Polycyclic Aromatic Hydrocarbons (PAHs) from Vehicle Emission in the Vegetation of Highway Roadside in Johor, Malaysia

Azliyana Azhari, Mohd Noh Dalimin, and Seow Ta Wee

Abstract— **Incomplete combustion of organic and fossil fuel produced a mixture of hazardous air pollutants including polycyclic aromatic hydrocarbons (PAHs). Abundance of PAHs occurrence in the atmosphere can be accumulated into vegetation. This research measures the concentration of PAHs collected in 8 selected species of plants to study the different composition of PAHs in different species of plant leaves to discover the ability of plants to absorb PAHs from the atmosphere. The study is concentrated on 3 toll station along PLUS' North-South Expressway in Johor for 6 months. Samples 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 PAHs. From the series of experiments, it shows that the plant leaves samples from highway roadside air contains various types of PAHs. There are also presence of PAHs of car exhaust characteristics such as phenanthrene, fluorene, and pyrene. Plant leaves have the ability to absorb the organic pollutant to facilitate the removal or reduce the pollutants from the atmosphere**

Index Terms— **Polycyclic Aromatic Hydrocarbons (PAHs), Vehicular-air pollution, plant leaves absorption,**

I. Introduction

Human activities such as waste incineration, industrial process and vehicular traffic have caused many types of anthropogenic pollution the environment[1]. Transportation has been widely recognized as the main source of air pollution worldwide[2]. The characteristic of pollutant throughout the world vary across cities because of the different combustion sources, but usually share the same primary pollutants such as sulfur dioxide (SO2), nitrogen oxides (NOx), carbon monoxide (CO) and other organic pollutant[3] known to be toxic such as Polycyclic aromatic hydrocarbons (PAHs). PAHs are a large group of organic compounds with two or more fused aromatic rings which do not contain heteroatoms or carry any substituents[4]. PAHs contamination from vehicular emission is of great concern to our world nowadays due to its abundance occurrence 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. 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[5].

In Malaysia, the most important source of PAHs in cities is expected to be vehicular emission since motor vehicle contributed as much as 82% of air pollutants as reported in the Environmental Quality Report on 1996, and until now 93% of carbon monoxide and hydrocarbon emission of the air pollutants are still contributed by motor vehicles[6]. PAHs from combustion sources are widespread and typically concentrated in the urban centers. The distribution pattern of PAHs in Kuala Lumpur shows that vehicular emission is the dominant source of PAHs in atmospheric particles[5].

PAHs may enter plants by partitioning from contaminated soil or from the atmosphere depending on chemical and physical properties of the pollutant or the environmental condition[7]. In general, the lighter, smaller PAHs tend to deposit into plants through dry gasses and/or wet deposition while the larger, heavier 5 PAHs are usually in particulate form and can be deposited on to plant surface in wet and dry deposition[8]. 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:

- equilibrium partitioning;
- kinetically limited dry vapour deposition;
- particle-bound deposition, depending on the physicochemical properties of the compound [9].

The contaminants are transported through air mass movements and deposited by dry and wet deposition before being intercepted by plant canopies. The plant leaves absorb gaseous compounds or accumulate airborne particulates by interception, impaction or sedimentation. 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[10].

The objective of this study is to determine the concentration of PAHs in leaves of roadsides plants and to study the difference composition of PAHs in different species of plant leaves.

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II. MATERIALS AND METHODOLOGY

A. Sampling Site Selection

The North-South Expressway comprises of nine toll stations in the closed system and 2 toll stations in the open system. Three sampling sites along the closed system of North-South Expressway in Johor were chosen according to the distance and density of vehicle utilizing the area. The sampling sites are Ayer Hitam toll station, Skudai toll station and Tangkak toll station as shown in figure 1 with the desity of traffic shown in table I.

Fig. 1. Map of PLUS' North-South Expressway Exits in Johor Region.

TABLE I: TOTAL NUMBER OF VEHICLE USING THE AYER HITAM, SKUDAI AND TANGKAK TOLL STATION (DATA ACQUIRED FROM PLUS UEM BHD.).

Month	*Ayer Hitam*		*Skudai*		*Tangkak*	
	Entry	Exit	Entry	Exit	Entry	Exit
Jun	262,900	267,300	669,200	668,700	195,800	198,000
July	249,300	257,200	658,300	637,200	180,700	187,100
August	237,800	239,400	624,500	623,800	176,400	173,300
September	293,000	296,600	694,100	688,000	214,600	217,900
October	248,400	253,300	655,800	647,700	178,300	179,900
November	265,700	270,100	676,600	675,000	195,400	196,300
December	289,200	296,400	744,500	742,500	211,900	217,100

B. Plant Leaves Sample Collection

Eight species of plants found in the three sampling sites were chosen as plant leaves sample in this study namely *Baphia* sp., *Bougainvillea* sp., *Codiaeum* sp., *Ficus* sp., *Heliconia* sp., *Hibiscus* sp., *Ixora coccinea* and *Ixora taiwanensis*. The presences of species are as shown in table 2.

