical structure of the most common PAHs (Buell & Girard, 1994)

PAHs may result from both organic matter digenesis and anthropogenic processes which will be elaborated in detail in Chapter three. PAHs are known to be carcinogenic, mutagenic and toxic to the marine environment. The toxicity of PAHs is increased by several orders of magnitude when combined with exposure to the ultraviolet portion of sunlight as mentioned by Peachey and Crosby, (1996). PAHs constitute a diverse class of organic compounds consisting two or more benzene rings fused in linear, angular or cluster orientation. Table 1.1 presents all the compounds monitored in this study. Non aromatic organic compounds fused together, such as BTEX and other VOCs compounds also contributed by oil and grease pollutant.

Table 1.1: Physical and Chemical properties of the most common PAHs

PAH	Molecular weight	Aqueous Solubility at 30^0C [mgL^{-1}]	Vapour Pressure [Nm^{-2} at $20\ ^0C$]	Log octanol/ water partition coefficient
Napthalene	128	31.7	6.56	3.37
Acenapthylene	152	3.93	3.87	4.07
Acenapthene	154	3.47	2.67	4.33
Fluorene	166	1.98	1.73	4.18
Phenanthrene	178	1.29	9.07×10^{-2}	4.46
Anthracene	178	7.30×10^{-2}	2.61×10^{-2}	4.45
Pyrene	202	1.35×10^{-1}	8.00×10^{-4}	5.32
Fluoranthene	202	2.60×10^{-1}	9.11×10^{-5}	5.33
Benz [a] anthracene	228	4.00×10^{-2}	6.67×10^{-7}	5.61
Chrysene	228	2.00×10^{-3}	8.40×10^{-5}	5.61
Benz [a] pyrene	252	4.00×10^{-3}	6.67×10^{-7}	6.04
Benzo [k] fluoranthene	252	1.20×10^{-3}	6.67×10^{-5}	6.57
Benzo [b] fluoranthene	252	5.50×10^{-4}	6.67×10^{-5}	6.84
Indeno [123cd] pyrene	276	6.20×10^{-2}	1.33×10^{-8}	7.66
Benzo [ghi] perylene	276	2.60×10^{-4}	1.33×10^{-8}	7.23
Dibenz [ah] anthracene	276	5.00×10^{-4}	1.33×10^{-8}	5.97

Source: Jensen, 2003.

1.2.3 Volatile Organic Compounds (VOCs)

Volatile Organic Compounds (VOCs) are organic compounds that have high vapour pressure under normal conditions, significantly vaporize and enter the atmosphere. The term VOC is also occasionally used as an abbreviation, especially in biological context for 'Volatile Organic Carbons' (Patnaik, 2006). Most common sources of VOCs include paint thinners, dry-cleaning solvents, and some constituents of petroleum fuels such as gasoline and natural gas. Another significant source of VOCs from crude oil tanking (Ramsden, 2006; Schneitzer, 2002).

U.S Environmental Protection Agency (USEPA), defines VOCs as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate which participates in atmospheric photochemical reactions. The European Union (EU) defines VOCs based on evaporation into the atmosphere, rather than reactivity.

Table 1.2 shows some of the VOCs that can be found in water. This study focuses on priority 32 of the listed compounds including BTEX which will be elaborated in detail in Chapter three. Transportation activities, vaporized gasoline, fire are example sources of VOCs to the environment (Khalik Wood *et al.*, 2004)

Common acute symptoms of VOC exposure include eye irritation, nose and throat irritation, headaches, vomiting, allergic skin reaction and visual disorders (UNEP, 1993). Long-term exposure to VOCs may cause serious conditions which include cancer, damage to the liver, kidney and central nervous system. VOCs can enter the water source from atmospheric decomposition during rainfall (Soh & Abdullah, 2007).

This work is similar to that carried out by Huybrechts *et al.,* (1995) to assess the concentrations of priority VOCs. Compounds were selected from the 'Priority Lists' established at the Third International Conference on the protection of the North Sea.

Table 1.2 : Volatile Organic Chemical (VOCs) List.

VOLATILE ORGANIC CHEMICALS (VOCs) LIST		
Alachor	Atrazine	Benzene
Bromodichloromethane	Bromoform	Carbofuran
Chloropicrin	2,4- D	Dibromochloromethane (TTHM)
Dibromochloropropane (DBCP)	o-Dichlobenzene	p-Dichlorobenzene
1,2- Dichloroethane	1,1-Dichloethylene	Cis-1,2-Dichloethylene
Trans-1,2-Dichloroethylene	1,2-Dichloropropane	Cis-1,3-Dichloropylene
Dinoseb	Endrin	Ethylbenzene
Ethylene Dibromide (EDB)	Halocetonitriles (HAN): Bromochloroacetonitrile Dibromoacetonitrile Dichloroacetonitrile Trichloroacetonitrile	Haloketones (KH): 1,1-dichloro-2-propanone 1,1,1-trichloro-2-propanone
Heptachlor	Heptachlor Expoxide	Hexachlorobutadiene
Hexachlorocyclopentadiene	Lindane	Methoxychlor
Pentachlorophenol	Simazine	Styrene
1,1,2,2-Tetrachloethane	Tetrachloroethylene	Tribromoacetic acid
Toluene	2,4,5-TP(silver)	1,2,4-trichlorobenzene
1,1,1-trichloroethane	1,1,2- Trichloroethane	Trichloroethylene
Trihalomethanes (surrogate chemical)	Xylenes (total)	
Volatile Organic Chemicals (VOCs) are contaminants that may be found in drinking water supplies across the nation. VOCs are those organic chemicals (pesticides, herbicides and other chemicals) that are 'readily vaporizable at a relatively low Temperature (Webster's Collegiate Dictionary). With no visible characteristics, smell or taste, VOCs are virtually undetectable in drinking ware by the consumer. The only way to know if your water has VOCs is to have it testes or to obtain Test results from local public water supplier. VOCs are often toxic and pose intimidating health risks.		

Source: Multi-Pure Drinking Water System, 2007

REFFERENCE

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