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Chracterization of solvent-extractable hydrocarbons in airborne and roadside soil particles of Kuala Lumpur, Malaysia

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ABSTRACT Solvent-extractable hydrocarbons were isolated from PM_{10} airborne particles and roadside soil particles collected during the period from November 1998 to January 1999 from the city centre and the suburb of Kuala Lumpur, Malaysia. Hydrocarbons identified were n-alkanes, polycyclic aromatic hydrocarbons (PAHs), and petroleum molecular markers including pristane, phytane, hopanes, and steranes. Molecular distributions of these compounds as well as geochemical diagnostic ratios were determined in order to identify the sources of hydrocarbons. Samples of lubricating oils were also analyzed for comparisons. The major source of hydrocarbons was petrogenic emissions with some contribution from biogenic sources such as waxes of higher plants.

ABSTRAK Sebatian-sebatian hidrokarbon terekstrak telah diasingkan daripada zarahan terampai PM_{10} dan zarahan tanah tepi jalan yang dikumpul dari November 1998 sehingga Januari 1999 daripada pusat bandaraya Kuala Lumpur dan kawasan di sekitarnya. Sebatian-sebatian yang telah dikenalpasti termasuklah n-alkana, hidrokarbon aromatik polisiklik, dan penunjuk molekul seperti pristana, pitana, hopana dan sterana. Taburan molekul sebatian-sebatian ini di samping nisbah diagnostik geokimia ditentukan untuk mengenalpasti sumber-sumber sebatian tersebut. Sampel minyak pelincir juga dianalisis sebagai bandingan. Kajian ini menunjukkan bahawa sumber utama hidrokarbon ialah pembebasan petrogenik dengan sedikit sumbangan daripada sumber biogenik seperti lilin tumbuhan.

(hydrocarbons, PAHs, air pollution, vehicular emission)

INTRODUCTION

Particles in the atmosphere, which range in size from about one-half of a millimeter down to molecular dimensions, are made up of a variety of materials and discrete objects that may consist of either solid or liquid droplets. They originate from a wide variety of sources and processes, ranging from simple to complicated chemical or biochemical syntheses [1]. Atmospheric particles have numerous effects. The most obvious of these is reduction and distortion of visibility. Also, they have a significant influence upon weather and may cause damage to materials and health [1].

Because of the widespread use of fossil fuels, hydrocarbons predominate among organic air pollutants. A study of particulate ($dp \leq 2$ μm) exhaust emissions from catalyst and non catalyst automobiles and heavy-duty diesel trucks has identified more than 100 organic compounds, including n-alkanes, n-alkanoic acids, benzaldehydes, benzoic acids, azanaphthalenes, polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs, pentacyclic triterpanes, and steranes [2].

The main objectives of this study are: (a) to determine PAH and n-alkane concentrations in airborne particles and roadside soil particles, (b) to identify petroleum molecular markers such as hopanes and steranes for source reconciliation, (c) to compare the hydrocarbons composition of airborne particles to that of roadside soil particles.

EXPERIMENTAL

Reagents and glassware

All solvents used were of HPLC grade. Dichloromethane and hexane were obtained from J.T.Baker (USA) and methanol was obtained from Mallinckrodt (USA). All glassware used in the analytical work was soaked overnight in 2-3% (v/v) Decon 90 (UK), rinsed with water, dried in the oven at 150°C, wrapped with aluminum foil, and rinsed with methanol and dichloromethane before use.

Sampling

Urban airborne particles and roadside soil particles were collected from eight sites (three samples for each site) in the city centre and the suburb of Kuala Lumpur, Malaysia (Figure 1) during the period from November 1998 to January 1999. Airborne particles were sampled with a PM_{10} high-volume air sampler (Ecotech, Australia) fitted with annealed (300°C for 8 h) glass fibre filters (20.3×25.4 cm^2, Whatman EPM 2000, England), and operated at a flow rate of ~ 1.12 m^3/h, sampling time was 24 h. Roadside soil particles were collected using a small brush and a trowel, air dried, and sieved (only particles ≤ 600 μm were used in this study).

Extraction

Samples were extracted three times with dichloromethane (15 min each time) by ultrasonication (Branson 1200, USA). The extracts were then filtered through a sintered glass funnel fitted with glass fibre filter and concentrated using a rotary-evaporator system (Büchi, Switzerland).

