Science Forum (Journal of Pure and Applied Sciences)

Journal Homepage: https://atbuscienceforum.com.ng/index.php/jpas

Source Apportionment of Carcinogenic Polycyclic Aromatic Hydrocarbons in Urban Road Dust

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Abstract

This study assessed and compared the concentrations of polycyclic aromatic hydrocarbons (PAHs) in road dust collected from various zones within Durban City, South Africa, including the city centre, residential areas, and industrial districts. The investigation aimed not only to quantify PAH levels but also to identify their likely sources and assess potential health risks. Measured concentrations of total PAHs varied across the different land-use areas: from 77 to 1488.85 $\mu g \cdot kg^{-1}$ in the city centre, up to 2108 $\mu g \cdot kg^{-1}$ in residential areas, and between 138 and 1409 $\mu g \cdot kg^{-1}$ in industrial zones. These variations reflect differing emission sources and traffic intensities across the city. To determine the origin of PAHs, several molecular diagnostic ratios were calculated, including phenanthrene/anthracene (0.03, 0.34, and 0.41), benz[a]anthracene/chrysene (0.99 and 0.85), benzo[b]fluoranthene/benzo[k]fluoranthene (1.51 and 1.53), and benzo[a]pyrene/benzo[e]pyrene (0.98 and 0.92). These ratios, alongside results from principal component analysis (PCA), indicated that the dominant sources of PAHs were related to the incomplete combustion of petroleum products—primarily vehicular emissions from gasoline and diesel engines. Furthermore, the study employed toxicity equivalency factors (TEFs) to estimate the carcinogenic potential of individual PAH compounds. Health risk assessments were conducted using the hazard index (HI) and incremental lifetime cancer risk (ILCR) metrics. Results indicated that, while PAHs were present in varying concentrations, the associated health risks—both non-carcinogenic and carcinogenic—were within acceptable limits, suggesting that road dust PAHs in Durban do not currently pose significant health concerns for the urban population.

Keywords
Road dust,
Polycyclic aromatic hydrocarbons,
High performance liquid Chromatography,
Source apportionment,
Cancer risk assessment.

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INTRODUCTION

Elevated levels of polycyclic aromatic hydrocarbons (PAHs) and other organic pollutants have been reported in soils and road dust (Baird et al., 2005; Iwegbue et al., 2020; Liu et al., 2007)

PAHs are formed by both natural and anthropogenic processes, and can travel long distances in the atmosphere due to their gas-to-particulate partitioning (Angeliki Karanasiou1, 2014). Petroleum products use for transportation and industry, such as steel and aluminum production, power generation, coal combustion, waste incineration, agricultural burning, and residential heating, have caused extensive environmental pollution (Angeliki Karanasiou1, 2014). PAH contamination in the environments can be attributed to anthropogenic sources such as vehicular emissions and industrial discharges. PAHs also enter the environment through crude oil, coal tar, and petroleum products (Neff et al., 2005; Stout et al., 2015). Natural sources of PAHs, such as forest fires, volcanoes, and algae/bacteria biosynthesis, are minor compared to anthropogenic sources (Wang et al., 2011; B. Yu et al., 2014). PAHs mainly come from human activities, such as burning fossil fuels, biomass, and industrial emissions (Lawal, 2017b; Lorenzi et al., 2011).

Incomplete oxidation of carbon leads to hydrocarbon fragments and complex polycyclic aromatic structures (Cantú et al., 1998; Mogashane et al., 2020; Shi et al., 2011). Anthropogenic PAHs come from pyrogenic and petrogenic sources, generated by incomplete fuel and biomass combustion. PAHs are found in vehicle exhaust, cigarette smoke, coal and wood smoke, and gas- and oil-fired burner emissions, creating many point sources of PAHs in cities. PAHs are complex mixtures of hundreds of isomers, some of which are carcinogenic, according to IARC and ASTDR (Us, 1995). Planar PAHs, such as benzo[a]pyrene (B[a]P) and dibenzo[a,h]anthracene (Db[a,h]A), are highly carcinogenic due to their high activities in the bay region. In contrast, nonplanar carcinogens usually act synergistically to cause carcinogenic or mutagenic effects.

The United Nations Environmental Programme (UNEP) (Adams et al., 2018; Motelay-Massei et al., 2005), United States Environmental Protection Agency (US EPA) (Cai et al., 2009; Fisner et al., 2013; Keith, 2015), Canadian Environmental Protection Act (CEPA) (Karbalaei et al., 2018; Sun et al., 2017), and European Environment Agency (EEA) (Guerreiro et al., 2014; Pacyna, 2011) have listed PAHs as priority pollutants due to pollution concerns (Karbalaei et al., 2018; Kumar et al., 2014; Sun et al., 2017).

The USEPA has identified 16 PAHs as "Consent Decree" priority pollutants, some of which are carcinogenic. IARC has classified seven PAHs as Group B2 probable human carcinogens, including benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), chrysene (Chry), dibenzo[a,h]anthracene (DahA), and indeno[c,d-1,2,3]pyrene (IndP). Benzo[a]pyrene is the most toxic PAH (Nisbet and LaGoy, 1992). IARC concluded that PAHs are a major carcinogenic risk in urban areas (Soltani et al., 2015; Straif et al., 2009). (al., 2005).

The US EPA 16 priority PAHs are divided into two groups: non-carcinogenic (2-4 benzene rings) and carcinogenic (4-6 benzene rings). Non-carcinogenic PAHs include naphthalene, acenaphthene, anthracene, phenanthrene,

acenaphthylene, fluorene, fluoranthene, and pyrene. Carcinogenic PAHs are benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[l,2,3-c,d]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i]perylene. HMW PAHs, mainly from urban activities, are more hazardous than LMW PAHs due to their stability and carcinogenic properties (Mogashane et al., 2020; Yu et al., 2014).

