

Source apportionment of particulate-associated polycyclic aromatic hydrocarbons (PAHs) on impervious urban surfaces

La répartition des sources de particules associées à des hydrocarbures aromatiques polycycliques (HAP) sur les surfaces imperméables en milieu urbain

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RÉSUMÉ

Le ruissellement induit par les eaux de pluie constitue l'une des pollutions diffuses les plus graves en zone urbaine. En se déplaçant sur et à travers les surfaces en milieu urbain, le ruissellement collecte, transmet et rejette des polluants de surface dans les milieux récepteurs. Les stratégies d'atténuation de la pollution des eaux pluviales doivent ainsi se baser sur la connaissance de la distribution et de la répartition des sources de polluants sur les surfaces en milieu urbain. Cette étude présente la distribution des particules associées à des HAP en fonction des caractéristiques de la surface, à savoir des types d'occupation des sols en zone urbaine. Des échantillons ont été prélevés sur six sites de la ville de Dresde, en Allemagne, en utilisant une méthode de prélèvement d'échantillons par aspiration humide. Les résultats montrent que la charge de surface la plus élevée de \sum_{16} PAHs correspond à une voie piétonne pavée de pierre naturelle avec $34,5 \mu\text{g}/\text{m}^2$. Par contre, la concentration en phase solide la plus élevée correspond à une route soumise à une circulation intense, avec $36 \text{ mg}/\text{kg}$. Grâce à la combinaison d'un ratio de diagnostic qualitatif et d'une répartition quantitative des sources par PCA-MLR, deux contributeurs significatifs aux HAP sur les voies de circulation automobile ont été identifiés : les sources avec ou sans combustion. 81,6 % de la charge HAP ont été attribués aux sources impliquant la combustion, dont les émissions des véhicules, la combustion du charbon et du bois ; 18,4% ont été attribués aux sources sans combustion, telles que les déversements d'huile-moteur ou les débris des pneus de véhicules.

ABSTRACT

The rainfall induced runoff is one of the most severe non-point source pollutions in the urban area. As the runoff moves over and through the urban surfaces, it picks up, transmits and ultimately discharges surface pollutants into receiving waters. The stormwater quality mitigation strategies, therefore, should be based on the knowledge of the distribution and source apportionment of pollutants on the urban surfaces. This study showcases the distribution of particulate-associated PAHs as a function of surface characteristic, i.e. "urban land-use" types. Samples were obtained from six sites in the city of Dresden, Germany, using a wet vacuum sample-taking method. Results show that the highest surface load of \sum_{16} PAHs was found at a natural stone paved pedestrian path with $34.5 \mu\text{g}/\text{m}^2$. By contrast, the highest solid-phase concentration occurred at a high traffic load road with $36 \text{ mg}/\text{kg}$. Through a combined qualitative diagnostic ratio and quantitative PCA-MLR source apportionment, two significant contributors to PAH at vehicular roads were primarily identified as burnt and unburnt sources. 81.6% of the PAH burden was ascribed to burnt sources which are included vehicle emission, coal and wood combustion; 18.4% was attributed to unburnt sources, such as spilled engine oil, vehicular tire debris.

KEYWORDS

PAHs, Source apportionment, Stormwater wash-off, Urban surface pollution

1 INTRODUCTION

As toxic, carcinogenic, mutagenic, and teratogenic pollutants (Phillips 1983), polycyclic aromatic hydrocarbons (PAHs) are extensively studied by environmental scientists in various matrices such as: the airborne particulate-bound PAHs and their corresponding adverse influences on human health through direct inhalation and unintentional consumption due to hand-to-mouth contacts (Lorenzi et al. 2011); the occurrence of PAHs in urban soil induced through dry and wet deposition as well as in aquatic sediment resulting from point and non-point sources. Meanwhile, little is known about the distribution and source apportionment of PAHs on urban surfaces.

In fact, due to rapid urbanization in the past decades, large unpaved areas (e.g. rangeland, pastureland and forestland etc.) were transformed to impervious areas (e.g. road, square and parking lot etc.). The increased percentage of impervious areas results in an increased volume of surface runoff induced by rainfall events. Natural and anthropogenic pollutants are picked up from the surface by runoff and transport, either through a combined or separate sewer system, into lakes, rivers, wetlands, coastal waters and ground water systems, ultimately contaminating receiving waters.

