Health Risks Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Cassava and Cocoyam Flours from Eke Awka Market in Anambra State

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DOI: https://doi.org/10.51244/IJRSI.2024.1107090

Received: 04 July 2024; Revised: 17 July 2024; Accepted: 20 July 2024; Published: 21 August 2024

ABSTRACT

Exposure to Polycyclic aromatic hydrocarbons (PAHs)presents a potential health risk to individuals through various routes, including dietary intake, particularly for non-smokers. The aim of this study was to measure the levels of PAHs in cassava and cocoyam flour commercially sold and consumed daily in Anambra State Nigeria, and to assess its quality and safety using 100 volunteer students of the School of Pharmacy, Nnamdi Azikiwe University, Awka to determine the daily consumption of cassava and cocoyam flour. Gas chromatography with flame ionization was used to detect the presence and levels of PAHs. Appropriate equations were used to calculate the estimated daily intake (EDI), hazard quotient (HQ), hazard index(HI), toxic equivalents(TEQ), and incremental life cancer risks(ILCR). Seven PAHs were detected in the cassava flour namely: Fluorene, Fluroranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluroanthene, and Dibenzo[a,h]anthracene. On the other hand, four PAHs were detected in the cocoyam flour namely: Fluorene, Phenanthrene, Benzo[a]anthracene, and Benzo[k]fluoranthene. While dibenzo[a,h]anthracene had the highest concentration in the cassava flour, phenanthrene had the highest concentration in the cocoyam flour. The control samples showed no presence of PAHs. The values of the Estimated Daily Intake of PAHs in the cocoyam sample ranged from 1.7966e-4 to $4.3419e^{-4}$ for children and from $1.2320e^{-4}$ to $3.2138e^{-4}$ for adults, exceeding the recommended reference doses for both adults and children. The values in the cassava sample ranged from $1.5973e^{-4}$ to $6.7722e^{-4}$ for adults and from $2.3294e^{-4}$ to $9.876e^{-4}$ for children. These values exceeded the recommended reference doses for both adults and children. However, the HQ, and HI values for the cassava samples were $1.497e^{-2}$for adults and $2.1831e^{-2}$ for children, and that of cocoyam was $7.4433e^{-3}$ for adults and $1.090e^{-2}$ for children were below 1, suggesting non-carcinogenic risk. However, the toxic equivalents significantly surpassed the screening values. The *ILCR* for 16PAHs ($5.08e^{-3}$ for adults), and ($7.4095e^{-3}$ for children) in the cassava flour samples were notably higher than the threshold, underscoring a significant health concern indicating a high cancer risk. The value for the cocoyam, ($2.32e^{-4}$ for adults), and ($4.841e^{-6}$ for children) does not portend any cancer risk.

Keywords: cassava *flour; cocoyam flour; risk assessment, polycyclic aromatic hydrocarbons, Anambra*

INTRODUCTION

Concern about the safety of foods has been on the increase in recent years due to the increased rate of pollution which releases a lot of contaminants into the environment. Anthropogenic activities linked to

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XI Issue VII July 2024

urban development produce substantial quantities of organic and inorganic chemical contaminants that ultimately find their path into the surrounding ecosystem, including soils, water bodies, the atmosphere, and even the food we eat(Qishlaqi and Beiramali, 2019). The presence of these contaminants in common agricultural produce and other matrices is a global environmental concern (Oyekunle *et al.,* 2023). The primary route of human exposure to environmental contaminants is through food consumption, constituting over 90% of intake, in contrast to inhalation or dermal pathways(Kiani *et al.*, 2021).Among the various environmental contaminants, polycyclic aromatic hydrocarbons (PAHs) stand out as highly harmful and have garnered significant interest from researchers and experts.

The term "polycyclic aromatic hydrocarbons" (PAH) refers to classes of substances that have diverse toxicological and carcinogenic characteristics and are made up of two or more benzene rings connected in different ways(Patel *et al.*, 2020). These compounds typically appear as colorless, white, or pale yellow solids. PAHs are categorized based on the number of rings they contain. They are divided into two groups: low-molecular-weight PAHs (LMW PAHs), which have two or three aromatic rings, and high-molecular-weight PAHs (HMW PAHs), which have four or more aromatic rings. The spatial arrangement of their aromatic rings can be angular, linear or clusters. Depending on their molecular weight, they are released into the atmosphere either as a gas (LMW PAHs) or as particulate matter (HMW PAHs)(Abdel-shafy and Mansour, 2016). PAHs may originate from natural sources such as forest fires, and volcanic activity or from numerous outdoor sources such as motor vehicle emissions, petrochemical and petroleum refining processes, wastewater treatment facilities, power plants, and oil spills, and exposure to PAHs is linked to several harmful health effects, including impaired pulmonary function, hormone imbalance, myocardial infarction, immune system alterations and failure, testicular lesions, carcinogenicity, and neurological diseases (Al-harbi *et al.*,2020).