Humans are exposed to PAHs through ingestion, inhalation, and dermal contact with PAH contaminated water, air, soil, sediment, and food (Šimko 2002; Veiga et al. 2014). non-smokers' PAHs intake ranges from 3 to 17 μg day^{-1} (Scherer et al., 2022). Many studies have examined PAHs' levels, distribution, and environmental fate due to their mutagenic, carcinogenic properties (Cantú; Godefroy et al.). Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic, endocrine-disrupting, and toxic to reproduction, posing risks to human and environmental health. PAH contamination is globally monitored in drinking water, wastewater, industrial emissions, soil, hazardous waste extracts, food, and biological fluids.

Urban road dust contains contaminants, including polybrominated diphenyl ethers (PBDEs) (Cao et al., 2014; Li et al., 2018; Shi et al., 2013), polychlorinated biphenyls (PCBs) (Cao et al., 2014; Li et al., 2018; Shi et al., 2013), PAHs, and toxic heavy metals (Hassanien & Abdel-Latif, 2008; Saeedi et al., 2012; Soltani et al., 2015). These contaminants harm the environment. Road dust PAHs comes from combustion of petroleum products, industry, power plants, waste incineration, and home heating. Poorly maintained vehicles and unburned fuels from car exhausts also contribute to the presence of petrogenic PAHs in rods dust. Tyres and asphalt debris also contain PAHs, making road dust a nonpoint source of these contaminants (Boonyatumanond et al., 2007). It noteworthy that PAHs manufactured for analytical purposes do not cause environmental contamination (K. B. Okona-Mensah et al., 2005).

Numerous studies have been conducted to investigate their levels, distribution, and fate in the environment, as they have been found to possess mutagenic, carcinogenic (Cantú; Godefroy et al., 2005), endocrine-disrupting (Scinicariello & Buser, 2014; Wang et al., 2011; Yu et al., 2014), and reproductive toxicity properties that pose threat to human and environmental health (Lawal, 2017; World Health, 1998). Consequently, PAH contamination is frequently monitored globally in a wide range of environmental matrices, including drinking water, wastewater, industrial emissions, soil, and hazardous waste extracts (Lawal, 2017), food (Giorgia Purcaro n, 2013; Yu et al., 2014) and biological fluids (Okona-Mensah et al., 2005; Ramesh et al., 2015).

Durban, South Africa's commercial and industrial activities have caused a rise in traffic density, resulting in high levels of polycyclic aromatic hydrocarbons (PAHs). Petroleum refining and cabotage are major sources of PAHs. Despite numerous reports on PAHs in urban road dust in Asian, European, and American cities, few studies have been done in African cities, especially Durban. The objective this study was to apportion possible sources to PAHs in urban road dust. The results are crucial for monitoring PAH pollution in urban environmental.

Materials and methods

The study area

Durban city (Zulu: eThekwini, from itheku meaning 'harbour') (29° 52′ 59.9988″ S and 31° 2′ 59.9964″ E) is a city located on the eastern coast of South Africa along the Indian Ocean. With a population of 3.5 million people and an area of approximately 225.91 km2, it is the third most populous urban area in the KwaZulu-Natal province (Statistics South, 2011; Tularam et al., 2020). It is a popular tourist destination and home to two major petrochemical refineries: a sugar refinery, a paper factory, a number of chemical processing industries, an airport, and the busiest port in South Africa (Vetrimurugan et al., 2017).

Durban Harbour ranks as the 4th-busiest in the southern hemisphere and the 9th largest harbour in the world (Tularam et al., 2020). The area experiences a humid subtropical climate, with hot and humid summers and pleasantly warm and dry winters, free from snow and frost. The city has an average annual rainfall of 1,009 mm and an average temperature of approximately 24 °C in the summer and 17 °C in the winter (Busari, 2018).

Sample collection

Fifty-five road dust samples were collected from several sampling locations: busy road junctions in the city centre, industrial locations, and residential areas. Geographic information on each sampling location (latitude and longitude coordinates) was determined with a hand-held global positioning device (Figure 3.2). The coordinates for each sample collected in this work are listed in Supplementary Materials Table SI 3.1. Approximately 500 g of road dust was collected with a pan and brush from each side of the road at each sampling point over a 100-meter-long and 0.3-meter-wide area. The pan and brush were rinsed with acetone after each sampling. Because PAHs undergo photo-degradation under relatively adequate oxidant and ultraviolet (UV) radiation conditions, direct exposure to sunlight and possible strong UV sources were avoided during handling, storage, and transportation.

After sampling, the samples were wrapped in aluminium foil, sealed in plastic bags, and transported to the laboratory in an ice chest. Samples were then dried in the dark in the laboratory at room temperature for 24 h. Large foreign objects, such as plant debris (sticks or leaves), stones (rocks), or any other synthetic waste, were handpicked and discarded. The samples were then homogenized, and fractionated into 53, 75, and 300 μm particle size fractions using an assemblage of stainless-steel sieves on an automated Retsch mechanical shaker. The fractionated samples were stored at 4 °C until analysis.

Figure 1. Map of the study area and sample locations.

Chemicals

A 2000 µg mL^{-1} in dichloromethane EPA 610 PAH certified reference standard mixture (CRM47940), of 16 PAHs was purchased from Sigma Aldrich. The PAHs present were as follows: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP),

dibenz[a,h]-anthracene (DahA), benzo[ghi]perylene (BghiP). This solution was diluted in methanol to desired concentrations for the establishment of calibration lines and other experiments. Deuterated chrysene (Chr-d_{12}). HPLC-grade methanol was purchased from Sigma Aldrich and 18 MΩ Millipore water was obtained from Millipore Milli-Q Elix 5 UV water purification system.

