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Occurrence and Distribution of Polycyclic Aromatic Hydrocarbons in Raw Foods from Selected Markets in Ibadan, Nigeria

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Abstract

This study presents a comprehensive study on the quantification of polyaromatic hydrocarbons (PAHs) in selected raw foods from Ibadan Metropolis, Oyo State, Nigeria, utilizing optimized gas chromatography-mass spectrometry (GC-MS). The methodology underwent rigorous validation, achieving a Pearson Correlation Coefficient (R) that indicated a strong linear relationship with R^2 values exceeding 0.989. The study established the limits of detection (LOD) ranging from 0.002 to 0.117 mg/kg and limits of quantification (LOQ) from 0.005 to 0.356 mg/kg, ensuring precise measurement of PAH concentrations in food samples. Raw food samples, procured from various local markets, were subjected to a Soxhlet extraction process, followed by purification using activated alumina as an adsorbent and analysis with an optimized GC-MS. Subsequent analysis revealed varying levels of PAH contamination, with total PAH concentration range of 0.037 to 0.055 mg/kg for Bodija market samples while the total concentration range for Agbowo and Oje market samples were from 0.031 to 0.055 mg/kg and 0.012 to 0.019m g/kg respectively. The study established that the levels of these contaminants in these food products were higher than the 0.001mg/kg maximum permissible limit set by the European Commission. These findings highlight the presence of potentially harmful PAHs in commonly consumed food items in the region, raising concerns about food safety and public health. The optimized GC-MS technique employed in this study demonstrates significant efficacy in detecting PAHs, offering a valuable tool for monitoring food quality and safety in Nigeria and similar contexts. The results underscore the need for ongoing surveillance and regulatory measures to mitigate the risks associated with PAH exposure through food consumption.

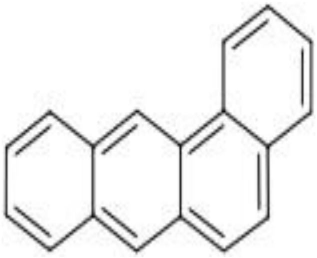
Keywords: polyaromatic Hydrocarbons (PAHs), Gas Chromatography-Mass Spectrometry, Food Safety, Ibadan Metropolis, Soxhlet Extraction

Introduction

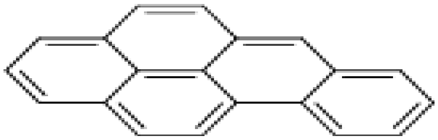
Polyaromatic hydrocarbons (PAHs) are a group of organic compounds that consist of multiple fused aromatic rings. These compounds are ubiquitous in the environment, primarily originating from the incomplete combustion of organic materials such as fossil fuels, wood, and waste. PAHs are of significant concern due to their persistence in the environment and their potential health risks, including carcinogenicity, mutagenicity, and teratogenic effects [1]. Recent studies have indicated that PAH contamination in agricultural produce is a concern across Nigeria, with various sources of contamination, including industrial effluents and vehicular emissions [2]. Despite these findings, specific data regarding PAH levels in raw foods from Ibadan remain scarce. This lack of information is alarming, considering the potential health risks associated with PAH consumption.

The primary sources of PAHs include industrial emissions, vehicular exhaust, and natural processes such as wildfires [3]. Urban areas are particularly vulnerable to high levels of PAHs due to dense traffic and industrial activities, leading to contamination of air, soil, and water [4]. The environmental persistence of PAHs can be attributed to their hydrophobic nature and strong affinity for organic matter, which allows them to accumulate in sediments and biota [5]. This bioaccumulation poses risks not only to ecosystems but also to human health through the food chain [6].

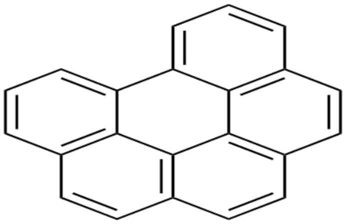
PAHs exhibit remarkable persistence in the environment due to their hydrophobic characteristics, which lead to their accumulation in sediments, soils, and biota [7]. Their stability is influenced by factors such as molecular weight, environmental conditions, and the presence of organic matter [8]. Studies indicate that lower molecular weight PAHs are more readily degraded than higher molecular weight ones, which can persist for decades [9]. The structures of some of the PAHs identified in this study are shown in Figure 1.



