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Speciation of the polycyclic aromatic hydrocarbons (PAHs) in scallions (*Alium chinese*; order; asterales; family; Asteraceae) cultivated on the shoulder of intracity highways in Lagos, Nigeria

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Abstract The comparative mean results obtained in this study showed the following: pyrene 2.94±0.11 µg/g, chrysene 3.01±0.23 µg/g, BaP; 2.94±0.13 µg/g, BaA; 3.01±0.12 µg/g and BbF; 3.04±0.13 µg/g. The results of the health evaluation showed that Beneze (a) pyrene had the highest value (14.71 µg/kg), followed by Benze (b) fluoranthene and Benzo (a) anthracene (1.52 and 1.51) of the toxicity equivalent factors. Meanwhile, the sum across the station was significantly higher than the standard limits. The CDI (chronic daily intake) results obtained for each PAH congener were considerably high and fluctuated across the station. However, the results for the ILCR (incremental life cancer risk) were higher than the threshold set for this study. The study concluded that the content of PAH investigation in the scallions was higher than the set threshold. It is recommended that the cultivation of scallions on the highway shoulders be discontinued. Farmer's advocacy and education were imperative to enlighten the farmers on the adverse effects of farming along the road shoulders, and the implications of producing such vegetables for human consumption.

Keywords: Highways, Scallion cultivation, PAHs, Bioaccumulation, Human health, Risk quantification

Introduction

Scallions (green and spring onions) are important vegetables that are highly cherished globally and utilized in various continents for culinary especially salad. Scallions contain essential nutrients such as vitamins A, B_2 (thiamine), C, copper,

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phosphorus, and magnesium (Barode, 2023). They provide pleasant and unique tastes in cuisines and dishes (Abike, 2020; Ogodu, 2023), aid digestion, and boost the immune system (Daudu, 2022). Scallion regulates blood sugar as sulfur stimulates insulin production (Oghenetega, 2023). They help to fight free radicals and prevent the growth of cancerous cells Belo (2021) and Bamgboye, (2019), prevent osteoporosis and make the bones and the stomach strong Ojugo (2021), prevent tissues from damage and inflammation (Olanipeku, 2022).

The greatest producer of scallion is China with an annual production volume of 869839 tons while Mali the second-world producer has an annual production output of 26.979 metric tons (Awojobi, 2022; Jimoh, 2023; Oshokoyo, 2022). Scallion production in Lagos City, Nigeria is done on parcels of land on the road shoulders of urban city highways for visibility to commuting clients (Awosika, 2018; Ayodele, 2019; Bamgboye, 2019). Cultivation of scallions along intracity highways exposes them to various contaminants and toxicants expelled by the exhaust fumes of vehicles (Clarke, 2022). The composition of exhaust fumes includes carbon dioxide, carbon monoxide, ammonia numerous oxides, and polycyclic aromatic hydrocarbons (PAHs). PAHs are organic or synthetic contaminants with high chemical stability and lipophilicity (Baxter, 2014; Bayat *et al*., 2015; Bayraktar *et al*., 2016). They are mutagenic, carcinogenic, and disruptors of endocrine systems (Araghi *et al*., 2014; Argyropoulos *et al*., 2012). PAHs cause deoxyribonucleic acid (DNA) damage, cause respiratory problems, and have harmful effects on cardiovascular systems (Pozo *et al*., 2015; Ranzi *et al*., 2013; Ratola *et al*., 2013; Sacchi *et al*., 2013). In vegetable food crops, studies have shown the linkages of PAH contents in the whole plant tissues that call for great concern (Paris *et al*., 2018; Kalteh *et al*., 2020). Kalteh *et al*. (2020) reported that there have been no slated MPLs (maximum permissible limits) found for PAHs regulation in edible vegetables. This consequence is a deficiency in ample studies about the presence of PAHs in leafy edible vegetables to collaborate with the threshold set by the EU (European Union) commissions (2011) on plants. Studies from different parts of Nigeria showed that PAH contents in leafy vegetables had varied impacts as regards probable health risks when consumed by humans (Tesi *et al*., 2021; Igwe *et al*., 2022).

