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Concentrations, Sources and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Vegetables Cultivated in the Environs of Rivers Niger - Benue Lokoja, Nigeria

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Abstract: This study determined the levels of polycyclic aromatic hydrocarbons (PAHs) in vegetables cultivated and consumed in five Local Government Areas around the Rivers Niger Benue confluence at Lokoja, in north central, Nigeria with the view of estimating the daily intake amount and the possible risks to consumers. Sixteen PAHs were determined in vegetable samples purchased from farmers in local markets using a GC-MS. Estimation of daily intake was done on generally exposed consumers. The margin of exposure was used to assess the risk to consumers. The concentration (in µg/kg) of Σ16 PAHs in vegetables were in the range of 2.12±1.5 in tomatoes to 99.88±29.18 in okro samples. Among individual PAH congeners, naphthalene showed very high values in about 60% of the vegetable samples. The concentration of ΣLMW- PAHs ranged from 1.10±0.84 in tomatoes to 90.51±26.71 in okro while that of ΣHMW- PAHs ranged from 1.02±0.66 in tomatoes to 16.65±9.15 in jute leaves. The benzo [a] pyrene (BaP) concentrations in all the samples were slightly below the recommended Food Standard Agency limits of 2µg/kg in food samples. The concentrations (in µg/kg) of Σ8 carcinogenic PAHs in the samples varied from 0.79±0.29 in tomatoes to 13.99±8.05 in jute leaves. The Margin of Exposure (MOE) based on BaP, PAH 2, PAH 4 and PAH 8 for the adults was 100% higher than 10,000 which indicated low concern for human health while in children, 7.14% was less than 10,000. The source determination indicated fuel combustion and pyrolytic emission sources. This study is the first of its kind in the Rivers Niger Benue confluence in particular and in north central Nigeria in general and can serve as a useful baseline for continuous monitoring of PAHs in the locally produced and consumed vegetables in order to ensure protection of human health in the area.

Keywords: Estimated Daily Intake, Human Health, Margin of Exposure, PAHs and Vegetable

1. Introduction

Environmental risk assessment of different food items is an important study for the healthy life of human beings. All over the world, vegetables have been part of the food system for generations. Vegetables are now among the most important cultivated food crops [1, 2]. They make up a major portion of the diet of humans, play a significant role in human nutrition and are the sources of most vitamins, minerals, dietary fiber and phytochemicals [3, 4]. Some phytochemicals in vegetables are strong antioxidants which reduce the risk of chronic diseases by protecting against free-radical damage, modifying metabolic activation and detoxification of carcinogens, as well as influencing processes that alter the course of tumor cells [5]. Vegetables in the daily diet have been strongly associated with overall good health [6], while their pollution by hazardous substances may become serious threat to public health [7].

PAHs are one of the major organic pollutants in foods [8-9]. They are generally lipophilic, non-soluble in water but soluble in organic matters [10]. An increase in the levels of environmental PAHs could be a major cause of high PAHs levels in food within industrialized and developing countries like Nigeria [11, 12]. Humans are exposed to PAHs through direct inhalation, ingestion of contaminated food or water, skin contact as well as smoking of cigarettes. Studies have shown PAHs contaminations in various foods and crops such as vegetables [13], legumes and cereals [14, 15], pasta products [16], meat [17] and fish [18]. PAHs have been reported to cause carcinogenic and mutagenic effects and are potent immune suppressants. They can interfere with the normal function of DNA [19]. Epidemiological studies indicate that dietary exposure to PAHs is associated with some human cancers [20]. Cancer has become a major source of morbidity and mortality globally [21, 22]. Accumulation of PAHs by vegetables may be an indirect exposure pathway to humans. Plants through their roots take up PAHs from soil and water. PAHs in plant roots are bio- concentrated and translocated to their storage organs which are usually eaten by man and animals [13, 23].