TABLE 2 PRESENCES OF SPECIES IN EACH SAMPLING SITE

Species	*Sampling site*		
	Ayer Hitam	Skudai	Tangkak
Baphia sp.	√		
Bougainvillea sp.	√	√	√
Codiaeum sp.	√		√
Ficus microcarpa	√	√	√
Heliconia sp.		√	
Hibiscus sp.			√
Ixora coccinea	√	√	√
Ixora taiwanensis		√	√

Leaves samples of the same species were collected from 3 different sites in one sampling area to ensure homogeneity of the samples. Leaves samples collected were as far as possible to be of the same maturity, size and healthy appearance and collected at approximately 1.0 – 1.5 m from the ground. The leaves were collected in aluminum containers separately according to the species and brought back for laboratory analysis. The samples were immediately kept in a freezer at -20°C if analysis was not done immediately. Plant leaves samples were collected once in 2 weeks for 6 months from June 2010 to December 2010 by random selection.

C. Laboratory Analysis

The method use for air sample extraction in this study is a typical ultrasonic extraction method[11] with some modifications. 5 g wet weight of sample were spiked with 50µL of Anthracene-D10 and Perylene-D12 as internal standard. The samples were extracted three times using ultrasonic agitation for a 15-min period each with 150 ml of dichloromethane.

1 mL dried extract dissolved in dichloromethane and applied to the top of a 20 cm column with 1 cm I.D prepared by adding 5 g activated silica gel (slurry packed with n-hexane) followed by 10 g activated aluminum oxide (dry packed). The extract was fractionate using eluent with increasing polarity and collected in different round bottom flask. The alkanes were collected in the first fraction (20 mL of n-hexane), the alkenes and polycyclic aromatic hydrocarbons (PAHs) were eluted in the second fraction (30 mL of 10% dichloromethane in n-hexane; 20 mL of 50% n-hexane in dichloromethane) and the polar compounds were obtained in the third fraction (40mL 10% methanol in dichloromethane)

Fraction I, II and III of sample were analyzed by gas chromatography – mass spectrometry (GC-MS) method. Compound identification was based on GCMS data. Quantification was made by comparing the retention time of each sample to the retention time of the external standard.

III. RESULTS AND DISCUSSION

Seven PAHs were identified and quantified in this study. Those PAHs were acenaphtylene (ACN), phenanthrene (PHE), fluorene (FL), pyrene (PY), chrysene (CHR).

Benzo[a]anthracene (BaA), and benzo[a]pyrene (BaP). Among the seven PAHs, three are of the 3-rings PAHs, namely CAN, PHE and FL, two are 4-rings, CHR and BaA while BaP is the only 5-rings PAHs detected from all three sampling station. There are presence of PAHs of car exhaust characteristics such as PHE, FL, PY and BaP while PHE, FL and PY are characteristic of diesel vehicle exhaust[12] showing that most of the PAHs found originated from exhaust emission.

The highest average concentration for all plant leaves sample is detected to be BaP except for *Codiaeum* sp. and *Ixora taiwanensis* in Tangkak toll station as shown in figure 2. The highest average concentration of PAHs among plant leaves sample are detected to be BaP in *Baphia* sp. in Ayer Hitam toll station, *Heliconia* sp. in Skudai toll station and *Hibiscus* sp. in Tangkak toll station. BaP is the largest compound detected in this study. Accumulation of particulate-bond compound is more plausible through deposition and leaf surface property compared to the gaseous contaminants[10] which may dissipate into plants through plant respiratory process through the stomata[7] .

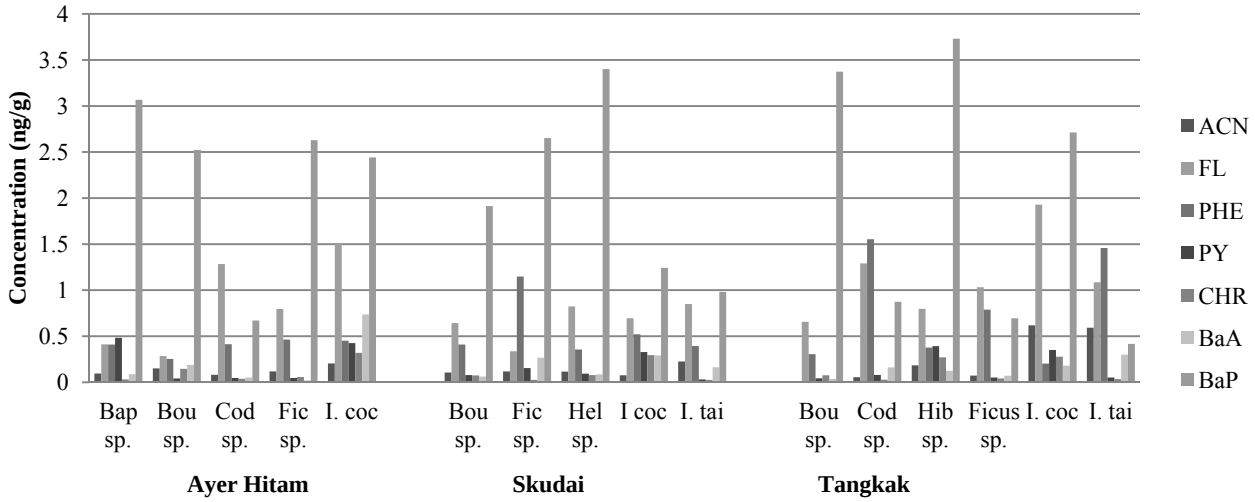

Fig. 2. Average concentration of PAHs in plant leaves samples from Ayer Hitam, Skudai and Tangkak toll station.