In Nigeria, several studies have been done regarding the health risks of PAH contents in animals and plants (Olayinka *et al*., 2019; Tesi *et al*., 2021; Igwe *et al*., 2022). However, no study had been conducted about PAHs in scallion vegetables grown or cultivated on road shoulder of intracity highways. Thus, the focus of this study was to determine the PAH content of scallions grown on vegetable farms located on highways shoulders in Lagos City Nigeria for its suitability for human consumption and the considerations for probable health

risk. The PAHs are investigated as pyrene, chrysene, benzo (a)pyrene (BaP) benz(a)anthracene (BaA), and benz (b)fluoranthene (BbF).

Materials and methods

Area of the study

Lagos state is one of the 36 states that make up the Federal Republic of Nigeria. It is located between a latitude of 6.465422°N and a longitude of 3.406448E (Figure 1) with a land area of 1,171 km^2 and a population of 24 million (National Population Commission, 2006). Lagos as a littoral state is the industrial hub and economic headquarters of Nigeria. It has 13 industrial estates and a high network of roads where Scallions are grown on the road shoulders of the majority of the highways.

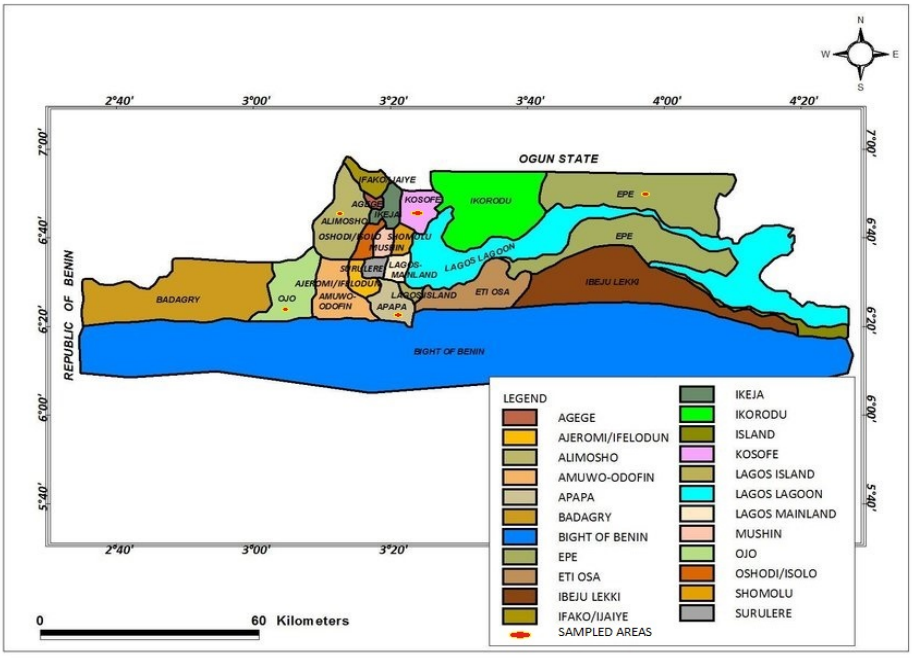

Figure 1. Map of Lagos showing the sampled locations

Ethical consideration

Scallion samples were collected from the vegetable farms after due permissions were obtained from the farm owners. No approval was sought or obtained from the government because there was no prohibiting law in place against such sample collection.

Sampling

Vegetable farms along the highways used for this study were Lagos State University - Iba Estate highways (LA-IB), Alapere to Old toll gate highways (AL-OT), Oko-Oba to Abulegba highway (OK-AB), Orile Iganmu to National Theatre highways (OR-NT) and Lekki to Epe highways (LK-EP). Five farms were randomly selected from the pools of farms along each highway. The selected farms were mapped out into sampling grids (SG), A, B, C, D, and E, and from each of the sampling grids (SG), scallion samples were randomly collected from 5 sports in each, wrapped in aluminum foils for analysis.