In this context, urban surface has been recognized as a primary receptor of the dry and wet deposition as well as a primary contributor to the runoff pollution which eventually contaminated the aquatic environment (Kose et al. 2008). Hence, the influence of surface characteristic on the adsorption behaviour of PAHs and the contributions of the various sources should be well understood to appropriately mitigate PAH levels in the environment.

The main objectives of the investigation presented in this paper were to investigate the distribution of particulate-associated PAHs on impervious surfaces with regard to their surface characteristic, to identify the primary origins of PAHs using qualitative diagnostic ratio assessment and quantitative principal component analysis with multiple linear regression (PCA-MLR) receptor model.

2 METHODS

2.1 Study area

Surface samples were obtained in the city of Dresden (51°02'55" N, 13°44'29" E) which is located in eastern Germany. The characteristics and locations of the selected sampling sites are given in Table 1 and Figure 1, respectively.

Table 1. Characteristics of sampling sites (see Figure 1).

Site	Abbr.	Material	Dimension ^a	Traffic load ^b
Flat roof	FR	Brick	235 × 115	- ^c
Natural stone paved pedestrian path	NP	Natural stone	80-100 × 80-100	-
Low traffic load road	LR	Asphalt	NA	NA ^d
Inner courtyard	IC	Brick	900 × 600	-
Brick paved pedestrian path	BP	Brick	195 × 95	-
High traffic load road	HR	Asphalt	NA	Ca. 13600 to 15000 cars per day with 5 % heavy traffic

^a The dimension of surface pavement, length (mm) × width (mm).

^b <http://www.dresden.de>, accessed June, 2011.

^d NA: not available.

^c "-": auto-free zone.

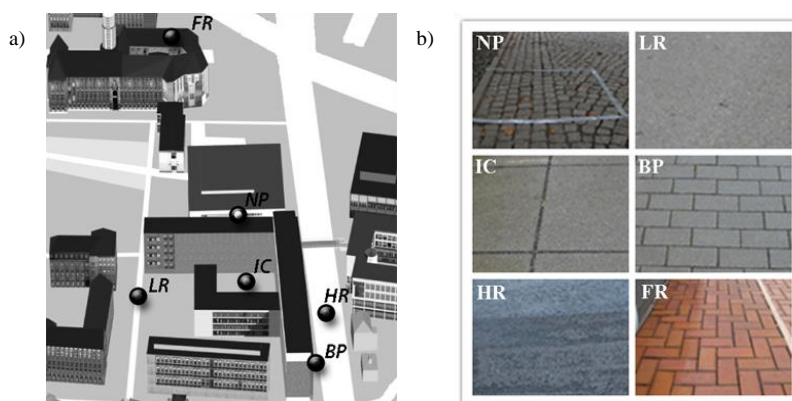


Figure 1. a) Sampling sites and b) surface pavements (see Table 1).

The selected 6 sampling sites represent different land-use types and surface characteristics. LR is a secondary road, whose traffic load is quite low and not quantified. IC was chosen not only because it is an auto-free zone, but also because it is separated from vehicular traffic (VT) by the surrounding buildings.

2.2 Sample collection

The sampling campaign was performed on August 2011. A wet vacuum sweeper (Puzzi 100 Super Kärcher) was employed in this study. During the sampling process, the vacuum nozzle was moved from the road curb to the bottom line of predefined sampling plot at approximately 10 cm/s in parallel stripes. The collected samples were then deposited into pre-cleaned 1-L amber-brown-glass bottles with bakelite caps before being transported to the laboratory. After sample collections at each site, additional 6 L of deionised water were passed through the sweeper three times to prevent cross-contamination. To avoid or reduce the potential of PAHs dissolution in the water (The concentrations of individual and \sum_{16} PAHs in water have been tested, and all of them were below the detection limit.), the samples were dried immediately when transferred to the laboratory. Specifically, samples were air dried for about 24 - 48 hours at room temperature (about 20 °C) in the ventilation laboratory. After they were completely dry, all the samples were labelled, sealed and refrigerated at 4 °C in preparation for analysis.

2.3 Laboratory analysis

Total and individual sixteen U.S. EPA criteria PAHs (www.epa.gov) were analysed by an independent commercial laboratory Team Umweltanalytik GmbH following the German Standard DIN EN 15527 and E DIN 38407-F 39. The details of experimental methods and related information can be found via (www.umweltanalytik-ebersbach.de). The analysis of total solids (TS) and total organic matters (TOM) was conducted following DIN 38409.

