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Influence of traffic characteristics on polycyclic aromatic hydrocarbon build-up on urban road surfaces

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Abstract
Traffic is one of the prominent sources of polycyclic aromatic hydrocarbons (PAHs) and road surfaces are the most critical platform for stormwater pollution. Build-up of pollutants on road surfaces was the focus of this research study. The study found that PAHs build-up on road surfaces primarily originate from traffic activities, specifically gasoline powered vehicles. Other sources such as diesel vehicles, industrial oil combustion and incineration were also found to contribute to the PAH build-up. Additionally, the study explored the linkages between concentrations of PAHs and traffic characteristics such as traffic volume, vehicle mix and traffic flow. While traffic congestion was found to be positively correlated with 6- ring and 5- ring PAHs in road build-up, it was negatively correlated with 3-ring and 4 ring PAHs. The absence of positive correlation between 3-ring and 4-ring PAHs and traffic parameters is attributed to the propensity of these relatively volatile PAHs to undergo re-suspension and evaporation. The outcomes of this study are expected to contribute effective transport and land use planning for the prevention of PAH pollution in the urban environment.

Keywords: Stormwater quality; Traffic emissions; Congestion; Traffic volume; Stormwater pollutant processes

1. Introduction
Stormwater pollution is a global issue (Phiri et al. 2005). The common pollutants that degrade the quality of urban receiving waters include suspended solids, heavy metals and polycyclic aromatic hydrocarbons (PAHs) (Chow et al. 2012; Herngren et al. 2010). Among several PAH species, the sixteen species listed by the United States Environmental Protection Agency (US EPA) as priority pollutants have received significant research attention. This is due to their bioavailability and potential toxicity and the resulting detrimental human and ecosystem health impacts (Samanta et al. 2002; Walker et al. 1999).

The PAHs are contributed to urban receiving waters via a diversity of sources, among which stormwater runoff is considered to be a primary source (Wakida et al. 2013; Beasley and Kneale, 2002). PAHs are incorporated into urban stormwater runoff when the pollutants deposited on urban impervious surfaces are washed off during rain events. This highlights the importance of investigating pollutant build-up on urban impervious surfaces, especially on urban road surfaces, which are considered as a major pollutant source to stormwater runoff (Brown and Peake, 2006).

The species and concentrations of PAHs present in urban road build-up are significantly influenced by the characteristics of the PAH sources. Therefore, vehicle mix (based on fuel type used to power the engine), traffic congestion, prescribed speed, age of vehicles (EPASGV 1999; Goonetilleke et al. 2009) and other traffic and land use characteristics can potentially influence PAH build-up on roads. Therefore, it is necessary to understand the influence of traffic and land use characteristics on PAH build-up in order to develop effective strategies to mitigate PAH related urban water quality degradation. Though the influence of traffic and land use characteristics on the build-up of pollutants such as heavy metals has been investigated (Gunawardena et al. 2013), studies that relate the PAH build-up process to the characteristics of the contributing sources are scarce in research literature. Consequently, the current study aimed to develop an understanding of the linkages between PAHs, categorised on the basis of the number of their benzene rings, and contributing source characteristics such as vehicle mix, traffic congestion, traffic volume and land use. The primary objectives of this study were: (a) to identify the sources of specific PAH species in the urban environment; and (b) to investigate the influence of traffic and land use characteristics on the PAH build-up process. The outcomes of this study are expected to contribute to effective transport and land use planning for the mitigation of PAH pollution in the urban environment. The research study was carried out at the Science and Engineering Faculty, Queensland University of Technology, Brisbane, Australia during the period April 2009 to April 2012.

2. Materials and methods
2.1 Site selection and sample collection
The build-up samples were collected from eleven road sites which encompass varying traffic characteristics within the Gold Coast region, Queensland, Australia (Fig. 1). The samples were collected from 2.0 m x 1.5 m plot areas in the middle of the traffic lanes using the wet and dry vacuuming method described by Mahbub et al. (2011b). This method employs a domestic vacuum cleaner fitted with a water filtration system and a vacuuming protocol summarised as follows: (1) firstly, the plots were dry vacuumed with the aim of collecting as much of the dust samples aa possible; (2) then, after spraying the plot with deionized water at 2 bar pressure, the remaining dust samples were collected by wet vacuuming. Prior to the field work, this protocol was tested under laboratory conditions and found to be 97.4% efficient in collecting and retaining road deposited dust with typical particle size distribution.