Fractionation

1 mL of the extract (concentrated to <0.2 mL) was applied to the top of a glass column (1.0 cm I.D.) containing 2.5 g of neutral alumina (dry packed; top) (Merck, 70-230 mesh, activity I, activated at 200°C for 4 h) and 1.5 g of silica (slurry packed with n-hexane; bottom) (Fluka, 230-400 mesh, activated at 200°C for 4 h), the adsorbents was capped with 1.0 g of sodium sulfate anhydrous (activated at 300°C for 4 h), and supported by a small plug of precleaned glass wool inserted at the narrow end of the column, the flow rate was ~ 1.0 mL/min. The alkanes were obtained in the first fraction (8 mL of n-hexane), the PAHs were collected in the second fraction (8 mL of 1:1 n-hexane-dichloromethane). The fractions were concentrated to 100 μL under reduced pressure at 40°C using a rotary-evaporator system.

Instrumental analysis, Identification and Quantification

Samples were analyzed by "full-scan" GC-MS (Hewlett-Packard Model 6890, USA) operated at the following conditions; Injection mode: splitless (1 min) (1.0-1.4 μL; hot needle technique), Temperature of injector: 290°C, Temperature of oven: 60°C (held for 2 min), then up to 280°C at 6°C/min, then held at 280°C for 20 min, Temperature of transfer line: 300°C. Compound identification was based on the GC-MS data (i.e. key fragment ions: n-alkanes, m/z 85; PAHs, m/z M^+; hopanes, m/z 191; steranes, m/z 217 and 218), retention times compared to that of external standards, and/or mass spectra). Typical ion chromatograms for PAHs are given in Figure 2.

Quantification was performed from the GC profiles using the external standard method. All quantifications were based on the compounds area derived from the ion fragmentogram.

RESULTS AND DISCUSSION

n-Alkanes

Crude petroleum, the primary source of gasoline, diesel fuel, and lubricating oil, contains n-alkanes ranging up to about C_{35} with essentially no carbon number predominance (CPI ~ 1) [3, 4] and C_{max} in the range of C_{22} to C_{25} [5, 6, 7]. n-Alkanes in vehicular exhaust are derived both from incomplete combustion of fuel (mainly diesel, gasoline fuel residues cannot be sampled by filtration technique) and from engine lubricating oil [4, 8].

Plant waxes contain n-alkanes ranging from about C_{21} to C_{37} [9]. Virtually, odd carbon number n-alkanes are predominant in plants and show a C_{max} in the range of C_{25} to C_{33}, which depends on the plant species as well as the season and locale [e.g., 7, 10, 11, 12, 13, 14].

In this study, the main n-alkanes determined were in the range of C_{19} to C_{34}. Airborne particles had total n-alkanes concentrations of 102.87 ± 50.60 ng/m^3 (Table 1). Roadside soil particles had total n-alkanes concentrations of 7.358 ± 4.768 µg/g (Table 1).

The Carbon Preference Index (CPI), a measure of the carbon number predominance, is useful to determine the degree of biogenic versus petrogenic input. The carbon number maximum of the most abundant n-alkanes (C_{max}) can also be used as an indicator of relative source input [15].

Airborne particles showed an odd C_{max} at C_{25} (Figure 3), which is characteristic of biogenic sources (i.e. higher plant waxes). CPI value was 1.08, which indicates a major contribution from petroleum residues derived from vehicular emissions.

Roadside soil particles exhibited a C_{max} at C_{31} (Figure 3). This C_{max} is indicative of higher plant waxes input. The CPI had a value of 2.05 reflecting a significant input from biogenic sources.

Comparison of n-alkanes distribution in airborne particles and roadside soil particles

From the previous discussion, it was obvious that airborne particles are more enriched in n-alkanes derived from petrogenic sources, whereas in roadside soil particles the biogenic input of n-alkanes is more apparent. This can be explained by particle size considerations that are important to particle deposition from the atmosphere. Petrogenic residues preferentially occur in the submicron particles [16] that deposit slowly from the atmosphere [17]. Biogenic materials (e.g., mechanically generated leaf and soil dusts) in contrast preferentially accumulate in the larger particles, which deposit more readily by gravitational sedimentation or impaction [16, 18]. Thus, roadside soil particles are enriched in biogenic materials, whereas airborne particles are more enriched in petrogenic residues.