Kogi and other five states make up the north central region of Nigeria, a unique agricultural belt producing varieties of crops including vegetables. The north central region are the major suppliers of vegetables such as cucumbers, garden egg, tomatoes, spinach and so on. The Rivers Niger and Benue confluence at Lokoja promotes vegetable farming in the dry and rainy seasons. Lokoja is strategically situated as the link between the north and south of Nigeria. Consequently, the Abuja Lokoja highway carries a great deal of traffic, including heavy duty vehicles travelling up north and down south. In other words, the Abuja-Lokoja highway is a region of very high vehicular emission of PAHs especially over the many bridges criss crossing the confluence. Vehicular emission is a major source of PAH. Other PAH sources considered to be significant are the annual heavy flooding of the confluence due to the overflow of Benue and Niger rivers, dumping of urban wastes from Lokoja township as well as burning of agricultural farmlands are other important factors that could enrich the water and soil of the confluence with PAH. The general populace in the study area could be exposed to PAHs through consumption of contaminated food crops such as vegetables [24-26].

The north central states, being a major vegetable producing area has scanty information on PAH contamination in vegetables. So, there is a need to study the contamination of these vegetables by PAH to avoid the public health problem due to PAH pollution in this area of study. Therefore, the objectives of this study were to: i) determine the levels of PAHs in some vegetable samples cultivated in the environs of the River Niger Benue confluence at Lokoja north central Nigeria and ii) estimate the potential health risks from the consumption of the vegetables for adults and children.

Risk assessment of PAHs in foods namely margin of exposure (MOE), benzo [a] pyrene (BaP), PAH 2, PAH 4 and PAH 8 [27] would be used.

2. Materials and Methods

2.1. Equipment and Reagents

Agilent 6890N GC coupled to 5973C inert MS, Micro pipette or Automatic pipettes, Injection vials of 1 and 5 ml suitable for GC, fume cup board, Decon Ps major laboratory sonicator, Uniscope laboratory oven SM 9023 model, PAH reference standard from RESTEK, anhydrous sodium sulphate, silica gel, dichloromethane, hexane, acetone, Deuterated (surrogate) PAH standards (acenaphthalene d_{10}, chrysene d_{12}, phenathrene d_{10} and perylene d_{12}) from Sigma Aldrich, USA. All reagents and solvents were of analytical grade.

2.2. Study Area, Sampling and Sample Preparation

The study area covers five Local Government Area (LGA) surrounding the Niger-Benue confluence at Lokoja, the capital of Kogi State, in north central Nigeria. The five LGAs are Ofu, Kabba- Bunu, Ajaokuta, Lokoja and Bassa. Vegetable samples were purchased directly from farmers at the fringes of a major market in each LGA as follows: Itobe market (Ofu LGA), Kabba market (Kabba – Bunu LGA), Ganaja market (Ajaokuta LGA), Karara/ Kakanda market (Lokoja LGA) and Shintaku Market (Bassa LGA). The study area is shown in figure 1.

2.3. Sampling and Sample Preparation

Samples of spinach, jute leaves, pumpkin, okro. tomatoes, garden egg and cucumber were purchased directly from farmers at the fringes of the markets in each Local Government Areas under study. Non leafy vegetable samples were washed and put in baskets to drip and air dry. Bunches of leafy vegetables (spinach, pumpkin leaves and jute leaves) were washed, allowed to drip in baskets and later put in an oven at 105°C until adhering water has completely evaporated. The samples were cut into small pieces with knife and 5 g of triplicate samples of each vegetable were put together and thoroughly mixed to produce a composite sample.

2.4. Extraction and Clean-Up

2 g of each composite sample were weighed and blended in a clean 250 ml conical flask. 20 mL mixtures of dichloromethane and n- Hexane (1:1 v/v) were added to the sample and sonicated in a high frequency ultrasonic bath for 30 min at 24°C. The sample extracts were cleaned up in a glass column and eluted with 2.5 mL of the same solvent mixture. The eluted sample was concentrated using rotary evaporator. The evaporated extract was reconstituted with 2 mL dichloromethane and transferred into vials for subsequent injection into the GC.

