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Inherent and external factors influencing the distribution of PAHs, hydroxy-PAHs, carbonyl-PAHs and nitro-PAHs in urban road dust

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Graphical Abstract
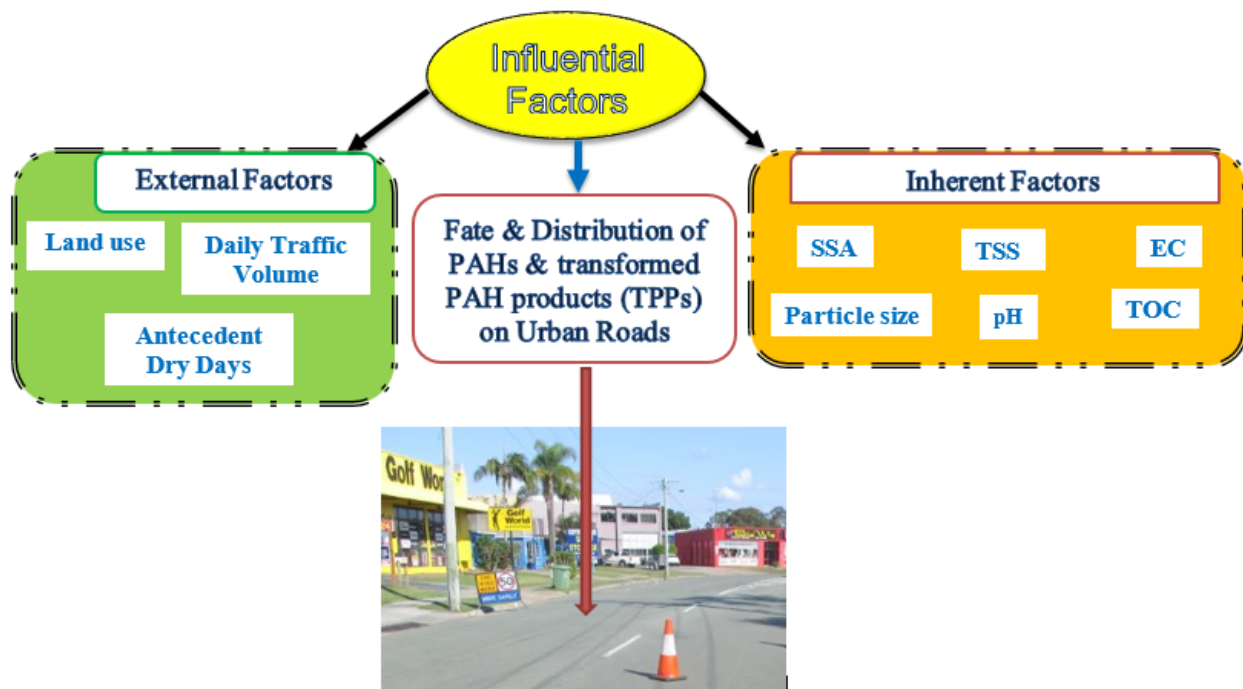
Highlights

- Commercial land use recorded the highest cumulative concentration of PAHs and TPPs
- Antecedent dry days have inverse effect on cumulative concentration of LMW-PAHs
- Antecedent dry days have no major influence on the total concentration of HMW-PAHs
- Small particle sizes inversely influence cumulative concentration of PAHs and TPPs
  - Higher quantities of PAHs and TPPs are sorbed to 0.45 – 150 µm road dust particles

Abstract

The distribution and fate of hazardous polycyclic aromatic hydrocarbons (PAHs) and their associated transformed PAHs products (TPPs) notably carbonyl-PAHs (CPAHs), hydroxy-PAHs (HoPAHs), and nitro-PAHs (NPAHs) on urban road surfaces are influenced by diverse factors to varying extent. The pollutants are eventually transported to urban receiving waters via stormwater runoff posing risks to human and ecosystem health. In order to formulate an effective mitigation strategy, it is essential to comprehensively examine the role of both inherent and external factors in the distribution and fate of these hazardous pollutants, and thus, the need for this study. The research study showed that commercial land use has the highest cumulative concentration of PAHs and TPPs. Antecedent dry days (ADDs) has an inverse influence on the distribution of the total concentrations of low-molecular weight PAHs (LMW-PAHs), PAHs, and (PAHs + TPPs) irrespective of the type of land use, whilst there was no major influence on the total concentrations of high molecular weight PAHs (HMW-PAHs), and TPPs. The high volatility of LMW-PAHs compared to HMW-PAHs is considered to account for the decreasing concentration of LMW-PAH with increasing ADD. Particle size range has significant inverse influence on the cumulative concentration of pollutants across all land uses, since smaller particles are characteristically associated with larger surface area leading to the higher sorption of pollutants. Multivariate analysis of the influential factors indicated that two particle size ranges (0.45 – 150 µm and 150 – 425 µm) constitute the major influential factors on the distribution and fate of PAHs and TPPs in urban road dust. Greater quantum of pollutants are sorbed to the 0.45 – 150 µm particles due to the relatively higher specific surface area (SSA), concentration of total organic carbon (TOC) and total suspended solids (TSS) concentration. Therefore, it is critical to effectively remove finer particles from road surfaces in order to reduce exposure to hazardous pollutants.

Keywords: Land use; Road dust; Hazardous PAHs; Transformed PAH products; Particle size

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are pollutants of global concern. They are widespread in the urban environment especially on urban road surfaces coupled with their significant deleterious ecological and human health impacts (Bandowe and Nkansah, 2016; Cachada et al., 2016; Gbeddy et al., 2020c; Zhao et al., 2009). These pollutants are typically found sorbed to road deposited particles referred to as road dust (Amato et al., 2011; Majumdar et al., 2012) which are eventually transported by stormwater runoff (Gbeddy et al., 2018) into receiving waterbodies, thereby causing deterioration in water quality (Liu et al., 2017).

Past studies on PAH pollution have primarily focused on the distribution, fate, health risk and influential factors of originally emitted PAHs with minimal or no attention given to the derivatives of PAHs (Majumdar et al., 2012) such as nitro-PAHs (NPAHs), carbonyl-PAHs (CPAHs) and hydroxy-PAHs (HoPAHs); collectively referred to as transformed PAH products (TPPs) (Gbeddy et al., 2020c). For example Ma et al. (2017) established a quantitative model to estimate the cancer risk posed by only originally emitted PAHs laden in urban dust. However, PAHs are prone to transform and degrade due to a range of environmental factors such as light and microbial action to yield TPPs. Most of the resultant TPPs are potentially more hazardous in the minutest quantities compared to their corresponding precursor PAHs (Gbeddy, 2020; Gbeddy et al., 2020c). In this regard, the holistic assessment and understanding of the factors influencing the distribution of both parent PAHs and TPPs are essential for formulating suitable stormwater remediation measures. This is due to the fact that the accumulation of pollutants on impervious road surfaces constitutes

a critical source of stormwater pollutants as a result of wash-off processes (Brown and Peake, 2006; Gbeddy et al., 2018; Gunawardena et al., 2014; Li et al., 2017). Consequently, the knowledge presented in this study will contribute to the creation of sustainable stormwater quality management strategies, as well as ensuring the better protection of human and ecosystem health.

The influential factors in relation to the fate and distribution of precursor PAHs and TPPs on urban road surfaces can be classified into two main categories, namely, external and inherent factors (Liu et al., 2017). The external factors include land use, catchment management practices, traffic characteristics, population density, and climate characteristics, whilst the inherent factors comprise of the physicochemical properties of both, the pollutants and their associated sorbents (Gunawardena et al., 2014; Hvitved-Jacobsen et al., 2010; Liu et al., 2017; Liu et al., 2016; Liu et al., 2007). Gunawardena et al. (2014) investigated the influence of external factors particularly traffic features such as vehicle mix, traffic volume and traffic flow on the distribution of PAHs. In addition, Li et al. (2017) reported that anthropogenic activities in the vicinity influence PAHs pollution trends in road dust rather than the type of associated land use. However, the studies by Gunawardena et al. (2014) and Li et al. (2017) did not include TPPs, although these pollutants can even be more hazardous (Gbeddy, 2020; Gbeddy et al., 2020c).

The effectiveness of any stormwater pollution mitigation process correlates with the state of knowledge with respect to the fundamental factors controlling stormwater quality (Gunawardena, 2012; Helmreich et al., 2010; Hvitved-Jacobsen et al., 2010). In this context, this study comprehensively elucidates the influence of inherent and external factors on the accumulation of both, precursor PAHs and associated TPPs on urban road surfaces. To the best of our knowledge, this is the first time such a holistic study has been undertaken on PAHs and TPPs distribution in an urban environment. The outcomes of this study are expected to bridge the current knowledge gap on the distribution and fate of PAHs and TPPs during build-up on urban road surfaces, thereby promoting effective stormwater management practices and protection of human and ecosystem health and thereby enhancing stormwater reuse.

2. Material and methods
2.1 Study area and sites

Urban areas are characterized by anthropogenic activities and thus, have two to ten (2-10) folds of PAH concentrations compared to rural areas (Sarma et al., 2016), thereby serving as a notable source area for stormwater pollution. The Gold Coast region located in south-east of Queensland, Australia was selected as the study area. This is a highly urbanized area with a range of urban land uses. Herngren et al. (2010) and Liu et al. (2017) have conducted background studies on the build-up and wash-off of precursor PAHs on the road surfaces in the study area, thus facilitating the comparison of results for better interpretation of the data.

Five road sites comprising of one commercial and two residential sites in Benowa suburb, and two industrial sites in Nerang suburb were selected. These sites have varied external characteristics such as land use, proximity to arterial road network and traffic characteristics such that they can provide samples with varied inherent physicochemical properties (Gbeddy et al., 2018; Gunawardena et al., 2014; Liu et al., 2017). In this regard, the emission sources of PAHs and TPPs at these sites were assumed to be different based on the findings by Gunawardena et al. (2014) and Liu et al. (2017) on the factors influencing the built-up of PAHs on road surfaces in the study

area. These past studies indicated that varied traffic volumes associated with different land uses constitute the major PAH emission and built-up factors. Fig. S1 in the Supplementary Information shows the locations of each sampling site.