Both dietary and non-dietary sources (such as inhalation and skin contact) can expose people to PAHs and more than 70% of non-smokers' exposure to PAHs is linked to food consumption, which is the main exposure pathway among these (Sampaio *et al.*, 2021).The contamination of food with PAHs has received great environmental concern due to their carcinogenicity, toxicity, mutagenicity, persistence, and mobility throughout the environment. As PAHs are lipophilic and semi-volatile compounds, they can be accumulated by plants, and some of such plants are ***Manihot esculenta*** and ***Colocasia esculenta,*** commonly known as cassava and cocoyam respectively**.**

Within numerous developing nations using Nigeria as a case study, cocoyam and cassava hold a pivotal role in ensuring household food security and generating income. These crops are characterized by their starch and fibre content, contributing to consumer satiety and energy provisioning. Notably, cocoyam and cassava are extensively cultivated in the West African region and serve as a vital food source for over 400 million individuals globally(Owusu-Darko *et al.*, 2014).Cocoyam and cassava exhibit a notable abundance of starch content, rendering it amenable for extraction and subsequent application in various industries contingent upon its compatibility. Nonetheless, a paramount strategy for cassava and cocoyam preservation and economic augmentation entails their conversion into starch through processing, capitalizing on their elevated starch proportions. Their transformation into flour via processing confers an extension to their shelf life, ensuring uninterrupted availability throughout the entire year (Falade and Okafor, 2013).

Major techniques involved in cassava and cocoyam processing include drying and grinding, and one of the cost-effective means of drying is the use of open-air drying which is majorly practiced. However, open-air drying exposes it to environmental contaminants, and PAHs being ubiquitous in the environment can become possible contaminants. The grinding process can also involve the use of heavy machines which also exposes the food substance to PAH contamination. Food chain contamination with PAHs harms human

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XI Issue VII July 2024

health as around 30% of human cancers have been always associated with low exposure to PAHs in the diet (Khillare *et al.,* 2012) hence it is important to determine the levels of polycyclic aromatic hydrocarbons

present in various food crops consumed, and most especially cocoyam which is globally consumed.Cassava and cocoyam flour are easily affordable and serve as staple food commonly consumed by the populace of Anambra State, South East Nigeria. A good quality control by safety assessment is therefore necessary to protect consumers from potential health risks. The study therefore investigates the levels of PAHs in cocoyam and cassava flour to determine their potential health risk.

MATERIALS AND METHODS

The research design was based on the United States Environmental Protection Agency (USEPA) method 8100 (EPA, 1984) as described by Udowelle *et al* (2017), whereby the cassava and cocoyam flours were randomly purchased from the study area as highlighted in Figure 1.

1. Study Area

This research was carried out in Anambra State, a tropical region situated in the south eastern part of Nigeria, characterized by a mean daily temperature of 29 °C. Its geographic coordinates are approximately 6.02 °N latitude and 6.05 °E longitude. Anambra State shares a border with four neighbouring states, namely Imo, Delta, Enugu, and Kogi. The state is further divided into three senatorial districts known as Anambra Central, Anambra North, and Anambra South. The Independent National Electoral Commission (INEC) for the year 2023 lists a total of 362 wards distributed across these senatorial zones. Within the state, there are approximately 193 communities spanning 21 Local Government Areas (LGAs).According to the 2006 census and 2016 prediction, it had a total population estimated at 4,177,828 and 5,527,809, respectively, with an 862 population density. The research samples were collected in the Eke Awka market in the Anambra State's Awka South Local Government Area.

2. Study Site Description/Sample Collection

Ethical approval for this study was sought for and received from the ethics committee of the Faculty of Basic Medical Sciences of the Nnamdi Azikiwe University Awka. A structured questionnaire and an oral interview were conducted among 100 students of the Nnamdi Azikiwe University School of Pharmacy Agulu before choosing the sample size. The questionnaire information was gathered from 10th April 2023 to 14th April 2023. The results of the questionnaire were used to calculate the average daily intake of cups of both cassava and cocoyam flour as they provide information such as demographic data of the individual, and several cups of flour each consumes daily. The cocoyam and cassava flour samples which served as a test sample were procured randomly from Eke Awka market, situated in Anambra Central Senatorial District. To ensure proper handling, the sample was carefully packaged and labelled using a nylon bag, with additional identification provided through the use of a marker and masking tape. Subsequently, the securely packaged tests and control samples were sent to the laboratory for thorough analysis of PAHs.

The control sample: Unprocessed tubers of both cassava and cocoyam were acquired from a residential quarter located approximately five kilometres away from any industrial area, following the methodology described by Asomugha *et al.,* (2005) and taken to Pharmacology and Toxicology Laboratory, Nnamdi Azikiwe University, Awka Nigeria. The tubers were peeled and thoroughly double-washed with distilled water and subsequently air-dried in a closed room for 14 days. Once completely dried, the peeled and dried cocoyam and cassava tubers were shredded separately using a clean mortar and pestle before the samples

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were carefully packaged and labelled in a nylon bag prior for laboratory analysis for the presence of PAHs.

