

Assessment of Petroleum Hydrocarbons in Selected Vegetables and Soil Samples from Gashua Bade Local Government Area Yobe State Nigeria

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Abstract

This study investigated contamination of vegetables and soils by petroleum hydrocarbons (PHCs/TPHs) in Karage, Dachia, and Amshi (Gashua Bade LGA, Yobe State, Nigeria) and assessed related human health risks using GC-MS analysis. PHCs are persistent, toxic mixtures from crude oil and petroleum products that can accumulate in agricultural soils and enter food crops, creating potential health risks through long-term consumption, especially for children. Vegetable samples showed TPH concentrations from 0.337 mg/kg in Amaranthus (Karage) to 7.66 mg/kg in okra (Dachia), all exceeding the USEPA limit of 0.2 mg/kg. Adult chronic daily intake values (10.3–504 mg/kg/day) were far above the WHO/USEPA safe threshold (0.345 mg/kg/day). Hazard quotient and hazard index values exceeded safe limits, indicating significant non-carcinogenic risk, while cancer risk values for adults and children also surpassed acceptable ranges, with children showing greater vulnerability. The highest risks were linked to roselle from Dachia and Amshi. Soil TPH levels ranged from 1.16 to 9.04 mg/kg, with diagnostic ratios suggesting mixed plant-derived and petroleum sources. Overall, contamination poses serious carcinogenic and non-carcinogenic health risks. Urgent remediation, stronger pollution control, reduced dietary exposure, and ongoing monitoring are recommended.

1. Introduction

Industrialization and urbanization have resulted in a large growth in consumption of sources of energy and severe environmental contamination. Among the different types of pollutions, Petroleum hydrocarbons (PHCs) contamination is one of the most common environmental issues encountered by environmental professionals. Hydrocarbon A “hydrocarbon” is any chemical compound that consists only of the elements carbon (C) and hydrogen (H). [35, 26, 42]. They all contain a C frame and have H atoms attached to the frame most hydrocarbons are combustible. Petroleum Hydrocarbons are a large class of chemicals made up of carbon and hydrogen that are the primary compounds found in common fuels such as kerosene, gasoline, diesel, motor oil, and different jet fuels, including JP-5.[10]. each type of fuel consists of a slightly different mixture of hundreds of types of petroleum hydrocarbons [38]. They contain a wide variety of thousands of different mixtures and concentrations of organic chemical compounds, but most of them include hydrogen and carbon with lower amounts of oxygen, sulphur, and nitrogen [14, 19, 42]. Petroleum hydrocarbons are classified as short-chain hydrocarbon (aromatic hydrocarbons, alicyclic, and paraffinic), diesel (n-paraffins, isoparaffins, naphthenes, and aromatics), kerosene, and gasoline [37]. Spillage of used engine oils, such as gasoline or aircraft engines, contaminates the natural environment [26]. When an oil spill occurs, oil floats being less dense than water [34]. As the most toxic hydrocarbons tend to evaporate immediately after the oil spills, it also contaminates the ecosystem by this route [27, 14, 19]. Environmental pollution caused by releases of petroleum to land, surface water, or the subsurface is of concern because chemicals in PHCs can present a risk to human and environmental receptors if concentrations in environmental media are high enough. Contamination of hydrocarbon occurs due to toxic organic substances, petroleum, and pesticides which is a serious concern for the environment. Crude oil contamination is common due to its extensive use and its related dumping process and accidental spills. “PHCs” is compounds of petroleum that consist almost entirely of the elements of C and H. They are not distinct entities but rather represent a continuum over a broad range by the molecular weight of individual hydrocarbons. Gasoline, diesel fuel, and related products contain hundreds and sometimes thousands of different PHCs. Alkanes (or paraffins) These hydrocarbons are saturated, which means that each carbon atom forms four single bonds with the H and other C atoms which make up each compound. These hydrocarbons are also aliphatic, which means that the carbon atoms are joined by straight or branched-chain arrangements. Examples of compounds in this group are hexane, heptane, octane, and decane [35]. Cycloalkanes (or naphthalenes) Hydrocarbons in this group are saturated hydrocarbons which are characterized by their ring-type structure. Methylcyclopentane and ethylcyclo-p-hexane are examples of hydrocarbons in this group. Alkenes (or olefins) Hydrocarbons in this group are unsaturated, which means they contain at least two carbon atoms joined by more than one covalent bond and aliphatic. Ethene and propene are examples in this group. Arenes (or aromatics) All compounds in this group contain at least one benzene ring. Benzene, toluene, ethylene, and xylene (BTEX) compounds fall into this group [35].

Vegetables are important edible crops and are an essential part of the human diet. Vegetables make up a major constituent of human diet, and they provide the body with additional minerals and vitamins due to their high nutritional values [9, 8] They are rich in nutrients required for human health, and are an important source of carbohydrates, vitamins, minerals, and fibers [12, 11]. It is estimated that sufficient intake of vegetables require consumption of at least 400g per day per capita (corresponding to 146 kg per year per capita). Evidence from various studies suggests that the daily consumption of vegetables can prevent the development of cardiovascular diseases and some cancers, especially gastrointestinal cancers [12, 11]. In tropical Africa, over hundred vegetable species are cultivated for consumption. Specifically, in Nigeria and other sub-Saharan African countries, tropical vegetables have been part of the food system for generations [48]. With increased awareness of the health protecting properties of vegetables immense attention has been drawn vegetable consumption in Nigeria. Vegetables are now among the most important cultivated food crops [12, 11] Therefore, their presence in plants constitutes a major health concern. Plants through their roots take up PHCs from soil and water. PHCs in plant roots are bio- concentrated and translocated to their storage organs which are usually eaten by man and other organisms [9, 8].

2. Materials and Methods

2.1 Study Area

The study area is Gashua Bade, located on latitude 12°52'5"N and longitude 11°2'47"E. Gashua is one of the largest and most developed towns in Yobe State. Since 1976, it has been headquarters of the Bade Local Government Area. The town lies near the Nguru-Gashua Wetlands, an economically and ecologically important ecological system. The town is situated close to the convergence of Hadeija and Jama'are rivers in the Chad Basin. The Chad Basin extends to Niger Republic, Chad and Cameroon. The Basin belongs to the West Africa rift subsystem and it has three water bearing horizons which are; the upper, middle and the lower zones. Gashua has a population of about 125, 000 according to 2006 National population census results. Gashua climate is known to have a characteristic short rainy season (June – September) and long dry season (October – May), with high temperatures of about 39°C to 45°C. The annual rainfall range from 500–1000 mm. Greater part of Gashua lies within the flood plain. Topographically, Gashua is relatively a lowland area which contribute to the flooding of Gashua and its environs.

3. Sample Collection

The sample collection was carried out by method described by [13]. Sample of matured vegetables (*Amaranthus*, *Roselle* and *Okra*) were collected within Gashua Bade, LGA, Yobe State, Nigeria in the location land within the study area. The samples were well labeled and preserved in a clean polyethene bags. The samples were transported to the Research Laboratory Department of Pure and Applied Chemistry University of Maiduguri, Nigeria pending the analysis.

3.1 Extraction of the Vegetables

The extraction was carried out by method described by [13,22]. The samples of vegetables were washed severally with distilled water. Having washed the root part of the plants with water, the roots, stem and the leaves were cut into pieces and crushed using mortar and pestle. Ten grams (10) of the crushed sample were weighed into a 100 ml beaker and mixed with acetone/dichloromethane mixture as extraction solvent. Using 400 mL hexane solvent, the mixture of the solution was then incubated for 15 min at 40°C. After filtration of the homogenate through filter paper Whatman No. 1, the solid was re-extracted with 200 mL of hexane and heated at 40°C while stirring for 15 minutes, and this treatment was repeated four times. The filtrate is collected and concentrated by rotary evaporator at 40°C to obtain oleoresin. The oleoresin was subjected to saponification with 50 mL of KOH/10% ethanol and heated at 65°C. After 2 hours, the extract was diluted with 100 mL of hexane and repeated three times, and then collected and dried with 20 g of Na₂SO₄.

