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THE ANALYSIS AND CHARACTERIZATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SELECTED AREAS : KUALA TERENGGANU CASE STUDY IN A STATE OF TERENGGANU, MALAYSIA.

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ABSTRACT.

Analysis and characterization of polycyclic aromatic hydrocarbons (PAHs) were measured at two selected industrial areas and four selected school areas in Kuala Terengganu, Malaysia. Airborne particles were collected using High Volume Air Sampler (HVAS) in school areas and 24 hours in industrial areas respectively. From the analyses, the highest concentration of PAHs on air particle samples obtained in oil palm industry which represent an industrial areas. The value of the concentration is 1342.87 µg/g dry weight. On the other industry area (paddy industry), the concentration value obtained is only 50.86 µg/g dry weight. Meanwhile, the highest concentration of PAHs on air particle samples obtained in representing school areas is in Agama Khairiah school area which is 39603.5 µg/g dry weight. The lowest concentration of PAHs obtained in school areas is in Paya Bunga school area with the value of 2214.719 µg/g dry weight. The results obtained from this study shows that school areas are the most contaminated place with PAHs compounds compared to an industrial areas

Key Words: Polycyclic Aromatic Hydrocarbons (PAHs). Airborne Particles. Naphthalene.

1.0 INTRODUCTION.

In Malaysia, the major sources of air pollution are comes from mobile sources, stationery sources, and open burning sources. For the past five years, emissions from mobile sources (i.e., motor vehicles) have been the major source of air pollution, contributing to at least 70-75% of the total air pollution. Emissions from stationery sources generally have contributed to 20-25% of the air pollution, while open burning and forest fires have contributed approximately 3-5% (DOE, 1996). According to the Department of the Environment (DOE), Malaysia, in 1996, the percentages, of the air emission load by type were motor vehicles, 82%; power stations, 9%; industrial fuel burning, 5%; industrial production processes, 3%;

domestic and commercial furnaces, 0.2%; and open burning at solid waste disposal sites, 0.8% (DOE, 1996).

As a result of rapid population growth, explosive industrialization and few environmental regulations, air or atmosphere pollution play a role in the incidence of respiratory diseases and cancers because a large number of chemical compounds that damage the ambient air quality are formed during incomplete combustion of organic materials. Among the compouns formed are polycyclic aromatic compounds. Polycyclic aromatic hydrocarbons (PAHs) comprise the largest class of chemical compounds known to be cancer-causing agents (Peter, 2002). By definition, PAHs consist solely of carbon and hydrogen (Baek, 1991). PAHs, predominantly the products of incomplete combustion, are ubiquitous in the atmosphere as the result of natural events, such as forest fires, and widespread anthropogenic sources, such as biomass burning (e.g. slash-and-burn agriculture), vehicle traffic, home heating and industrial emissions (Baek *et al*., 1991; Howsam and Jones, 1998). Incomplete combustion of wood and petroleum products is responsible for a large proportion of their formation. In the development of oil palm and paddy industries in Malaysia, PAHs pollution level from this industry emissions were studied. In addition, some sample were collected which situated nearby the road since it is one of the most important sources of PAHs in urban area.

However, the concern and awareness of the sources and effects of PAHs on human health are still very low among the people in Malaysia especially in Kuala Terengganu. Therefore, the objectives of this study were to determine and compare the concentration of total PAHs, and to identify the types and characteristics of PAHs compounds in selected school and industrial areas of Kuala Terengganu. The results from this study provide a baseline reference for a global database as well as for regulatory action to improve air quality in the city of Kuala Terengganu.

2.0 LITERATURE REVIEW

Aromatic hydrocarbons are the molecule that contains one or more benzene compound, which sometimes called as unsaturated cyclic hydrocarbons. Unsaturated hydrocarbons are compounds that have less hydrogen atom attach to the carbon atom (e.g. alkenes and alkynes). Besides, aromatic hydrocarbons also referred as Arene which are derived from benzene, C_6H_6. Benzene (C_6H_6) is the most basic compound of these hydrocarbons. Although benzene is a good solvent in fractionating organic compounds in all kind of media, but the usage of its has been band due to its carcinogenic effect to human. According to Masterton and Hurley (1997), chronic exposure to benzene vapor leads to various blood disorders and, in extreme cases, aplastic anemia and leukemia.

