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Exposure and comparative risk assessment of PAHs in dust from roadside solid surfaces in three semiurban areas of Eastern Nigeria†

John Kanayochukwu Nduka, [ID] *[ad] Chideraa Courage Offor, [ID] *[a] Henrietta Ijeoma Kelle[b] and Perpetua Chioma Okafor[c]

Settled road dust is a sink for polycyclic aromatic hydrocarbons (PAHs), which have hazardous effects on ecosystems. Sampled dust from the solid surfaces of Awka, Ekwulobia, and Rumuodomaya-Ogale, Eastern Nigeria, was collected between December 2019 and March 2020, sieved to obtain uniform particle size, subjected to solvent extraction, and subsequently purified using silica gel/Na_2SO_4 column. The extracts were analyzed using gas chromatography coupled with a flame ionization detector (GC-FID), and the measured PAH concentrations followed the decreasing order: Rumuodomaya-Ogale > Ekwulobia > Awka. Dusts from the Eze-Uzu junction, Ekwulobia roundabout axis, Victoria hospital premises, Eleme junction, and Elelenwo-Akpajo bypass had total PAH concentrations ($\mu g\ g^{-1}$) that ranged from 0.480−0.613, 0.672−0.926, 0.739−1.388, 1.497−7.915, and 1.423−7.037, respectively. The concentration of benzo(*a*)pyrene equivalent (BaPE) ($\mu g\ g^{-1}$) in dust samples varied across locations as follows: Eze-Uzu junction (0.0047−0.0690), Government house (0.0047−0.0689), Ekwulobia roundabout (0.0720−0.1942), Victoria hospital premises (0.0720−0.2291), Eleme junction (0.2570−1.4930), and Elelenwo-Akpajo bypass (0.2455−1.3934). Benzo(*a*)pyrene total toxicity equivalence (BaP-TEQ) values in dust of all the sampled locations indicated no cancer risk (CR) to residents, with benzo(*a*)pyrene as the main contributor. In all cases, CRing values were higher in children than in adults. PAHs in dust indicate contamination *via* vehicular emissions, waste burning, and incomplete diesel or gasoline combustion. The point source of PAH in the study areas—open waste burning and the explosion of diesel-laden vehicles—should be regulated.

Environmental significance

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants found in ambient air, occurring both in the gas phase and attached to aerosol particles. They are toxic to the ecosystem and human health, and dust serves as a sink for them. More than 75% of economic and outdoor activities, such as roadside hawking, petty trading, shops, residential areas, transporters, garages, and auto-workshops, are situated on Nigerian roads, and roadside dwellers are exposed to PAH-contaminated dust. Herein, we observed that significant concentrations of PAHs were present in dusts in the three semi-urban areas of Eastern Nigeria, which are sufficient to cause non-cancer effects. Data from this study will provide baseline information for reference and assist policymakers and public health providers in Nigeria with information regarding the PAH pollution status in semi-urban areas of Eastern Nigeria.

[a]Environmental Chemistry and Toxicology Research Unit, Pure and Industrial Chemistry Department, Nnamdi Azikiwe University, P.M.B 5025 Awka, Anambra State, Nigeria. E-mail: johnduka2000@yahoo.co.uk; co.offor@unizik.edu.ng; Tel: +234 7039541583; +234 7061658455

[b]Department of Chemistry, Faculty of Science, National Open University, Abuja, Nigeria

[c]Department of Natural Sciences, School of General Studies, Federal Polytechnic, Oko, Nigeria

[d]Department of Industrial Chemistry, Madonna University, Elele, Rivers State, Nigeria

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1 Introduction

The growing human population in Nigeria and the rise in the middle class, occasioned by more oil revenue between 1999 and 2015 and heralded by a return to democratic rule and attendant wage increases, have led to a high volume of vehicular usage. Records from Nigeria's Federal Road Safety Commission (FRSC)[1] state that more than seven million vehicles plied Nigerian roads in 2007. Additionally, statistics showed that automobile ownership in Nigeria grew by 693% from 1970 to 2010.[2] These figures must have increased between 2010 and 2020 before this study. Nigeria's road transport sector depends on cross-border importation of "second-hand vehicles" that

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easily wear and decompose owing to corrosion of auto components and poor road infrastructure.[3] Therefore, the rapid growth in automobile ownership in Nigeria partly implies severe traffic congestion and vehicle exhaust emissions, thereby releasing a reasonable concentration of polycyclic aromatic hydrocarbons (PAHs) into the environment.[2] The PAHs, consisting of two or more fused aromatic rings in different structural configurations, primarily originate from pyrogenic, petrogenic, and biological sources.[4,5] When dispersed into the atmosphere, PAHs exist in vapour and solid phases.[6] High molecular weight (HMW) PAHs, with characteristic 4–6 rings, easily form bonds with dust particulates in the outdoor environment.[5]

Atmospheric PAHs from automotive exhaust, wood and waste burning, oil and gas exploration, paintings, asphalt pavement operation, and solvent application in small industries and workshops[7,8] interact with road dust and form sinks *via* wet and dry depositions. This interaction worsens during periods of high traffic density (hours of commuting to and from work and school). The small particle size and pore size of dust aid in easy PAH movement from one location to another.[6] Humans are generally exposed to PAHs in dust from roadside solid surfaces *via* inhalation, ingestion, and dermal contact. Breathing contaminated ambient air, eating smoked fish, smoking cigarettes, or inhaling smoke from open fireplaces have been reported as major routes of PAH exposure.[6,9–11] Children between ages 1 and 4 are mostly at a higher risk of exposure to contaminated dust owing to their regular habit and activity of hand-to-mouth contact while playing on the floor, tender and weak developing bodies, and non-advanced immune systems.[12,13] When inhaled, dust containing PAHs may have carcinogenic, mutagenic, and teratogenic effects on different body organelles[14,15] and interrupt hormone secretion in animals and humans.[16,17] Benzo(*a*)pyrene, benzo(*a*)anthracene, benzo(*k*)fluoranthene, and benzo(*b*)fluoranthene are lung cancer triggers in humans.[18] Chronic health problems, such as decreased immune function, cataracts, kidney damage, breathing problems, asthma-like symptoms, and lung function abnormalities, are associated with exposure to high PAH concentrations.[6] PAH concentrations in road/street dust in Asia,[19,20] Australia,[21] America[22,23] and Europe[24] have been studied. In Africa, and particularly in Nigeria, more than 75% of economic and outdoor activities, such as roadside hawking, petty trading, shops, residential areas, transporters, motor parks, mechanic workshops, markets, hotels, and food vending, are situated on Nigerian roads, which might pose risks to humans. Despite this, PAH studies on outdoor dust in the Nigerian environment have been studied only by Iwegbue and team[25–28] and Yusuf *et al.*[29] These Nigerian researchers conducted a single-month study of PAHs in dust without considering the direct effect of traffic density on PAH concentration. Hence, this study is primarily aimed at monitoring PAH concentrations in road dust on different solid roadside surfaces at selected locations in Awka, Ekwulobia, and Rumuodomaya-Ogale localities of Eastern Nigeria from December 2019 to March 2020 and their potential health risk impacts on children and adults. Presently, there is no reported

study on PAH concentrations in dust at these sample locations. Hence, data from this study will provide baseline information for reference and assist policymakers and public health providers in Nigeria with information regarding PAH pollution status in the semi-urban areas of Eastern Nigeria.

2 Materials and methods

2.1 Study area

The sampling areas of Awka, Ekwulobia, and Rum-Ogale, as shown in Fig. 1, were identified and selected to accommodate for differences in PAH pollution across functional zones. Awka, a university town and the capital of Anambra State, represents a zone with a mixture of residential and commercial activities and minor industrial activities. It covers an area of 1425 km^2 with a density of 760 people per km^2. The city is located between latitudes 06° 06′ N and 06° 16′ N and longitudes 07° 01′ E and 07° 10′ E. The dry season begins from late October to March, with prevailing dust-laden winds, while the rainy season starts from April to October. Ekwulobia, a small, semi-urban town located in Anambra State, is known for its moderate residential and commercial activities. The South-Eastern town (lat. 6.024628 with GPS coordinates 6° 1′28.6608″N and long. 7.079426 with GPS coordinates of 7° 4′45.9336″E) has an altitude of 276 m. The area has a prevailing tropical savannah climate with an annual average temperature and rainfall of 320 °C and 1033 mm, respectively. Awka and Ekwulobia have an estimated population of 2.9 million according to the National Population Commission Census.[30] Rum-Ogale (4.88°N, 7.02°E; 4.79°N, 7.12°E) located in the Niger Delta (Rivers State), known for numerous industrial activities, represents PAH pollution in an industrialized zone. These towns are oil and gas-rich enclaves of Eastern Nigeria. Large-scale industrial manufacturing outfits, such as oil and gas exploration companies, gas plants, fertilizer plants, refineries, filling stations, recycling companies, and plastics and paper companies, are located in Rivers. Rumuodomaya and Ogale have population densities of over one million according to the 2018 National Bureau of Statistics.[30]

2.2 Sample collections

There are no globally accepted sampling methods for road/street dusts.[8] Therefore, road dust samples were collected from solid surfaces (signposts, billboards, roundabout pavement, roof sheets, *etc.*), as may be available on busy roads at each sampling location of the three semi-urban areas of Awka (Enugu-Awka highway and Eke-Awka road), Ekwulobia (Ekwulobia-Uga highway and Ekwulobia-Oko road), all in Anambra State, and Rumuodomaya-Ogale roads, Rivers State, between December 2019 and March 2020. PAH particulates from recent traffic emissions, industrial activities and atmospheric deposition adhere so easily to surface dust and could be easily inhaled, ingested and deposited on human skins.