Sample preparation

An ultrasound-assisted extraction (UAE) technique was used for the extraction of PAHs from solid samples such as road dust. UAE is an attractive extraction method because it is less expensive than other methods and has fewer instrument requirements (Mussatto, 2015). It has advantages such as short extraction time at low temperature, less energy requirement and retention of the quality of the extract (Kumar et al., 2021). Extraction is carried out by using an ultrasonic bath or an ultrasonic probe system. It consists of passing ultrasonic energy in the form of waves through a liquid solvent containing solid particles. As the waves hit the surface of the material, a force that is either perpendicular or parallel to the surface is generated. Sonic energy is converted into mechanical energy in the form of shock waves equivalent to several thousand atmospheres of pressure (Mussatto, 2015).

Before extraction of PAHs the fractionated road dust samples were placed in desiccator for 24 h to minimize weight measurement errors to obtain a constant weight. A mass of 500 mg of each dried dust sample fraction was sonicated for 30 min with 10 mL of methanol in a 50 mL flask (thrice) in ultrasonic bath maintained at 30 °C. The extracts were combined and then filtered through 0.45 Whatman filter paper (#4; Whatman, UK) and the filtrate was reduced to 2 mL by using a gentle current of nitrogen gas and then filtered through a 0.45 µm syringe filter into HPLC vials for analysis. The recovery was further evaluated by spiking the road dust sample with deuterated chrysene (Chr-d_{12}), at 1, 2, and 5 µg mL^{-1} concentrations, extracted and analysed.

Quality control

To ensure the dependability of the results, quality assurance procedures and measures were followed. Spiked blanks (standards spiked into solvent), matrix spikes, matrix blank, procedural blanks (solvent), and standard reference material analysis (Dr. Ehrenstorfer GmbH Alkanes-Mix 10, and Sigma-Aldrich Co. LLC EPA 525 PAH Mix A and EPA 525 PAH Mix B) were all carried out. In procedure blank samples, none of the target PAHs were found. For the 16 studied PAHs, the average recoveries based on surrogate deuterated PAHs in dust were roughly 88-95%. The minimal detection limit of PAHs, defined as the lowest analyte concentration detectable in a sample (signal-to-noise ratio = 3:1), ranged from 0.05 to 0.4 g/kg, with precisions ranging from 4-8%.

Potential health risk assessment of PAHs

A number of methods have been employed to assess the possible health risks posed to humans from exposure to dust particles containing PAHs. These methods include the BaP carcinogenic (BaP_{TEQ}) and BaP mutagenic (BaP_{MEQ}) equivalency factors (Iwegbue et al., 2020; Jiang et al., 2014; US Department of Health and Human Services & 7-28-0006, 1995), non-carcinogenic and incremental

lifetime cancer risks (ILCR) (Jiang et al., 2014; Nisbet & LaGoy, 1992; Shabbaj et al., 2018; Soltani et al., 2015). The aforementioned methods were used to evaluate the possible health risks from exposure to PAHs in the dust of children and adults in the area of study.

BaP-toxic equivalent

The toxicity factor (BaP_{TEF}) and mutagenic factors (BaP_{MEF}) have been used to evaluate the toxicity and mutagenic potency of PAHs relative to BaP (Nisbet & LaGoy, 1992). The toxic equivalent, BaP_{TEQ} and mutagenic equivalent BaP_{MEQ} is also use for a more accurate assessment of potential health risk (Jung et al., 2010; Qi et al., 2019). BaP_{TEF} and BaP_{MEF} values, together with the determined PAH concentrations, have been used to calculate toxic equivalent, BaP_{TEQ}, and mutagenic equivalent, BaP_{MEQ}, relative to BaP in environmental samples (Qi et al., 2019). Table 3.2 provides the TEFs and MEFs used in this study. Equations 1 and 2 were used to evaluate the BaP_{TEQ} and BaP_{MEQ} in the dust samples.

$$BaP_{TEQ} = \sum C_i \times BaP_{TEF} \quad (1)$$

$$BaP_{MEQ} = \sum C_i \times BaP_{MEF} \quad (2)$$

where BAP_{TEQ} and BaP_{MEQ} are the toxic equivalent, mutagenic equivalent relative to BaP. C_i denotes the $UCL_{95\%}$ concentration of the individual PAH. The $UCL_{95\%}$ (upper confidence limit on the mean) was computed based on Student's t-value using the formula (Usepa, 2002):

$$UCL_{95\%} = \overline{X} + (t_{0.05}, n\text{-}1 * \sigma) / \sqrt{n}$$

where $\overline{X}$ is the mean concentration of PAH in the sample, $t_{0.05}$, n-1 is the t-value at the 0.05 level for n-1 degrees of freedom, σ is standard deviation of PAH concentrations in the sample, and n the sample size.

BaP_{TEF} and BaP_{MEF} represent the toxicity and the mutagenicity factor respectively. BaP_{TEQ} and BaP_{MEQ} for the sum of seven carcinogenic PAHs ($\sum PAH_{7C}$) in the road dust were calculated as follows:

BaP_{TEQ} for $\sum PAH_{7C}$ = [BaA] x 0.1 + [Chry] x 0.01 + [BbFA] x 0.1 + [BkFA] x 0.1 + [BaP] x 1 + [IP] x 0.1 + [DahA] x 5

BaP_{MEQ} for $\sum PAH_{7C}$ = [BaA] x 0.082 + [Chry] x 0.017 + [BbFA] x 0.25 + [BkFA] x 0.11 + [BaP] x 1 + [IP] x 0.31 + [DahA] x 0.29

