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Distribution and Source Apportionment of Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Soils from Five Different Locations in Klang Valley, Malaysia

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Abstract The concentrations of polycyclic aromatic hydrocarbons (PAHs) in soil samples were measured at five different sites within Klang Valley, Malaysia. The results showed that the total concentrations of the fourteen priority PAHs ranged from 64 to 155 μg/kg. Irrespective of the land use, all the measured soil PAH concentrations in this study were significantly lower than that found in soil samples in temperate regions. The profile of PAHs in the soils was dominated by the LMW PAHs. The PAHs in Klang Valley soils originated from pyrogenic sources, with a combination of petroleum and biomass combustion in vehicles, industries and non-point sources.

Keywords PAHs · Soil · Source apportionment · Isomer ratio

Polycyclic aromatic hydrocarbons (PAHs) are mutagenic and carcinogenic organic compounds mostly rendered from pyrogenic origins which are initiated by incomplete combustion of hydrocarbon-containing fuels (United States Environmental Protection Agency 2008). Apart from pyrogenic sources, PAHs in the environment can derive from petrogenic sources. The formation of petrogenic PAHs is a long process occurring at moderate temperatures and is linked to fossil fuels such as petroleum and coal (Soclo et al. 2000). Atmospheric PAHs mainly settle onto soil via wet or dry deposition processes. In wet deposition, PAH compounds dissolve in precipitation such as rain or snow while dry deposition occurs when compounds are deposited onto soil as dry particles or gases from atmospheric turbulence, molecular diffusion or gravitational settling (Rey-Salgueiro et al. 2008). Once produced, PAHs are inevitably dispersed widely into the environment, finally accumulating in soils and sediments which have large holding capacities for these pollutants (Wild and Jones 1995).

Soil quality is an excellent indicator of environmental pollution and risks since soil is continuously subjected to pollution in the open-system nature (Chung et al. 2007). Qualitative understanding of sources of PAH pollutants in soil is important, especially in the case of non-point sources of PAHs such as the combustion of domestic and garden waste as well as uncontrolled situations like smoke from regional forest fires in tropical Asian cities (Omar et al. 2006; Boonyatumanond et al. 2007). Various methods of PAH source apportioning have been employed to identify PAH sources in environmental matrices. These methods include using isomer ratios, cluster analysis, principal components analysis (PCA) and chemical mass balance (CMB) (Li et al. 2001; Boonyatumanond et al. 2007; Liu et al. 2009).

Klang Valley is an area in southwestern Peninsular Malaysia surrounded by highlands over 1,500 m altitude in the east and the Straits of Malacca in the west. The region comprises Kuala Lumpur and its suburbs, as well as the adjoining cities and towns within the state of Selangor. To

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the best knowledge of the authors, PAH concentration levels as well source apportioning in surface soils of this region have yet to be documented although there have been studies reporting on PAH levels in atmospheric cum roadside particles in Kuala Lumpur (Omar et al. 2002, 2006). This study will provide data for comparison of PAH pollution in Klang Valley with other places worldwide. Apart from that, the study could potentially be useful for environment policy makers in Malaysia to gain insights into the source apportioning of PAHs in the country. Thus, it is the aim of the present study to determine firstly, the concentration levels of PAHs in surface soils collected from five locations in Klang Valley and secondly, to carry out source apportionment via isomer ratio.

Materials and Methods

Five different locations for soil sampling were selected around Klang Valley, as shown in Fig. 1. The details of each sampling site are as listed in Table 1. Four surface soil samples were collected from every site (0–10 cm upper layer), making a total of 20 samples in this work. Every sample was air-dried and sieved to <2 mm after removing stones and residual roots. The soil pH, moisture content, soil organic matter (SOM), total organic carbon content (TOC) and soil textural class were measured and are compiled in Table 1 under Electronic Supplementary Material. The SOM was determined using the loss-on-ignition (LOI) method whereas the TOC was obtained according to the Walkley–Black method.