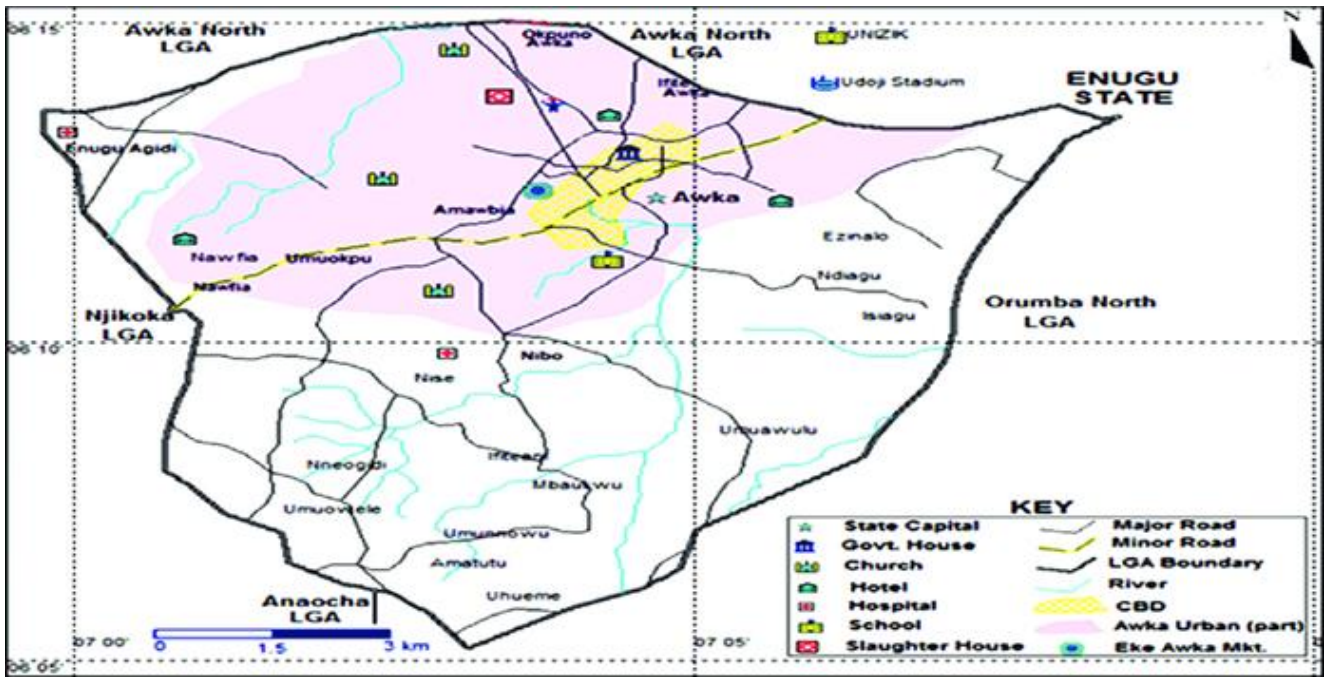

Fig 1: Map of Awka metropolis showing the location of Eke Awka in Anambra state, Nigeria.

3. Chemicals and Equipment

Sodium sulphate, anhydrous silica gel, Dichloro methane, Filter Paper, Buchner's Funnel, Measuring Cylinder, Beaker, 20ml Vial Bottles, Amber Bottles with Plastic Cover, Spatula, Weighing Balance, Ceramic Mortar and Pestle, Pasture Pipette, Analytical Weighing Balance, Chromatographic Column, 600mm long by 30mm Glass Vials, Gas Chromatograph (GC), Flame ionization detector (FID)(Claurus 680, PerkinElmer Inc., Waltham, MA, USA).The reasons why the equipment and chemicals were used in this study are explained in the PAHs analysis below.

4. Polycyclic aromatic hydrocarbons(PAH) Analysis

The polycyclic aromatic hydrocarbons (PAHs) present in the cassava flour, cocoyam flour and control samples were analyzed according to the method of the United States Environmental Protection Agency (USEPA, 2007).