2.2 Sampling and sample preparation

Dry and wet vacuum sampling approach using a Delonghi Aqualand vacuum cleaner (92% efficiency) was used to collect road dust samples from an area of one metre by the half-metre width at each study site as described in Gbeddy et al. (2018) and Jayarathne et al. (2018). Sampling was done in 2017 at the first (1st), fourth (4th), seventh (7th), and eleventh (11th) antecedent dry day (ADD) in order to assess the influence of particle built-up time on the distribution of PAHs and TPPs. In the context of particle build-up, ADD refers to dry weather periods during which no rainfall and road sweeping occurred. The samples were collected into a de-ionized water bath in the vacuum cleaner, and together with road dust were filtered through a 425 µm stainless steel sieve. The residue on the sieve was discarded as debris. The filtrate was initially filtered through a 75 µm glass fibre filter paper and then a 0.45 µm glass fibre filter with the help of a suction pump. The wet samples on the filter papers were air dried at room temperature of 27 ^{o}C to constant weight and then segregated into four particle size ranges of 0.45—75 µm, 75—150 µm, 150—300 µm and 300—425 µm using stainless steel sieves. Particles less than 0.45 µm were considered as the dissolved component in the de-ionized water (Gbeddy et al., 2018). The de-ionized water with the dissolved components was transferred into pre-cleaned brown-coloured 500 mL glass bottles and kept in the refrigerator below 4 ^{o}C until analysis for PAH and TPP analytes. Particle size distribution influences the distribution and fate of pollutants such as PAHs and TPPs in the environment, thus road dust fractionation was essential for this study (Deletic and Orr, 2005; Gbeddy et al., 2018).

2.3 Measurement of road dust physicochemical parameters

The analytical methods used in determining the pH, electrical conductivity (EC), specific surface area (SSA), total suspended solid (TSS), and total organic carbon (TOC) which is the sum of particulate organic carbon (POC) and dissolved organic carbon (DOC) are shown in Table S1 in the Supplementary Information. SSA quantification using ethylene glycol monoethyl ether (EGME) approach ensured the simultaneous determination of both, external and internal surface area of the road dust particles. Further information on these physicochemical methods can be found in Gbeddy (2020) and Jayarathne et al. (2018).

2.4 Extraction and analysis of PAHs and TPPs in road dust

A total of 26 precursor PAHs and 14 TPP pollutants (see Table S3) laden in road dust samples of 0.45—75 µm, 75—150 µm, 150—300 µm and 300—425 µm particle size ranges were extracted using DIONEX ASE 350 simultaneous in-cell clean-up pressurized fluid extraction (PFE) method developed by Gbeddy et al. (2020a). The extraction cell contained a glass filter at the outlet, 10 g deactivated (3%) silica gel and 5g activated alumina mixture, glass filter, mixture of 0.15 g road dust and 0.075 g activated diatomaceous earth, and a third filter paper at the inlet. The extraction was performed using n-hexane/dichloromethane (9:1, v/v) solvent mixture at 14 MPa and 150 ^{o}C, with 7 min of dynamic extraction, two static cycles of 5 min each, one cell volume for rinsing, and a purge time of 60 s. Liquid–liquid extraction using dichloromethane was used to extract de-

ionized water laden with dissolved sample constituents. The extract mixture was rotary evaporated to dryness and the solvent phase changed to HPLC-grade hexane.

The cleaned extracts were analyzed using a Shimadzu Triple Quadrupole (TQ) 8040 Gas Chromatography–Mass Spectrometry (GC-MS) System containing Rxi-5Sil MS column (30 m x 0.25 μm thickness× 0.25 mm ID) with constant column flow of 1.2 mL min^{-1}. The concentrations of the analytes in the water soluble phase were below the detection limit of the GC–MS instrument. The method of extraction and extract analysis are described in the previous studies of Gbeddy et al. (2020a), Gbeddy et al. (2020b) and Gbeddy et al. (2021).

2.5   Quality control (QC) and quality assurance (QA)

In order to facilitate precision and accuracy of the results of analysis, QA and QC protocols were used. Blank analysis, duplicate extract analysis, spiking using deuterated surrogate standards, repeat analysis of duplicate extracts with more than ±20% relative percent difference in the results, daily calibration of reference standards, cross-checking of calibration standards after the analysis of ten extracts, and analysis of standard reference material (SRM 1649b) were some of the protocols deployed in this study. The standard calibration curves have regression coefficients ranging from 0.995 to 1.0. The mean recovery percentage for benzophenone-d10, 1-nitropyrene-d9, 9-nitroanthracene-d9, 1-hydroxypyrene-d9, acenaphthene-d10, anthracene-d10, naphthalene-d8, pyrene-d10, and phenanthrene-d10 surrogate standards were 96, 71, 43, 76, 58, 111, 53, and 114, respectively. The percentage recovery of analytes with certified mass fraction values in the SRM 1649b were 73, 50, 65, 60, 87, and 118 for benzo(a)pyrene, triphenylene, benzo(k+j)fluoranthene, benzo(e)pyrene, picene, and 1-nitropyrene, respectively. Negligible analyte concentrations were measured in the blank samples. The estimated analyte concentrations reported in this study were not corrected for recoveries since most of the analytes lack corresponding surrogate standards. Further information on the QC/QA can be found in Gbeddy et al. (2020a).

2.6   Potential influential parameters

External factors including three varied land uses (residential, commercial and industrial), daily traffic volume (DTV) and four different antecedent dry days (1, 4, 7 and 11) were selected. Inherent factors comprised of road dust physicochemical parameters (four particle size ranges (0.45─75 μm, 75─150 μm, 150─300 μm and 300─425 μm), specific surface area, total suspended solids concentration, and total organic carbon concentration as specified in Table S2. These parameters were selected based on their potential influence on the fate and distribution of PAHs and TPPs in the environment (Akortia et al., 2019; Gbeddy, 2020; Jayarathne et al., 2018). However, external factors such as climate characteristics on PAHs patterns were not evaluated in this study due to the lack of relevant data for the various study sites. For instance, the study sites do not have weather monitoring stations in the immediate vicinity to measure pertinent climate characteristics with the required degree of accuracy such as temperature, light intensity, ultraviolet radiation and wind speed.

2.7   Data analysis

The influence of inherent and external factors on the fate and distribution of PAHs and TPPs is complex (Jonsson et al., 2007) and therefore, requires thorough scrutiny in order to clearly

distinguish the important parameters and patterns and to eliminate noisy variables. In this context, the generated data was analysed using factor analysis (FA), a multivariate statistical technique using StatistiXL Version 2.0 software. FA technique was chosen because it can identify the relationship between various observed variables and the underlying unseen variables referred to as factors. The factors were extracted via principal component (PC) method thereby ensuring that data reduction was undertaken with minimal correlation existing between the generated factors. In addition, the correlation matrix model was employed during the factor extraction process to overcome the differences in the units, magnitude of estimates and variance of the observed variables (StatistiXL, 2022). Further information on these methods can be found in Akortia et al. (2021) and Gbeddy et al. (2020b).

3. Results and discussion

3.1 Distribution of the cumulative PAHs and TPPs on urban roads

Commercial land use recorded the highest cumulative concentration of LMW-PAHs, HMW-PAHs, PAHs, TPPs, and PAHs plus TPPs whilst the variations in the cumulative concentrations for these pollutants across other land uses (residential and industrial) can be described as negligible (see Fig. S2). Although the average daily traffic volume estimated for the commercial land use is 3000 compared 3500 for industrial land uses (refer to Table S2), it is hypothesized that the differences in vehicular type and the length of time spent by these vehicles led to greater release and accumulation of these pollutants in commercial land use areas. Moreover, commercial areas are associated with mixed sources of PAHs and TPPs arising from smoke food preparation activities, thus the observed relatively higher accumulation of these pollutants.

The mean concentrations with standard deviation of low molecular weight PAHs ($\sum$LMW-PAHs), high molecular weight PAHs ($\sum$HMW-PAHs), $\sum$PAHs, $\sum$TPPs and $\sum$ (PAHs + TPPs) for each land use site were 2.54 ± 2.07 mg/kg, 3.42 ± 1.79 mg/kg, 5.95 ± 3.36 mg/kg, 2.46 ± 1.66 mg/kg, and 8.41 ± 4.49 mg/kg, respectively, as shown in Table S4. LMW-PAHs and HMW-PAHs refer to PAHs containing two to three, and more than three fused aromatic rings, respectively (Jonsson et al., 2007). The mean concentration of the $\sum$PAHs in this study is more than twice the 2.57 mg/kg (0.18 – 7.60 mg/kg concentration range) reported by Bandowe and Nkansah (2016) in road dust from Kumasi, a major city in Ghana, whilst the $\sum$TPPs is thrice the Kumasi estimate of 0.83 mg/kg (0.057 – 4.20 mg/kg concentration range). However, the mean $\sum$PAHs concentration in this study is approximately three times less than the 15.77 mg/kg reported by Wei et al. (2015), whilst the $\sum$TPPs is twice less than the 5.64 mg/kg quantified in urban road dust from Xi'an, Central China. Finally, the concentration range for the $\sum$PAHs (0.31 – 18.65 mg/kg, see Table S4) in this study is broader than the 0.45 – 2.03 mg/kg recorded by Zhang et al. (2019) in size dependent road dust particles from the city of Dresden, Germany. The variations in land use characteristics (land use type, vehicle type, age and daily traffic volume), climatic condition, and the number of pollutants investigated in each study could account for the observed differences.