2.4 Source apportionment

PAHs are always emitted as a mixture, and the relative molecular concentration ratios are considered to be characteristic for a given emission source. Therefore, PAH diagnostic ratios (DRs) have been widely used to qualitatively distinguish source assignments of PAH (Benner et al. 1990).

PCA-MLR is a multivariate analytical tool used for receptor modelling in environmental source apportionment (Larsen and Baker 2003). In this study, the PCA-MLR receptor model was explored after the DRs assessment, to confirm the proposed sources by DRs and quantitatively estimate the mean percentage contribution of each source.

3 RESULTS AND DISCUSSION

3.1 Spatial distribution of TS and TOM

PAHs are largely associated with particulate matter, and the road-deposited sediments (substituted as total solids) are regarded as a major carrier of PAHs to sewer system and eventually receiving waters (Boonyatumanond et al. 2006). Prior to the discussion of PAH, therefore, the mass of TS and TOM per

unit surface area (g/m^2) at various antecedent dry-weather periods (ADPs) are given in Figure 2 for the investigated land-use types. The build-up process during two dry-weather periods is displayed by solid lines, whilst the dashed lines represent precipitation periods or days when the surfaces were still wet after rainfall events.

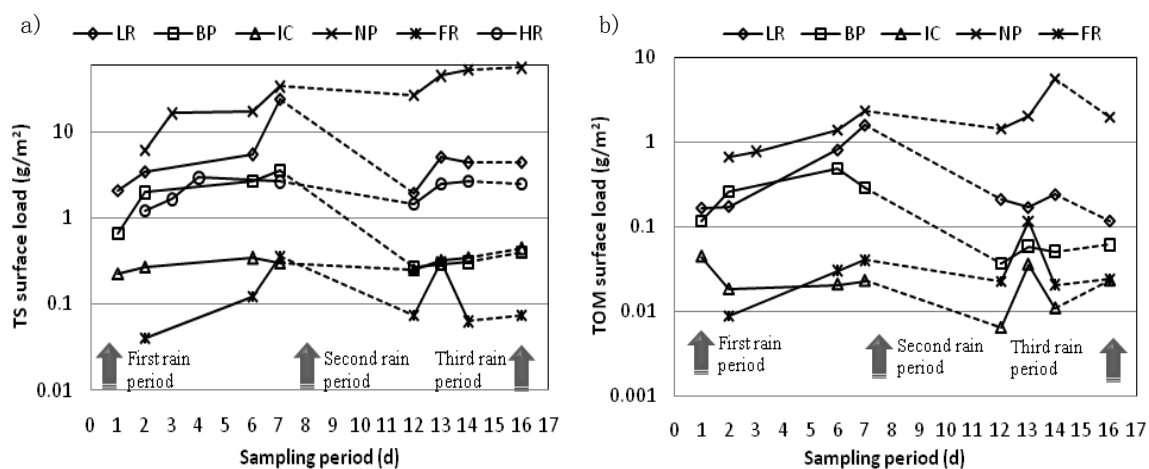


Figure 2. Spatial distribution and temporal accumulation and of a) TS and b) TOM.

According to Figure 2, the surface characteristics and the rain volumes (from Deutscher Wetterdienst, DWD) significantly influence the TS and TOM accumulation. The detailed interpretation and explanation is described in Zhang et al. (2012). Generally speaking, increasing tendencies of TS and TOM were apparent at all sites over ADPs, the highest TS and TOM surface loads were found at NP site. This can be explained by the large gaps between the natural stones filled with sandy materials which have a higher retention capacity for particulate matters. Besides, rough surfaces such as natural stones, can trap more sediments than smooth surfaces.

3.2 Spatial distribution of PAHs

PAHs concentrations were determined at the 6 sampling sites defined in Figure 1. The following 16 PAHs concentrations were quantified: Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLUH), Pyrene (PYR), Benz(a)anthracene (BaA), Chrysene (CHY), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IDP), Dibenzo(a,h)anthracene (DBA), Benzo(g,h,i)perylene (BgP). In order to represent the pollutant accumulation process and the pollution sorption ability of sediments, the measurements were interpreted using the forms of i) the mass of PAHs per unit surface area ($\mu\text{g}/\text{m}^2$), referred to as “surface load”, and ii) the mass of PAHs per unit mass of total solids (mg/kg), referred to as “solid-phase concentration”. The distributions of individual and sum PAHs after 3-day ADP in the second rain period are shown in Table 2.

