UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN ATMOSPHERIC AEROSOLS COLLECTED FROM SELECTED LOCATIONS IN PENINSULAR MALAYSIA

POURYA SHAHPOURY BAHRY

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By

POURYA SHAHPOURY BAHRY

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

December 2007

DEDICATION

To my dear mother, close friends, my family, and my supervisor who have been the most important reasons of hopefulness during my study.

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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Chairman: Associate Professor Mohamad Pauzi Zakaria, PhD

Faculty: Environmental Studies

With rapid modernization and development of Malaysia during the recent years, atmospheric hydrocarbons have been increasing due to increase in industrialization, motorization, biomass burning and deforestation in this country. One of the most important classes of hydrocarbons is polycyclic aromatic hydrocarbon (PAHs) that has long been of interest in the field of environmental forensic. It is very important to characterize the Polycyclic Aromatic Hydrocarbons in the environment because of the known carcinogenic and mutagenic effect of theses compounds to human health especially on the endocrine system. Generally, anthropogenic PAHs are released from both pyrogenic and petrogenic sources. Particulate phase PAHs have significant contribution from the total concentration of PAHs in the atmosphere. This study specifically focuses on characteristics of this group of compounds in total suspended particulates at nine sampling stations in peninsular Malaysia. The objectives of this project are to determine the sources, distribution and concentrations of compound specific PAHs in selected locations. For this

purpose, atmospheric aerosols are collected using high volume air samplers. The samples are further soxhlet extracted using high-grade dichloromethane then purified and fractionated by a two-step column chromatography. Subsequently, PAHs fraction with 3-5 benzene rings is analyzed by gas chromatography coupled with mass spectrometer (GC-MS). The results of this study revealed that concentration of PAHs ranged from 0.28 to 13.02 ng/m^3 with the mean value of 2.73 ng/m^3. The ratio of the sum of methylphenanthrenes to phenanthrene (MP/P) was under unity for 16 samples from the 18 samples analyzed. This result indicated that the atmospheric PAHs are from pyrogenic sources. Interestingly samples from Tanah Rata station MP/P ratio were found to be above unity that may come from petrogenic input of PAHs. Application of lower molecular weight (LMW) to higher molecular weight (HMW) PAHs proportion provided very useful supportive data to identify the origin of PAHs. The results indicated that distribution of compound specific PAHs during the sampling period are strongly controlled by dominance of higher molecular weight PAHs, which is consistent with results of MP/P ratio. The only exceptions consist of two samples from Alor Setar and Tanah Rata stations that LMW/HMW and MP/P ratios do not relate to each other, suggesting unique source of PAHs in the study area that contains both pyrogenic and petrogenic PAHs. Finally, it has concluded that the atmospheric environment of peninsular Malaysia during the period of sampling has influenced by pyrogenic sources of PAHs.

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

PENCIRIAN HIDROKARBON AROMATIK POLISIKLIK DALAM AEROSOL ATMOSFERA DARI BEBERAPA LOKASI TERPILIH DALAM SEMENANJUNG MALAYSIA

Oleh

POURYA SHAHPOURY BAHRY

December 2007

Pengerusi : Profesor Madya Mohamad Pauzi Zakaria, PhD

Fakulti : Pengajian Alam Sekitar

Pembangunan yang pesat di Malaysia dalam beberapa tahun kebelakangan ini telah meningkatkan kepekatan hidrokarbon dalam atmosfera. Peningkatan tersebut adalah berpunca daripada pengindustrian, pemotoran, pembakaran biojisim dan penebangan hutan di negara ini. Salah satu kelas hidrokarbon yang penting ialah hidrokarbon polisiklik beraromatik yang telah mendapat perhatian dalam bidang alam sekitar forensik. Mengenalpasti hidrokarbon polisiklik beraromatik dalam alam sekitar adalah penting kerana ia bersifat karsinogenik dan mutagenik. Ia juga memberi kesan kepada kesihatan manusia dan boleh menjejaskan sistem endokrin. Pada kebiasaannya, hidrokarbon polisiklik beraromatik yang dihasilkan daripada aktiviti manusia terdiri daripada dua jenis iaitu sumber pirogenik dan petrogenik. Hidrokarbon polisiklik beraromatik wujud dalam fasa partikulat secara siknifikan di dalam atmosfera berbanding dengan fasa lain. Oleh itu kajian ini memfokus sifat sebatian tersebut dalam jumlah partikulat terampai dari sembilan stesen persampelan di semenanjung Malaysia. Objektif bagi projek ini termasuk