5. Procedure

The control sample was sliced into small pieces before being grounded and crushed into a powdered state. Then about 2 to 5g of the sample was weighed using an analytical weighing balance and put into the extraction vessel. Fifty grams (50g) of sodium sulfate was measured, added into the solution, and thoroughly homogenized by stirring with a spatula that helped remove all water molecules in the sample. Then 25ml of Dichloromethane was added to the mixture, which helped release all the PAHs present. Stirring was continued through the wrist action until all the contents were thoroughly homogenized. The mixtures were allowed to stay for an hour before mixing with silica gel that removed all polar compounds in the sample. Then the solution was filtered through a Buchner funnel equipped with the 0.500mm Whatman

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filter paper into a graduated measuring cylinder. Then the filtrate was further cleaned by passing it through the chromatographic column that had been packed with glass wool for further purification. This filtrate was concentrated by passing it over nitrogen gas. The concentrated hydrocarbon fractions were then transferred into the glass vials via the Teflon rubber crimp caps for gas chromatographic (GC)analysis. One micro litre of the concentrated sample was injected using a hypodermic syringe through a rubber septum into the column. Separation occurs as the vapour constituent partitions the gas and liquid phases. Then the sample was automatically detected as it emerged from the column by the FID detector whose response is dependent upon the composition of the vapor.

The ultraviolet (UV) absorbance spectra of PAHs are extremely distinctive. Each isomer's UV absorbance spectrum differs from the others because each ring structure has a distinct UV spectrum. This is particularly helpful in identifying PAHs. The majority of PAHs are fluorescent as well, stimulated by light absorption (when molecules absorb light), and emitting certain light wavelengths. Gas chromatography with a flame ionization detector (Claurus 680, PerkinElmer Inc., and Waltham, MA, USA) was used to quantify sixteen PAHs. The sixteen (16) PAHs that were quantified are Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene and Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3)pyrene, Dibenzo(a,h)anthracene and Benzo(g,h, i)perylene.

Target analytes were separated using an HP-5 capillary column (30m × 0.25mm i.d. with a 0.25μm film thickness) while the detector was heated to 300°C.Moreover, the carrier gas is helium (99.99%), set at 1 milliliters per minute. Then a splitless injection of a 1 um treated sample was made at 250 °C. The column temperature was originally set at 80°C for 1 minute, then increased to 225°C at a rate of 15°C per minute, 265°C at a rate of 2.5°C per minute, and ultimately 300°C at a rate of 2.5°C per minute for 5 minutes. The determination of the presence of PAHs was made by comparing the peak's retention durations to those obtained from a standard PAH combination (standard provided by the instrument manufacturer). The standard solution of each PAH was used to create external calibration curves that served as the foundation for quantification.

6. Quality Control

To ensure the reliability of the data, rigorous quality assurance procedures were implemented, including the analysis of duplicate samples and blank samples. Additionally, before sample pretreatment and quantified analysis, the recovery rate was assessed using the method of external standards. The calibration curves exhibited high correlation coefficients, all exceeding 0.998, validating the accuracy of the quantification of PAHs. The analytical conditions utilized in this study allowed for a detection limit of 0.56-4.21 ng/L for the 16 PAHs, with a signal-to-noise ratio of 3, and a limit of quantization set at a signal-to-noise ratio of 10.

7. *Health Risk Assessment*

Health risk assessment is defined as the process that evaluates the toxic properties of chemical substances and their effects upon human exposure (Dokubo and Igwe, 2019).

The evaluation of human health risk in studies involves assessing the likelihood of severe health impacts arising from an individual's exposure to substances that may have carcinogenic or non-carcinogenic properties over a specific duration (Tay *et al.*, 2022).

To assess the non-carcinogenic health risks due to exposure to PAHs through the consumption of cocoyam

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flour by dietary intake, several models were employed such as the Estimated Daily Intake (EDI), Hazard Quotient (HQ), and Hazard Index (HI).

Additionally, the carcinogenic risks were also estimated by computing the carcinogenic potencies of the concentrations of different PAHs (B[a]Pteq), the toxic equivalent quotients (TEQs), screening value (SV) and the increased lifetime cancer risk (ILCR) (Onojake *et al.,* 2020; Tarawneh *et al.,* 2023).

8. Non-carcinogenic Risk Assessment

a. Estimated Daily Intake: The Estimated Daily Intake (EDI) of PAHs via consumption of powdered cassava was assessed for adult and children population (mg/kg/day) using Equation

EDI = (CPAHs x IR) / (BW)

Where CPAHs is the concentration of PAHs in the powdered cassava (mg/kg),

IR is the ingestion rate (kg/day)

BW is the average body weight (kg)

The adult daily average ingestion rate of cassava flour was calculated from the questionnaire to be 1 cup which weighs 500g = 0.5kg and that of children was assumed to be half of the average adult daily ingestion rate which is 250g = 0.25kg. The average adult body weight was assumed to be 70kg (Dokubo & Igwe, 2019) and that of children to be 24kg (Halfadji and Naous, 2021).

b. Hazard Quotient: The hazard quotient (HQ) is defined as the estimation of the non-carcinogenic risk level caused by the exposure to a pollutant concerning EDI (estimated daily intake) which is calculated from the following equation:

HQ = EDI/RfD

Where RfD is the reference dose for oral exposure.