On the Enugu-Awka highway, two points were designated for sampling: the Eze-Uzu junction (Point 1) and the Government House road (Point 2), while on the Eke-Awka road, the Coca-Cola
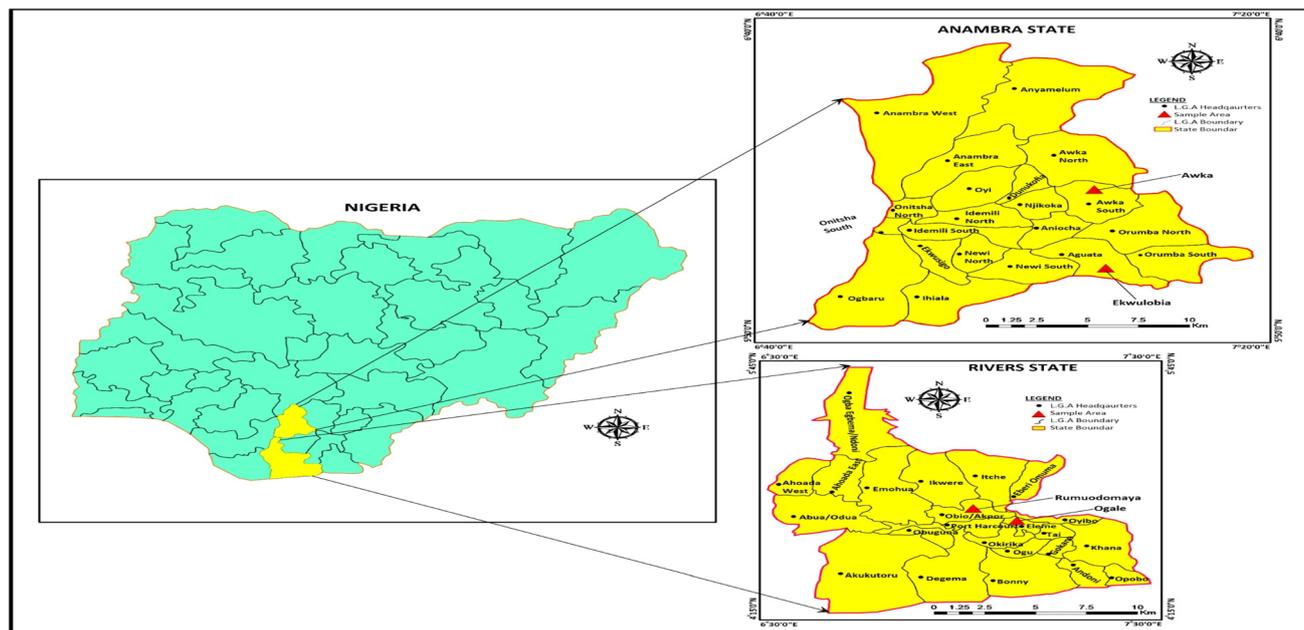
Fig. 1 Map of Nigeria showing the study area of Awka, Ekwulobia and Rumuodomaya–Ogale.

junction (Point 1) and the Eke-Awka roundabout (Point 2) were marked for sampling. On the Ekwulobia-Oko road, Vonic Hotel junction (Point 1) and First-Hill Secondary School premises (FHSS) (Point 2) were marked for sampling, while on the Ekwulobia-Uga highway, Ekwulobia roundabout axis (Point 1) and Victoria hospital premises (Point 2) were sampled. In Rivers State, each of the Eleme petrochemical junctions (Point 1) and Elelenwo-Akpajo junctions (Point 2) on Eleme road, and the Eliozo-Eligbolo bridge (Point 1) and Police Post Link road (Point 2) on Rumuodomaya road were also sampled. A total of 288 dust samples were collected from the mentioned available solid surfaces on the roads of each sampling point of the semi-urban areas using brushes and parkers.[1,19,30–32] In each month,

triplicate samples of dust from the solid surfaces were collected twice in the identified sampling locations and thoroughly mixed together to form a composite sample, which was transferred into a polythene bag, tightened, labelled, and taken to Springboard Laboratory Awka, Nigeria. In the laboratory, the samples were air-dried at room temperature, sieved through a 100-μm mesh, and stored at ambient temperature before analysis. The terms and abbreviations used for the various sampling locations are presented in Table 1. To study the contributions and correlations of high traffic density periods to PAH concentrations in dust of the study areas, traffic counts were manually taken weekly/monthly between 7–9 am and 4–6 pm (depicting rush hour periods with attendant high vehicular movement) by the research team, as there was no available data from Nigeria's Federal Road Safety Commission on the traffic densities of most of the study locations. The rush-hour counts did not cover the off-peak hour differences; however, they captured the vehicular-type variations that contribute to PAH emissions in the study areas (Table S1†) and also represented the highest traffic volumes of the day.

Table 1 Terms and abbreviations of the various sampling locations

S/N	Term	Abbreviations
1	Enugu-Awka highway	EAH
2	Eze-Uzu junction	EUJ
3	Government House road	GHRd
4	Eke-Awka road	EARd
5	Coca-Cola junction	CCJ
6	Eke-Awka roundabout	EARt
7	Ekwulobia-Uga highway	EUH
8	Ekwulobia roundabout	ERt
9	Victoria hospital premises	VHP
10	Ekwulobia-Oko road	EORd
11	Vonic hotel junction	VHJ
12	First Hill Secondary School premises	FHSSP
13	Ogale road	ORd
14	Eleme Petrochemical junction	EPJ
15	Elelenwo-Akpajo junction	EAJ
16	Rumuodomaya road	RRd
17	Eliozo bridge	EB
18	Police post link road	PPLRd

2.3 Reagents

The reagents used for the analysis were *n*-hexane (HPLC grade), anhydrous sodium sulfate/anhydrous magnesium sulfate (purity 99%), silica gel (BDH Poole, UK), acetonitrile, and a 1000 μg mL^{-1} mixed standard containing the USEPA 16 priority PAHs (obtained from Supelco Sigma-Andrich Inc., USA).

2.4 Sample extraction and clean-up

For each of the studied months, 10 g of composite dust samples from Enugu-Awka highway (EAH), Eke-Awka road (EARd), Ekwulobia-Uga highway (EUH), Ekwulobia-Oko road (EORd), Ogale road (ORd), and Rumuodomaya road (RRd) were each

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homogenized with 6.0 g of anhydrous sodium sulfate to remove moisture. The homogenate was extracted using a Soxhlet extractor with 300 mL of n-hexane. The Soxhlet extraction for each sample was carried out for 6 hours at 75 °C. The extraction procedure was repeated three times with fresh portions of n-hexane on the residue. The extract was pooled together and concentrated to 1 mL using a rotary evaporator. The concentrated extract was purified on a silica gel/Na_2SO_4 column loaded top to bottom with 3 g of silica gel and 1 g of Na_2SO_4. The PAHs in the extract were eluted with acetonitrile and dried over 2 g of anhydrous magnesium sulfate through filter paper into a 50-mL round-bottom flask.

2.5 PAH analysis by GC-FID

A Buck M910 gas chromatograph with a flame ionization detector was used to separate and quantify the PAHs in the sample. The separation of the PAH compounds and the effect of PAH isomers on the analytical results were accounted for by utilizing a capillary GC column with high PAH selectivity: VF-5 column (30 m × 0.25 mm internal diameter × 0.25 μm film thickness). The injector and detector temperatures were set at 250 °C and 300 °C, respectively, to achieve the baseline or near-baseline of separation of the PAH isomer pair. The initial temperature of the oven was set at 70 °C for 5 min, raised to 120 °C for 4 min, ramped at 10 °C min^{-1} to 180 °C, held for 2 min, and finally ramped at 5 °C min^{-1} to 300 °C. Helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1} and a detector make-up gas of 29 mL min^{-1}. The injection volume of the GC was 10.0 μL. The total run time for a sample was 43 minutes.

2.6 Quality control/assurance

Quantification of PAH was performed by applying the linear regression method ($r^2 > 0.99$) using five-point calibration curves established between the authentic standard concentrations and corresponding peak areas. Each PAH compound was calibrated using individual PAH standards to ensure accurate quantification of the co-eluting isomers. Analysis of serial dilutions of the PAH standard showed a limit of detection of the chromatographic method between 7.0×10^{-6} and 1.6×10^{-4} μg g^{-1} for the PAH compounds. The limit of quantification (LOQ) ranged from 1.8×10^{-7} to 4.10×10^{-5} μg g^{-1}. The recovery efficiency of the method was evaluated by the analysis of filters spiked with known concentrations of standard PAH compounds, and the compounds provided recovery mean values ranging from 70% to 80%. Field and laboratory blanks were routinely analysed for quality control. The blank levels of individual analysts were normally very low and, in most cases, below detection.

2.7 Statistical analysis

Data analyses were performed with Microsoft Excel Package 2016, XRealStats (add-in), and PAST 4.03 software. Microsoft Excel was used to calculate the incremental lifetime cancer risk (ILCR), benzo(a)pyrene equivalent carcinogenic power (BaPE), and benzo(a)pyrene equivalent as total toxicity equivalence (BaPeq as TEQ). A preinstalled add-in, XRealStats, was used to execute Pearson's coefficient correlation of PAHs in the dust

samples. Correlation analysis (CA) was used to show the inter-relationships between the analyzed PAH components, especially regarding their origins. Parameters with association coefficients $r < 0.5$, $0.75 > r > 0.5$, and $r > 0.75$ were considered weak, moderate, and strong, respectively.[33]

Principal component analysis (PCA) was carried out to identify the possible sources of PAHs in the dust samples using PAST software. The software was also utilized to provide information on the graphical representation of the correlation analysis and factor loadings. The Bray–Curtis hierarchical cluster analysis tool was used to determine the differences and similarities among different study months.[34]

The study employed US EPA's Positive Matrix Factorization (PMF) (v5.0.14) modelling to improve the source identification of PAHs in the study area.[35] To understand the inter-location differences, one-way ANOVA was used, while the mean of the total PAH concentrations between locations was compared using Dunn's *post hoc* test.[36] A two-sample t-test (independent t-test) was used to determine whether there is a statistically significant difference between the mean of PAH concentration in the two locations of the study areas using PAST software. The following hypothesis test was adopted for this study: there is no significant difference in total PAHs between sample locations. The null hypothesis was accepted at $p > 0.05$ and rejected at $p < 0.05$.