3.2 Extraction and Cleanup Methods for PHCs in Vegetable Samples

The most commonly used extraction method for PHC in aqueous samples is the EPA 3510 liquid-liquid extraction. The liquid-liquid extraction (LLE) technique involves the use of a separatory funnel for multiple extraction of the sample with an organic solvent of choice with the intent of achieving good recovery of the desired analytes. The technique requires strong shaking of the liquid sample with an organic solvent in a funnel shaped piece of glassware for a couple of minutes, followed by the separation of the organic layer (extract) from the aqueous phase [13, 22]. The extract is then filtered through a desiccant to remove moisture before a final concentration prior to the analytical procedure. Extraction efficiency of the organic analytes in aqueous samples was frequently monitored by the addition of surrogate standard solution.

3.3 Collection of Soil Sample

The collection of soil sample was carried out by method described by [55]. Soil samples were collected with spiral auger at the depths in the ranged 0 to 5.0 cm, 5 to 10 cm, and 10 to 15 cm. After collection, the soil samples were homogenized in clean plastic containers that were previously washed. The homogenized portion of soil samples were taken into a clean amber bottle and stored in an ice - chest until pending analysis.

3.4 Extraction of Soil Sample

The extraction was carried out by method described by [55]. Ten (10 g) of soil sample was added into an amber glass bottle. Anhydrous sodium sulphate (Na₂SO₄) was also added into the glass bottle containing the soil sample. The sample was stirred. The addition of Na₂SO₄ was to remove moisture from the soil sample. 150µg/ml of surrogate (solution contains a mixture of a 50:50 mix diesel and mineral oil) standard where added to the soil sample. 30 ml of dichloromethane (DCM) was added to the sample as extracting solvent and the bottle containing soil sample where corked very tight and transferred to a mechanical shaker. The sample was agitated between 2 to 3 hours at room temperature using a mechanical shaker. After agitation, the sample was allowed to settle for 1 hour and then filtered through 110 mm filter paper into a clean beaker. The filtrate was allowed to concentrate to 1 ml by evaporation overnight in a fume cupboard.

3.5 Risk Assessment of Petroleum Hydrocarbons (PHCs) in Vegetable Samples

3.6 Carcinogenic Risk Assessment of PHCs in Vegetable Samples

Carcinogenic risk (CR) values of petroleum a hydrocarbon (PHCs) in vegetable via ingestion pathway was predicted from their chronic daily intake (CDI) obtained from the Eq. 1 predicted by [55,59, 57].

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \dots\dots\dots \text{Equation (1) [55]}$$

$$CR = CDI \times SF \dots\dots\dots \text{Equation (2) [55]}$$

Where:

CDI: Chronic Daily Intake

C = Concentration

IR = Intake Rate

BW = Body Weight

EF = Exposure Factor

ED = Age Specific Exposure Duration

AT = Average Time

CR = Cancer risk

SF = Slope factor is used to estimate the risk of cancer associated with exposure to a carcinogenic or potentially carcinogenic substance Chronic daily intake via ingestion. These exposure assumptions were made to be consistent with [58]. guidance on assumption on reasonable maximum exposure [55,57]. The average vegetable consumption rate set at 68.5 g/day per person from the annual per capital vegetable consumption of 59 to 170g for Nigeria [25, 55]. CF is the conversion factor ($0.000001 \text{ mg } \mu\text{g}^{-1}$) and BW represents body weight which is set at 70 kg.

4. Results and Discussion

4.1 Mean Concentrations of Some Petroleum Hydrocarbons (mg/kg) in Vegetable Samples from Karage, Dachia, and Amshi locations Gashua LGA, Yobe State, Nigeria

The vegetables shows the mean concentration of some Petroleum Hydrocarbons in Vegetables sample Amaranthus, Roselle and Okra, from Gashua Bade, LGA, Yobe State, Nigeria, ranging from n-C₁₀;ND to 2.40E + 00 mg/kg, n-C₁₁;ND to ND, n-C₁₂;ND to 2.82E + 00 mg/kg, n-C₁₃;ND to ND mg/kg, n-C₁₄; 1.56E + 00 to 4.53E + 00 mg/kg, n-C₁₅; ND to ND mg/kg, n-C₁₆; 6.30E-01 to 6.24E + 00 mg/kg, n-C₁₇; 3.43E-01 to 9.70E-01 mg/kg, n-C₁₈; 1.04E + 00 to 6.54E + 00 mg/kg, n-C₁₉; 2.00E + 00 to 4.71E + 00 mg/kg, n-C₂₀; 2.34E + 00 to 5.44E + 00 mg/kg, n-C₂₁; 2.97E + 00 to 3.63E + 00 mg/kg, n-C₂₂; 3.43E-01 to 4.08E + 00 mg/kg, n-C₂₃; 3.27E + 00 to 4.09E + 00 mg/kg, n-C₂₄; 2.08E + 00 to 3.45E + 00 mg/kg, n-C₂₅; 3.41E + 00 to 4.69E + 00 mg/kg, n-C₂₆; 3.16E + 00 to 5.94E + 00 mg/kg, n-C₂₇; 9.59E-01 to 7.66E + 00 mg/kg, n-C₂₈; 1.68E + 00 to 6.44E + 00 mg/kg, n-C₂₉; 8.97E-01 to 5.49E + 00 mg/kg, n-C₃₀; 1.26E + 00 to 4.48E + 00 mg/kg, n-C₃₁; 3.07E + 00 to 4.21E + 00 mg/kg, n-C₃₂; 4.03E-01 to 2.89E + 00 mg/kg, n-C₃₃; 3.37E-01 to 4.47E + 00 mg/kg, n-C₃₄; 1.09E + 00 to 5.37E + 00 mg/kg, n-C₃₅; 3.52E + 00 4.29E + 00 mg/kg, n-C₃₆; 5.30E-01 to 5.68E + 00 mg/kg, n-C₃₇; 3.95E + 00 to 4.57E + 00 mg/kg, n-C₃₈; 8.43E-01 to 2.75E + 00 mg/kg, n-C₃₉; ND to 2.86E + 00 mg/kg and n-C₄₀; ND to 1.64E + 00 mg/kg. Mean concentration recorded maximum in Okra (41.71%) followed by Amaranthus (35.10%) and Roselle (23.2%) in comparison total Mean concentration.

4.2 Mean Concentrations of Some Petroleum Hydrocarbons (mg/kg) in Soil Samples from Karage, Dachia and Amshi locations Gashua Bade, LGA, Yobe State, Nigeria

The soil samples shows the mean concentration of some Petroleum Hydrocarbons in soils sample from Gashua Bade, LGA, Yobe State, Nigeria, ranging from n-C₈; ND to n-C₃₀ not detected in soil (samples) mg/kg, n-C₃₁; 7.77E + 00 to 9.04E + 00 mg/kg, n-C₃₂; ND to 8.85E + 00 mg/kg, C₃₃; ND to ND mg/kg, n-C₃₄; ND to ND mg/kg, n-C₃₅; ND to ND mg/kg, n-C₃₆; ND to ND mg/kg, n-C₃₇;ND to ND mg/kg, n-C₃₈;ND to ND mg/kg, n-C₃₉;ND to ND mg/kg and n-C₄₀;ND to ND mg/kg. Soil recorded maximum in Amshi10-15cm (41.5%), followed by Dachia 10-15cm (30.7%) and Karage10-15cm (30.6%) in comparison total soil.

Table 1
Mean Concentrations of Petroleum Hydrocarbons (mg/kg) in Vegetable
Samples from Karage, Dachia, and Amshi locations Gashua Bade, LGA,
Yobe State, Nigeria

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amshi location (Roselle)
n-C8	ND	ND	ND
n-C9	ND	ND	ND
n-C10	ND	2.40E + 00	ND
n-C11	ND	ND	ND
n-C12	ND	2.83E + 00	ND
n-C13	ND	ND	ND
n-C14	4.53E + 00	1.56E + 00	1.66E + 00
n-C15	ND	ND	ND
n-C16	1.49E + 00	6.30E-01	6.24E + 00
n-C17	3.43E-01	9.70E-01	9.70E-01
Pristane	1.97E + 00	ND	ND
n-C18	2.08E + 00	6.54E + 00	1.04E + 00
Phytane	4.49E + 00	4.28E + 00	1.17E + 00
n-C19	4.71E + 00	ND	2.00E + 00
n-C20	ND	5.44E + 00	2.34E + 00
n-C21	1.49E + 00	2.97E + 00	3.63E + 00
n-C22	3.43E-01	2.90E + 00	4.08E + 00
n-C23	1.97E + 00	3.27E + 00	4.09E + 00
n-C24	2.08E + 00	3.02E + 00	3.45E + 00
n-C25	4.49E + 00	3.41E + 00	4.69E + 00
n-C26	4.71E + 00	3.16E + 00	5.94E + 00
n-C27	4.43E + 00	7.66E + 00	9.57E-01
n-C28	4.53E + 00	6.44E + 00	1.68E + 00
n-C29	4.87E + 00	5.49E + 00	8.97E-01
n-C30	4.48E + 00	3.83E + 00	1.26E + 00
n-C31	3.07E + 00	4.21E + 00	3.08E + 00
n-C32	4.09E + 00	2.89E + 00	4.03E-01
n-C33	3.37E-01	1.62E + 00	4.47E + 00
n-C34	5.37E + 00	2.31E + 00	1.09E + 00
$\chi^2 = 3.23 (P > 0.05)$			