3.2 $\sum$LMW-PAHs and $\sum$PAHs, and influential factors

Antecedent dry days (ADDs) influence the distribution of LMW-PAHs on urban road surfaces considerably irrespective of the type of land use as shown in Fig. 1*a*. The concentration of total LWM-PAHs as presented in Table S4 decreases sharply from the 1st ADD to the 11th ADD. The decrease is more evident on the 7th and 11th ADDs, whilst there was no appreciable difference in

concentrations between 1st and 4th ADDs. This is an indication of potential susceptibility of LMW-PAHs to environmental transformation, degradation, translocation and long-range transport with extended ADDs (7 to 11 ADDs) due to their relative volatility. This observation presents an interesting perspective on the effectiveness or otherwise of current stormwater management practices (SWMP) with respect to PAHs accumulation on urban road surfaces. In this regard, the conduct of any SWMP, such as street sweeping after the 4th ADD may not lead to the effective removal of LMW-PAHs from urban road surfaces.

The concentration of LMW-PAHs also decreases sharply with increasing particle sizes as illustrated in Fig. 1a. Smaller road dust particles are associated with higher specific surface area (SSA), thereby facilitating the sorption of LMW-PAHs compared to larger particles. Furthermore, smaller particles may have higher organic matter content with more binding sites for LMW-PAHs compared to larger particles. This distribution characteristics of LMW-PAHs calls for the deployment of SWMPs that are capable of retaining smaller particles from the urban environment. Moreover, since smaller particles are more prone to suspension and translocation caused by natural and anthropogenic forces such as wind and vehicular movements, it is advisable to carry-out street sweeping in under 4 ADDs.

Finally, from Fig. 1b, the distribution of total PAH concentration (∑PAHs) with respect to land use, ADD and particle size distribution follows similar pattern as ∑LMW-PAHs. This indicates the significant contribution of LMW-PAHs to the total concentration of PAHs on urban road surfaces and thus, the need to adopt best SWMPs in order to curb the rapid distribution of PAHs across various environmental matrices such as soil, waterbodies, sediments, roof surfaces and buildings. As shown in Fig. 1, commercial land use generally exhibited higher cumulative concentration of LMW-PAHs and PAHs across the different particle sizes for different ADDs. This trend can be attributed to the reasons adduced above in sub-section 3.1.

3.1 ∑HMW-PAHs and ∑TPPs, and influential factors

Irrespective of the land use type, ADD does not have any significant effect on the distribution of total HMW-PAHs and total TPPs on urban road surfaces as shown in Fig. 2a and 2b, respectively. However, commercial land use generally exhibited higher cumulative concentration of HMW-PAHs and TPPs across the different particle sizes for the different ADDs. This trend can be attributed to the reasons offered above. The inherent properties of HMW-PAHs to resist transformation, degradation, translocation and long-range transport compared to LMW-PAHs are key underlying factors in their environmental distribution. HMW-PAHs have low volatility and as a result, changes in climatic conditions such as atmospheric temperature and UV index during different ADDs may not affect the fate and distribution of this category of PAHs considerably. In the event of volatilization, HMW-PAHs may undergo dry and wet deposition close to their origins. HMW-PAHs are more lipophilic compared to LMW-PAHs and thus, sorb more readily to organic matter. Moreover, the high resonance energy associated with HMW-PAHs makes them more thermodynamically stable in the environment (Gbeddy et al., 2020).

(a)

(b)
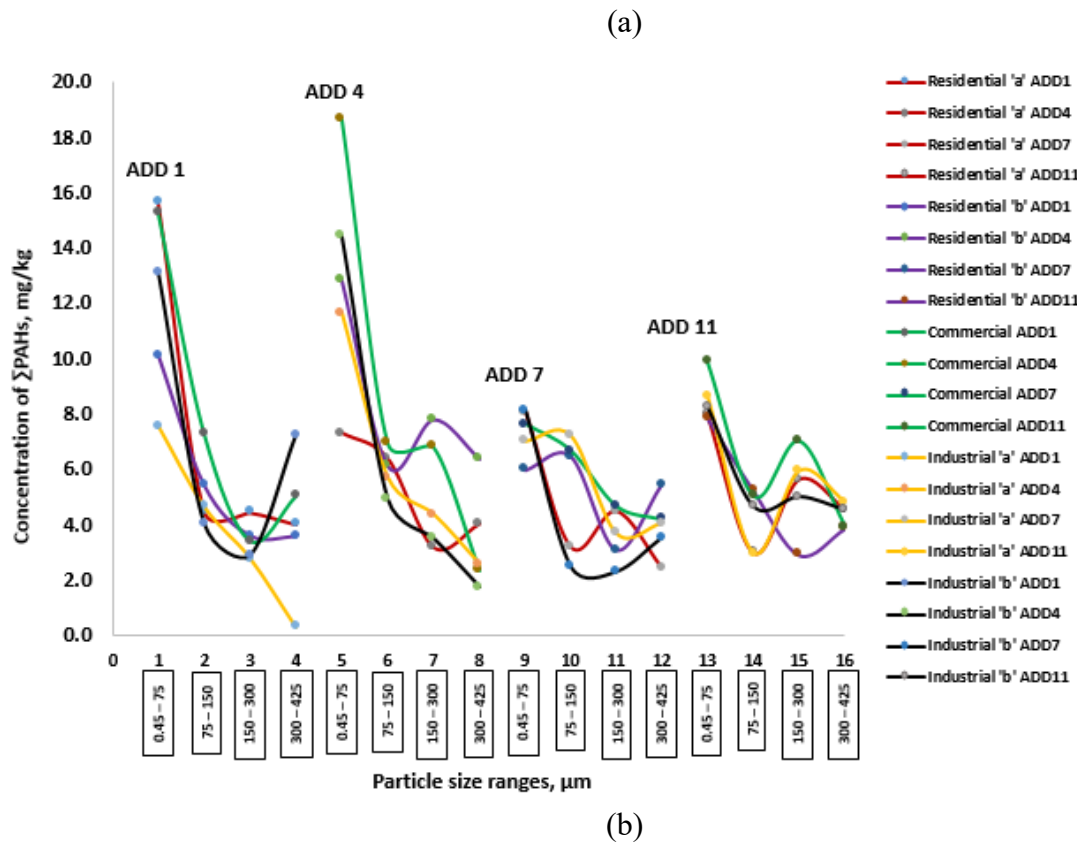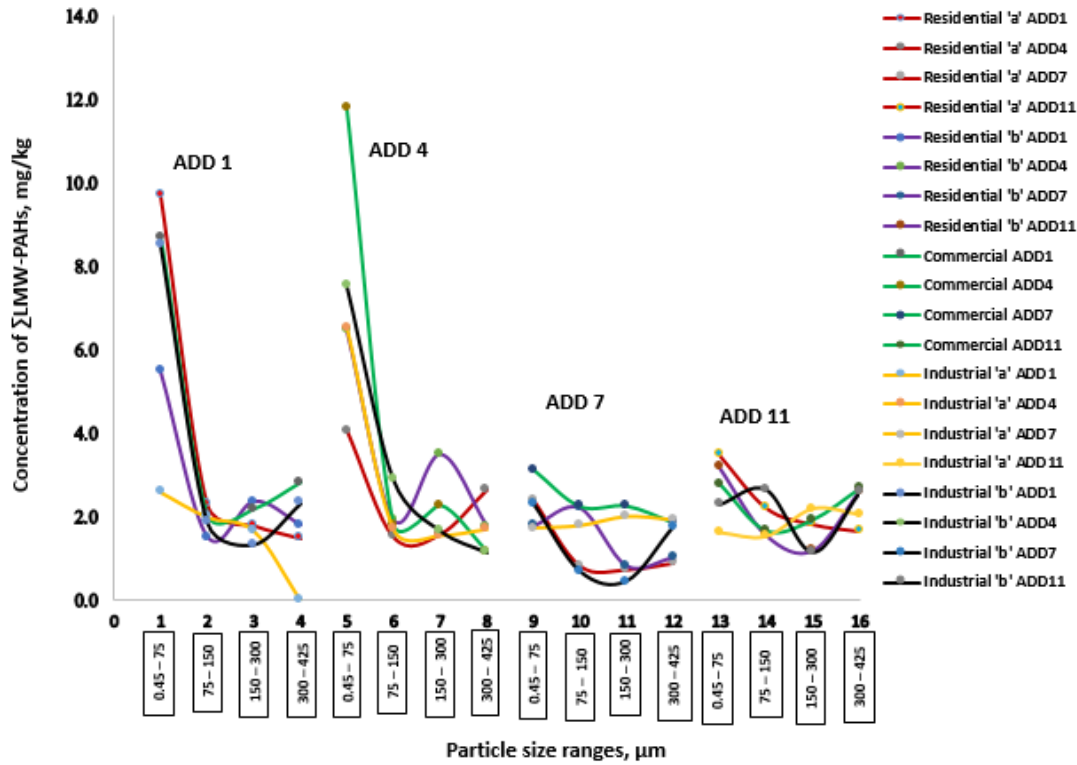
Fig 1: Distribution of total LMW-PAHs (a) and total PAHs (b) concentration in various particle size range road dust and ADDs across different land uses
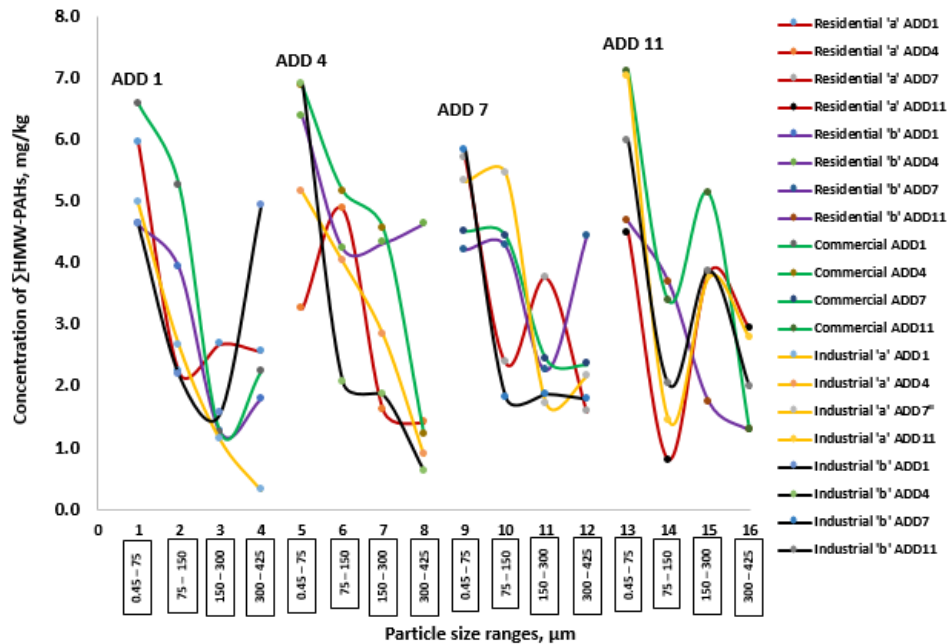
(a)
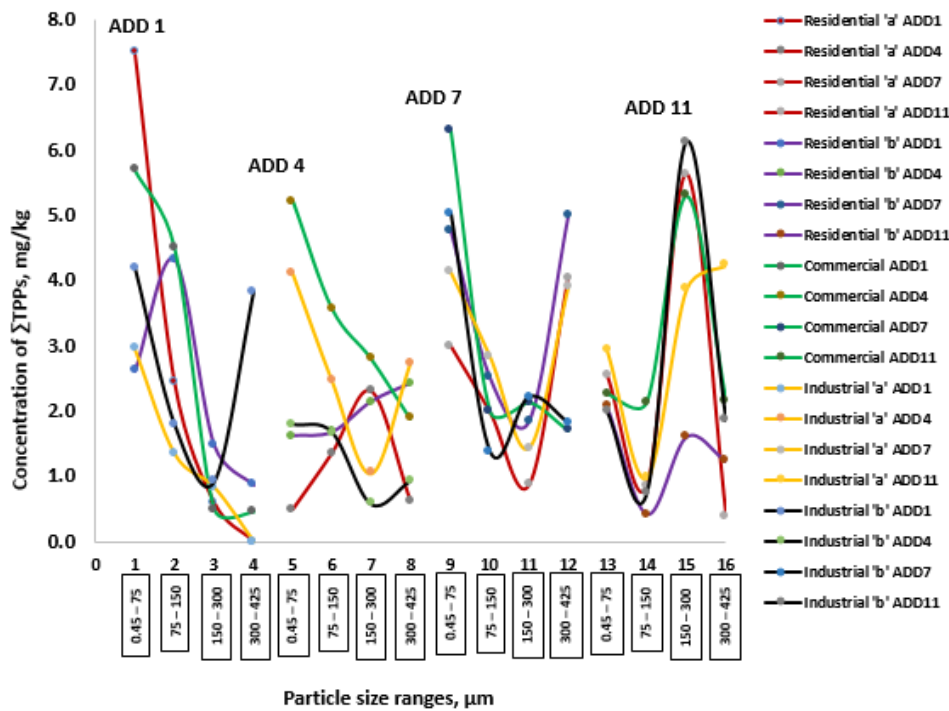
(b)