NB: only the RfD of some of these PAHs have been derived (Nap = 20, Flu = 40, Phe = 30, and Pyr = 30 μ/kg-bw day).

c. Hazard index: This is the total sum of all the hazard quotients for all chemicals to which an individual is exposed (USEPA, 2011). HI (Hazard Index) is employed when numerous dangerous substances are found, all of which impact a common target organ or system. Its purpose is to assess the cumulative risk stemming from multiple routes of contamination. HI values of pollutants less than one are considered as safe and hence denote non-carcinogenic adverse effects (USEPA, 2011).

HI = Σ HQ

d. Carcinogenic Risk Assessment: This assessment was done following USEPA guidelines. This involves calculating the B[a]P equivalents of each PAH present in the sample. This is done by multiplying the concentration of each PAH with its toxic equivalent factor. B[a]P is used as the index carcinogen to which toxicity of PAHs is measured because it is the most widely studied and most information on the occurrence

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and toxicity of PAHs is related to it (Abdel-shafy and Mansour, 2016).

e. Toxic Equivalency Factor (TEF): This describes the toxicities of dioxins, furans, and polychlorinated biphenyls in terms of the dioxin 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), which is the most toxic form of the substance (ATSDR, 2011). Each congener might have a different level of toxicity. TEFs allow for the expression of the toxic equivalency (TEQ), which measures the degree of toxicity of a mixture of dioxins and dioxin-like compounds. The sum of the concentration and each congener's individual TEF values yields one single number (ATSDR, 2011).

The product of the concentration of each unique PAH congener and their toxicity equivalency factor (TEF) was used to calculate each PAH's carcinogenic potency using this equation;

Carcinogenic potencies for PAHs B (A)Pteq = Concentration of PAH × TEF.

Benzo (a) pyrene has frequently been examined as a marker representing the full group of chemicals to determine the PAH concentration of foodstuffs to determine health risk. Additionally, only benzo (a) pyrene had its maximum amounts in the foods specified.

The total sum of the product of the concentration and the **toxic equivalent factor** of each PAH

$$TEQ = \Sigma [C \times TEF]$$

A chemical's relative carcinogenicity about B(a)P is estimated by the TEF values because it has the highest characterized risk as a probable human carcinogen among PAHs, hence Benzo(a)pyrene was chosen as the reference compound. Subsequently, the B(a)P equivalency of each PAH is added together to determine the overall risk assigned to all PAHs present in the sample.

f. Incremental Life Cancer Risk (ILCR): This represents the likelihood of a person developing any form of cancer as a result of daily exposure to a carcinogenic pollutant throughout their lifetime. ILCR is calculated by utilizing the cancer slope factor, which assesses the probability of an individual developing cancer from the ingestion of contaminant levels throughout a lifetime. The slope factor for cancer through ingestion is measured in units of $(mg/kg/day)^{-1}$.

ILCR was estimated using the equation below;

$$ILCR = \frac{TEQ \times IR \times EF \times ED \times SF}{BW \times ATn}$$

Where TEQ = toxic equivalent quotients for all the PAHs present.

IR is the ingestion rate

EF is the exposure frequency which is 360 days/year(Tarawneh *et al.*, 2023)

ED is the exposure duration which is 70 years (Tarawneh *et al.*, 2023)

SF is the oral cancer slope factor (7.3 per mg/kg/day) (Tarawneh *et al.*, 2023)

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BW is the body weight

ATn is the average lifespan which is 70 years (25,550 days) (Tarawneh *et al.*, 2023).

According to USEPA (2013) guidelines, an ILCR value below 10^{-6} indicates a negligible cancer risk. Conversely, an ILCR exceeding 10^{-4} is considered an unacceptable level of cancer risk, while an ILCR within the range of 10^{-6} to 10^{-4} is deemed acceptable in terms of carcinogenic risk assessment for the public.

g. Screening Value (SV): This represents the minimum allowable concentration of chemicals in edible tissue, where public health concerns may arise. This value is determined through the formula:

$SV = (RL / SF \times BW) / IR$

Where RL = Maximum acceptable risk level (10^{-5}).

RESULTS AND DISCUSSION

1) Table 1 lists each PAH concentration in each of the samples. Although no PAH was found in the cassava or cocoyam control samples, the values ranged from 4.71062 e^{-3} to 9.48105 e^{-2} mg/kg and 1.72478e^{-2} to 4.49938e^{-2} mg/kg for the test samples, respectively. This could be explained by the absence of anthropogenic activities such as waste disposal or burning, industrial operations.