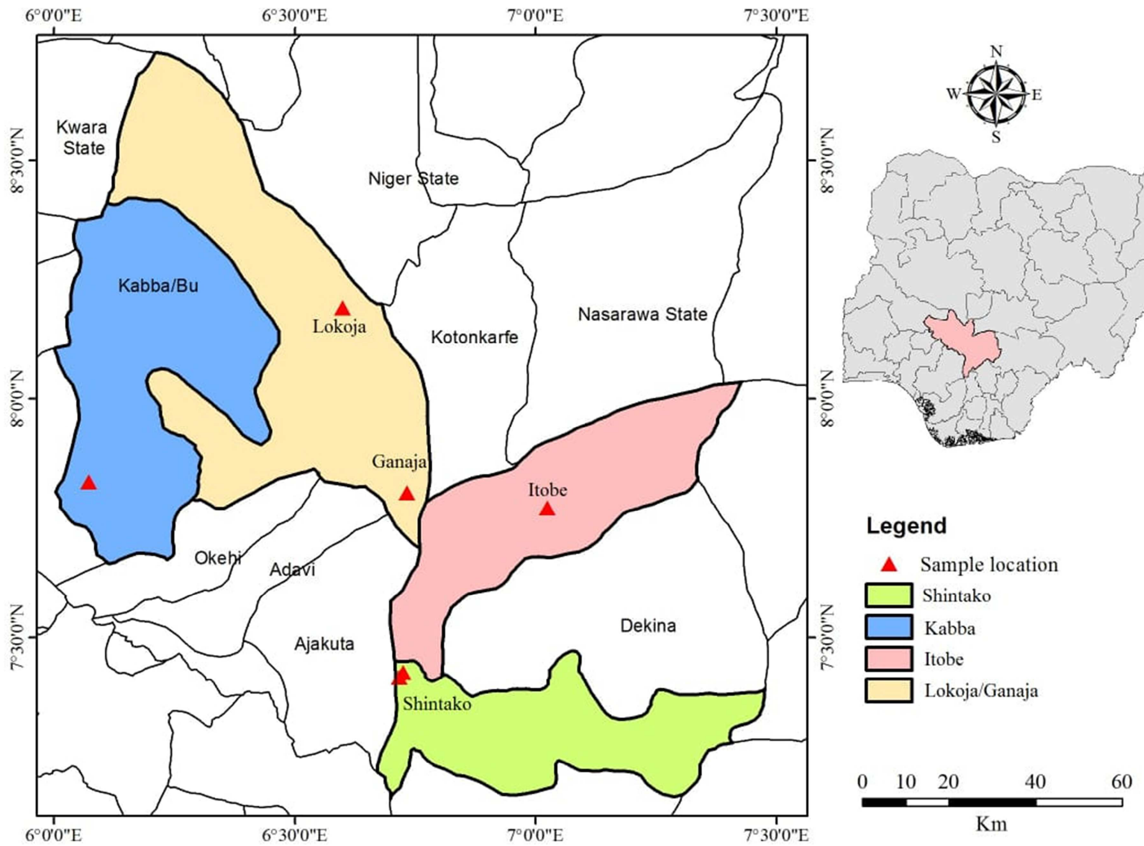

Figure 1. *Map of Kogi State Showing the Sampling Locations.*

2.5. Quality Assurance and Control

Recovery analyses of four surrogate PAHs mixtures: acenaphthene d_{10}, chrysene d_{12}, phenanthrene d_{10} and perylene d_{12} (Sigma Aldrich USA) was carried out to evaluate the validity of the analytical procedure. Mixed standard solutions containing equal concentrations of each surrogate PAH were prepared and used to spike three 2 g portion of a vegetable sample in ascending order of concentration (0.1, 0.5, 1.0 ppm) The three spiked samples were then taken through the extraction process.

The limit of detection (LOD) and limit of quantification (LOQ) were determined by the signal-to noise method. The peak-to-peak noise for the analyte retention time was measured, and subsequently, the concentration of the analyte that yielded a signal equal to the noise-to-signal ratio was estimated. A signal-to noise ratio of three is generally accepted for estimating LOD and signal-to-noise ratio of ten is used for estimating LOQ [28].

2.6. Determination of PAHs

PAHs analysis was carried out with an Agilent 6890N gas chromatograph coupled to inert 5973C mass spectrometer (with triple axis detector) and electron impact source (Agilent Technologies). An HP-5 capillary column coated with 5% Phenyl-Methyl Siloxane (30 m length × 0.32 mm diameter × 0.25 µm film thickness) was used. The carrier gas was hydrogen used at constant flow of 1.48 mL/min, at an initial nominal pressure of 1.49 psi, and average velocity of 44.22 cm/sec. 1µL of the samples were injected in splitless mode at an injection temperature of 300°C. Purge flow to spilt vent was 15.0 mL/min at 0.75 min with a total flow of 16.67 mL/min; gas saver mode was switched off. Oven was initially programmed at 40°C (1 min) then ramped at 12°C/min to 300°C (10 min). Run time was 32.67 min with a 3 min solvent delay. The mass spectrometer was operated in electron-impact ionization mode at 70eV with ion source temperature of 230°C, quadrupole temperature of 150°C and transfer line temperature of 300°C.