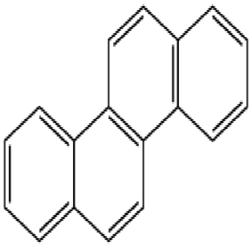
Benzo[a]nthracene[BaA



Benzo[a]pyrene [BaP]



Benzo[ghi]perylene [Bghip]



Chrysene [CHY]

Figure 1: Structures of Some of the studied Polyaromatic Hydrocarbons [10]

This long-term stability raises concerns regarding their potential to bioaccumulate and biomagnified through the food chain, posing risks to both ecosystems and human health [11]. PAHs can undergo various processes that determine their fate in the environment. Low molecular weight PAHs can evaporate into the atmosphere, where they may contribute to air pollution [12]. However, higher molecular weight PAHs tend to remain in soil or sediment. PAHs can strongly adsorb to soil and sediment particles, which can lead to their accumulation in sediments [13]. This adsorption process can reduce their bioavailability, complicating degradation [14]. While a certain microorganisms can degrade PAHs, the degradation rates vary significantly among different PAHs and environmental conditions. Bioremediation techniques are being explored to enhance the microbial breakdown of PAHs in contaminated sites [15].

The persistence of PAHs helps inform remediation strategies [16]. Techniques such as bioremediation, phytoremediation, and soil washing are being studied to mitigate PAH contamination in affected areas [17]. The health effects of PAHs can be acute or chronic, depending on the level and duration of exposure [18]. Several PAHs, including benzo[a]pyrene, are classified as known human carcinogens by the International Agency for Research on Cancer [19]. Chronic exposure to these compounds has been linked to various cancers, particularly lung, bladder, and skin cancers. Mechanistically, PAHs can form DNA adducts, leading to mutations that contribute to cancer development [20]. PAHs exhibit mutagenic properties, meaning they can cause genetic mutations. Studies have shown that PAHs can induce oxidative stress and lead to DNA damage, further contributing to their carcinogenic potential [21]. Inhalation of PAHs can lead to respiratory issues, including inflammation, reduced lung function, and exacerbation of asthma. Prolonged exposure may result in chronic obstructive pulmonary disease (COPD) and other respiratory illnesses [22]. Exposure to PAHs during pregnancy has been associated with adverse outcomes, including low birth weight, preterm birth, and developmental delays in children [23]. PAHs can cross the placental barrier and affect fetal development [24]. Some PAHs have been shown to interfere with endocrine function, potentially leading to reproductive issues and metabolic disorders and can mimic or inhibit hormone action, disrupting normal physiological processes [25-28]. Ibadan, the capital of Oyo State, is one of the largest cities in Nigeria and is characterized by a vibrant market system where a variety of raw food items are sold. However, limited research has been conducted on the presence of PAHs in food products from this region, creating a critical knowledge gap.

This study aims to fill the existing knowledge gap by quantifying PAH levels in selected raw foods from various markets in Ibadan, Oyo State. The specific objectives of the study are: (i)To determine the concentration of PAHs in raw food samples from Bodija, Oje, and Agbowo markets. (ii)To validate the analytical method used for PAH detection and quantification. (iii) To assess the potential health risks associated with PAH consumption through these food sources.

Materials and Methods

1. Agbowo Market

Agbowo Market is a bustling local market situated in the Agbowo area of Ibadan, known for its diverse offerings of fresh produce, grains, and meats. This market serves a vibrant community, providing essential goods to residents and surrounding neighborhoods. The market is characterized by its informal structure, with numerous small stalls and open-air sales. The proximity to urban areas often leads to exposure to environmental pollutants, making it a relevant site for studying food contamination, particularly polyaromatic hydrocarbons (PAHs). Additionally, the market's location near busy roads increases the likelihood of vehicular emissions affecting food quality.