Fig. 2: Distribution of total HMW-PAHs (a), and total TPPs (b) in various particle size range road dust and ADDs across different land uses

Similar to LMW-PAHs, the concentration of ∑HMW-PAHs and ∑TPPs decreases with increasing particle size of road dust sorbent as represented in Fig. 2(a) and 2(b), respectively. However, unlike LMW-PAHs the concentrations of HMW-PAHs and TPPs increased in large 150-300 μm particles on the 11th ADD before decreasing in the larger 300-425 μm particles, thus indicating high affinity

for high molecular weight PAH pollutants. In general, the high specific surface area, more organic matter content and more binding sites associated with smaller particles account for the observed pattern. The large molecular weight associated with TPPs can also account for the similar distribution pattern on urban road surfaces as that of HMW-PAHs. However, it is not very evident from the univariate analysis why there is high affinity for HMW-PAHs and TPPs by the 150-300 μm particles on the 11th ADD. The multivariate analysis in sub-section 3.5 provides greater insight into this observation.

3.2   Distribution of ∑PAHs + ∑TPPs, and influential factors

As depicted in Fig. 3, ADDs and particle size distribution have significant influence on the sum of PAHs and TPPs across different land uses. The distribution patterns from one (1) to seven (7) ADDs follow that of ∑LMW-PAHs whilst that on the 11th ADD is similar to ∑HMW-PAHs and ∑TPPs. This implies that LMW-PAHs are typically released to urban road surfaces in higher quantities compared to HMW-PAHs and TPPs within 1st to 7th ADDs. It is hypothesized that the relative volatility coupled with potential transformation and degradation of LMW-PAHs led to the decreased concentration on the 11th ADD, and subsequent increase in the concentration of TPPs and HMW-PAHs. Secondly, the wet and dry deposition of HMW-PAHs close to their environmental sources would also contribute to the higher concentration of HMW-PAHs on later ADDs. Finally, commercial land use recorded relatively higher cumulative concentration of PAHs and TPPs across different particle sizes for the different ADDs. This trend can be attributed to the reasons given above.
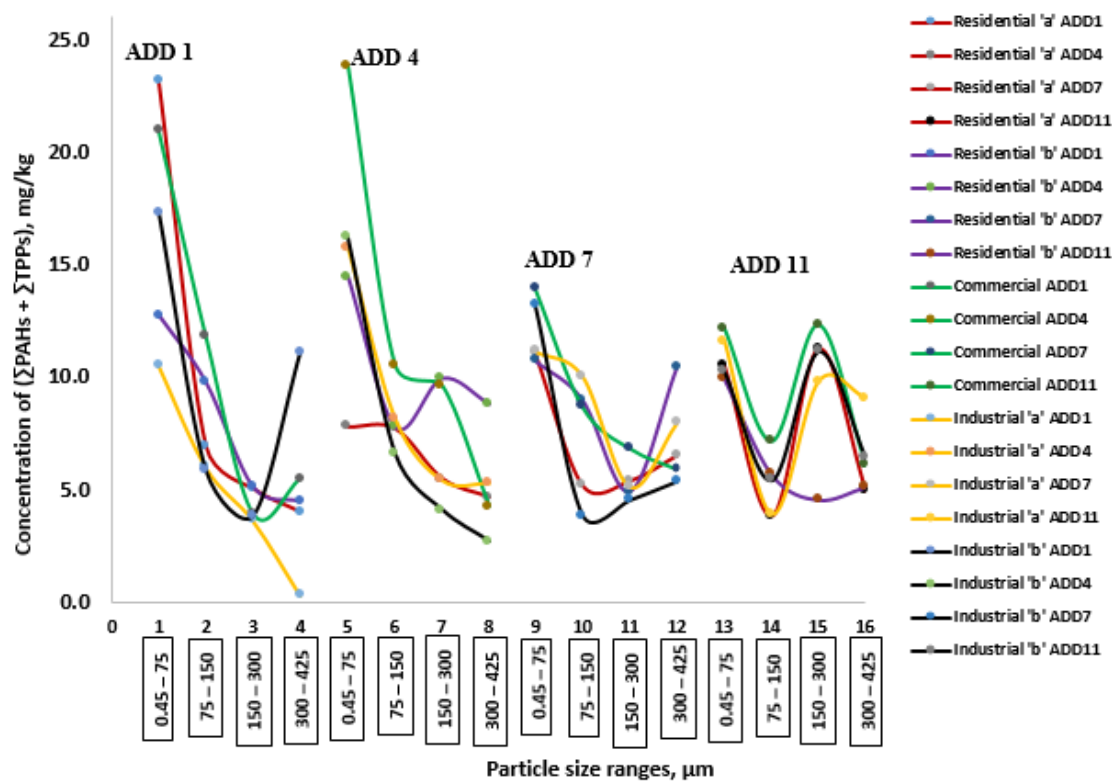
Fig. 3: Distribution of the cumulative concentration of PAHs and TPPs in various particle size range road dust and ADDs across different land uses

3.3   Multivariate characterization of influential factors on PAHs and TPPs distribution on urban roads using factor analysis (FA)

The data matrix comprising of 39 variables x 80 objects (sample) was subjected to factor analysis (FA) in order to assess the influence of both inherent and external factors on the distribution of PAHs and TPPs on urban road surfaces. The variables comprised of inherent and external factors, and pollutant concentrations. The data was pre-processed using standardization to overcome the differences in units and variance of the different variables. The factors were selected using the principal component (PC) method without any rotation. Using Eigenvalues > 1, thirteen (13) factors were found to be significant and they account for 75% variance in the data.