2.7. Statistical Analysis

Analysis of variance (ANOVA) was used to determine whether the concentrations of the PAHs varied significantly within and between the groups ($P<0.05$). Data were analyzed using SPSS version 16.0 for Windows.

2.8. PAH Diagnostic Analysis

The sources of the PAHs detected in this study was determined using the diagnostic ratios. They allow to distinguish between PAH pollution from petrogenic (liquid fuel spills), pyrolytic (combustion of gas and liquid fuels) and burning biomass or coal sources [29].

2.9. Estimated Daily Intake

The dietary intakes of the detected PAHs were estimated, using a deterministic approach. A fixed value for the consumption of an individual food was multiplied by a fixed value for the contaminant concentration in that food [16]. The total exposure was obtained by summing the intakes from all foods, using the Estimated daily Intake (EDI) equation:

$$EDI = CxCR/BW$$

Where

EDI is an estimated daily dose (mg/kg/day), C is the concentration of PAHs determined in the vegetables (mg/kg), CR is the consumption rate of vegetables (37.23 g/day) [30], BW is the body weight, 60 kg for an adult and 15 kg for children [31].

Risk Assessment

The risk was estimated using the Margin of Exposure

$$MOE = BMDL_{10}/EDI$$

Where

$BMDL_{10}$ is the benchmark dose lower confidence limit at 10% incidence level. Considering a $BMDL_{10}$ of 0.07, 0.17, 0.34 and 0.49 all in mg/kg bw per day for BaP, PAH 2, PAH 4 and PAH 8 respectively, for adult and children scenario, where:

BaP = Benzo [a] pyrene

PAH 2 = Benzo [a] pyrene and chrysene

PAH 4 = Benzo [a] anthracene, benzo [a] pyrene, benzo [b] fluoranthene and chrysene

PAH 8 = Benzo [a] anthracene, benzo [b] fluoranthene, benzo [k] fluoranthene, benzo [g, h, i] perylene, benzo [a] pyrene, chrysene, dibenz [a, h] anthracene and indeno [1, 2, 3- C, d] pyrene. [23]

3. Results and Discussions

Percentage recovery (%R) obtained from the analyses of the spiked samples were in the range of 94.0% - 99.2%. These values obtained were within the 70 – 120% range for acceptable recovery values stipulated by European Commission's guidelines for evaluating accuracy and precision of a method. The LOD (0.008µg/kg) and LOQ (0.024µg/kg) were obtained for anthracene, benzo [b] pyrene and pyrene while LOD (0.004µg/kg) and LOQ (0.012µg/kg) were obtained for the remaining PAH.

The mean concentrations of PAHs in the vegetable samples studied presented in Table 1 are on fresh weight basis since vegetables are normally consumed fresh. The fact that almost all samples in the current study contained majority of the PAHs demonstrates the widespread nature and persistence of these compounds.

The highest concentration of total PAHs (Σ 16 PAH) was detected in Okro (99.88±29.18µg/kg) while the least concentration was found in tomatoes (2.12±1.5µg/kg). Benzo [a] pyrene (BaP) was detected in all of the samples at concentrations ranging from 0.09±0.03 in cucumbers to 0.84±0.20 µg/kg in jute leaf samples. The mean concentration levels of eight probable carcinogenic PAHs, Σ8 PAHs, varied from 0.79±0.29 in tomatoes to 13.99±8.06 in jute leaf samples. The mean concentration levels of lower molecular weight, LMW PAHs (2, 3 and 4 ring compounds) ranged from 1.10±0.84 in tomatoes to 90.51±26.71 in okro while that of higher molecular weight, HMW PAHs (more than 4 ring compounds) ranged from 1.02±0.66 in tomatoes to 16.65±9.15 in jute leaf. Okro is a rich source of fats [32] and since most of the PAHs are lipophilic, this can explain the high concentration of the PAH in the okro samples.