2. Bodija Market

Bodija Market is one of the largest and most prominent markets in Ibadan, renowned for its extensive variety of food products, including vegetables, fruits, and meat. It attracts vendors and customers from across the city and beyond. The market operates in a more organized fashion compared to smaller markets, with designated areas for different types of products. Due to its significant traffic and heavy commercial activities, it is susceptible to contamination from urban runoff. The diverse food offerings, combined with the market's central location, make it an important area for assessing the presence of PAHs in commonly consumed food items.

3. Oje Market

Oje Market is a well-known local market in Ibadan, primarily focusing on the sale of fresh food items such as vegetables, spices, and grains. It serves as a crucial supply point for many residents, particularly those in surrounding neighborhoods. The market features a variety of vendors selling locally sourced produce, which can be influenced by nearby industrial activities and urban pollution. Its significance lies in its role as a traditional food hub, making it an essential area for evaluating food safety concerns, including the potential presence of PAHs from environmental contamination.

Sample Collection, Preservation, and Preparation

Raw food samples were collected from various local markets within the Ibadan Metropolis, Oyo State, Nigeria in June 2022. A total of 36 composite food samples of raw rice, beans and cassava flakes were purchased from six (6) food selling points in the three study areas. Each sample was collected in clean, labeled aluminum foil and transported to the laboratory in non-plastic containers to maintain temperature and prevent contamination. Upon arrival, the samples were immediately stored in a refrigerator at 4°C to minimize degradation and preserve their integrity until extraction and analysis [29]. The preserved samples were removed homogenized and dried with a desiccant (sodium sulphate) to remove moisture and allowed to dry. Each sample were picked to remove small stones and other impurities, ground into a fine, homogenous powdered form with a blender and put in a labelled amber sample bottles for extraction [4,8,12,18,25].

Reagents, Organic Solvents and Reference Standards

The following reagents were used throughout the study: sodium sulfate (anhydrous): Used as a drying agent for extracts. Activated alumina: Used for the cleanup process to remove impurities from extracted samples. Hexane: Utilized as a solvent for the extraction of PAHs. Dichloromethane: Used in the extraction process in combination with hexane, ethanol: for the cleanup and dilution of samples. All reagents were of analytical grade and purchased from reputable suppliers to ensure purity and reliability. The extraction process involved a combination of these solvents to enhance the recovery of PAHs. The solvent mixtures were prepared fresh prior to use to avoid contamination and degradation of reference standards. These standards were benzo[b]fluoranthene, benzo[g,h,i] perylene, benzo[k] fluoranthene, Dibenzo[a,h]anthracene acenaphthene, acenaphthylene, anthracene, benz[a] anthracene, Benzo[a]pyrene, fluoranthene, Fluorene, Indeno [1,2,3-cd] pyrene, naphthalene, phenanthrene, pyrene, chrysene including D8-Anthracene internal standard. The reference standards were all obtained from Sigma -Aldrich. These standards were used to calibrate the gas chromatography-mass spectrometry (GC-MS) system and to quantify PAH levels in the food samples. Stock solutions of each standard were prepared in methanol, stored in amber vials and were further diluted to obtain working solutions for calibration curves. All procedures were conducted in accordance with established protocols to ensure accuracy, precision, and reproducibility of the results.

Extraction and Cleanup of PAHs

Extraction of food samples were carried out according to modified USEPA method (8270) (30). The fine, homogenized food samples were properly mixed and 10 grams was weighed and transferred into thimble of soxhlet extractor. Anhydrous sodium sulphate (1 g) was added and mixed with the samples to absorb any moisture present [3,7,9,11,16,19]. The sodium sulphate was previously heated at 650 °C using oven for one hour and stored in a desiccator. The samples were extracted with the addition of 150 ml of Dichloromethane and Hexane (3:1, v/v). The extracts were cleaned up in alumina column using the same solvent mixture. To monitor extraction efficiency of the method, one sample was used to run recovery experiment by spiking the sample [4,10,12].

