



Human health risks of PAHs in soil and vegetables from Tiga, Kano State, Nigeria

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ABSTRACT

This study evaluates the concentrations of seventeen polycyclic aromatic hydrocarbons (PAHs) in soil and selected vegetable samples (onions, tomatoes, hot peppers, sweet peppers, and garden eggs) from Tiga agricultural locations in Kano State, Nigeria. Soil samples were collected from ten plots (depth profiles of 0–10 cm, 10–20 cm, and 20–30 cm) and combined at each depth to create composite samples. Additionally, 20 g of each vegetable were collected and divided into fruit, stem, and root components. Standard procedures were used for the extraction and clean-up of PAHs from both soil and vegetable samples, and instrumental analysis was conducted using SHIMADZU GC-MS (GC-17A). PAH levels in soil ranged from 1.20E-02 mg/kg to 3.80E-02 mg/kg, while vegetables showed concentrations from 1.00E-03 mg/kg to 8.90E-02 mg/kg. The 0–10 cm soil samples displayed higher PAH concentrations among all the depths studied, while the vegetables with the highest PAH concentration followed the trend: Onions > Sweet Pepper > Tomatoes > Hot Pepper > Garden Egg. Overall, total PAH concentrations in vegetables exceeded those in soil. Estimated daily PAH doses were below the Tolerable Daily Dose Limit set by FAO, indicating low health risks. Incremental lifetime cancer risk values also fell below US EPA acceptable levels (10E-06), suggesting negligible cancer risk while the hazard index was less than 1, implying no appreciable non-cancer health risks. PAH pollution was attributed to both petrogenic and pyrogenic sources. The findings of this study indicate that under the assessed conditions, the five vegetables evaluated from Tiga pose no significant risk and are considered safe for consumption.

1. Introduction

Environmental pollution stands as a paramount global issue, and a leading contributor to morbidity and mortality [1]. Human activities, notably mining, urbanization, industrialization, exploration, and agriculture, have spearheaded widespread environmental pollution on a global scale. Consequently, the focus has intensified on polycyclic aromatic hydrocarbons (PAHs) due to their known toxicity, mutagenic potential, and carcinogenic properties when exposed [2].

PAHs are defined as organic environmental pollutants featuring two or more carbon-hydrogen aromatic rings, primarily originate from the incomplete combustion of organic materials associated with anthropogenic activities [3]. The Agency for Toxic Substances and Disease Registry [4] has identified over 100 different PAHs. These highly mobile compounds can be transported considerable distances from their sources [5,6].

Research by Purcaro et al. [7] indicates that over seventy percent of the global population is exposed to PAHs, with contamination levels

influenced by food sources and preparation methods. PAHs have been detected in a wide range of food products, including vegetables, meat and fish [2,8].

In Kano State, Nigeria, the second most populous state, commercial activities and a diverse economy spanning both industry and agriculture have been pivotal. The increasing population has led to a surge in demand for food, particularly vegetables. To address this, the Tiga Dam was constructed to provide water for irrigation along the floodplains. However, Tiga dam receives large amounts of effluent from nearby industries and municipal wastewaters. This discharge contains organic wastes in high concentrations that are harmful to aquatic ecosystem and local population depending on the water.

Industrial areas, particularly those close to Tiga Dam, are major sources of air pollution, especially due to industrial emissions. These activities release PAHs into the air as gases or particulate matter, and can travel long distances before settling on the soil, crop or water bodies.

In a similar manner, Tiga dam also receives agricultural run-offs from extended farm lands along Tiga flood plain. These cultivated lands have

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a history of practicing intensive modern agriculture, characterized by substantial use of agrochemicals, fertilizers (including sewage sludge wastewater), and mechanized farm tools to improve yield and satisfy the increasing food demand. As a result, emissions from mechanized tools, trucks, industrial effluents discharge, and waste burning, have significantly contributed to environmental pollution.

In other words, irrigation water sourced from the TIGA Dam becomes contaminated due to the indiscriminate disposal of sewage, agricultural waste, and other anthropogenic activities. Consequently, contaminated farm products are consumed locally and distributed. This scenario has spurred research into the associated risks of consuming contaminated foods [9,10].

Several studies have examined PAHs in soils and vegetables, identifying industrial activities as key sources of contamination and the need for health risks assessment [2,11–16].

Therefore, there is a pressing need to assess the contamination of PAHs in soil and some selected vegetables samples cultivated around

TIGA Dam agricultural location, Kano State, Nigeria and assess associated health risks.

2. Methodology

2.1. Study area

Constructed between 1971 and 1974, TIGA Dam aimed to enhance food security through irrigation farming. Positioned at Latitude 11° 15' to 11° 29' N and Longitude 8° 16' to 8° 38' E, the dam spans an area of 178 square kilometers, boasting a maximum capacity close to 2,000,000 cubic meters. Specifically, the dam measures approximately 40.40 km in length, 24.40 km in width, and 40.00 m in depth, with a surface area of 178.00 km² and a storage capacity of around 1978.49 × 106 m³ liters of water [17].

2.2. Sample collection

2.2.1. Collection of soil and vegetable samples

The soil sampling procedure followed Akan et al. [18,19] in the TIGA Dam agricultural areas. This study, titled 'Human Health Risks of PAHs in Soil and Vegetables from TIGA, Kano State, Nigeria', aimed to evaluate PAHs contamination in soil and vegetables. Ten plots were selected, and soil samples were collected at three depths (0–10 cm, 10–20 cm, 20–30 cm) using a 2.5 cm diameter spiral auger. Composite samples were formed by combining samples from different depths, placed in clean glass containers, labelled and transported to the Department of Pure and Applied Chemistry at the University of Maiduguri. Simultaneously, 20 g samples of five vegetables (onions (*Allium cepa*), tomatoes (*Lycopersicon esculentum*), hot pepper (*Capsicum chinense*), sweet pepper (*Capsicum annum*), and garden egg (*Solanum melongena*)) with root lengths between 7 and 11 cm, 48–85 cm, 32–44 cm, 33–45 cm, and 16–24 cm respectively were collected from five plots, ensuring replicates for each crop. According to GAPCS [17], these five vegetables were the most consumed in TIGA agricultural areas. The vegetable samples were placed in clean glass containers, labelled, and transported to the lab. They were stored at 4°C for preservation. Sampling was repeated three times a month over four months.