Petroleum molecular markers

Molecular markers are either biolipids, synthesized by living organisms and preserved in crude petroleum and sediments, or geolipids, derived from biolipids precursors by change in the molecule but survival of the carbon skeleton [19]. In environmental chemistry, these compounds can be utilized as source identifiers [e.g., 4, 8]. Petroleum molecular markers include pristane, phytane, hopanes, and steranes [4, 8]. Pristane and phytane are present in diesel fuel, lubricating oil, and in both auto and diesel engine exhaust. On the other hand, hopanes and steranes are not present in gasoline and diesel fuel because they belong to the higher boiling fraction of crude petroleum, but they are found in lubricating oil and in both auto and diesel engine exhaust [4, 8].

In the present study, the hopanes identified were Ts (C_{27}), Tm (C_{27}), 17□(H),21□(H)-hopanes that consist of the C_{29} to C_{35} pseudohomologs (including 22S and 22R epimers for C_{31} to C_{35} homohopanes). Steranes identified on the m/z 217 were C_{27} to C_{29} □□□ (20S + 20R), while those identified on the m/z 218 were C_{27} to C_{29} □□□ (20S + 20R).

As shown in Figure 4, the molecular distribution of hopanes and steranes in airborne particles and roadside soil particles resembles that of lubricating oil indicating that these compounds are chiefly derived from the engine lubricating oil. Thus, the presence of hopanes and steranes together with pristane and phytane reflects the contamination by petroleum residues.

Polycyclic aromatic hydrocarbons (PAHs)

PAHs are ubiquitous in the environment and have been identified to have carcinogenic and mutagenic effects. The formation of PAHs is due to two major causes: (a) endogenic synthesis in the environment by microorganism, phytoplankton, algae, and higher plants, which create the natural background, and (b) man-controlled high temperature pyrolitic reactions, open burning, and natural volcanic activities [21, and references cited therein]. In combustion processes, PAHs are produced due to chemical recombination of organic radical intermediates produced by cracking of larger organic molecules [21].

In this study, the main PAHs determined were phenanthrene (PHEN), anthracene (ANTH), 4,5-methylenephenanthrene (45MPHEN), fluoranthene (FLT), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), enzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (PER), indeno[1,2,3-cd]pyrene (IP), dibenz(a,h)anthracene (dBahA), benzo[g,h,i] perylene (BgP), anthanthrene (ANTN), and coronene (COR).

Airborne particles had total PAHs concentrations of 6.28 ± 4.35 ng/m^3 (Table 2). The molecular distribution of PAHs shows that BgP and COR as the most abundant compounds (Figure 5). The high abundance of BgP and COR is indicative of gasoline vehicle emissions [2, 22].

The ratio of BeP/(BeP + BaP) was 0.55. This ratio value was close to gasoline vehicle emissions [0.53 ± 0.05 [17, and references cited therein] indicating the petrogenic pyrolytic source of PAHs. This ratio also indicates that the samples were fresh and no photochemical oxidation had occurred [23].

In roadside soil particles, the total PAHs concentrations was found to be 0.224 ± 0.108 µg/g (Table 2). The molecular distribution showed the highest abundance at lower molecular weight PAH namely PHEN, FLT, and PYR (Figure 5). The high abundance of the low molecular weight PAHs is indicative of diesel vehicle emissions [2, 22].

The ratio of BeP/(BeP + BaP) was 0.68, which is close to that value measured for diesel vehicle emissions (0.66, calculated from [2]) and reflects a decay in BaP that indicates that these samples are aged and exposed to solar radiation [23].

Comparison of PAHs distribution in airborne particles and roadside soil particles

Lower molecular weight PAHs were more enriched in roadside soil particles, whereas high molecular weight ones were more abundant in airborne particles. This may be due to one or more of the following reasons: (a) lower molecular weight PAHs predominate in larger particles, which deposit faster and easier, whereas high molecular weight ones predominate in the smaller particles that deposit slowly from the atmosphere [17, 24], (b) lower molecular weight PAHs have higher hydrophilicity. Thus, wet deposition is more effective in removing these compounds from the atmosphere compared to the high molecular weight ones, and (c) evaporation of lower molecular weight PAHs during air sampling due to their volatilization.