Table 2. The spatial distribution of surface loads and solid-phase concentrations of PAHs at each sampling site.

Site	FR		NP		LR		IC		BP		HR	
	mg/kg	µg/m ²	mg/kg	µg/m ²	mg/kg	µg/m ²	mg/kg	µg/m ²	mg/kg	µg/m ²	mg/kg	µg/m ²
NAP	BDL ^a	- ^b	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-
ACY	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-
ACE	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-
FLU	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-
PHE	BDL	-	0.042	2.19	BDL	-	0.20	0.069	0.11	0.033	3.11	1.43
ANT	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	0.41	0.19
FLUH	0.69	0.043	0.088	4.60	0.10	0.43	0.40	0.14	0.15	0.046	5.64	2.56
PYR	0.61	0.038	0.069	3.60	0.085	0.37	0.32	0.11	0.14	0.043	5.13	2.31
BaA	0.62	0.039	0.066	3.45	0.077	0.33	0.24	0.083	0.20	0.061	2.92	1.27
CHY	0.53	0.033	0.077	4.02	0.081	0.35	0.25	0.086	0.16	0.049	3.03	1.36
BbF	0.62	0.039	0.085	4.44	0.062	0.27	0.20	0.069	0.22	0.067	4.26	1.86
BkF	0.37	0.023	0.039	2.04	BDL	-	0.11	0.038	BDL	-	1.85	0.80
BaP	0.46	0.029	0.073	3.81	0.062	0.27	0.16	0.055	0.15	0.046	3.88	1.69
IDP	0.39	0.024	0.062	3.24	0.05	0.22	0.1	0.034	0.14	0.043	2.9	1.26
DBA	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	0.25	0.064
BgP	BDL	-	0.054	2.82	0.055	0.24	0.11	0.038	0.16	0.049	2.55	1.11
∑ ₇ carcPAHs ^c	2.99	0.19	0.40	21.00	0.33	1.44	1.06	0.37	0.87	0.27	19.09	8.30
∑ ₁₆ PAHs ^d	4.88	0.31	0.66	34.48	0.57	2.46	2.09	0.72	1.43	0.44	35.96	15.91

^a BDL: below detection limit.

^b The unit cannot be transferred due to corresponding PAHs contents are below detection limit.

^c ∑₇carcPAHs: The sum of seven analyzed carcinogenic PAHs (∑₇carcPAHs) are Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Chrysene, Dibenzo(a,h)anthracene, and Indeno(1,2,3-cd)pyrene.

^d ∑₁₆PAHs: The sum of 16 analyzed individual PAH.

As shown in Table 2, the concentrations of the individual and sum PAHs at each sampling site varied in a wide range. In terms of surface load, the highest value was found at NP site with 34.5 µg/m² which is twice the second high value occurred at HR site with 15.9 µg/m². The solid-phase concentration at NP site, in contrast to the surface load, was fairly low with 0.66 mg/kg. The solid-phase concentration at HR site was 36 mg/kg. The different rankings for the two sites in respective two units indicate the different pollution distribution mechanisms, although both sites have high surface loads. Compared with HR site, the lower solid-phase concentration indicates that each individual sediment (i.e. TS) at NP site adsorbed less PAHs and does not significantly contribute to the high value of surface load. Therefore, as opposed to the HR site, the high surface load at NP site was attributed to a high specific surface load of TS rather than its low adsorption ability. In other words, the potential pollution contributor was the "TS-quantity" not the "TS-quality". An explanation for the high solid-phase concentration at HR site is the contribution of auto tire debris and asphalt pavement which consisted of high PAHs fractions and were regarded as significant contributors to PAHs content in road-deposited sediments by Boonyatumanond et al. (2007) and Kose et al. (2008). In addition, the low TOM to TS ratio (7.6% ±

1.2%) at NP site indicates relatively low sorption potential, as organic matter provides interfaces for PAHs adsorption