The biplot for the first three (3) factors were considered since they contributed the largest percentages to the total variance in the data, as well as higher factor loadings as presented in Tables S5 and S6, respectively. As shown in Fig. 4, the most significant factor influencing the distribution of the pollutants is particle size range which is an inherent factor. Two particle size ranges of 0.45 – 150 μm and 150 – 425 μm exert distinctive influence on the distribution of the pollutants regardless of the land use type. The biplot for factors 1 and 2 as represented by Fig. 4a indicated three clusters whilst that for factors 1 and 3 (see Fig. 4b) showed two clusters. However, it was identified that the two clusters on the positive factor 1 of Fig. 4a were both influenced primarily by 150 – 425 μm particle range, although the cluster on the negative factor 2 is influenced additionally by daily traffic volume (DTV), pH, EC, ADD, benzo(c)phenanthrene (BcPH), 9,10-anthraquinone (AQN) and 9-nitroanthracene (9NAN). Furthermore, BcPH HMW-PAH, and AQN and 9NAN TPPs that are highly correlated with DTV and closely associated with the 150 – 300 μm road dust particles in Fig. 4a, can be considered as the primary contributory factors for the increased cumulative concentration of HMW-PAHs and TPPs in the 11th ADD as evident from Fig. 1b, 2 and 3.
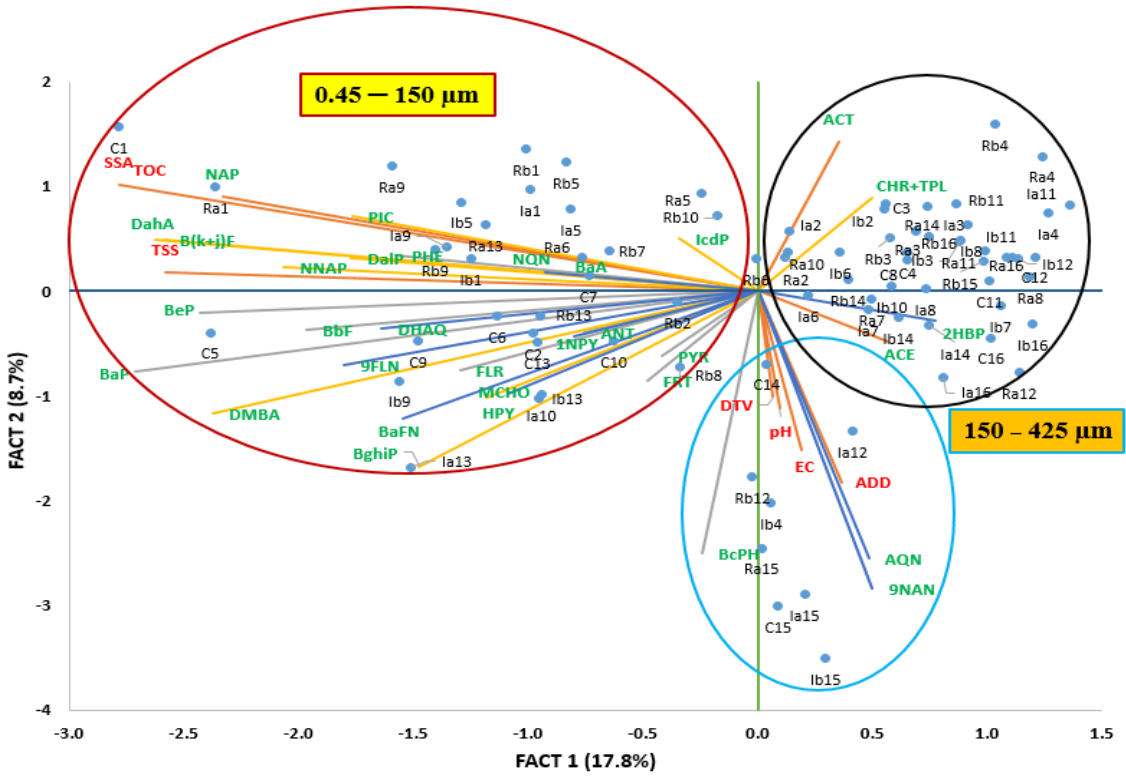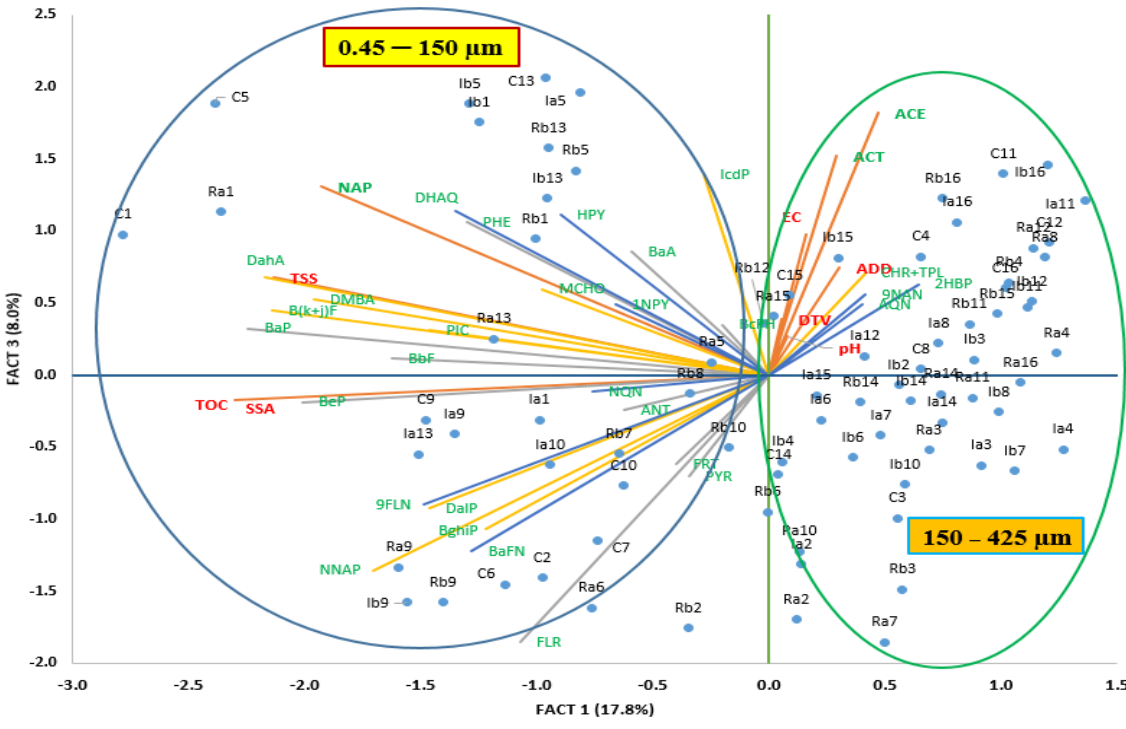
Fig. 4: Biplots for the most significant factors: (a) factors 1 and 2; (b) factors 1 and 3

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Large number of the PAH and TPP pollutants are sorbed (adsorbed and absorbed) to the $0.45 - 150$ μm particles especially during shorter antecedent dry days (ADDs) as evident in the large ellipses on the negative factor 1 in Fig. 4. The Fig. 4 further indicates that small road dust particles have high positive correlation with three critical inherent road dust properties, namely, the specific surface area (SSA), total organic carbon (TOC) concentration and total suspended solids (TSS) concentration. The significant sorption relationship between most of the pollutants and the $0.45 - 150$ μm particles can be attributed to the relatively higher SSA, and concentrations of TOC and TSS of the smaller sorbent particles. This observation implies that in order to minimize the potential exposure of living organisms to hazardous PAHs and TPPs laden in road dust, the efficacy of current mitigation measures such as street sweeping for removing smaller particles on urban road surfaces has to be enhanced. As Gbeddy et al. (2018) noted, smaller particles with their attendant high pollutant concentration have greater probability of navigating the respiratory system into the most sensitive alveoli to cause deleterious health effects. In this regard, it is quintessential to remove and retain the smaller road dust particles from the urban environment to engender greater protection of human and ecosystem health.

On the other hand, a smaller number of pollutants including acenaphthylene (ACT), acenaphthene (ACE), chrysene (CHR), triphenylene (TPL), 2-hydroxybiphenyl (2HBP), BcPH, 9NAN and AQN are found to be associated with the $150 - 425$ μm particles as shown in Fig. 4. It is not very obvious why these particular eight (8) pollutants out of the total number of forty (40) investigated have a good sorption relationship with the larger particles. Further research has to be conducted to clarify the reasons for this close relationship. However, the minimal number of pollutants can be attributed to the inverse relationship that exists between larger particles and SSA, and the concentrations of TOC and TSS. External factors such as DTV and ADD influence the distribution of pollutants in road dust especially during longer ADDs. The turbulence associated with higher DTV might lead to suspension and redistribution of smaller particles with their associated high pollutants to other parts of the urban environment. Unlike smaller particles, larger road dust particles are normally retained on road surfaces during longer ADDs and high DTV (Egodawatta and Goonetilleke, 2006; Gbeddy et al., 2018). Inherent road dust properties such as pH and electrical conductivity (EC) exert influence on the sorption of PAHs and TPPs (mostly benzo(c)phenanthrene, 9,10-anthraquinone and 9-nitroanthracene) in larger particles (see Fig. 4). Higher pH (alkaline) sorbent and EC promote the accumulation of these pollutants in larger particles during longer ADDs. However, the reason for the observed relationship between these two parameters and these particular PAHs and TPPs is not very clear.

4.   Conclusions and recommendations

The findings of this study show that the concentration ranges for the sum of low-molecular weight PAHs (∑LMW-PAHs), high-molecular weight PAHs (∑HMW-PAHs), PAHs (∑PAHs), transformed PAH products (∑TPPs) and ∑(PAHs + TPPs) in size dependent road dust particles are $0.00 - 11.77$, $0.31 - 7.12$, $0.31 - 18.65$, $0.00 - 7.49$, and $0.31 - 23.86$ mg/kg, respectively. The outcomes also indicated that particle size ranges of $0.45 - 150$ μm and $150 - 425$ μm are the key inherent sorbent factors controlling the distribution of pollutants across all land uses. External factors such as the daily traffic volume (DTV) and antecedent dry day (ADD) influence the distribution of pollutants in the larger particles especially during prolonged ADDs. A smaller

number of pollutants comprising of acenaphthene (ACE), acenaphthylene (ACT), triphenylene (TPL), chrysene (CHR), benzo(c)phenanthrene (BcPH), 2-hydroxybiphenyl (2HBP), 9,10-anthraquinone (AQN) and 9-nitroanthracene (9NAN) were found to be sorbed to the larger 150 – 425 µm range particles. The inverse relationship between larger particles and inherent factors, notably specific surface area (SSA), and concentrations of total organic carbon (TOC) and total suspended solids (TSS) account for the small quantity of sorbed pollutants. The outcomes of this study provide fundamental knowledge for the development of effective stormwater management strategies for the protection of human and ecosystem health. However, further study is recommended for assessing the influence of other external factors such as population density and climate characteristics (for example temperature, solar radiation intensity, ultraviolet radiation index and wind speed) on PAHs and TPPs distribution patterns on urban road surfaces. Moreover, the transformation of PAHs for different ADDs and under other external environmental factors such as temperature, radiation intensity and UV requires further investigation in order to derive a greater understanding of the fate of these deleterious pollutants.

