

Distribution of Gas Phase Polycyclic Aromatic Hydrocarbons (PAHs) in Selected Indoor and Outdoor Air Samples of Malaysia: a Case Study in Serdang, Selangor and Bachang, Malacca

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Abstract

Distribution of 10 polycyclic aromatic hydrocarbons (PAHs) in the gas phase of air from selected indoor and outdoor areas of Selangor and Malacca, Malaysia has been investigated. A locally designed Semi Permeable Membrane Device (SPMD) was applied for passive air sampling for 37 days at selected locations. Cleanup was carried out with Gas Purge - Micro Syringe Extraction (GP-MSE) and the final analysis was using Gas Chromatography-Mass Spectrometry (GC-MS). In this study, 6 indoor and 12 outdoor locations were selected for air sampling. A total of 10 compounds of PAHs (Σ_{10} PAHs) were determined in the range of 0.218 ng/m³ - 1.692 ng/m³ and 0.378 ng/m³ - 1.492 ng/m³ in outdoor and indoor samples respectively. In the outdoor samples, locations such as near a petrol station and heavy traffic showed the maximum levels of Σ_{10} PAHs, while rooftop samples showed the lowest Σ_{10} PAHs. The distribution of gas phase Σ_{10} PAHs was influenced by vehicular emission. Low molecular weight (LMW) compounds (2-3 rings) were dominant in all samples (>70%) indicating that SPMD has successfully sampled the gas phase of the air.

Keywords: polycyclic aromatic hydrocarbons (PAHs); indoor /outdoor air; semi permeable membrane device (SPMD)

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are well known as hazardous air pollutants. Some of the compounds such as benzo(a)anthracene, benzo(a)pyrene and dibenzo(ah)anthracene were classified as carcinogenic to humans. PAHs consist of two and more fused aromatic benzene rings and can be classified into two categories; low molecular weight (LMW) (2-3 rings) and high molecular weight (HMW) (≥ 4 rings). LMW PAHs often associated with gas phase and HMW PAHs occur mainly in the particulate phase. Both gas and particulate phases are important in finding out the point sources and their possible toxic impacts. Park *et al.* (2001) suggested that although the lighter PAH compounds are considered to be less toxic, they are able to react with other pollutants (such as ozone, nitrogen oxides, and sulfur dioxide) to form diones, nitro- and dinitro-PAHs, and sulfuric acids, which may have more toxic significance.

The presence of PAHs in the environment is primarily due to emissions from incomplete combustion of carbon containing materials from natural, industrial, commercial, vehicular and residential sources (Kim *et al.*, 2012). Studies on particulate PAHs in ambient air of Malaysia had been done by many researchers (Omar *et al.*, 2006; Bahry *et al.*, 2009; Jamhari *et al.*, 2014). They found that PAHs distribution in ambient air in Malaysia was mainly contributed by vehicular and traffic emissions. Unfortunately, no information is available on gas phase PAHs in Malaysia. However, He and Balasubramanian (2010) reported the concentration of gaseous PAHs (5.3 ng/m³ to 277.2 ng/m³) in Singapore. Meanwhile, Wu *et al.* (2012) reported the ambient level of gaseous PAHs in Taiwan as 628.8 \pm 545.1 ng/m³ in summer and 2189 \pm 1194 ng/m³ in winter.

The objective of this study is to investigate the level of gas phase PAHs in indoor and outdoor air located at Serdang, Selangor and Bachang, Malacca.

We have simplified the procedure with a Semi Permeable Membrane Device (SPMD) for passive air sampling followed by Gas Purge Micro Syringe Extraction (GP-MSE) cleanup and GC-MS determination.