Table 1. *Mean concentrations (ug/kg FW) of PAH in vegetable from Rivers Niger-Benue confluence at Lokoja, Northcentral, Nigeria.*

	Spinach	Jute leaf	Pumpkin leaf	Okro	Tomatoes	Garden egg	Cucumber	Average	RfD
Naphthalene	0.40±0.12^{b*}	22.61±19.31^{b}	17.08±16.75^{b}	88.64±26.07^{a}	0.14±0.08^{b*}	38.71±36.47^{ab}	0.31±0.11^{b*}	23.98±8.40	20
Acenaphthylene	ND	ND	ND	0.018±0.018^{a}	0.012±0.010^{a*}	ND	0.29±0.29^{a*}	0.05±0.04	0.06
Acenaphthene	0.71±0.49^{a*}	0.45±0.25^{a*}	0.45±0.23^{a*}	0.84±0.35^{a*}	0.60±0.60^{a*}	1.48±0.58^{a*}	0.10±0.06^{a*}	0.66±0.16	60
Fluorene	0.28±0.11^{ab*}	0.33±0.16^{ab*}	0.15±0.04^{b*}	0.69±0.17^{a*}	0.12±0.08^{b*}	0.70±0.23^{a*}	0.18±0.07^{b*}	0.35±0.06	40
Phenanthrene	0.25±0.09^{a}	0.75±0.30^{a}	0.22±0.07^{a}	0.25±0.05^{a}	0.13±0.05^{a}	0.27±0.09^{a}	0.49±0.20^{a}	0.34±0.06	NA
Anthracene	0.10±0.06^{a*}	0.13±0.08^{a*}	0.11±0.07^{a*}	0.07±0.05^{a*}	0.10±0.03^{a*}	0.07±0.04^{a*}	0.05±0.02^{a*}	0.09±0.02	0.03
Fluoranthene	0.65±0.31^{abc*}	1.46±0.23^{a*}	0.24±0.11^{bc*}	0.87±0.28^{abc*}	0.05±0.02^{c*}	0.90±0.40^{ab*}	0.44±* 0.25^{bc*}	0.66±0.12	40
Pyrene	0.27±0.10^{ab*}	0.29±0.12^{ab*}	0.10±0.03^{b*}	0.15±0.04^{b*}	0.05±0.02^{b*}	0.45±0.13^{a*}	0.27±0.10^{ab*}	0.23±0.04	30
Benz [a] anthracene	1.55±0.54^{bc}	2.64±0.82^{b}	1.09±0.52^{bc}	5.85±1.26^{a}	0.08±0.03^{c}	0.97±0.74^{bc}	0.04±0.02^{c}	1.75±0.40	NA
Chrysene	0.07±0.05^{a}	0.07±0.04^{a}	0.02±0.02^{a}	0.03±0.02^{a}	0.02±0.01^{a}	ND	0.02±0.01^{a}	0.03±0.01	NA
Benzo [b] fluoranthene	0.22±0.07^{ab}	0.54±0.22^{a}	0.31±0.05^{ab}	0.25±0.05^{ab}	0.03±0.02^{b}	0.60±0.17^{a}	0.02±0.02^{c}	0.28±0.05	NA
Benzo [a] pyrene	0.28±0.14^{b}	0.84±0.20^{a}	0.29±0.08b	0.43±0.25^{ab}	0.11±0.04^{b*}	0.15±0.01^{b*}	0.09±0.03^{b*}	0.31±0.06	0.3
Benzo [ghi] perylene	0.72±0.48^{a}	8.22±6.34^{a}	5.93±2.99^{a}	0.40±0.13^{a}	0.21±0.11^{a}	0.89±0.31^{a}	0.32±0.14^{a}	2.39±1.05	NA
Dibenz [a, h] anthracene	0.35±0.18^{a}	1.40±0.62^{a}	0.46±0.15^{a}	0.43±0.14^{a}	0.17±0.12^{a}	0.39±0.16^{a}	0.13±0.04^{a}	0.48±0.11	NA
Indeno [1, 2, 3-cd] pyrene	0.10±0.10^{bc}	1.10±0.51^{a}	0.04±0.04^{c}	0.89±0.27^{ab}	0.28±0.28^{bc}	0.42±0.20^{abc}	0.15±0.09^{bc}	0.42±0.11	NA
Benzo [k] fluoranthene	0.09±0.06^{a}	0.09±0.06^{a}	0.09±0.06^{a}	0.07±0.04^{a}	0.02±0.01^{a}	0.03±0.02^{a}	0.02±0.01^{a}	0.06±0.02	NA
Σ16 PAH	6.05±2.9	40.92±29.26	26.58±21.2	99.88±29.18	2.12±1.5	46.02±39.54	2.31±0.76		
BaP	0.28±0.14	0.84±0.20	0.29±0.08	0.43±0.25	0.11±0.04	0.15±0.01	0.09±0.03		
PAH 2	0.35±0.19	0.91±0.24	0.31±0.10	0.46±0.27	0.13±0.05	0.15±0.01	0.38±0.08		
PAH 4	1.84±0.65	3.25±1.08	1.43±0.59	6.13±1.32	0.12±0.06	1.57±0.91	2.39±0.51		
PAH 8	3.02±1.33	13.99±8.06	7.92±3.76	7.89±1.62	0.79±0.29	3.31±1.40	6.15±1.87		
Σ LMW – PAH	4.30±2.02	24.27±20.11	18.00±17.16	90.51±26.71	1.10±0.84	41.22±37.41	29.48±9.96		
Σ HMW – PAH	1.75±0.88	16.65±9.15	8.58±4.04	9.37±2.47	1.02±0.66	4.80±2.13	7.45±2.24		

