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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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 heteroatoms or carry any substituents (WHO Regional Office for Europe, 2000). Natural crude oil and coal deposits contain significant amounts of PAHs, arising from chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons. They are also found in processed fossil fuels, tar and various edible oils. PAHs are formed mainly as a result of pyrolytic processes, especially the incomplete combustion of organic materials during industrial and other human activities, such as processing of coal and crude oil, combustion of natural gas, including for heating, combustion of refuse, vehicle traffic, cooking and tobacco smoking, as well as in natural processes such as carbonization.

1.2 Problem statement

PAHs in the atmosphere released by various anthropogenic sources mainly from vehicle combustion are widespread and typically concentrated in the urban centers. The distribution of PAHs in Kuala Lumpur shows that vehicular emission is the dominant source of PAHs in atmospheric particles (Omar *et al.*, 2001). Abundant presence of PAHs in the environment caused pollution and can be a hazard to human health due to its carcinogenic, mutagenic and teratogenic characteristics. The use of plants as bioindicators are much simpler and cheaper and the findings of this study can also lead to treating the environmental pollution problems. It is important to study the relationship between the composition of PAHs in plants and the degree of PAHs pollution in the atmospheric environment to discover the ability of plants to absorb PAHs from the atmosphere to be a potential medium for bioremediation.

The three major source of pollution in Malaysia are mobile sources, stationary sources and open burning sources. For the past five years, emissions from mobile source such as motor vehicles has been the major source of air pollution, contributing at least 70 – 75 % of the total air pollution (Afroz, 2002). Combustion of fossil fuels for transportation, power generation, and other human activities produces a complex mixture of pollutants containing literally thousands of chemical constituents (Cohen *et al.*, 2004). The precise characteristics of mixture would vary across cities, through different combustion sources, but all mixtures contain certain primary gaseous pollutants, such as sulfur dioxide (SO_2), nitrogen oxides (NO_x) and carbon monoxide (CO). The mixture of pollutant also contains organic compounds from the incomplete combustion of fossil or biogenic sources of energy and some of these compounds are known to be carcinogens mainly of polycyclic aromatic hydrocarbons (PAHs) group.

Although polycyclic aromatic hydrocarbons (PAHs) are not among the ‘dirty dozen’ of the Stockholm convention on Persistent Organic Pollutants, they were included in the Convention on Longrange Transboundary Air Pollution Protocol on Persistent Organic Pollutants by United Nations Economic Commission for Europe and their toxic effects on both human and ecosystem health are well documented. Human exposure to PAHs has been widely associated with elevated levels of DNA adducts and mutations and also with reproductive defects (Gaspari *et al.*, 2003). There are several hundred PAHs; the best known is benzo[a]pyrene (BaP). In addition a number of heterocyclic aromatic compounds (e.g. carbazole and acridine), as well as nitro-PAHs, can be generated by incomplete combustion. About 500 PAHs and related compounds have been detected in air, but most measurements have been made on BaP (WHO Regional Office for Europe, 2000). Sixteen PAHs are considered priority pollutants in terms of health effects, included in US EPA’s list of 188 hazardous air pollutant: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene (US EPA, 1990, WHO,1998). As pollutants, they are of concern because some compounds have been identified as carcinogenic, mutagenic and teratogenic (Wu *et al*., 1998, Omar *et al.*, 2006).

The most important source of PAHs in Malaysia is vehicular emission since motor vehicle contributed as much as 82% of air pollutants as reported in the Environmental Quality Report by the Department of Environment in 1996. Until now 93% of carbon monoxide and hydrocarbon emission of the air pollutants are still contributed by motor vehicles (DOE, 2007). Particulate matter released by these vehicles associated with PAHs from the incomplete combustion of organic fuel may contribute to various health problems. PAHs in the atmosphere can also come from natural sources such as forest fires and volcanic eruptions, but if their presence are especially in densely populated areas, then it must be significantly affected by anthropogenic sources (Li *et al*., 2009).

Fate of these organic compounds depends on the physical and chemical properties of the compound itself. The transport of organic contaminants between atmosphere and plants has been a subject of growing interest in the community. Atmospheric pollutants are transported to vegetation from their source by wind and turbulence. During the atmospheric transport, pollutants are dispersed by turbulence and also transformed chemically usually by oxidation into secondary pollutants and often into aerosol (Fowler, 2002)

PAHs released from many types of pollution source floats in the air for some times, but the organic matter will later be removed from the atmosphere both in vapour – phase and condensed form, absorbed and deposited on water, soil and plant foliage (Nicola *et al*., 2008). In general lighter, less hydrophobic particulates are dispersed in the environment at greater distance than heavier, more hydrophobic particulates. As for PAHs, the important property is their lipophilicity: they may accumulate in fat tissue of vertebrates and invertebrates, also in lipophilic parts of plants, accumulation can take place (Keymulen *et al.*, 1995), so leaves represent a convenient passive sampler for monitoring the presence of hydrocarbon. In addition, leaf characteristics such as leaf surface, waxes, hairs and number of stomata play an important role in PAH uptake and accumulation (Prajapati and Tripathi, 2007).

Plant exposure to PAHs can occur in various ways. The particulate accumulation on the leaf surface depends on particle size, speed of deposition and leaf surface properties. Particulate-bonded PAHs may be taken up directly via the stomata or be deposited on the leaf surface, while gaseous PAHs may be accumulated in leaves by:

(i) equilibrium partitioning;
(ii) kinetically limited dry vapour deposition;
(iii) particle-bound deposition, depending on the physicochemical properties of the investigated compound

(McLachlan, 1999).