Table I: shows the concentration of the PAHs present in the samples and controls

Polycyclic Aromatic Hydrocarbons	**Concentration (mg/kg)**			
	cassava sample	**Control sample**	**Cocoyam sample**	**Control sample**
Naphthalene	NA	NA	NA	NA
Acenaphthylene	NA	NA	NA	NA
Acenaphthene	NA	NA	NA	NA
Fluorene	2.23621e^{-2}	NA	4.16821e^{-2}	NA
Phenanthrene	NA	NA	4.49938e^{-2}	NA
Anthracene	NA	NA	NA	NA
Fluoreanthene	1.72062 e^{-2}	NA	NA	NA
Pyrene	3.31945 e^{-2}	NA	NA	NA
Benzo[a]anthracene	1.88641e^{-2}	NA	2.63410e^{-2}	NA
Chrysene	2.03342 e^{-2}	NA	NA	NA
Benzo[b]fluoranthene	4.71062 e^{-3}	NA	NA	NA
Benzo[k]fluoranthene	NA	NA	1.72478e^{-2}	NA
Benzo[a]pyrene	NA	NA	NA	NA
Benzo[g,h,i]perylene	NA	NA	NA	NA
Di-benz[a,h]anthracene	9.48105 e^{-2}	NA	NA	NA
Indeno[l,2,3-c,d]pyrene	NA	NA	NA	NA

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The concentration of each PAH present in the samples are shown in Table 1. The values ranged from 4.71062 e^{-3} to 9.48105 e^{-2} mg/kg and 1.72478e^{-2} to 4.49938e^{-2} mg/kg for both cassava and cocoyam test samples respectively while no PAH was detected in both cassava and cocoyam control samples this could be attributed to the fact that the site where control samples were harvested is free of anthropogenic activities like dumping and burning of refuse, industrial activities, etc. Also, their processing was done in a controlled environment inside the laboratory. Out of 16 priority PAHs listed by USEPA, seven were presented in the cassava test sample with Di-benzo[a,h]anthracene concentration (9.48105 e^{-2} mg/kg) the highest in the cassava sample while only four were present in cocoyam test sample with phenanthrene concentration (4.49938e^{-2} mg/kg) the highest in the sample. The total value for PAHs present was higher in cassava than in cocoyam. The variations in the PAH concentration may be attributed to different processing procedures and equipment, transportation, and storage conditions involved in the production of the cassava and cocoyam flour. The environment where they are being stored and marketed is highly polluted as there is a lot of anthropogenic activities like residual burning and refuse dumping, fumes from the exhaust pipes of automobiles etc.

2) The EDI (mg/kg) of PAHs from eating cocoyam and cassava for adults and children is shown in Table 2. The values obtained in the cocoyam sample ranged from 1.2320e^{-4} to 3.2138e^{-4} for adults and from 1.7966e^{-4} to 4.3419e^{-4} for children with Phenanthrene having the highest concentration and Benzo[k]fluoranthene having the lowest concentration in both adults and children. These values greatly exceed the recommended oral reference dose (RfD) of 4–10 ng/kg-bw day (WHO, 2006).

The EDI (mg/kg) of PAHs through consumption of cocoyam and cassava for both adults and children are presented in Table 2 below. The obtained values in the cassava sample ranged from **1.5973e^{-4}** to **6.7722e^{-4}** for adults and from **2.3294e^{-4}** to **9.876e^{-4}** for children with Dibenzo[a,h]anthracene having the highest concentration and fluoranthene with the lowest concentration in both adults and children. The obtained values in the cocoyam sample ranged from **1.2320e^{-4}**to**3.2138e^{-4}** for adults and **1.7966e^{-4}** to**4.3419e^{-4}** for children with Phenanthrene having the highest concentration and Benzo[k]fluoranthene with the lowest concentration in both adults and children These values greatly exceed the recommended oral reference dose (RfD) 4-10 ng/ kg-bw day (WHO, 2006).

Table II: show the EDI of PAHs present in both samples and for both adults and children

Polycyclic Aromatic Hydrocarbons	**Estimated daily intake (mg/kg/day) Cassava sample**		**Polycyclic Aromatic Hydrocarbons**	**Estimated daily intake (mg/kg/day) Cocoyam sample**	
	Adults (≥ 18years)	**Children (2-12 years)**		**Adults (≥ 18years)**	**Children (2-12 years)**
Fluorene	1.5973e^{-4}	2.3294e^{-4}	Flourene	2.9773e^{-4}	4.3419e^{-4}
Fluoreanthene	1.229e^{-4}	1.7923e^{-4}	Phenanthrene	3.2138e^{-4}	4.6869e^{-4}
Pyrene	2.371e^{-4}	3.458e^{-4}	Benzo[a]anthracene	1.8814e^{-4}	2.7439e^{-4}
Benzo[a]anthracene	1.3474e^{-4}	1.965e^{-4}	Benzo[k]fluoranthene	1.2320e^{-4}	1.7966e^{-4}
Chrysene	1.4524e^{-4}	2.1181e^{-4}			
Benzo[b]fluoranthene	3.3647e^{-5}	4.9069e^{-5}			
Di-benz[a,h]anthracene	6.7722e^{-4}	9.876e^{-4}			

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The results indicated that regular consumption of food products made from this cassava flour from this study location could potentially harm human health, causing neurological and liver cell damage, gastrointestinal bleeding, vascular diseases, and oxidative stress (Dokubo and Igwe, 2019).