2. Materials and Methods

2.1 SPMD design

Principles of SPMD as explained by Esteve-Turrillas *et al.* (2007) have been applied in developing a simple sampling device with locally available materials. Briefly, the sampler consisted of a 2 ml vial smeared inside with 10 μ l of Triolein (99%) and enclosed in a non-woven fabric bag (5-15 μ m pore size) which acted as a semi permeable membrane filter. The SMPD sampler housed in a rain proof casing was hung at study locations where only gas phase volatile and semi volatile compounds were trapped.

2.2 Sampling

Six indoor (ID) and twelve outdoor (OD) locations were sampled for this study. SPMD passive air samplers were hung at selected locations as in Table 1. Indoor air samples included shops (ID1-ID4) and cars (ID5 and ID6). Meanwhile, outdoor samples included places with heavy traffic, petrol station (OD4 and OD12), industrial/waste dump site areas (OD5-OD8), university area (OD11), parks and lake-side (OD1-OD3). Indoor sampling was done at Serdang, Selangor except for an Old Car (ID 6) at Bachang, Malacca. OD1-OD5 represented outdoor samples from Serdang, Selangor while OD6-OD12 were samples from outdoor areas in Bachang, Melacca. Air samples OD6-OD9 were collected near electronics waste dump sites or factories manufacturing electronic equipments. The interest was to identify any gaseous emission of PAHs from those sites. All samples were exposed for 37 days (27th August 2014 - 3rd August 2014) for sampling in Selangor and (28th August 2014 - 4th August 2014) for sampling in Malacca. The exposure period was set based on PCBs equilibration in Triolein (Ockenden *et al.*, 2001) during the sampling period, haze occurrence was reported by Department of Environment (DOE), Malaysia. It occurred from 17 September to 12 October in the year 2014, in the west coast and northern parts of Peninsular Malaysia. However, our sampling locations were not much influenced by the haze according to the reported

API (Air Pollution Index) of (30-40) and (20-30) in Bachang and Serdang respectively. This is considered 'moderate' by DOE.

2.3 Extraction

Triolein in each sample vials were dissolved and rinsed with minimum volume of n-hexane (GR grade, Merck, Germany). The extracts were concentrated down to 40 μ l using nitrogen blow and then further extracted with GP-MSE[®] (ME-101 Multifunctional Micro-extraction, China). GP-MSE[®] sample pretreatment technology was developed by Yang *et al.* (2011) and the setup parameter for PAHs extraction was selected based on the evaluation of He *et al.* (2014). Approximately 100 μ l of sample extracts were collected and transferred to GC vials for the analysis.

2.4 Analysis

Samples were identified and quantified using gas chromatography (GC) - Agilent 6890N, USA equipped with Mass Selective Detector (MSD) - Agilent 5975C. HP-5MS capillary column with 30 m length, 0.25 mm i.d, 0.25 μ m film thickness (Agilent J&W, USA) was used for the separation. The GC temperature was programmed as follows: initial 40°C, 30°C/min to 150°C, 4°C/min to 310°C, hold 5 min. The mass spectrometry was operated under electron ionization (EI) mode. Helium gas was used as a carrier at a flow rate of 1.0 mL/min.

External calibration was performed with the PAH-MIX 18, Dr.Ehrenstorfer, GmbH, Germany. Only PAH compounds with quality value (Qvalue) more than 60% were measured for the QC screening. Thus, 10 compounds of PAHs namely Naphthalene (Nap), Acenaphthylene (Ace), Fluorene (Flu), Anthracene (Ant), Phenanthrene (Phe), Pyrene (Pyr), Benzo(a) Anthracene (BaA), Chrysene (Chy), Benzo(a)Pyrene (BaP) and Benzo(ghi)Perylene (BgP) were selected for further quantification with SIM mode. Linear calibration of 10, 30 and 50 μ g/L for all compounds showed very good linearity (r^2). Calculation of individual and total PAHs (Σ_{10} PAHs) amount was in pg/m^3 and ng/m^3 respectively and based on equation suggested by Kannan and Petrick (2009).

