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SPATIAL DISTRIBUTION AND SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SURFACE SEDIMENT OF LANGAT RIVER, SELANGOR, MALAYSIA

NURUL AFIQAH BINTI MOHAMD TAHIR

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By

NURUL AFIQAH BINTI MOHAMD TAHIR

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

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

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November 2012

Chairman: Professor Mohamad Pauzi Zakaria, PhD
Faculty: Environmental Studies.

The rapid growth of infrastructure in Selangor, the Langat River has experienced change in land use and this subsequently caused the river to carry a significant load of material in the dissolved or particulate phases. PAHs can probably enter into the aquatic ecosystem through atmospheric transportation, storm water carrying surface runoff during rainy season, direct discharge of effluent from sewage treatment plants, or accidental spillage of oil from traffic boats or ships. This study was carried out on the collected surface sediments samples from 22 sampling locations at Langat River, Selangor. The objective of this study is to determine the concentration and pattern distribution of Polycyclic Aromatic Hydrocarbons (PAHs) on the surface sediments. Besides that, this work have identified the possible anthropogenic sources of PAHs by using Principal Component Analysis (PCA) followed by the apportionment of PAH sources using Multiple Linear Regression (MLR). The samples underwent Soxhlet Extraction (SE) method to extract the target compounds using dichloromethane (DCM). Then, the extracts were cleaned and separated using two steps of column chromatography with silica gel. The concentrations of 23 individual PAHs were determined and quantified using gas chromatography mass spectrometry (GC-MS) detector. The total concentrations of PAHs were ranged from 60.61 to 426.07 ng/g dry weight with a mean of 221.43 ng/g dry weight. This finding revealed that the level of PAHs pollution in Langat River fell within low to moderate. Cluster analysis (CA) showed that six sampling locations can be classified as having high pollution loading of PAHs due to the rapid growing in residential areas and industrial area as well as shipping boat traffic. Five possible PAHs sources were generated: automobile emission (70.86%), spillage from petroleum derivative product (20.06%), unburned fuel from transportation (5.07%), wood combustion (2.79%); and road dust (1.22%). This study uncovered the usefulness of PCA as an alternative technique in order to

identify the PAHs sources. Besides that, MLR of the generated data (factor scores) from PCA was used to apportion the PAHs sources. The strong correlation between observed and predicted total concentration of PAHs proved that MLR is convincing technique in identifying the percentage contribution of PAHs sources.

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

TABURAN RUANGAN DAN PENGAGIHAN SUMBER HIDROKARBON AROMATIK POLISIKLIK DI PERMUKAAN SEDIMEN DI SUNGAI LANGAT, SELANGOR, MALAYSIA

Oleh

NURUL AFIQAH BINTI MOHAMD TAHIR

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Pertumbuhan infrustruktur yang pesat di Selangor, Sungai Langat telah mengalami perubahan guna tanah dan seterusnya sungai membawa muatan yang tertentu dalam bentuk bahan terlarut dan partikal yang kecil. PAH mungkin boleh masuk ke dalam ekosistem akuatik melalui pengangkutan atmosfera, air hujan yang membawa air larian permukaan semasa musim hujan, pelepasan bahan pembuangan dari loji rawatan kumbahan, atau tumpahan minyak dari bot atau kapal. Kajian ini telah dijalankan ke atas sampel permukaan sedimen yang telah diambil dari 22 lokasi persampelan di Sungai Langat, Selangor. Objektif kajian ini adalah untuk menentukan kepekatan dan corak taburan hidrokarbon aromatik polisiklik (PAH) pada permukaan sedimen. Selain itu, kajian ini telah mengenalpasti sumber antropogenik PAH dengan menggunakan analisis komponen prinsipal (PCA) diikuti oleh pengagihan sumber PAH menggunakan analisis regresi linear berganda (PCA-MLR). Permukaan sedimen telah menjalani kaedah Pengekstrakan Soxhlet dengan sebatian sasaran telah diekstrak menggunakan dicholoromethane (DCM). Kemudian, ekstrak dibersihkan dan dipisahkan menggunakan kolum kromatografi dengan gel silika. Kepekatan 23 individu PAHs telah ditentukan dan dikira menggunakan kromatografi gas yang ditambah dengan pengesan jisim spektrometri (GC-MS). Jumlah kepekatan 23PAHs antara 60.61 426.07 ng / g berat kering dengan purata 221.43 ng/g berat kering. Penemuan ini telah menunjukkan tahap pencemaran di Sungai Langat berada pada tahap pencemaran rendah ke sederhana. Analisis pengkelasan menunjukkan bahawa enam lokasi pensampelan boleh diklasifikasi sebagai pencemaran yang tinggi kerana kepesatan kawasan perumahan, kawasan perkilangan dan peningkatan lalu lintas kapal dan bot. Lima kemungkinan sumber PAH telah dihasilkan: pelepasan asap kenderaan