mengenalpasti sumber, taburan dan kepekatan sebatian spesifik hidrokarbon polisiklik beraromatik. Untuk tujuan tersebut, aerosol atmosfera telah diambil dengan menggunakan alat pemungut udara sampel isipadu tinggi. Sampel yang diambil seterusnya diekstrak secara sokslet dengan menggunakan diklorometana bergred tinggi. Seterusnya, langkah pemurnian dan pengasingan dijalankan dengan kaedah dua langkah kromatografi kolum. Seterusnya, fraksi hidrokarbon polisiklik beraromatik dengan cincin benziena 3-5 dianalisis dengan menggunakan kromatografi gas yang digabungkan dengan pengesan jisim selektif (GC-MS). Keputusan kajian menunjukkan kepekatan julat hidrokarbon polisiklik beraromatik dari 0.28 hingga 13.02 ng/m^3 dengan nilai min adalah 2.73 ng/m^3. Nisbah jumlah metilfenantrina bahagi fenantrina adalah kurang daripada uniti untuk 16 daripada 18 sampel. Keputusan tersebut menunjukkan sumber hidrokarbon polisiklik beraromatik adalah pirogenik. Menariknya, nisbah MP/P bagi sampel yang diambil di stesyen Tanah Rata menunjukkan nilai yang lebih tinggi daripada nilai uniti yang mungkin terhasil daripada sumber hidrokarbon polisiklik beraromatik dari petrogenik. Aplikasi nisbah berat molikul rendah bahagi berat molikul tinggi boleh memberikan data sokongan untuk mengenalpasti sumber hidrokarbon polisiklik beraromatik. Keputusan kajian ini menunjukkan taburan hidrokarbon polisiklik beraromatik didominasikan oleh berat molikul tinggi. Keputusan tersebut adalah konsisten dengan nisbah metilfenantrina bahagi fenantrina. Dua stesen yang menunjukkan keputusan nisbah LMW/HMW dan MP/P yang berbeza membuktikan sumber hidrokarbon polisiklik beraromatik yang bercampur diantara petrogenik dan pirogenik. Akhir sekali, kesimpulan boleh dibuat

bahawa atmosfera di semenanjung Malaysia pada bulan Julai 2006 dipengaruhi oleh sumber pirogenik.

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I would like to take this opportunity to appreciate all of the persons who contributed individually in this study. First, I would like to present my warmest gratitude to my supervisor, Associate Professor Dr. Mohamad Pauzi Zakaria, for his helpful support, guidance and encouragement through my period of study. This appreciation also goes to the respectable members of my supervisory committee, Professor Dr. Dzulkefly Kuang Abdullah and Associate Professor Dr. Ahmad Makmom Bin Abdullah who gave me lots of comments to improve this project. I want to respectfully give my sincerest gratitude to Ms Siniarovina Urban from the meteorology department of Malaysia, for her worthwhile help and counseling. My special thanks also to my dear friends from the environmental forensic laboratory, Mr Mahyar Sakari, Mr Alireza Riahi, Ms Azadeh Shahbazi and Ms Sofia Anita for their rewarding advice and consultations. Unsparing gratitude to my esteemed mother and other members of my family for their kind and perpetual support that has enabled me to reach higher levels of knowledge.

I certify that an Examination Committee has met on 18th December 2007 to conduct the final examination of Pourya Shahpoury Bahry on his Master of Science thesis entitled "Characterization of Polycyclic Aromatic Hydrocarbons in Atmospheric Aerosols Collected from Selected Locations in Peninsular Malaysia" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the degree of Master of Science.

Members of the Examination Committee were as follows:

Mohammad Ismail Yaziz, PhD
Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Chairman)

MD. JELAS HARON, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mohd Ali Hassan, PhD
Professor
Faculty of Biotechnology and Biomolecular Sciences
Universiti Putra Malaysia
(Internal Examiner)

Mhd. Radzi Bin Abas, PhD
Professor
Faculty of Science
University of Malaya
(External Examiner)

_____
HASANAH MOHD. GHAZALI, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 21 February 2008

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

Mohamad Pauzi Zakaria, PhD
Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Chairman)

Ahmad Makmom Bin Abdullah, PhD
Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Member)

Dzulkefly Kuang Abdullah, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

_____
AINI IDERIS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 21 February 2008

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 submitted for any other degree at UPM or other institutions.

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POURYA SHAHPOURY BAHRY

Date: 28 January 2008

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LIST OF ABBREVIATIONS

Ant	Anthracene
Ant-d10	Anthracene-d10
BaA	Benzo(a)anthracene
B(a)P	Benzo(a)pyrene
B(e)Acep	Benzo(e)acephenanthrylene
B(e)P	Benzo(e)pyrene
B(k)F	Benzo(k)fluoranthene
Chry	Chrysene
Chry-d12	Chrysene-d12
DBahA	Dibenzo(a,h)anthracene
DBT	Dibenzothiophene
DCM	Dichloromethane
Flu	Fluoranthene
GC/MS	Gas Chromatography Mass Spectrometry
LMW/HMW-PAHs	Lower Molecular Weight PAHs / Higher Molecular Weight PAHs

Hex	Hexane
HMW	Higher Molecular Weight
IIS	Internal Injection Standard
LMW	Lower Molecular Weight
2-MA	2-methylanthracene
MeOH	Methanol
1-MP	1-methylphenanthrene
2-MP	2-methylphenanthrene
3-MP	3-methylphenanthrene
9-MP	9-methylphenanthrene
MP/P	Methylphenanthrene/ Phenanthrene
1MPyr	1-methylpyrene
Naph-d8	Naphthalene-d8
P-terph-d14	P-terphenyl-d14
PAHs	Polycyclic Aromatic Hydrocarbons
Pery-d12	Perylene-d12