Appendix A. Supplementary material

References

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Inherent and external factors influencing the distribution of PAHs, hydroxy-PAHs,

Fig. S1: Study area and sites; (a) & (b) residential, (c) commercial, and (d) & (e) industrial land uses (adopted from Gbeddy et al. (2018))

Table S1: Measurement of road dust physicochemical parameters

Physicochemical property	Analytical method
pH	Method 4500H (APHA, 2005) and Method 4A1 (Rayment and Lyons, 2011) using smartCHEM-Cond/pH instrument
EC	Method 2520B (APHA, 2005) and Method 3A1 (Rayment and Lyons, 2011) using smartCHEM-Cond/pH instrument
SSA	Ethylene glycol monoethyl ether (EGME) method (Gunawardana, 2011)
TSS	Method 2540B (APHA, 2005)
TOC:	
Dissolved organic carbon (DOC)	Method 5310C (APHA, 2005) using Shimadzu TOC-VSH Analyser (Gunawardana, 2011; Ma, 2015)
Particulate organic carbons (POC)	Loss-on-ignition (LOI) (Ma, 2015; Rayment and Lyons, 2011)

Table S2: Relevant inherent and external influential factors for PAHs and TPPs distribution on urban road surfaces

Site	IDs	Particle size range (µm)	Antecedent dry day, ADD (day)	Daily Traffic Volume, DTV	Specific surface area, SSA (m²/g)	Total suspended solids, TSS (g/mL)	Total organic carbon, TOC (mg/L)	Electrical conductivity, EC (µS/cm)	pH @ 25ºC
BVH 1,1	Ra1	0.45-75	1	750	37.660	0.000948	37.661	38.4	6.17
BVH 1,2	Ra2	75-150	1	750	12.570	0.000290	12.570	38.4	6.17
BVH 1,3	Ra3	150-300	1	750	9.080	0.000114	9.080	38.4	6.17
BVH 1,4	Ra4	300-425	1	750	6.290	0.000198	6.290	38.4	6.17
BVH 4,1	Ra5	0.45-75	4	750	37.690	0.000766	37.691	63.2	6.15
BVH 4,2	Ra6	75-150	4	750	34.190	0.000332	34.190	63.2	6.15
BVH 4,3	Ra7	150-300	4	750	3.490	0.000010	3.490	63.2	6.15
BVH 4,4	Ra8	300-425	4	750	2.790	0.000004	2.790	63.2	6.15
BVH 7,1	Ra9	0.45-75	7	750	57.310	0.000912	57.311	53.9	5.93
BVH 7,2	Ra10	75-150	7	750	27.960	0.000376	27.960	53.9	5.93
BVH7,3	Ra11	150-300	7	750	6.270	0.000238	6.270	53.9	5.93
BVH 7,4	Ra12	300-425	7	750	1.400	0.000254	1.400	53.9	5.93
BVH 11,1	Ra13	0.45-75	11	750	45.380	0.001056	45.381	88.9	6.17
BVH11,2	Ra14	75-150	11	750	23.040	0.000310	23.040	88.9	6.17
BVH 11,3	Ra15	150-300	11	750	7.690	0.000212	7.690	88.9	6.17
BVH 11,4	Ra16	300-425	11	750	4.880	0.000112	4.880	88.9	6.17
BMT 1,1	Rb1	0.45-75	1	750	18.880	0.001828	18.882	41	6.25
BMT 1,2	Rb2	75-150	1	750	19.570	0.000196	19.570	41	6.25
BMT 1,3	Rb3	150-300	1	750	4.900	0.000256	4.900	41	6.25
BMT 1,4	Rb4	300-425	1	750	21.670	0.000132	21.670	41	6.25
BMT 4,1	Rb5	0.45-75	4	750	19.580	0.001200	19.581	64.7	5.88
BMT 4,2	Rb6	75-150	4	750	17.470	0.000478	17.470	64.7	5.88
BMT 4,3	Rb7	150-300	4	750	16.070	0.000140	16.070	64.7	5.88
BMT 4,4	Rb8	300-425	4	750	27.260	0.000070	27.260	64.7	5.88
BMT 7,1	Rb9	0.45-75	7	750	40.540	0.001208	40.541	66	5.74
BMT 7,2	Rb10	75-150	7	750	23.760	0.000494	23.760	66	5.74
BMT 7,3	Rb11	150-300	7	750	7.690	0.000382	7.690	66	5.74
BMT 7,4	Rb12	300-425	7	750	24.480	0.000244	24.480	66	5.74
BMT 11,1	Rb13	0.45-75	11	750	36.360	0.002084	36.362	158.2	5.61
BMT 11,2	Rb14	75-150	11	750	13.990	0.000296	13.990	158.2	5.61
BMT 11,3	Rb15	150-300	11	750	13.270	0.000162	13.270	158.2	5.61
BMT 11,4	Rb16	300-425	11	750	36.350	0.000258	36.350	158.2	5.61
BST 1,1	C1	0.45-75	1	3000	74.100	0.001434	74.101	57.5	6.35
BST 1,2	C2	75-150	1	3000	37.000	0.000134	37.000	57.5	6.35
BST 1,3	C3	150-300	1	3000	31.430	0.000118	31.430	57.5	6.35
BST 1,4	C4	300-425	1	3000	13.980	0.000228	13.980	57.5	6.35
BST 4_1	C5	0.45-75	4	3000	42.620	0.001222	42.621	82.2	6.33

BST 4,2	C6	75-150	4	3000	45.430	0.000152	45.430	82.2	6.33
BST 4,3	C7	150-300	4	3000	32.160	0.000314	32.160	82.2	6.33
BST 4,4	C8	300-425	4	3000	29.340	0.000016	29.340	82.2	6.33
BST 7,1	C9	0.45-75	7	3000	29.320	0.000986	29.321	53.5	6.7
BST 7,2	C10	75-150	7	3000	13.270	0.000392	13.270	53.5	6.7
BST 7,3	C11	150-300	7	3000	0.700	0.000148	0.700	53.5	6.7
BST7,4	C12	300-425	7	3000	0.700	0.000216	0.700	53.5	6.7
BST 11,1	C13	0.45-75	11	3000	30.710	0.001418	30.711	106.6	6.48
BST 11,2	C14	75-150	11	3000	4.880	0.000318	4.880	106.6	6.48
BST 11,3	C15	150-300	11	3000	2.790	0.000082	2.790	106.6	6.48
BST 11,4	C16	300-425	11	3000	1.400	0.000042	1.400	106.6	6.48
NSS 1,1	Ia1	0.45-75	1	3500	19.720	0.001326	19.721	37	6.25
NSS 1,2	Ia2	75-150	1	3500	7.690	0.000176	7.690	37	6.25
NSS1,3	Ia3	150-300	1	3500	4.190	0.000176	4.190	37	6.25
NSS 1,4	Ia4	300-425	1	3500	3.500	0.000100	3.500	37	6.25
NSS 4,1	Ia5	0.45-75	4	3500	9.780	0.000962	9.781	63.4	6.36
NSS 4,2	Ia6	75-150	4	3500	5.590	0.000404	5.590	63.4	6.36
NSS 4,3	Ia7	150-300	4	3500	4.900	0.000016	4.900	63.4	6.36
NSS 4,4	Ia8	300-425	4	3500	0.700	0.000066	0.700	63.4	6.36
NSS 7,1	Ia9	0.45-75	7	3500	22.370	0.001934	22.372	48.6	6.49
NSS 7,2	Ia10	75-150	7	3500	12.590	0.000938	12.591	48.6	6.49
NSS 7,3	Ia11	150-300	7	3500	2.800	0.000182	2.800	48.6	6.49
NSS 7,4	Ia12	300-425	7	3500	2.800	0.000146	2.800	48.6	6.49
NSS 11,1	Ia13	0.45-75	11	3500	21.670	0.003354	21.673	114.6	6.53
NSS 11,2	Ia14	75-150	11	3500	5.590	0.001192	5.591	114.6	6.53
NSS11,3	Ia15	150-300	11	3500	2.800	0.000286	2.800	114.6	6.53
NSS 11,4	Ia16	300-425	11	3500	0.700	0.000152	0.700	114.6	6.53
NHC 1,1	Ib1	0.45-75	1	3500	23.780	0.001332	23.781	71.8	6.31
NHC 1,2	Ib2	75-150	1	3500	11.190	0.000314	11.190	71.8	6.31
NHC 1,3	Ib3	150-300	1	3500	8.510	0.000082	8.510	71.8	6.31
NHC1,4	Ib4	300-425	1	3500	6.290	0.000248	6.290	71.8	6.31
NHC 4,1	Ib5	0.45-75	4	3500	16.780	0.001064	16.781	72.5	6.27
NHC 4,2	Ib6	75-150	4	3500	10.540	0.000092	10.540	72.5	6.27
NHC 4,3	Ib7	150-300	4	3500	2.800	0.000020	2.800	72.5	6.27
NHC 4,4	Ib8	300-425	4	3500	0.700	0.000156	0.700	72.5	6.27
NHC 7,1	Ib9	0.45-75	7	3500	24.460	0.000946	24.461	47.8	6.61
NHC 7,2	Ib10	75-150	7	3500	16.780	0.000622	16.781	47.8	6.61
NHC 7,3	Ib11	150-300	7	3500	0.700	0.000228	0.700	47.8	6.61
NHC 7,4	Ib12	300-425	7	3500	8.380	0.000208	8.380	47.8	6.61
NHC 11,1	Ib13	0.45-75	11	3500	18.160	0.001428	18.161	129.5	6.68
NHC 11,2	Ib14	75-150	11	3500	11.870	0.000490	11.870	129.5	6.68
NHC 11,3	Ib15	150-300	11	3500	5.590	0.000162	5.590	129.5	6.68
NHC 11,4	Ib16	300-425	11	3500	8.390	0.000102	8.390	129.5	6.68

Table S3: PAHs, TPPs, surrogate and internal standards used in this study (adopted from Gbeddy et al. (2021); Gbeddy et al. (2020a); Gbeddy et al. (2020b))