Table 1 Locations and land uses of soils collected in Klang Valley

Location	Land use	Abbreviation
Cheras	Residential	R
Hulu Langat Forest Reserve	Forest	F
Hulu Kelang (SEH) free trade zone	Light industry (electronics processing plant site)	LI
PKNS development site	Light industry (new industrial development site)	LI(2)
Batu Caves Industry	Heavy industry (medium to heavy manufacturing factories)	HI

100 grams of each soil sample was extracted in 140 mL of 1:1 acetone:hexane (v/v) and horizontally shaken in a

Fig. 1 Sampling locations of surface soils in Klang Valley

mechanical shaker at 100 rpm at room temperature for 24 h. The soil solvent mixture was then filtered and solvent exchanged to cyclohexane using evaporation. The cleanup of the cyclohexane sample extract was carried out according to US EPA Method 3630C. After cleanup, the samples were concentrated to 0.1 mL volume for analysis. Quantitative analysis of PAHs in the soil extracts were conducted by gas chromatography (GC) using a 30 m × 0.25 mm i.d. × 0.25 μm film thickness fused silica capillary column (DB5-MS) installed in a Clarus 400 GC equipped with a flame ionisation detector (FID) (Perkin Elmer). A 1.0 μL aliquot of the final extract was injected in splitless mode with helium as the carrier gas. The temperatures at both injector and detector ports were set at 290 and 300°C respectively. The GC-FID operating conditions were as follows: isothermal at 35°C for 2 min, followed by 10°C/min ramp rate to a final temperature of 310°C which was held for 15 min. The following fourteen PAHs that are classified by the US EPA as priority pollutants were analysed (United States Environmental Protection Agency 2008): acenaphthene (ACN), fluorene(FLU), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo (b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), benzo(g,h,i)perylene (BgP) and indeno(1,2,3-c,d)pyrene (IND). Method detection limits in ng/g were as follows:- ACN:50, FLU:5, PHEN:2, ANT:1, FLUO:2.5, PYR:5, BaA:2.5, CHR:2.5, BbF1:, BkF:1, BaP:2.5, DahA:10, BgP:4, IND:2.5. Quantification was carried out using the external standard method whereby average response factors were calculated for individual PAHs. All of the samples taken were analysed in duplicate. The procedure was checked for recovery efficiencies by analysing soil samples spiked with PAH standards. The recoveries of individual PAHs ranged from 49.3% to 106.8% with a mean value of 74.4%. Replicate analyses resulted in errors within ±15%.

Results and Discussion

Taking the averages of the four samples from each sampling site within Klang Valley, the total concentrations of the priority PAHs in the 5 sites ranged from 64 to 155 μg/kg. The highest total PAH concentration was found in a forest area (155.2 ± 91.4 μg/kg) followed by two light industrial areas (95.8 ± 46.2 and 92.2 ± 57.0 μg/kg for LI and LI(2) respectively), a heavy industrial area (82.9 ± 43.7 μg/kg) and finally a residential area (64.9 ± 7.3 μg/kg). Although the forest area soil (F) had the highest PAH concentration, the forest is located within the urban area of Klang Valley and hence was not necessarily expected to have the lowest concentration. On the contrary, the results indicated that more PAH atmospheric deposition occurred in the forest area compared to the other sites sampled. Forest soils receive high PAH inputs due to the large interception deposition caused by foliage which eventually falls to the ground, leading to PAH accumulation in the soil organic layer (García-Falcón et al. 2006). Within the organic matter, PAHs tend to adsorb onto humic substances by interacting with the π electrons associated with their aromatic moieties (Arias-Estévez et al. 2007). Table 2 is a compilation of measured PAH concentrations in various locations worldwide. The concentrations obtained in this study are only slightly smaller to a previous study (Omar et al. 2002). This difference can be attributed to the fact that in the previous study, the samples were collected off the roadsides which tend to have increased PAH concentrations (Butler et al. 1984). The total PAH concentrations at all studied sites in the Klang Valley are comparable to other urban places located in tropical or sub-tropical regions such as Uberlândia, Brazil (Wilcke et al. 1999a), Bangkok, Thailand (Wilcke et al. 1999b) and Hong Kong (Chung et al. 2007). However, compared to urban places with temperate climates such as Dalian, China (Wang et al. 2007), Tallinn, Estonia (Trapido 1999) and Beijing, China (Tang et al. 2005), these concentrations are significantly lower. The possible reasons for such low PAH concentrations in the Klang Valley include faster photo-oxidation of PAHs due to higher ultraviolet radiation and enhanced volatilisation due to high soil temperature and moisture (Wilcke 2000).

Environmental standards for PAHs in soil have been established in several countries such as the Netherlands, Denmark and Canada for risk assessments at contaminated sites and for setting targets in remediation efforts (Tang et al. 2005; Chung et al. 2007). Presently, such standards have yet to be established in Malaysia. The PAH concentrations in all the soil samples in this study were at least one order of magnitude below the target value of 1,000 μg/kg for 10 PAHs set by the Netherlands, indicating very low PAH soil contamination in Klang Valley.