Analysis

The samples from each sampling grid in each farm were thoroughly washed with clean water and rinsed with deionized water. They were then pulverized with a motorized shredder pulverized and later homogenized with an Agilent blender/homogenizer model 430A. 5g of the homogenized was weighed out into a flask and 50 mL dichloromethane was added. This was followed by the addition of 25 microlitres (µl) of 20 parts per million of surrogate standards for recovery and sonicated for 15 minutes deploying an ultra sonicator. The digest obtained was transferred into another flask and anhydrous sodium sulfate was added to expel any available moisture and left at room temperature to allow dichloromethane to evaporate to about 2 ml. The extracts were then passed through silica gel with an alumina column for fractionation. 30 ml of n-hexane was added, and the supernatant was used in the determination of the PAH using Agilent single quadrupole GC/MSD 5977C.

Computation of data

Using the Statistical Package for Social Scientists (SPSS) 29 and Microsoft Excel 2019, Windows 10 pro application, an analysis of variance (ANOVA) and the computation of the mean and standard error (SE) were carried out to determine if there were any significant differences in the samples acquired.

The software Microsoft Excel 2019 and Windows 10 Pro were used to assess the possible health hazards associated with the samples.

Evaluation of exposure

The PAH levels in Nigerian scallions are used as the basis for the PAH 15 health risk assessment. BaP was utilized as the main example to show how the

toxicity equivalent factors (TEFs) of PAH and the carcinogenic risk of PAH15 are related. The TEF in this study was demonstrated to consist of BaP-Benz(a)pyrene (1), BaA-Benz(a)anthracene and BaF-Benzo(b) fluoranthene (0.1), Chr-Chrysene (0.01), and Pyr-Pyrene (0.001). The BaPeq, or BaP-Benz(a)pyrene equivalent, was computed using formula (1):

$$TEQBap = \sum_{i=1}^{n} Ci * TEFi \quad \textbf{1}$$

where the values of TEFi and Ci reflect the TEF congener (i) in the scallion species and the quantity of PAH in the acquired scallion species sample. The total of all PAHs, or TEQBaP-Bapeq 15, was used to calculate the carcinogen risk.

The CDI (chronic daily intake) of PAHs was computed using equation 2 (Dadar *et al.,* 2022; US EPA, 1992) using BaP as the standard equivalent level:

$$CDI\ (ng * BaPeq\ per\ bw.d) = \sum Ci * lRi * ED * \frac{ET}{Bw*AT} \quad \textbf{2}$$

Where the value of Ci is the predicted quantity of PAH15 for BaPeq in ng BaPeq/g for the scallions. The daily intake (IRi) for the age scallion species is reported in grams per day. Exposure days (ED)- 53. The exposure frequency (EF)- 365 days in a year. According to a 2008 study by the European Food Safety Agency, the values for body weight (BW), ingestion rate (IR), and average time (AT) were 65 kg, 70 years, and carcinogenic for 25,550 days.

The carcinogenic risk was computed using the formula (3).:

$$ILCR = CDI*SF*CF \quad \textbf{3}$$

The conversion factor (CF) is 10^{-6} mg/mg, and the slope factor (SF) for ingesting PAH for BaP is 7.3 mg/kg/day, where the incremental life cancer risk (ILCR) is dimensionless US EPA (1992).

Results

Characterization of PAHs in scallion species

The results of the analysis of the PAHs in scallions cultivated on the road shoulders of intracity highway in Lagos Nigeria were shown in Figures 2-6 and the comparative PAHs content of the scallion cultivated in all the highways selected in Lagos in Figure 7.

The group mean of the PAHs in the scallions in intracity highways in Lagos was subjected to the test of significance deploying special package for Social Sciences (SPSS) model 29 (IBM) at 0.05 level of significance and the p-value was 0.42 thus rejecting H_0.