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amshi location (Roselle)
n-C35	3.52E + 00	4.29E + 00	ND
n-C36	3.24E + 00	5.68E + 00	5.30E-01
n-C37	3.95E + 00	4.57E + 00	ND
n-C38	8.43E-01	2.75E + 00	ND
n-C39	2.86E + 00	ND	ND
n-C40	ND	1.64E + 00	ND
TPHs	6.07E + 01 (35.1%)	7.21E + 01 (41.71%)	4.02E + 01 (23.2%)
$\chi^2 = 3.23 (P > 0.05)$			

Figures with parentheses indicate proportion (%) of TPHs in each vegetable with respect to total petroleum hydrocarbons

Keys: ND: Not detected PHCs = Petroleum Hydrocarbons mg/kg = Milligram per kilogram TPHs = Total Petroleum Hydrocarbons.

Table 2
Mean Concentrations of Some Petroleum Hydrocarbons (mg/kg) in Soil Samples from Karage, Dachia and Amshi
locations Gashua Bade, LGA, Yobe State, Nigeria

PHCs	Karage			Dachia			Amshi		
	0-5cm	5-10cm	10-15cm	0-5cm	5-10cm	10- 15cm	0-5cm	5-10cm	10-15cm
n-C8	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C9	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C10	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C11	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C12	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C13	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C14	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C15	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C16	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C17	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pristane	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C18	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phytane	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C19	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C20	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C21	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C22	ND	ND	ND	ND	ND	ND	ND	ND	ND

Continuation of Table 2									
Karage location				Dachia location			Amshi location		
PHCs	0-5cm	5-10cm	10-15cm	0-5cm	5-10cm	10-15cm	0-5cm	5-10cm	10-15cm
n-C23	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C24	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C25	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C26	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C27	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C28	1.38E + 00	1.35E + 00	1.42E + 00	1.32E + 00	1.18E + 00	1.43E + 00	1.16E + 00	1.57E + 00	1.45E + 00
n-C29	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C30	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C31	ND	8.61E + 00	ND	ND	7.77E + 00	ND	ND	ND	9.04E + 00
n-C32	ND	ND	ND	ND	ND	ND	ND	ND	8.85E + 00
n-C33	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C34	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C35	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C36	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C37	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C38	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C39	ND	ND	ND	ND	ND	ND	ND	ND	ND
n-C40	ND	ND	ND	ND	ND	ND	ND	ND	ND
TPHs	1.38E + 00 (29.7%)	9.96E + 00 (21.5%)	1.42E + 00 (30.6%)	1.32E + 00 (28.4%)	8.95E + 00 (19.3%)	1.43E + 00 (30.7%)	1.16E + 00 (24.9%)	1.57E + 00 (33.8%)	1.93E + 01 (41.5%)
$\chi^2 = 62.6$ (P < 0.05)									

Figures with parentheses indicate proportion (%) of TPHs in each soil with respect to total petroleum hydrocarbons

Key: ND: Not detected, PHCs = Petroleum Hydrocarbons, mg/kg = Milligram per kilogram, TPHs = Total Petroleum Hydrocarbons

Table 3
Chronic Daily Intake of Some Petroleum Hydrocarbons (mg/kg) in
Vegetable Samples in Adult from Karage, Dachia and Amshi locations
Gashua Bade, LGA Yobe State, Nigeria

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amashi location (Roselle)
n-C8	ND	ND	ND
n-C9	ND	ND	ND
n-C11	ND	ND	ND
n-C12	ND	ND	ND
n-C13	ND	ND	ND
n-C14	ND	1.23E + 01	ND
n-C15	ND	1.45E + 01	ND
n-C16	ND	ND	ND
n-C17	ND	8.13E + 00	ND
Pristane	ND	3.50E + 00	ND
n-C18	2.33E + 01	5.53E + 00	9.33E + 00
Phytane	ND	ND	ND
n-C19	7.81E + 00	3.37E + 01	3.19E + 01
n-C20	2.05E + 00	2.24E + 01	5.20E + 00
n-C21	1.03E + 01	2.82E + 01	5.57E + 00
n-C22	1.08E + 01	1.59E + 01	6.20E + 00
n-C23	2.31E + 01	1.55E + 01	1.04E + 01
n-C24	2.34E + 01	1.23E + 01	1.20E + 01
n-C25	2.32E + 01	1.61E + 01	1.92E + 01
n-C26	2.37E + 01	1.81E + 01	2.14E + 01
n-C27	2.53E + 01	1.68E + 01	2.15E + 01
n-C28	2.34E + 01	3.93E + 01	1.83E + 01
n-C29	1.64E + 01	3.33E + 01	2.45E + 01
n-C30	2.15E + 01	2.85E + 01	3.07E + 01
n-C31	2.02E + 00	2.02E + 01	5.04E + 02
n-C32	2.78E + 01	2.21E + 01	9.40E + 00
n-C33	1.86E + 01	1.55E + 01	5.15E + 00
n-C34	1.72E + 01	9.10E + 00	6.95E + 00
n-C35	2.08E + 01	1.26E + 01	1.61E + 01
$\chi^2 = 19.16$ (P < 0.05)			

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amashi location (Roselle)
n-C36	4.88E + 00	2.24E + 01	2.35E + 00
n-C37	1.53E + 01	2.94E + 01	2.34E + 01
n-C38	ND	2.35E + 01	5.77E + 00
n-C39	ND	1.41E + 01	ND
n-C40	ND	8.53E + 00	2.98E + 00
TPHs	3.41E + 02 (20.8%)	5.02E + 02 (30.6%)	7.92E + 02 (48.3%)
$\chi^2 = 19.16$ (P < 0.05)			

Figures with parentheses indicate proportion (%) of TPHs in each vegetable with respect to total petroleum hydrocarbons

Keys: ND: Not detected, PHCs = Petroleum Hydrocarbons mg/kg = Milligram per kilogram TPHs

= Total Petroleum Hydrocarbons

Table 4
Chronic Daily Intake of Some Petroleum Hydrocarbons (mg/kg) in
Vegetable Samples in Children from Karage, Dachia and Amshi
locations Gashua Bade, LGA Yobe State, Nigeria

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amshi location (Roselle)
n-C8	ND	ND	ND
n-C9	ND	ND	ND
n-C10	ND	ND	ND
n-C11	ND	ND	ND
n-C13	ND	ND	ND
n-C14	ND	2.87E + 01	ND
n-C15	ND	3.40E + 01	ND
n-C16	ND	ND	ND
n-C17	ND	1.90E + 01	ND
Pristane	ND	8.13E + 00	ND
n-C18	5.44E + 01	1.29E + 01	2.17E + 01
Phytane	ND	ND	ND
n-C19	1.82E + 01	7.87E + 01	7.47E + 01
n-C20	4.80E + 00	5.22E + 01	1.21E + 01
n-C21	2.40E + 01	6.59E + 01	1.30E + 01
n-C22	2.52E + 01	3.70E + 01	1.45E + 01
n-C23	5.38E + 01	3.61E + 01	2.41E + 01
n-C24	5.45E + 01	2.87E + 01	2.81E + 01
n-C25	5.40E + 01	3.76E + 01	4.47E + 01
n-C26	5.52E + 01	4.21E + 01	4.99E + 01
n-C27	5.91E + 01	3.92E + 01	5.01E + 01
n-C28	5.46E + 01	9.17E + 01	4.26E + 01
n-C29	3.81E + 01	7.74E + 01	5.71E + 01
n-C30	5.00E + 01	6.65E + 01	7.14E + 01
n-C31	4.70E + 00	4.70E + 01	1.27E + 01
n-C32	6.50E + 01	5.15E + 01	2.19E + 01
n-C33	4.34E + 01	3.61E + 01	1.20E + 01
n-C34	4.01E + 01	2.13E + 01	1.62E + 01
n-C35	4.84E + 01	2.93E + 01	3.75E + 01
$\chi^2 = 9.69\%$ (P < 0.05)			