(70.86%), pengaliran produk terbitan petroleum (20.06%), bahan api yang tidak terbakar daripada pengangkutan (5.07%), pembakaran kayu (2.79%); dan debu jalanraya (1.22%). Selain dari itu, MLR bagi data yang dijana (skor faktor) dari PCA telah digunakan untuk mengagihkan sumber PAHs. Korelasi yang kuat antara jumlah kepekatan PAHs yang dicerap dan yang diramal membuktikan bahawa MLR adalah teknik yang menyakinkan dalam mengenal pasti sumbangan peratusan sumber PAHs.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory committee were as follows:

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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 it's not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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(NURUL AFIQAH BINTI MOHAMD TAHIR)

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LIST OF ABBREVIATIONS

PAHs	Polycyclic Aromatic Hydrocarbons
PCA	Principal Component Analysis
MLR	Multiple Linear Regression
DCM	Dichloromethane
GCMS	Gas Chromatography Mass Spectrometer
WQI	Water Quality Index
USEPA	United State Environmental Protection Agency
EDC	Endocrine Disrupting Compounds
CA	Cluster Analysis
POPs	Persistent Organic Pollutants
LMW	Low Molecular Weight
HMW	High Molecular Weight
LPL	Low Pollution Loading
MPL	Moderate Pollution Loading
HPL	High Pollution Loading
OSHA	Occupational Safety and Health Administration
LMW/HMW	Low Molecular Weight/High Molecular Weight
BaA/(BaA/Chry)	Benzo(a)Anthracene/(Benzo(a)Anthracene+Chrysene)
Fluo/(Fluo+Pyr)	Fluoranthene/(Fluoranthene+Pyrene)
Ant/(Ant+Phe)	Anthracene/(Anthracene+Phenanthrene)
PCs	Principal Components
VFs	Varimax Factors
SPM	Suspended Particulate Matter
SS	Surface Sediment
SIS	Surrogate Internal Standard
IIS	Internal Injection Standard
Naph	Naphthalene
AceNapy	Acenaphthylene
AceNaph	Acenaphthene
Flu	Fluorene
Phe	Phenanthrene
Ant	Anthracene
Fluo	Fluoranthene
Pyr	Pyrene
BAnt	1,2-benzanthracene
Chry	Chrysene
B(a)P	Benzo(a)pyrene
B(b)Fluo	Benzo(b)luoranthene
BaA	Dibenzo[a,h]anthracene
IP	Indeno[1,2,3-cd]pyrene
Bghi	Benzo[g,h,i]perylene
Ret	Retene
1-MNaph	1-methylnapthalene
1,2-MNaph	1,2-dimethylnapthalene
3,6-DMNaph	3,6-dimethylnapthalene

2-MAnt	2-methylanthracene
DBT	dibenzothiophene
2-MPhe	2-methylphenanthrene
B(e)P	Benzo (e)pyrene
POPs	Persistent organic pollutants

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Many studies have been conducted by researchers around the world, in identifying Polycyclic Aromatic Hydrocarbons (PAHs) pollution in atmosphere, water column, sediment, soil as well as organisms. PAHs form a widespread class of environmental chemical pollutants which has been identified mostly originated from anthropogenic activities (Neff, 1979). Malaysia is not an exception as previous studies have been carried out to evaluate the current status of PAHs generated and released into the environment (Shahbazi et al., 2010; Saha et al., 2009; Bahry et al., 2009; Bakhtiar et al., 2009; Chandru et al., 2008; Zakaria et al., 2002). According to a report by Abdullah (1995), Malaysia has transformed its development strategy in order to compete with world's market target from agriculture based economy to manufacturing industries in the 1990s.

There is also a continuous increase in the urbanization areas with the population exceeding 28.3 million (Population and Housing Census of Malaysia, 2010). Malaysia which is located in Southeast Asia has a unique tropical environment and climate surrounded by the Straits of Malacca and the South China Sea in the western and eastern shores, respectively. In Malaysia, more than 90% of our water supply comes from rivers and streams. Such vast economic growth during the past two decades has contributed significantly to an increase in pollution and diversity of waste that have been poured out into the rivers. The rivers are used as an outlet for the waste discharge from various surrounding activities. In 2004, Department of Environment (DOE) Malaysia issued reports on 17,991 water pollution point sources contributed mainly from sewage treatment plants (54%), manufacturing industries (38%), animal farms (5%) and agro-based industries (3%). Rivers have always played an essential role in the human life to be used as transportation, support agriculture activities and productivity, domestic and industrial water supply, recreational area and an important food sources. Therefore, the quality of rivers should become a priority in order to maintain the balance ecosystem.