2.3. Soil sample preparation for PAHs analysis

The soil samples were air-dried at room temperature for 48 h, then

Table 1

Mean concentrations of PAHs in soil samples within TIGA dam agricultural location.

Concentration (mg/kg)				
PAHs	MAC's	0–10 cm	10–20 cm	20–30 cm
Naphthalene	1	ND	ND	1.03E–03
2-Methyl Naphthalene	1	7.73E–04	ND	ND
Acenaphthylene	3	1.91E–02	ND	ND
Acenaphthene	3	1.28E–04	ND	ND
Fluorene	3	3.75E–04	1.03E–04	ND
Phenanthrene	3	7.34E–05	6.53E–05	ND
Anthracene	3	1.47E–03	3.30E–04	4.30E–04
Fluoranthene	3	ND	1.02E–04	7.73E–04
Pyrene	3	8.78E–04	1.61E–03	1.67E–03
Benz(a)anthracene	0.15	2.93E–04	ND	1.75E–03
Chrysene	-	9.54E–03	6.94E–03	8.45E–03
Benz(b)fluoranthene	0.3	2.80E–04	ND	1.46E–04
Benz(a)pyrene	0.3	1.93E–05	2.97E–05	9.43E–04
Benz(k)fluoranthene	-	1.08E–04	ND	8.26E–03
Dibenz(a,h)anthracene	0.3	7.23E–05	6.27E–05	2.07E–03
Indinol(1,2,3 cd)pyrene	-	ND	ND	1.45E–03
Benz(g,h,i)perylene	-	4.94E–03	2.76E–03	1.03E–03
TOTAL		3.80E–02	1.20E–02	2.80E–02

MAC's = maximum allowable concentration [4], ND = Not detected

Note: Values represent the mean ± standard deviation, calculated at a 95 % confidence level.

Table 2

Mean concentrations of PAHs of stem part of sweet pepper, tomatoes, hot pepper, onion and garden egg cultivated within TIGA dam agricultural location.

Concentration (mg/kg)						
PAHs	MAC's	Sweet Pepper	Tomato	Hot Pepper	Onion	Garden Egg
Naphthalene	1	ND	8.68E–04	3.91E–04	1.06E–03	1.93E–04
2-Methyl Naphthalene	1	ND	ND	ND	ND	ND
Acenaphthylene	3	ND	ND	ND	4.12E–03	8.88E–04
Fluorene	3	ND	ND	1.26E–05	1.75E–04	ND
Acenaphthene	3	ND	ND	ND	ND	1.15E–05
Phenanthrene	3	3.89E–05	ND	ND	5.41E–05	ND
Anthracene	3	8.29E–04	9.99E–05	1.24E–05	9.79E–04	ND
Fluoranthene	3	1.04E–03	ND	2.30E–05	9.30E–04	1.07E–04
Pyrene	3	3.82E–03	2.37E–04	2.03E–04	2.65E–03	4.64E–04
Benz(a)anthracene	0.15	1.92E–03	8.32E–05	1.74E–04	2.16E–03	2.52E–04
Chrysene	-	3.71E–03	2.09E–04	1.02E–03	5.33E–03	7.34E–04
Benz(b)fluoranthene	0.3	1.41E–03	ND	ND	7.89E–04	2.74E–04
Benz(a)pyrene	0.3	7.31E–03	1.62E–03	ND	1.25E–03	1.49E–04
Benz(k)fluoranthene	-	7.13E–03	3.11E–03	ND	5.93E–03	1.64E–03
Dibenz(a,h)anthracene	0.3	2.74E–02	6.20E–03	ND	ND	2.99E–03
Indinol(1,2,3-cd)pyrene	-	2.38E–02	1.15E–02	ND	ND	1.86E–03
Benz(g,h,i)perylene	-	7.63E–03	ND	3.39E–03	6.36E–02	1.86E–03
TOTAL		8.60E–02	2.39E–02	5.23E–03	8.90E–02	1.14E–02

MAC's = maximum allowable concentration [4], ND = Not detected

Note: Values represent the mean ± standard deviation, calculated at a 95 % confidence level.

sieved through a 2 mm mesh to remove the coarse fraction, and stored in airtight containers prior to extraction [20].

2.4. Vegetable samples preparation for PAHs analysis

The vegetable samples underwent a process of being finely chopped, followed by oven drying. Subsequently, they were crushed using a laboratory mortar and sieved through a 0.5 mm sieve. Afterward, the purified vegetable samples were further ground using a blender and stored in airtight containers in preparation for the extraction process [21].

2.5. Extraction and clean-up of soil and vegetable samples for PAHs analysis

Soil samples were extracted using the method of Itodo et al. [20]. Ten grams (10 g) of arid soil were measured into a pre-cleaned extraction thimble, oven-dried, and extracted with n-hexane and acetone (4:1 v/v) in a soxhlet extractor for eight hours. The extract was evaporated to dryness at 40°C using a rotary evaporator, redissolved in 10 mL of n-hexane, and subjected to clean-up.

Vegetables were prepared using the method of Okereke et al. [21]. Two grams (2 g) of sample mixed with 10 g sodium sulfate were combined with 10 mL dichloromethane and allowed to settle. The mixture was filtered into a clean container, concentrated to 2 mL, and cleaned using a column packed with anhydrous sodium sulfate. The extract was further concentrated using a rotary evaporator, dissolved in 1 mL dichloromethane, and 1 µL was injected into the GC for analysis.