Being hydrophobic these organic compounds may be absorbed by the leaf surfaces. Therefore leaves of plants grown by the roadside are expected to contain high levels of organic compounds originating from vehicular exhaust.

Due to the various factors, some plants have high tolerance, hence might have the ability to absorb PAHs in the atmosphere. These plants can be an excellent agent for biomonitoring. They can also assist in the removal of pollutants from the environment (bioremediation).

1.3 Significance of study

Over the years, motor vehicles are the main transportation of people causing pollution problems to increase. When the main food sources are from the environment, it caused a major concern in terms of human health. This research is carried out to determine the relationship between motor vehicle emission pollution and the absorption of pollutants by plants.

Different types of combustion yield different distributions of PAHs in both relative amounts of individual PAHs and in which isomers are produced. Present in the form of particulate matters or in gaseous form, PAHs have the ability to enter human body system through respiration and food intake. Therefore, it is important to recognize the ways and means of transportation of PAHs in the atmosphere can be incorporated into the food chain and consequently to increase the knowledge of limiting the intake of PAHs into human body system.

The discovery of relationship between the absorption of PAHs in plants and the concentration of atmospheric PAHs will allow the determination of species suitable for biomonitoring of PAHs level in the atmosphere. Biomonitoring allows continuous observation of an area with the help of bioindicators with a simple and inexpensive sampling procedure. The ability of certain species of plants to absorb PAHs from ambient air could lead to treatment of environmental pollution through bioremediation.

1.4 Research question

The issue and problems stated raise questions such as

(i) What is the concentration of PAHs in air and plant leaves of a sampling area?

(ii) Is there any relationship between the concentration of PAHs in the air and plant leaves?

(iii) How can leaf characteristic affect absorption of PAHs and help as biomonitoring agent?

1.5 Objectives

Specifically this study is aimed to

(i) determine the concentration PAHs in the air

(ii) determine the concentration PAHs in vegetation

(iii) determine the relationship of concentration of PAHs in vegetation and air

(iv) study the different composition of PAHs in different species of plants to determine the potential biomonitoring agent

1.6 Scope

Different locations in urban areas and roadsides with different profile of pollution were selected as sampling sites. The study was concentrated on 3 exits along PLUS' North-South Expressway in Johor region; Ayer Hitam toll station, Skudai toll station and Tangkak toll station.

Two types of samples were employed to achieve the objectives of the study; air particulate sample and plant leaves sample. Plant leaves were taken from eight different species in the three sampling site and analyzed and compared according to the species.

Out of hundreds of different PAHs, Sixteen PAHs are considered priority pollutants: naphthalene, acenaphthylene, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene are the main focus in this study.

A six months study was carried out every two weeks from June to December 2010. Samples were taken for 12 weeks.

1.7 Thesis outline

The thesis is represented in 6 chapters as described below

Chapter 1 introduces the study, the research questions and the objective that needed to be achieved to address the problem. Chapter 2 explores the literature of various researches carried out prior to this research. Chapter 3 explains the research methodology used in carrying out the research from sampling methods, extraction, determination of PAHs in samples and result analysis.

Chapter 4 and chapter 5 show the data analyses and interpretation of the research. Chapter 6 summarizes the results of the research and provides recommendations for future research

1.8 Conclusion

Air pollution problem is a big issue in our country and the major source for air pollution is from mobile sources such as vehicle emission. This study focused on the PAHs pollution in the atmosphere and the ability of plants to absorb and contain the pollutant thereby becoming the agent for biomonitoring and also removing the pollution from the environment.

CHAPTER 2

LITERATURE REVIEW

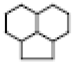
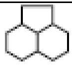
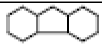
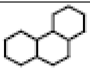
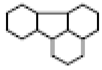
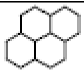
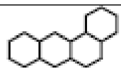
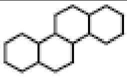
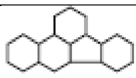
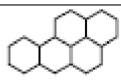
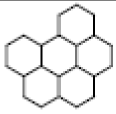
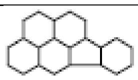
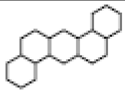
2.1 Introduction

This chapter reviews in details the literature from various studies regarding the ability of PAHs deposited or absorbed by plants which leads to the idea of this research. It discusses the details of vehicular emission, organic pollutants accumulation, chemical uptakes by plants, relationship between PAHs and plants and the process of biomonitoring and bioremediation.

2.2 Definition of Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are very large number of naturally occurring and man-made chemicals characterized by two or more fused aromatic rings. In pure form they are as white or yellowish crystalline solids. However, they are not usually found in this pure form, they are commonly found as environmental pollutants that belong to the hydrophobic organic compounds (HOCs) group based on their properties (Ou, 2000). The fate of PAHs in nature are becoming a pollutant of great environmental and human health concerns due to their widespread occurrence, strong persistence, long-range transportation potential carcinogenic, mutagenic and teratogenic properties as well as their high concentration and frequency found in the environment. Table 2.1 shows the 16 priority PAHs as listed by the United States Environmental Protection Agency (USEPA).

Table 2.1: US EPA 16 priority PAHs (Joa *et al.*, 2009).