The solid-phase concentration of PAH at HR site was about an order of magnitude higher than those at other sites. However, the HR site was notably characterized by the vehicular traffic (VT). It is therefore suggested that PAHs and VT are highly linked. Actually the vehicle emission was considered as one of the primary contributors to PAH pollution (Albinet et al. 2007). The particulate matter at this site has a higher surface adsorption capacity than auto-free zones. Therefore, in contrast to NP site, the high value of solid-phase concentration at HR site was attributed to "TS-quality" rather than to "TS-quantity". Relatively low PAH surface loads can be found at FR, IC and BP sites. All three sites were characterised by low TS contents and no VT access. Special concern should be paid to the individual PAH of BaP which is regarded as the most potent carcinogen. Except for NP and LR sites, the BaP concentrations at other sites are higher than the BaP generic soil screening level (SSL) of 0.09 mg/kg used by U.S. EPA. However the BaP concentrations at all sampling sites are lower than a more tolerant BaP soil guideline of 5 mg/kg proposed by Fitzgerald et al. (2004).

3.3 Source apportionment of PAHs

3.3.1 Source estimates from diagnostic ratios

To assess the possible diverse origins of PAHs, the diagnostic ratios (DRs) were employed in qualitative source assessment. The reviewed reference of DRs is compiled in Table 3.

Table 3. Diagnostic ratios used for source apportionment of PAHs.

Diagnostic ratio ^c	Transition point	Source assignment
ANT/(ANT + PHE)	< 0.1	Petroleum
	> 0.1	Grass, wood or coal combustion
BaA/(BaA + CHY)	< 0.50	Petroleum
	> 0.50	Grass, wood or coal combustion
BaP/BgP	< 0.6	Non-vehicle emission
	> 0.6	Vehicle emission
BbF/BkF	2.5 - 2.9	Aluminum smelter emission
FLUH/(FLUH + PYR)	< 0.40	Petroleum
	0.40 - 0.50	Liquid fossil fuel (vehicle and crude oil)
	> 0.50	Grass, wood or coal combustion
IDP/(IDP + BgP)	< 0.20	Petroleum
	0.20 - 0.50	Liquid fossil fuel (vehicle and crude oil)
	> 0.50	Grass, wood and coal combustion
LMW ^a /HMW ^b	< 1	Pyrogenic
	> 1	Petrogenic

^a LMW: Low molecular weight (LMW) PAHs which have a high vapour phase fraction with two or three aromatic rings.

^b HMW: High molecular weight (HMW) PAHs which have a high particulate phase fraction with four to six aromatic rings.

^c Reference: Tobiszewski and Namieśnik (2012).

For characterization of the PAHs sources, the ratio of BaP to BgP has been compared on the premise that BgP originates mainly from vehicular traffic. A BaP to BgP ratio of 0.60 is defined as the transition point to distinguish between dominant traffic influence ($BaP/BgP > 0.60$) and minor (or none) traffic influence ($BaP/BgP < 0.60$). As shown in Table 4, the BaP/BgP ratios from each site are higher than 0.60, indicating a dominant source of vehicle emissions. The FLUH/(FLUH + PYR) ratio has been used to detect petroleum-derived PAH. However, the FLUH/(FLUH + PYR) ratios are above 0.50 for all sites. It suggests a controversial conclusion compared with from the value of BaP/BgP ratio which indicates that the surface PAH has been attributed to combustion source. Overall, both diagnostic ratios underline the influence of the anthropogenic activity on PAHs content.

Table 4. Diagnostic ratios of PAHs calculated in each sampling site.

Site	ANT/(ANT + PHE)	BaA/(BaA + CHY)	BaP/BgP	BbF/BkF	FLUH/(FLUH + PYR)	IDP/(IDP + BgP)	LMW/HMW
BP	- ^a	0.556	0.938	-	0.517	0.467	-
FR	-	0.539	-	1.676	0.531	-	-
HR	-	0.491	1.522	2.303	0.524	0.532	-
IC	-	0.490	1.455	1.818	0.556	0.476	-
LR	-	0.487	1.127	-	0.541	0.476	-
NP	-	0.462	1.352	2.179	0.561	0.534	-

^a The ratio cannot be calculated due to corresponding PAH contents are below detection limit.

Furthermore, some source-specific interpretations have been provided for the FLUH/(FLUH + PYR) ratio. For example, Grimmer et al. (1981) detected a FLUH/(FLUH + PYR) ratio of about 0.74 in re-refined and used motor oils in Germany. Fraser et al. (1998) measured ambient concentrations of PAH in the city of Los Angeles, and FLUH/(FLUH + PYR) ratios of 0.55 - 0.57 were found. Explicitly, the spilled used engine oil and the ambient PAHs content which was transferred by wet deposition from the atmosphere to surfaces could have a potential influence on the behaviour of road-deposited sediment associated PAHs, and consequently lead to the various DRs transition points.