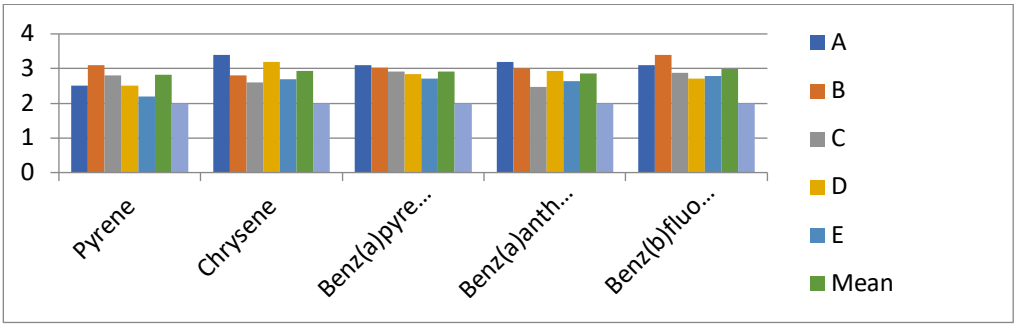

Figure 2. The PAHs contents of the scallions cultivated along Lagos University Iban estate high (LA-IB) and EU Regulation 1255/2020 MPC for PAHs in vegetables in µg/kg

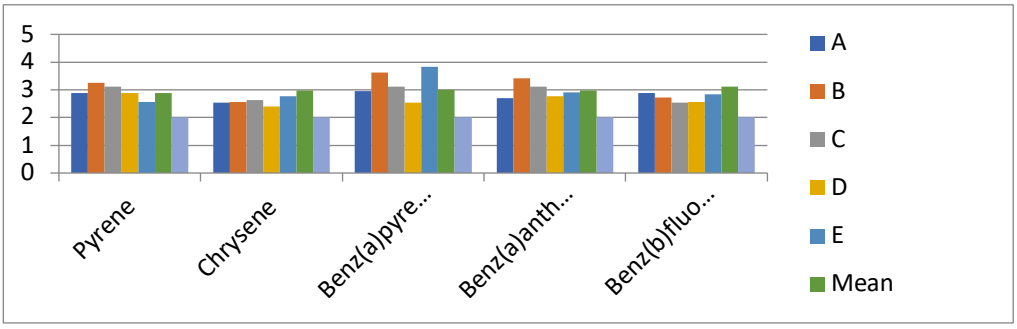

Figure 3. The PAHs content of scallion cultivated at the Alapere-old Tollgate highway (AL-OT) and the EU Regulation 1255/2020 MPC for PAHs in vegetables in µg/kg

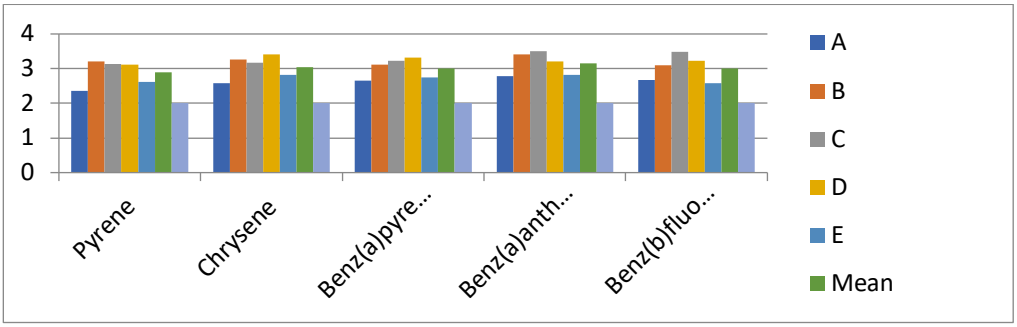

Figure 4. The PAHs content of scallions grown at the road shoulders of Oko-Oba-Abulegba highways (OK-AB) and the EU Regulation 1255/2020 MPC for PAHs in vegetables in µg/kg

