Science Forum (Journal of Pure and Applied Sciences)

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

Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons in Urban Road Dust

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Abstract

In this study, a cost-effective and environmentally sustainable analytical method was developed for the detection and quantification of 16 polycyclic aromatic hydrocarbons (PAHs) identified under the US EPA Consent Decree in urban road dust. Methanol was employed both as the sole extraction solvent and as the organic phase in a methanol–water gradient high-performance liquid chromatography (HPLC) system, enabling efficient separation and analysis. Road dust samples were collected from diverse urban environments, including residential, industrial, and city center locations. Ultrasound-assisted extraction was applied to enhance PAH recovery. The measured concentrations of PAHs ranged from 77 to 1488.85 $\mu g\ kg^{-1}$ in city center dust, up to 2108 $\mu g\ kg^{-1}$ in residential areas, and between 138 and 1409 $\mu g\ kg^{-1}$ in industrial zones. The method achieved low detection (0.33–37.98 $\mu g\ kg^{-1}$) and quantification limits (0.99–22.87 $\mu g\ kg^{-1}$), along with satisfactory average recovery rates ranging from 69% to 88%. Precision was demonstrated through acceptable intra-day (78.91%–110.43%) and inter-day (75.30%–114.65%) variability. Health and ecological risks associated with the detected PAHs were assessed using toxicity equivalency factors (TEFs), hazard indices (HIs), incremental lifetime cancer risks (ILCRs), and ecological risk quotients (ERQs). While the PAHs in road dust were not found to pose significant human health risks, a moderate ecological risk was identified. Source apportionment analysis indicated that the predominant contributors to PAH contamination were combustion-related, specifically from gasoline and diesel fuel sources. Overall, the study demonstrates the potential of this simplified, green analytical approach for effective environmental monitoring of PAHs in urban road dust, especially in resource-limited settings.

Keywords
Road dust,
Polycyclic aromatic hydrocarbons,
High performance liquid Chromatography,
Methanol extraction,
Ecological risk assessment.

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INTRODUCTION

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of pervasive organic environmental contaminants. They are characterised by their multiple fused aromatic rings comprised of carbon and hydrogen, which make them both hydrophobic and lipophilic (Godefroy et al., 2005). Although PAHs may exhibit similar behaviour in the environment, each PAH compound possesses a distinct set of physical and chemical properties. At room temperature, solids made of pure PAH compounds are colorless, white, or pale yellow (Abdel-Shafy & Mansour, 2016; Kim et al., 2013). PAHs are generally characterised by their high melting and boiling points, low vapour pressures, low water solubilities, and high Henry's Law constants. Due to their hydrophobic nature, PAHs have a greater tendency to bind to organic matter in soil. PAHs are formed by both natural and anthropogenic processes and have the ability to move over long distances in the atmosphere due to their tendency to partition from the gas phase to the particulate phase.

The use of petroleum products for transportation, industrial operations like steel and aluminium production, power generation, coal combustion, waste incineration, agricultural burning, and residential heating, among numerous other activities, has resulted in widespread environmental pollution. The major sources of anthropogenic PAHs are pyrogenic and petrogenic, generated by incomplete combustion of fuels and biomass. PAHs are present from various sources, such as engine exhaust, cigarette smoke, coal and wood smoke, and gas and oil-fired burner emissions, leading to numerous point sources of PAHs in urban areas. Therefore, the sources of PAH contamination of the environment are mainly anthropogenic activities such as incomplete combustion of fossil fuels (petroleum and coal) and biomass, vehicular traffic, and industrial emissions (Lawal, 2017a; D. Lorenzi et al., 2011). Instead of undergoing complete oxidation into carbon dioxide, the carbon undergoes intricate pyrolysis and pyro-synthesis mechanisms that result in the generation of hydrocarbon fragments and complex polycyclic aromatic structures during these processes (Cantú; Connection et al., 1998; T. M. Mogashane et al., 2020; Shi et al., 2011) . Additionally, PAHs enter the environment through crude oil and coal tar contamination, as well as various petroleum products from refineries (Neff et al., 2005; Stout et al., 2015). Although natural processes such as forest fires, volcanic eruptions, and biosynthesis by algae and bacteria also generate PAHs, their contribution is negligible in comparison to the anthropogenic processes (Wang et al., 2011; B. Yu et al., 2014).