Analyte/Chemicals	Symbol	Rings; Class	Conc/Quantity	Manufacturer
A. Parent PAHs				
1. Picene (H184S, CAS:213-46-7)	PIC	5;HMW	50μg/mL in Toluene	AccuStandard, USA
2. Triphenylene (N-13711, CAS:217-59-4)	TPL	4;HMW	100mg neat	Chem Service Inc, USA
H-QME-01 Quebec Ministry of Environment PAH Mix (24 PAHs):			500μg/mL in DCM:Benzene (50:50)	AccuStandard, USA
1. Acenaphthene	ACE	3;LMW		
2. Acenaphthylene	ACT	3;LMW		
3. Anthracene	ANT	3;LMW		
4. Benz[a]anthracene	BaA	4;HMW		
5. Benzo[b]fluoranthene	BbF	5;HMW		
6. Benzo[j]fluoranthene	BjF	5;HMW		
7. Benzo[k]fluoranthene	BkF	5;HMW		
8. Benzo[ghi]perylene	BghiP	6;HMW		
9. Benzo[c]phenanthrene	BcPH	4;HMW		
10. Benzo[a]pyrene	BaP	5;HMW		
11. Benzo[e]pyrene	BeP	5;HMW		
12. Chrysene	CHR	4;HMW		
13. Dibenz[a,h]anthracene	DahA	5;HMW		
14. Dibenzo[a,h]pyrene	DahP	6;HMW		
15. Dibenzo[a,i]pyrene	DaiP	6;HMW		
16. Dibenzo[a,l]pyrene	DalP	6;HMW		
17. 7,12-Dimethylbenz[a]anthracene	DMBA	4;HMW		
18. Fluoranthene	FRT	4;HMW		
19. Fuorene	FLR	3;LMW		
20. Indeno[1,2,3-cd]pyrene	IcdP	6;HMW		
21. 3-Methylcholanthrene	MCHO	5;HMW		
22. Naphthalene	NAP	2;LMW		
23. Phenanthrene	PHE	3;LMW		
24. Pyrene	PYR	4;HMW		
B. Carbonyl-PAHs				
1. 1,4-Naphthaquinone (C 15425000, CAS: 130-15-4)	NQN	2;TPP	0.25 g neat	Dr. Ehrenstorfer GmbH, Germany
2. 9-Fluorenone (C 20805000, CAS: 486-25-9)	9FLN	3;TPP	0.25 g neat	Dr. Ehrenstorfer GmbH, Germany
3. Benzo[a]fluoren-11-one (TRC-B203590, CAS: 479-79-8)	BaFN	4;TPP	100mg neat	Toronto Research Chemicals (trc), Canada
			0.25 g neat	Dr. Ehrenstorfer GmbH, Germany
4. 9,10-Anthraquinone (C 10281000, CAS: 84-65-1)	AQN	3;TPP		
C. Hydroxy-PAHs				
1. 2-Hydroxybiphenyl (HBP-001N, CAS: 90-43-7)	2HBP	2;TPP	100mg neat	AccuStandard, USA
2. 4-Hydroxybiphenyl (HBP-003N, CAS: 92-69-3)	4HBP	2;TPP	100mg neat	AccuStandard, USA
			10mg neat	AccuStandard, USA
3. 1-Hydroxypyrene (R-096N, CAS: 5315-79-7)	HPY	4;TPP	0.1g neat	Dr. Ehrenstorfer GmbH, Germany
4. 1,8-Dihydroxyanthraquinone (Danthron) (C 11961000, CAS: 117-10-2)	DHAQ	3;TPP		
D. Nitro-PAHs				
1. 5-Nitroacenaphthene (N-10899, CAS: 602-87-9)	5NAC	3:TPP	500mg neat	Chem Service Inc, USA
			100mg neat	AccuStandard, USA

Name	Code	TPP	Amount	Source
2. 1-Nitronaphthalene (R-016N, CAS: 86-57-7)	NNAP	2;TPP	5mg neat	AccuStandard, USA
3. 9-Nitroanthracene (R-003N, CAS: 602-60-8)	9NAN	3;TPP	5mg neat	AccuStandard, USA
4. 3-Nitrofluoranthene (R-013N, CAS: 892-21-7)	3NFR	3;TPP	5mg neat	AccuStandard, USA
5. 1-Nitropyrene (R-022N, CAS: 5522-43-0)	1NPY	4;TPP	100μg/mL in Toluene	AccuStandard, USA
6. 6-Nitrobenz(a)pyrene (R-004S, CAS: 63041-90-7)	NBaP	5;TPP		
E. Internal & Recovery Standards				
1. Naphthalene (D8, 99%) (DLM-365-1, CAS: 1146-65-2)	NAPd		1g neat	Cambridge Isotope Laboratories, Inc. (CIL), USA
			0.1g neat	CIL, USA
2. Phenanthrene (D10, 98%) (DLM-371-0.1 (CAS: 1517-22-2)	PHEd		1g neat	CIL, USA
			0.1g neat	CIL, USA
3. Anthracene (D10, 98%) (DLM-102-1, CAS: 1719-06-8)	ANTd		50μg/mL in Toluene-D8	CIL, USA
			50μg/mL in Toluene-D8	CIL, USA
4. Pyrene (D10, 98%) (DLM-155-0.1, CAS: 1718-52-1)	PYRd		1mg neat	trc, Canada
			0.1g neat	CIL, USA
5. 9-Nitroanthracene (D9, 98%) (DLM-4712-1.2)	9NANd		5g neat	CIL, USA
6. 1-Nitropyrene (D9, 98%) (DLM-1528-1.2)				
7. 1-Hydroxypyrene-d9 (TRC-H952702-1)	1NPYd			
8. Fluoranthene (D10, 98%) (DLM-2140-0.1, CAS: 93951-69-0)	HPYd			
9. Benzophenone-D10, 98%	FRTd			
	BZPd			
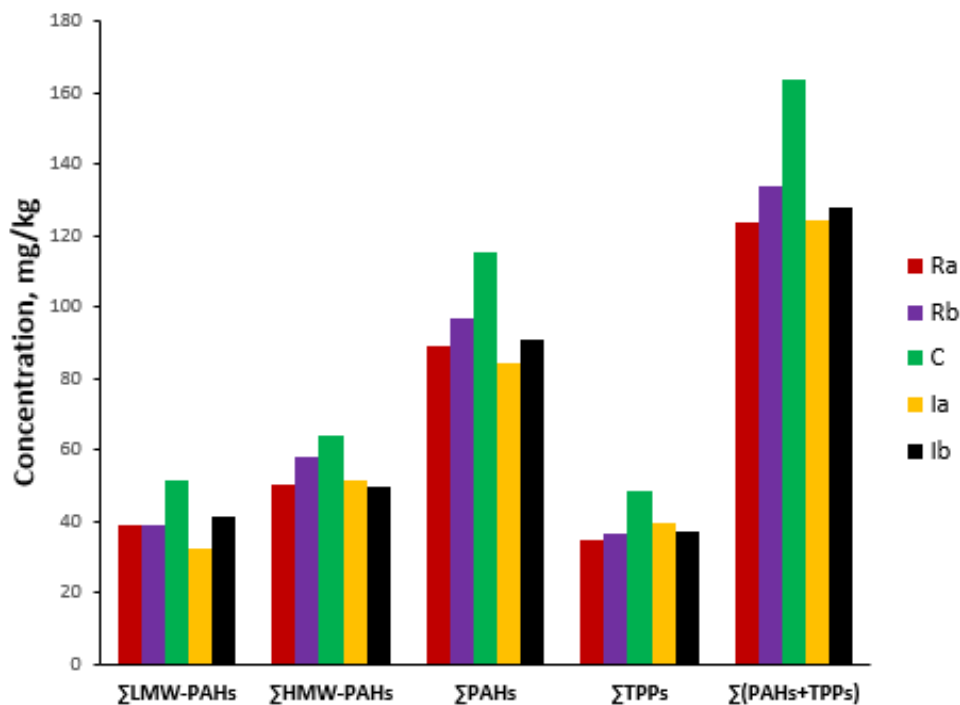
Fig. S2: Influence of land use on the cumulative distribution of PAHs and TPPs on urban roads

Table S4: Cumulative distribution of different classes of PAHs in road dust particles

ID	∑LMW-PAH (mg/kg)	∑HWM-PAH (mg/kg)	∑PAHs (mg/kg)	∑TPPs (mg/kg)	∑(PAHs + TPPs) (mg/kg)
Ra1	9.69	5.96	15.65	7.49	23.14
Ra2	2.29	2.23	4.52	2.44	6.95
Ra3	1.79	2.68	4.47	0.60	5.06
Ra4	1.48	2.56	4.04	0.00	4.04
Ra5	4.05	3.27	7.32	0.49	7.81
Ra6	1.51	4.88	6.39	1.36	7.75
Ra7	1.58	1.61	3.19	2.31	5.50
Ra8	2.64	1.40	4.04	0.63	4.68
Ra9	2.38	5.71	8.09	3.00	11.09
Ra10	0.82	2.38	3.20	1.99	5.19
Ra11	0.73	3.77	4.50	0.88	5.38
Ra12	0.88	1.59	2.47	4.05	6.52
Ra13	3.49	4.49	7.98	2.54	10.52
Ra14	2.22	0.80	3.01	0.85	3.87
Ra15	1.82	3.85	5.66	5.64	11.30
Ra16	1.65	2.93	4.58	0.39	4.97
Rb1	5.48	4.64	10.12	2.62	12.74
Rb2	1.51	3.93	5.44	4.32	9.76
Rb3	2.36	1.27	3.63	1.49	5.12
Rb4	1.80	1.80	3.60	0.88	4.48
Rb5	6.46	6.38	12.84	1.63	14.46
Rb6	1.91	4.24	6.15	1.68	7.82
Rb7	3.49	4.33	7.81	2.14	9.96
Rb8	1.76	4.64	6.40	2.42	8.82
Rb9	1.78	4.22	6.00	4.77	10.76
Rb10	2.22	4.28	6.50	2.52	9.02
Rb11	0.82	2.26	3.08	1.85	4.93
Rb12	1.02	4.45	5.46	4.99	10.45
Rb13	3.18	4.68	7.86	2.08	9.94
Rb14	1.56	3.70	5.26	0.42	5.68
Rb15	1.19	1.74	2.93	1.61	4.54
Rb16	2.61	1.28	3.89	1.24	5.13
C1	8.70	6.58	15.28	5.69	20.97
C2	2.05	5.25	7.31	4.51	11.81
C3	2.19	1.25	3.44	0.50	3.94
C4	2.82	2.23	5.05	0.46	5.51
C5	11.77	6.88	18.65	5.21	23.86
C6	1.80	5.17	6.97	3.57	10.54
C7	2.26	4.56	6.83	2.80	9.63
C8	1.16	1.23	2.38	1.89	4.27
C9	3.13	4.51	7.64	6.29	13.93
C10	2.25	4.43	6.69	2.01	8.70
C11	2.26	2.45	4.71	2.14	6.85