Regardless of the inconsistent suggestions from the first two DRs, the ratios of BaA/(BaA + CHY) and IDP/(IDP + BgP) with higher molecular masses were conducted. Both of them were recommended by Dvorská et al. (2011) for better distinction between vehicle emission and residential heating sources. The values of both DRs suggest a mixture of petroleum and combustion sources. The results have a good agreement with the conclusion that VT and coal combustion are major contributors of atmospheric PAHs and are consistent with the sources of PAHs in urban surface dust (Liu et al. 2007). According to the value of BaA/(BaA + CHY) ratio, the PAHs contents at BP and FR sites are attributed to combustion source. In contrast, the other four sites including two VT roads are characteristic of petroleum source. However, with regard to the value of IDP/(IDP + BgP) ratio, the PAHs at BP, IC, and LR sites have a petroleum-related source. The PAHs contents at HR and NP sites appear to be affected by combustion-related source. In addition, the value of BbF/BkF ratio reported herein implies that there is no aluminium smelter emission in the vicinity of sampling sites.

The reliability of DRs source apportionment is challenged by many uncertainties. The DRs transition points could be revised based on better time-resolved PAH data. More than one DR was recommended to be used to confirm the results, because the reliance on a single ratio to infer source can be highly misleading. Nevertheless, the source apportionment using DRs is advantageous because of the user-friendly application and is therefore still commonly used as a tool for qualitatively identifying potential sources.

3.3.2 Source estimates from principal component analysis

Principal component analysis (PCA) followed by stepwise multiple linear regression (MLR) of the data was performed using SPSS statistics 19. The purpose of PCA is to reduce the dimensionality of the original PAH data to a minimum number of components. Each component is a linear combination of the original variables. All the components are orthogonal to each other, which results in the smallest possible covariance (Zhang et al. 2012). In this study, PCA was applied to estimate the potential sources which are responsible for each component. Principal components were computed using Varimax Rotation Method with Kaiser normalization. The components were extracted based on

eigenvalue greater than 1. The rotated component matrix of individual PAHs from both low and high traffic load roads is shown in Table 5.

Table 5. Rotated component matrix of individual PAH from both low and high traffic load roads.

Individual PAH		Component	
		1	2
Variable	Abbr.	Burnt source ^a	Unburnt source ^a
Phenanthrene	PHE	0.939	0.312
Anthracene	ANT	0.845	-0.166
Fluoranthene	FLUH	0.971	0.173
Pyrene	PYR	0.975	0.174
Benz(a)anthracene	BaA	0.995	-0.024
Chrysene	CHY	0.956	0.209
Benzo(b)fluoranthene	BbF	0.951	0.284
Benzo(k)fluoranthene	BkF	0.965	0.172
Benzo(a)pyrene	BaP	0.967	0.206
Indeno(1,2,3-cd)pyrene	IDP	0.945	0.292
Dibenzo(a,h)anthracene	DBA	0.116	0.971
Benzo(g,h,i)perylene	BgP	0.900	0.401
% of Variance ^b		86.333	9.107
Cumulative % ^c		86.333	95.440

^a Proposed source assignments according to corresponding assessment.

^b The percent of the total variability explained by each principal component.

^c The amount of variance accounted for by each component.

As shown in Table 5, two components were extracted whose eigenvalues are greater than 1. The sum of the variances of the first two components exceeds 95% of the total variance of the original data. The first component is responsible for 86.33% of the total variance. This component is heavily weighted by nearly all given individual PAH with the exception of DBA. According to Harrison et al. (1996), BgP has been identified as a tracer of vehicle emissions. Elevated levels of BkF relative to other PAHs have been proposed to indicate diesel-powered vehicle exhausts. IDP was also found in both diesel and gas engine emissions. Consequently, the profile of IDP, BgP and BkF appears highly indicative of vehicular sources. By contrast, PYR, FLUH, PHE and ANT in the same component have been reported as strongly associated with coal combustion (Harrison et al. 1996). In addition, Benner et al. (1995) reported the use of PHE and ANT as a marker for wood combustion. It means that no single source could explain the PAH profiles in the first component, suggesting that multiple sources contribute to those PAHs. Accordingly, the rotated loadings in the first component indicate a combination of vehicle emission, coal and wood combustion sources. All of them were categorized as burnt sources. It is therefore suggested that the first component was attributed tentatively to the burnt sources.