PAHs occur as complex mixtures of hundreds of isomers, and both the International Agency for Research on Cancer (IARC) and the Agency for Toxic Substances and Disease Registry (ASTDR)(Us, 1995) have found that some of these isomers are human and animal carcinogens (Us, 1995). PAHs with planar structures, such as benzo[a]pyrene and dibenzo[a,h]anthracene, are highly potent carcinogens due to their high activity in the bay region. In contrast, non-planar

carcinogens tend to act as synergists to carcinogenic or mutagenic activity.

Because of the growing concern about pollution from persistent organic pollutants, the United Nations Environmental Programme (UNEP) (Adams et al., 2018; Motelay-Massei et al., 2005), the United States Environmental Protection Agency (US EPA) (Cai et al., 2009; Fisner et al., 2013; Keith, 2015), the Canadian Environmental Protection Act (CEPA) (Karbalaei et al., 2018; Sun et al., 2017), and the European Environment Agency (EEA) (Guerreiro et al., 2014; Pacyna, 2011) have listed polycyclic aromatic hydrocarbons (PAHs) as priority environmental pollutants (Karbalaei et al., 2018; Kumar et al., 2014; Sun et al., 2017).

The United States Environmental Protection Agency (USEPA) has identified 16 unsubstituted PAHs as "Consent Decree" priority pollutants, out of the hundreds present in the environment. Some of these PAHs are possible or probable human carcinogens. The International Agency for Research on Cancer (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[1,2,3-c,d]pyrene (IndP) [23]. Benzo[a]pyrene is considered the most toxic PAH (Nisbet & LaGoy, 1992). The International Agency for Cancer Research (IARC) has determined that exposure to PAHs is the major carcinogenic risk in urban environments (Soltani et al., 2015; Straif et al., 2005).

The 16 US-EPA priority PAHs are classified into two groups: non-carcinogenic and carcinogenic PAHs. The non-carcinogenic PAHs consist of those low molecular weight with 2- to 4-benzene rings and include: naphthalene, acenaphthene, anthracene, phenanthrene, acenaphthylene, fluorene, fluoranthene, and pyrene. The carcinogenic PAHs are those high molecular weight with 4- to 6-benzene rings, such as benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[l,2,3-cd] pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i] perylene. High molecular weight PAHs (HMW PAHs) are primarily produced by anthropogenic activities in urban areas. They pose a more significant threat to the environment and human health than the low molecular weight PAHs (LWM PAHs) due to their stability and carcinogenic potential (Tumelo M. Mogashane et al., 2020; B. Yu et al., 2014). Human exposure to PAHs occurs through ingestion, inhalation, and dermal contact with water, air, sediment, soil, and food (Šimko, 2002; Veiga et al., 2014). The estimated intake of PAHs by non-smokers ranges from 3 to 17 $\mu g\ day^{-1}$ (Scherer et al., 2022).

Many 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; Binbin Yu et al., 2014), and reproductive toxicity properties that pose threat to human and environmental health (Lawal, 2017b; 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, 2017b), food (Giorgia Purcaro n, 2013; Binbin Yu et al., 2014) and biological fluids (K. Okona-Mensah et al., 2005; Ramesh et al., 2015).

Many analytical methods have been reported for detecting and quantifying PAHs in various media (Ali Najmeddina, 2018; Lawal, 2017b; Lee et al., 1981; Scinicariello & Buser, 2014; Šimko, 2002; Traviesa-Alvarez et al., 2007; Veiga et al., 2014). High performance liquid chromatography with ultraviolet or fluorescence detection (HPLC-UV/FLD), is considered suitable for the analysis of the PAHs in any type of medium due to its high sensitivity and selectivity in distinguishing structural isomers, making it a more favourable technique than gas chromatography with flame ionisation detection (GC-FID) or gas chromatography-mass spectrometry (GC-MS) (Çorman et al., 2017; Šimko, 2002). HPLC-UV/FLD has been widely used in official methods recommended by agencies like the US EPA and the International Standards Organisation. For instance, according to US EPA Method 610, HPLC-UV/FLD is the best method for analysing the 16 EPA priority PAHs since GC-MS is unable to effectively differentiate between four isomeric pairs: anthracene and phenanthrene, chrysene and benzo[a]anthracene, benzo[b]fluoranthene and benzo[k]fluoranthene, and dibenzo[a,h]anthracene and indeno[1,2,3-c,d]pyrene (Wise et al., 1990).