C12	1.87	2.35	4.23	1.71	5.93
C13	2.79	7.12	9.91	2.27	12.17
C14	1.66	3.39	5.05	2.14	7.19
C15	1.92	5.13	7.05	5.30	12.35
C16	2.67	1.28	3.95	2.16	6.11
Ia1	2.59	4.97	7.56	2.96	10.52
Ia2	1.99	2.66	4.66	1.35	6.00
Ia3	1.66	1.14	2.80	0.84	3.63
Ia4	0.00	0.31	0.31	0.00	0.31
Ia5	6.52	5.15	11.68	4.10	15.78
Ia6	1.69	4.02	5.72	2.47	8.19
Ia7	1.55	2.83	4.38	1.06	5.43
Ia8	1.70	0.89	2.58	2.73	5.31
Ia9	1.71	5.33	7.03	4.13	11.16
Ia10	1.77	5.46	7.23	2.84	10.07
Ia11	2.00	1.71	3.71	1.43	5.14
Ia12	1.92	2.15	4.07	3.89	7.97
Ia13	1.63	7.04	8.67	2.94	11.61
Ia14	1.54	1.44	2.98	0.97	3.96
Ia15	2.19	3.77	5.96	3.87	9.83
Ia16	2.05	2.78	4.83	4.24	9.07
Ib1	8.49	4.65	13.14	4.20	17.33
Ib2	1.87	2.18	4.05	1.80	5.85
Ib3	1.34	1.55	2.89	0.92	3.82
Ib4	2.32	4.93	7.25	3.83	11.09
Ib5	7.52	6.92	14.44	1.80	16.23
Ib6	2.88	2.06	4.93	1.68	6.61
Ib7	1.66	1.85	3.52	0.59	4.10
Ib8	1.14	0.62	1.76	0.94	2.70
Ib9	2.32	5.85	8.16	5.03	13.19
Ib10	0.68	1.81	2.49	1.38	3.88
Ib11	0.44	1.87	2.31	2.22	4.53
Ib12	1.75	1.79	3.54	1.83	5.36
Ib13	2.30	5.98	8.28	2.00	10.29
Ib14	2.66	2.03	4.69	0.76	5.45
Ib15	1.16	3.87	5.03	6.13	11.16
Ib16	2.58	1.98	4.56	1.87	6.43
Range	**0 – 11.77**	**0.31 – 7.12**	**0.31 – 18.65**	**0 – 7.49**	**0.31 – 23.86**
Mean	**2.54±2.07**	**3.42±1.79**	**5.95±3.36**	**2.46±1.66**	**8.41±4.46**

LMW-PAHs and HMW-PAHs refer to PAHs containing two to three, and more than three aromatic rings, respectively

Table S5: Factor variance with Eigenvalues > 1

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Factor 9	Factor 10	Factor 11	Factor 12	Factor 13
Value	6.9	3.4	3.1	2.6	2.5	1.9	1.6	1.5	1.4	1.3	1.1	1.1	1.0
% of Var.	17.8	8.7	8.0	6.7	6.4	4.8	4.1	3.7	3.6	3.3	2.9	2.8	2.6
Cum. %	17.8	26.5	34.4	41.2	47.6	52.3	56.5	60.2	63.8	67.1	70.0	72.8	75.4

Table S6: Unrotated factor loadings of factors with Eigenvalues > 1

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Factor 9	Factor 10	Factor 11	Factor 12	Factor 13
ADD	0.099	-0.488	0.242	-0.529	-0.293	0.107	-0.070	0.020	0.275	0.211	-0.007	0.241	0.007
DTV	0.018	-0.270	0.124	0.577	-0.521	0.194	-0.201	-0.028	-0.102	-0.013	0.008	-0.092	0.009
SSA	-0.744	0.273	-0.055	-0.369	0.018	0.005	0.066	0.103	-0.178	-0.175	-0.199	0.047	-0.121
TSS	-0.690	0.050	0.219	-0.149	-0.210	0.072	-0.123	-0.144	0.253	0.149	0.073	-0.103	0.040
TOC	-0.744	0.273	-0.055	-0.369	0.018	0.005	0.066	0.103	-0.178	-0.175	-0.199	0.047	-0.121
EC	0.052	-0.405	0.316	-0.530	-0.130	0.302	-0.041	0.221	0.097	0.195	-0.048	0.178	-0.039
pH	0.025	-0.298	0.087	0.561	-0.529	0.112	-0.316	-0.043	-0.052	-0.007	-0.109	-0.103	-0.119
NAP	-0.623	0.243	0.424	0.286	0.377	0.089	-0.174	-0.021	-0.072	0.039	-0.103	0.008	-0.070
ACT	0.094	0.382	0.493	-0.072	-0.048	-0.014	-0.056	0.222	-0.246	0.042	0.137	-0.122	-0.380
ACE	0.152	-0.128	0.588	-0.150	-0.120	0.236	0.071	0.016	-0.180	-0.160	-0.117	-0.337	0.188
FLR	-0.347	-0.201	-0.599	0.128	-0.248	-0.096	0.144	-0.146	-0.001	0.073	0.034	0.072	0.113
PHE	-0.422	0.090	0.343	-0.253	-0.230	0.062	-0.128	0.394	-0.015	0.076	0.036	-0.067	0.310
ANT	-0.202	-0.105	-0.079	0.173	0.177	0.080	0.213	0.728	-0.007	0.193	-0.097	-0.028	-0.104
FRT	-0.129	-0.229	-0.200	-0.364	0.420	0.267	-0.215	-0.226	0.000	0.115	0.370	-0.119	-0.235
PYR	-0.112	-0.166	-0.227	-0.096	0.520	0.353	-0.435	-0.010	0.055	0.087	0.206	-0.119	0.029
BaP	-0.726	-0.205	0.104	-0.101	-0.188	-0.108	-0.219	-0.007	0.128	0.102	-0.061	-0.087	0.156
BeP	-0.650	-0.054	-0.060	0.115	-0.065	-0.004	0.337	0.059	-0.177	0.263	0.151	0.101	0.077
BaA	-0.191	0.036	0.278	0.271	-0.157	-0.070	-0.181	0.188	-0.280	-0.127	0.518	0.459	0.111
BcPH	-0.065	-0.669	0.113	-0.079	-0.341	-0.008	0.105	-0.098	-0.064	-0.082	-0.086	-0.072	-0.301
BbF	-0.526	-0.098	0.037	0.023	0.272	0.151	0.101	-0.127	0.309	-0.266	0.015	0.252	0.206
B(k+j)F	-0.692	0.131	0.145	0.169	0.115	0.151	-0.129	-0.176	0.074	-0.029	-0.007	0.150	-0.295
CHR+TPL	0.133	0.239	0.229	-0.206	-0.134	0.271	0.254	-0.299	-0.086	0.123	0.152	0.061	-0.070
DahA	-0.702	0.133	0.220	0.196	0.033	-0.073	0.141	-0.018	0.147	0.225	0.024	-0.169	-0.197
MCHO	-0.316	-0.271	0.193	-0.157	0.156	-0.197	-0.065	-0.092	-0.291	-0.475	0.127	-0.286	-0.054
DMBA	-0.635	-0.313	0.170	-0.011	-0.040	0.025	0.144	-0.365	-0.042	0.084	-0.125	-0.035	0.069
IcdP	-0.091	0.136	0.450	-0.309	-0.181	-0.368	0.117	-0.025	0.068	-0.135	0.255	-0.153	0.248
BghiP	-0.394	-0.449	-0.345	-0.010	0.122	0.227	0.067	0.215	-0.265	0.105	0.013	-0.093	0.141
DalP	-0.473	0.086	-0.300	-0.308	-0.231	-0.315	-0.115	-0.120	-0.309	-0.067	-0.004	0.253	-0.023
PIC	-0.473	0.190	0.100	0.196	-0.198	-0.062	0.368	-0.047	0.293	0.164	0.396	-0.214	-0.103
NNAP	-0.552	0.062	-0.438	-0.166	-0.319	-0.184	-0.112	-0.054	0.057	-0.006	-0.195	-0.112	-0.037
9NAN	0.134	-0.759	0.180	-0.059	0.278	-0.249	0.217	0.030	0.001	-0.123	0.037	-0.049	-0.129
1NPY	-0.214	-0.115	0.158	0.134	0.264	0.402	0.090	-0.237	-0.423	0.167	-0.148	-0.064	0.325
BaFN	-0.414	-0.325	-0.396	-0.054	-0.271	0.164	-0.195	0.177	-0.137	-0.102	0.205	0.004	-0.169
9FLN	-0.482	-0.190	-0.290	0.276	0.110	0.104	0.409	0.141	0.060	-0.204	0.167	-0.113	0.097
NQN	-0.247	0.048	-0.038	0.073	-0.062	0.305	-0.181	0.176	0.440	-0.559	0.034	-0.047	0.077
AQN	0.129	-0.681	0.159	0.024	0.290	-0.422	0.105	0.064	0.066	-0.017	0.009	0.039	-0.057
HPY	-0.291	-0.262	0.359	0.260	0.255	-0.399	-0.285	-0.073	-0.080	0.103	0.028	0.200	0.103
2HBP	0.207	-0.077	0.204	0.028	-0.197	0.477	0.415	-0.120	-0.081	-0.280	0.016	0.316	-0.122
DHAQ	-0.438	-0.097	0.368	0.302	0.241	-0.028	0.025	0.052	0.195	-0.032	-0.304	0.217	-0.111

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