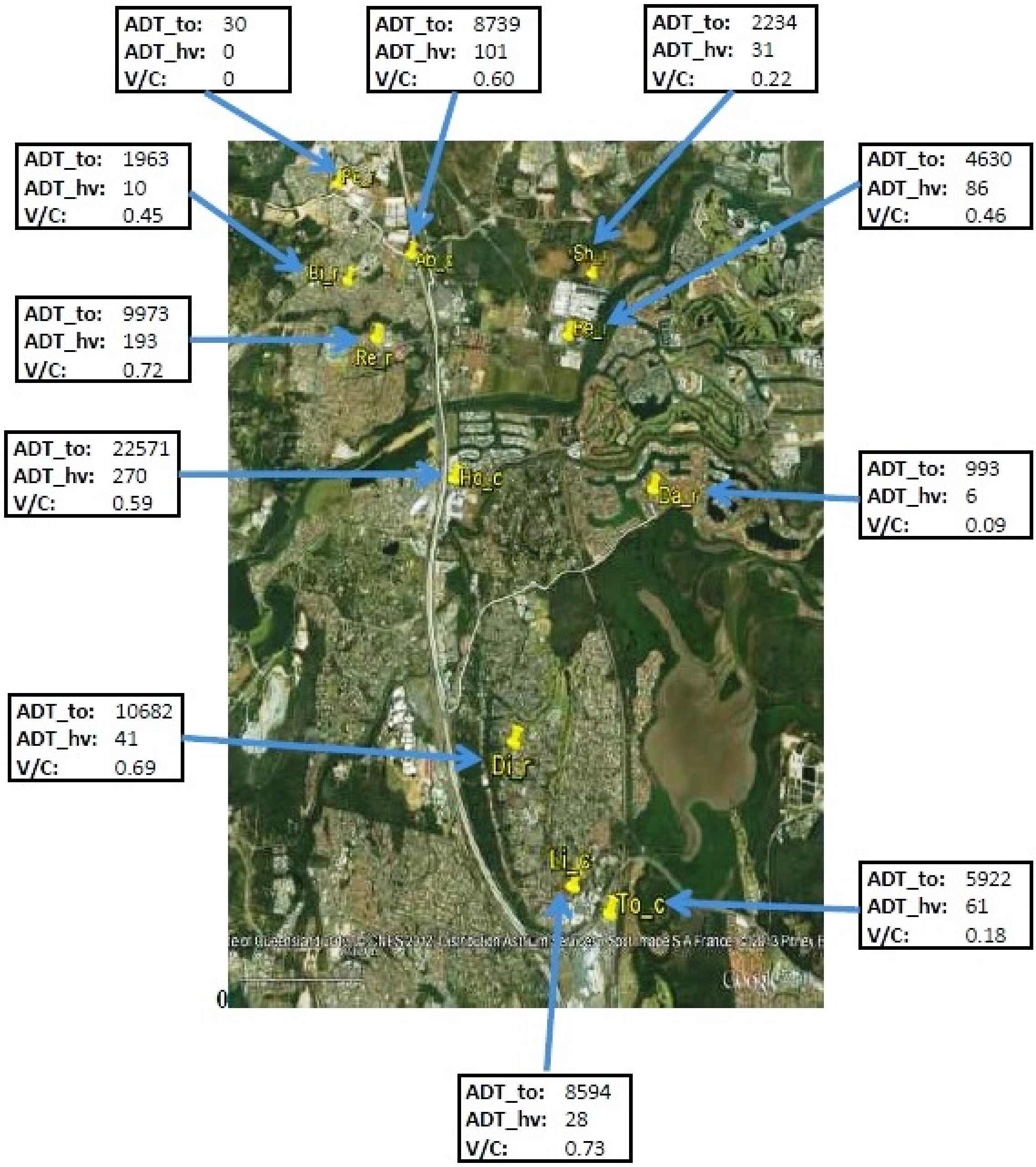

Fig. 1 Study sites (R, C and I denote residential, commercial and industrial sites, respectively; (ADT_to - Annual average daily traffic volume; ADT_hv - total heavy duty traffic volume; V/C - Volume to capacity ratio)