2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Poly (or polycyclic or polynuclear) aromatic hydrocarbons more simply known as polyarenes, are one of the largest classes of organic molecules found in nature. PAHs are chemical compounds with a similar structure comprising two or more (up to seven) condensed aromatic and other cyclic rings. The simplest form of these chemicals is naphthalane which consist of two fused benzene ring. PAHs are formed naturally in the environment, during such processes as thermal geological reactions and natural fires. Human activities are more significant sources to the environment, as PAHs are formed in all processes involving incomplete combustion of carbon-based fuels, and are therefore emitted during burning of common fuels, such as coal, oil, wood and gas. PAHs concentrations in atmosphere which consist a great level where lower molecular weight forms of PAHs account are greater than 90% of total atmospheric load. The main sources that emit PAHs into the air are from stationary sources and mobile sources. Exposure to PAHs has long been identified as an environmental concern whereby the PAHs were found to exhibit a wide spectrum of acidity as mutagens and carcinogens, which range from inactive to highly potent (Harvey, 1997). Some PAHs are present at ambient temperatures in air, both as gases and associated with particles of their low vapour pressure. PAHs with four or fewer rings usually remain as gases when they are released into the air. Nevertheless, they do undergo degradation by the sequence of free radical reactions after several hours and PAHs with more than four benzene rings do not exists long in the gaseous state.

2.2 Health Effect of PAHs.

The PAHs have high molecular-mass (4 and more condensed aromatic rings) are considered to be more dangerous than two and three rings PAHs in view of their potential (Tuhackova *et al.*, 2001). For the past three decades, PAHs have been of environmental concern due to their toxicity and their ubiquitous in the environment. Men exposed occupationally to high concentrations of PAH mixtures show an increased incidence of tumors of the lung, skin and possibly bladder and other sites. Of these various tumors, lung cancer is the one most obviously linked to exposure to PAHs through inhaled air. Most carcinogenic PAHs occur almost exclusively in the long-lived particulate phase. Irrespective of their physical properties and initial routes of exposure, the tumour-inducing effects of carcinogenic PAHs depend on their conversion in the body into compounds which, unlike the parent substances, are capable of reacting with and damaging the genetic material (DNA) in the nuclei of cells which called as genotoxic carcinogens.

2.3 Mobile Source

Motor vehicle is a significant source of ambient polycyclic aromatic hydrocarbons (PAHs) in urban areas where the emission coming from gasoline and diesel vehicles, as well as from small two-stroke engines such as mopeds and lawn movers. PAHs include a large number of species representing a whole range of boiling points and volatility. Even if these compounds all have boiling points exceeding 200 ºC, they are distributed between the gas and particulate phase in emissions from an internal combustion engine, and the enrichment technique used has to be adjusted accordingly.

3.0 THE COLLECTION OF DATA.

3.1 Location of Sampling

The data were collected at annurban areas of Kuala Terengganu, capital city of Terengganu State, Malaysia. It is located in the east coast of Malaysia (about 500 km north east coast of Kuala Lumpur. Figure 1 shows the site locations of the study. Four sampling locations of school area that chose were based on the sources of PAHs from vehicle traffic which are namely ; 'Sekolah Rendah Chung Hwa Wei Sin' (S1), 'Sekolah Kebangsaan Paya Bunga' (S2), 'Sekolah Menengah Agama Khairiah' (S3) and 'Sekolah Rendah Sultan Sulaiman 1' (S4). In addition, two sampling locations which represented an industrial areas were chosen based on the sources of PAHs from combustion process and non-combustion process. The site location for these sampling are namely ; Nazra Paddy Industry Sdn. Bhd (non-combustion process) andSungai Tong Palm Oil Mill (combustion process)

Figure 1. Location of the study area.