Table 3.2. TEFs and MEFs values used for toxicity and mutagenic potencies

PAH	TEF[a]	MEF[b]
BaA	0.10	0.08
Chr	0.01	0.02
BbF	0.10	0.25
BkF	0.10	0.11
BaP	1.00	1.00
IP	0.10	0.31
DBahA	5.00	0.29

Non-cancer risk

The hazard index (HI) serves as an approximation of non-carcinogenic risk and is determined by summing the hazard quotients (HQs) of individual exposure routes. The HQ is determined by dividing the chronic daily intakes (CDI) with the reference dose (RfD). The chronic daily intakes (CDIs) and HQs were determined by using the upper confidence level, $UCL_{95\%}$ concentrations of nine PAHs (NaP, Acy, Ace, Flu, Ant, Phen, Flt, Pyr, and BghiP) in samples (Iwegbue et al., 2021; Suman et al., 2016). In this study, hazard indices (HI) or quantified non-carcinogenic risk were used to analyse each exposure pathway for non-carcinogenic effects. Equations 3-11 were used to determine the non-carcinogenic risks from exposure to PAHs in road dust via inhalation, oral ingestion, and dermal contact for both adults and children.

$$Hazard\ index\ (HI) = \sum HQ = HQ_{ingestion} + HQ_{inhalation} + HQ_{dermal} \quad (3)$$

$$HQ = \frac{CDI_{nc}}{RfD} \quad (4)$$

$$CDI_{ing-nc} = \frac{C_{UCL} \times IngR \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \quad (5)$$

$$CDI_{inhal-nc} = \frac{C_{UCL} \times InhR \times EF \times ET \times ED}{PEF \times 24 \times AT_{nc}} \quad (6)$$

$$CDI_{derm-nc} = \frac{C_{UCL} \times SA \times AF \times ABS_d \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \quad (7)$$

where CDI is the chronic daily intake, denoted as $CDI_{ing\text{-}nc}$, $CDI_{inhal\text{-}nc}$ and $CDI_{derm\text{-}nc}$ are the chronic daily intake for non-cancer ingestion, inhalation and dermal absorption respectively. C_{UCL} is the upper confidence level, $UCL_{95\%}$ concentration, IngR is the ingestion rate (mg dust day^{-1}), EF is the exposure frequency (day $year^{-1}$), ED is the exposure duration (year), BW is body weight (kg), AT_{nc} represents the averaging time for non-carcinogenic effects (period over which exposure is averaged, days), InhR is the average daily inhalation rate (mg kg^{-1}-day), ET is the exposure time (hr d^{-1}), PEF is the particle emission factor (m^3 kg^{-1}), SA is the dermal surface exposure (cm^2 day^{-1}), AF is the dermal adherence factor (mg cm^{-2}), ABS_d is the dermal adsorption factor and CF is the conversion factor 10^{-6} is conversion factor.

Note: exposure via the inhalation pathway typically involves the low molecular weight volatile PAHs.

Cancer risk assessment

In this study, cancer risk assessment from environmental PAH exposures was used using USEPA standard models (residential scenarios) for evaluating ILCR (USEPA 1991; Peng et al. 2011).The incremental lifetime cancer risk (ILCR) was established to quantitatively assess the potential cancer risk from human exposure (adults and children) to environmental PAH contaminants based on the U.S. EPA standard models (Means, 1989; Shabbaj et al., 2018; Wang et al., 2011). The following assumptions form the basis for the models: (1) Humans are exposed to PAHs in dust through ingestion, inhalation, and dermal contact; (2) soil particle intake rates and emission rates are representative of PAH exposure; (3) some exposure parameters for the observed population are similar to those of reference populations; (4) the total carcinogenic risk is calculated by summing individual risks for each exposure pathway; and (5) lifetime exposure under a particular land use pattern is used to evaluate cancer risk (Man et al.,

2013; Qi et al., 2019). The incremental lifetime cancer risk for the three exposure routes is denoted as $ILCR_{ingestion}$, $ILCR_{inhalation}$ and $ILRC_{dermal}$. The ILCR (unitless) and is estimated based on the concentrations of the seven carcinogenic PAHs (Means, 1989; Soltani et al., 2015; United States. Environmental Protection Agency. Office of & Remedial, 1989; Zhang et al., 2016). The ILCR is calculated separately for ingestion, dermal contact, and inhalation (Equations 8–10). The total risk of cancer is determined by summing up the ILCR values (Equation 11), obtained from equations 8 to 10. The acceptable risk range for carcinogens established by the US EPA is between 10^{-6} and 10^{-4}. If the calculated risk falls below 10^{-6}, no further action is required. However, if the risk exceeds 10^{-4}, it is considered a cause for concern, and additional measures are required to reduce exposure and consequent risk (Ali Najmeddina, 2018; Keshavarzi et al., 2018). Based on these parameters, the lifetime cancer risks can be qualitatively described as follows: Risks less than or equal to 10^{-6} are classified as "very low," "risks ranging from 10^{-6} to 10^{-4} are considered low," "risks between 10^{-4} and 10^{-3} are classified as moderate," "risks ranging from 10^{-3} to 10^{-1} are deemed high," and "risks equal to or greater than 10^{-1} are classified as very high." (Iwegbue & Obi, 2016).

$$ILCR_{ingestion} = \frac{C_{ucl} \times IngR \times EF \times ED \times CF \times SFO_{ing}}{BW \times AT_{ca}} \quad (8)$$

$$ILCR_{inhalation} = \frac{C_{ucl} \times Inhal \times EF \times ED \times IUR}{PEF \times AT^{*}} \quad (9)$$

$$ILCR_{dermal} = \frac{C_{ucl} \times SA \times AF \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times AT_{ca}} \quad (10)$$