2.2 Sample testing

The samples were transported and stored in the laboratory under the prescribed conditions detailed in AS/NZS (1998). PAH analyses were the undertaken following the guidelines described in USEPA Method 610 (USEPA 1991). The samples were analysed using Gas Chromatography-Mass Spectrometry (GC/MS) and EPA 525 Semivolatiles Calibration mix, internal standards (10-Acenaphthene, D12-Perylene, D12-Chrysene and D10-Phenanthrene), surrogate standards (D10-Fluorene and D10-Fluoranthene) and certified reference material (1649b urban dust, National Institute of Standards and Technology, USA) were employed for quality assurance and quality control purposes. The recoveries from the certified reference material were within 85%-115% of the values given in the standard certificate.

Since the pollutant build-up process is influenced by the particle size (Mahbub et al. 2011a), the samples were wet-sieved into the following five particle size fractions: > 300 µm, 150-300 µm, 75-150 µm, 1-75 µm and < 1 µm. The size resolved samples were analysed for the following PAH species: Acenaphthene (ACE), Acenaphthylene (ACY), Anthracene (ANT), Benz(a)anthracene (BaA), Benzo(a)pyrene (BaP), Benzo(e) pyrene (BeP), Phenanthrene (PHE), Chrysene (CHR), Indeno(1,2,3-c,d)pyrene (IND), Benzo(g,h,i)perylene (BgP), Pyrene (PYR), Fluorene (FLU), Dibenz(a,h)anthracene (DbA) and Fluoranthene (FLA).

2.3 Traffic variables

As PAHs commonly present on road surfaces are primarily generated by traffic (EPASGV 1999), a range of traffic parameters were incorporated into the analysis undertaken. Annual average daily traffic volume (ADT_to) was used as an exploratory variable to represent traffic volume. In terms of PAH build-up, the volume of diesel fuelled vehicles was considered to be an important indicator for vehicle mix. The total heavy duty traffic volume (ADT_hv) was used as a surrogate for vehicle mix. It was found that when ADT_hv is used together with ADT_to, it facilitates the discrimination of gasoline related PAHs from diesel related PAHs in road build-up. Volume to capacity ratio (V/C), which is defined as the ratio between the actual number of vehicles using a road and the design traffic volume was used as a surrogate for traffic congestion. The required traffic data was obtained from a traffic survey conducted using automatic traffic counters at the study sites.

2.3 Analytical tools

Diagnostic ratios, factor analysis and multi criteria decision making methods PROMETHEE and GAIA were used for analysis of PAH load in pollutant build-up (Table S1-S5 in Supplementary Materials). Various diagnostic ratios have been proposed in the literature (Tobiszewski and Namieśnik 2012) and the choice of suitable diagnostic ratios primarily depends on the potential sources of the PAHs at the study sites. Since this study investigated the influence of traffic activities, the following diagnostic ratios were used: BaP/BgP and IND/(IND+BgP). A BaP/BgP ratio greater than 0.6 suggests that the source is potentially traffic related, while less than 0.6 indicates that it is potentially non-traffic source (Katsoyiannis et al. 2011). IND/(IND+BgP) ratio can be used to further discriminate the traffic sources into gasoline (ratio < 0.5) and diesel (ratio > 0.5) sources (Ravindra et al. 2006).

Factor analysis (FA) was used as a complementary technique to identify the PAH sources and it was performed using principal component extraction method with orthogonal VARIMAX rotation. The factors were extracted based on the initial eigenvalue criteria ≥ 1 (Egodawatta et al. 2013). This technique results in the extracted factors that are strongly correlated to a specific set of variables, while weakly correlated with other variables (Egodawatta et al. 2013). Since each variable is primarily associated with a certain factor, the interpretation of a complex data set is simplified after the rotation (Abdi 2003).