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amshi location (Roselle)
n-C36	1.14E + 01	5.25E + 01	5.50E + 00
n-C37	3.57E + 01	6.85E + 01	5.45E + 01
n-C38	ND	5.49E + 01	1.35E + 01
n-C39	ND	3.29E + 01	ND
n-C40	ND	1.99E + 01	6.97E + 00
TPHs	7.95E + 02 (30.0%)	1.17E + 03 (44.1%)	6.85E + 02 (25.8)
$\chi^2 = 9.69\%$ (P < 0.05)			

Figures with parentheses indicate proportion (%) of TPHs in each vegetable with respect to total petroleum hydrocarbons

Keys: ND: Not detected, PHCs = Petroleum Hydrocarbons mg/kg = Milligram per kilogram TPHs

= Total Petroleum Hydrocarbons

Table 5
Hazard Quotient (HQ) and Hazard Index (HI) of Petroleum Hydrocarbons (PHCs) in Vegetable Samples in Adult from Karage, Dachia and Amshi locations Gashua Bade, LGA Yobe State, Nigeria

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amshi location (Roselle)
n-C30	4.30E + 02	5.70E + 02	6.14E + 02
n-C31	3.37E + 01	3.37E + 02	8.40E + 03
n-C32	2.53E + 02	2.01E + 02	8.55E + 01
n-C33	9.30E + 02	7.75E + 02	2.58E + 02
n-C34	1.72E + 02	9.10E + 01	6.95E + 01
n-C35	1.04E + 02	6.30E + 01	8.05E + 01
n-C36	6.97E + 00	3.20E + 01	3.36E + 00
n-C37	1.70E + 02	3.27E + 02	2.60E + 02
n-C38	ND	1.18E + 02	2.89E + 01
n-C39	ND	7.05E + 01	ND
n-C40	ND	2.31E + 01	8.05E + 00
HI	2.10E + 03 (15.0%)	2.61E + 03 (19.0%)	9.81E + 03 (66.0%)
$\chi^2 = 7.402$ (P < 0.05)			

Figures with parentheses indicate proportion (%) of HI in each vegetable with respect to total Hazard Index

Key: ND: Not detected, PHCs = Petroleum Hydrocarbons, HI =Hazard Index, HQ = Hazard Quotient

Table 6
Hazard Quotient (HQ) and Hazard Index (HI) of Petroleum Hydrocarbons (PHCs) in Vegetable Samples in Children from Karage, Dachia and Amshi locations Gashua Bade, LGA Yobe State, Nigeria

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amshi location (Roselle)
n-C30	1.00E + 03	1.33E + 03	1.43E + 03
n-C31	7.83E + 01	7.83E + 02	2.12E + 02
n-C32	5.91E + 02	4.68E + 02	1.99E + 02
n-C33	2.17E + 03	1.81E + 03	6.00E + 02
n-C34	4.01E + 02	2.13E + 02	1.62E + 02
n-C35	2.42E + 02	1.47E + 02	1.88E + 02
n-C36	1.63E + 01	7.50E + 01	7.86E + 00
n-C37	3.97E + 02	7.61E + 02	6.06E + 02
n-C38	ND	2.75E + 02	6.75E + 01
n-C39	ND	1.65E + 02	ND
n-C40	ND	5.38E + 01	1.88E + 01
HI	4.90E + 03 (10.0%)	6.07E + 03 (13.0%)	3.49E + 03 (78.0%)
$\chi^2 = 6.902$ (P < 0.05)			

Figures with parentheses indicate proportion (%) of HI in each vegetable with respect to total Hazard Index

Key: ND: Not detected, PHCs = Petroleum Hydrocarbons, HI =Hazard Index, HQ = Hazard Quotient

Table 7
Cancer Risk Assessment (CRA) of Some Petroleum Hydrocarbons
(mg/kg/day) in Vegetable Samples in Adult from Karage, Dachia
and Amshi locations Gashua LGA Yobe State, Nigeria

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amshi location (Roselle)
n-C30	1.08E + 00	1.43E + 00	1.54E + 00
n-C31	2.42E-01	2.42E + 00	6.55E-01
n-C32	2.17E + 00	3.31E + 00	1.41E + 00
n-C33	3.29E + 00	3.09E + 00	1.03E + 00
n-C34	1.29E + 00	2.73E-01	2.09E-01
n-C35	3.59E + 00	3.78E-01	4.82E-01
n-C36	1.83E-01	1.01E + 00	1.06E-01
n-C37	5.91E-01	1.32E + 00	1.05E + 00
n-C38	ND	2.31E + 00	5.67E-01
n-C39	ND	8.17E + 00	ND
n-C40	ND	8.53E-02	2.98E-02
ILCR	1.24E + 01	2.38E + 01	7.08E + 00
	(28.7%)	(54.9%)	(16.4%)
$\chi^2 = 10.07$ (P < 0.05)			

Figures with parentheses indicate proportion (%) of ILCR in each vegetable with respect to total ILCR

Key: ND: Not detected, PHCs = Petroleum Hydrocarbons, CRA =Cancer Risk Assessment, ILCR; Incremental Lifetime Cancer Risk, mg/kg/day = milligram per kilogram per day

Table 8
Cancer Risk Assessment (CRA) of Some Petroleum Hydrocarbons
(mg/kg/day) in Vegetable Samples in Children from Karage,
Dachia and Amshi locations Gashua LGA Yobe State, Nigeria

PHCs	Karage location (Amaranthus)	Dachia location (Okra)	Amshi location (Roselle)
n-C30	2.50E + 00	3.32E + 00	3.57E + 00
n-C31	5.63E-01	5.64E + 00	1.52E + 00
n-C32	9.73E + 00	7.72E + 00	3.29E + 00
n-C33	8.68E + 00	7.22E + 00	2.41E + 00
n-C34	1.20E + 00	6.38E-01	4.87E-01
n-C35	1.45E + 00	8.81E-01	1.13E + 00
n-C36	5.13E-01	2.37E + 00	2.48E-01
n-C37	1.60E + 00	3.08E + 00	2.45E + 00
n-C38	ND	5.39E + 00	1.32E + 00
n-C39	ND	1.91E + 01	ND
n-C40	ND	1.99E-01	6.97E-02
ILCR	2.63E + 01 (26.8%)	5.55E + 01 (56.5%)	1.65E + 01 (16.7%)
$\chi^2 = 17.1$ (P < 0.05)			

Figures with parentheses indicate proportion (%) of ILCR in each vegetable with respect to total ILCR

Key: ND: Not detected, PHCs = Petroleum Hydrocarbons, CRA =Cancer Risk Assessment, ILCR; Incremental Lifetime Cancer Risk, mg/kg/day = milligram per kilogram per day

Table 9
Diagnostic Ratio of Some Petroleum Hydrocarbons (PHCs) in Soil Sample from Karage location, Gashua Bade, LGA, Yobe State, Nigeria

Soil Depth	CPI	CPI %	Σ LMW/HMW	Σ LMW/HMW %	Σ LCH/SCH	C13/19	PRI/PHY	C17/PRI	C18/PRI
0–5cm	1.11E + 01	(24.7%)	1.38E + 00	(46.7%)	ND	ND	ND	ND	ND
5–10cm	2.13E + 01	(45.8%)	1.57E-01	(5.4%)	ND	ND	ND	ND	ND
10-15cm	1.41E + 01	(30.3%)	1.42E + 00	(47.9%)	ND	ND	ND	ND	ND
CPI $\chi^2 = 3.43$ (P > 0.05)									
LMW/HMW $\chi^2 = 1.05$ (P > 0.05)									

Figures with parentheses indicate proportion (%) of CPI and LMW/HMW in each soil with respect to total CPI and LMW/HMW

Keys: CPI; Carbon Preference Index, LMW: Lower Molecular Weight, High Molecular Weight, HMW: High Molecular Weight, LCH: Long Chain Hydrocarbon, SCH: Short Chain Hydrocarbon, PRI; Pristan, PHY: Phytene ND: Not Detected, cm; Centimeter, C: Carbon