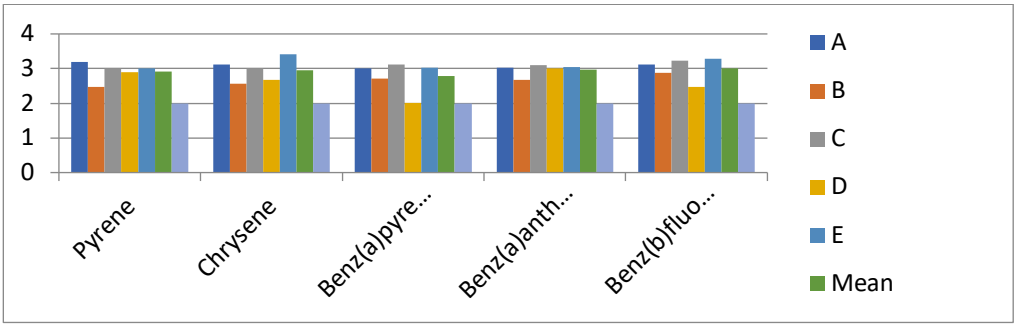

Figure 5. The PAHs content of scallions grown at the road shoulders of Orile-Iganmu-National Theatre intra-highway and EU Regulation 1225/2020 MPC for PAHs in vegetables in µg/kg

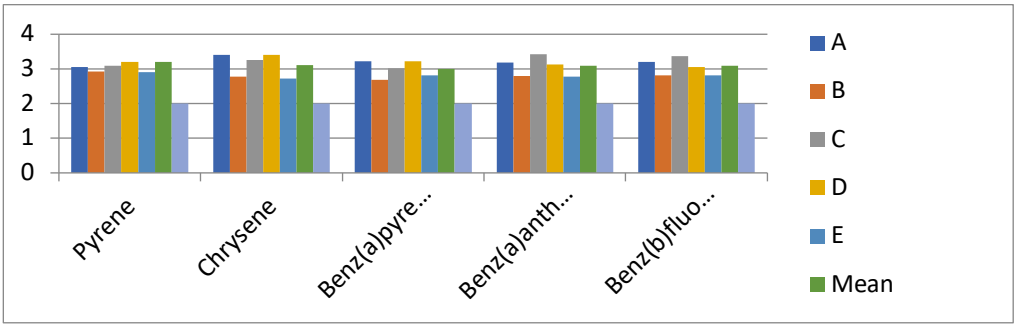

Figure 6. The PAHs contents in scallions grown on road shoulders of Lekki-Epe intra-highway and European 1255/2020 for PAHs in vegetables in µg/kg

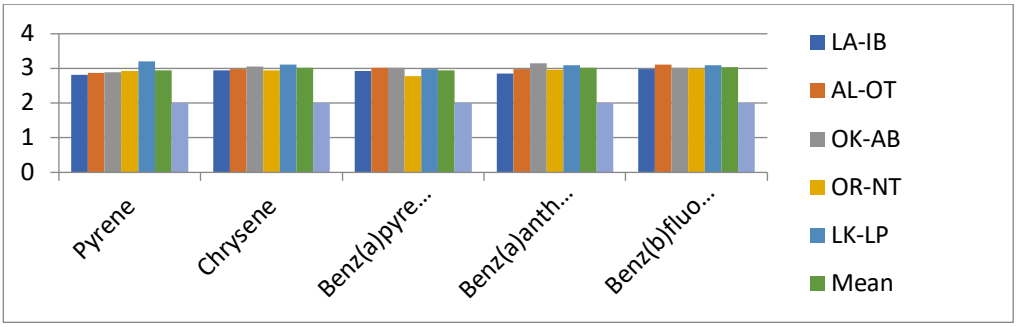

Figure 7. Mean comparisons of the PAHs in scallions grown in intra-highway shoulders in Lagos city and European Union Regulation 1255/2020 for PAHs in vegetables in µg/kg

Health risk calculation of PAHs in Scallion species

The results for the non-carcinogenic risks from the possible ingestion of PAH congeners in the scallion sourced from different locations in Lagos city of Nigeria are shown in Tables 1 and 2. The results showed that Beneze (a) pyrene had the highest value (14.71 µg/kg), followed by Benzo (b) fluoranthene and Benzo (a) anthracene (1.52 and 1.51) of the toxicity equivalent factors. Meanwhile, the sum across the station was significantly higher than the standard limits (Table 1). The CDI results obtained in this study for each of the PAH congeners were considerably high and fluctuated across the station (Table 2).

However, the results for the ILCR showed that the values were higher than the threshold set for this study (Table 3).