Figure 2 shows the distribution of PAH concentrations according to the number of rings as follows: 3-ring (ACY, ACN, FLU, PHEN, ANT); 4-ring (ANT, FLT, PYR, BaA, CHR); 5-ring (BbF, BkF, BaP); and 6-ring (DahA, BgP, IND). The 3-ring PAHs were found to dominate in most sites, with a total PAH contribution of 39.9%, 53.5%, 47.9% and 58.2% for soil samples R, F, LI and HI respectively. In the LI(2) sample, however, the total PAH concentration was fairly contributed by 32.8% of 3-ring PAHs and 33.8% of 6-ring PAHs. The high concentration of 6-ring PAHs in the LI(2) soil was distinctly different from all the other soils which had very low concentrations of HMW PAHs. The HMW PAHs only constituted 14.4%, 8.7%, 2.2% and 14.0% to the total PAH concentrations in R, F, LI and HI soils respectively. Considering the volatility and degradability of LMW PAHs, it is therefore

Table 2 The concentrations of priority PAHs in soils in different locations worldwide

Location	Concentration (μg/kg)	Climate	Reference
Residential site (R), Klang Valley	64.9 ± 7.3	Tropical	Present study
Forest site (F), Klang Valley	155.2 ± 91.4	Tropical	Present study
Light industrial site (LI), Klang Valley	95.8 ± 46.2	Tropical	Present study
Light industrial site (LI(2)), Klang Valley	92.2 ± 57.0	Tropical	Present study
Heavy industrial site (HI), Klang Valley	82.9 ± 43.7	Tropical	Present study
Roadside, Kuala Lumpur, Malaysia	Average = 224	Tropical	Omar et al. (2002)
Urban sites, Uberlândia, Brazil	Range = 7–390[a]	Tropical	Wilcke et al. (1999a)
Urban sites, Bangkok, Thailand	Range = 11.7–376.2	Tropical	Wilcke et al. (1999b)
All land uses, Hong Kong	Range = n.d.–19500[b] Median = 140	Subtropical	Chung et al. (2007)
Traffic sites, Dalian, China	Average = 6,506 ± 5,726	Temperate	Wang et al. (2007)
Urban sites, Dalian, China	Average = 650 ± 252	Temperate	Wang et al. (2007)
Suburban sites, Dalian, China	Average = 407 ± 78	Temperate	Wang et al. (2007)
Rural sites, Dalian, China	Average = 223 ± 16	Temperate	Wang et al. (2007)
Urban sites, Tallinn, Estonia	Average = 2,200 ± 1,396[c]	Temperate	Trapido (1999)
Central urban sites, Tallinn, Estonia	Average = 9,015 ± 6,363[c]	Temperate	Trapido (1999)
Rural sites, Harjumaa, Estonia	Average = 232 ± 153[c]	Temperate	Trapido (1999)
Rural sites, Pärnumaa, Estonia	Average = 584 ± 379[c]	Temperate	Trapido (1999)
Urban sites, Beijing, China	Range = 219–27,825 Average = 3,917	Temperate	Tang et al. (2005)

n.d. non-detected

[a] Summation of 20 PAHs

[b] The maximum PAH concentration is due to localised hotspots

[c] Summation of 12 PAHs

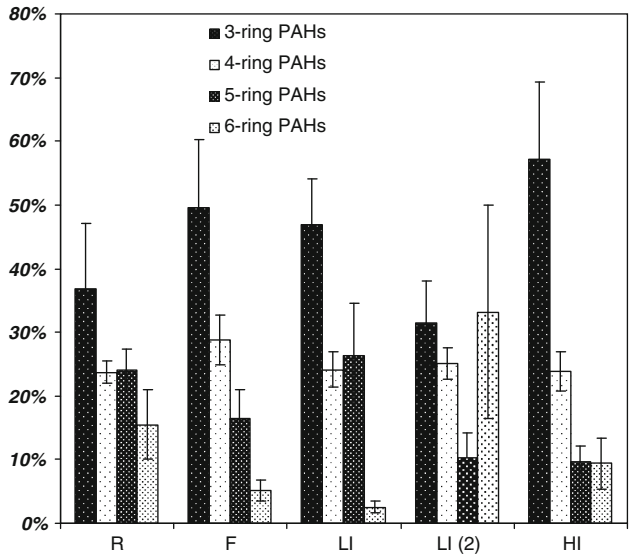

Fig. 2 PAH profiles in soils in Klang Valley

surprising that this category of PAHs was dominant in most sites. The results obtained from this study indicate that there are specific sources for these PAH compounds. In the LI(2) soil, it is possible that a highly regional source of PAHs exist, with its high concentration of 6-ring PAHs.