2.8 Human health risk assessments

BaPE, BaPE as TEQ, and ILCR were used to determine the possible health risks arising from human exposure to PAH-laden dust particles.

2.8.1 BaPE. Extended-period exposure to PAHs causes various health effects. Epoxides and dihydro diols (reactive metabolites) present in some PAHs bind to cellular proteins and DNA, causing biochemical disruptions and cell damage, which further leads to mutation, malformation development, tumors, and cancer.[6] Previous studies have reported that high-carcinogenic and molecular-weight PAHs such as Benzo(a)pyrene (BaP), benzo(a)anthracene (BaA), benzo(k)fluoranthene (BkF), dibenzo(a,h)anthracene (IcdP), and dibenzo(a,h)anthracene (DahA) from petrogenic, pyrogenic, and biological sources are transported into the kidney, liver, spleen, fat, ovaries, and respiratory tracts, where they cause tissue damage on prolonged exposure.[5,37] Since numerous health effects could be associated with exposure to PAHs, the benzo(a)pyrene equivalent carcinogenic power (BaPE) was calculated following eqn (1):[38,39]

$$BaPE = 0.06 \times BaA + 0.07 \times BbF + BkF + BaP + 0.6 \times DahA + 0.08 \times IcdP \quad (1)$$

where BaA is the Benzo(a)anthracene concentrations (μg g^{-1}), BkF is the benzo(k)fluoranthene concentrations (μg g^{-1}), BbF is the benzo(b)fluoranthene concentrations (μg g^{-1}), BaP is the benzo(a)pyrene concentrations (μg g^{-1}), DahA is the dibenzo(a–h)anthracene concentrations (μg g^{-1}), and IcdP is the indeno(1,2,3-cd)pyrene concentrations (μg g^{-1}).

2.8.2 BaPE as TEQ. BaP$_{eq}$ as TEQ was calculated using eqn (2):

$$\text{BaP}_{eq} \text{ as TEQ} = \sum C_n \times \text{TEF} \qquad (2)$$

where C_n is the average concentration ($\mu g\ g^{-1}$) of an individual PAH in the settled dust and TEF ($\mu g\ g^{-1}$) is the toxic equivalence factor of that PAH.[40,41] The toxic equivalent factor (TEF) for fluoranthene (Flu), phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(g,h,i) perylene (BghiP), indeno (1,2,3-cd)pyrene (IcdP), dibenzo(a,h) anthracene (DahA), benzo(a)pyrene (BaP), benzo(k)fluoranthene (BkF), and benzo(b)fluoranthene (BbF) were 0.001, 0.001, 0.01, 0.001, 0.1, 0.01, 0.01, 0.1, 1, 1, 0.1, and 0.1, respectively.[39,40]

2.8.3 Incremental lifetime cancer risk (ILCR). ILCR is an important model for assessing the carcinogenic risk of a given population, allowing for comparative analyses across different pollutants and exposure pathways. The model estimates the number of excess cancer cases that arise per one million population exposure to PAH pollutants and intake levels over a 70-year lifetime. However, it does not infer the actual risk of an individual owing to differences in lifestyle, mobility and environmental factors.[42]

To evaluate the cancer risk among residents (children and adults) of the studied areas, we used the ILRC model as suggested by Yang *et al.*:[43]

$$\text{ILCRs}_{\text{inhalation}} = \frac{\left(C \times \left\{ \text{CSF(inh)} \times \sqrt[3]{\left(\dfrac{\text{BW}}{70}\right)} \right\} \times \text{IR(inh)} \times \text{EF} \times \text{ED} \right)}{\text{BW} \times \text{AT} \times \text{PEF}}, \quad (3)$$

$$\text{ILCRs}_{\text{dermal}} = \frac{\left(C \times \left\{ \text{CSF(der)} \times \sqrt[3]{\left(\dfrac{\text{BW}}{70}\right)} \right\} \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{ED} \right)}{\text{BW} \times \text{AT} \times 1\text{E}6}, \quad (4)$$

$$\text{ILCRs}_{\text{ingestion}} = \frac{\left(C \times \left\{ \text{CSF(ing)} \times \sqrt[3]{\left(\dfrac{\text{BW}}{70}\right)} \right\} \times \text{IR(ing)} \times \text{EF} \times \text{ED} \right)}{\text{BW} \times \text{AT} \times 1\text{E}6}, \quad (5)$$

where CSF_{ing}, CSF_{der} and CSF_{inh} of BaP are 7.3, 25, and 3.85, respectively, determined by the cancer-causing ability of BaP. BW is body weight (70 kg for adults; 15 kg for children), AT is the average life span (25, 550), EF is the exposure frequency (350 days per year), ED is the exposure duration (24 and 6 years for adult and children, respectively), IR_{inh} is the inhalation rate (20 m^3 per day for adult and 7.6 m^3 per day for children), IR_{ing} is the dust intake rate (100 mg per day for adult and 200 mg per day), SA is the dermal surface exposure (5700 cm^2 for adult and 2800 cm^2 for children), AF is the dermal adherence factor (0.07 mg per cm^2 per h for adult and 0.2 mg per cm^2 per h for children), ABS is the dermal adsorption fraction (0.13 both adult and children), and PEF is the particle emission factor (1.36×10^9 m^3 kg^{-1}). CS ($\mu g\ g^{-1}$) is the $\sum$PAH concentrations based on the TEF of all PAHs and BaPE as TQE for more carcinogenic PAHs.[44–46]

3 Results and discussion

3.1 Concentrations of PAHs in roadside dust and their effects

The concentration of PAHs in road dust and the monthly traffic densities of Awka localities are presented in Table S1† and Fig. 2. Generally, the total concentrations of PAHs in dust from the Enugu-Awka highway (EAH) were higher than those from the Eke-Awka road (EARd). Dust from Eze-Uzu junction (EUJ), on EAH, had a total PAH concentration that ranged from 0.480 to 0.613 $\mu g\ g^{-1}$ within the sampling period of December 2019 to March 2020. There was a decrease in total PAH concentration in dust from Government House road (GHRd) (0.285–0.612 $\mu g\ g^{-1}$) on EAH when compared to EUJ (0.480–0.613 $\mu g\ g^{-1}$). The higher PAH concentrations in dust from EAH, and more particularly at EUJ, could be related to the proximity of the sampling site to the production source. There is a constant fall and explosion of diesel-laden tankers and other heavy-duty vehicles at EUJ due to the dilapidated state of the road.[47] The resultant accidental fossil fuel spills form a complex mixture with soil, which is considered a matrix of road dust.[48] Studies confirming high concentrations of PAHs in fossil fuel products have been reported.[49–51] Moreover, traffic congestion and emissions at the EUJ release unburnt carbon into the environment, which invariably contributes to the high PAHs observed in the sample location. Data from our traffic count showed a total of 956 269 vehicles plied the EAH in all the months during rush hours, as shown in Table S1.† Dust from the Coca-Cola junction (CCJ) and Eke-Awka roundabout (EARt) on Eke-Awka road (EARd) had a total PAH concentration that ranged from 0.160 to 0.672 μg g^{-1} and 0.346 to 0.609 $\mu g\ g^{-1}$. Eke-Awka road (EARd) is a major hub for economic activities. Several industries, such as the plastic, foam, and lubricant industries, are located within the area. These industries utilize diesel-powered generators as a source of power, enhancing the transport of PAH-containing particles, which later settle on the solid surface *via* wet and dry deposition. Additionally, emissions from organic waste dumps littered around the popular Eke-Awka market and uncontrolled burning of waste products near the market may have added to the PAH-laden samples in the area. The highest total PAH concentration in EUJ (0.613 $\mu g\ g^{-1}$) and CCJ (0.672 μg g^{-1}) (Table S1†) correlates with the highest traffic densities of 242 707 and 260 332 vehicles, respectively, (February 2020) observed during rush hours (7.00–9.00 am and 4.00–6.00 pm). This finding agrees with Lawal,[52] who states that traffic congestion and vehicular exhaust emissions, which geometrically increase during work and school hours, are major sources of outdoor PAH pollution.

Owing to the lack of universally accepted methods for road dust sampling, data from this study were therefore compared locally and globally with those of similar sampling methods employed (brush and parker), as presented in Table S1.† In Nigeria, few studies on PAH pollution in road/street dust exist, as mentioned earlier; Iwegbue *et al.*[27] and Iwegbue and Obi,[28] used the sampling methods employed in this study. The total PAH concentrations of Awka dust were lower than those