Table 1. Toxicity-equivalent factors of selected PAH congeners in scallions

No of vegetable sample	Designate	Beneze (a) pyrene (µg/kg)	Pyrene (µg/kg)	Chrysene (µg/kg)	Benzo (a) anthracene (µg/kg)	Benzo (b) fluoranthene (µg/kg)	
		TEQBaP	TEQBaP	TEQBaP	TEQBaP	TEQBaP	Sum
5	LA-IB	2.92	0.00	0.03	0.29	0.30	**3.54**
5	AL-OT	3.01	0.00	0.03	0.30	0.31	**3.65**
5	OK-AB	3.01	0.00	0.03	0.32	0.30	**3.66**
5	OR-NT	2.78	0.00	0.03	0.30	0.30	**3.41**
5	LK-EP	2.99	0.00	0.03	0.31	0.31	**3.64**
	Σ	**14.71**	**0.01**	**0.15**	**1.51**	**1.52**	

*EU 1255/2020 MPC for PAHs in scallions is 2.0 µg/kg

Table 2. Potential CDI of selected PAH congeners in scallions

No of vegetable sample	Designate	Benzo (a) pyrene (µg/kg)	CDI	Pyrene (µg/kg)	CDI	Chrysene (µg/kg)	CDI	Benzo (a) anthracene (µg/kg)	CDI	Benzo (b) fluoranthene (µg/kg)	CDI
5	LA-IB	2.92	456.77	2.82	441.13	2.94	459.90	2.85	445.82	2.98	466.16
5	AL-OT	3.01	470.85	2.88	450.51	2.98	466.16	2.98	466.16	3.11	486.49
5	OK-AB	3.01	470.85	2.89	452.08	3.05	477.11	3.15	492.75	3.01	470.85
5	OR-NT	2.78	434.87	2.92	456.77	2.95	461.46	2.97	464.59	3	469.29
5	LK-EP	2.99	467.72	3.2	500.57	3.11	486.49	3.1	484.93	3.1	484.93

*EU 1255/2020 MPC for PAHs in scallions is 2.0 µg/kg

Table 3. Probable ILCR of selected PAH (Benzo (a) pyrene) in scallions

No of vegetable sample	Designate	Benzo (a) pyrene (µg/kg)	ILCR
5	LA-IB	2.92	0.02
5	AL-OT	3.01	0.02
5	OK-AB	3.01	0.02
5	OR-NT	2.78	0.02
5	LK-EP	2.99	0.02

US EPA (1992) standard for ILCR: *1×10^{-6} to 1×10^{-4}

Discussion

PAHs contents quantification in scallion species

Research evidence attested to the contamination and bioaccumulation of PAHs in vegetables on highways shoulder from the soil and particulate droplets in other climes (Albanese *et al.,* 2014; Anyakora and Coker, 2006; Qin *et al*., 2014; Sazakli *et al*., 2015). More research is being constantly carried out on ways to ameliorate the impact of PAHs on human health (Azah *et al*., 2015 Aziz *et al*., 2014; Baldantoni *et al*., 2014; Ogwu *et al*., 2022) However, research on the same in Lagos City remains largely unavailable in this study.

Findings from this study revealed varying contamination levels of the PAHs investigation. The mean content of pyrene in the scallions varied from 2.82µg/kg on the Lasu-Iba estate highway to 3.20 µg/kg on the Lekki-Epe highway with a mean concentration of 2.94 µg/kg. This increased content of PAHs is the consequence of the bioaccumulation of the contaminants on the scallion leaves. The result is in agreement with the reports of (Barakat *et al*., 2011). Pyrene affects endocrine activities and damages the DNA (Al-Thukair and Malik, 2016; Ogwu *et al*., 2022).

Chrysene concentration distribution was 2.94µg/kg in the Lasu-Iba estate to 3.05 ug/kg at Oko-Oba-Abulegba highways with a comparative mean concentration of 3.01µg/kg. The elevation of chrysene in the scallions is anthropogenic, from particulate droplets and bioaccumulation of chrysene from the soil emanating from vehicular exhaust fumes. This report agrees with the studies conducted by (Alagić *et al.,* 2015; Bandowe *et al*., 2014) Chrysene contamination has been classified as a cancer-causing agent (Amezcua-Allieri *et al*., 2012; Ogwu *et al.,* 2022; Rodgers-Vieira *et al*., 2015).