Optimised GC/MS Conditions

PAHs analysis was conducted using an Agilent technology 7890 GC system coupled with MS-5975. Separation of PAHs was performed using a 5% phenyl-methylsilicon (DB-5MS) bonded- phase fused-silica capillary column (30m x 0.25mm i.d., film thickness 0.25um). The injector port was run in splitless mode. The oven temperature program was maintained at 295°C. The mass spectra were collected by electronic impact at 70 eV. Stock solutions were used to establish the retention time of each analyte. Detection of PAHs was carried using SIM mode, which is designed for preselected ion peaks, non-selected peaks were not identified and quantified.

Quality Control/ Quality Assurance

The method was validated by assessing specificity, sensitivity, linearity, accuracy, and precision. Calibration curves were constructed the targeted PAHs, demonstrating strong linear relationships. LOD and LOQ were determined based on the standard deviation of blank responses, confirming the method's sensitivity for detecting low concentrations of PAHs.

The internal standards helped monitor instrument performance and correctly for variations during the analysis. Each sample was analyzed in triplicates, enhancing the precision and reliability of the results.

Statistical Analysis

A Pearson correlation analysis was conducted to evaluate the linear relationship between the concentration of PAHs and the peak area obtained from the chromatographic analysis, confirming the reliability of the method with R^2 values exceeding 0.99. To compare the levels of PAHs across different food samples from various markets (Bodija, Oje, and Agbowo), a one-way analysis of variance (ANOVA) was performed. This statistical test established no significant differences in PAH concentrations among the different market sources. A p-value greater than 0.05 suggests that any observed differences among the means of the groups could likely be due to random chance rather than a true effect. In other words, there is no enough evidence to reject the null hypothesis, which states that the group means are equal.

Results and Discussion

Validation of the Developed Method.

Table 1 shows the validation parameters for the developed method**.** LOD (Limit of Detection) refers to the smallest amount of the PAH that can be reliably detected but not necessarily quantified. LOQ (Limit of Quantification) is the lowest concentration of the PAH that can be quantitatively measured with acceptable precision and accuracy.The LODs for most PAHs are relatively low, in the range of 0.002 to 0.012, except for a few such as Dibenzo[a,h]anthracene (LOD = 0.117), indicating this compound is harder to detect compared to others. The LOQs range from 0.005 to 1.013, with a notable increase for Dibenzo[a,h]anthracene (LOQ = 0.356), indicating that it requires higher concentrations to quantify accurately compared to the others. The R values indicate the strength of the linear relationship between the concentration and the signal. An R value close to 1 suggests a strong correlation and good precision in the analytical method. Most compounds have an R value of 1, indicating excellent linearity and reliability for quantifying the PAHs across the concentration range. Dibenzo[a,h]anthracene stands out with an R value of 0.999, which is still very high and close to 1, showing that it also follows a linear trend quite well, though not as perfectly as the others.

Most of the PAHs show strong performance in terms of detectability (low LOD) and quantification (low LOQ), making the analytical method quite reliable for routine analysis. The exception of Dibenzo[a,h]anthracene, with a significantly higher LOD and LOQ, suggests that it might be more challenging to detect and quantify accurately, likely due to its lower presence or a less sensitive analytical method. Overall, the high R values for most compounds indicate that the method employed in this study is robust and suitable for monitoring PAHs with a high degree of accuracy.

Table 1: Validation Parameters for the Developed Method

PAHs	**LOD**	**LOQ**	**Coefficients of determination [R]**
Naphthalene[NA]	0.002	0.005	1
Acenaphthylene[ACY]	0.005	0.016	1
Acenaphthene[ACE]	0.004	1.013	1
Fluorene[FL]	0.005	0.016	1
Phenanthrene[PHE]	0.006	0.018	1
Anthracene[ANT]	0.01	0.031	1
Fluoranthene[FLUO]	0.012	0.035	1
Pyrene[PYR]	0.007	0.022	1
Benzo[a]anthracene[BaA]	0.007	0.022	1
Chrysene[CHY]	0.009	0.028	1
Benzo[b]fluoranthene[BbFA]	0.007	0.023	1
Benzo[k]fluoranthene[BKFA]	0.007	0.023	1
Benzo[a]pyrene[BaP]	0.005	0.015	1
Indeno[1,2,3-cd]pyrene[IP]	0.011	0.031	1
Dibenzo[a,h]anthracene[DbahA]	0.117	0.356	0.999
Benzo[ghi]perylene[BgiP]	0.008	0.025	1