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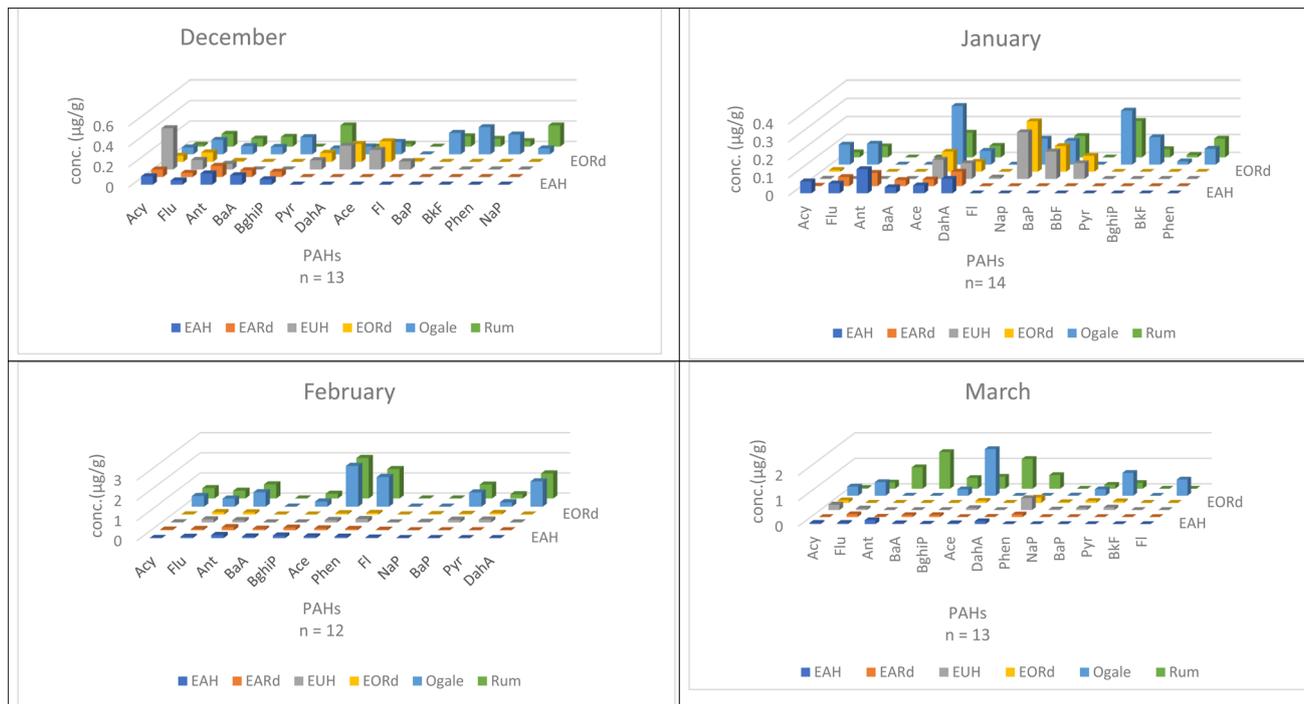*Environ. Sci.: Atmos.*, 2025, **5**, 831–847 | **835**

Fig. 2 Concentrations (trends) of PAHs among different locations from December 2019 to March 2020.

reported in the street dust of Abadan, Iran[19] and Guangzhou, China[31] but higher than those found in Tehran, Iran[8] and Warri metropolis, Nigeria[28] (Table S2†). The differences under meteorological conditions of Guangzhou and Abadan compared to Awka may have contributed to the variations in PAH concentrations. Awka experiences higher rainfall, which tends to dilute and wash-out PAHs in the road dust unlike in Guangzhou and Abadan, where low wind dispersion traps PAH pollutants in the dust matrix. It was also observed that acenaphthylene (Acy) and fluoranthene (Flu) in road dust from EUJ were higher than those reported in an industrialized area of Lagos, Nigeria.[27] The high vehicular movement in the more population dense and highly industrialized city of Lagos might lead to the disturbance and resuspension of dust-containing Acy and Flu in the area. There are no established safety standards for PAHs in dust.[27] Consequently, the reference values of PAHs in the soil were adopted and used to ascertain the extent of the risk posed by PAHs in dust. This assumption is based on the fact that pollutants in soil constitute a significant fraction of road dust, and both utilize the same analyte unit.[48,53] The total PAH concentration in dust from sampling locations in Awka was below the Dutch soil target and intervention values of 1.5 µg g^{-1} and 40 µg g^{-1}, respectively.[54] In addition, PAH contamination was categorized into four levels: not contaminated (<0.2 µg g^{-1}), slightly contaminated (0.2–0.6 µg g^{-1}), contaminated (0.6–1.0 µg g^{-1}), and heavily contaminated (>1.0 µg g^{-1}).[55] Based on these criteria, the total PAHs in dust sampled in February 2020 from EAH and EARd showed that they were slightly contaminated (Table S1†), while others fell within the "not contaminated" category. The fluoranthene, benzo[a]anthracene, and benzo [g,h,i] perylene in Awka dust were within the background soil

concentrations of PAHs in urban soil of the USA, as set by the Agency for Toxic Substances and Disease Registry.

The composition of PAHs in the settled road dust from the EAH and EARd showed the dominance of 3- and 4-ring PAHs over 5- and 6-ring PAHs in all the months. This finding varied with the study carried out in the street dust of Lagos, in which high molecular weight (HMW) PAHs (4–6 rings) showed prevalence.[27] The dominance of 3-ring low molecular weight (LMW) PAHs (Phenanthrene, Anthracene, Acenaphthene, Acenaphthylene, and Fluorene) observed in Awka dust could be related to their long-distance transport characteristics. LMW PAHs are usually influenced by seasonal and diurnal temperature changes and deposited on a surface through an air-surface exchange that allows their gradual migration over a long distance.[56] The 4-ring medium molecular weight (MMW) PAHs (fluoranthene and benzo[a]anthracene) in dust are affected by their wide dispersion through winds and vehicle-generated turbulence.[57] Acute exposure to a mixture of 3- and 4-ring PAHs by roadside dwellers (hawkers, petty traders, shop owners, transporters, roadside auto-engineers, and food vending) in Awka causes skin irritation and inflammation. Anthracene and benzo(a)pyrene are direct skin irritants. Reports have shown that they both cause allergic reactions in human and animal skins.[6] Further, non-cancer effects, such as cataracts, decreased immune function, kidney and liver damage and asthma, are all associated with long-term exposure to PAH mixtures.[6]

Generally, the differences in composition of the PAHs in road dust from the EAH and EARd could be related to their varying traffic densities, vehicular type, economic activities, and photo-degradation strength of PAHs in dust. EAH had 1.4% total traffic densities in all the months higher than EARd, apart

from the diesel and petrol engine vehicles that consistently ply the highway.

When compared with those of Awka, the total PAH concentration in the dust from Ekwulobia was higher (Table S1† and Fig. 2). Dust from the Ekwulobia roundabout (ERt) axis, on EUH, had a total PAH concentration that ranged from 0.672 to 0.926 µg g^{-1} and 0.739 to 1.388 µg g^{-1} at Victoria Hospital premises (VHP) from December 2019 to March 2020. It was also observed that dust from the Vonic Hotel junction (VHJ) and First Hill Secondary School premises (FHSSP), on EORd, had a total PAH concentration that ranged from 0.454 to 0.982 µg g^{-1} and from 0.401 µg g^{-1} to 0.564 µg g^{-1}. The high PAH concentration in the dust of Ekwulobia localities, particularly the roundabout axis (when compared to Awka), could be traceable to its activities. The ERt sampling point is surrounded by a popular garage called "Ekwulobia Park", which hosts numerous PAH-laden activities, such as smoking, barbecuing, traffic congestion and emissions, and burning of abandoned tires as waste, in addition to the use of the generator by roadside food vendors for their businesses. Hence, there is a greater chance of inhalation of these PAHs by roadside hawkers, shop owners, workers in roadside offices, traffic police personnel, drivers, and passengers who consistently visit the park. Additionally, the PAHs in dust could undergo photochemical and chemical oxidation by absorbing solar radiation from the ultraviolet region, leading to the formation of transformed PAH products (TPPs), which could be more hazardous than the parent PAHs upon inhalation.

The month of December (mid-dry season) 2019 showed the highest PAH concentration of 0.913 µg g^{-1} and 1.388 µg g^{-1} in dust from the ERt axis and VHP. This correlates with the highest traffic density of 332 292 vehicles observed owing to the Christmas holiday festivities (December), as well as the possible release of decomposing organic wastes from the hospital and their interaction with dust particles common in the study season (harmattan). Based on the Maliszewska-Kordybach[55] criteria for PAH contamination, dust from ERt and VHP on the Ekwulobia-Uga highway can be said to be completely contaminated; however, this was not the case with dust from the Ekwulobia-Oko road (EORd), as some locations showed a "slightly contaminated status". In general, the total PAH concentration in Ekwulobia dust for all the months was below the Dutch soil target value of 1.5 µg g^{-1}.[54] This finding agrees with the PAH concentrations in soils from the commercial and industrial areas of Lagos, Nigeria, which were below the Dutch limit for industrial land use.[58] A comparison of the total PAH concentrations in the road dust of Ekwulobia localities based on previous studies showed some variations. For instance, the $\sum$PAH concentrations in Ekwulobia road dust were lower than those in the street dust of Kuala, Lumpur[59] and Ilam, Iran,[60] but higher than those from industrial areas in the Babylon governorate, Iraq[61] and Dhaka, Bangladesh[62] (Table S2†). The environmental conditions, pollution control policies and mechanisms, combustion sources and traffic densities of these areas contribute to their PAH variations.

The composition of PAHs in the settled road dust from EUH and EORd showed the dominance of 2-, 3-, and 5-ring PAHs over 4-ring PAHs in all the months. This differed from the 3- and 4-ring PAHs that dominate in Awka: dust but agreed with a PAH study in the urban soil of the Niger Delta, Nigeria.[63] The dominance of 5-ring HMW PAHs (benzo(a)-pyrene and dibenzo(a,h)anthracene) detected in the study area (Table S1†) may indicate the petrol-engine cars that frequently ply the road and their retention power close to the source point. LMW PAHs (2- and 3-rings) are traceable to diesel engines. A study by Majumdar et al.[56] confirmed petrol and diesel engines as major sources of HMW and LMW PAHs. Considering the number of hours spent daily on roads by hawkers, there might be a potential breakdown of their red blood cells owing to inhalation and/or ingestion of dominant 2-ring naphthalene.[30] Moreover, 5-ring benzo(a)pyrene and dibenzo(a,h)anthracene, dominant in the dust of Ekwulobia localities, are notable for causing cancer.[64] Further, these concentrations of PAHs could bio-accumulate in the environment and be absorbed by terrestrial mammals, plants and aquatic organisms, leading to immuno-suppression, genotoxic effects and teratogenicity.[6]