3. Results and Discussion

Table 1 shows the concentration of Σ_{10} PAHs among the indoor and outdoor samples. The concentration range for indoor air was 0.31 ng/m^3 -

1.49 ng/m³ and for outdoor air was 0.22 ng/m³ - 1.97 ng/m³. Concentration of Σ_{10} PAHs in the gas phase was obviously lower than the reported values in particulate phase in air. For example, during non-haze situation in Malaysia the ambient air concentration (mean) was 3.69 ng/m³ (Okuda *et al.*, 2002). In comparison, Kim *et al.* (2012) found the annual arithmetic average concentrations of gaseous and particulate Σ_{14} PAHs were 1.4 ng/m³ and 2.9 ng/m³, respectively in Gosan, Korea. Chang *et al.* (2006) reported that gaseous phase of PAHs in urban, suburban and rural areas in Taiwan still carries 50-90% of PAHs compared to particulate phase. Interestingly, a measurement of 16 PAHs in gaseous phase of air in Singapore ranged between 5.3 to 277.2 ng/m³ with a median value of 98.3 ng/m³ (He and Balasubramanian, 2010). The difference could be due to different sampling methodology, metrological factors and sampling locations. This could also be attributed to an increase in the number of on-road vehicles in highly industrialized and small city state like Singapore.

Based on the table 1, it was observed that indoor air concentration of Σ_{10} PAHs in a car workshop was the highest with a value of 1.49 ng/m³ and a photocopy shop showed the lowest with 0.31 ng/m³. A radio repair shop showed the second highest value of 1.30 ng/m³. On the other hand, a motorcycle workshop revealed only 0.35 ng/m³. Indoor air samples of two cars were investigated as well. An old car showed a concentration of 0.49 ng/m³ slightly higher than a new car - 0.46 ng/m³. High concentration of PAHs in a car workshop was obviously from automobile repair activity and also the engine fuel combustion within the area. Diesel trucks were the major source of LMW PAHs, whereas light-duty gasoline vehicles were the dominant source of HMW PAHs (Srogi, 2007). As illustrated in Fig. 1, Fluorene (Flu) was the most abundant PAH in the car workshop pointing to the fact that fuel exhaust fumes could be a source in that area. Naphthalene (Nap) existed in all samples, especially at high concentration in the radio repair shop and in the automobile workshop. The occurrence of naphthalene, a LMW PAH, reflects the sampling efficiency of SPMD in capturing the gaseous phase of the air.

Table 1. Concentration of Σ_{10} PAHs for indoor and outdoor sample

Sample	Description	Σ_{10} PAHs (ng/m ³)
<i>Indoor</i>		
ID 1	Car workshop	1.49
ID 2	Motorcycle workshop	0.35
ID 3	Radio repair shop	1.30
ID 4	Photocopy shop	0.31
ID 5	New car	0.46
ID 6	Old car	0.49
<i>Outdoor</i>		
OD 1	Herb Garden	1.03
OD 2	Forest	1.03
OD 3	Small Lake	0.92
OD 4	/Heavy Traffic	1.74
OD 5	Car scrap yard	0.48
OD 6	Electronic waste site A	0.40
OD 7	Electronic waste site B	0.56
OD 8	Electronic waste site C	0.75
OD 9	Electronic waste site D	0.44
OD 10	Industrial Area	0.54
OD 11	Roof top	0.22
OD 12	Petrol station	1.97