3.2 The PAHs Data Analyses

Generally, the analytical method that been used in this study referred to the US EPA Method TO-13 (USA EPA, 1999). In this study, the airborne samples were collected by using a High-Volume Air Sampler (HVAS), which fitted with glass fiber filters. Sampling was carried out over an eight hours period for school areas while 24 hours for industrial areas. Exposed filter then were cut into small pieces, stored in a 100 ml beaker to which 10 ml of dichloromethane were added to inhibit microbial activity, wrapped with aluminum foil and kept in refrigeration until the day of analysis. Each sample was extracted three times using ultrasonic agitation (Barnson 1200 (USA) Ultrasonic Cleaner) for a 30-min period with the addition of 50ml dichloromethane for each extraction. Column chromatography (CC) technique was used for the separation of hydrocarbons fraction. In this step, the column used was alumina-silica column where the silica gel and alumina acted as the stationary phase, the sample was ready to analyze by gas chromatography-flame ionization detector (GC-FID). Quantification and identification of individual hydrocarbon component from fraction 2 (aromatic) were performed on a Shimadzu GC17A chromatography fitted with a fused silica capillary column (30m x 0.25mm SUPELCO PTE^{TM}) and a standard Flame Ionization Detector (FID). 'Hot needle' / sandwich technique (air-sample-air) was used to inject the sample in order to achieve the exact amount of sample injected in the GC-FID.

4.0 RESULTS AND DISCUSSION

4.1 PAHs of air particle samples in selected industrial areas

The concentration of individual aromatic hydrocarbons identified in air particle samples was showed in Table 1. The table clearly showed that the concentration of PAHs from air particle samples in Sungai Tong Palm Oil Mill was generally higher than the samples from Nazra Paddy Industry Sdn. Bhd. The total concentration of PAHs in air particle samples from Palm Oil Mill was in the range of 239.831 µg/g.D.W to 2214.390 µg/g.D.W, which was 26 times higher than the samples in paddy industry (152.957 µg/g.D.W).

Thus, the air quality in oil palm industry was poorer than paddy industry. This indicates that the oil palm industry has a combustion process resulted in formation of relatively stable aromatic hydrocarbons. The results shows that biomass fires are pyrolysis processes causing the formation of PAHs from the process of either high temperature thermal alteration of natural product precursors in the source organic matter or process of recombination of molecular fragment in the smoke. Besides the factor of combustion process, the second factor that result the high PAHs concentration of air particle samples in oil palm industry was the high mass combustion of waste. The total PAHs concentration between two sites is shown in Figure 2.

The results also indicates that ,there are some similarities in PAHs profile in both of industries samples. Acenaphthylene and benzo[k]fluoranthene were found to be present in both industries samples. The highest concentration of acenaphthylene was observed in oil palm industry on November, where about 116.359 µg/g is obtained, followed by paddy industry sample on November (2.881 µg/g). However, benzo[k]fluoranthene was found in oil palm industry on November with the highest concentration 261.949 µg/g. Meanwhile, 3.326 µg/g of this compound is obtained in paddy industry on January.

Table 1 : Concentration of individual aromatic hydrocarbons identified in air particle samples

Compound	Nov		Dec		Jan	
	Paddy Filter[a]	Oil Filter[b]	Paddy Filter	Oil Filter	Paddy Filter	Oil Filter
Naphthalene	41.709	1196.012	43.592	239.831	45.158	1501.305
Acenaphthylene	2.881	116.359	n.d	n.d	n.d	n.d
Acenaphthene	1.908	n.d	n.d	n.d	4.529	n.d
Pyrene	n.d	n.d	n.d	n.d	n.d	713.085
Benzo[a]anthracene	n.d	n.d	n.d	n.d	4.248	n.d
Benzo[b]fluoranthene	n.d	n.d	n.d	n.d	5.606	n.d
Benzo[k]fluoranthene	n.d	261.949	n.d	n.d	3.326	n.d
Total Concentration (µg/g.D.W)	46.498	1574.320	43.592	239.831	62.867	2214.390

[a] Air particle sample from Nazra Paddy Industry Sdn. Bhd.
[b] Air particle sample from Sungai Tong Palm Oil Mill
n.d = not detectable