The studies also revealed that BaP concentration in the scallions ranged from 2.92µg/kg in the Lasu-Iba estate highway to 3.01µg/kg at the Oko-Oba-Abulegba intracity highway with a comparative mean of 2.94 µg/kg. The visible

increase in the contents of BaP in the scallion was concomitant to the vehicular exhaust fumes emission resulting in foliar accumulation of some and also through bioaccumulation of the toxicant in the plant physiology through the roots. This result is in tandem with the reports (An *et al*., 2016; Anyanwu and Seample, 2015; Ogwu *et al*., 2022; Rodriguez *et al*., 2012). The health effects of BaP on humans include lung and skin cancer Ogwu *et al*. (2022), Ren *et al*. (2014), and Ren *et al*. (2015), bladder cancer (Rosales *et al*., 2013).

The study equally revealed that the concentrations of BaA were between 2.85 µg/kg in the Lasu-Iba estate high to 3.10 µg/kg in the Lekki-Epe intracity highway with a comparative mean of 3.01 µg/kg; this increase in the concentrations of BaA is associated with human activities. This result of increased BaA in the scallions aligns with the reports recorded by (Seegar, 2015; Semedo *et al*., 2014; Scheurer *et al.,* 2014). BaA is known to cause skin damage, coughing Ramdine *et al*. (2012), Ré *et al*. (2015), Sather *et al*. (2006), lung cancer shortness of breath throat cancer (Aly Salem *et al*., 2014).

BbF concentration in the scallions in this study was between 2.98 µg/kg at Lasu-Iba estate intra highways to 3.11 µg/kg at Alapere-Old tollgate with a comparative mean of 3.04 µg/kg. The high level of BbF is attributed to the direct effects of exhaust emissions causing particulate droplets resulting in bioaccumulation and biomagnification of BbF in the scallion. This result corroborates the studies carried out by (Al-Daghri *et al*., 2014; Angioni *et al*., 2014; Araghi *et al*., 2014; Bandowe *et al*., 2014). Human, prolonged exposure to BbF has been implicated in skin, liver, and lung cancer (Al-Daghri *et al*., 2014; Alharbi *et al*., 2014; Bacosa and Inoue, 2015; Sarria-Vila *et al*., 2016).

Probable risk quantification of PAH contents in Scallions

There was a sufficient concentration of the chosen PAHs in scallions according to the results of the health risk assessment of the species. The TEFs were noteworthy since the scallions of Beneze (a) pyrene, Benzo (b) fluoranthene, and Benzo (a) anthracene had substantial quantities of PAHs. If the species under investigation is taken more than the recommended daily intake, there may be a non-carcinogenic health risk. The CDI (chronic daily intake) data demonstrated a beneficial synergy between the TEF results. The TEFs and CDI levels were both significantly higher than the EU's regulation criteria for scallion species (2011 and 2020). Tesi *et al*. (2021), Igwe *et al*. (2022), and Liu *et al.* (2023) have also reported similar instances.

In comparison to the US EPA (1992) (1×10^{-6} to 1×10^{-4}) and Liu *et al*., (2023) standards for exposure valuation for PAHs compounds, the ILCR result

(1×10^{-2}) in this study demonstrated a significant increase. As a result, eating scallions by people carries the danger of developing cancer.

The findings from this study confirmed the detrimental consequences of growing vegetables near highway shoulders because the crops are exposed to pollution from gasoline-powered cars' exhausts through contaminant expulsions. According to the study, scallions were contaminated with PAHs, which not only made the vegetables unsafe for human consumption but also prevented them from being exported since Codex Alimentarius huddles for export products could not be scaled. As a result, it is advised that laws be passed to forbid growing scallions on the shoulders of highways, as the crop is unfit for human consumption and should not be exported. Farmers must get education on the detrimental effects of their operations.

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