PROMETHEE (Preference Ranking Organisation Method for Enrichment Evaluation) is a non-parametric method that ranks the objects according to the variables, whereas GAIA (Graphical Analysis for Interactive Assistance), which is a visual complement to PROMETHEE, is a principal component analysis-like biplot that is useful to analyse object-object, variable-variable and object-variable relationships (Khalil et al. 2004). PROMETHEE was used as a data pre-treatment method prior to GAIA analysis. Based on the outcomes of the PROMETHEE analysis, GAIA biplot is developed and the rules outlined by Espinasse et al. (1997) are used to interpret the relationships between objects and variables. Accordingly, two variables are considered positively correlated if the angle between their corresponding vectors is acute, while they are considered negatively correlated if they are obtuse. The variables are considered unrelated if the vectors are orthogonal. Further details about these methods can be found in Kokot and Ayoko (2004).

The PROMETHEE algorithm requires the definition of a number of modelling parameters such as the choice of a weighting condition and specific preference function for each variable. In addition, PROMETHEE requires the user to specify whether higher variable or lower variable values are preferred by choosing the “maximum” or “minimum” modelling option for each variable. In the current work, the “maximum” option was chosen for each variable in order to identify conditions that lead to high concentrations of PAHs at each of the selected study sites. A weight of 1 was selected for all the variables so that they have equal significance in the analysis. In the Visual PROMETHEE software used for PROMETHEE and GAIA analysis, six preference functions are available (Brans and Mareschal 2005) and each preference function describes a certain data characteristics. In this study, the V-Shaped function was selected since this preference function has been found to be applicable for environmental work (see for example Gunawardena et al., 2012).

3. Results and Discussions

3.1 PAH source identification

Diagnostic ratios and factor analysis have been widely used to identify the PAH sources (Kavouras et al. 2001). These two approaches complement each other, thereby increasing the accuracy of PAH source identification.

Table 1 presents the outcomes of diagnostic ratio analysis while Table 2 presents the outcomes of factor analysis.

According to the BaP/BgP ratios for different particle fractions shown in Table 1, traffic activities are the predominant sources of PAHs in the urban areas investigated. Additionally, IND/(IND+BgP) ratios suggest that gasoline vehicles are the primary sources of PAHs in most of the study sites, while PAHs are contributed by the diesel vehicles at industrial sites, possibly due to frequent stops and slow moving traffic.

The results of FA shown in Table 2 are for loadings higher than 0.5 based on the suggestion that loading less than 0.5 is not significant (Harrison et al. 2003). It is reported that PAHs emitted by the same sources tend to be grouped under the same factor (Harrison et al. 1996). Accordingly, based on the FA results, it can be argued that the PAHs are contributed to the study sites by multiple sources since more than one factor exists. Furthermore, specific PAH species have been used as source markers. For example, PHE, FLU and PYR are considered as typical diesel vehicle markers, while IND and BgP are gasoline vehicle markers (Khalili et al. 1995; Ravindra et al. 2006). Consequently, it can be concluded that gasoline vehicles are the major source of PAHs since Factor 1 (F1), which explains the largest variance, for different particle size fractions is generally associated with gasoline vehicle markers, i.e. IND and BgP. This is in agreement with the conclusions derived using diagnostic ratios.

In the particle size range > 300 µm, Factor 2 had a high loading of ACY, which may be associated with a diesel emission source (Simcik et al. 1999). In the 150-300 µm particle size range, F1 has high loadings of typical diesel markers such as FLU and PHE, while F2 is associated with gasoline markers. Hence, traffic is the primary source of PAHs in this particle size fraction. F3 can be associated with the PAHs loaded on F3 (PYR, FLA, BaA, CHR) which are markers of sources such as industrial oil combustion and incineration (Harrison et al. 1996). Accordingly, these sources are important contributors of PAHs to the build-up for this particle size range. In the 75-150 µm range, gasoline emissions, diesel emissions and industrial emissions are again the main PAH sources as evidenced by the high loadings of gasoline, diesel and industrial emission markers on F1, F2, and F3, respectively. The results for the 1-75 µm and <1 µm fractions again reflect the importance of vehicle emissions (both gasoline and diesel) as sources of PAHs in the build –up samples.