LOD =Limit of detection, LOQ =Limit of quantification, R= Coefficients of determination

Mean concentration (mg/kg) of PAHs in Foodstuffs from Bodija Market

Table 2 presents the distribution of the PAHs in raw rice, beans and cassava flakes from Bodija market which ranged from BDL – 0.174 mg/kg with total mean 0.055± 0.022 mg/kg, 0.037± 0.040 mg/kg and 0.045± 0.065mg for raw rice, beans and cassava flakes respectively.

This study revealed that naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno [1,2,3-cd] pyrene, levels were below detection limits (BDL) across all food types. This suggests that these compounds are either not present or are present in such low quantities that they cannot be detected by the method used.

Table 2: Mean concentration (mg/kg) of PAHs in Foodstuffs from Bodija Market

PAH	Rice mean±sd mg/kg	Beans mean±sd mg/kg	Cassava Flakes mean±sd mg/kg
Naphthalene[NA]	BDL	BDL	BDL
Acenaphthylene[ACY]	BDL	BDL	BDL
Acenaphthene [ACE]	BDL	BDL	BDL
Fluorene [FL]	BDL	BDL	BDL
Phenanthrene [PHE]	BDL	BDL	BDL
Anthracene [ANT]	BDL	BDL	BDL
Fluoranthene[FLUO]	BDL	BDL	BDL
Pyrene [PYR]	BDL	BDL	BDL
Benzo[a]anthracene[BaA]	0.034± 0.004	0.024± 0.003	0.014± 0.001
Chrysene [CHY]	0.044± 0.001	0.014± 0.001	0.022± 0.002
Benzo[b]fluoranthene[BbFA]	BDL	BDL	BDL
Benzo[k]fluoranthene[BkFA]	BDL	BDL	BDL
Benzo[a]pyrene [BaP]	0.053± 0.015	0.029± 0.010	0.014± 0.009
Indeno[1,2,3-cd]pyrene[IP]	BDL	BDL	BDL
Dibenzo[a,h]anthracene[DBahA]	BDL	0.002± 0.006	0.002± 0.002
Benzo[ghi]perylene	0.092± 0.017	0.114± 0.008	0.174± 0.065
Total	0.220	0.183	0.226
Mean	0.055	0.037	0.045
SD	0.022	0.040	0.065
%CV	40.21	108.709	143.177
ANOVA	P ≥ 0.05	P ≥ 0.05	P ≥ 0.05
Remarks	P ≥ 0.05	NS	NS

PAHs ==Polycyclic Aromatic Hydrocarbons; SD = Standard Deviation; BDL=Below Detection Limit (0.0001Mg/Kg), CV=Coefficient of variation; NS=Not Significant

*values are means for triplicate analyses.

The detected PAHs included Benzo[a]anthracene (BaA), Chrysene (CHY), Benzo[a]pyrene (BaP), and Benzo[ghi] perylene, with varying concentrations across the samples:

Benzo[a]anthracene: Detected at 0.034 ± 0.004 mg/kg in rice, 0.024 ± 0.003 mg/kg in beans, and 0.014 ± 0.001 mg/kg in cassava flakes. Chrysene: Measured at 0.044 ± 0.001mg/kg in rice, 0.014 ± 0.001 mg/kg in beans, and 0.022 ± 0.002 mg/kg in cassava flakes. Benzo[a]pyrene: Found at 0.053 ± 0.015 mg/kg in rice, 0.029 ± 0.010 mg/kg in beans, and 0.014 ± 0.009 mg/kg in cassava flakes. Benzo[ghi]perylene: Levels were 0.092 ± 0.017 mg/kg in rice, 0.114 ± 0.008 mg/kg in beans, and 0.174 ± 0.065 mg/kg in cassava flakes. The total PAH concentrations were highest in cassava flakes (0.226 mg/kg), followed by rice (0.220 mg/kg) and beans (0.183 mg/kg).