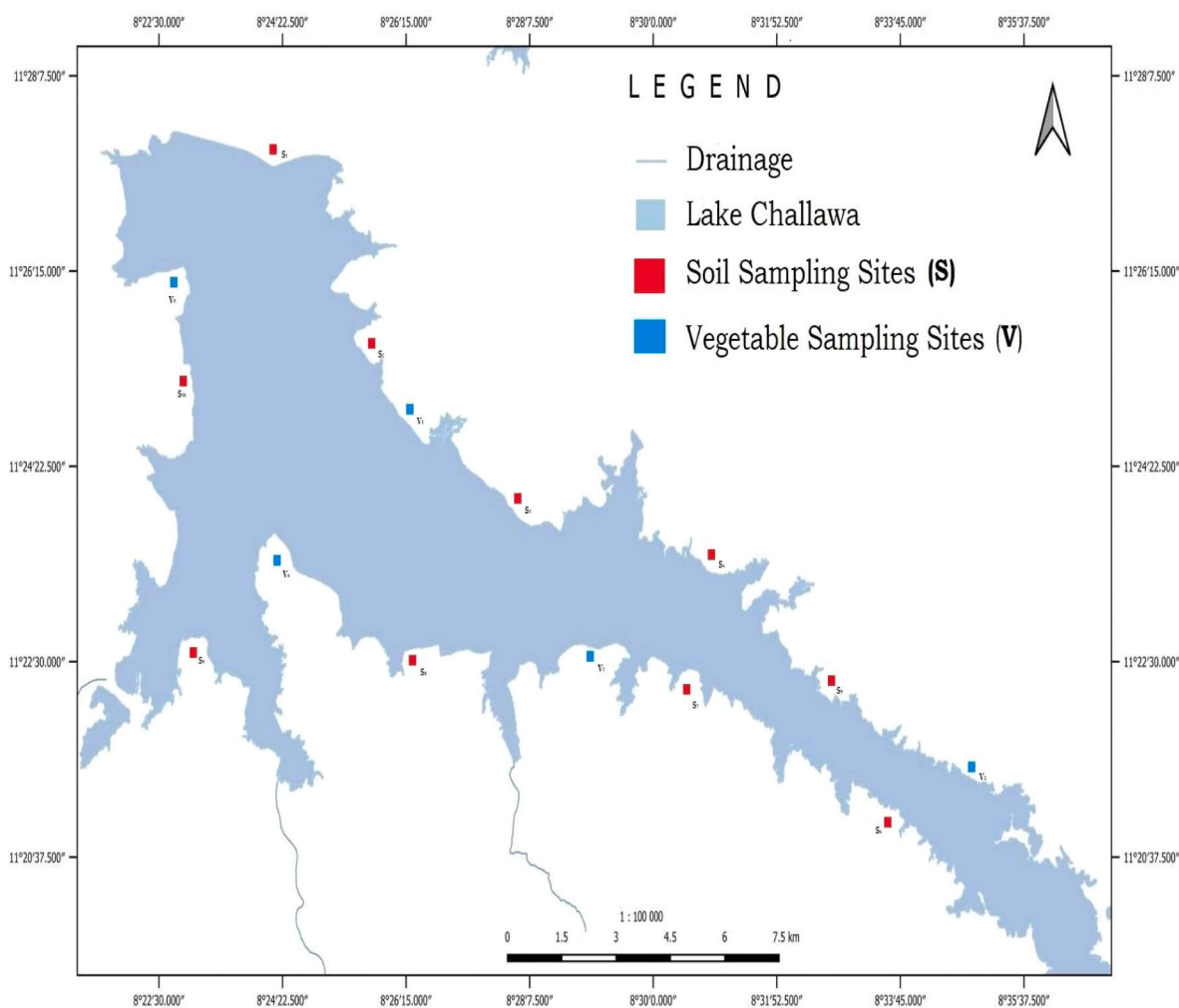
2.5.1. Instrumental analysis for analyte (PAHs) using GS-MS

The sample, consisting of soil and vegetable samples, was analyzed using a SHIMADZU GC/MS (GC-17A) that had been calibrated with PAHs standards. The equipment accurately determined the concentration of PAHs, utilizing the provided sample details.

2.6. Risk assessment of PAHs

2.6.1. Identification of PAHs sources in soil samples

Diagnostic ratios were employed to differentiate potential sources of PAHs in the soil. The following ratios were utilized as indicators of sources: Ant/Ant+Phe, BaA/BaA+Chr, Fluo/Fluo+Pyr, and the ratio of LMW-PAHs to HMW-PAHs.



Map 1: Map of Tiga Dam

Source: Cartography Lab, Department of Geography, University of Maiduguri (2021)

2.6.2. Carcinogenic risk assessment of PAHs in soil samples

The assessment of health risks linked to Polycyclic Aromatic Hydrocarbons (PAHs) in soil samples employed the Toxicity Equivalence Factor (TEF) method outlined by Nisbet and Lagoy [22] and adopted by Okereke et al. [21]. The TEF for each PAH was calculated to gauge its relative toxicity compared to Benzo[a]pyrene (BaP). The overall equivalent concentration was quantified and expressed as BaP equivalent (BaPeq). The BaPeq for each specific PAH was determined using the following equation:

$$BaPeq = \sum Cn \times TEFn$$

BaPeq = Benzo(a)pyrene Equivalence, Cn = Concentration, TEF = Toxic Equivalence Factor

2.6.3. Ecological risk assessment of PAHs in soil samples

The assessment of potential ecotoxicity of PAHs in the soil utilized the Mean Ecological Risk Medium Quotient (mERM-Q) approach. The calculation of mean ERM quotient values followed the formula method proposed by Long et al. [23], as outlined below:

$$m-ERM-q = \sum \left(\frac{Ci}{ERMi} \right) / n$$

m-ERM-q = Ecological Risk Medium Quotient, C = Concentration

2.6.4. Non-cancer hazard, carcinogenic risk calculation for vegetable samples

Risk associated with dietary exposure to non-carcinogenic PAHs was evaluated using hazard quotient approach. Hazard quotient is calculated by representing a ratio of the exposure dose (Average daily dose) for each PAH divided by an oral chronic reference dose (RfD).

$$Average\ Daily\ Dose\ (ADD) = \frac{TEQ_{BAP} \times IR \times CF}{BW}$$

TEQ_{BAP} = Toxic equivalence concentration, IR = Ingestion rate of carcinogenic PAHs based on average vegetable consumption rate per capita in Nigeria, CF = Conversion factor (0.000001 mg/μg), BW = Average body weight in Nigeria estimated at 70 kg [24].