3.2 Influence of traffic characteristics on PAH build-up

The influence of traffic characteristics on PAH build-up was investigated separately for each particle size fraction using PROMETHEE and GAIA. Additionally, the PAH loads were grouped according to the number of benzene rings before undertaking the analysis since properties such as volatility depend on the number of benzene rings present in PAHs (Wilson and Jones 1993). Accordingly, the data matrix for each particle size fraction consisted of:

a) 7 variables: Cumulative PAH loads for 4 PAH groups, i.e. 3-, 4-, 5- and 6-ring benzene groups (Table 2), and the 3 traffic variables, i.e. ADT_to, ADT_hv and (V/C);
b) 11 objects: 11 study sites.

The resulting GAIA biplot for each particle fraction is given in Fig. 2. For all fractions, the lengths of the vectors for 5-ring and 6-ring PAHs were generally longer than those for the 3-ring and 4-ring PAHs, suggesting that they account for more of the variability in the data. In terms of the relationship of the variables to land use, the 5-ring and 6-ring PAHs are mainly associated with the two industrial sites while the 3-ring and 4-ring PAHs are associated with residential and commercial sites.

As evident in Fig. 2, the 5-ring and 6-ring PAHs also generally correlate with each other while there is a reasonable degree of correlation between the vectors for the 3-ring and 4-ring PAHs in keeping with the gasoline and diesel emissions sources of 5/6-ring and 3/4 ring PAHs, respectively. In almost all of the build- up fractions, the vectors for V/C and 5/6 ring PAHs show positive (albeit weak) correlation, but those for the 3/4 ring PAHs and traffic characteristics such as ADT_to, ADT_hv and V/C show no correlation or negative correlation. The lack of positive correlation of the 3/4 ring PAHs with traffic congestion and other traffic characteristics could be attributed to their relatively higher volatile nature which makes them more susceptible to re-suspension and evaporation.