Total Cancer Risk = $ILCR_{ing}$ + $ILCR_{inh}$ + $ILCR_{derm}$ (11)

where $C_{UCL95\%}$ is the PAH upper concentration limit of dust (μg kg^{-1}) (Kurt-Karakus, 2012). The $C_{UCL95\%}$ (exposure-point upper confident limit) is thought to provide an estimate of the "reasonable maximum exposure"(Kurt-Karakus, 2012), which is the upper limit of the 95 percent confidence interval for the mean. To account for the non-normal distribution of PAH concentrations in dust samples, the "modified central limit theorem (CLT)" was used in determining the 95 percent upper confidence limit (UCL) in this study (Hazardous, 2002; Kurt-Karakus, 2012). IngR is the ingestion rate of dust (mg day^{-1}), EF is the exposure frequency (day $year^{-1}$), ED is the exposure duration (year), CF is the conversion factor, SFO is the oral slope factor for BaP based on causing cancer ability: $SFO_{Ingestion}$, $SFO_{Inhalation}$ and SFO_{Dermal} of BaP, are 7.3, 3.85 and 25 (mg kg^{-1} $day^{-1})^{-1}$, respectively (Jiang et al., 2014; Soltani et al., 2015), BW is average body weight, AT_{ca} is the average life span (day) for cancer effects, IUR is inhalation unit risk (3.85), PEF is the particle emission factor (cm^3 kg^{-1}), AT^* is the averaging time for exposure. SA is skin area (cm^2 day^{-1}), AF is skin adherence factor (mg cm^{-2}), and ABS is the dermal absorption fraction. GIABS is the gastrointestinal absorption factor. Values of exposure parameters and factors used for the incremental lifetime cancer risk assessment are given in Supplementary Information Table 3.

Results and discussion

Determination of the 16 US EPA priority PAHs in road dust was carried out on a C_{18}

reversed phase SUPELCOSIL® LC-PAH (250 × 4.6 mm, 5 m particle size) chromatographic column by a methanol: water gradient elution method to obtain a satisfactory separation of the PAHs in this study. All PAHs were detected except for dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene. A typical chromatogram of certified reference standard mixture (CRM47940), of the16 US EPA PAHs and sample obtained under the same optimal chromatographic conditions are provided in Supplementary Information Figures S1 – S4.

The accuracy of the analytical procedure was evaluated through recovery experiments by spiking 2 g of road dust sample with aliquots of a certified mixed standard at three different concentrations (5, 10, and 20 µg mL^{-1}) in triplicate. The RSD ranged from 0.033 to 4.846%. The mean recoveries of individual fifteen PAHs ranged between 100.602 to 118%. The recovery was further evaluated by spiking the road dust sample with deuterated chrysene (Chr-d_{12}), at 1, 2, and 5 µg mL^{-1} concentrations, extracted and analysed. The RSD ranged from 0.566 to 1.033%. The mean recovery ranged from 98.52 to 109.55%. Thus, the accuracy of the method was deemed adequate for all PAHs analysed, except for dibenzo[a,h]anthracene which has a very low solubility in methanol.

Spatial distribution

PAH concentrations in road dust samples collected from the city centre, residential and industrial areas varied between from 77 to 1488.85 µg kg^{-1}, 1192 to 2108 µg kg^{-1}, and 138 to 1409 µg kg^{-1} respectively. Due to the non-normal distribution of PAH concentrations, the study relied on median concentrations for comparison purposes. Median values were preferred over mean values as they are less influenced by outliers (Iwegbue et al., 2020; Keshavarzi et al., 2017; Soltani et al., 2015).

The observed trend of PAH concentrations in road dust from different areas of Durban is as follows: residential area > city centre > industrial area. The burning of biomass and other materials in residential areas is the primary contributor to the elevated levels of PAHs in the road dust. The highest concentration of carcinogenic PAHs was detected in road dust samples from residential areas, followed by those from the city centre, and then the industrial area. The high concentration of carcinogenic PAHs in the residential area samples could be attributed to the burning of biomass for cooking and heating, as well as garbage incineration, both of which contribute to the PAH load.

In contrast, the concentration of carcinogenic PAHs in the city centre was relatively lower when compared to that of the residential and industrial areas. The city centre is the central business district of Durban, and the presence of shops and shopping malls has led to increased traffic load. However, effective sweeping and washing of the roads and pavements has helped mitigate the potential increase in PAH load. The relatively low levels of PAHs observed in the industrial area may be due to the compliance of industries with environmental quality standards set out by environmental regulatory agencies.

BaA has the highest average concentration among PAH species in road dust from Durban city, with a value of 251.77 µg kg^{-1} in residential area samples. Ace follows with average concentrations of 195.78, 153.28, and 94.63 µg kg^{-1} in industrial areas,

residential areas, and the city center, respectively. Therefore, BaA and Ace are the dominant PAHs in the samples. On the other hand, BbF, Flt, and Acy have the lowest measurable concentrations among the PAHs, with average concentrations of 0.06, 0.52, and 0.76 μg kg^{-1} found in residential areas, the city center, and industrial areas, respectively.

The average concentration of low molecular weight PAHs (LMW 2-3 rings) is 709.24 μg kg^{-1}, accounting for 44.23% of the total PAHs (ΣPAHs). In contrast, the average concentration of high molecular weight PAHs (HMW 4-6 rings) is 635.85 μg kg^{-1}, which represents 39.66% of the ΣPAHs. The relatively high concentration of HMW PAHs in the ΣPAHs suggests that petrogenic sources are the major contributors. This is because the ratio of ΣLMW PAHs to ΣHMW PAHs is > 1 (1.12) (Ali Najmeddina, 2018; Liu et al., 2007; Soltani et al., 2015; Suman et al., 2016; Tobiszewski & Namieśnik, 2012; Yu et al., 2014). The ratio of carcinogenic PAHs (BaA, Chr, BbF, BaP, BghiP, and IndP) to the total PAHs (CanPAHs/ΣPAHs) is 0.40. This indicates a low cancer risk from exposure to PAHs in road dust.