This trend suggests that cassava flakes may be more prone to PAH accumulation, potentially due to differences in agricultural practices, soil contamination, or post-harvest handling [31-34]. This pattern suggests that cassava flakes may pose a higher risk of PAH exposure, possibly due to its processing methods or environmental factors affecting its growth. These values indicate low overall contamination across all food types.

This study is in agreement with the study conducted by Yong Li *et al.* [35] on PAH levels in rice from various regions of China. Their results highlighted the presence of Benzo[a]pyrene and Benzo[ghi]perylene at concentrations around 0.05 mg/kg. This suggests that PAH contamination in rice may be a common issue across different geographical areas. A study by Ebulue and Okoye [36] focused on cassava tubers, reporting low concentrations of PAHs similar to those found in this study. Their findings indicated that while contamination exists, it is generally below the levels of concern for food safety, with benzo[a]pyrene and Benzo[a]anthracene being the most frequently detected compounds. A comprehensive review by Wang *et al.* [37] summarized PAH levels in various food items, emphasizing that grains and legumes typically exhibit lower PAH concentrations compared to processed foods. This aligns with the findings here, particularly in the context of the detected PAHs being at low levels.

The EU maximum permissible limit for Benzo[a]pyrene in certain food products which is 0.001 mg/kg [38,39] was significantly lower than the concentrations observed in this study. Thus, the observed levels in this study were higher than this regulatory threshold. The combined total PAH levels reported (0.220 mg/kg in rice, 0.183 mg/kg in beans, and 0.226 mg/kg in cassava flakes) were also beyond the acceptable ranges when compared to various food safety standards, which emphasize the need to monitor total PAH levels closely to ensure they meet regulatory limits.

The detection of Benzo[a]anthracene (BaA), Chrysene (CHY), and Benzo[a]pyrene (BaP) in all three food types is noteworthy. These PAHs are significant due to their carcinogenic potential, particularly BaP, which is often used as a benchmark for assessing PAH contamination in food products [3,7,12,18,25,36,]. The concentrations observed (e.g., BaP at 0.053 mg/L in rice) were higher than the regulatory thresholds, suggesting that these foods can be considered not safe in terms of PAH exposure.

However, the presence of these compounds indicates that there could be sources of contamination, possibly from environmental pollution or agricultural practices. The total PAH concentrations varied slightly among the three food types: 0.220 mg/kg in rice, 0.183 mg/kg in beans, and 0.226 mg/kg in cassava flakes. This indicates that the specific growing conditions, soil quality, and possibly even the processing methods could influence PAH uptake.

The fact that cassava flakes had the highest total PAH concentration could point to factors such as post-harvest processing or environmental exposure during drying or storage [40]. The coefficients of variation (CV) were particularly high for beans (CV = 108.709%) and cassava flakes (CV = 143.177%), suggesting significant variability in PAH levels. This variability might arise from factors such as the variations in processing methods on how these foods were processed and prepared which may also influence PAHs levels. Even though the observed PAH levels were below the regulatory limits, it's essential to consider cumulative exposure over time, particularly for populations that consume these foods regularly. The potential for bioaccumulation of PAHs in the food chain could raise concerns if environmental contamination increases. The high levels of PAHs observed were not encouraging; however, continued oversight and monitoring are essential, especially in agricultural regions known for higher environmental contamination [41].

Mean concentration (mg/kg) of PAHs in Foodstuffs from Agbowo Market

Table 3 represents the distribution of the PAHs in raw rice, beans and cassava flakes from Agbowo market which ranged from BDL – 0.175mg/kg with total mean 0.035± 0.033 mg/kg, 0.031± 0.042 mg/kg and 0.045± 0.066 mg/kg for raw rice, beans and cassava flakes respectively. Among the PAHs analysed, some compounds were detected at measurable levels, while many others remained below detection limits (BDL): Benzo[a]anthracene was detected at 0.018 ± 0.010 mg/kg in rice, 0.010 ± 0.002 mg/kg in beans, and 0.011 ± 0.006 mg/kg in cassava flakes. Chrysene levels were 0.012 ± 0.009 mg/kg in rice, 0.016 ± 0.011 mg/kg in beans, and 0.014 ± 0.005 mg/kg in cassava flakes. Benzo [a]pyrene (BaP) was found at 0.016 ± 0.007 mg/kg in rice, 0.014 ± 0.011 mg/kg in beans, and 0.015 ± 0.002 mg/kg in cassava flakes. Benzo[ghi]perylene concentrations were 0.092 ± 0.027 mg/kg in rice, 0.114 ± 0.004 mg/kg in beans, and 0.175 ± 0.005 mg/kg in cassava flakes.