PAHs compound were detected in plant leaves sample from all sampling area at different level of concentration proves possibility of PAHs and other organic compound to accumulate in plant leaves through absorption from the air into leaf surfaces [7]. The increasing pattern of PAHs concentration collected in the plant leaves also shows accumulation pattern of PAHs compound in the plant leaves collected. Presence of PAHs in plant leaves shows that PAHs in the atmosphere are attracted to natural surfaces such as plant leaves[13].

Pollutants can be absorbed into the plant leaves and collected until a certain period of time. The vegetation – atmosphere partition process shows atmospheric deposition is to bring the vegetation into equilibrium with the gas phase in the atmosphere[9].

The total concentration of PAHs increase over the 12 weeks of sampling is shown in figure 3. The highest total concentration of PAHs was found in *Ixora coccinea* for Ayer Hitam and Tangkak toll station, and in *Heliconia* sp. for Skudai toll station.

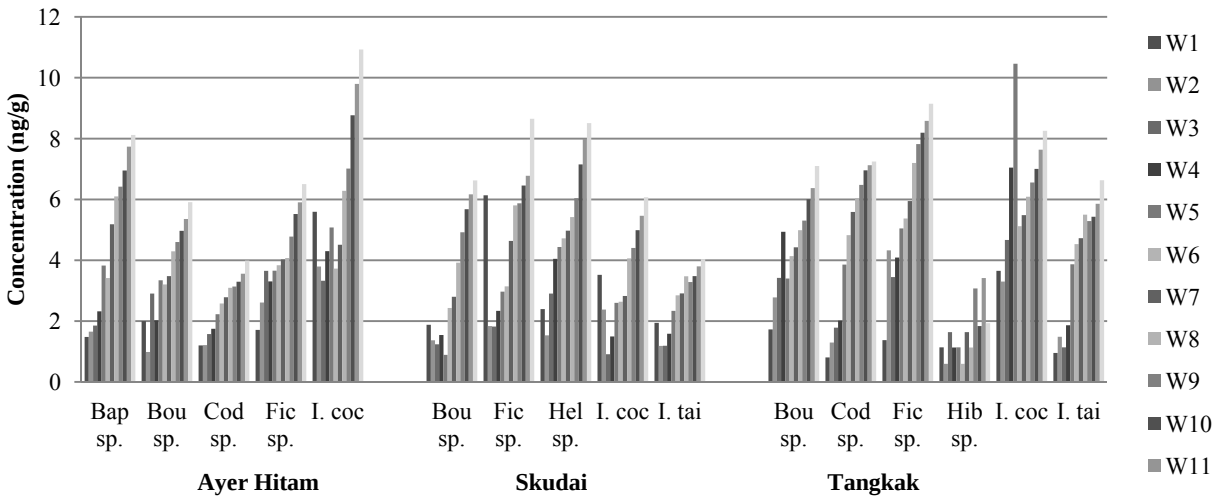

Fig. 3. Total concentration of PAHs in plant leaves sample from Ayer Hitam, Skudai and Tangkak toll station for 12 weeks

The increasing trend of total concentration over the 12 weeks confirming the accumulation of PAHs in the plant leaves sample. The total concentration of PAHs from Skudai toll station show lowest accumulation even though it is the most utilized station among all three, probably because the different distribution and layout of the toll station compared with Ayer Hitam and Tangkak toll station.

Based on the physical appearance of the plant leaves, *Ficus microcarpa*, *Ixora coccinea* and *Baphia nitida* have the waxiest surface of leaves therefore have the ability to accumulate more organic pollutant in the leaves. The highest total concentration of PAHs in the plant leaves, the species with highest accumulation of PAHs compounds are *Ficus microcarpa*, *Ixora coccinea* and *Baphia nitida*. These species have the ability to be introduced into the environment to reduce and remove PAHs pollution in the atmosphere to help mitigate the organic air pollution problem.

IV. CONCLUSION

Plant leaves are able to absorb PAHs pollution in the atmosphere. The concentration of PAHs in plant leaves samples show increasing pattern throughout the 12 weeks showing the accumulation of PAHs in the plant leaves samples. Based on the findings of this research, PAHs pollutants in the environment are able to be reduced or removed by using plants. However, further development of this study is needed to provide more data on this matter and also to help in mitigation of the problem.

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