The distribution of PAHs in dust samples differed depending on the location. In the city centre, the most prevalent PAHs were 3-ring PAHs, followed by 4-rings, 2-rings, 5-rings, and 6-rings. In residential and industrial areas, the most common PAHs were 4-ring PAHs, followed by 3-rings, 5-rings, 2-rings, and 6-rings. Figure 2 displays the profiles of the different ring PAHs found in road dust samples from these areas.

The abundance of low molecular weight (LMW) PAHs in road samples can be attributed to their origin from petrogenic sources (Liu et al., 2007). LMW PAHs have high vapour pressures, making them more susceptible to long-range transport and deposition on surfaces through air-surface exchange. This exchange allows for gradual transfer over long distances, facilitated by seasonal and diurnal temperature changes (Suman et al., 2016).

In contrast, high molecular weight (HMW) PAHs have low vapour pressures, causing them to preferentially partition into the particulate phase from the gas phase. This results in "single-hop" transport behaviour, and once deposited on a surface, they are resistant to air-surface exchange due to their low vapour pressure. Additionally, HMW PAHs are resistant to degradation and are not easily weathered by oxidation and photodegradation (Ali Najmeddina, 2018; Iwegbue et al., 2020; Soltani et al., 2015; Suman et al., 2016). These aforementioned factors likely contributed to the observed PAH distribution patterns.

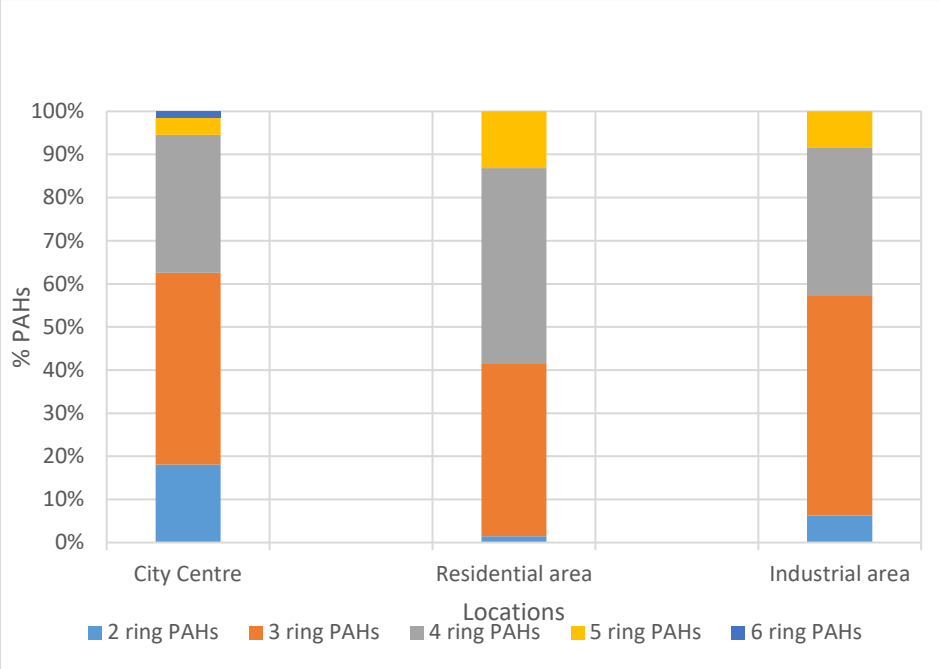

Figure 2. Profile of various ring PAHs in road dust from sampled areas.

Human health risk assessment

Non-cancer risk

The non-cancer risk expressed as the hazard quotient and hazard index of exposure to PAHs in road dust for child and adult in the study areas is shown in Table 3.8. The HQs of exposure to PAHs in road dust for child through ingestion, inhalation and dermal contact in city centre, residential and industrial areas ranged from 9.08×10^{-7} to 1.02×10^{-6}, 9.72×10^{-9} to 1.09×10^{-8}, and 4.42×10^{-4} to 5.08×10^{-4} respectively. The HQs of exposure to PAHs in road dust for adult through ingestion, inhalation and dermal contact in city centre, residential and industrial areas ranged from 2.72×10^{-7} to 9.93×10^{-7}, 1.19×10^{-8} to 8.61×10^{-7}, and 1.08×10^{-4} to 3.96×10^{-4} respectively. The contribution of exposure routes to the HI value in all the study areas for both children and adults followed a similar trend for HQs in the order: dermal > ingestion > inhalation.

The HIs of exposure to PAHs in road dust for both children and adults in the study areas are of the same order of magnitude in the following order: city centre > residential area > industrial area. The values are below the HI threshold value (HI > 1) to pose a considerable non-cancer risk. An HI value > 1 is considered a cause for concern for any potential adverse non-carcinogenic health effects (Means, 1989). This approach differs from the probabilistic method used for evaluating carcinogens. An HQ value of 0.01 does not imply a 1 in 100 chance of experiencing adverse effects, but rather indicates that the estimated intake is 100 times lower than the threshold level at which adverse health effects may occur (Means, 1989). However, dermal contact and ingestion have been determined to be the primary exposure pathways to PAHs for both children and adults at non-cancer risk in this study.