Table 10

Diagnostic Ratio of Some Petroleum Hydrocarbons (PHCs) in Soil Sample from Dachia location, Gashua Bade, LGA, Yobe State, Nigeria

Soil Depth	CPI	CPI %	Σ LMW/HMW	Σ LMW/HMW %	Σ LCH/SCH	C13/19	PRI/PHY	C17/PRI	C18/PRI
0–5cm	1.21E + 01	(20.3%)	1.32E + 00	(45.5%)	ND	ND	ND	ND	ND
5–10cm	3.24E + 01	(54.3%)	1.52E-01	(5.3%)	ND	ND	ND	ND	ND
10–15cm	1.51E + 01	(25.4%)	1.43E + 00	(49.0%)	ND	ND	ND	ND	ND
CPI χ^2 = 12.07 (P < 0.05)									
LMW/HMW χ^2 = 1.34 (P > 0.05)									

Figures with parentheses indicate proportion (%) of CPI and LMW/HMW in each soil with respect to total CPI and LMW/HMW

Keys: CPI; Carbon Preference Index, LMW: Lower Molecular Weight, High Molecular Weight, HMW: High Molecular Weight, LCH: Long Chain Hydrocarbon, SCH: Short Chain Hydrocarbon, PRI; Pristan, PHY: Phytene ND: Not Detected, cm; Centimeter, C: Carbon

Table 11

Diagnostic Ratio of Some Petroleum Hydrocarbons (PHCs) in Soil Sample from Amshi location Gashua Bade, LGA, Yobe State, Nigeria

Soil Depth	CPI	CPI %	Σ LMW/HMW	Σ LMW/HMW %	Σ LCH/SCH	C13/19	PRI/PHY	C17/PRI	C18/PRI
0–5cm	1.10E + 01	(23.9%)	1.16E + 00	(12.6%)	ND	ND	ND	ND	ND
5–10cm	2.00E + 01	(43.5%)	1.57E + 00	(17.1%)	ND	ND	ND	ND	ND
10–15cm	1.50E + 01	(32.6%)	6.45E + 00	(70.3%)	ND	ND	ND	ND	ND
CPI χ^2 = 2.65 (P > 0.05)									
LMW/HMW χ^2 = 5.66 (P > 0.05)									

Figures with parentheses indicate proportion (%) of CPI and LMW/HMW in each soil with respect to total CPI and HMW/HMW

Keys: CPI; Carbon Preference Index, LMW: Lower Molecular Weight, High Molecular Weight, HMW: High Molecular Weight, LCH: Long Chain Hydrocarbon, SCH: Short Chain Hydrocarbon, PRI; Pristan, PHY: Phytene ND: Not Detected, cm; Centimeter, C: Carbon

5. Discussion

5.1 Mean Concentrations of Petroleum Hydrocarbons (mg/kg) in Vegetable Samples from Karage, Dachia, and Amshi locations Gashua Bade, LGA, Yobe State, Nigeria

Mean Concentrations of Petroleum Hydrocarbons (mg/kg) in Vegetable Samples from Karage, Dachia, and Amshi locations Gashua Bade, LGA, Yobe State, Nigeria. Table 1, presents the mean concentrations of some total petroleum hydrocarbons (TPHs) in various vegetable samples collected from different agricultural locations. The analysis revealed the presence of petroleum hydrocarbons ranging from n-C₈ to n-C₄₀ in all examined samples. Among the studied vegetables, okra samples collected from Dachia location exhibited the highest mean TPHs concentration, with a value of 7.66E mg/kg, while the lowest concentration was recorded in Amaranthus samples from Karage location, at 3.37E-01 mg/kg. These recorded concentrations significantly exceed the maximum permissible limit of 0.2 mg/kg, as recommended by the United States Environmental Protection Agency [24, 55]

This deviation indicates a substantial level of petroleum hydrocarbon contamination in the vegetables grown in the study area. Mean concentration in vegetable recorded maximum in Okra (41.71%) followed by Amaranthus (35.10 %) and Roselle (23.2%) in comparison total Mean concentration [52], evaluated total petroleum hydrocarbon (TPHs) concentrations in edible vegetables cultivated on crude oil polluted soils in Nigeria. Their study revealed that okra contained TPH levels ranging from 24.5 to 71.2 mg/kg, values that exceeded the permissible limits set by the [23,62]. Similarly[18]. investigated TPHs contamination in okra cultivated in Egypt and reported concentrations between 12.3 and 45.6 mg/kg, with higher levels observed in location located closer to oil spill zones. These results are consistent with the concentrations recorded in the present study. In Bangladesh [50], assessed petroleum hydrocarbon residues in vegetables grown in industrial regions, including okra from roadside and industrial-area location, where TPHs concentrations ranged from 15.7 to 39.9 mg/kg, posing potential health risks. In another Nigerian study[63], measured TPHs levels in okra from oil-polluted farmlands in the Niger Delta, reporting concentrations between 18.4 and 62.7 mg/kg and highlighting their possible implications for human health.

Comparative analysis with previous studies underscores the elevated TPHs burden in the present investigation. For instance [17], assessed TPHs levels in spinach and lettuce irrigated with contaminated water in the Assiut region of Egypt and reported much lower concentrations, ranging between 0.125–0.326 mg/kg. This discrepancy emphasizes the severe contamination present in the current study, which ranged from 40.2 mg/kg to 72.1 mg/kg. The significantly higher concentrations observed may be attributed to extensive petroleum-related activities in the study area, including oil spills, pipeline leaks, proximity to gas flaring sites, and waste discharge, all contributing to elevated hydrocarbon levels in the soil and subsequently in crops [43,32] Further supporting the present findings [43], reported mean TPHs concentrations in leafy vegetables ranging from 0.75–2.1 mg/kg, identifying widespread contamination across sampled locations. Similarly [51], observed accumulation of hydrocarbons in vegetables such as tomatoes, carrots, onions, and cabbages grown in oil-polluted regions of Russia, with TPHs levels in tomatoes ranging between 1.2–1.9 mg/kg.

Their findings noted greater accumulation in root vegetables due to direct soil contact, a conclusion that aligns with the patterns observed in the current research. Contrasting findings were reported by [61], who examined urban garden vegetables and found that carrot and lettuce samples contained TPHs concentrations between 0.15–0.82 mg/kg, significantly lower than those found in the present study. Similarly [31], documented TPHs residues in vegetables from Delta State, Nigeria, within a range of 0.47–1.63 mg/kg [44], also contributed to the body of knowledge on petroleum hydrocarbon contamination, reporting values between 2.4–9.6 mg/kg in vegetables cultivated in polluted soils of the Niger Delta. Comparable results were recorded by [49], who found TPHs concentrations ranging from 0.01–8.94 mg/kg in crops grown in contaminated sites across Nigeria. These findings, while higher than regulatory limits, remain significantly lower than the values reported in the present research [16], analyzed TPHs concentrations in vegetables from oil-polluted regions of the Niger Delta and reported a value of 1.68 mg/kg in okra (*Abelmoschus esculentus*), indicating contamination but still markedly below the levels detected in this study [45]. also reported TPHs accumulation in edible vegetables from oil-impacted areas, with values such as 1.32 mg/kg in pumpkin 1.51 mg/kg in spinach, and the highest in parsley.

These values are consistent with the trend of contamination but again fall well below those observed in the current analysis. Other related studies provide further context.[64], conducted a human health risk assessment of TPHs in tomatoes and cabbages grown on contaminated soils, reporting values of 0.3 mg/kg and 0.7 mg/kg, respectively [3], assessed TPHs levels in vegetables from crude oil-impacted soils in the Niger Delta and found concentrations ranging between 0.15–0.55 mg/kg, while[39], investigated leafy vegetables from oil-polluted agricultural lands in northern Nigeria and observed TPHs concentrations between 0.09–0.45 mg/kg. Furthermore, the TPHs concentrations found in the current study (40.2–72.1 mg/kg) are significantly higher than those reported in related literature and exceed established safety limits. The elevated levels of petroleum hydrocarbons in vegetables from the study area likely result from extensive environmental contamination due to agricultural activities [24, 38]. This situation raises serious public health concerns regarding the long-term consumption of contaminated vegetables and underscores the need for remediation strategies and stricter environmental monitoring in petroleum-impacted agricultural zones.