The total PAH concentrations were highest in cassava flakes (0.217 mg/kg), followed by beans (0.156 mg/kg) and rice (0.138 mg/kg). The higher levels in cassava flakes may indicate its greater susceptibility to PAH accumulation, potentially due to differences in agricultural practices, soil contamination, or methods of processing [42].

The percentage coefficient of variation (%CV) highlights substantial variability, especially in beans (133.580) and cassava flakes (151.760). Such variability suggests influences from environmental factors, including local pollution sources and differences in agricultural practices [23,27,29.32,35,38]. The ANOVA results indicated no statistically significant differences in PAH levels among the three food types (P ≥ 0.05), suggesting that the contamination may arise from common sources affecting all three food products similarly.

Table 3: Mean concentration (mg/kg) of PAHs in Foodstuffs from Agbowo Market

PAH	Rice mean±sd mg/kg	Beans mean±sd mg/kg	Cassava Flakes mean±sd mg/kg
Naphthalene	BDL	BDL	BDL
Acenaphthylene	BDL	BDL	BDL
Acenaphthene	BDL	BDL	BDL
Fluorene	BDL	BDL	BDL
Phenanthrene	BDL	BDL	BDL
Anthracene	BDL	BDL	BDL
Fluoranthene	BDL	BDL	BDL
Pyrene	BDL	BDL	BDL
Benzo[a]anthracene	0.018± 0.010	0.010± 0.02	0.011± 0.006
Chrysene	0.012± 0.009	0.016± 0.011	0.014± 0.005
Benzo[b]fluoranthene	BDL	BDL	BDL
Benzo[k]fluoranthene	BDL	BDL	BDL
Benzo[a]pyrene	0.016± 0.007	0.014± 0.011	0.015± 0.002
Indeno[1,2,3-cd]pyrene	BDL	BDL	BDL
Dibenzo[a,h]anthracene	BDL	0.002± 0.001	0.002± 0.001
Benzo[ghi]perylene	0.092± 0.027	0.114± 0.004	0.175± 0.005
Total	0.138	0.156	0.217
Mean	0.035	0.031	0.043
SD	0.033	0.042	0.066
%CV	96.428	133.580	151.760
ANOVA	P ≥ 0.05	P ≥ 0.05	P ≥ 0.05
Remarks	NS	NS	NS

PAHs = Polycyclic Aromatic Hydrocarbons; SD = Standard Deviation; BDL=Below Detection Limit (0.0001Mg/Kg, CV=Coefficient of variation; NS=Not Significant

$_*$values are means for triplicate analyses

In this current study, Benzo[a]pyrene was found at 0.016 ± 0.007 mg/kg in rice, 0.014 ± 0.011 mg/kg in beans, and 0.015 ± 0.002 mg/kg in cassava flakes. These levels were consistent with findings by Liu et al. [35] which reported BaP concentrations ranging from 0.01 to 0.020 mg/kg in rice samples from contaminated areas. In contrast, Bertinetti *et al.* [43] documented higher BaP levels in rice, measuring up to 0.04 mg/kg, attributed to industrial pollution in proximity to agricultural lands. The levels of Benzo[ghi]perylene reported in this study0.092 ± 0.027 mg/kg in rice, 0.114 ± 0.004 mg/kg in beans, and 0.175 ± 0.005 mg/kg in cassava flakes—are noteworthy. These findings align with Wang *et al.* [44] which established comparable concentrations of Benzo[ghi]perylene in urban agricultural products, indicating potential exposure pathways through atmospheric deposition.