BaP toxicity

The BaP_{TEQ} and BaP_{MEQ} values for the carcinogenic PAHs found in the road dust samples from various locations within Durban city are presented in Table 3.9. The range of BaPTEQ and BaP_{MEQ} values determined were between 21.48 to 183.5 µg kg^{-1} and 23.96 to 176.75 µg kg^{-1} respectively. The samples from residential areas had higher BaP equivalent concentrations compared to samples from the city centre and industrial areas. This

suggests that a potential mutagenic and carcinogenic risk to residents from exposure to road dust. However, the BaP_{TEQ} concentrations determined in Durban city road dust samples were lower than those reported in urban road dust from other cities such as Lanzhou, Northwest China (Liu et al., 2019); Sao Paulo, Brazil (Bourotte et al., 2019); Bushehr, Iran (Keshavarzi et al., 2017); and Lagos, Southwest Nigeria (Iwegbue et al., 2020).

Table 3. BaP_{TEQ} and BaP_{MEQ} (μg kg^{-1}) concentrations in samples from the three areas.

	BaA	Chr	BbF	BaP	IndP	BaP_{TEQ}	BaA	Chr	BbF	BaP	IP	BaP_{MEQ}
City centre	10.12	0.02	1.89	8.91	0.54	21.48	8.3	0.166	4.72	8.91	1.68	23.96
Residential area	42.34	0.05	0.01	141.1	ND	183.5	34.72	0.92	0.01	141.1	ND	176.75
Industrial area	14.02	0.05	ND	19.64	ND	33.71	11.5	0.9	ND	19.64	ND	32.03

Carcinogenic risk

The carcinogenic risk (CR) factors linked with human exposure to PAHs in road dust from Durban city are presented in Table 3.10. The CR factors for accidental ingestion, inhalation, and dermal contact in children and adults were determined. For childhood and adult exposure by ingestion, inhalation, and dermal contact, the CR factors ranged from 1.07×10^{-3} to 4.55×10^{-3}, 1.81×10^{-7} to 9.07×10^{-7}, and 9.39×10^{-4} to 5.68×10^{-3}; and 2.93×10^{-6} to 5.51×10^{-4}, 2.93×10^{-6} to 5.51×10^{-4}, and 3.28×10^{-4} to 3.52×10^{-3} respectively. The CR values for the dermal contact route for the city centre for both children and adults, and the ingestion routes for adults are in the same order of magnitude (10^{-4}). The total CR values for residential areas for children and adults are also within the same order of magnitude (10^{-3}). In the industrial area, the CR values for the ingestion and dermal contact routes for children and the dermal contact route for adults in the industrial areas are in the same order of magnitude (10^{-3}). CR values $< 10^{-6}$ are generally considered as negligible, however, CR values $> 10^{-4}$ are of significant concern. The CR values between 10^{-6} and 10^{-4} are potentially carcinogenic to humans (Assessment, 2001; Khpalwak et al., 2019). Hence, the CR values indicate that accidental ingestion and dermal contact with PAH-laden urban dust particles substantially raise the total CR. Due to their growing organs, neurological systems, and immune systems, "hand-to-mouth" practices, and playing contact with dust, children are particularly susceptible to carcinogens. The overall CR values for children exposed to road dust by ingestion and dermal contact were greater than those for adults. The CR for inhalation in children was modest (10^{-7}), however the CR values for inhalation in adults are of the order of magnitude (10^{-6} to 10^{-4}) which indicate a significant potential for CR. The incremental lifetime cancer risk factors for exposure to PAHs in Durban city road dust are in the following order: residential areas > city centre > industrial areas, which indicates that the CR for residential areas is higher than for the other areas. The CR values for ingestion, dermal contact and the overall cancer risk are higher than the acceptable risk level of 10^{-6} to 10^{-4} (Assessment, 2001; Iwegbue et al., 2020; Khpalwak et al., 2019). Overall, the study highlights the significant CR associated with exposure to PAHs in road dust, especially for children, and the need for effective measures to mitigate this risk

Sources of PAHs in urban road dust

Diagnostic ratios

The main anthropogenic sources of PAHs in the environment are the incomplete burning of fossil fuels or biomass, crude oil spills, lubricating oils, and refined petroleum products. The types of PAHs emitted by a source are determined by the mechanisms that produce them (Tobiszewski & Namieśnik, 2012). Low-molecular-weight PAHs, for example, are typically produced by low-temperature processes, such as wood burning, whereas high-molecular-weight PAHs are typically produced by high-temperature processes, such as fuel combustion in engines (Ravindra et al., 2008; Tobiszewski & Namieśnik, 2012). Consequently, identifying the likely origins of PAHs is necessary for understanding the fate of PAHs in the environment and implementing measures to preserve and improve human and environmental health.

Some PAHs have been found to be useful markers, tracers, or signatures for different processes that release PAHs into the environment. The determination of the concentration profile and ratio of these PAHs enables the identification of the sources that contribute to their concentrations in various environmental matrices (Ravindra et al., 2008). According to the literature, certain individual PAHs or groups of PAHs can be used as indicators for various sources: (a) The primary source of low molecular weight PAHs (those with 4 rings), such as fluoranthene and pyrene, are heavy-duty vehicles or diesel trucks. These vehicles emit significantly higher levels of benzo[g, h, i]perylene and phenanthrene (Liu et al., 2015; Ravindra et al., 2008). On the other hand, the prevalence of high molecular weight PAHs like benzo[a]pyrene and dibenzo[a,h]anthracene is indicative of light-duty petrol vehicles (Ali Najmeddina, 2018; Ravindra et al., 2008). (b) Salt particles (used for salting roads during winter) are associated with phenanthrene, fluoranthene, and pyrene, which appear to adsorb volatile PAH emissions from motor vehicles (Keyte et al., 2013; Ravindra et al., 2008). (c) Pyrene, fluoranthene, and phenanthrene emissions are relatively high in incineration processes (Ravindra et al., 2008; Smith et al., 1995). (d) Chrysene and benzo[k]fluoranthene are the predominant emissions from coal combustion sources (Dong & Lee, 2009; Ravindra et al., 2008; Smith et al., 1995).