PAH	Abbrevation	Structure	Molecular mass
Naphtalene $C_{10}H_8$	NA		128
Acenaphtene $C_{12}H_{10}$	AC		154
Acenaphtylene $C_{12}H_8$	ACN		152
Fluorene $C_{13}H_{10}$	FL		166
Phenanthrene $C_{14}H_{10}$	PHE		178
Anthracene $C_{14}H_{10}$	AN		178
Fluoranthene $C_{16}H_{10}$	FA		202
Pyrene $C_{16}H_{10}$	PY		202
Benzo[a]anthracene $C_{18}H_{12}$	B[a]A		228
Chryene $C_{18}H_{12}$	CHR		228
Benzo[b]fluoranthene $C_{20}H_{12}$	B[b]F		252
Benzo[k]fluoranthene $C_{20}H_{12}$	B[k]F		252
Benzo[a]pyrene $C_{20}H_{12}$	B[a]P		252
Benzo[ghi]perylene $C_{22}H_{12}$	B[ghi]P		276
Indeno[1,2,3-cd]-perylene $C_{22}H_{12}$	IP		276
Dibenzo[a,h]anthracene $C_{22}H_{14}$	D[ah]A		278

2.3 Theoretical framework

The research is explained in a theoretical framework as shown in Figure 2.1. The framework shows that combustion of organic fuel by vehicle emits numerous kinds of pollutants including carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO_2) and PAHs. PAHs, a type of organic compound, are possibly absorbed by plants due to their physical and chemical characteristics. The ability of plants to absorb these contaminants can promote the use of plants to be a qualitative indicator of contaminant levels and to further assist in bioremediation. This is supported by a theory by Simonich and Hites (1995) that accumulation of organic pollutants by vegetation can be divided into three areas;

(i) The mechanism of uptake by vegetation.

(ii) The use of vegetation as a qualitative indicator of contaminant levels.

(iii) The importance of vegetation as a pollutant sink.

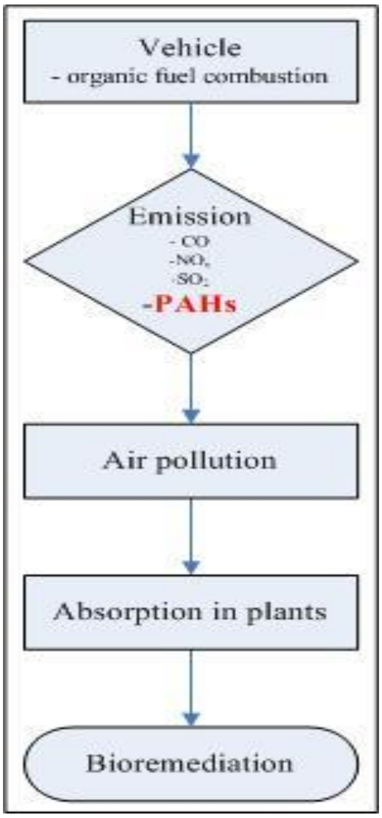


Figure 2.1: Theoretical framework of the research.

Based on the theory proposed by Simonich and Hites (1995), the research was carried out in a framework as shown in figure 2.2. This research concentrated on the accumulation of PAHs in plant leaves over time. The ability of plants to absorb PAHs released to the atmosphere by vehicle emission was observed by measuring the PAHs concentration in air sample and comparing with the concentration of PAHs in plant leaves sample in between time and sampling station.

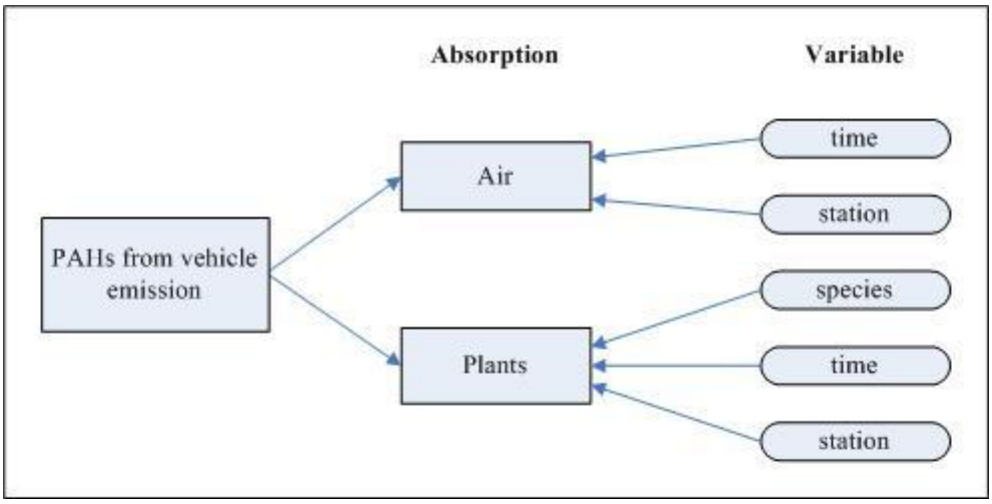


Figure 2.2: Research framework.

2.4 Vehicular emission and environment

Vehicles are mechanical means of conveyance mostly manufactured, propelled, pulled by animals or powered by fuel engine such as petroleum or diesel which is the most popular means of vehicle in the new age. Emission means something sent forth or out, any form of pollution discharged into the atmosphere from smokestacks, vents, surface areas of commercial or industrial facilities, residential chimney and motor vehicle, locomotive or aircraft exhaust (US EPA, 1990). Vehicular emission is something sent out from a vehicle, particularly from the exhaust. According to the Terms of Environment, Glossary, Abbreviations and Acronyms, environment is the sum of all external factors, both biotic and abiotic, to which organism is exposed that act upon the existence and development of an organism or an ecological community and ultimately determines its form and survival (US EPA, 1990).