Hazard Quotient (HQ) = Average daily dose (ADD)/RfD

The total risk due to exposure to mixture of carcinogenic PAHs in the product of the dietary carcinogen exposure dose (mg kg⁻¹ BW⁻¹) and

Table 3
Risk assessment based on benz(a)pyrene equivalent of PAHs in soil samples within Tiga dam agricultural location.

Concentration (mg/kg)				
PAHs	USEPA TEF	0–10 cm	10–20 cm	20–30 cm
Naphthalene	0.001	-	-	-
2-Methyl Naphthalene	0.001	-	-	-
Acenaphthylene	0.001	2.00E-06	-	-
Acenaphthene	0.001	-	-	-
Fluorene	0.001	-	-	-
Phenanthrene	0.001	-	-	-
Anthracene	0.1	1.00E-05	-	-
Fluoranthene	0.001	-	-	-
Pyrene	0.001	-	-	-
Benz(a)anthracene	0.1	3.00E-05	-	1.80E-04
Chrysene	0.001	1.00E-05	1.00E-05	1.00E-05
Benz(b)fluoranthene	0.1	3.00E-05	-	1.00E-05
Benz(a)pyrene	0.1	2.00E-05	3.00E-05	9.40E-04
Benz(k)fluoranthene	1	1.00E-05	-	8.30E-04
Dibenz(a,h)anthracene	1	7.00E-05	6.00E-05	2.07E-05
Indinol(1,2,3-cd)pyrene	0.01	-	-	1.00E-05
Benz(g,h,i)perylene	-	5.00E-05	3.00E-05	1.00E-05
ΣBaPTEQ		1.00E-04	1.30E-04	2.01E-03

USEPA TEF = United State Environmental Protection Agency, Toxic Equivalent Factor, BaPTEQ = Benzo(a)pyrene Toxic Equivalent Quotient. Note: Values represent the mean ± standard deviation, calculated at a 95 % confidence level.

benzo(a)pyrene’s slope factor value.

Risk (carcinogenic) = Average daily dose x slope factor

3. Results

3.1. Mean concentration of PAHs in soils from Tiga

Table 1 summarizes the mean concentrations of polycyclic aromatic hydrocarbons (PAHs) in soil samples from three depths (0–10 cm, 10–20 cm, and 20–30 cm) at the Tiga agricultural location. Naphthalene concentrations ranged from 0.00 to 1.03E-03 mg/kg, while 2-Methyl Naphthalene varied between 0.00 and 7.73E-04 mg/kg. Acenaphthylene spanned 0.00–1.91E-02 mg/kg, Acenaphthene 0.00–1.28E-04 mg/kg, and Fluorene 1.03E-04–3.75E-04 mg/kg. Other PAHs, including Phenanthrene (6.53E-05–7.34E-05 mg/kg), Anthracene (3.30E-04–1.47E-03 mg/kg), and Fluoranthene (7.73E-04–1.02E-04 mg/kg), showed similar variability.

Higher-molecular-weight PAHs, such as Chrysene (6.94E-03–9.54E-03 mg/kg), Benz(a)anthracene (2.93E-04–1.75E-03 mg/kg), and Benz(a)pyrene (1.93E-05–9.43E-04 mg/kg), also exhibited depth-dependent variation. The highest total PAH concentration (3.80E-02 mg/kg) occurred at 0–10 cm depth, while the lowest concentration (1.20E-02 mg/kg) was recorded at 10–20 cm.

3.2. Mean concentration of PAHs in vegetables from Tiga

Table 2 and supplementary Tables S1 and S2 present the average concentrations of polycyclic aromatic hydrocarbons (PAHs) in various vegetable parts (root, stem, and fruit) of onion, tomato, hot pepper, sweet pepper, and garden egg from the Tiga agricultural location. Naphthalene concentrations ranged from 3.91E-04 to 1.19E-02 mg/kg, Acenaphthylene from 8.88E-04 to 7.97E-03 mg/kg, and Acenaphthene from 1.15E-05 to 3.33E-04 mg/kg. Similarly, concentrations of Fluorene (1.26E-05–8.57E-03 mg/kg), Phenanthrene (3.89E-05–6.99E-04 mg/kg), and Anthracene (1.24E-05–9.79E-04 mg/kg) showed variability across samples.

The highest cumulative concentration (8.90E-02 mg/kg) was found in the roots and stems of onion, while the lowest (1.00E-03 mg/kg) was recorded in the roots of sweet pepper. Supplementary tables (S1, S2) provide detailed data.

3.2.1. Benzo(a)pyrene equivalent concentration of PAHs in soils from Tiga

Table 3 shows BaP equivalent concentrations of PAHs at different soil depths (0–10 cm, 10–20 cm, and 20–30 cm) in Tiga. Benz(a)pyrene had the highest levels (2.00E-05–9.40E-04 mg/kg), while Acenaphthylene and Indinol(1,2,3-cd)pyrene were among the lowest (0.00–2.00E-06 mg/kg and 0.00–1.00E-05 mg/kg, respectively).