Several environmental forensics researchers have used diagnostic ratios or relative abundances to distinguish between diesel and petrol combustion emissions (Tobiszewski & Namieśnik, 2012; Yu et al., 2014), biomass combustion, and crude oil product PAH sources (Ravindra et al., 2008). Previous studies have shown that PAH isomer ratios is effective in PAH source identification (Ali Najmeddina, 2018; Bandowe & Nkansah, 2016; Jiang et al., 2014; Wang et al., 2008; Yu et al., 2014). Various diagnostic ratios of PAHs, such as the ratio of LMW (2-3 ring PAHs) to HMW (4-6 ring PAHs), Ant/(Phe + Ant), and Flt/(Flt + Pyr), can aid in emission sources identification, as outlined in Table 3.12. However, the Phe/Ant diagnostic ratio has limited discrimination ability, as the Phe and Ant pair have relatively small differences in thermodynamic capacity between these isomers, rendering it ineffective for PAH source identification (Lawal, 2017). On the other hand, the Flt/(Flt + Pyr) ratio has a

higher relative difference in thermodynamic stability between these isomers than the Phe and Ant pair, so it gives more accurate information about their combustion sources. This suggests that the Flt/(Flt + Pyr) ratio is an effective indicator for determining the origin of PAHs (Lawal, 2017). Additionally, mass 276 and 202 isomers have a good range in stability, indicating their potential as indicators of thermodynamic versus kinetic sources (e.g., petroleum vs. combustion), while masses 278 and 228 exhibit little promise as such indicators (Yunker et al., 2002).

The Ant/(Ant + Phe) ratios in the city centre samples are 0.03, while in residential and industrial areas, they are 0.34 and 0.41, respectively. The Flt/(Flt + Pyr) ratios for the city centre and industrial areas are 0.01 and 0.04, respectively, while for residential areas, it is 0.34. These ratios are typical of liquid fossil fuel and coal combustion (Liu et al., 2019; Liu et al., 2007; Yunker et al., 2002). The LMW/HMW PAHs ratios in the city centre and industrial areas are 1.67 and 1.34, respectively. LMW/HMW ratio > 1 indicates the predominance of a petrogenic source (Ali Najmeddina, 2018; Liu et al., 2007; Tobiszewski & Namieśnik, 2012). In contrast, the LMW/HMW PAHs ratio from residential areas is 0.71, which indicates a prevalence of pyrogenic sources. Overall, the PAH sources from the samples indicate both petrogenic and pyrogenic signatures, with the city centre samples showing major sources of petrogenic origin. Samples from the residential and industrial areas have both petrogenic and pyrogenic contributions.

Principal component analysis

The principal component analysis (PCA) method was used on individual PAH components to improve the accuracy of emission source identification of PAHs in Durban city road dust. PCA with varimax rotation was employed to investigate the main sources and to also statistically select source fingerprints. All factors with eigen values > 1 were extracted and subjected to rotation using the varimax method and Kaiser normalization, with the rotation converging after six iterations. The analysis revealed three principal components, corresponding to three categories of emission sources (see Table 3). Component 1, which accounts for 24.57% of the variance, exhibits high loading values for BaA and BaP, known markers of petrol emissions (Soltani et al., 2015) indicating that vehicular emissions (both petrol and diesel) constitute a significant proportion of PAHs in Durban city road dust. Additionally, component 1 also shows high Acy loading, a marker of wood combustion sources (Dong & Lee, 2009; Soltani et al., 2015), as well as Flt loading, a marker of oil combustion and coal combustion (Soltani et al., 2015), while BaA is attributed to natural gas combustion BaA (Annibal D. Pereira Netto1, 2006; Suman et al., 2016). Therefore, component 1 represents vehicular emissions and biomass combustion sources.

Component 2, which accounts for 17.04% of the overall variation, has high loading values for Flu and BbF, both of which are markers of wood combustion (Dong & Lee, 2009) and petrol emissions (Soltani et al., 2015) respectively. Component 3, which accounts for 10.15 % of the overall variation, exhibits solely a loading for Phe, a marker for combustion linked to wood and fossil fuels such as liquefied petroleum gas (LPG), natural gas, and coal (Soltani et al., 2015).

These findings imply that vehicular emissions, combustion related to petroleum products, and biomass combustion are likely the primary sources of PAHs in Durban city road dust.

Table 3. Principal component analysis of Durban city road dust PAHs.

	Component		
	1	2	3
Nap	-.332	.113	-.827
Acy	.666	.084	-.145
Ace	-.657	-.302	.188
Flu	.070	.878	-.027
Phe	-.117	.107	.581
Ant	-.233	-.344	.209
Flt	.539	-.457	.366
Pyr	-.353	.078	.336
BaA	.887	.089	.014
Chr	-.289	-.225	.373
BbF	-.333	.778	.070
Bap	.831	-.225	.127
BghiP	-.061	-.326	-.028
Eigenvalues	3.19	2.26	1.32
Variance (%)	24.57	17.04	10.15
Cumulative (%)	24.57	41.60	51.76

Note: Bold data (> 0.500) represent higher weightage of PAHs.

Conclusion and Recommendations

The study reported PAH concentrations in road dust from different areas of urban city, providing essential data for future assessments of PAH pollution related to urban traffic in Africa. Human toxicity assessment revealed potential mutagenic and carcinogenic risks, emphasizing the need for regulatory measures to reduce PAH emissions and protect human health. This research contributes valuable insights into PAH contamination in urban road dust and its environmental and health implications.

Recommendations

Government regulatory agencies should enact legislation to prevent PAH emissions into the environment from anthropogenic sources in order to manage the potential impact on human health.

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