NA- Not accessed; RfD-Reference dose; means with different alphabet along each row are significantly different at $p < 0.05$ using Duncan New Multiple Range Test; *- Significant difference between the concentration and the reference dose using one sample t-test

Most of the naphthalene entering the environment are discharged to the air. The largest releases result from the combustion of wood and fossil fuels and the off-gassing of naphthalene-containing moth repellents [33]. Naphthalene in the atmosphere is subject to a number of degradative processes, including reaction with photochemically produced hydroxyl radicals [34]. The occurrence of naphthalene in the environment is also attributable to recent combustion, bush burning and vehicular emissions close to the farmland.

The concentrations of Bap in all the vegetable samples range from 0.09 to 0.84μg/kg, being lower than the maximum permissible level of 1μg/ kg specified by EU for different baby foods [35] and the recommended Food Standard Agency limits of 2μg/kg in food samples. Concentrations of lower molecular weight (LMW) compounds (those having 2-4 rings) were found to be higher than those of the high molecular weight (HMW) compounds (5 or more rings). This is in agreement with the study [36] on the quantification of PAHs in fruits and vegetables in Mumbai.

Table 2 shows the characteristic PAH Diagnostic Ratios for Particular Emission Sources while Table 3 shows the calculated PAH Diagnostic Ratios of various emission sources. For Anth/(Anth + Phen), ratios obtained for all the samples were > 0.1, indicating fuel combustion emission source. Diagnostic ratios for Fla/(Fla + Pyr) in all the samples were > 0.5, indicating emission from combustion of biomass (in this case burning of farm lands and bushes for game and land preparation for agricultural purposes), while for B [a] A/B [a] A+ Chr, the ratio were > 0.35, indicating fuel (petroleum) combustion emission. For the I [cd] P/I [cd] P+B [ghi] emission, the ratio obtained were < 0.2 for spinach, jute leaf and pumpkin indicating a petrogenic (spillage) sources, and were in the range of 0.2 – 0.5 and > 0.5 for garden egg, cucumber and tomatoes respectively indicating emission from fuel combustion and biomass combustion respectively. Thus, the major PAH emission sources are fuel combustion and burning of biomass into the soil and water of the Niger- Benue confluence and its environment. Thus, it is clear from Tables 2 and 3 that the abundance of PAH from the study area follows this order of importance: vehicular emission and combustion processes based on the diagnostic ratio over the confluence, the annual heavy flooding of the confluence due to the overflow of Benue and Niger rivers and the dumping of urban wastes from Lokoja township.