Rapid urbanization has resulted in increasing air pollution emissions, typically arising from transportation, energy production and industrial activities, concentrated in densely populated areas (D'Angiola *et al.*, 2010). The increasing need for mobility and derivation of new technology has provided faster locomotion and triggered people to the use of more speedy and comfortable means of transportation. Behind the contribution of transportation, it has been widely recognized as the main source of air pollution worldwide (Colvile *et al.*, 2001). Transport sector's share of green house gases emission rose by 35% in 15 years from 1990 (European Commission, 2009). Moreover, the share of road modes is about 72% of emissions released by transport compared to other modes of transportation such as air and railway transportation. For a given type of fuel, the gas emissions from vehicles are directly correlated with energy consumption, based on a number of phenomena, which may be grouped into three categories:

(i) Phenomena related exclusively either to driver behavior or to vehicle performance.
(ii) Phenomena that depends on road infrastructure properties: slopes, curves, pavement stiffness, surface unevenness, and surface texture.
(iii) Road works, by adding to traffic congestion, also impact fuel consumption patterns.

(European Commission, 2009)

Road traffic has grown distinctly over the years. Data acquired from the Department of Statistics Malaysia, shows that total number of private vehicles increased greatly from year 1999 to 2007 as shown in Figure 2.3 and Figure 2.4, and from the total number of on road vehicle, almost 80% are privately owned vehicle. These vehicles mostly run on petrol and diesel, a complex mixture of hydrocarbons (HCs).

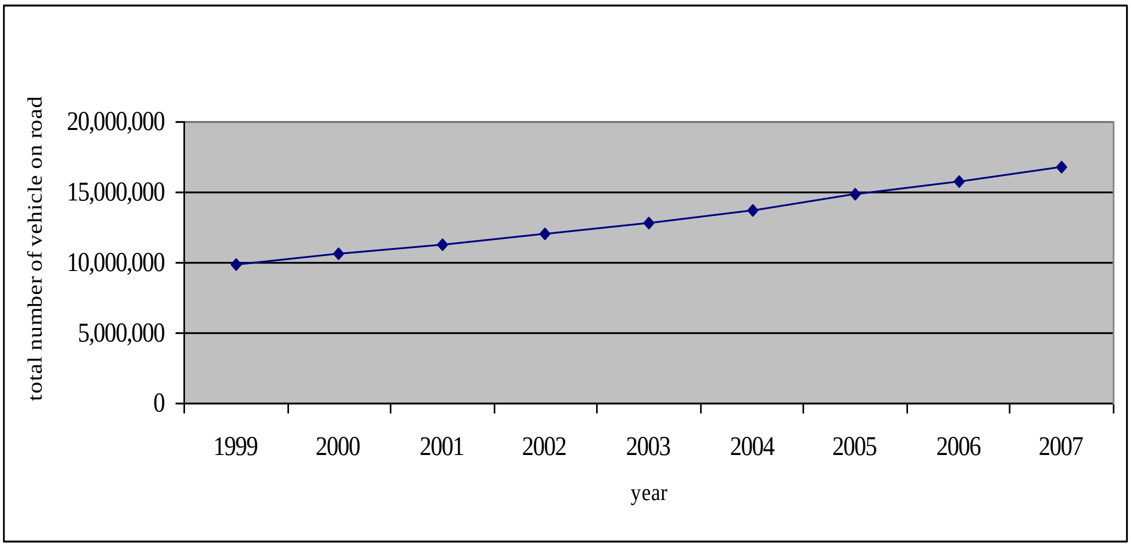


Figure 2.3: Total number of vehicle on the road from 1999 to 2007
(source: Department of Statistics Malaysia, 2009).

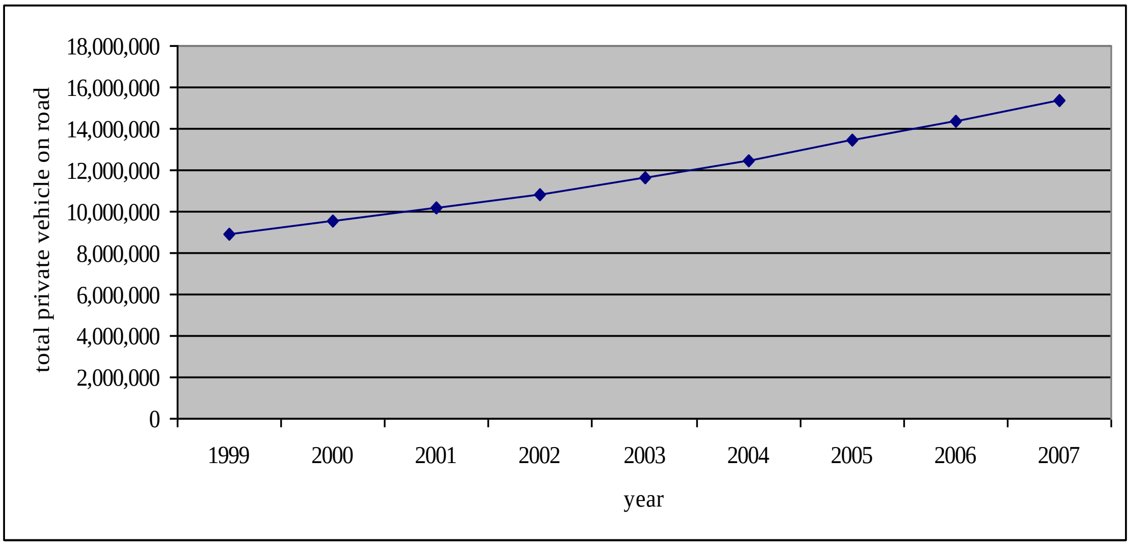


Figure 2.4: Total number of privately owned vehicle on the road from 1999 to 2007
(source: Department of Statistics Malaysia, 2009).