5.2 Mean Concentrations of Some Petroleum Hydrocarbons (PHCs) (mg/kg) in Soil Samples from Karage, Dachia and Amshi locations Gashua LGA, Yobe State, Nigeria

The results of the mean concentration of PHCs analysis in soil as shown at various depths of contaminated soil samples ranged from 0-5cm, 5-10cm and 10-15cm respectively. Table 2, show the values of PHCs in soil samples from study area ranged from n-C₂₈ 1.16E+00 to n-C₃₁ 9.04E+00 mg/kg in 0-5cm and 10- 15 cm both are in Amshi sampling location respectively, the ranged of these values are higher than maximum permissible limit according to [55]. The highest values of PHCs were observed at Amshi with the values of n- C₃₁ 9.04E+00 mg/kg at the depth of 10 – 15 cm, while the lowest values of n-C₂₈ 1.16E+00 mg/kg at depth of 0 – 5 cm was observed at Amshi sampling location too. Soil recorded maximum in Amshi10-15cm (41.5 %), followed by Dachia 10-15cm (30.7 %) and Karage10-15cm (30.6%) in comparison total soil [61], conducted an assessment of petroleum hydrocarbon contamination and associated health risks in vegetables and soils from urban gardens, reporting total petroleum hydrocarbon (TPHs) concentrations in soils reaching up to 4,250 mg/kg. These values are consistent with the findings of the present study. In a related investigation [3], evaluated exposure and health risks associated with petroleum hydrocarbons in vegetables cultivated in crude oil–impacted soils of the Niger Delta, Nigeria, and recorded TPHs concentrations in soils of up to 3,600 mg/kg, which also align with the present results. Similarly [39], assessed petroleum hydrocarbon residues in leafy vegetables from oil-polluted agricultural soils in northern Nigeria, reporting TPHs concentrations in soils ranging from 1,300 to 2,400 mg/kg. These reported ranges are in agreement with the values obtained in this study, further confirming the comparability of petroleum hydrocarbon contamination levels across different geographical locations and agricultural contexts.

TPHs concentrations in the soil sample from three different locations are higher than maximum permissible limit of 100 mg/kg [56]. Several studies have investigated total petroleum hydrocarbons (TPHs) contamination in soils from oil-impacted regions across the globe, reporting varying concentrations influenced by proximity to pollution sources and the intensity of petroleum-related activities [53], assessed TPHs levels in crude oil–polluted soils in Nigeria using gas chromatography, reporting concentrations ranging from 1,524 mg/kg to 3,685 mg/kg.

Although these values were below the 100 mg/kg threshold typically considered hazardous for direct consumption, they still indicate significant petroleum contamination. Similarly [51], documented elevated petroleum hydrocarbon levels in soils from oil-producing regions in Russia, with concentrations ranging from 116 mg/kg to 6,948 mg/kg. The highest TPHs levels occurred near oil extraction and transportation infrastructure, including pipelines and spill sites. These results are consistent with the findings of [17], who evaluated petroleum hydrocarbon contamination in soils and vegetables irrigated with polluted water in the Assiut region. Their analysis revealed soil TPHs concentrations ranging from 1.64 mg/kg to 3.92 mg/kg. The authors cautioned that chronic exposure to petroleum-contaminated vegetables could pose carcinogenic and mutagenic health risks, particularly in communities experiencing prolonged oil exploitation. In Nigeria's Imo River Basin, [4] reported soil TPHs concentrations ranging from 408.4 mg/kg to 9,263.2 mg/kg, with values decreasing with distance from spill points [7] investigated soils at a fuel service station in Accra, Ghana, finding concentrations between 44.1 mg/kg and 894

mg/kg, with several samples exceeding permissible limits set by the United States Environmental Protection Agency [56]. [21], examined soils and groundwater around petroleum storage facilities in Enugu State, Nigeria, recording mean soil TPHs concentrations between 102.60 mg/kg and 1,102.42 mg/kg.

The highest values occurred in areas adjacent to oil facilities, indicating contamination primarily linked to oil production and storage activities. Similarly,[54], measured TPHs in soils and groundwater within a crude oil-producing community, reporting concentrations from 19.5 mg/kg to 1,800 mg/kg. The study noted that mean TPHs concentrations exceeding 500–1,000 mg/kg present significant environmental and health concerns, with parsley samples exhibiting the highest accumulation levels among assessed plants.

5.3 Chronic Daily Intake of Some Petroleum Hydrocarbons (mg/kg/day) in Vegetable Samples in Adult from Karage, Dachia and Amshi locations Gashua Bade, LGA Yobe State.

Table 3, presents the chronic daily intake (CDI) values of selected petroleum hydrocarbons in vegetable samples consumed by adults. The CDI ranged from 2.02 mg/kg/day for n-C31 to 5.04E+02 mg/kg/day for n-C31. Notably, the highest CDI of total petroleum hydrocarbons (TPHs) was recorded in Roselle at the Amshi sampling location, with a value of 5.04E+02 mg/kg/day, while the lowest was observed in Amaranthus from the Karage location at 1.03E+01 mg/kg/day. These intake levels significantly exceed the maximum permissible limits established by the United States Environmental Protection Agency [55], which are 0.345 mg/kg/day for adults and 0.232 mg/kg/day for children respectively. CDI recorded maximum in Roselle (48.3%) followed by Okra (36.6 %) and Amaranthus (20.8%) in comparison total CDI.

Comparatively, studies by [61], reported maximum CDI values for children at 3.6E-03 mg/kg/day, with even lower values for adults, highlighting a stark contrast to the present findings. Similarly [40], observed CDI values between 6.0E-03 to 1.4E-02 mg/kg/day for children and 0.003–0.010 mg/kg/day for adults in vegetables from oil-contaminated regions substantially lower than those obtained in this study [20], reported values ranging from 1.3E-02 to 2.8E-02 mg/kg/day across both age groups in vegetables grown near auto-mechanic workshops, while[64] documented a CDI ranged of 1.1E-03 to 3.8E-03 mg/kg/day depending on the consumer's age. In agreement with the current findings,[44], documented CDI values ranging from 2.4 to 9.6 mg/kg/day in edible vegetables cultivated in petroleum contaminated soils within the Niger Delta. Similarly, [3] reported CDI values of 2.2E-03 mg/kg/day for adults and 4.5E-03 mg/kg/day for children, while [39], found ranges between 1.6E-03 and 3.9E-03 mg/kg/day in leafy vegetables from oil-impacted farmlands in northern Nigeria. These studies, however, reported exposure levels within or below the [58] permissible limits, thus contrasting with the elevated levels observed in the present research.

The substantially higher CDI values reported in this study may be attributed to localized environmental pollution sources, including industrial discharges, oil spills, and intensive agricultural activities within the study areas, CDI recorded maximum in Okra (44.1%) followed by Amaranthus (30.0 %) and Roselle (25.8%) in comparison total CDI. as similarly suggested by [17].

5.4 Hazard Quotient and Hazard Index of Petroleum Hydrocarbons (PHCs) in Vegetable Samples in and Adult and Children from Karage, Dachia, and Amshi locations Gashua Bade, LGA, Yobe State

Table 4. to 5, shows hazard quotient and hazard index of petroleum hydrocarbons (PHCs) in vegetable samples ranged from n-C30 to n-C40 respectively. The highest value of HI of 9.81E+03 was observed in the Roselle sample at Amshi sampling location, while the lowest HI values of 2.10E+03 was obtained in Amaranthus in Karage sampling location. The values of HI in all the vegetable samples (Amaranthus, Okra, and Roselle) ranged from 9.81E+03 to 2.10E+03 are higher than maximum permissible limit of 1.00, according to [55], HI recorded maximum in Okra (45.8%) followed by Amaranthus (36.9 %) and Roselle (17.2%) in comparison total Hazard index [6]. conducted a human health risk assessment of petroleum hydrocarbon residues in edible vegetables cultivated near oil-contaminated sites in Rivers State, Nigeria. Their results indicated hazard quotient (HQ) values ranging from 0.021 to 0.327 and hazard index (HI) values between 0.084 and 0.921, all of which were below the threshold value of 1, suggesting no immediate non-carcinogenic health risk not consistent with

the present study's results, further highlighting variability in petroleum hydrocarbons risk levels across different geographical locations. Similarly [47], in their study on dietary exposure and carcinogenic risk of petroleum hydrocarbons in leafy vegetables from oil-impacted communities in the Niger Delta, reported HQ values ranging from 0.014 to 0.258 and HI values between 0.109 and 0.674. These results were comparatively lower than those obtained in the present study [60], assessed the human health implications of total petroleum hydrocarbons in edible vegetables from crude oil-polluted farmlands in Bayelsa State, Nigeria, and recorded HQ values between 0.031 and 0.412, with HI values ranging from 0.124 to 1.032. Notably, some HI values exceeded 1, indicating a potential non-carcinogenic health risk. These findings were still lower than the values observed in the present investigation.