The highest cumulative BaP equivalence (2.01E-03 mg/kg) occurred at 20–30 cm, while the lowest (1.00E-04 mg/kg) was at 0–10 cm, indicating depth-related variations likely influenced by deposition and leaching.

Table 4
Diagnostic ratio of PAHs in soil samples within Tiga dam agricultural location.

PAHs	BaA/ BaA+Chr	Ant/ Ant+Phe	Flua/ Flua+Pyr	LMW/ HMW
0–10 cm	2.98E-02	9.52E-01	-	1.36E+ 00
10–20 cm	-	8.35E-01	5.96E-02	4.33E-02
20–30 cm	1.72E-01	1.00E+ 00	3.16E-01	5.50E-02
Mean	7.00E-02	9.30E-01	1.30E-01	1.46E+ 00
Ratio				

BaA = Benzo(a)anthracene, Chr = Chrysene, Ant = Anthracene, Phe = Phenanthrene, Fluo = Fluoranthene, Pyr = Pyrene, LMW = Low Molecular Weight, HMW = High Molecular Weight. Note: Values represent the mean ± standard deviation, calculated at a 95 % confidence level.

3.3. Ecological risk assessment of PAHs in Tiga soils

Table S3 presents the ecological risk assessment results for PAHs in soil samples from the Tiga agricultural location. The concentrations of various PAHs ranged as follows: Naphthalene (0.00–4.90E-07 mg/kg), 2-Methyl Naphthalene (0.00–1.15E-06 mg/kg), Acenaphthylene (0.00–2.98E-05 mg/kg), Acenaphthene (0.00–2.56E-07 mg/kg), Fluorene (1.91E-07–6.94E-07 mg/kg), and others, including Benz(a)pyrene (1.21E-08–5.89E-07 mg/kg) and Benz(g,h,i)perylene (8.36E-06–1.50E-05 mg/kg).

The highest mean effect range medium quotient (MERMQ) was observed at 0–10 cm (5.25E-05 mg/kg), while the lowest was recorded at 10–20 cm (1.23E-05 mg/kg).

3.4. Diagnostic ratio of PAHs in Tiga soils

Table 4 shows the diagnostic ratios of specific PAHs in soil samples from Tiga agricultural locations. The BaA/BaA + Chr ratio ranged from 2.98E-02–1.72E-01, the Ant/Ant + Phe ratio from 8.35E-01–1.00E+ 00, the Flua/Flua + Pyr ratio from 5.96E-02–3.16E-01, and the LMW/HMW ratio from 4.33E-02–1.36E+ 00. The highest mean ratio (1.46E+00) was observed in LMW/HMW, while the lowest (7.00E-02) was in BaA/BaA + Chr.

3.5. Average daily dose (ADD) of vegetables from Tiga

Tables S4 to S6 present the average daily dosage of specific PAHs in the root, stem, and fruit of vegetable samples (onion, tomato, hot pepper, sweet pepper, and garden egg) from the Tiga agricultural location. The Naphthalene concentration ranged from 3.91E-04 to 1.16E-08 mg/kg/day. Acenaphthylene varied between 4.03E-09 and 8.69E-10 mg/kg/day, while Acenaphthene ranged from 3.26E-10 to 5.75E-11 mg/kg/day. Other PAHs, such as Fluorene, Phenanthrene, and Benz(a)pyrene, had values from 1.23E-11 to 8.39E-09, 3.81E-11 to 6.84E-10, and 1.46E-10 to 1.59E-09 mg/kg/day, respectively. The highest total daily dose (8.71E-08 mg/kg/day) was in the root and stem of onions, while the lowest (9.79E-10 mg/kg/day) was in the root of sweet pepper.

3.5.1. Cancer risk assessment of carcinogenic PAHs in vegetable from Tiga

Tables S7 to S9 present the cancer risk assessment of carcinogenic polycyclic aromatic hydrocarbons in vegetable samples (onion, tomato, hot pepper, sweet pepper, and garden egg) from the Tiga agricultural location. Cancer risk values for Benz(a)anthracene ranged from 5.94E-11–1.54E-09 mg/kg day-1; Chrysene from 1.50E-12–3.81E-11 mg/kg day-1; Benz(b)fluoranthene from 3.50E-11–1.01E-09 mg/kg day-1; Benz(a)pyrene from 1.07E-11–5.22E-10 mg/kg day-1; Benz(k)fluoranthene from 1.17E-08–9.13E-08 mg/kg day-1; Dibenz(a,h)anthracene from 2.14E-08–1.96E-07 mg/kg day-1; and Indinol(1,2,3-cd)pyrene from

1.33E-09–1.70E-08 mg/kg day-1. The highest ILCR value (2.67E-07 mg/kg day-1) was observed in the stem of sweet pepper, while the lowest (1.31E-10 mg/kg day-1) was in the root of sweet pepper.

3.5.2. Hazard quotient and hazard index of non-carcinogenic PAHs in vegetables from Tiga

Tables S10 to S12 present the hazard quotient and hazard index values for polycyclic aromatic hydrocarbons (PAHs) in vegetable samples from the Tiga agricultural location. The highest hazard index (1.93E-07 mg/kg day-1) was observed in onion roots and stems, while the lowest (3.33E-09 mg/kg day-1) was found in sweet pepper roots. For the hazard quotient, Naphthalene ranged from 9.45E-10 to 5.80E-08 mg/kg day-1, Acenaphthylene from 4.35E-09 to 3.90E-08 mg/kg day-1, and Acenaphthene from 1.8E-11 to 5.43E-10 mg/kg day-1. Other PAHs like Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, and Benz(g,h,i)perylene showed values ranging from 3.08E-11 to 2.10E-08 mg/kg day-1, 9.53E-11 to 1.71E-09 mg/kg day-1, 4.03E-12 to 3.19E-10 mg/kg day-1, 5.63E-11 to 2.55E-09 mg/kg day-1, 6.63E-10 to 1.25E-08 mg/kg day-1, and 2.02E-09 to 1.56E-07 mg/kg day-1, respectively.