Table 2. *Characteristic PAHs Diagnostic Ratios for Particular Emission Sources.*

PAHs Emission	Diagnostic Ratio		
	Petrogenic	Fuel combustion	Coal, grass, wood (Biomass) burning
Anth /(Anth + Phe)	<0.1	>0.1	-
Fla/(Fla + Pyr)	<0.4	0.4 – 0.5	>0.5
B [a] A/(B [a] A + Chr)	<0.2	>0.35	0.2 – 0.35
I [c, d] P/(I [c, d] P+B [g, h. i] P	<0.2	0.2 – 0.5	>0.5

Source: [29]

Table 3. *PAH Diagnostic Ratios Analysis for apportionment of Emission Sources.*

Sample	Anth /Anth +Phen	Fla/Fla+Pyr	B [a] A/B [a] A+Chr	I [cd] P/I [cd] P+B [ghi] P
Spinach	0.29	0.71	0.96	0.12
Jute leaf	0.15	0.83	0.97	0.12
Pumpkin leaf	0.33	0.71	0.98	0.01
Okro	0.22	0.85	0.99	0.69
Tomatoes	0.43	0.50	0.80	0.57
Garden egg	0.21	0.67	1.00	0.32
Cucumber	0.10	0.62	0.67	0.32

Table 4 presented the estimated daily intakes of indicators of the occurrence of carcinogenic PAHs such as BaP, PAH2, PAH4 and PAH8 of generally exposed children and adults who consumed the studied vegetable samples. It was reported that the total dietary exposure of adult to carcinogenic PAHs in vegetables for BaP ranged from 0.07 to 0.52×10^{-6}, PAH 2 from 0.08 to 0.57×10^{-6}, PAH 4 from 0.07 to 3.80×10^{-6} and for PAH 8 from 0.49 to 8.68×10^{-6} while for children the total dietary exposure were BaP (0.27 to 2.09×10^{-6}), PAH 2 (0.32 to 2.26×10^{-6}), PAH 4 (0.30 to 15.20×10^{-6}) and PAH 8 (1.96 to 34.70×10^{-6}). A careful study of the indicators for the occurrence of carcinogenic PAHs such as BaP, PAH2, PAH4, and PAH8 of generally exposed children and adults who consumed these vegetables follow the same trend. For example, jute leaf which was the most important source of BaP and PAH2 in adults followed by okro was the same for children, for PAH4 okro was the most important source followed by jute leaf for both adults and children and for PAH8, jute leaf was the most important source followed by pumpkin leaf for both children and adults. Tomatoes was the least important source of these indicators for the occurrence of carcinogenic PAH in both children and adults. The dietary intakes of PAHs are usually expressed in mg/kg bw/day and thus are age dependent. The concentration of the least important source of PAH in tomatoes for children (0.27×10^{-6} mg/kg bw/day) is higher than the concentration in adults (0.07×10^{-6} mg/kg bw/day) for BaP. This is the same for PAH2, PAH4 and PAH8. Nwaneshiudu, O. C. et al and Yoon, E. et al reported in their studies that children risks are always higher than those for adults. This is in agreement with the result in this present study as the children's risk is higher than those of the adults.

Table 4. *Estimated daily intakes (× 10^{-6}mg/kg bw/day) of carcinogenic PAH Residues in the analysed Vegetables by generally exposed individuals.*

Samples	BaP		PAH 2		PAH 4		PAH 8	
	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Spinach	0.17	0.70	0.22	0.87	1.14	4.57	1.87	7.50
Jute leaf	0.52	2.09	0.57	2.26	2.02	8.07	8.68	34.70
Pumpkin leaf	0.18	0.72	0.19	0.77	0.89	3.55	4.91	19.70
Okro	0.27	1.07	0.29	1.14	3.80	15.20	4.90	19.60
Tomatoes	0.07	0.27	0.08	0.32	0.07	0.30	0.49	1.96
Garden egg	0.09	0.37	0.09	0.37	0.97	3.90	2.05	8.22
Cucumber	0.22	0.87	0.24	0.94	1.48	5.93	3.82	15.30

Table 5. *Margin of Exposure (MOE) of generally exposed individuals to carcinogenic PAH residues in the analysed Vegetables.*