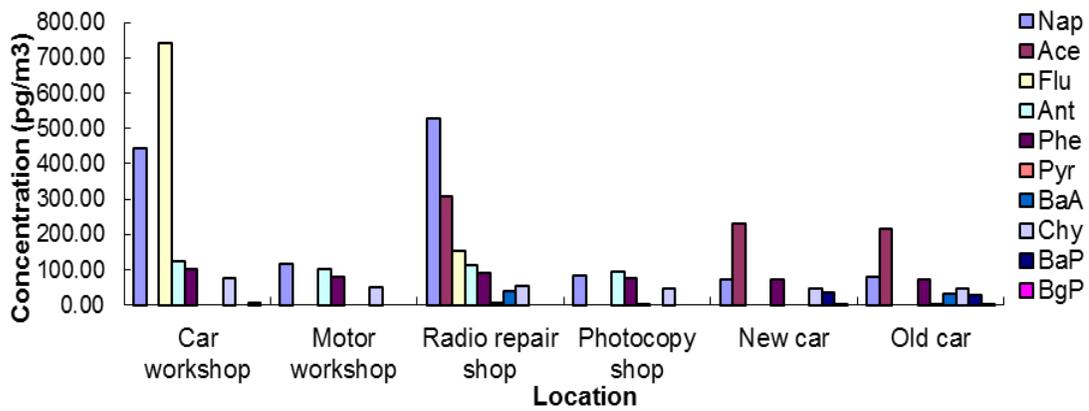


Figure 1. Distribution of individual PAHs in the indoor area

Among the outdoor samples, a location near petrol station (OD12) and a location nearby heavy traffic (OD4) showed the highest concentrations namely, 1.97 ng/m³ and 1.74 ng/m³ respectively. It can be concluded that vehicular emissions from the traffic are the main sources of gas phase PAHs in those areas. Studies by Okuda *et al.* (2002); Omar *et al.* (2006); Bahry *et al.* (2009) and Jamhari *et al.* (2014) also found out the contribution of motor vehicle emissions in higher concentration of PAHs in Malaysia. According to Chang *et al.* (2006), the major sources of PAHs in most Asian countries are traffic exhaust. The lowest Σ₁₀PAHs concentration of 0.22 ng/m³ was found at the roof top (OD11) of the residential area in Bachang, Malacca indicating the site was less polluted with gas phase PAHs.

Fig. 2 shows the distribution of individual PAHs in outdoor areas. Generally, LMW compounds were dominant, with Acenaphthylene (Ace) as a significant compound in all samples except the roof top sample. Fluorene was rich at heavy traffic and petrol station samples reflecting vehicular emissions and petroleum-based fuels (Fang *et al.*, 2005).

Fig. 3 shows the percentage of LMW and HMW in all samples. The LMW PAHs were dominant in all air samples as expected and found to be more than 70% of Σ₁₀PAHs. In general, LMW PAHs are present in gaseous phase and those with four rings occur in both phases while those with five or more rings are found in particulate phase (Rao *et al.*, 2007).