4. Discussion

4.1. Occurrence and distribution of PAHs in soil samples from Tiga agricultural location

Table 1 displays the concentrations of 17 polycyclic aromatic hydrocarbons (PAHs) in soil samples from the Tiga agricultural location, Kano State, Nigeria. The PAHs were categorized into light (2–3 ring), 4-ring, and heavy (5–6 ring) groups based on the number of aromatic rings, following classifications by Boehm and Farrington [25], Akbari-Adergani et al. [10], and Wang et al. [26]. In this study, 4-ring PAHs had the highest concentration, totaling 3.20E-02 mg/kg, accounting for 39 % of the PAH content in the soil samples. In contrast, heavy (5–6 ring) PAHs had the lowest concentration, totaling 2.22E-02 mg/kg, representing 27 % of the samples (Fig. 1).

The concentration of PAHs varied by soil depth, with the highest concentration (1.91E-02 mg/kg) observed in the 0–10 cm soil depth, while the lowest (1.93E-05 mg/kg) was also recorded at the same depth. This indicates that PAH contamination in the study location is primarily due to atmospheric deposition, rather than from irrigation water or fertilizers. The binding of PAHs to soil organic matter reduces their mobility, explaining why contamination is more concentrated in the topsoil, with minimal leaching into deeper layers (10–20 cm and 20–30 cm).

This pattern suggests that industrial emission as well as agricultural practices, such as burning chaff and weeds, may contribute to PAH contamination in the area. These findings align with previous studies by Eze et al. [13], Haixu et al. [14], and Sizhuo et al. [27], which also found

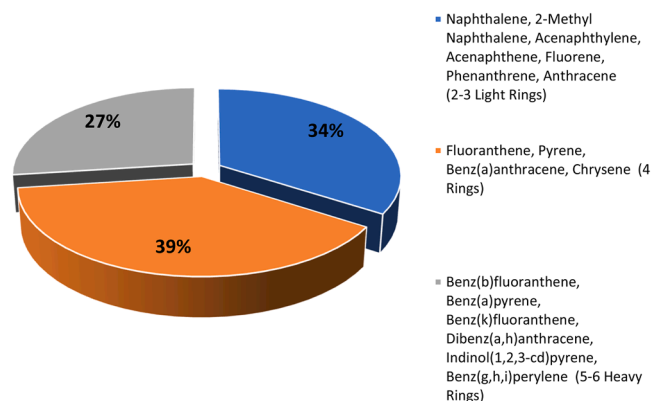


Fig. 1. Compositional pattern of PAHs in soil from Tiga dam agricultural location.

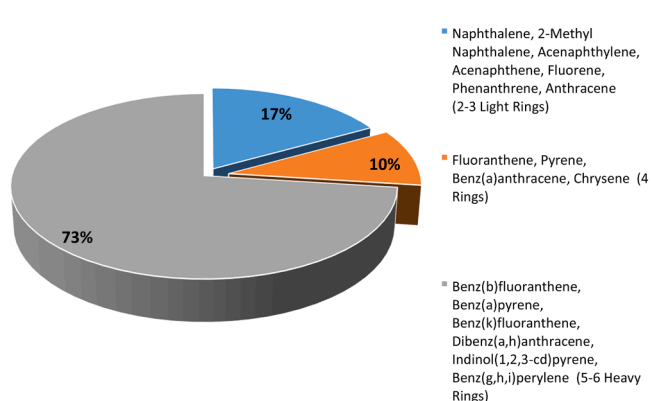


Fig. 2. Compositional pattern of PAHs in sweet pepper samples from Tiga dam agricultural location.

higher PAH concentrations in topsoil, attributing the contamination to anthropogenic activities like gas flaring and industrial operations.

Polycyclic Aromatic Hydrocarbons (PAHs) are a diverse group of organic compounds, characterized by multiple fused benzene rings, primarily originating from both natural sources (e.g., volcanic eruptions, forest fires) and anthropogenic activities (e.g., vehicle emissions, industrial processes) [28]. Their toxicity, mutagenic potential, and carcinogenic properties make PAHs a significant environmental concern [2]. Due to their hydrophobic and lipophilic nature, PAHs are widely dispersed in the environment and can undergo long-range transport.

Soil, serving as an indicator of environmental pollution, showed detectable levels of all investigated PAHs in the Tiga agricultural location. These results highlight the ubiquitous, persistent, and mobile nature of PAHs, consistent with the findings of Yendry et al. [6]. The concentrations of certain PAHs in the study were elevated compared to others but were lower than those reported in studies by Karaca [29] and Kukharchyk et al. [30].

Despite these elevated levels, PAH concentrations in the current study were below the maximum allowable limits (see Table 1), suggesting regional variation and the need for continuous monitoring to ensure environmental safety and regulatory compliance.

4.2. Occurrence and distribution of PAHs in vegetable samples from Tiga agricultural location

The GC-MS method was used to measure the concentration of 17 polycyclic aromatic hydrocarbons (PAHs) in vegetable samples (onion, tomato, hot pepper, sweet pepper, and garden egg) from Tiga agricultural locations, Kano State, Nigeria. Table 2, and Tables S1 and S2 show the detection of all 17 PAHs, highlighting their widespread presence in the area.

The study found that 5–6 ring PAHs were the most prevalent, with concentrations of 73 % in sweet pepper, 94 % in tomato, 80 % in onion, and 76 % in garden egg. In contrast, 4-ring and 2–3 ring PAHs were present in lower amounts, representing only 10 % and 2 % in sweet pepper and tomato, respectively, and 7 % and 10 % in onion and garden egg (Fig. 2, S1–S4). Figures labelled with an 'S' are available in supplementary materials.