Selangor is the most developed area in Malaysia with good infrastructure such as highways and transportation. As a result of rapid growth of infrastructure in Selangor, Langat River also experienced change in land use and subsequently caused rivers to carry a significant load of matter in dissolved or particulate phases. DOE Malaysia reported that Langat River is seriously being contaminated by industrial discharge (58%), domestic sewage from treatment plant (28%) construction project (12%) and pig farm (2%). In other words, Langat River is strongly correlated with the increase of population and consequently increases in anthropogenic activities. Based on study that conducted by Lee et al. (2006), this river is classified as average polluted overall where the value of Water Quality

Index (WQI) is approximately 36-89. However, it is found that the upstream area (Hulu Langat area before Sungai Lui) falls in relatively low pollution. On the contrary, the downstream area (Sungai Balak and Sungai Batang Benar) is polluted and extensive treatment required.

1.2 Problem Statements

Langat River is an important river system which is providing the potable water for drinking purposes, supplies water for manufacturing, recreational, and agriculture production. Nowadays, insufficient treatments of domestic sewage effluents and hydrocarbons pollution from anthropogenic sources are directly discharged into the adjacent river. The major concern on PAHs pollution in the environment is due to their toxicity and carcinogenic potential towards animal and human health (Beg et al., 2003). Other than that, PAHs have ability to persistence in environment as well as has long-range transport properties (Li et al., 2012). Based on these characteristics, PAHs is one of the most concerned contaminants in the global region (Xu et al., 2006). Among the 16 PAHs, seven of them are probably carcinogenic (Neff et al., 2005) i.e. benzo(a)anthracene (BAnt), Chrysene (Chry), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoramthene (BkF), dibenzo(a,h)anthracene (BaA) and indeno(1,2,3-cd)pyrene, (IP). PAHs have the ability to accumulate in the lipid of organisms (Baumard et al., 1998) due to its hydrophobic characteristic and thereafter will indirectly deteriorate human's health given the consumption of polluted organisms.

Humans may also face the threat of contracting cancer. In addition, PAHs are also known as Endocrine Disrupting Compounds (EDC) owing to their ability to mimic human hormones (Qiao et al., 2006). In order to identify the possible sources of PAHs, diagnostic ratios have been applied (Wang et al., 2009). However, the diagnostic ratios have several limitations (Fang et al., 2004). There will be conflicts between ratios where certain ratio shows pyrogenic sources but the other ratio concludes different result. On the other hand, the diagnostic ratios are not sensitive enough to be applied in determining the multiple point source of pollution. The inconsistencies from the usage of diagnostic ratios to identify the pyrogenic and petrogenic sources of PAHs have resulted to the use of Principal Component Analysis (PCA) for further confirmation.

Recently, there have been advances in investigating the possible sources of PAH contamination. Instead of using only limited number of compounds in diagnostic ratios, PCA 'looks' at all the compounds which would prevent misinterpretation of the collected data. Multivariate statistical tools such as Cluster Analysis (CA), Principal Component Analysis (PCA) and Multiple Linear Regression (MLR) can be used in the analysis to avoid misinterpretation and unbiased approaches in the analysis of complex environmental data (Singh et al., 2004). These approaches have been successfully applied in evaluating the surface water and freshwater quality (Juahir et al., 2010; Helena et al., 2000). Lately the usage has been extended

to determine the source of organic contaminants such as faecal sterol in the environment (Hu et al., 2011; Cao et al., 2011; Jiang et al., 2009; Osman et al., 2009; Kavouras et al., 2001). Other countries such as China have extensively applied these approaches in PAHs fingerprinting analysis, however in Malaysia the PAHs studies that involved these method is rather scarce.

1.3 Significance of Study

The background information on PAHs distributions that exist in the collected surface sediment will be known. The results obtained are useful for future monitoring of anthropogenic pollution in Langat River. PAHs detected in the sediment samples may contributed from the pollution that directly discharged into the adjacent river or long range transport from the origin sources through atmospheric transportation via wind rise and volatilization or storm water carrying surface runoff during rainy season. PCA is using as an confirmation technique to identify the possible PAHs sources in Langat River, and then PCA-MLR was executed to apportion the possible sources that contributed to the PAHs pollution in Langat River.

1.4 Hypotheses

i) The PAHs distribution in the sampling locations is depends on the activities in the Langat River.

ii) Multivariate statistical analysis can be used as optional technique to identify the possible PAHs sources however diagnostic ratios is used as a reliable molecular marker to determine the PAHs sources.

1.5 Objectives of Study

i) To determine the concentration and spatial distribution of PAHs from selected surface sediments in the Langat River, Selangor.

ii) To identify the possible PAHs sources using diagnostic ratios and further confirmation using multivariate statistical analysis.

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