Table 1. Concentrations of n-alkanes in airborne particles and roadside soil particles

Compound		**Concentrations (ng/m^3) Airborne particles**	**□ (n =24)**	**Concentrations (µg/g) Roadside soil particles**	**□ (n =24)**
No.	**Name**				
1	C_{19}	0.23	0.09	0.326	0.295
2	C_{20}	1.70	1.01	0.320	0.223
3	C_{21}	2.88	1.73	0.336	0.229
4	C_{22}	4.73	2.87	0.373	0.369
5	C_{23}	7.25	4.38	0.358	0.316
6	C_{24}	9.69	5.71	0.375	0.326
7	C_{25}	12.39	6.90	0.486	0.364
8	C_{26}	11.95	6.69	0.345	0.297
9	C_{27}	11.01	5.84	0.451	0.405
10	C_{28}	8.13	4.30	0.327	0.251
11	C_{29}	6.85	3.12	0.584	0.401
12	C_{30}	4.94	2.46	0.337	0.282
13	C_{31}	6.12	2.80	1.008	0.653
14	C_{32}	5.75	2.02	0.283	0.224
15	C_{33}	4.39	2.32	0.980	0.615
16	C_{34}	4.87	3.16	0.471	0.416
Total		**102.87**	**50.60**	**7.358**	**4.768**
CPI*		1.08		2.05	
C_{max}		C_{25}		C_{31}	

* CPI = 0.5 (□$C_{25} - C_{33}$/ □$C_{26} - C_{34}$ + □$C_{25} - C_{33}$/ □$C_{24} - C_{32}$) (Bray and Evans, 1961)

Table 2. Concentrations of PAHs in airborne particles and roadside soil particles

Compound		**Concentrations (ng/m^3) Airborne particles**	**□ (n =24)**	**Concentrations (µg/g) Roadside soil particles**	**□ (n =24)**
No.	**Name**				
1	PHEN	0.17	0.11	0.043	0.024
2	ANTH	0.09	0.05	0.005	0.004
3	45MPHEN	0.03	0.02	0.004	0.003
4	FLT	0.12	0.08	0.028	0.013
5	PYR	0.33	0.21	0.039	0.016
6	BaA	0.16	0.12	0.005	0.005
7	CHR	0.19	0.13	0.020	0.007
8	BbF	0.35	0.27	0.007	0.004
9	BkF	0.24	0.18	0.001	0.003
10	BeP	0.57	0.40	0.013	0.007
11	BaP	0.47	0.36	0.006	0.005
12	PER	0.18	0.14	0.004	0.004
13	IP	0.69	0.57	0.006	0.004
14	dBahA	0.05	0.05	0.001	0.001
15	BgP	1.35	0.95	0.020	0.016
16	ANTN	0.17	0.19	0.002	0.006
17	COR	1.11	0.94	0.020	0.023
Total		**6.28**	**4.35**	**0.224**	**0.108**
BeP/(BeP+BaP)		0.55		0.68	

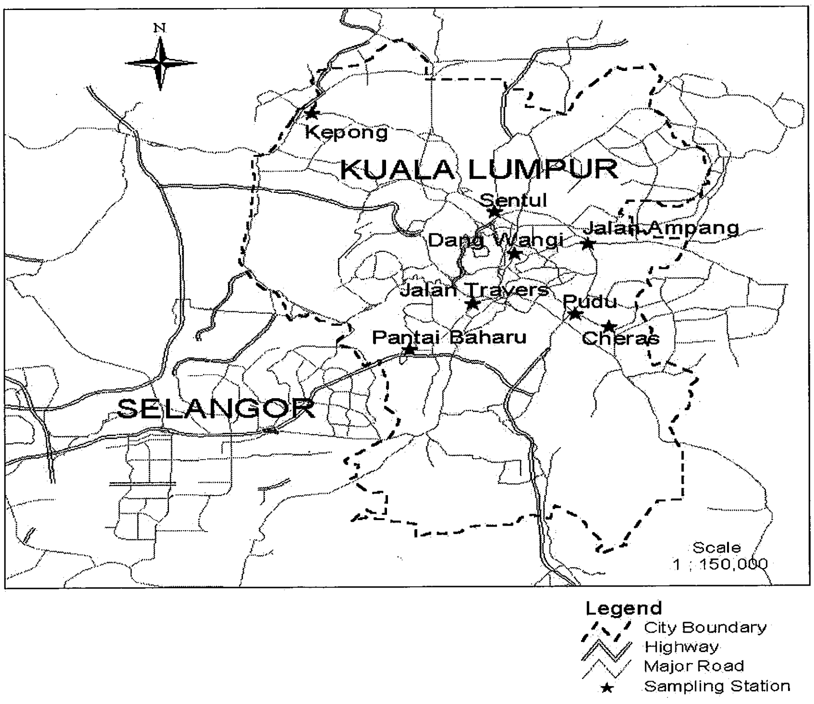

Figure 1. Location map of the sampling sites in Kuala Lumpur.