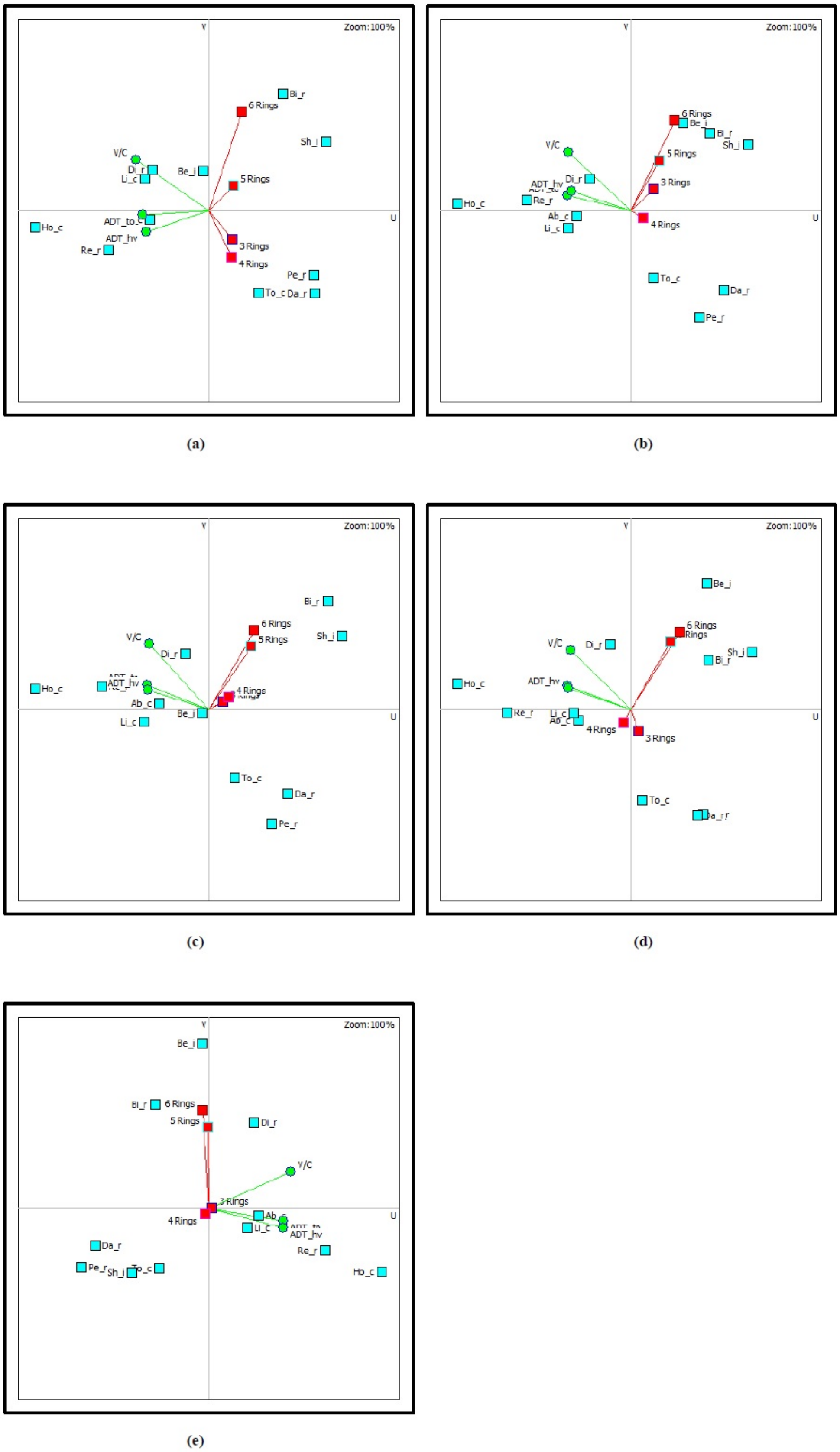

Fig. 2 GAIA biplots for different particle size fraction: (a) > 300 µm; (b) 150-300 µm; (c) 75-150 µm; (d) 1-75 µm; (e) < 1 µm. Variance described > 71% (ADT_to - Annual average daily traffic volume; ADT_hv - total heavy duty traffic volume; V/C - Volume to capacity ratio)

4. Conclusions

The research study found that polycyclic aromatic hydrocarbon (PAH) build-up on urban road surfaces were primarily contributed by traffic sources, especially gasoline vehicles. However, both diesel vehicles and industrial emissions also contribute to the PAHs found in the road build- up, although the species of PAHs are usually different from those associated with gasoline emissions. Although traffic congestion was positively correlated with 6-ring and 5-ring PAHs in the road build-up, it is negatively correlated with 3-ring and 4-ring PAHs. The absence of positive correlation between 3-ring and 4-ring PAHs and traffic parameters is attributed to the propensity of these relatively volatile PAHs to undergo re-suspension and evaporation relatively easily. However, further studies are required to confirm this hypothesis. The outcomes of this study are expected to contribute effective transport and land use planning for the prevention of PAH pollution in the urban environment.

Supplementary Material

Supplementary Materials contain PAH pollutant loads used for the calculation of values presented in Table 1 and Table 2.

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Supplementary Materials

Influence of traffic characteristics on polycyclic aromatic hydrocarbon build-up on urban road surfaces

Polycyclic aromatic hydrocarbon (PAH) load in different particle size fractions

Table S1: PAH load in particle size fraction > 300 µm (mg/m^2)

Sites	ACY	ACE	FLU	ANT	PHE	PYR	FLA	BaA	CHR	BaP	BeP	BgP	DbA	IND
Li_c	0.06	0.16	0.24	0.11	0.00	0.00	0.01	0.00	0.00	0.37	0.37	0.13	0.15	0.10
To_c	2.33	0.28	0.93	4.11	2.93	1.18	2.91	0.04	0.31	0.39	0.39	0.13	0.15	0.10
Ab_c	0.40	0.62	3.16	0.93	0.70	0.19	0.57	0.90	0.00	0.39	0.40	0.19	0.38	0.10
Di_r	6.39	0.15	1.63	0.51	0.18	0.09	0.58	0.00	0.00	0.04	0.10	0.79	1.12	0.87
Be_i	2.88	0.69	2.42	0.86	0.60	0.06	0.40	0.00	0.00	0.03	0.19	1.18	1.62	1.15
Re_r	0.29	2.32	2.76	1.38	0.74	1.27	1.98	0.00	0.94	0.44	0.43	0.14	0.15	0.10
Ho_c	0.06	0.17	1.38	0.68	0.54	0.00	0.42	0.00	0.00	0.39	0.40	0.13	0.15	0.10
Sh_i	4.43	9.06	2.22	0.03	0.15	0.45	0.60	0.05	0.79	0.48	0.94	1.91	2.68	2.15
Bi_r	2.03	0.69	1.06	0.27	0.42	0.42	0.00	1.24	0.00	0.00	0.92	2.72	3.77	2.46
Pe_r	0.79	0.20	7.04	0.38	2.10	0.27	1.57	0.00	0.21	0.39	0.40	0.14	0.18	0.10
Da_r	2.95	6.47	3.50	1.17	0.19	0.80	0.60	2.00	0.92	0.42	0.45	0.17	0.29	0.10