Onion, sweet pepper and tomato samples showed higher PAH levels due to their close proximity to industrial areas. Onion's shorter root length (7–11 cm) which is closer to the polluted topsoil contributes to its higher uptake of PAH compared with other vegetables. Onion has high lipid layers in its tissues which explains its significant root uptake of Benz(g,h,i)perylene, a highly lipophilic PAH. Benz(g,h,i)perylene found in onion sample showed the highest concentration of PAHs among the 17 PAHs analyzed in vegetable samples (Table S1).

PAH concentrations were also found to be higher on the plant surface (outer leaves and peel) than in internal tissues, as confirmed by Hussein and Mona [3]. Studies by Kacmaz et al. [31], Akbari-Adergani et al. [10], Al-Dmour et al. [11], and Tesi et al. [15] showed that vegetables with larger surfaces, like sweet pepper and tomatoes, are more prone to PAH contamination due to greater exposure to airborne PAHs. Additionally, the higher transpiration rates and waxy cuticles contribute to the uptake and retention of airborne PAHs.

While vegetables provide essential nutrients, the elevated PAH levels in some samples (Table 2, S1, and S2) may pose a potential hazard. However, these concentrations were lower than those reported by Tesi et al. [15], Al-Dmour et al. [11], Alina et al. [9], Banerjee et al. [32], and Nwaichi et al. [33], but higher than reports by Akbari-Adergani et al. [10] and all except Tesi et al. [15], remained below the maximum allowable limits.

4.2.1. Diagnostic ratio and source identification of PAHs in soil from Tiga agricultural location

Previous studies [16,34–36] have highlighted the utility of diagnostic ratios in identifying pollution sources, a crucial step in

understanding pollutants and developing remediation strategies. These ratios, also known as isomeric ratios, use compounds with similar molar masses and physicochemical properties to differentiate between petrogenic (petroleum/combustion) and pyrogenic (biomass/coal burning) sources of PAHs [37]. Key ratios include BaA/BaA+Chr, Ant/Ant+Phe, Flua/Flua+Pyr, and LMW/HMW.

Yunker et al. [38] suggest that a BaA/BaA+Chr ratio < 0.2 indicates a petrogenic origin, while a ratio > 0.35 suggests a pyrogenic source. Similarly, an Ant/Ant+Phe ratio > 0.1 indicates heavy fuel combustion, and a Flua/Flua+Pyr ratio < 0.4 implies a petrogenic source [39]. The LMW/HMW ratio > 1 points to a pyrogenic source, while a ratio < 1 suggests petrogenic origins.

Table 4 displays the diagnostic ratios of PAH compounds in Tiga agricultural location. In Tiga, the BaA/BaA+Chr ratios (0.03–0.17) indicate a petrogenic origin, while the Ant/Ant+Phe ratios (0.84–1.00) suggest a pyrogenic source. The Flua/Flua+Pyr ratios (0.06–0.32) point to a petroleum source, and the LMW/HMW ratios (1.36, 0.04, and 0.06) suggest a petrogenic origin across different soil depths.

In Tiga, nearby combustion-related industrial processes and incineration release PAHs, depositing them through atmospheric deposition. These are notable sources of petrogenic and pyrogenic PAHs, respectively. However, a significant source of pyrogenic PAHs in Tiga may be attributed to the habitual practice of burning agricultural waste in selected areas within each farm lands. The presence of agricultural machinery, irrigation systems may also contribute significantly to pyrogenic PAHs. Contamination of water used for irrigation farming with organic wastes and industrial effluents are the major contributors to petrogenic PAHs. Run-offs containing residues of agrochemicals and fertilizers from agricultural fields are other sources of petrogenic PAHs pollution in Tiga agricultural location. These findings align with previous studies on PAH emissions from industrial effluents, automobiles, fuel combustion, and agricultural waste burning [39–43].

4.3. Ecotoxicity studies of some PAHs in soil from Tiga agricultural location

Environmental experts use effect range median (ER-M) and effect range-low (ER-L) values to assess the toxicity of polycyclic aromatic hydrocarbons (PAHs) in soil and other media. PAH levels below ER-L (4.00 mg/kg) indicate no toxicity, while levels above ER-M (44.79 mg/kg) suggest harmful effects on the ecosystem and human health [44,45].

At Tiga agricultural locations, PAH levels are below ER-M, indicating minimal risk to the ecosystem and human health. However, accumulation over time may lead to higher concentrations. This conforms with findings from Howard et al. [45] and Huanling et al. [46], who reported low ER-M values in Nigeria and China respectively. The Mean ER-M values at Tiga (Table S3) are consistently below 0.1, categorizing the area as low priority for PAH pollution control, consistent with Long et al. [23] and other studies [47,48].

4.4. Benz(a)pyrene equivalent concentration of some PAHs in soil samples from Tiga agricultural location

Benzo[a]pyrene (BaP) is the most toxic and carcinogenic PAH, often used as a benchmark to assess the toxicity of other PAHs. To evaluate the risks of PAHs in environmental matrices like soil and vegetables, the BaP carcinogenic equivalent factor (BaPTEQ) is commonly used. Toxic equivalency factors (TEFs) compare the carcinogenicity of PAHs to BaP, which has the most comprehensive toxicological data [5,16].

In Tiga agricultural locations, BaPTEQ in soil samples from different depths (0–10 cm, 10–20 cm, and 20–30 cm) was calculated (Table 3). BaP and Dibenzo[a,h]anthracene contributed the most to the total BaP equivalent, comprising 40.29 %. The overall BaPTEQ concentration in the soil was 2.24E-03 mg/kg, indicating low carcinogenic potential compared to Cao et al. [49] and Bortey-Sam et al. [50], who reported

higher values. According to Julius et al. [51], the Canadian Soil Environmental Quality Standard sets a threshold of 6.00E-01 mg/kg for Σ 16BaPeq, deeming the soil at Tiga safe.