The second component is responsible for 9.11% of the total variance. This component is predominantly weighted in DBA. Irwin et al. (1997) have reviewed that high loadings of DBA were contained in coal tar (2.5 mg/kg), soot (64 - 705 mg/1000 cu m), and cigarette smoke condensate (0.1 - 0.15 mg/kg). This profile indicates that the burnt sources do not directly contribute the high rotated loading in this component. In addition, the used motor oil typically has much higher concentrations of PAHs than new motor oil. Upshall et al. (1993) has detected 1.5 mg/kg of DBA in the used engine oil. The application of used oil to roads as a dust suppressant and the spilled used oil on the road surface has been reported in other reference. It could be another plausible explanation. However, whether it is performed in the presented sampling sites need to be further investigated. Nevertheless, this indication is consistent with the diagnostic ratio analysis that the used motor oil to some extent contributes to PAHs concentration

at given sampling sites. Accordingly, the highly weighted DBA loading suggested that the second component was attributed tentatively to the unburnt sources.

3.3.3 Stepwise multiple linear regression

In order to quantitatively estimate the percentage contribution of significant PAH sources, a multiple linear regression analysis was performed after the application of PCA. Thus a PCA-MLR receptor model was established and follows the model described elsewhere by Larsen and Baker (2003). A stepwise method which combines forward selection and backward elimination of each variable was used, and a significance level of 0.05 was set. The PCA-MLR was conducted by regressing the component score (CS) computed by PCA against the corresponding pre-standardized \sum PAH concentration using the standard score (see Eq. 1).

$$Z_i = \frac{x_i - \mu_i}{\sigma_i} \quad (1)$$

Z_i is the standardized value of variable i ; x_i is the raw value of variable i ; μ_i is the mean of variable i over all samples; and σ_i is the standard deviation of variable i .

Afterwards, the multiple linear regression equation for the standardized \sum PAH values was determined to be:

$$\hat{Z}_{\sum PAH} = 0.975CS_1 + 0.220CS_2 \quad (R^2 = 0.997) \quad (2)$$

$\hat{Z}_{\sum PAH}$ is the standardized concentration of \sum PAH; CS_i is component score i ; 0.975 and 0.220 are partial regression coefficients B_i .

By expanding $\hat{Z}_{\sum PAH}$ and rearranging terms, the multiple linear regression equation becomes:

$$\sum PAH = 0.975\sigma_{PAH}CS_1 + 0.220\sigma_{PAH}CS_2 + \mu_{\sum PAH} \quad (3)$$

The percentage contributions to the mean for the two components, which were defined as $B_i / \sum B_i \times 100\%$ for each source, were 81.6% for CS_1 (attributed to burnt source) and 18.4% for CS_2 (attributed to unburnt source). The results agree with the findings of Sofowote et al. (2008) who reported that about 80% of the PAH burden was ascribed to burnt related sources.

4 SUMMARY AND CONCLUSIONS

The concentrations of individual and \sum_{16} PAHs of surface samples were measured from six sampling sites with various surface characteristics. The PAHs contents were reported as surface load and solid-phase concentration. Both are important contaminant indicators in surface and runoff management. The characteristics of surface pavements exert a significant influence on PAHs distribution, and to some extent govern the behavior of PAHs adsorption on urban surfaces. The highest surface load of \sum_{16} PAHs was found at NP site with $34.5 \mu\text{g}/\text{m}^2$. By contrast, the highest solid-phase concentration was measured at a high traffic load road HR site with $36 \text{ mg}/\text{kg}$.

Through a combined qualitative diagnostic ratio and quantitative PCA-MLR source apportionment, two significant contributors to PAH at vehicular roads were tentatively identified as burnt and unburnt sources. 81.6% of the PAHs burden was ascribed to burnt sources which are included in vehicle emission, coal and wood combustion, while 18.4% were attributed to unburnt sources, such as spilled engine oil, vehicular tire debris.

The results reported herein could be used for source oriented mitigation of rainfall-induced runoff pollution. This work belongs to a series of research topics which are aiming at predicting the transport of particulate-associated contaminants from urban surfaces to receiving water bodies.

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(No. 2010605021). Any mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

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