Table S2: PAH load in particle size fraction 150 - 300 µm (mg/m^2)

Sites	ACY	ACE	FLU	ANT	PHE	PYR	FLA	BaA	CHR	BaP	BeP	BgP	DbA	IND
Li_c	0.43	0.29	0.74	0.23	0.00	0.00	0.06	0.00	0.00	0.37	0.37	0.13	0.15	0.10
To_c	0.12	0.24	4.43	1.96	1.80	0.07	1.01	0.00	0.00	0.37	0.43	0.13	0.15	0.10
Ab_c	0.26	0.45	2.66	1.50	1.20	0.15	1.19	0.25	0.37	0.42	0.46	0.27	0.53	0.17
Di_r	7.39	0.17	3.13	0.61	0.28	0.19	0.68	0.00	0.00	0.05	0.30	0.99	1.42	0.87
Be_i	10.18	0.19	7.85	3.35	2.27	0.11	1.42	0.03	0.00	0.44	1.37	1.49	1.91	1.44
Re_r	0.28	2.26	2.75	1.33	0.92	0.73	1.72	0.04	1.10	0.40	0.54	0.13	0.18	0.10
Ho_c	0.06	0.17	1.03	0.52	0.40	0.00	0.18	0.00	0.00	0.37	0.39	0.13	0.16	0.10
Sh_i	4.24	8.70	1.34	0.84	0.25	0.44	1.17	0.00	0.28	1.21	0.53	1.96	2.80	1.99
Bi_r	2.66	3.48	1.45	0.66	0.28	0.12	0.35	0.00	0.36	0.29	0.54	2.41	2.89	2.25
Pe_r	0.11	0.28	1.01	0.37	0.17	0.00	0.11	0.00	0.00	0.37	0.37	0.13	0.15	0.10
Da_r	0.16	5.10	3.95	2.56	1.36	1.46	1.18	2.50	0.93	0.43	0.48	0.34	0.50	0.10

Table S3: PAH load in particle size fraction 75 - 150 µm (mg/m^2)

Sites	ACY	ACE	FLU	ANT	PHE	PYR	FLA	BaA	CHR	BaP	BeP	BgP	DbA	IND
Li_c	0.06	0.16	0.26	0.14	0.00	0.00	0.02	0.00	0.00	0.37	0.37	0.13	0.15	0.10
To_c	0.72	0.20	8.64	3.39	2.44	0.67	1.98	0.00	0.05	0.38	0.38	0.13	0.15	0.10
Ab_c	0.14	0.32	3.82	1.99	1.50	0.23	1.25	0.24	0.47	0.42	0.40	0.32	0.73	0.19
Di_r	8.39	0.18	4.63	1.61	1.28	0.29	0.78	0.00	0.00	0.07	0.50	1.19	1.72	1.07
Be_i	3.99	1.19	5.20	1.44	1.03	0.20	0.71	0.00	0.00	0.00	0.01	0.24	1.97	2.04
Re_r	3.20	2.54	1.08	0.88	0.55	0.49	1.87	0.00	0.49	0.39	0.40	0.13	0.15	0.10
Ho_c	0.05	0.18	1.28	0.64	0.47	0.00	0.40	0.00	0.00	0.37	0.39	0.13	0.18	0.10
Sh_i	0.81	8.89	2.46	0.95	0.29	0.40	0.68	0.00	0.57	1.48	0.66	2.21	3.11	2.45
Bi_r	3.08	6.42	3.01	0.18	0.44	0.51	1.35	0.69	0.37	1.11	0.79	2.51	3.18	2.35
Pe_r	0.06	0.17	0.87	0.43	0.32	0.00	0.20	0.00	0.00	0.37	0.39	0.13	0.15	0.10
Da_r	2.84	6.09	3.58	0.57	0.66	1.10	0.64	3.59	0.24	0.43	0.45	0.16	0.34	0.11