Various researches have shown that petrol or diesel fueled vehicle are the main source of air pollutant emission. An inventory of Turkish road transport emissions in the atmosphere was calculated and the contributions of road transport to global and local air pollutant emissions were examined for the year 2004 and it was observed that passenger cars are the main source of CO, HCs, and lead (Pb) emissions while heavy duty vehicles are mainly responsible for NO_x, particulate matter (PM), and SO_2 emissions (Solyu, 2007). As shown in Figure 2.5, diesel and petrol road transport comprises more than 70% of fine particulate matter smaller than 10 µm aerodynamic diameter (PM_{10}) in London in the year 1995 and 1996. Ideally, a complete combustion of fossil fuel would lead to a complete conversion of fuel into energy, but this is unachievable. Changes occurred during combustion and passed out unburned fuel and partially burnt fuel. The partially burnt fuel changes form into a number of gases, impurities combine in the process principally with air to form other compounds e.g. oxides of sulphur, nitrogen from the air participate in the combustion process to form oxides of nitrogen i.e nitrogen oxide (NO) and nitrogen dioxide (NO_2) depending on the prevailing conditions in the combustion chamber. The products of combustion are mainly gases or particulate matters are then emitted into the environment as exhaust gases (Enemari, 2001).

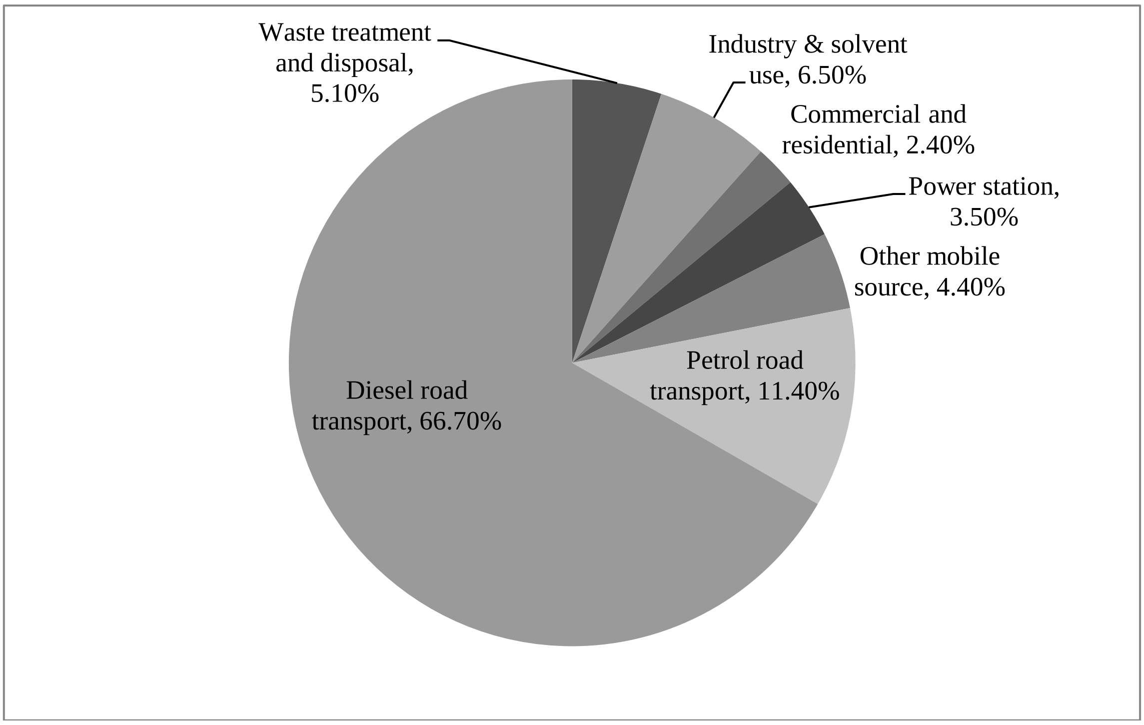


Figure 2.5: Emissions of fine particulate matter smaller than 10 µm aerodynamic diameter in London in 1995/1996 (Colvile *et al.*, 2001).

An annual emission for metropolitan area for Buenos Aires, one of the megacities in the world for 2006 determined that gasoline light-duty vehicles are the most abundant contributor to air pollution, while diesel light and heavy-duty vehicle are the main contributors towards air pollution even though they occur in fewer numbers. The main pollutant caused by both gasoline and diesel fueled vehicle are

CO, carbon dioxides (CO_2), methane (CH_4), NOx, SO2 and PM as shown in Figure 2.6 (D'Angiola *et al.*, 2010).