Urban road dust contains a variety of 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 have a negative impact on the environment. PAHs found in road dust come from a variety of sources, including the combustion of petroleum products for transportation, industrial processes, power generation, waste incineration, and domestic heating. Leaks from poorly maintained vehicles and unburned fuels from car exhausts also contribute to the presence of petrogenic PAHs in street dust. Tyres and asphalt debris also contain PAHs, making road dust a non-point source of these contaminants (Boonyatumanond et al., 2007). It is important to note that individually manufactured PAH compounds for analytical purposes do not constitute environmental contamination (K. B. Okona-Mensah et al., 2005).

Durban, South Africa's thriving commercial and industrial activities, have led to a significant increase in traffic density, resulting in a substantial amount of polycyclic aromatic hydrocarbons (PAHs). Certain industries, including petroleum refining and cabotage, contribute significantly to the PAH load. Despite the numerous reports available on the distribution, sources, and potential risks of PAHs in urban road dust in Asian, European, and American cities, only a limited number of studies have been conducted in African cities, particularly

Durban, South Africa. Therefore, the study aimed to establish a simple and cost-effective method for the determination of concentrations, sources, and exposure risks of PAHs in Durban Road dust. The results of this study are critical for managing urban environmental quality with regards to PAH contamination in urban settings, implementing pollution abatement strategies, and serving as a valuable resource for the scientific community.

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 km^2, 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, which 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 around 24 °C in the summer, while in the winter it is 17 °C (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 1). The coordinates for each sample collected in this work are listed in Supplementary Materials Table SI 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.

Ecological risk of PAHs in road dust

The risk quotient (RQ) method can be used to evaluate the potential risk posed to organisms by exposure to PAHs in road dust. Equation 1 was used to calculate the risk of organisms being exposed to each PAH in a medium.

$$RQ_j = \frac{C_{PAHs}}{C_{QV}}$$

where C_{PAHs} is the average concentration of a specific PAH in the medium and C_{QV} is its quality value.

The RQs were determined from the maximum permissible concentrations (MPCs) and negligible concentrations (NCs) for the specific PAH, as given by Equations 2 and 3. The environmental quality for negligible concentrations (NCs) and maximum permissible concentration (MPCs) were obtained from (Di Wang 1 ID 2018; Gereslassie et al., 2018; Kalf et al., 1997). PAH congeners with the same toxicity equivalence factor (TEF) have similar human and ecological health impacts (Gereslassie et al., 2018). Therefore, the environmental quality risk quotient was calculated using PAH congeners with the same TEF values. The individual and total risk quotient were calculated using Equations 2 and 3 (Gereslassie et al., 2018; Qi et al., 2016):

$$RQ_{(MPCs)} = \frac{C_{PAHs}}{C_{QV(MPCs)}}$$

$$RQ_{(NCs)} = \frac{C_{(PAHs)}}{C_{(QV(NCs)}}$$

The $C_{QV(MPCs)}$ are the concentrations above which the risk of adverse effects on an ecosystem is unacceptable, whereas $C_{QV(NCs)}$ are concentrations below which the occurrence of adverse effects is regarded as negligible (Cao et al., 2010; Kalf et al., 1997). Kalf et al. (Kalf et al., 1997) investigated the toxicity of ten PAHs, excluding Acy, Ace, Flu, Pyr, BbF, and DahA. The toxic equivalency factors (TEFs) of the individual PAHs (Kalf et al., 1997; Nisbet & LaGoy, 1992) were used to evaluate the NCs and MPCs of the remaining six PAH compounds, with the premise that compounds with similar TEF values exhibit similar toxicity.