Sources of PAHs may have individual profiles or signatures which can then be linked to the profiles found in environmental matrices such as soils. Due to physical–chemical transformation activities, the original distribution patterns of emitted PAHs may be modified. PAH isomer ratios based on evolution kinetics of individual PAH compounds were developed to determine the various origins of these pollutants in the environment (Soclo et al. 2000). Table 3 shows the calculated PAH isomer ratios for the soils from the five sites in Klang Valley. An ANT/(ANT + PHEN) ratio >0.1 and a FLT/(FLT + PYR) ratio >0.4 indicate that the PAHs originate from pyrogenic sources whereas an ANT/(ANT + PHEN) ratio <0.1 and a FLT/(FLT + PYR) ratio <0.4 indicate petrogenic sources of PAHs (Yunker et al. 2002). In all samples, the ANT/(ANT + PHEN) and FLT/(FLT + PYR) ratios ranged from 0.10 to 0.65 and 0.40 to 0.89 respectively which showed a strong pyrogenic influence existed on the PAHs in all the soils sampled in Klang Valley. More specifically, PAHs in soil samples from R with $0.5 > \text{FLT}/(\text{FLT} + \text{PYR}) > 0.4$ mainly originated from petroleum combustion while PAHs in the rest of the samples mainly originated from combustion of grass, wood, and coal with $\text{FLT}/(\text{FLT} + \text{PYR}) > 0.5$. The calculated CHR/BaA ratios presented in Table 3 also pointed to a predominance of pyrogenic sources since a CHR/BaA ratio <1 imply pyrogenic PAH sources while a CHR/BaA ratio = 1 imply petrogenic sources (Soclo et al. 2000). More specifically, it

Table 3 Isomer ratios of PAHs in soils in Klang Valley

Soil sample	ANT/ (ANT + PHEN)	FLT/ (FLT + PYR)	CHR/ BaA	PHEN/ ANT
R1	0.19	0.44	0.76	4.31
R2	0.16	0.40	0.65	5.22
R3	0.10	0.42	0.85	9.00
R4	0.13	0.46	0.82	6.69
F1	0.42	0.82	0.78	1.37
F2	0.57	0.58	0.94	0.74
F3	0.17	0.89	0.86	4.99
F4	0.32	0.84	0.96	2.13
LI1	0.41	0.78	0.87	1.47
LI2	0.45	0.67	0.84	1.22
LI3	0.65	0.81	0.68	0.55
LI4	0.53	0.88	0.76	0.90
LI(2)1	0.17	0.83	0.63	5.05
LI(2)2	0.40	0.63	0.95	1.48
LI(2)3	0.51	0.72	0.88	0.96
LI(2)4	0.14	0.65	0.84	6.26
HI1	0.43	0.64	0.53	1.34
HI2	0.31	0.56	0.57	2.20
HI3	0.40	0.69	0.70	1.47
HI4	0.37	0.80	0.63	1.72

has been reported that a PHEN/ANT ratio of approximately 4 indicated that the PAHs originate from motor vehicle exhaust, while a ratio of over 50 implied that the PAHs are derived from mineral oil (Yang et al. 1991). The PHEN/ANT ratios of several soil samples were close to 4 which suggested the likelihood of vehicular emissions contributing to the PAHs in these soils.

In Klang Valley, the main sources of air pollution are motor vehicles, industrial activities and non-point sources such as open burning and forest fires, with motor vehicles contributing the most (70%–75%) followed by industrial activities (20%–25%) and lastly by open burning and forest fires (3%–5%) (Afroz et al. 2003). The isomer ratios findings indicate that the PAHs in the soils collected are pyrogenic in origin, with a combination of petroleum and biomass combustion in vehicles, industries and non-point sources. Since approximately 90.2% of the total energy consumption in Malaysia comes from crude oil, petroleum products, natural gas liquids, refinery feedstocks and natural gas while coal represents a mere 4% of the total energy consumption (World Resources Institute 2005), it is unlikely that coal combustion is a dominant source of PAHs.

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