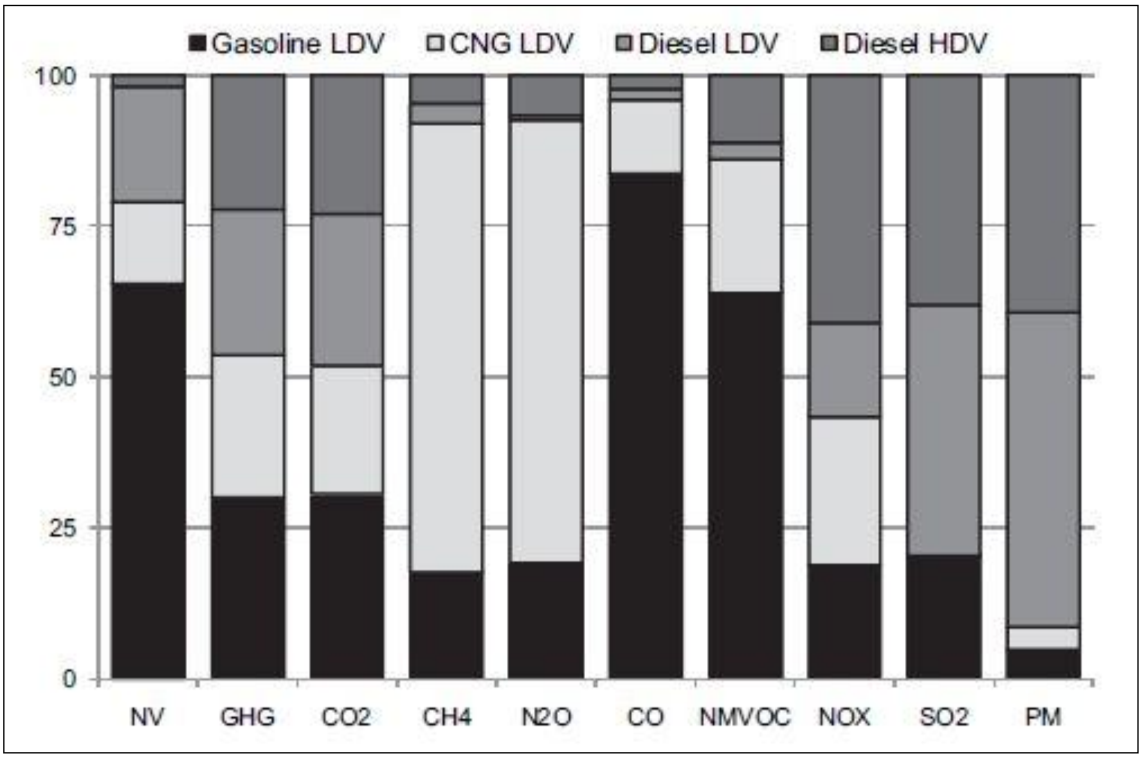


Figure 2.6: Emissions distribution by fuel type (compressed natural gas (CNG), diesel oil and gasoline) and main vehicle category (light and heavy-duty vehicles), GHG represents the sum of CO2, CH4 and N2O emissions (CO2: 1, CH4: 21 and N2O: 310); NV stands for number of vehicles (D'Angiola *et al.*, 2010).

2.5 Organic pollutant

An organic compound is any member of a large group of chemical compound consisting entirely of hydrogen and carbon and is also known as hydrocarbon. There are thousands of different hydrocarbon compounds that are comprised solely of hydrogen and carbon and can be found in gaseous, liquid or solid states at room temperature. Hydrocarbon can be classified into two main classes:

(i) aliphatic hydrocarbons which can later be classified into two types, saturated hydrocarbon (containing only sp^3 carbon), also known as alkanes and unsaturated hydrocarbon, alkenes and alkynes which each has double bonded carbons and triple bonded carbons,

(ii) aromatic hydrocarbons which possess benzene ring as their unit structure are known as arenes

(Mahmood, 2004).

Organic substances comprise a potentially large group of air pollutants, particularly in urban environments. Organic pollutant is organic substances introduced in an environment and cause instability, disorder, harm or discomfort to ecosystem physically, chemically and/or biologically. Even at low levels, some of these organic pollutants can be hazardous to human health, particularly if the exposure is long term. Some organic pollutants also play an important role in the formation of photochemical smog.

Many anthropogenic sources of organic pollutants such as waste incineration, industrial processes and, most importantly, vehicular traffic emits both trace elements and hydrocarbons into the atmosphere. As organic substances enter the atmosphere through natural or anthropogenic sources, removal of the compounds will take place. Once in the atmosphere, their fate and transfer to the natural surfaces are controlled by atmospheric deposition. Various studies have been done over the years to determine the fate of these organic compounds in sediments, soil, air and water (Simonich and Hites, 1994). Precipitation scavenging is an important atmospheric removal mechanism for relatively volatile and semi-volatile organic compounds, while the larger molecular weight compounds tend to attach themselves to particulate matter and settled in the soil, sediments or ended up in plant tissues.

Several methods of human absorption of organic compounds are known to risk human health. They include inhalation of contaminated air, ingestion of contaminated foods and drinks and absorption through cuts when accidents happen. Industries where occupational exposure is likely to occur include coke ovens and coal tar use, iron and steel works, aluminum casting, foundries, carbon electrodes and carbon black manufacture, asphalt manufacture and use, and also pollution via road traffic (Dejean *et al.*, 2008). The known effects of organic substance to human health includes risk of damaging lungs from metabolism of organic material inhaled through breathing (Sun *et al.*, 1983) and sperm damage which can result to infertility of men or mutation and abnormalities in babies (Gaspari *et al.*, 2003).