The risk quotients ($RQ_{\sum PAHs}$) based on the maximum permissible concentrations ($RQ_{\sum PAHs(MPCs)}$) and PAH negligible concentrations ($RQ_{\sum PAHs(NCs)}$) are summed up using Equations 4 – 9. Only RQ values greater than one are included in the sums when calculating these total risks.

$$RQ_{\sum PAHs} = \frac{C_{\sum PAHs}}{C_{QV(\sum PAHs)}}$$

$$RQ_{\sum PAHs(MPCs)} = \frac{C_{\sum PAHs}}{\sum C_{QV(MPCs)}} \quad (5)$$

$$RQ_{\sum PAHs(NCs)} = \frac{C_{\sum PAHs}}{\sum C_{QV(NCs)}}$$

$$RQ_{\sum PAHs} = \sum_{i=1}^{16} RQ_j \ (RQ_j \geq 1) \quad (7)$$

$$RQ_{\sum PAHs(MPCs)} = \sum_{i=1}^{16} RQ_{j(MPCs)} \ (RQ_j \geq 1) \quad (2) \quad (8)$$

$$RQ_{\sum PAHs(NCs)} = \sum_{i=1}^{16} RQ_{j(NCs)} \ (RQ_j \geq 1) \quad (3) \quad (9)$$

The following is a qualitative classification of RQ values: $RQ_{(NCs)} < 1.0$ indicates that the individual PAH is likely of negligible concern, whereas $RQ_{(MPCs)} > 1$ indicates that contamination by the individual PAH is severe and necessitates some control and remedial action to reduce the risk.

The ecosystem risk assessment of 16 US EPA PAHs, the $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ for specific PAH were determined. RQ(NCs) < 1.0 indicate that contamination from an individual PAH was of negligible concern. $RQ_{(NCs)} \geq 1.0$ and $RQ_{(MPCs)} < 1.0$ indicated that individual PAH contamination was of moderate risk. $RQ_{(MPCs)} > 1.0$ indicate that contamination from individual PAH posed a high risk and necessitates some control

and remedial action to reduce the risk. The $RQ\sum PAHs_{(NCs)}$ and $RQ\sum PAHs_{(MPCs)}$ for all the PAHs are calculated by summing up the $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ for all the PAHs determined respectively. The total ecological risk, $RQ\sum PAHs$ was calculated by taking into account the individual RQMPCs and RQMPCs ≥ 1. Table 1 provides an overview of the ecological risk associated with individual PAHs and the total PAHs. The carcinogenic risk of individual PAHs was determined by the concentration of each PAH and its corresponding toxicity equivalency factor.

Table 1. Ecological risk grading of individual PAH and ∑PAHs (Gereslassie et al., 2018).

Individual PAHs			**∑PAHs**		
Risk grade	$RQ_{(NCs)}$	$RQ_{(MPCs)}$	Risk grade	$RQ\sum PAHs_{(NCs)}$	$RQ\sum PAHs_{(MPCs)}$
Low risk	< 1	< 1	Risk-free	< 1	< 1
Medium risk	≥ 1	< 1	Low risk	≥ 1; < 800	< 1
High risk	≥ 1	≥ 1	Medium risk 1	≥ 800	< 1
			Medium risk 2	< 800	≥ 1
			High risk	≥ 800	≥ 1

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.

The method developed is appropriate for the cost-effective and environmentally friendly determination of PAHs in environmental matrices such as road dust. The method employs a one-step sample extraction procedure for road dust samples. There was no need for clean-up because the injection of sample extracts caused no significant backpressure in the analytical column. The LC chromatograms revealed that all of the PAH molecules were selectively eluted under the optimised chromatographic conditions. Methanol is a better organic phase eluent than acetonitrile, which is both more expensive and toxic.

Spatial distribution and composition of PAHs in Durban city road dusts

The concentrations and corresponding statistics of PAHs found in road dust from the different areas of Durban city studied are presented in Table 3.6. 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.