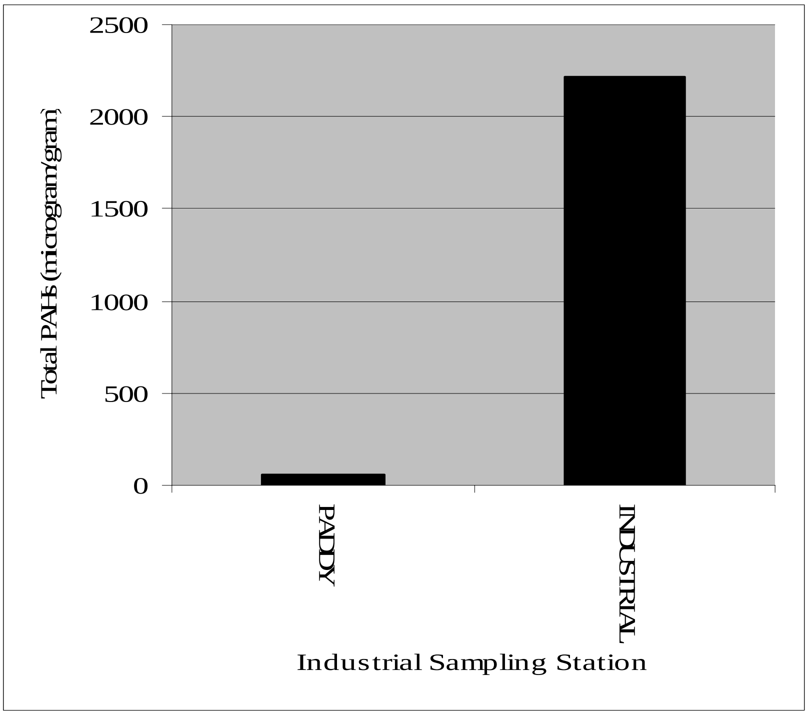

Figure 2 : Total PAHs for sampling station representing industrial area.

4.1 PAHs of atmospheric particles in school areas

The results of the 16 priority PAHs and the total PAHs representing school areas obtained from this study in is shown in Table 2. From the observation, it is clear that the concentration of S3 air samples shows the highest total PAHs with a value of 39603.50 µg/g compared to other samples. The lowest total identified concentration is found in S2 air samples where its concentration is 2214.719 µg/g. In other samples, the analyzed results show the average concentration of total identified PAHs fall in the range of 2872.812 µg/g to 7502.976 µg/g. The total PAHs according to the different sampling station are illustrated in Figure 3. The highest total PAHs value obtained in S3 air samples which located near road junctions where are most probably emitted from vehicle exhaust system. In addition, production of PAHs is greatly influenced by change of speed in which the largest production of all PAHs occurred during acceleration and deceleration. S1 sampling station which is located near the T-road junctions shows very low concentrations compared to the total PAHs concentrations in S3 sampling station. This can be concluded that the traffic flow in the S3 sampling station gives an impact on the concentration of PAHs compared to S1 sampling station. Total PAHs for sampling station representing school area is shown in Figure 4. From the analyses, only 13 PAHs compound were identified in all of the air samples which include naphthalene, acenaphthylene, acenapthene, fluorene, phenanthrene, anthracene, pyrene, benz[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene. In addition, it is clear that naphthalene is the majority dominant and abundant compound detected in air samples for each sampling station.

Table 2 : Results of PAHs compounds (µg/g) obtained from different sampling.

Name of Compound [a]	Composition	Molecular Weight & Target Ion	S1	S2	S3	S4
Naphthalene	$C_{10}H_8$	128	5613.380	1545.210	21981.500	2303.090
Acenaphthylene	$C_{12}H_8$	152	111.476	N.D	817.131	N.D
Acenapthene	$C_{12}H_{10}$	154	N.D	N.D	2565.915	N.D
Fluorene	$C_{13}H_{10}$	166	N.D	N.D	810.615	N.D
Phenanthrene	$C_{14}H_{10}$	178	N.D	N.D	705.318	N.D
Anthracene	$C_{14}H_{10}$	178	586.749	226.316	1022.462	569.722
Pyrene	$C_{16}H_{10}$	202	N.D	N.D	300.414	N.D
Benz[a]anthracene	$C_{18}H_{12}$	228	142.948	271.188	4628.148	N.D
Chrysene	$C_{18}H_{12}$	228	1048.423	100.561	135.119	N.D
Benzo[k]fluoranthene	$C_{20}H_{12}$	252	N.D	N.D	1684.591	N.D
Benzo[b]fluoranthene	$C_{20}H_{12}$	252	N.D	N.D	2402.437	N.D
Benzo[a]pyrene	$C_{20}H_{12}$	252	N.D	N.D	1053.630	N.D
Indeno[1,2,3-	$C_{22}H_{12}$	276	N.D	71.444	1496.220	N.D
Total PAHs			7502.976	2214.719	39603.500	2872.812