Different locations of Rumuodomaya-Ogale have appreciable levels of PAHs higher than those of Ekwulobia and Awka (Table S1† and Fig. 2). Dust from Eleme Petrochemical Junction (EPJ) on Ogale road had a total PAH concentration that ranged from 1.497 to 7.915 µg g^{-1} and 1.423 to 7.037 µg g^{-1} in Elelenwo-Akpajo (EAJ) bypass from December 2019 to March 2020. Dust from Eliozu-Eligbolo Bridge (EEB) and Police Post Link Road (PPLRd), on Rumuodomaya Road, had total PAH concentrations ranging from 0.872 to 7.915 µg g^{-1} and 0.749 to 7.037 µg g^{-1}, respectively. The month of February 2020 had the highest PAH concentrations of 7.915 µg g^{-1}, 7.037 µg g^{-1}, 7.915 µg g^{-1}, and 7.037 µg g^{-1} in dust from EPJ, EAJ, EEB, and PPLRd, respectively. The highest total PAH concentrations in EPJ and EEB (7.915 µg g^{-1}) locations were higher than the total PAHs in the soil of Choba (7.42 mg kg^{-1}), Khana (6.33 mg kg^{-1}), Eleme (6.79 mg kg^{-1}), and Yenogoa (7.39 mg kg^{-1}), as demonstrated by Okoye et al.[65] The high concentrations of PAHs in the dust of the Rum-Ogale locations compared with those of previous studies could be attributed to the combined effect of oil and gas industrial operations, unregulated artisanal refining emissions, traffic density (421, 286 and 361, 293), and open organic waste dumping practices rampant in the marshy environment. Rum-Ogale is known generally for its gas flaring, oil and gas exploration and refining, high traffic counts, and fuelling stations. Recently, residents of Obio-Akpor, Eleme, Ikwerre, and Okirika local councils carried out public demonstrations against rampart atmospheric fallout of deadly black soot (unburnt hydrocarbons), known to contain PAHs, in the atmosphere estimated to have risen to almost 11 times above the recommended safety level of the World Health Organisation (WHO) standard, which is considered to emanate majorly from the activities of artisanal refining, oil and gas bunkering.[66] Black soot interacts with dust particles and forms a bond with toxic 4–6-ring PAHs inhalable by residents. Aromatic hydrocarbon sheets originating from soot can physically wrap around sperm cells and bacteria and inactivate some of them.[14,16,67] A Nigerian daily tabloid (Guardian Newspaper) reported that about 22 077 persons have suffered from related respiratory ailments associated with soot-

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particulate matter in the last five years in Port Harcourt city,[66] which shared a boundary with our study area. March 2020 data showed evidence of high pyrene concentrations in road dust from Ogale and Rumuodomaya, indicating incomplete combustions and tobacco smoke.[41,68] The levels of PAHs obtained in Ogale and Rumuodomaya are worrisome considering that inhabitants are mostly low-income earners, students, transporters, peasant farmers, petty businessmen and women, who spend quality time outdoors in pursuit of daily assignments.[69,70] The concentrations of PAHs in dust from Rum-Ogale showed that settled roadside dusts are a sink for environmental toxicants, such as PAHs. The PAH concentrations of the Rum-Ogale localities were comparable with those reported in other selected cities globally. Acenaphthylene and fluoranthene in dusts from EPJ and EEB were all higher than those reported in the street dust of Huizhou[71] and Lagos.[27] The status of the total PAHs in the dust of Rum-Ogale localities ranged from contaminated (0.6–1.0 μg g^{-1}) to heavily contaminated (>1.0 μg g^{-1}).[55] Specifically, in February 2020 (Table S1†), anthracene and benzo(a)pyrene in dust from EPJ and EEB were "contaminated", while acenaphthylene, dibenzo(a–h)anthracene and phenanthrene were "heavily contaminated". In March 2020, fluoranthene and pyrene in dust from EPJ were "contaminated", while benzo(a)anthracene and dibenzo(a–h)anthracene in dust from EEB were "heavily contaminated".

The composition of PAHs in the settled road dust of EPJ and EAJ, on Ogale road, showed the dominance of 5- and 3-ring PAHs over 2-, 4- and 6-ring PAHs in all the months of study. This differed from the 4-ring PAHs that were mostly abundant in the soil and sediment of the Awotan-Asunle community in Ibadan, Oyo State, Nigeria.[72] Characteristically, the HMW PAH dominant in EPJ and EAJ are insoluble in water, less volatile and have increased bioaccumulation and carcinogenic tendencies.[73] Therefore, pedestrians and other inhabitants of EPJ and EAJ would probably suffer from health effects in the near future after prolonged exposure. The 3- and 4-ring PAH dominants in EEB and PPLRd agree with the findings from the Enugu-Awka highway (EAH) and Eke-Awka road (EARd) in this study.

A correlation analysis was performed as shown in Tables S3 and S4† to study the relationships between the rush hour traffic and the total traffic density, and average traffic densities and the PAH level to suggest that PAHs from the roadside were mostly or partially emitted from traffic. The total traffic density had a strong positive correlation with the Lux bus (Dec); Mini-bus and Tanker/trailer (Feb); and Lux-bus and Tanker/trailer (Mar) (Table S3†). Further, a strong significant positive correlation exists among the mean traffic density and Ace, Pyr, BkF and BghiP (Jan); Acy, Flu, Ant, Ace, Phen, BaP, Pyr, and Daha (Feb); and Acy, Flu, Ace, BaP, Pyr, and Flu (Mar) (Table S3†).

3.2 Statistical significance of PAHs in dust of the study areas: independent t-test and one-way ANOVA

An independent sample t-test (Tables S5–S7†), one-way ANOVA (Table S8†) and Dunn's *post hoc* test (Table S9†) were conducted to compare the PAHs in the sample locations. There was no statistically significant difference ($t = 0.54$, $p = 0.60$) in PAHs for EAH ($M = 0.46$) and EARd ($M = 0.41$). The magnitude of the difference in the means (mean difference $= 0.05$, 95% CI: 0.14 to 0.29) was very small; hence, the null hypothesis was accepted (Table S5†). This implies that PAHs in the dust of Awka locations may be attributed to chance. Additionally, there was sufficient evidence to accept the null hypothesis and conclude that the mean PAH values in Ogale locations are not statistically different from those in Rumuodomaya because $p > 0.05$ (Table S6†). However, these findings differed from those of the Ekwulobia sample locations, which showed a statistically significant difference ($t = 3.46$, $p = 0.01$) in PAHs with the mean concentrations of EUH ($M = 0.93$) higher than the EORd ($M = 0.57$). The magnitude of the difference in the mean (mean difference $= 0.34$, 95% CI: 0.44 to 0.63) was significant (Table S7†). To investigate whether PAH concentrations in dust differ across different levels within the sample locations, ANOVA was conducted. Sample locations were divided into six groups: ORd, RRd, EUH, EORd, EAH and EARd. The ANOVA results (Table S8†) suggest that the PAH concentrations of the groups differ significantly ($F5$, $18 = 3.3$, and $P = 0.027$). Equal variance was not assumed because Levene's statistics was significant. Dunn's *post hoc* comparison, as shown in Table S9,† was used to check for individual differences between the groups. The result indicated that the mean of the total PAHs in dust from EORd, EAH and EARd differed significantly from that of ORd and RRd. Additionally, the mean of the total PAHs in dust from EARd differed significantly from EUH. The mean difference was significant at the 0.05 level. However, there were no statistically significant differences between RRd *vs.* ORd, EUH *vs.* ORd, EUH *vs.* RRd, EORd *vs.* EUH, EAH *vs.* EUH, EAH *vs.* EORd, EARd *vs.* EORd and EARd *vs.* EAH.

3.3 Health risk assessment of PAHs in road dust

3.3.1 BaP toxicity. The BaP_{TEQ} values of the road dust of the three studied localities (Awka, Ekwulobia and Rumuodomaya-Ogale) are shown in Table 2. Dust from Ogale and Rumuodomaya road showed higher BaP_{TEQ} concentrations than those from Ekwulobia and Awka. This implies that there is a potential carcinogenic risk to the residents of Ogale and Rumuodomaya. The compound benzo(a)pyrene was the main contributor to the BaP_{TEQ} concentrations in dust from Rumuodomaya-Ogale. The BaP_{TEQ} values in dust from EPJ and EAJ, on Ogale road, ranged from 0.2167 to 2.0406 μg g^{-1}, and 0.2143 to 1.8715 μg g^{-1}. However, EEB and PPLRd, on Rumuodomaya road, had BaP_{TEQ} concentrations that ranged from 0.1313 μg g^{-1} to 2.0406 μg g^{-1} and from 0.1099 μg g^{-1} to 1.8715 μg g^{-1}. The BaP_{TEQ} concentrations observed in the dust from Ogale road (0.2143 to 2.0406 μg g^{-1}) and Rumuodomaya road (0.1099 to 2.0406 μg g^{-1}) were higher than those reported in Mifalan, Iran,[74] but lower than those reported in Ulsan, Korea[75] and Tianjin, China.[76] Furthermore, our study differed slightly from the values of urban wet deposition reported by Mu *et al.*[77] in the rainy season of 2020; only 7 of the 16 PAHs were detected and 6-ring PAHs were not detected in the North-Eastern Chinese city. It may not be a surprise that PAH values of Rumuodomaya-Ogale are higher than others because the area is also home to constant