Currently, there are no regulatory guidelines for PAHs in road dust, despite the potential risks associated with exposure to PAHs in road dust. However, exposure limits for PAHs do exist for atmospheric PAHs, water, food products and soil. Therefore, the limits for PAHs in soil were used as a reference value in this study. This is a reasonable assumption since soil contributes approximately 30–40% to dust (Cachada et al., 2016; Maliszewska-Kordybach, 1996). In the Netherlands, the limit for PAHs in soil is 1500 µg kg^{-1}, while the intervention limit is set at 40,000 µg kg^{-1} (Cachada et al., 2016; Iwegbue et al., 2020). The Dutch government has also established national maximum limits for various land use categories; 6,800 µg kg^{-1} for residential land and 40,000 µg kg^{-1} for industrial land.

Similarly, the German government has set precautionary limits of 300 and 1000 $\mu g\ kg^{-1}$ for BaP in soils with organic matter contents ≤ 8% and > 8%, respectively (Cachada et al., 2016; Iwegbue et al., 2021).

Maliszewski-Kordybach has proposed four categories for classifying the contamination levels of polycyclic aromatic hydrocarbons (PAHs) in soil, which are as follows: heavily contaminated (>1000 $\mu g\ kg^{-1}$), slightly contaminated (600-1000 $\mu g\ kg^{-1}$), contaminated (200-600 $\mu g\ kg^{-1}$), and not contaminated (< 200 $\mu g\ kg^{-1}$) (Maliszewska-Kordybach, 1996).

A comparison between the concentrations of PAHs in road dust for various cities worldwide and those found in Durban shows that while PAH concentrations in Durban road dust are higher than those in Tehran, Iran, they are lower than those in Newcastle upon Tyne, North East England, Bangkok, Thailand, Cairo, Egypt, Lagos, Nigeria, and Xincheng, China. This difference in concentration could be attributed to the effective street sweeping and washing practices implemented in Durban, especially in the city centre (Angeliki Karanasiou, 2014).

Based on the Maliszewski-Kordybach classifications of PAH contamination levels in soil (Maliszewska-Kordybach, 1996), it was determined that all road dust samples taken in Durban were below the safe level. The results show that the level of PAH contamination in the road dust of Durban is relatively low in toxicity. Nonetheless, the median BaP concentrations for all samples analyzed ranged from 1.65 to 13.41 µg kg^{-1}, which is below the German precautionary levels for soil with organic matter compositions of ≤ 8 and > 8%, which are 300 µg kg^{-1} and 1000 µg kg^{-1}, respectively.

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; Binbin Yu et al., 2014).

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.