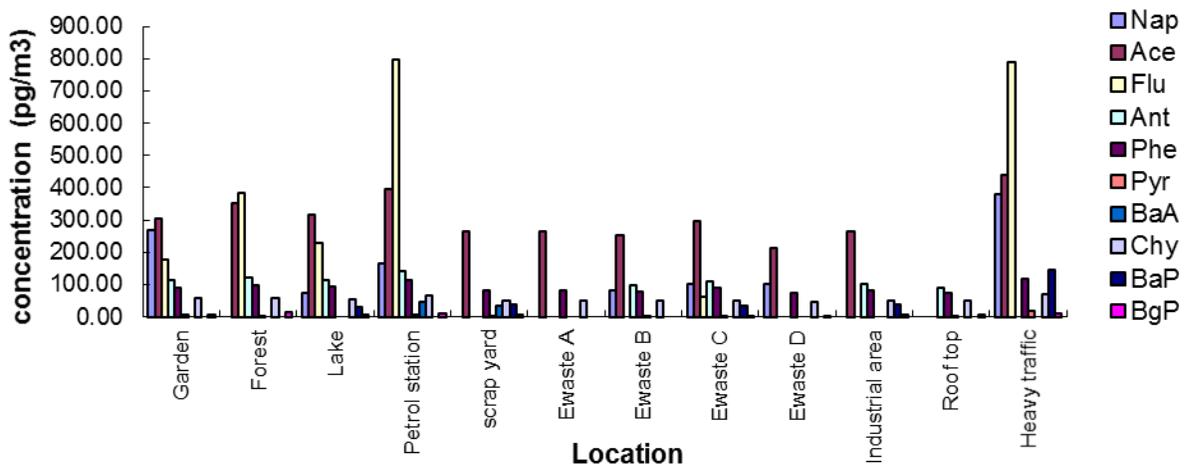


Figure 2. Distribution of individual PAHs in outdoor area

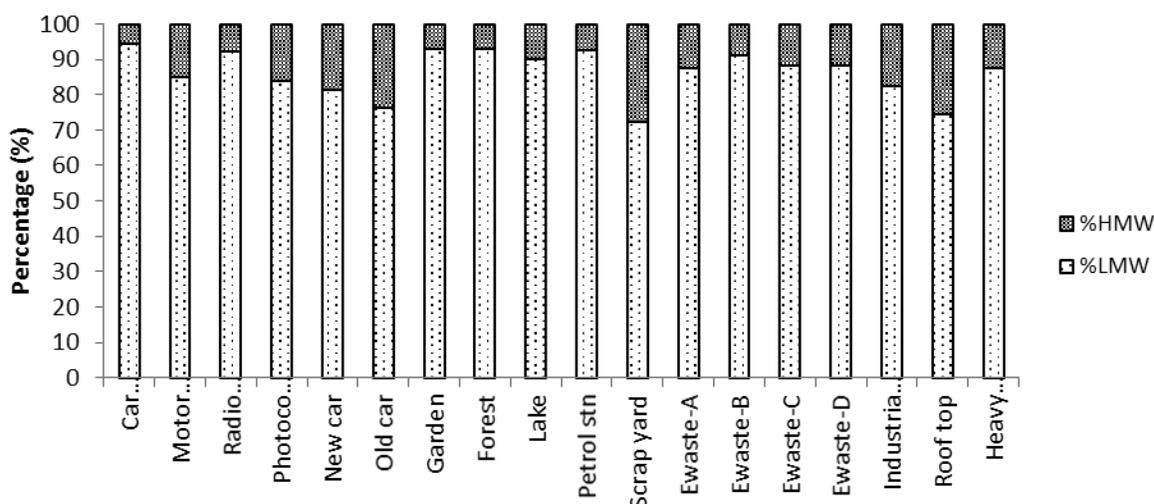


Figure 3. Percentage of LMW Vs HMW

Even though the diagnostic ratios of LMW to HMW seem to show a petrogenic source, it is hard to conclude with only gas phase composition. Unfortunately, SPMD sampler captures only gaseous phase. Tobiszewski and Namieśnik (2012) suggested that total concentration of atmospheric PAHs (gas + particulate) should be used to calculate diagnostic ratio.

4. Conclusions

The concentration of gas phase Σ_{10} PAHs as determined by SPMD passive air sampler in indoor and outdoor samples was dominated by LMW PAHs. Outdoor samples with highest concentration of PAHs were from heavy traffic and near petrol station locations indicating vehicular emission as a possible source. Similarly, an indoor sample at a car workshop was found to have high gaseous PAHs indicating fuel combustion from motor vehicles as a source. Application of SPMD techniques for gaseous PAHs determination shows comparable results with other such passive sampling methods (e.g. Polyurethane Foam (PUF)). However, more studies are needed to verify various quantitative methods. In summary, these data clearly suggest that a new design of SPMD used in this study, along with the cleanup using GP-MSE[®] could be utilized as useful techniques in detecting gas phase PAHs.

Acknowledgements

We thank the generous gift of GP-MSE[®] by Professor Dr. Donghao Li of Key Laboratory of Nature Resources of Changhai Mountain and Functional Molecular (Yanbian University), Ministry of Education, Jilin, China .

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Received 31 January 2017

Accepted 10 May 2017

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