Phe	Phenanthrene
Pyr	Pyrene
SIS	Surrogate Internal Standard

CHAPTER 1

INTRODUCTION

1.1 Background of Study

There is a strong relation between life on earth and the nature of earth's atmosphere that determines its suitability for life. After discovery of fire, due to its special dynamic character, atmosphere has been transformed into a dumping ground to dispose pollutant materials by human being. After the industrial revolution in the late 1800's, industries confronted rapid development in various point of views especially by invention of internal combustion engines that played a particular role in human history. Considering that these engines have used fossil fuels, the interest of human regarding this new invention led them in a search for more supplies of fossil fuels especially petroleum. Nowadays, exploration of petroleum is obvious in every corner of the world and this is the trigger point that releases the petroleum pollution to the environment. Usually utilization of petroleum as source of energy can emit various types of chemicals from the exploration points and the refining process to combustion in industrial power plants and engines. Some of these chemicals may be non-hazardous but the rest could remain in the environment as persistent organic chemicals and cause carcinogenic and mutagenic effect on organisms. Signs of petroleum pollution produced by human activities are obvious in different phases of the environment, especially in the atmosphere.

Atmospheric pollution is one of the most important concerns humankind faces these days. The air contamination causes damage on human health and harm to wildlife and vegetation. Among the released chemical to the atmosphere by utilization of petroleum, hydrocarbons has a share of more than 50-98% of the total composition. This truth is another proof that crude oil contains thousands of chemicals of which hydrocarbons are the most abundant compounds depending on the specific locations where the oil was found.

Hydrocarbon contamination (HC) in atmosphere has increased globally due to growth in urbanization, industrialization, motorization and deforestation. Natural sources are the most important contributors of organics in the atmosphere, and hydrocarbons generated and released by human activities constitute only about one seventh of the total hydrocarbons in the atmosphere. On the other hand, more than 80% of petroleum hydrocarbons are produced by anthropogenic sources and the other 20% are released naturally through oil seeps and biogenic sources. Among petroleum hydrocarbons, the major compounds are straight chain alkanes (*n*-alkanes), cycloalkanes and aromatics. The petroleum hydrocarbons of greatest concern are PAHs that are widespread in the environment. Polycyclic aromatic hydrocarbons (PAHs) are one of the most important classes of micro organic pollutants produced mostly by means of incomplete combustion of organic material containing carbon, hydrogen and other minor compounds.

Until the last two decades, it was generally presumed that PAHs were formed only during the high temperature pyrolysis of organic materials. The discovery of complex mixture of PAHs spanning a wide molecular weight range in fossil fuels such as coal and crude petroleum has led to the conclusion that given significant time, pyrolysis of organic materials at temperature as low as 100-150° C can cause production of PAHs. Besides, there has been considerable speculation in recent years and some experimental evidence in its favor that PAHs are synthesized by bacteria and plants. Thus, PAHs are probably formed in three ways, high temperature pyrolysis of organic materials, low to moderate temperature of diagenesis of sedimentary organic material to form fossil fuels or direct biosynthesis by microbes and plants.

Although PAHs could be produced naturally, a wide variety of human activities increases the environmental load of these substances. Incineration of industrial and domestic wastes, forest and grass fires, power generation from fossil fuels, and the combustion of fuels in internal combustion engines also produce emission rich in PAHs. These anthropogenic PAHs may reach the aquatic environment in industrial and domestic sewage effluents, surface runoffs from land, deposition of air born particulates and spillage of petroleum and petroleum products into water bodies.

Polycyclic aromatic hydrocarbons in atmospheric particles have received a great deal of attention due to the known carcinogenic effects of some of these compounds. Prominent among these compounds are benzo(a)pyrene,

benzo(a)anthracene, chrysene, benzo(e)pyrene, benzo(e)acephenanthrylene, benzo(j)fluoranthene, and indenol. The most often cited example of a PAHs compounds is benzo(a)pyrene, a compound that the body can metabolize to a carcinogenic form.

Over 120 PAHs compound have been identified in urban pollution and are produced by the combustion of organic matter. Organic compounds in combustion exhaust consist mainly of unburned alkanes and series of PAHs. Individual PAHs compounds from combustion sources enter the ambient atmosphere as gases or associated with the particles. Airborne particulate matters consists of a complex mixture of solid and liquid that contains PAHs and are emitted to the atmosphere from a variety of sources. Typically 2 to 3 rings condensed PAHs are partitioned with the gas phase while 4 to 6 ring PAHs are partitioned on particles.

What is the nature of particulate matter? Particle in the atmosphere that range from about 0.5 mm down to molecular dimensions, are made up of an amazing variety of materials and discrete objects. Particulates are believed to cause the most visible and obvious form of air pollution. Atmospheric aerosols are solid or liquid particles smaller than 100 μm in diameter. Pollutant particles in the 0.001 to 10 μm range are commonly suspended in the air near sources of pollution such as the urban atmosphere, industrial plants, highways and power plants.