In contrast [1], examined petroleum hydrocarbon contamination in vegetables from peri-urban location in Lagos, Nigeria, reporting HQ values between 0.016 and 0.194 and HI values ranging from 0.092 to 0.562. Similarly [30], recorded HQ values from 0.011 to 0.238 and HI values between 0.078 and 0.614. Both sets of findings were [2], reported Total Hazard Quotient (THQ) values ranging from 0.017 to 0.065, while the Hazard Index (HI) ranged from 0.042 to 0.158. All recorded values were below the threshold of 1, indicating no immediate non-carcinogenic health risk. Similarly [17], found HQ values for adults of 0.015 in tomato, 0.029 in onion, and 0.047 in parsley, with the overall HI remaining below 1, suggesting negligible non-carcinogenic health concerns. In the work of the assessed vegetables *Telfairia occidentalis*, *Amaranthus spp* and *Vernonia amygdalina* had HQ values ranging from 0.082 to 0.437, with children exhibiting higher HQs than adults. HI values were 0.347 for adults and 0.587 for children, both below 1, implying no significant non-carcinogenic risk. HI recorded maximum in roselle (78.0%) followed by Okra (13.0 %) and Amaranthus (10.0%) in comparison total Hazard index.

Similarly [33], evaluated petroleum hydrocarbon contamination in vegetables cultivated near industrial zones in Dhaka, Bangladesh. HQ values for adults ranged from 0.022 to 0.091, and for children from 0.035 to 0.112, while HI values were 0.126 for adults and 0.219 for children. These findings indicated generally low chronic health risks, though the elevated values in children suggested a relatively higher vulnerability. The present study's results differ from these previous reports. The health risk assessment showed the lowest chronic daily intake (CDI) rate of 1.05×10^{-1} mg/kg for n-C₃₂ at the Karage sampling site, and the highest CDI rate of 9.00×10^{-3} mg/kg for nC₃₅ at the Dachia sampling site. However, in contrast to the earlier studies where HQ and HI values were consistently below 1, the HQ and HI values for all petroleum hydrocarbons (PHCs) in vegetables from the current study area exceeded 1. An HI value greater than 1 indicates that long-term consumption may pose significant non-carcinogenic health risks, rendering vegetables from the study locations unsafe for human consumption.

5.5 Cancer Risk Assessment of Some Petroleum Hydrocarbons (PHCs) in Vegetable Samples in Adult and Children from Karage, Dachia and Amshi locations Gashua Bade, LGA Yobe State.

Cancer risk refers to the likelihood of a person developing cancer. It's influenced by various factors, including genetics, lifestyle choices, and environmental exposures. Having risk factors doesn't guarantee cancer development, but it increases the probability compared to someone with fewer or no risk factors [6]. The lowest cancer risk value for children was observed in the n-C₄₀ hydrocarbon fraction, with a value of 6.97E-02 mg/kg/day in *Abelmoschus esculentus* (Roselle) from the Amshi sampling location. In contrast, the highest cancer risk value of 9.73E+00 mg/kg/day was recorded in Karage (*Amaranthus*) from the Karage sampling location. All the cancer risk values for children recorded in this study exceeded the United States Environmental Protection Agency [58]. recommended threshold range of 1.0E-06 to 1.0E-04 mg/kg/day [55]. For adults, the lowest cancer risk value (1.06E+01 mg/kg/day) was observed in the n-C₃₆ hydrocarbon fraction in *Hibiscus sabdariffa* from Amshi, whereas the highest value (8.17E+00 mg/kg/day) occurred in *Abelmoschus esculentus* from Dachia. Similar to the findings in children, these adult cancer risk values also exceeded the [58] 's threshold limit. ILCR recorded maximum in Okra (54.9%) followed by Amaranthus (28.7 %) and Roselle (16.4%) in comparison total ILCR. Across all vegetable samples analyzed, *Abelmoschus esculentus* have the highest cancer risk of value of petroleum hydrocarbons (PHCs), followed by *Amaranthus hybridus* (amaranthus), while *Hibiscus sabdariffa* consistently exhibited the lowest values in all sampling locations. This trend indicates that consumption of these vegetables particularly okra and amaranthus from the study area poses a significant carcinogenic risk and may contribute to the development of cancer and other related

health disorders. Notably, cancer risk values for children were higher than those for adults in all three vegetable species examined in this study. ILCR recorded maximum in Okra (56.5%) followed by Amaranthus (26.8 %) and Roselle (16.7%) in comparison total ILCR [6], conducted a human health risk assessment of petroleum hydrocarbon residues in edible vegetables cultivated near oil-contaminated sites in Rivers State, Nigeria, and reported cancer risk (CR) values ranging from $3.6\text{E-}06$ to $1.2\text{E-}05$ mg/kg/day. These values fall within the [58] acceptable range of $1.0\text{E-}06$ to $1.0\text{E-}04$ mg/kg/day, but are not consistent with the findings of the present study.

A similar discrepancy was observed when compared with the results of [47], who investigated dietary exposure and carcinogenic risk of petroleum hydrocarbons in leafy vegetables from oil-impacted communities in the Niger Delta and obtained cancer risk values between $2.8\text{E-}06$ and $9.5\text{E-}06$ mg/kg/day. In the same vein,[60], reported cancer risk values in vegetables ranging from $4.1\text{E-}06$ to $2.4\text{E-}05$ mg/kg/day, which are lower than the values observed in the current research. Likewise [1], assessed petroleum hydrocarbon-contaminated vegetables from peri-urban locations in Lagos, Nigeria, and recorded cancer risk values from $1.9\text{E-}06$ to $8.1\text{E-}06$ mg/kg/day, which are also not in agreement with the present study's results.

Similarly [30], documented cancer risk values ranging from $1.1\text{E-}06$ to $7.4\text{E-}06$ mg/kg/day, both below the maximum permissible limit and significantly lower than those obtained in the present research. The comparatively higher cancer risk values recorded in the current study, particularly among children, may be attributed to intensified agricultural activities, urban runoff, and other anthropogenic factors that contribute to elevated concentrations of total petroleum hydrocarbons (TPHs) in vegetable samples from the study area. Comparable findings were documented by[46], in their study on the human health risk assessment of petroleum hydrocarbon pollutants in vegetables cultivated within petroleum-producing regions of Nigeria.

The reported cancer risk (CR) values ranged from $2.8\text{E-}04$ to $8.2\text{E-}04$ mg/kg/day, which fall within the established safe limit, indicating minimal carcinogenic risk. Similarly [40], investigated petroleum hydrocarbon contamination in vegetables and the associated human health risks in areas surrounding oil installation sites in India. The study focused on spinach and cabbage, with CR values ranging from $2.5\text{E-}04$ to $1.6\text{E-}03$ mg/kg/day, aligning closely with the findings of the present research. Furthermore, their risk assessment revealed potential health risks for both adults and children, with cancer risk value of $3.45\text{E-}01$ mg/kg/day for leafy vegetables in adults and approximately $2.32\text{E-}01$ mg/kg/day in children. These comparable values reinforce the consistency of results across different geographical locations and vegetable types.