2.5.1 Organic pollutant accumulation in the atmosphere

The atmosphere plays an important role in the transport and cycle of chemicals that are volatile in nature. Commonly found organic compounds in the atmosphere are derived from biogenic sources such as vascular plant wax, anthropogenic utilization of fossil fuel products and natural sources such as vegetation, forest fires, and volcanoes. Hart *et al.* (1993) has measured the concentrations of organic pollutants such as n-alkanes, PAHs, polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzodioxins (PCDDs), phenols, and a variety of volatile organic compounds (VOCs) in snow, rain, fog, and the ambient air in Central and Northern Switzerland. From the research carried out the pollutants measured were:

(i) strongly influenced by artifacts associated with sampling, extraction, and analyses;

(ii) dependent on the local meteorological conditions; and

(iii) can be modeled quite well by equilibrium partitioning theory between the gaseous, aqueous, and particulate phases in the atmosphere

(Hart *et al.*, 1993).

A comparison of composition was carried out to see the different occurrences of organic pollutant between a normal climate and a haze episode in Kuala Lumpur by Abas and Simoneit (1996) and interpreted to be due to the local build-up of organic contaminants as a result of atmospheric stability changes, photochemical reactions and unidentified anthropogenic stability. Some of the organic contaminants are also suspected to be brought in from outside of the Klang Valley region (Abas and Simoneit, 1996). PAHs are subjected to photodegradation (Sear, 2001) and therefor can be broken into smaller PAHs compounds and the gas-phase PAHs usually have shorter atmospheric lifetimes than those found on particulate (Abas and Simoneit, 2006).

2.5.2 Organic pollutant accumulation in plants

For many years studies were done on environmental fate of organic pollutants in sediments, soil, air and water, only in the mid 1980s the attention turns towards vegetation (Paterson *et al.*, 1990). As organic pollutants floats in the atmosphere after being released, these compounds would naturally be attracted to natural surfaces; one of the most common natural surfaces is leaves of plants grown close to the emission sources other than the sedimentation around them. Such contaminants, transported through air mass movements, are deposited by dry and wet deposition and intercepted by plant canopies: the leaves absorb gaseous compounds or accumulate airborne particulates by interception, impaction or sedimentation.

Organic pollutants may enter plants by partitioning from contaminated soil to enter the roots and translocated in the plants through xylem or from the atmosphere by gas-phase and particle phase deposition onto the waxy cuticles or by uptake through stomata and translocated by phloem as shown in Figure 2.7. Both pathways depend on the chemical and physical properties of the pollutant, the environmental condition such as ambient temperature and organic content of the ambient air or soil, and the plants species (Simonich and Hites, 1995).

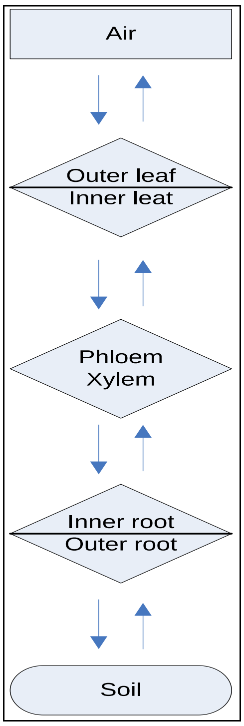


Figure 2.7: Simplified mechanism of pollutant uptake by vegetation (Simonich and Hites, 1995)

The particulate accumulation on the leaf surface depends on particle size, speed of deposition and leaf surface properties. Leaf morphology and the chemistry of the waxy components affect airborne particle retention on the leaf surface and air-to-foliage gas transfer, thereby affecting the accumulation of particle-bound and gaseous contaminants in vegetation (Alfani *et al*., 2001).

2.5.3 Effects of chemical and physical factors towards organic pollutant accumulation in plants

Accumulation of organic pollutant in plants is mostly affected by the physical and chemical factors of the organic compounds themselves. Uptakes of compounds from soil through plant roots are usually a pathway of organic compounds with high water solubility. These hydrophilic compounds move into the inner roots and distributed within the plant.

Organic compounds are non-polar which makes most of them lipophilic in nature. These pollutants such as PAHs, PCDFs, PCDDs and PCBs partition through the epidermis of the root and not drawn into the inner xylem therefore not transported to the other parts of the plants. However, for most species examined under controlled exposure experiments, uptake of lipophilic organic pollutants through roots are generally not a significant way of accumulation (Paterson *et al.*, 1994, Simonich and Hites, 1995). The main accumulation pathways of lipophilic organic pollutants are through absorption from the air into leaf surface.

Molecular weight of the organic pollutant also determines the pathway of accumulation in plants (Orecchio, 2007). Since the form of organic pollutant is dependent on the molecular weight. Smaller organic matter may dissipate into plants through plant respiration process through the stomata while heavier compounds usually exist in particulate form depending on deposition onto the waxy leaves surfaces to enter the plants (Simonich and Hites, 1995).

Vegetation-atmosphere partition coefficient accounts for the vegetation synthetic organic chemical (SOC) concentration, the lipid content of the vegetation, and the atmospheric gas-phase SOC concentration. The long-term partitioning process is primarily governed by the atmospheric gas-phase concentrations and is temperature dependent, while particle-phase SOCs may be scavenged by vegetation, but not temperature dependent; these SOCs may be more tightly bound to the particles than to the vegetation. (Simonich and Hites, 1994)

Experiments was conducted using ryegrass, an important agricultural grassland species in Central Europe as samples, have shown that the primary mechanism of atmospheric deposition for many semi-volatile organic compounds to be dry gaseous deposition. Dry gaseous deposition is a diffusive process, which chemicals being deposited to bring the vegetation into equilibrium with the gas phase (McLachlan *et al.*, 1995). Field studies, also with ryegrass, indicated that equilibrium is not approached for very nonvolatile compounds due to slow uptake kinetics compared to the contaminant storage capacity of the vegetation. However, for persistent chemicals of intermediate volatility such as the higher chlorinated benzenes or the lower chlorinated biphenyls, an approximate equilibrium can be expected for many plant species (Komp and McLachlan, 1997, McLachlan *et al.*, 1995).