3) Exposure to multiple PAHs was evaluated for possible health risks to humans using the hazard index (HI), which is the total of the individual PAH-based Hazard Quotients (HQs) added together. A value of 0 for the HQ or HI indicates no significant non-cancer risks (no hazard), whereas a value of 1 or higher indicates notable non-cancer risks shown in table 3.

Table III: shows the hazard quotient and hazard index of the PAHs in the two samples and for adults and children.

PAHs	**Hazard Quotient**		**PAHs**	**Hazard Quotient**	
Cassava sample	**Adults**	**Children**	**Cocoyam sample**	**Adults**	**Children**
Fluorene	**$3.9933e^{-3}$**	**$5.8233e^{-3}$**	**Fluorene**	$7.4433e^{-3}$	$1.090e^{-2}$
Fluoreanthene	**$3.0735e^{-3}$**	**$4.4808e^{-3}$**	**Phenanthrene**	**NA**	**NA**
Pyrene	**$7.9033e^{-3}$**	**$1.1527e^{-2}$**	**Benzo[k]fluoranthene**	**NA**	**NA**
Benzo[a]anthracene	**NA**	**NA**	**Benzo[a]anthracene**	**NA**	**NA**
Chrysene	**NA**	**NA**	**Hazard Index**	$7.4433e^{-3}$	$1.090e^{-2}$
Benzo[b]fluoranthene	**NA**	**NA**			
Di-benz[a,h]anthracene	**NA**	**NA**			
Hazard Index	**$1.497e^{-2}$**	**$2.1831e^{-2}$**			

The potential risk to human health resulting from exposure to multiple PAHs was assessed using the hazard index (HI). The HI represents the cumulative sum of individual PAH-based Hazard Quotients (HQs). An HQ or HI value less than 1 indicates no significant non-cancer risks (no hazard), while a value of 1 or higher signifies noteworthy non-cancer risks (hazard) (Dokubo and Igwe, 2019). The degree of risk increases with higher HQ or HI values. In this study, the calculated HI values for the cassava sample is **$1.497e^{-2}$**for adults and **$2.1831e^{-2}$**for children which are less than 1, indicating that the non-carcinogenic adverse health risks associated with the levels of PAHs found in the cassava sample is negligible.

For the cocoyam sample, the HQ values in both adults and children were calculated only for Fluorene and other polycyclic aromatic hydrocarbons present were not computed due to limited information about their oral reference doses in the literature. However, both the HQ and HI values obtained were well below 1 thus the non-cancer risk associated with the consumption of cocoyam is largely negligible.

4) As the carcinogenic PAH with the greatest amount of research, benzo (a)pyrene (BaP) is commonly used as the reference material. According to the findings, there were no PAHs found in any of the control samples, or those that were present were at undetected levels as shown in Table 4..This indicates that there were few or no anthropogenic activities in the area where the samples were collected, such as disposing of agricultural waste or burning residual materials, and that there were fewer automobiles in the area because the roads there were not paved.

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XI Issue VII July 2024

Table IV: shows the B (a) P equivalent and TEQ of PAHs present in both samples

PAH	TEFs	Conc. (mg/kg) in cassava	B(a)P	Conc.(mg/kg) in cocoyam	B(a)P
Naphthalene	0.001	NA	NA	NA	NA
Acenaphthylene	0.001	NA	NA	NA	NA
Acenapthene	0.001	NA	NA	NA	NA
Fluorene	0.001	$2.23621e^{-2}$	$2.23621e^{-5}$	$4.16821e^{-2}$	$4.1682e^{-5}$
Phenanthrene	0.001	NA	NA	$4.4994e^{-2}$	$4.4994e^{-5}$
Anthracene	0.01	NA	NA	NA	NA
Fluoranthene	0.001	$1.72062e^{-2}$	$1.72062e^{-5}$	NA	NA
Pyrene	0.001	$3.31945\ e^{-2}$	$3.31945e^{-5}$	NA	NA
Benzo(a)anthracene	0.1	$1.88641\ e^{-2}$	$1.88641e^{-3}$	$2.63410e^{-2}$	$2.63410e^{-3}$
Chrysene	0.01	$2.03342\ e^{-2}$	$2.03342e^{-4}$	NA	NA
Benzo(b)fluoranthene	0.1	$4.71062\ e^{-3}$	$4.71062e^{-4}$	NA	NA
Benzo(k)fluoranthene	0.1	NA	NA	$1.72478e^{-2}$	$1.72478e^{-3}$
Benzo(a)pyrene	1.0	NA	NA	NA	NA
Indeno(1,2,3,d)pyrene	0.1	NA	NA	NA	NA
Dibenzo(a,h)anthracen	1.0	$9.48105\ e^{-2}$	$9.48105e^{-2}$	NA	NA
Benzo(g,h,i)perylene	0.01	NA	NA	NA	NA
TEQ			0.09744		$4.4456e^{-3}$