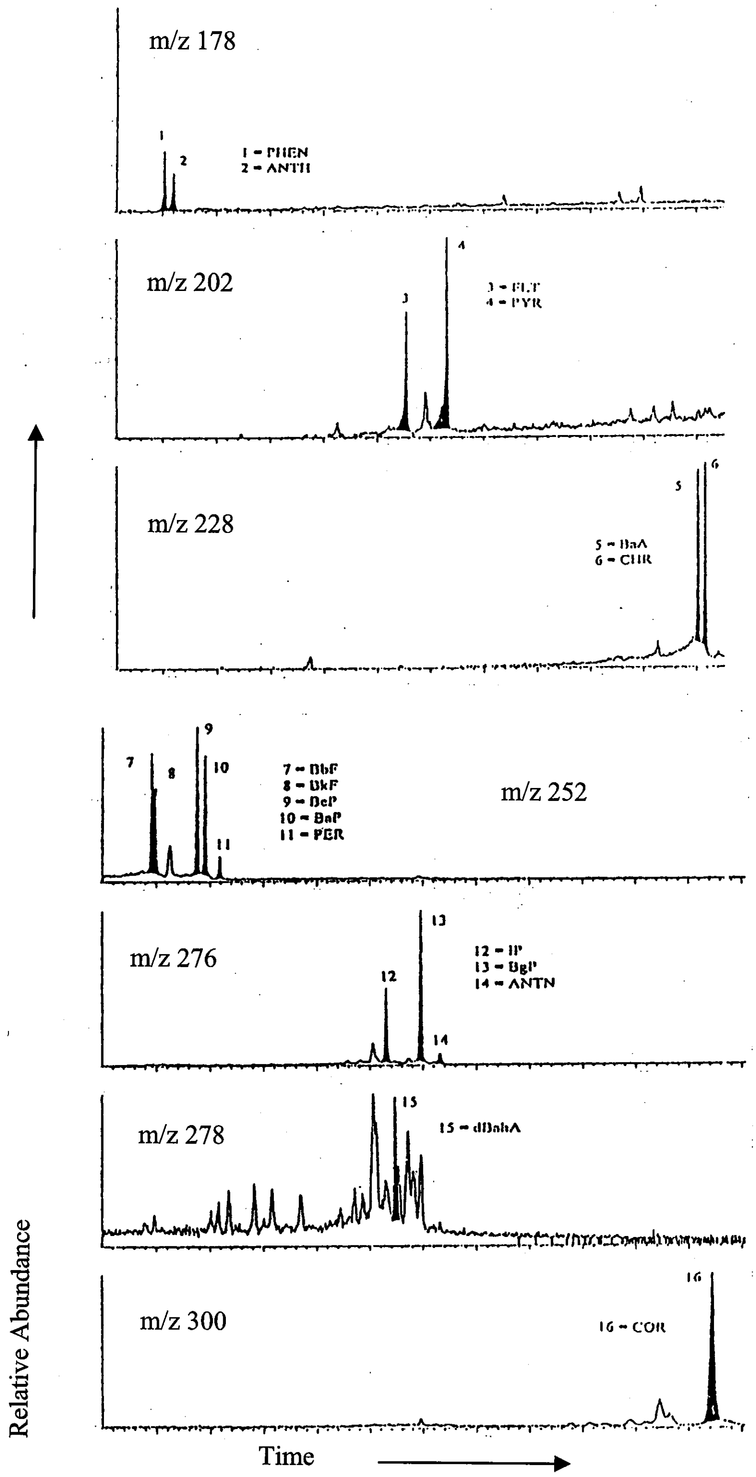

Figure 2. Typical ion chromatograms for PAHs

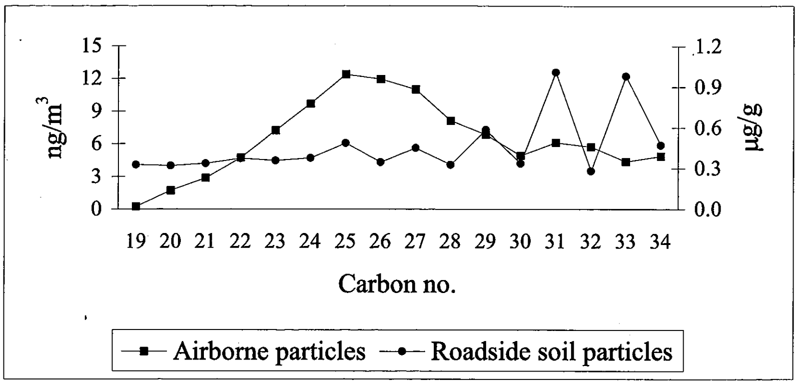

Figure 3. Molecular distribution of n-alkanes in urban airborne particles and roadside soil particles.