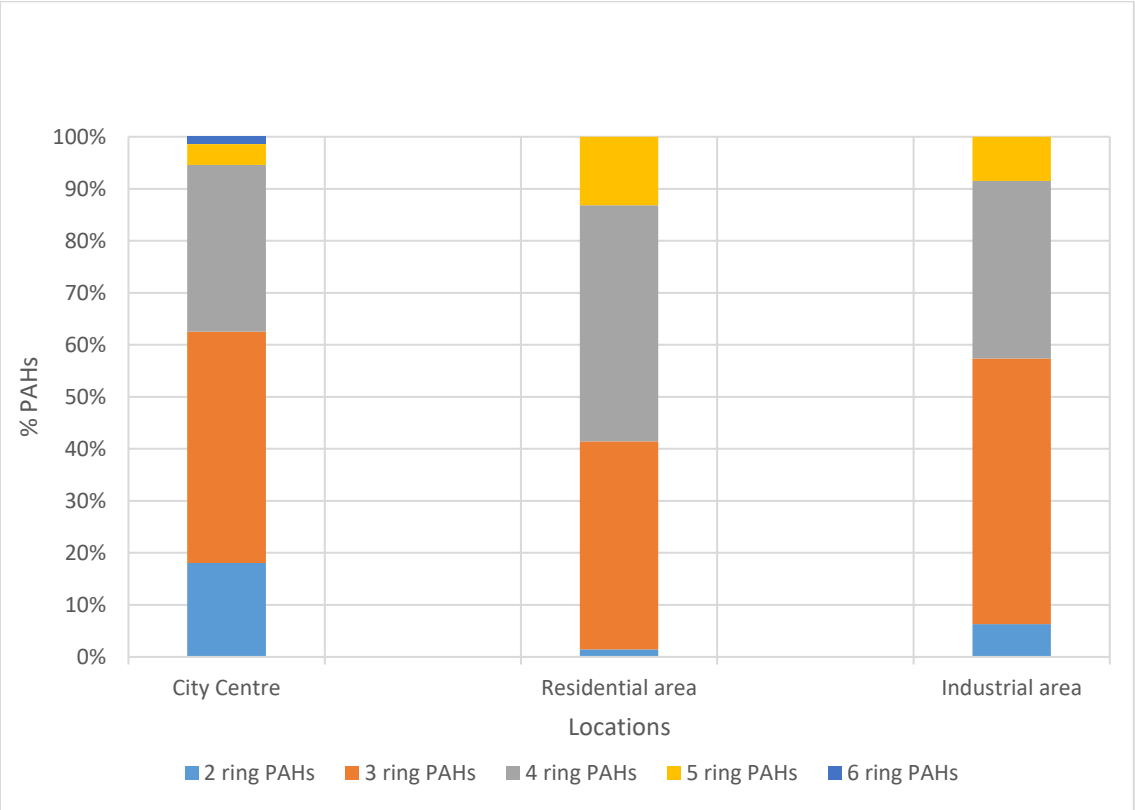

Figure 2. Profile of various ring PAHs in road dust from sampled areas.

Ecological risk assessment

Environmental assessment of organic pollutants such as PAHs is crucial for safeguarding public health. Road dust have been identified as the predominant source of organic pollutants such as PAHs. The ecological risk of PAHs in urban road dust is a complex issue that depends on various factors,

such as the concentration of PAHs, organisms' exposure routes, and species. PAHs in urban road dust pose immense ecological risk due to their influence on the quality of the soil and water. Another possible ecological risk of PAHs in urban road dust is their potential to bio-accumulate and magnify in the food chain. Ecological risk assessment model for PAHs in road dust is still limited without a suitable model (Anh et al., 2019). Therefore, in this study, the potential ecological risk assessment of PAHs road dust was by direct comparison with environmental quality guideline values for related environmental media such as soil. This assumption is reasonable since dust is a type of soil type that primarily consists of sand-sized particles (López et al., 2015; Maliszewska-Kordybach, 1996; Pettijohn et al., 1987).

The risk quotient for negligible concentrations ($RQ_{(NCs)}$) for the individual PAHs were above 1 in most of the studied areas except for Acy, Ant, Flt, Chr and IndP. On the other hand, the risk quotient for the maximum permissible concentrations ($RQ_{(MPCs)}$) of individual PAHs were generally less than 1 in most of the areas, suggesting that exposure to individual PAH concentrations in the city road dust particles poses a low ecological risk to organisms.

The $RQ_{\sum PAHs(NCs)}$ for the 15 PAHs ranged from 181.57 to 389.80 µg kg^{-1} with none of the areas having values > 800. In addition, the $RQ_{\sum PAHs(MPCs)}$ for these areas were also > 1, indicating a low ecosystem risk associated with an organism's exposure to PAHs in dust particles from these areas in Durban city. The $RQ_{\sum PAHs(NCs)}$ for PAHs in road dust from city centre, and residential and industrial areas were less < 800 but their $RQ_{\sum PAHs(MPCs)}$ > 1, indicating a medium risk 2 associated with an organism's exposure to PAHs in dust from these areas.

Sources apportionment

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; Binbin 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; Binbin 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, 2017b). 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, 2017b). 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 (refer to Table 3.12), 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 3.13). 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.

Conclusion and Recommendations

In this study, a validated HPLC method was developed for the extraction and quantification of fifteen priority PAHs in road dust samples, utilizing a methanol-water gradient elution, which is a novel approach in environmental sample analysis. The method is cost-effective and environmentally friendly and employs a one-step sample extraction, because methanol is a better organic phase eluent than acetonitrile, which is both more expensive and toxic. The method demonstrated excellent recovery, selectivity, sensitivity, precision, and accuracy for these PAHs. It was successfully applied to quantify these PAHs in road dust samples, revealing a change in elution order compared to the conventional acetonitrile-based method. This approach using methanol offers cost savings without compromising resolution. 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. Ecological risk assessment indicated a moderate risk to organisms, while 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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