Since Benzo (a)pyrene (BaP) is the most extensively researched carcinogenic PAH, it is frequently chosen as the reference substance. The findings revealed that the total BaPeq (sum of 16 BaPeq) of each of the control sample was zero as there was no PAH found in the sample or the PAHs present in the samples are in undetected levels which reflects the little to absent industries in that area where the samples were

collected, reduced anthropogenic activities such as dispose of agricultural wastes or residual burning in that area and reduced use of automobiles in that area as the road is not tarred. The total BaPeq (sum of 16 BaPeq) of tested PAHs in the cassava sample was 0.09744 mg/kg and that of cocoyam was $4.4456e^{-3}$ mg/kg. The result demonstrates that Dibenzo(a,h)anthracene is the most significant contribution to the risk of carcinogenicity according to the TEQ in the cassava sample. The toxic equivalents (TEQ) value, measuring at $9.744e^{-2}$ mg/kg, significantly surpassed the screening values (SV) of $3.913e^{-8}$ for adults and $2.2831e^{-7}$ for children. This suggests a heightened likelihood of carcinogenic effects from the total PAHs when consuming foods derived from the sample, such as cassava flour which is employed nowadays in bakery industries (Dokubo and Igwe, 2019).

The [B(a)P] equivalent concentrations B(a)Peq ranged between 0.0449-1.72 µg/kg. The B(a)Pteq results suggest that consumption of cocoyam at the rate of 0.5kg/day in adults and 0.25kg/day in children poses potential adverse health effects such as cancer, mutations and birth defects in terms of B(a)P to humans. The TEQ value obtained $4.4456e^{-3}$ was greater than the screening values obtained in both adults and children thus indicating that the assessed PAHs in cocoyam were of potential carcinogenic risk to both adults and

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XI Issue VII July 2024

children since they are known to cause cancer, mutations and birth defects in humans and, therefore of potential health concern to the consuming public.

5) As per USEPA guidelines, an ILCR of 10-6 or less indicates a risk level that is considered acceptable or negligible, whereas an ILCR of 10-4 or more indicates a threat that needs immediate action. Furthermore, an ILCR ranging from less than 10−6 to less than 10−4 indicates a possible risk to human health. Results indicate that the calculated ILCR for the cassava sample is 7.4095e-3 for children and 5.081e-3 for adults, both of which are significantly greater than 10-4. This indicates that the sample from the Eke Awka market needs high-priority attention to enhance the consumption of meals made from it as shown in Table 5.

Table V: shows the ILCR of the PAHs in both samples for adults and children

ILCR		
Cassava sample	**Adults = $5.081e^{-3}$**	**Children = $7.4095e^{-3}$**
Cocoyam sample	**Adults = $2.32e^{-4}$**	**Children = $4.841e^{-6}$**

According to USEPA standards, An ILCR of $10^{-6}$and below is described as the level of risk that is deemed acceptable or insignificant, $10^{-4}$and above as a danger that requires high-priority attention, and an ILCR from $< 10^{-6}$to $<10^{-4}$ reflects a potential risk to human health. From the results, the value of the calculated ILCR for the cassava sample is **$5.081e^{-3}$**for adults and **$7.4095e^{-3}$**for children which are significantly higher than 10^{-4} which shows that the sample from the Eke Awka market requires high-priority attention as increased consumption of foods made from the sample e.g. bread that has a high accumulation of PAHs will predispose individuals in that area to the development of cancer in the future unlike what is seen in the case of cocoyam where the values of ILCR for both adults and children were within acceptable range posing negligible or no carcinogenic risk. This is in line with the work of Udowelle *et al*(2017).

CONCLUSION

This study suggests that the consumption of processed cassava and cocoyam flours from the Eke-Awka market, Anambra State, possesses a high risk of exposure to PAHs when compared to unprocessed soil free of anthropogenic activity. However, exposure to PAHs from cocoyam consumption has fewer health effects in the long term and an absence of risk in individuals.

The incremental life cancer risks of 16 PAH in the cassava sample for adults and children require high-priority attention as there is potential carcinogenic risk due to high accumulation of carcinogenic PAHs in foodstuffs in that area, even though the values of HI and HQ are indicating the absence of non-carcinogenic adverse health risks associated with the levels of PAHs found in the sample, but for cocoyam sample the value of the ILCR shows no carcinogenic threat. The result from this study should elicit awareness and constitute a baseline line information for further studies. This will lead to appropriate efforts to limit sources of contamination and thereby protect the ecosystem. However, the Anambra State Government should endeavor to pass legislation on the sale and processing of cassava and cocoyam flours in open markets across the state to ameliorate the health hazards that may result in its consumption.

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