Table 2 BaPE and BaPE as TEQ of PAHs in settled road dust of the study areas

| Study area | Month/year | Parameters ($\mu g\ g^{-1}$) | Sampling locations | | | |
| | | | Enugu-Awka highway | | Eke-Awka road | |
			Point 1	Point 2	Point 1	Point 2
Awka	December 2019	BaPE	0.0110	0.0000	0.0040	0.0040
		BaPE as TEQ	0.0201	0.0017	0.0084	0.0083
	January 2020	BaPE	0.0506	0.0506	0.0506	0.0506
		BaPE as TEQ	0.0860	0.0859	0.0846	0.0859
	February 2020	BaPE	0.0047	0.0047	0.0046	0.0046
		BaPE as TEQ	0.0109	0.0109	0.0108	0.0108
	March 2020	BaPE	0.0690	0.0683	0.0130	0.0060
		BaPE as TEQ	0.0058	0.0046	0.0090	0.0083

| Study area | Month/year | Parameters ($\mu g\ g^{-1}$) | Sampling locations | | | |
| | | | Ekwulobia-Uga highway | | Ekwulobia-Oko road | |
			Point 1	Point 2	Point 1	Point 2
Ekwulobia	December 2019	BaPE	0.1248	0.1554	0.1056	0.0000
		BaPE as TEQ	0.0018	0.0015	0.0007	0.0005
	January 2020	BaPE	0.1942	0.2291	0.2292	0.1374
		BaPE as TEQ	0.2292	0.2701	0.2705	0.1471
	February 2020	BaPE	0.1480	0.1260	0.0280	0.0380
		BaPE as TEQ	0.1497	0.1277	0.0294	0.0395
	March 2020	BaPE	0.0720	0.0720	0.0720	0.0720
		BaPE as TEQ	0.0729	0.0730	0.0725	0.0725

| Study area | Month/year | Parameters ($\mu g\ g^{-1}$) | Sampling locations | | | |
| | | | Ogale road | | Rumuodomaya road | |
			Point 1	Point 2	Point 1	Point 2
Rumuodomaya-Ogale	December 2019	BaPE	0.3119	0.2455	0.1200	0.1064
		BaPE as TEQ	0.3805	0.2665	0.1313	0.1099
	January 2020	BaPE	0.8123	0.8103	0.8092	0.7618
		BaPE as TEQ	0.2167	0.2143	0.2124	0.1627
	February 2020	BaPE	1.4930	1.3934	1.4930	1.3934
		BaPE as TEQ	2.0406	1.8715	2.0406	1.8715
	March 2020	BaPE	0.2570	0.2570	1.0278	0.8494
		BaPE as TEQ	0.2632	0.2644	1.3361	1.3302

atmospheric thermal activities (high temperature reactions) owing to intense gas flaring, shipping operations and petrochemical activities with the potential to release total petroleum hydrocarbon (TPH), phenols, straight chain hydrocarbons (alkanes, alkenes, and alkynes), nitrate, nitrite, ammonia, and PAHs into the atmosphere.[78,79] This is evidenced by the presence of PAHs and straight chain hydrocarbons in the surface water of the area.[79] Rainwater samples of the area contain organic and inorganic nitrogen that are precursors of nitrate and nitrite, which activate nitrosation, a cancer trigger.[78] These occurrences together with PAHs in dusts of the study area indicate the level of atmospheric pollution to which the unsuspecting public is exposed.

3.3.2 Incremental life cancer risk (ILCR). The ILCR associated with human exposure to PAHs in the dust of all sample locations are shown in Table S10† and Fig. 3. The total ILCR values arising from children's exposure to PAHs in Awka dust *via* inhalation, dermal contact and ingestion ranged from 5.345×10^{-12} to 9.243×10^{-7}, 4.521×10^{-13} to 9.232×10^{-7}, 2.233×10^{-12} to 9.093×10^{-7} and 2.207×10^{-12} to 9.232×10^{-7} at EUJ, GHRd, CCJ and EARt, respectively, from December 2019 to March 2020. In adults, the total ILCR values ranged from 5.521×10^{-8} to 8.167×10^{-7}, 4.379×10^{-8} to 8.177×10^{-7}, 8.567×10^{-8} to 8.053×10^{-7} and 7.901×10^{-8} to 8.177×10^{-7} in EUJ, GHRd, CCJ and EARt, respectively. From the study, the ingestion cancer risk (CR) values of children's exposure to Awka dust were higher than their adult counterparts in all the months except December 2019. This finding varied with the CR values of adults *via* the dermal contact and inhalation routes, which appeared to be higher than those of the children in all the months except for December 2019. The high CR values of children *via* ingestion could be due to their hand-to-mouth habits
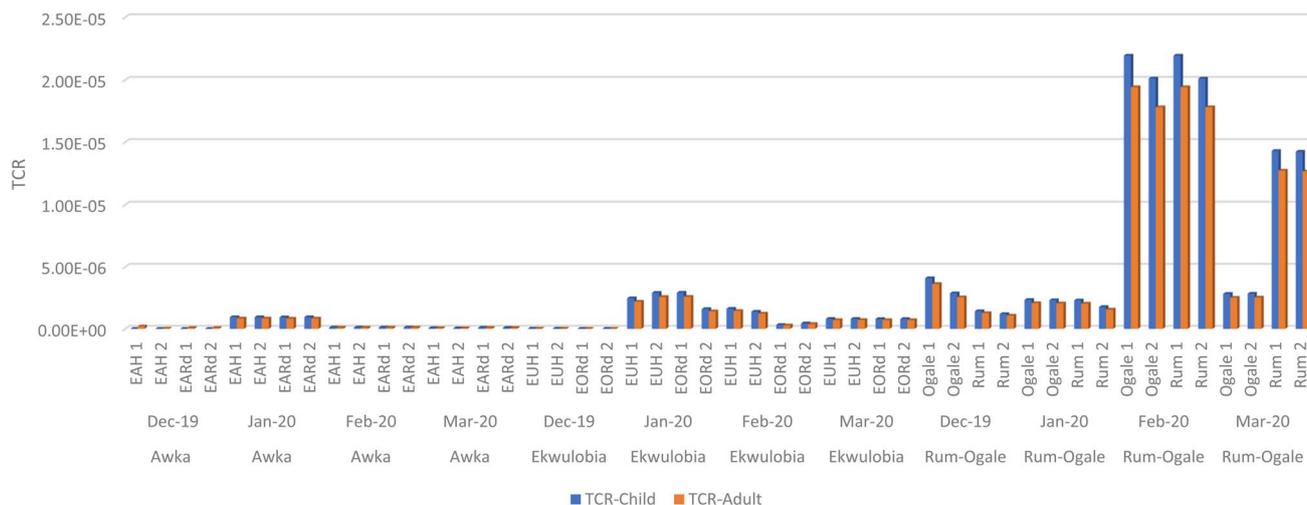
Fig. 3 Total cancer risk (TCR) of PAHs in road dust at different locations for children and adults.

while crawling. Shop owners (nursing mothers) within the study area often do business with infants, who are exposed to settled dust on the floor laden with PAHs during playtime. The CR values for children and adults through the exposure routes followed the order dermal contact > ingestion > inhalation.

The total ILCR values in dusts from the different sampling points of Ekwulobia were higher than the values in Awka but lower than those of Rumuodomaya-Ogale. The total ILCR values arising from children's exposure to PAHs in dust from Ekwulobia via inhalation, dermal contact and ingestion ranged from 1.935×10^{-8} to 2.463×10^{-6}, 1.612×10^{-8} to 2.903×10^{-6}, 7.523×10^{-9} to 2.907×10^{-9} and 5.374×10^{-9} to 1.581×10^{-6} in ERt, VHP, VHJ, and FHSSP, respectively. Total ILCR values (adult) ranged from 1.714×10^{-8} to 2.182×10^{-6}, 1.428×10^{-8} to 2.571×10^{-6}, 6.664×10^{-9} to 2.575×10^{-6} and 4.760×10^{-9} to 1.400×10^{-6} in ERt, VHP, VHJ, and FHSSP, respectively. Generally, children and adults in the study area would be more exposed to cancer risk via dermal contact and ingestion
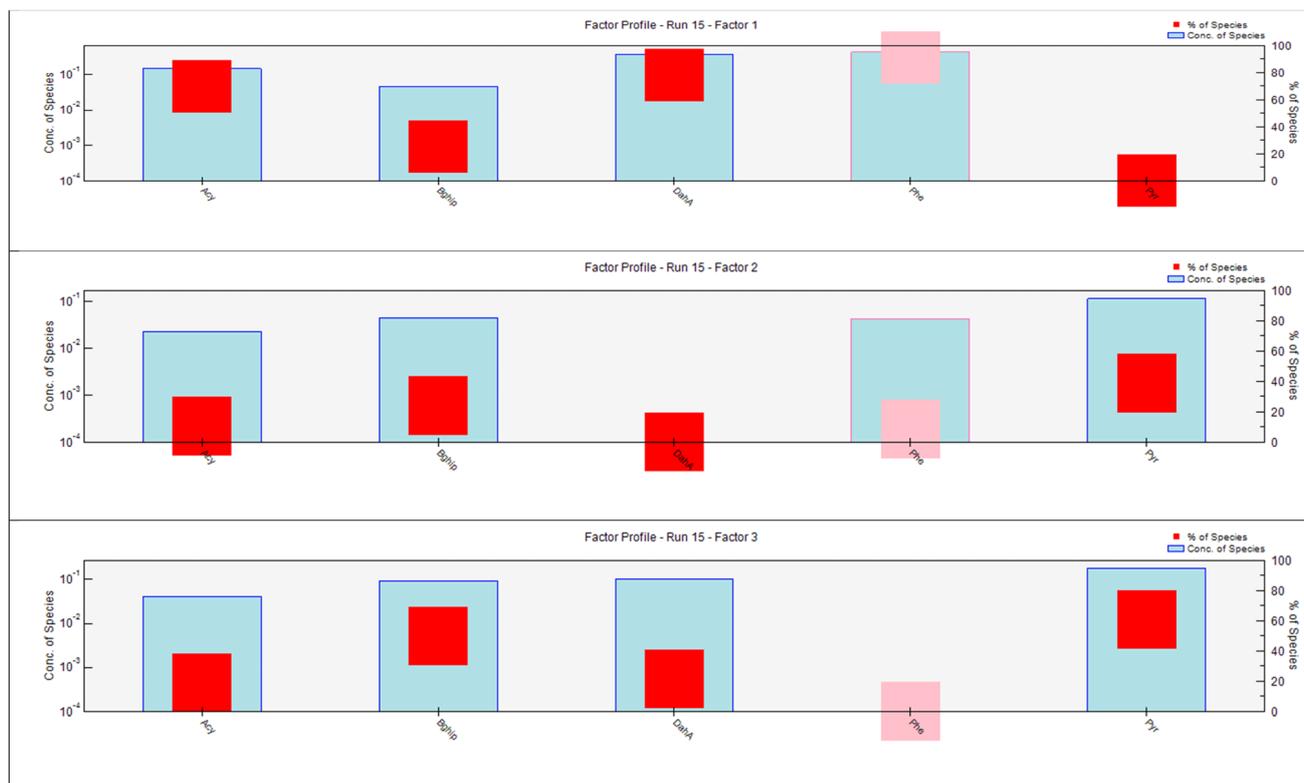

Fig. 4 Source contribution of PAHs in Rum-Ogale roadside dust for Dec 2019 to March 2020.

routes as PAH concentrations increase in all the months than through the inhalation pathway. The ILCR values of Ekwulobia dust followed the same trend as those of Awka dust; adult inhalation and dermal contact CR values were higher than the children's counterparts. Adult's high exposure to PAHs in dust through inhalation and dermal contact could be related to their frequent business activities close to the point of PAH sources and active and passive smoking prevalent in the study area. Furthermore, the CR values of adults implied that skin contact and inhalation of road dusts contributed significantly to the overall CR effects.