4.5. Dietary intake of PAHs through vegetable consumption from Tiga agricultural location

The Average Daily Dose (ADD) refers to the amount of chemical residues an individual is exposed to daily, typically calculated over a lifetime. Dietary intake is a significant pathway for exposure to polycyclic aromatic hydrocarbons (PAHs), especially among non-smokers [52]. Tables S4 to S6 show the dietary intake concentrations of PAHs in Tiga agricultural locations. Among the vegetables analyzed, onions had the highest PAH intake (6.22E-08 mg/kg/d), while garden egg had the lowest (1.13E-11 mg/kg/d). When compared to the Tolerance Daily Dose Limit (7.00E-02 kg or 68.5 g per capita for Nigeria), all values were below the acceptable limits. The results indicate that vegetable consumption from Tiga agricultural locations poses minimal health risks regarding PAH exposure.

4.6. Cancer risk assessment of PAHs in vegetables from Tiga agricultural location

A human cancer risk assessment was conducted on PAHs; benz(a)anthracene, chrysene, benz(b)fluoranthene, benz(a)pyrene, benz(k)fluoranthene, dibenz(a,h)anthracene, and indinol(1,2,3-cd)pyrene found in vegetable samples from Tiga agricultural sites. The assessment used Incremental Lifetime Cancer Risk (ILECR) considering dermal, ingestion, and inhalation exposure pathways [53]. According to the USEPA guidelines [54], ILECR values $\leq 10E-06$ indicate negligible risk, while values $\geq 10E-04$ indicate high risk. For the Tiga location, ILECR values ranged from 2.67E-07–1.31E-10, suggesting negligible cancer risk, consistent with previous studies [12,55]. These findings contrast with Tarafdar and Sinha's [56] higher cancer risk values for children and adults (3.64E-02–7.21E-02). In conclusion, this study indicates negligible cancer risk from PAH exposure in Tiga vegetable samples, aligning with past research. However, it highlights divergent results in some studies, underscoring the need for continuous monitoring of PAH-related health risks. Notably, vegetables showed higher PAH concentrations than soils, due to their greater surface area and ability to bioaccumulate contaminants [11,15].

4.7. Hazard quotient and hazard index of non-carcinogenic PAHs via consumption of vegetables from Tiga agricultural location

The hazard quotient represents the ratio between potential exposure to non-carcinogenic PAHs and the threshold of no adverse effects, especially through vegetable consumption in the Tiga agricultural location [57]. Calculated using the reference dose (RFD) for PAHs, these reference doses are considered safe and are based on an average adult body weight of 70 kg [57]. The hazard index, a cumulative measure of hazard quotients, serves as a risk indicator for PAH exposure through various contaminated pathways. In Tiga, the analysis revealed varying hazard quotients for different vegetables, with the highest (1.56E-07) and lowest (4.03E-12) values found in the root and stem of onions, respectively, and the highest (1.93E-07) and lowest (3.33E-09) hazard index values in the root and stem of onions and sweet pepper (see Tables S10 to S12). The result from the study revealed that both the values for hazard quotient and the hazard index from Tiga were less than 1. A level suggested by USEPA as generally having no appreciable health risk for the development of non-cancer health effect through the exposure of PAHs residues on vegetables.

4.8. Strengths and limitations of the study

This study provides invaluable insights into the levels of PAH

contamination in both soil and vegetables from Tiga Dam agricultural areas. A strength of this study is the use of GC-MS as an advanced tool with high sensitivity that ensures the accuracy and reliability of the PAH measurements. By analyzing soil at different depths (0–10 cm, 10–20 cm, 20–30 cm) and vegetable parts (root, stem, and fruit), the study provides a detailed understanding of PAH transfer, absorption, and translocation within crops, shedding light on bioaccumulation processes. This approach offers a more comprehensive view of how PAHs move through the soil and plants. In addition, the inclusion of human health risk assessments strengthens the practical relevance of the findings especially to local population.

However, there are limitations. The scope of the study focuses on just five vegetable types among foods cultivated in the area. This does not fully represent the variety of crops grown in the area, limiting the generalization of the findings. Similarly, soil sampling was also restricted to a maximum depth of 30 cm, which might miss contamination at deeper layers and previous depositions that could impact groundwater contamination.

To improve future research, it is essential to expand the range of vegetables studied and include deeper soil samples to assess the full extent of PAH contamination. Long-term studies that account for seasonal variations would also offer a more comprehensive insight. Farmers education on sustainable practices would be beneficial in minimize PAH contamination. The adoption of new policies focusing on regulations for monitoring PAH levels in soil and crops will also be beneficial in ensuring public health safety.

5. Conclusion

In the Tiga agricultural location, Kano State, Nigeria, seventeen polycyclic aromatic hydrocarbons (PAHs) were detected in both soil and vegetable samples, with vegetable PAH concentrations surpassing those in soil. Chi-square tests showed no significant differences between observed and expected PAH concentrations, as the test statistics were consistently lower than the critical values at a 0.05 significance level, with degrees of freedom ranging from 1 to 2. The results indicated that PAHs originated from both petrogenic and pyrogenic sources. The location was categorized as a low-priority site for pollution control, as the mean effect range medium quotient values in soil samples were below 0.1, suggesting an 11 % probability of toxicity. Daily PAH doses in vegetables revealed that onions and hot pepper had the highest values. The incremental lifetime cancer risk assessment for vegetable samples showed values below 10E-06 for Tiga agricultural location. This means that the levels of PAHs in the vegetables are so small that they pose no significant cancer risk. Therefore, these five vegetables (onions, tomatoes, sweet pepper, hot pepper and garden egg) from the Tiga agricultural area are considered safe for human consumption, as the associated health risk is negligible.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.toxrep.2025.101905](https://doi.org/10.1016/j.toxrep.2025.101905).

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