Note :[a] Compound listed were in its elution order , N.D = Not Detected

From the analyses it's indicates that naphthalene is majority dominant and abundant compound detected in air samples. The lowest concentration of PAHs compound is pyrene in which only one sample showed the presence of this compound that is in S3 air samples with the concentration of 300.414 µg/g. Since Naphthalene and Anthracene are the low molecular weight PAHs, therefore it can be concluded that the combustion and traffic vehicle emissions are the dominant sources of total PAHs in ambient air in Kuala Terengganu.

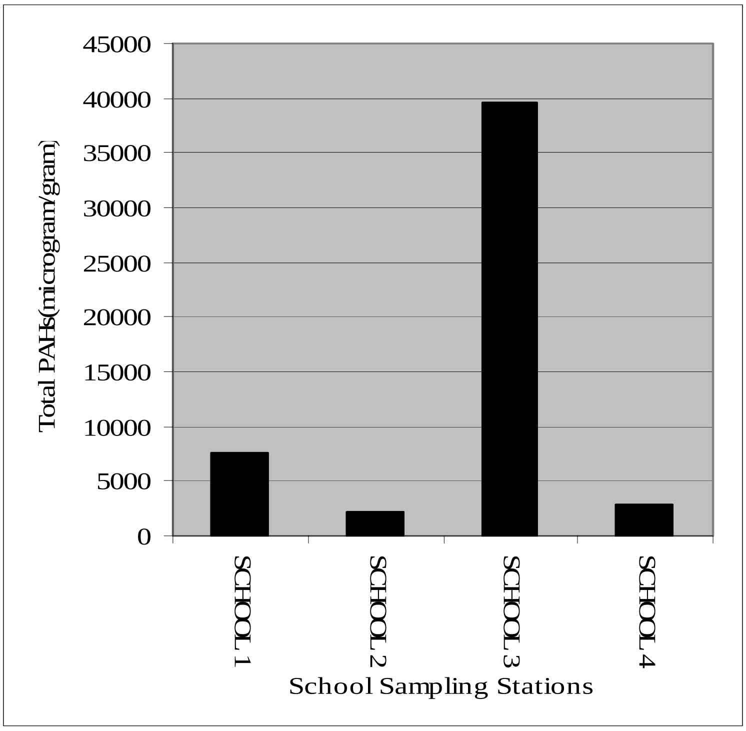

Figure 3 : Total PAHs for sampling station representing school area.

5.0 CONCLUSION AND SUGGESTIONS

As the conclusion, in comparing between two selected industry areas, the concentration of PAHs for air particle samples in oil palm industry was higher than the air particle samples from paddy industry which was 26 times higher than the air particle samples in paddy industry. It can be concluded that the air quality around the area of oil palm industry was polluted than the area around paddy industry. The highest concentration of PAHs air samples obtained is in S3 (39603.50 µg/g) sampling station compared to other sampling station can be concluded that the air particles located near the roadsides especially at road junctions are most probably emitted from vehicle exhaust system. Although the traffic volume and the speed of motor vehicles parameter are not included in this study, the results shows that that the production of higher PAHs collected especially when the areas situated nearby to the traffic junction. It's also can be concluded that the driving mode of the vehicles during acceleration and deceleration of the motor vehicle operations contributes to the emitted of higher pollutants concentrations.

However, the existence of variations could be attributed from other factors such as sites characteristics, topography of surrounding area, frequency of vehicles passing through, type of vehicles utilizing the road and history of the location of concern are not included in this study. The meteorological factors such as wind speed, relative humidity and atmospheric pressure and temperature parameter study can be included in future study.

In conclusion, the results of analyses provides as an indicator of the air pollution levels and database as well as for regulatory action references to improve the air quality particularly in the city of Kuala Terengganu and Malaysian as a general.

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