Uptake of PAHs also depends on physiological parameters of plants including specific area of leaves, surface hair, stomata density, lipid content and cuticle structure. For instance, PAHs concentrations in hairy leaves are significantly higher than those in smooth leaves (Howsam et al, 2000). Stomatal pores are important in uptake processes. Leaf surfaces vary greatly between plant species, both in morphology and chemistry of the waxy cuticle, the number and distribution of stomata, and in the presence or absence of hairs (pubescence). The water repellence of leaves has been shown to be important in determining how effectively the leaves can `clean themselves' of particulate contamination on their surfaces (Wang *et al.*, 2008)

Comparison between hazel leaves, which have the densest covering of hairs on both adaxial (upper) and abaxial (lower) surfaces, oak leaves with relatively shorter and less hair, and ash leaves which are essentially hairless with recessed capitates hairs present on the adaxial surface only (Howsam et al, 2000) shows that there were significant but small differences between PAHs concentrations in the three species and leaf pubescence may provide one explanation for the observed difference. Supporting evidence for the influence of leaf hairs on PAHs concentrations was found in the higher PAHs for concentrations of the majority of the particle bounded 4-, 5- and 6-ring PAHs are found in hazel (Howsam et al, 2000).

Wang *et al.* (2008) found that the concentrations of all individual PAHs compounds in the cuticles were higher than those in the inner tissues. There were also general decreasing trends in both cuticle and tissue concentrations from the lower molecular weight compound to the higher molecular weight compounds. The inner tissue concentrations seemed to decrease faster than the cuticle concentration did (Wang *et al.*, 2008). The low molecular weight PAHs were derived primarily from volatile PAHs in the air while high-molecular weight PAHs come from particulate PAHs deposition. Simonich and Hites (1994) collected the samples of the bark, leaves, needles and seeds of sugar maple and white pine and found a positive correlation between PAHs and lipid content. This shows that the different amount of PAHs concentration among the different plant tissues from the same site can vary according to the lipid content of the plants.

Temporal and seasonal variation provides different degree of absorption of organic pollutant in plants. Prajapathi and Tripathi (2008) observed that maximum concentration of PAHs in *Ficus benghalensis* leaves was in January (winter) and the concentration decreases in May (summer) and least during rainy season in August. Even though there is no linear quantitative relationship between air and leaf concentration, the higher values during winter can be assumed caused by greater accumulation of PAHs on leaf surface from more emission source during winter, more condensation and less photolytic degradation activity of PAHs under the sunlight (Prajapathi and Tripathi, 2008).

2.6 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic Aromatic Hydrocarbons (PAHs) are a large group of organic compounds which have two or more benzene rings fused together and does not contain any heteroatoms or carry any other substituents (Ou, 2000). PAHs are usually formed from incomplete burning of certain organic fuel, waste or other carbonaceous materials. They are formed during the combustion of a wide variety of materials such as fossil fuels, saturated and unsaturated hydrocarbons, peptides, and carbohydrates and are often absorbed onto particles of soot emitted from combustion sources and can dispersed regionally and intercontinentally through atmospheric long-range transport because they are usually absorbed onto particulate matter from the source of burning (Ou, 2000). Some major sources of PAHs are heat and power generation, refuse burning, motor vehicle emissions, industrial processes, petroleum leakage and spills, fallout from urban air pollution, forest fires and cigarette smoke (Ou, 2000).

When PAHs entered the natural atmosphere, they are found in both gaseous and solid particle phases. PAHs wit 2-3 aromatic rings almost usually exist in gaseous phase while those with 4 or more aromatic rings are usually associated with the particulate fraction (Li *et al.*, 2009). PAHs-associated particles exist predominantly as fine particles in congested traffic areas, and since most of the carcinogenic PAHs are of 4 and more aromatic rings, many studies on PAHs in ambient air are focused on PAHs bound to particulate matter (Li *et al.*, 2009, Omar *et al.*, 2006, Wu *et al.*, 1998, Wild and Jones, 1994). These are dependent on the molecular weight of the PAHs itself as heavier molecules tend to exist in particulate form rather than gaseous or liquid form (Mahmood, 2004). With an increase in molecular weight, their solubility in water decreases; melting and boiling point increase and vapour pressure decreases.

Through the environment, human exposure to PAHs may cause adverse health effect. The relationship between cancer and the environment is largely conditioned by investigations involving exposures to PAH. Several individual PAHs such as benzo[a]pyrene (B[a]P), chrysene, indeno[1,2,3-c,d]pyrene, and benzo[b]fluoranthene have produced carcinogenic, mutagenic, and genotoxic effects in animal experiments (Sun *et al.*, 1983, Gaspari *et al.*, 2003, Chen and Liao, 2006, Johnson *et al.*, 2008, Quinn and Arnold, 2009). Long-term studies of workers exposed to mixtures of PAHs and other workplace chemicals have shown an increased risk of skin, lung, bladder and gastrointestinal cancers (Johnson *et al.*, 2008). Biological effects of PAHs have also been associated with metabolic activation and elevated level of DNA adducts leading to mutation and transformation such as PAH-DNA adducts and P53 mutations in persons who smoke or are exposed to PAH in the workplace and ambient air (Chen and Liao, 2005). Chronic or long-term exposure to PAHs may include cataracts, kidney and liver damage and jaundice, may induce redness and skin inflammation (Quinn and Arnold, 2009).

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