	BaP		PAH 2		PAH 4		PAH 8	
	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Spinach	402000	101000	783000	196000	298000	74400	262000	65300
Jute leaf	134000	33500	301000	75200	168000	42100	56500	14100
Pumpkin	389000	97200	885000	221000	383000	95800	99800	24900
Okro	262000	65400	596000	61400	89500	4610	100000	3570
Tomatoes	1020000	256000	2110000	217000	4560000	235000	1000000	35700
Garden egg	752000	188000	1825994	188000	349000	17900	230000	8520
Cucumber	323000	80600	720000	74200	230000	11800	128000	4580

Table 5 presented the margin of exposure (MOEs) of generally exposed individuals to the carcinogenic PAHs as a result of the consumption of the analyzed vegetables. All values of MOE for adults were far above 10,000, indicating low risk, while for the children, values below 10000 were obtained for PAH 4 with respect to okro, and PAH 8 with respect to okro, garden egg and cucumber, showing high risk. This according to EFSA indicated low concern for human health and considered low priority for risk management actions. The children consuming these vegetables are at a high risk of exposure to PAH4 and PAH8. Values of MOE in okro (4610 and 3570), garden egg (8520) and cucumber (4580) were below 10,000. The consumption of these vegetables suggest a low public health concern for adults but a high public health concern to the children around the study site especially as it regards the importance of vegetables. Food Standard Agency (FSA) in the UK. reported that the mean MOE value of all PAHs in cereal and vegetables ranged from 267700-323800 in adults. The MOE values of the indicators for adults in this study varied between 56,500 and 4,560,000.

Reports have shown that children risks are always higher than those for adults [21,22]. Bishnoi, N. R. et al. have reported a higher intake of total PAHs from food for children (0.307µg/kg/day) than that for senior adults (0.102µg/kg/day) [37]. The values obtained in this study were in line with the values obtained by [14, 16, 20, 31, 38]. The study of Minmin W. et al on Distribution and Health Risk Assessment on Dietary Exposure of Polycyclic Aromatic Hydrocarbons in Vegetables in Nanjing showed that the values of MOE in children are lower than 10,000 and in adults the values were higher than 10,000. They attributed this to the fact that children were more sensitive and were easier to be exposed to the environmental pollutants. The study of Odika, I. M. et al. on the Health Risk Assessment of PAHs from Wheat (Tritcum specie) Bambara Nut (Vigna subterranea) and Pigeon Peas (Cajanus cajanifolia) Consumed in Nigeria also reported the values of MOE obtained ranged from 48,110 to 392,943 in adult male and female individuals [14]. These values being very much higher than 10,000 indicated low concern for human health and considered low priority for risk management actions. Iwegbu, C. M. A. et al. on Polycyclic aromatic hydrocarbon concentrations on commercially available infant formulae in Nigeria showed that the values of all the indicators-BaP, PAH2, PAH4, PAH8 were greater than 10,000 and that of Ihedioha, J. N. et al on Risk assessment of polycyclic aromatic hydrocarbons in pasta products consumed in Nigeria revealed that the MOE values for adult consumers were far higher than 10,000 and but children consuming Nigerian brands of pastas were at risk of exposure to PAH4 and PAH8 since these brands have MOE values below 10,000. Also the study by Lee et al. on the Occurrence and Risk characterization of PAHs of edible oils reported the values of MOEs (between 66094 and 1729776) were over 1.0 ×10^4 indicating that the risk of 4 PAHs in edible oils were of low concern from a public health point of view. [39]

From the analysis of variance of all the analyzed vegetables, means with different alphabet along each row are significantly different at $P < 0.05$ using Duncan New Multiple Range Test.

4. Conclusion

The study determined the concentrations of Σ16 PAHs in different vegetables. All vegetable samples analyzed had PAH concentrations less than the permissible limit specified for foods by the European Commission and the Food Standard Agency. The MOE values for the adults were higher than 10,000 in vegetables. According to the European Food Safety Authority (EFSA), a MOE value higher than 10,000 indicates a low concern for the consumer's health. Therefore, there is a low concern for the adults who consume these vegetables around this area in Nigeria. However, about 7.14% of the vegetables in children have MOE values lower than 10000 which suggests a risk of exposure to PAH4 and PAH8. There is a potential concern for children who consume these vegetables. Continuous demand for analytical monitoring and increased research efforts concerning Nigerian foods should be advocated to ensure adequate protection of human health and the risk management actions.

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