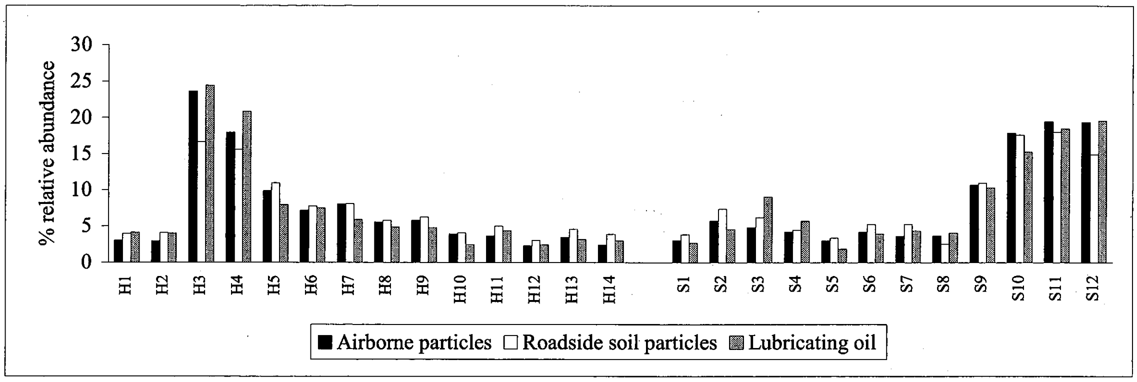

Figure 4. Molecular distribution of hopanes (H1=Ts, H2=Tm, H3=C_{29}□□, H4=C_{30}□□, H5=C_{31}S, H6=C_{31}R, H7=C_{32}S, H8=C_{32}R, H9=C_{33}S, H10=C_{33}R, H11=C_{34}S, H12=C_{34}R, H13=C_{35}S, H14=C_{35}R) and steranes (S1=C_{27}□□□S, S2=C_{27}□□□R, S3=C_{27}□□□S, S4=C_{27}□□□R, S5=C_{28}□□□S, S6=C_{28}□□□R, S7=C_{28}□□□S, S8=C_{28}□□□R, S9=C_{29}□□□S, S10=C_{29}□□□R, S11=C_{29}□□□S, S12=C_{29}□□□R).

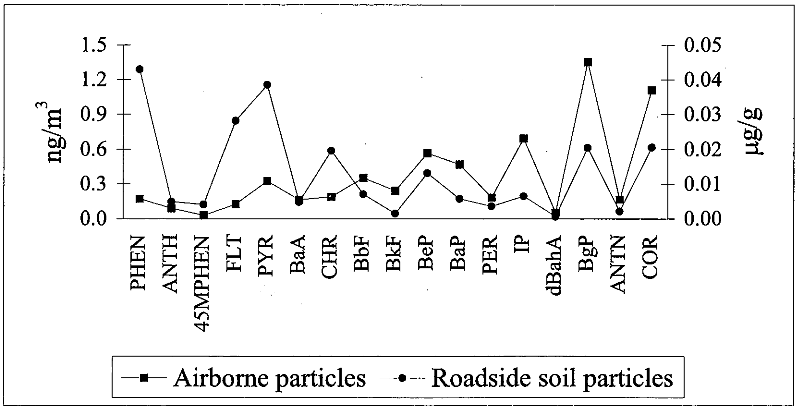

Figure 5. Molecular distribution of PAHs in urban airborne particles and roadside soil particles.

CONCLUSION

The total concentrations of n-alkanes in airborne particles and roadside soil particles collected in Kuala Lumpur, Malaysia are 102.87 ± 50.60 ng/m^3 and 7.36 ± 4.77 μg/g, respectively. The molecular distribution of n-alkanes, CPI, and C_{max} indicate that n-alkanes are of mixed petrogenic and biogenic sources.

Molecular distribution of hopanes and steranes closely matches that of lubricating oil reflecting that engine lubricants are the major source of these compounds.

The total concentrations of PAHs in airborne particles and roadside soil particles are 6.28 ± 4.35 ng/m^3 and 0.224 ± 0.108 μg/g, respectively. The distribution patterns of PAHs and the BeP/(BeP + BaP) diagnostic ratio indicate that PAHs are of mixed petrogenic pyrolytic sources (i.e. gasoline and diesel vehicles emissions).

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