Table S4: PAH load in particle size fraction 1 - 75 µm (mg/m^2)

Sites	ACY	ACE	FLU	ANT	PHE	PYR	FLA	BaA	CHR	BaP	BeP	BgP	DbA	IND
Li_c	0.46	0.30	0.89	0.29	0.03	0.00	0.10	0.00	0.00	0.37	0.37	0.13	0.15	0.10
To_c	0.52	0.72	7.40	3.03	2.36	0.31	1.68	0.00	0.11	0.37	0.38	0.13	0.15	0.10
Ab_c	4.03	0.25	8.36	2.47	1.74	1.59	2.29	1.34	1.20	0.55	0.48	0.56	1.59	0.30
Di_r	1.55	4.17	1.09	0.52	0.09	0.03	0.32	0.00	0.17	0.62	1.05	1.05	1.52	0.85
Be_i	5.00	1.05	2.57	0.29	0.73	0.73	1.34	0.43	0.24	2.02	1.71	2.11	3.85	2.08
Re_r	0.13	4.95	3.82	1.82	1.03	0.96	2.49	0.14	1.73	0.42	0.43	0.14	0.21	0.10
Ho_c	0.05	0.18	1.51	0.78	0.52	0.14	0.57	0.00	0.00	0.37	0.39	0.13	0.17	0.10
Sh_i	2.25	6.13	1.21	0.83	0.23	0.44	0.93	0.11	0.04	1.17	0.64	2.11	4.14	2.33
Bi_r	2.21	2.92	1.78	0.87	0.39	0.41	1.15	0.00	0.04	1.07	0.88	1.71	2.25	1.12
Pe_r	0.24	0.21	2.76	0.99	0.73	0.13	0.34	0.00	0.00	0.37	0.38	0.13	0.21	0.10
Da_r	0.15	5.89	4.60	2.59	1.45	1.34	1.09	4.31	0.28	0.55	0.57	0.21	0.60	0.12

Table S5: PAH load in particle size fraction < 1 µm (mg/m^2)

Sites	ACY	ACE	FLU	ANT	PHE	PYR	FLA	BaA	CHR	BaP	BeP	BgP	DbA	IND
Li_c	0.06	0.23	4.31	2.06	1.98	0.07	0.99	0.00	0.00	0.37	0.42	0.13	0.15	0.10
To_c	0.11	0.27	5.70	2.62	2.18	0.13	1.42	0.00	0.00	0.37	0.44	0.13	0.15	0.10
Ab_c	0.09	0.29	2.39	1.19	1.09	0.72	0.93	0.42	1.24	0.48	0.51	0.48	1.12	0.27
Di_r	5.17	8.84	2.17	0.75	0.19	0.23	0.43	0.00	0.17	0.84	0.66	1.01	1.44	1.02
Be_i	4.80	1.02	2.27	0.09	0.53	0.51	1.14	0.13	0.04	1.72	1.32	1.68	3.25	1.70
Re_r	2.05	4.52	3.07	1.56	0.87	0.83	2.14	0.00	0.79	0.40	0.41	0.13	0.24	0.10
Ho_c	0.06	0.17	1.11	0.59	0.46	0.05	0.28	0.00	0.00	0.37	0.38	0.13	0.15	0.10
Sh_i	2.14	2.14	0.99	0.05	0.03	0.02	0.15	0.00	0.00	0.28	0.14	0.08	0.16	0.14
Bi_r	0.78	2.42	1.68	0.61	0.15	0.21	0.61	0.20	0.12	0.54	0.50	1.38	1.68	1.50
Pe_r	0.07	0.19	1.81	0.93	0.72	0.15	0.55	0.00	0.00	0.37	0.37	0.14	0.15	0.10
Da_r	0.26	4.73	2.51	2.23	0.23	1.15	2.88	5.39	0.58	0.59	0.62	0.17	0.64	0.11