The total ILCR values arising from children's exposure to PAHs in the dust of Rumuodomaya-Ogale *via* inhalation, dermal contact and ingestion ranged from 2.329×10^{-6} to 2.193×10^{-5}, 2.303×10^{-6} to 2.011×10^{-5}, 1.411×10^{-6} to 2.193×10^{-5}, 1.181×10^{-6} to 2.011×10^{-5} in EPJ, EAJ, EEB, and PPLRd from December 2019 to March 2020, respectively. Considering adult exposure, the total ILCR values ranged from 2.063×10^{-6} to 1.943×10^{-5}, 2.040×10^{-6} to 1.781×10^{-5}, 1.250×10^{-6} to 1.943×10^{-5}, and 1.046×10^{-6} to 1.782×10^{-5} in EPJ, EAJ, EEB, and PPLRd from December 2019 to March 2020, respectively. The highest total ILCR values for children and adults observed in January 2020 (Awka and Ekwulobia) and February 2020 (Rumuodomaya-Ogale) indicate that the level of PAHs in these sampling stations might not cause any cancer effect on humans through inhalation, dermal contact and ingestion routes since values $\leq 10^{-6}$ to 10^{-4} acceptable risk threshold.[54]

3.4 PAH source apportionments and inter-relationships

Pearson coefficient correlation (PCC), cluster analysis (CA), principal component analysis (PCA) and diagnostic ratio (DR) are utilized by researchers across the globe to study the inter-relationship among contaminants in road dust and their possible sources.[80,81] However, in this study, only PCA, CA, and PCC were utilized.

3.4.1 PCA of PAHs. The PCA loading components of PAHs in the dust of different locations of Awka were resolved into three components that explained 100% of the total variance (Table S11†). Factor 1 contributed 51.44% of the total variance with a strong positive loading of fluoranthene (EUJ and GHRd), benzo(*a*)anthracene (GHRd), benzo(*g,h,i*)pyrene (all locations), acenaphthene (all locations), phenanthrene (EUJ and GHRd) and fluorene (all locations). High molecular weight (HMW) fluoranthene, benzo(*a*)anthracene, and benzo(*g,h,i*)pyrene may be attributed to fossil fuel and diesel combustion.[32] However, the presence of low molecular weight (LMW) acenaphthene, phenanthrene, and fluorene in the dust samples could be traceable to incomplete combustion processes.[82] Factor 2 accounted for 28.45% of the total variance and had a strong positive loading of fluoranthene (CCJ and EARt), anthracene (EUJ and GHRd), and dibenzo(*a–h*)anthracene (EUJ and GHRd). The 2-ring anthracene and 6-ring dibenzo(*a–h*)anthracene are derived from uncombusted petroleum products[32] and diesel-powered engines.[83] Factor 3 contributed 20.11% of the total variance and was dominated by 4-ring benzo(*a*)anthracene (CCJ and EARt).

The PCA of PAHs for Ekwulobia was resolved into three components that explained 99.99% of the total variance (Table S12†). Strong positive loading of acenaphthylene (VHJ), fluoranthene (VHJ), anthracene (ERt) and pyrene (VHJ and FHSSP) accounted for 48.05% of the total variance in Factor 1. HMW fluoranthene and pyrene in dust indicate pyrogenic products, such as coal combustion.[84] However, LMW-PAHs, acenaphthylene and anthracene are related to low temperature combustion processes, such as wood and biomass burning,
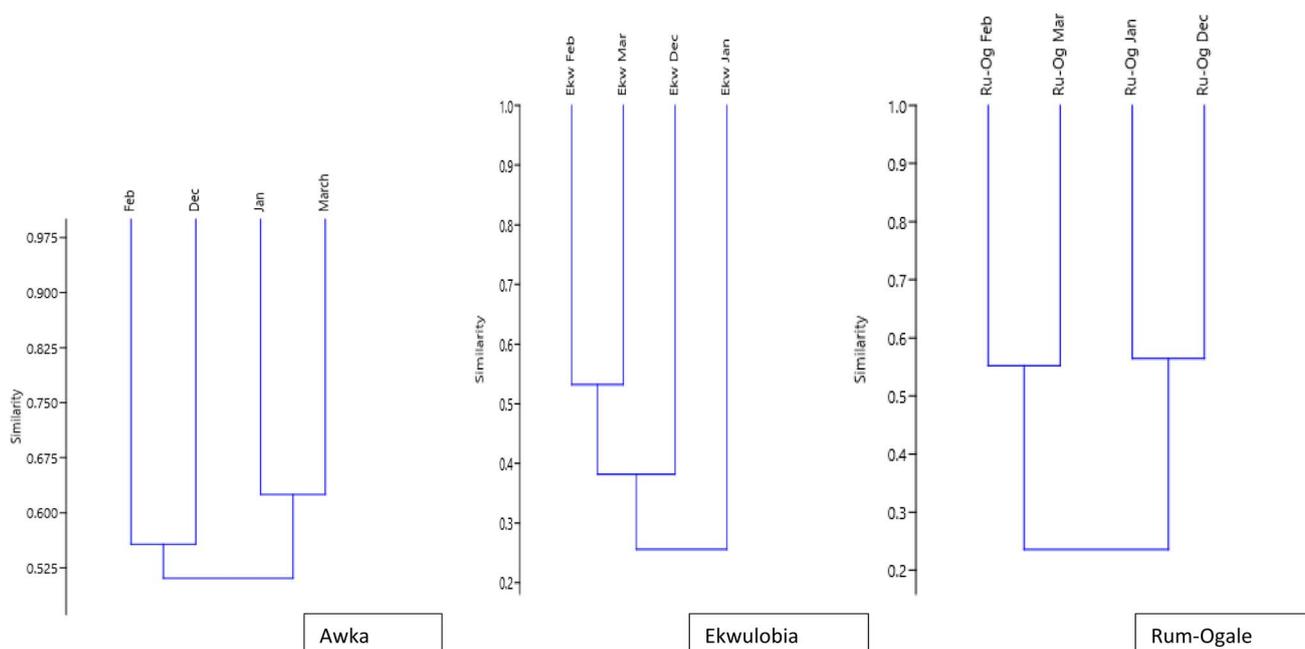

Fig. 5 Bray–Curtis cluster analysis of sample months (December 2019 to March 2020) for Awka, Ekwulobia and Rumuodomaya-Ogale.

liquified petroleum gas, natural gas and coal. Factor 2 accounted for 32.68% of the total variance and had strong positive loading of acenaphthene (VHJ and FHSSP), dibenzo(*a*–*h*) anthracene (ERt, VHP, VHJ) and fluorene (VHP). Factor 3 was dominated by fluoranthene (VHP and FHSSP) and anthracene (VHP, VHJ and FHSSP) and accounted for 19.26% of the total variance. Dibenzo(*a*–*h*)anthracene is a 5-ring PAH traceable to automobile emissions, while anthracene, acenaphthene and fluorene are tricyclic PAHs that indicate a low temperature combustion process.[75]

The loading component of PAHs in dust from Rumuodomaya-Ogale localities explained 100% of the total variance in the data (Table S13†). Factor 1, which accounted for 62.76% of the total variance, had a strong positive loading of acenaphthylene (all locations), Fluoranthene (EAJ, EEB, and PPLRd), anthracene (all locations), benzo(*g,h,i*)pyrene (EAJ and PPLRd), acenaphthene (all locations), dibenzo(*a*–*h*)anthracene (all locations), phenanthrene (all locations), benzo(*a*)pyrene (all

locations) and pyrene (EEB). Factor 2 accounted for 36.34% of the total variance and had a strong positive loading of fluoranthene (Eleme Petrochemical junction), benzo(*a*)anthracene (EEB), benzo(*g,h,i*)pyrene (EAJ and PPLRd), fluorene (EAJ and EEB), and pyrene (EPJ and EAJ). In Factor 3, the high loading of benzo(*a*)anthracene (EAJ), naphthalene (EEB) and benzo(*k*)fluoranthene (EAJ) contributed 0.90% of the total variance. LMW naphthalene is a tracer for incomplete combustion processes, while HMW benzo(*k*)fluoranthene originates from diesel-powered engines.[76]