5.6 Diagnostic Ratio of Petroleum Hydrocarbons (PHCs) in Soil Sample Location from Karage, Dachia, and Amshi locations Gashua Bade, LGA, Yobe State, Nigeria

Diagnostic ratios serve as valuable analytical tools for determining the potential sources of petroleum hydrocarbons in environmental matrices. These ratios facilitate the differentiation between petrogenic inputs, typically originating from crude oil or refined petroleum products, and pyrogenic inputs, which arise predominantly from the incomplete combustion of organic matter. Accurate source apportionment is essential for tracing the origin of contamination and for guiding the selection of effective mitigation and remediation strategies. A predominance of petrogenic signatures often suggests recent petroleum discharges, such as oil spills or leakages, whereas pyrogenic profiles are generally indicative of hydrocarbon contamination resulting from atmospheric deposition linked to industrial processes, vehicular exhaust, or other combustion-related activities. The carbon preference index (CPI) values measured across the three sediment depths (0–5 cm, 5–10 cm, and 10–15 cm) varied between $1.10\text{E+}01$ and $3.24\text{E+}01$ across all sampling locations. Similarly, the ratio of low molecular weight to high molecular weight hydrocarbons ($\Sigma\text{LMW}/\text{HMW}$) ranged from $1.52\text{E-}01$ to $6.45\text{E+}00$ across the investigated depths in all the tables (Table 9 to Table 11). Diagnostic ratio in Karage location of recorded maximum in CPI (45.8%) followed by CPI (30.3 %) and CPI (24.7%) in comparison total CPI. of recorded maximum in LMW/HMW (47.9%) followed by LMW/HMW (46.7 %) and LMW/HMW (5.4%) in comparison total LMAW/HMW. In contrast, the ratios of long-chain hydrocarbons to short-chain hydrocarbons ($\Sigma\text{LCH}/\text{SCH}$), $\text{C}_{13}/\text{C}_{19}$, pristane/phytane (PRI/PHY), C_{17}/PRI , and C_{18}/PRI were not detected at any depth in any of the sampling sites in the Table 9 to Table 11 respectively. Looking at the CPI values

across all depths of the soil samples, this indicates that the source of PHCs or TPHs in soil samples is from Biogenic source (higher plant waxes), since the values of CPI obtained is greater one. A Pr/Ph ratio less than 1 generally indicates anoxic, petroleum-related inputs (petrogenic), while a ratio greater than 1 suggests terrestrial or pyrogenic origin [5,41], n-C17/Pri and n-C18/Phy Ratios > 1 often indicate fresh petroleum input; values < 1 may suggest biodegradation [29,36]. CPI (Carbon Preference Index), A CPI near 1 is typical of petroleum, whereas values > 1 suggest biogenic inputs [5,28]. Diagnostic ratio in Dachia location of recorded maximum in CPI (54.3%) followed by CPI (25.4 %) and CPI (20.3%) in comparison total CPI. of recorded maximum in LMW/HMW (49.0%) followed by LMW/HMW (45.5 %) and LMW/HMW (5.3%) in comparison total LMW/HMW. Diagnostic ratio in Amshi location of recorded maximum in CPI (43.5%) followed by CPI (32.6 %) and CPI (23.9%) in comparison total CPI. of recorded maximum in LMW/HMW (70.3%) followed by LMW/HMW (17.1 %) and LMW/HMW (12.6%) in comparison total LMW/HMW.

Conclusion

The present study demonstrates that vegetables and soils from Karage, Dachia, and Amshi locations in Gashua Bade LGA are heavily contaminated with petroleum hydrocarbons, with concentrations substantially exceeding [58] and [25,62] safety limits. CDI, HQ, HI, and CR values indicate both carcinogenic and non-carcinogenic health risks, especially for children. Soil analysis confirmed high PHCs concentrations, and diagnostic ratios suggested mixed biogenic and petrogenic origins, implicating petroleum-related activities as major contributors. Given the magnitude of contamination, immediate interventions such as soil remediation, enforcement of pollution control measures, and restriction of vegetable consumption from affected sites are essential. Continuous monitoring and public health awareness campaigns should be prioritized to mitigate long-term exposure risks.

Declarations

Data Availability Statement

All data generated or analysed during this study are included in this published article.

“Consent to participate”

Not Applicable

“Consent to Publish”

Not Applicable

“Ethics declaration”

Not Applicable

“Funding Declaration”

No Funding

“Ethics and consent to participate”:

Not Applicable

“Permissions to collect the soil and plants/plant parts”

Soil and plant samples were collected in accordance with the standard guidelines established by the committee of the Department of Agriculture, University of Maiduguri, led by Professor Umar Abdullahi Postiskum and Professor Mohammed

Saqiq.

“Clinical trial number”

Not Applicable

Authors Contribution Declaration

A. Amahyel Muas: writing/drafting of the research, data Curation, methodology

B. Zakari Mohammed: Interpretation of results, conceptualization

C. Haruna B. Wayar: Methodology, formal analysis

D. Ayuba J. Maina: Data Curation, formal analysis

E. Mohammed A. Shettima: formal analysis, Methodology

F. Hadiza Bukar: Methodology, conceptualization

G. Aisha Abubakar: conceptualization, formal analysis

H. Joseph C. Akan: Supervisor

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Figures

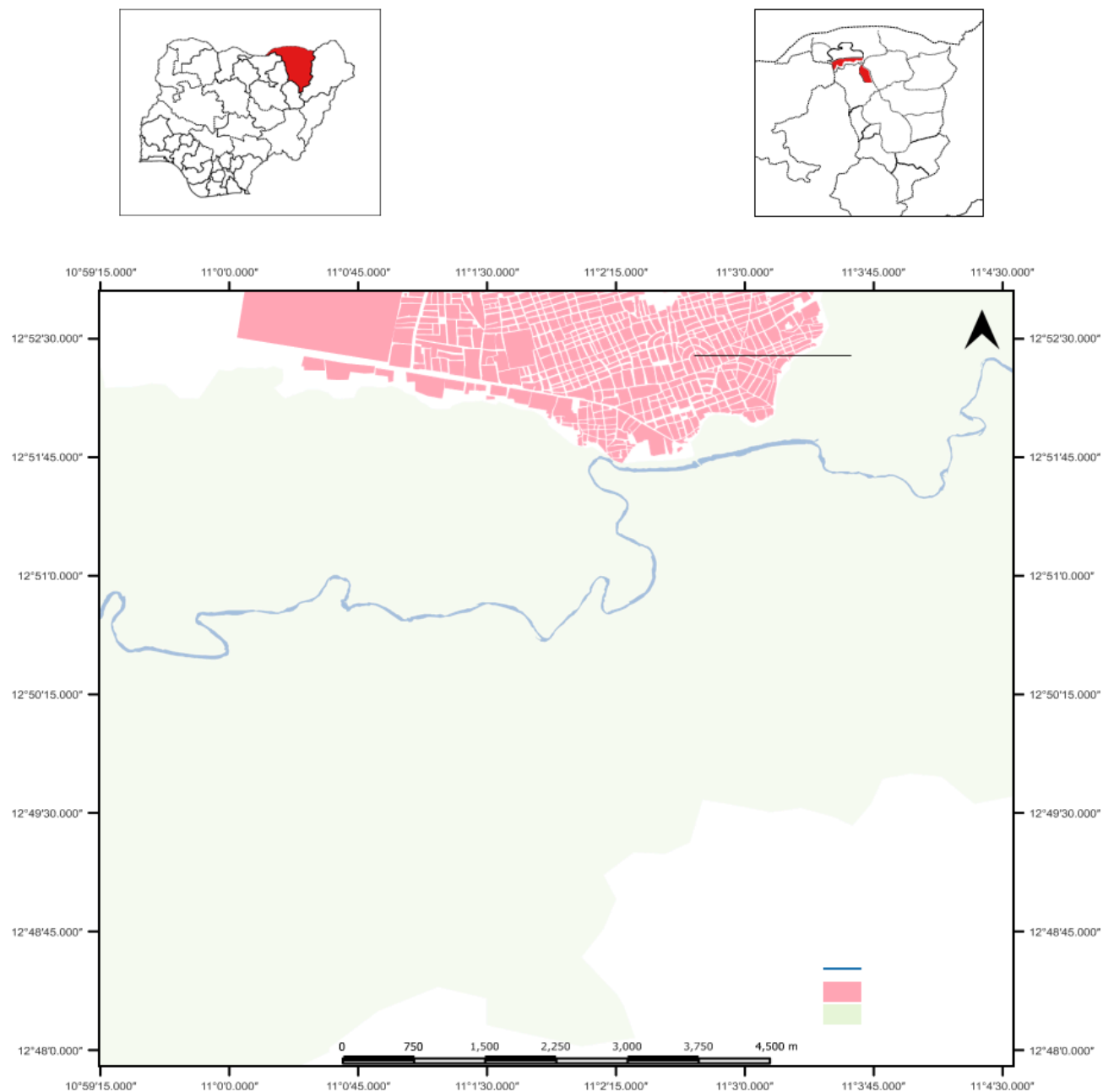


Figure 1

Unnumbered image in Materials and Methods section.