POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN AIR AND VEGETATION: CASE STUDY AT THREE SELECTED TOLL STATIONS ALONG NORTH SOUTH EXPRESSWAY IN JOHOR, MALAYSIA

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Dedicated to
the late Prof. Dr. Azhari bin Saleh, for his inspirations

Alfatihah

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) from vehicular emission are products of the incomplete combustion of organic fuel, and are usually attached to the particulate matter from the emission and can caused pollution and hazard to human health due to its carcinogenic, mutagenic and teratogenic characteristics. The objective of this study is i) to determine the concentration PAHs in the air of sampling area, ii) to determine the concentration PAHs in vegetation, iii) to determine the relationship of concentration of PAHs in plants and air of sampling area and iv) to study the different composition of PAHs in different species of plants to determine the potential biomonitoring agent. The study is carried out at three toll stations along PLUS' North-South Expressway in Johor. Air sample and plant leaves sample collected were extracted with ultrasonic agitation in dichloromethane and fractionated according to polarity before submitted to gas chromatography – mass spectrometry analysis to determine the concentration of the PAHs compounds. Spearman's rank correlation test was carried out using SPSS to determine the correlation between concentration of PAHs in air and plant leaves sample. Seven PAHs were identified and quantified in the atmospheric sample and plant leaves sample. Those PAHs were acenaphtylene (ACN), phenanthrene (PHE), fluorene (FL), pyrene (PY), chrysene (CHR), benzo[a]anthracene (BaA), and benzo[a]pyrene (BaP). Significant correlation at 0.05 level (2-tailed) was observed in samples of *Ficus microcarpa*, *Cordyline fruticosa*, *Hibiscus* spp., and *Ixora coccinea* with the value 0.622, 0.643, 0.680 and 0.608 respectively. The positive correlation shows that the plants have capabilities to absorb organic pollutants from the environment. Based from this research, the most suitable species to be introduced into the environment as a biomonitoring agent and to be further studied as a medium for low and medium level pollution bioremediation is *Ficus microcarpa*, *Cordyline fruticosa*, and *Ixora coccinea.*

ABSTRAK

Hidrokarbon polisiklik beraroma (PAHs) yang dibebaskan oleh kenderaan adalah hasil daripada pembakaran tidak lengkap bahanapi organik yang lazimnya bersama – sama zarah jirim yang dibebaskan dari pembakaran dan boleh menyebabkan pencemaran dan kesan kepada kesihatan manusia. Objektif kajian ini adalah i) menetukan kepekatan PAHs dalam udara di kawasan kajian, ii) menentukan kepekatan PAHs dalam tumbuh – tumbuhan, iii) menentukan hubungan antara kepekatan PAHs dalam daun pokok dan udara di kawasan kajian dan melihat perbezaan kandungan PAHs di dalam spesis tumbuhan yang berbeza untuk menentukan tumbuhan yang berpotensi menjadi ajen pemonitoran biologi. Kajian ini tertumpu di tiga plaza tol di sepanjang Lebuhraya Utara-Selatan PLUS di negeri Johor. Sampel udara dan daun pokok yang dikumpulkan diekstrak menggunakan kaedah pengocakan ultrasonik di dalam diklorometana dan dipecahkan mengikut kekutuban sebatian sebelum ujian kromatografi gas – spektometri jisim dilakukan ke atasnya untuk menentukan kepekatan sebatian – sebatian PAHs. Analisis korelasi Spearman's rank dijalankan menggunakan perisian SPSS untuk menentukan korelasi di antara kepekatan PAHs di dalam sampel udara dan sampel daun pokok. Tujuh sebatian PAHs telah dikenalpasti di dalam sampel – sampel udara dan daun pokok iaitu acenaphtylene (ACN), phenanthrene (PHE), fluorene (FL), pyrene (PY), chrysene (CHR), benzo[a]anthracene (BaA), and benzo[a]pyrene (BaP). Korelasi signifikan pada tahap 0.05 (2-tailed) dapat dilihat pada sampel *Ficus microcarpa*, *Cordyline fruticosa*, *Hibiscus* spp., dan *Ixora coccinea* masing – masing bernilai 0.622, 0.643, 0.680 dan 0.608. Korelasi positif menunjukkan kebolehan tumbuh – tumbuhan untuk menyerap bahan pencemar organik dari alam sekitar. Berdasarkan kajian ini, spesis yang paling sesuai untuk diperkenalkan sebagai ejen kawalan biologi dan seterusnya dikaji untuk menjadi media bioremediasi pencemaran tahap rendah dan sederhana ialah *Ficus microcarpa*, *Cordyline fruticosa*, dan *Ixora coccinea*.

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LIST OF SYMBOLS AND ABBREVIATION

AC	-	Acenaphtene
ACN	-	Acenaphthylene
Al_2O_3	-	Aluminum oxide
AN	-	Anthracene
B[a]A	-	Benzo[a]anthracene
B[a]P	-	Benzo[a]pyrene
B[b]F	-	Benzo[b]fluoranthene
B[ghi]P	-	Benzo[ghi]perylene
CH_4	-	Methane
CHR	-	Chrysene
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
D[ah]A	-	Dibenzo[ah]anthracene
DCM	-	Dichloromethane (CH_2Cl_2)
DNA	-	Deoxyrybonucleic acid
DOE	-	Department of Environment
FA	-	Fluoranthene
FL	-	Fluorene
GTN	-	Glyceryl trinitrate
H_2	-	Hidrogen molecule
H_2O	-	Water molecule