3.4.2 Positive matrix factorization (PMF). To improve the source identification of PAHs in road dust of Rum-Ogale (known for industrial activities), the quantitative receptor model EPA's PMF was run (Fig. 4). The model could not be used for other locations because of the zero uncertainty in PAH concentrations in some months of study (they were below the detection limit), thereby reducing the variability that PMF need to distinguish between sources. The PAH components were
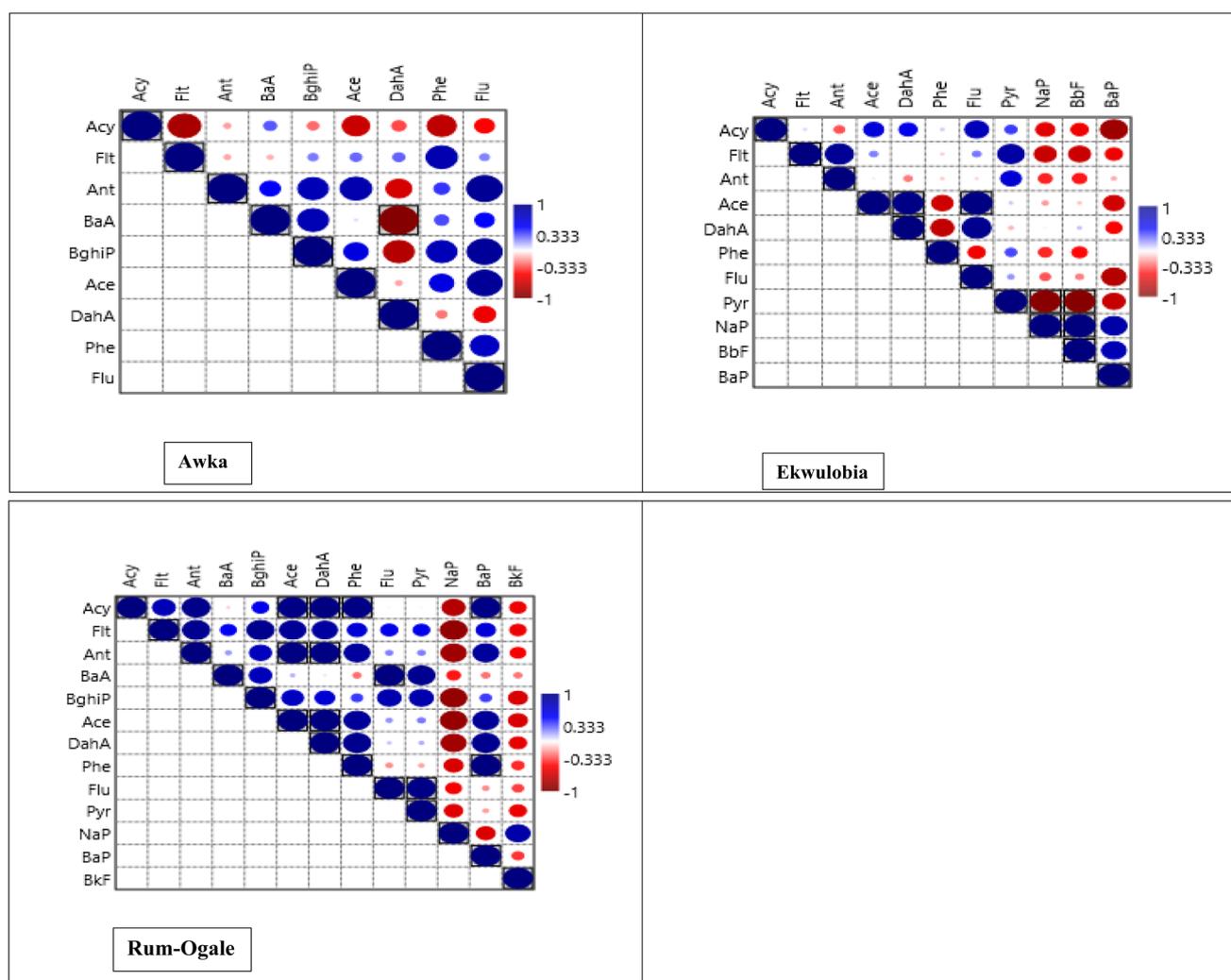
Fig. 6 Pearson's correlation between PAHs in roadside dust of Awka, Ekwulobia and Rumuodomaya-Ogale. Correlation is significant at the 0.05 level (boxed dots). The dot size represents the magnitude (strength) of the correlation coefficient between the two PAHs. The larger dot indicates a stronger correlation, while the smaller dots imply a weaker correlation. Additionally, the blue dot indicates a positive correlation, while the red dot shows a negative correlation.

categorized as strong with S/N values ranging from 3.58 to 5.65. The PMF random seed and number of factors were 84 and 3, respectively.

Considering Factor 1, the % contributions of the PAH species are as follows: Acy (25%), BghiP (70%), DahA (23%), Phe (<1%), and Pyr (89%). Factor 1 showed high loadings of BghiP and Pyr, which are indicators of vehicular emission and oil combustion, respectively;[85] hence, Factor 1 represents vehicular emission and oil combustion-related sources. In Factors 2 and 3, the PAHs % contributions were in the following order: Acy (67%, 14%), BghiP (26%, 26%), DahA (77%, 0.6%), Phe (85%, 13%), and Pyr (<1%, 42%). Factor 2 showed a high dominance of DahA and Phe in the road dust. Phe is a 3-ring LMW PAH, indicating unburnt fossil fuels,[86] while 5-ring HMW DahA could be traceable to oil refining activities and vehicular emissions.[31] Therefore, Factor 2 was designated as a petrogenic- and pyrogenic-related source. Factor 3 was characterized by weak PAH loadings, with Pyr having the highest contribution of 42%, suggesting that the factor represents a non-specific background source.

3.4.3 Bray–Curtis hierarchical cluster analysis. The Bray–Curtis hierarchical cluster analysis of all sample locations is shown in Fig. 5. This was carried out to determine the similarities among the different sampling months of the roadside dust.[34] In Awka, the cophenetic correlation was 0.89 among all sample locations, with January and March showing a maximum similarity of 60%. The months of February and December had a maximum similarity of 52%. In Ekwulobia, the cophenetic correlation was 0.99, with February and March having a maximum similarity of 50%. The month of December exhibited a similarity of 40% with March and February. Additionally, the month of January had the least similarity with December, February and March. Rumuodomaya-Ogale with a cophenetic correlation of 0.98 showed the same maximum similarity of 50% with December/January and February/March, as shown in Fig. 5. Hence, it could be concluded that PAHs in Awka dust had the highest maximum similarity.

3.4.4 Pearson correlation: PAH inter-relationships. The Pearson's correlation of PAHs in dust from the studied localities is presented in Tables S14–S16† and Fig. 6. For clarity and easier interpretation purposes, the mean of PAH in each sample location was determined and then used to carry out the correlation analysis. Sample data showed that some PAHs were not detected in the dust; hence, analysis was carried out for those detected using PAST software. In Awka, 3-ring PAHs strongly correlated positively with each other among Flu, Ant, and Ace. There was a high positive correlation between 3- and 4-ring (Phe and Flt), 6- and 3-ring (Bghip, Ant, Phe, and Flu) and 6- and 5-ring (BghiP and BaA) PAHs. Additionally, the 3-ring PAHs (Flu and Phe) moderately correlated positively among themselves, while Acy and DahA showed no significant positive correlation with other PAH components, as shown in Table S14.† The positive correlation of 3-ring PAHs with each other indicates compounds that could be of similar origin. The 6- and 5-ring PAHs are HMW compounds, and their high correlation in the dust samples also suggests a common anthropogenic source. As illustrated in Table S15,† a significant positive correlation

existed among 3- and 4-ring PAHs (Ant and Flt), 5- and 2-ring PAHs (BbF, BaP and NaP) and 5- and 3-ring PAHs (DahA and Ace) in Ekwulobia dust, indicating that the PAH source in the dust is a mixture of diesel and petrol engine cars.[56] Some PAH compounds (3 rings, 4 rings, and 5 rings) correlated positively with each other, confirming a possible common origin. High positive correlations were observed in dust from Rumuodomya-Ogale locations (Table S16†) among 4- and 3-ring PAHs in Flt, Ace, Ant, Flu, BaA, and Pyr. Other PAH pairs with strong positive correlations are 5 and 2 rings (BkF and NaP), 5 and 3 rings (DahA, Acy, BaP, Ant, Ace, and Phe), 6 and 3 rings (BghiP, Ant, and Flu), and 6 and 4 rings (BghiP, Flt, BaA, and Pyr). Additionally, 3-, 4-, and 5-ring PAHs correlated strongly with each other; hence, there were a greater number of strong and positive correlations between PAH pairs in the Rumuodomaya-Ogale sample location when compared with other study areas.

4 Conclusion

The appreciable concentration of PAHs was observed in the dust of the studied locations: Awka, Ekwulobia and Rumuodomaya-Ogale, from December 2019 to March 2020, with February and March showing the highest total PAH concentrations. Based on the Incremental Life Cancer Risk model, the PAH concentrations would not likely cause any cancer risk to the roadside dwellers: hawkers, petty traders, shop owners, drivers, passengers, automobile repairers, and food vendors, who spent quality time in outdoor activities. However, it was observed that non-cancer effects, such as skin irritation and inflammation, cataracts, decreased immune function, kidney and liver damage and asthma, could occur during short- and long-term exposure. The concentrations of PAHs in the road dust of the sample areas followed the order Rumuodomaya-Ogale > Ekwulobia > Awka, indicating that inhabitants of Rumuodomaya-Ogale are more exposed to PAHs in dust. In all the months of the study, children had higher ingestion cancer risk (CR) values than their adult counterparts owing to their frequent hand-to-mouth habits at playtime. The CR values of adults showed that they are more exposed to PAHs in dust *via* skin contact and inhalation routes. Traffic densities, congestion and emissions from petrol and diesel engine cars contribute majorly to the PAH load of the environment, considering their correlations from the study. Careful environmental management remains key to the regulation of PAHs in the environment and wholesome environmental cleanliness; hence, the environmental monitoring team, in conjunction with the health policy makers of Anambra and River States, Nigeria, should ban illegal artisanal refinery and open burning of waste and biomass near major roads as well as ensure repairs of damaged roads that often lead to fall and explosion of petrol/diesel laden vehicles to reduce PAH contaminations of the environment.

Data availability

Data used for the study were already contained in the manuscript.

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Author contributions

Conceptualization: JKN; data curation: CCO; formal lab analysis: CCO; investigation: JKN, CCO; writing – original draft: CCO, JKN; writing – review and editing: JKN, HIK; methodology: JKN, CCO; statistical analysis: CCO; funding acquisition: CCO, JKN, PCO.

Conflicts of interest

The authors declare that they have no conflict of interest.

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