He	-	Helium
HCs	-	Hydrocarbons
IP	-	Indeno[1,2,3-cd]perylene
N_2	-	Nitrogen molecule
Na_2SO_4	-	Sodium sulphate anhydrous
NA	-	Naphtalene
ND	-	Not detected
NO	-	Nitric oxide
NO_2	-	Nitrogen dioxide
NO_x	-	Nitrogen oxides
PAHs	-	Polycyclic aromatic hydrocarbons
Pb	-	Lead
PCBs	-	Polychlorinated biphenyls
PCDDs	-	Polychlorinated dibenzodioxines
PCDFs	-	Polychlorinated dibenzofurans
PHE	-	Phenanthrene
PM	-	Particulate matter
PM_{10}	-	Particulate matter with diameter less than 10µm
PY	-	Pyrene
RDX	-	Cyclonite
SiO_2	-	Silica gel
SO_2	-	Sulfur dioxide
SOCs	-	Synthetic organic chemicals
sp^3	-	Tetrahedral carbon

TNT	-	Trinitro toluene
US EPA	-	United States Environmental Protection Agency
VOCs	-	Volatile organic carbons
WHO	-	World Health Organisation

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) contamination from vehicular emissions is of great concern to our world nowadays due to its abundance in the atmosphere and the effects it could give towards the environment and human health. Long term exposure to PAHs can cause various disturbances in human life in terms of comfort and health. Learning the relationship between PAHs concentration in atmosphere and in plant leaves is important to determine the ability of plants in containing or removing PAHs from the atmosphere.

Earth's atmosphere comprises of various gases primarily of nitrogen, oxygen and carbon dioxide as well as minor component like helium and neon. The air contains oxygen which are vital for our bodies to live. A clean air supply is essential to our own health and for the environment. However, the growth of population on earth is causing more substances being released to the environment. Though most of the world's most populous countries are spread across region, and the characteristics vary quite significantly, these countries usually have one thing in common, where the residents usually suffer from severe air pollution (Soubbotina, 2004). Quite obviously, the biggest environmental problem is the increasing number of human beings who are just crowding our planet earth. The worldwide energy consumption has increased over the years relative to the increase of human population. The enormous number of human beings living on this planet and their ever increasing and unevenly distributed need for energy is the main problem with which caused more environmental problems (Gruden, 2003)

Since the industrial revolution, the quality of the air we breathe has deteriorated mainly as a result of human activities. Urbanization and industrialization

leads to degradation of the environment, depletion of fisheries, food, water, and air supplies. Rising industrial and energy production, the burning of fossil fuels and the rise of traffic on our roads just to meet the daily human needs all contribute to pollution in our towns and cities which, in turn, can lead to serious health problems. Among them, air pollution is the major issue affecting human health and the ecosystem. The abundance of anthropogenic sourced substances in the atmosphere contributes to a very uncomfortable environment to live in. The complex mixture of air pollutants of which the exact composition varies both over time and between individual towns and cities due to changes in patterns and sources of emissions results into complications of management of the pollution as a whole. Typically, however, urban air quality is dominated by emissions from road traffic. These are the results of the need for mobility from the urbanization and industrialization of the society. Various traffic systems were developed to allow mobility, and road traffic undoubtedly is the most preferred system for the transports of passengers and goods which result to the use of diesel and petrol fuelled vehicles (Gruden, 2003). These vehicles are responsible for the generation of a wide range of pollutants, with concentrations and relative proportions of pollutants depending on vehicle technology and operating conditions (Honour *et. al*., 2008).

1.1.1 Air pollution

Generally, air pollution is defined as 'the presence in the atmosphere of substances or energy in such quantities and such duration liable to cause harm to human, plant, or animal life, or damage to human-made materials and structures, or changes in the weather and climate, or interference with the comfortable enjoyment of life or property or other human activities' (Omar, 2001). Many atmospheric pollutants are naturally occurring substances such as carbon dioxide or methane. Human intervention in the natural environment commonly leads to the enhancement in the rate of production of these compounds. The largest point sources are natural processes, such as volcanic eruptions and the greatest anthropogenic contributor to air pollutant is combustion process (DiNardi, 1994). Atmospheric pollutants can be categorized as either primary pollutant: environmentally damaging materials product

of man-made or natural processes and secondary pollutant: products of chemical changes of the primary pollutants.

When pollutants are first released from a source, their concentrations are usually high, and will cause immediate effects on environmental quality. Dispersion takes place quickly in a limited portion of atmosphere and dilutes the pollutants. Deposition of pollutants on earth surface whether dry (dry particles or gases) or wet (rain or snow) causes pollution to the land or water according to where they deposited.

Air pollutants can give following effects:

(i) Atmospheric effects which may include changes in visibility, the urban and global climate, frequency of rainfall and stratospheric ozone level.

(ii) Direct or indirect health effect.

(iii) Welfare effects including damage to vegetation, injury to livestock, reduce visibility and odor pollution.

(Soubbotina, 2004).

The level of pollution usually depends on a country's technologies and pollution prevention and controlling method including the type of initial energy used for energy production. Using cleaner fossil fuels with less impurities, burning these fuels more effectively and increasing reliance on even cleaner, renewable source of energy are some of the best way to control and reduce air pollution (Soubbotina, 2004).

1.1.2 Polycyclic aromatic hydrocarbons (PAHs)

Aromatic compound, as basic as benzene, is defined as a cyclic compound containing some number of conjugated double bonds, characterized by unusually large resonance energy. These compounds had low hydrogen-to-carbon ratios and characteristic aromas, and they could be converted to benzene or closely associated compounds. The term 'aromatic' can be applied to compounds with this unusually stable ring system, regardless of their odors (Wade, 1987).

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings which do not contain

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