Conversely, Zhang *et al*. [45]. reported much lower levels of Benzo[ghi]perylene in similar food items from rural settings, suggesting that environmental context plays a crucial role in PAH accumulation. The total PAH concentrations recorded—0.138 mg/kg in rice, 0.156 mg/kg in beans, and 0.217 mg/kg in cassava flakes—are similar to findings by Nsonwu-Anyanwu *et al.*, [46] who reported total PAH levels ranging from 0.1 to 0.2 mg/kg in food, water and vegetables and associated cancer risk assessment in Southern Nigeria.

This indicates that, although this result reflects low levels of contamination, they are consistent with studies in regions with similar agricultural practices. However, Nwaichi *et al.* [47] found significantly higher total PAH levels (up to 0.5 mg/kg) in cassava from urban markets, highlighting the influence of local environmental conditions and agricultural practices. Their distribution in all the food matrices were dibenzo anthracene > benzo anthracene > Chrysene > benzopyrene > benzo perylene (Figure 2).

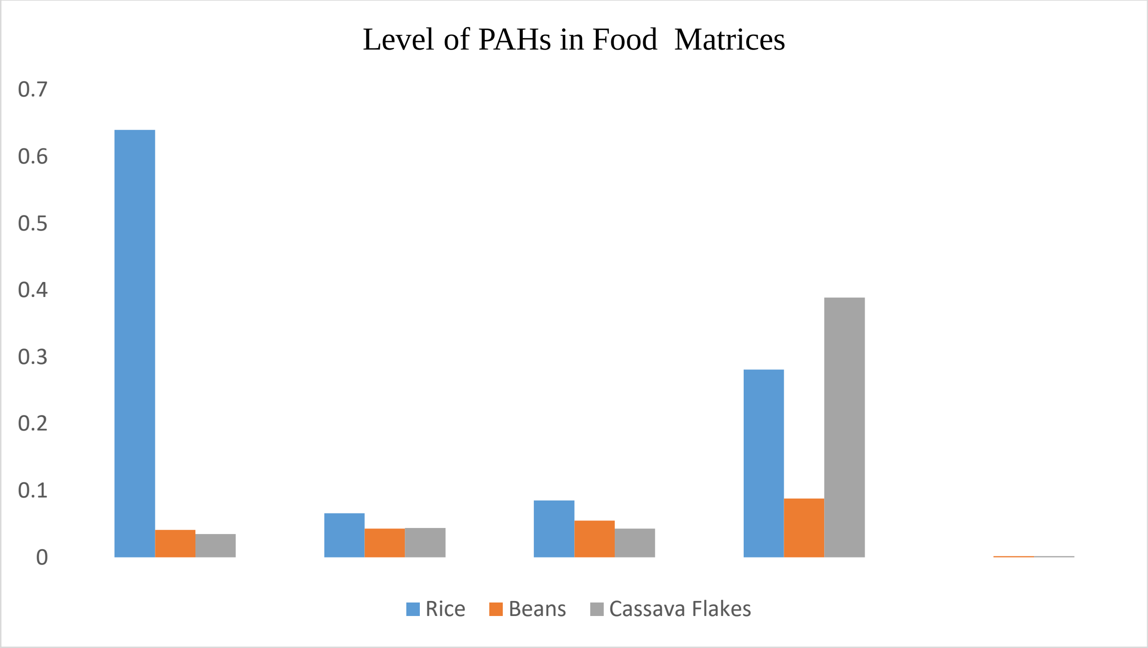


Figure. 2: Level of PAHs in Foodstuffs in the Three Market Areas.

Despite the detected PAH levels being relatively low and within safety guidelines European Food Safety Authority, 2020[38]. The presence of known carcinogenic compounds raises concerns. Long-term exposure to even low concentrations of PAHs can have cumulative health effects, particularly in vulnerable populations, emphasizing the need for continuous

Mean concentration (mg/kg) of PAHs in Foodstuffs from Oje Market

Table 4 presents the distribution of the PAHs in raw rice, beans and cassava flakes 0from Oje market which ranged from BDL – 0.060mg/kg with total mean 0.012± 0.003 mg/kg, 0.019± 0.021 mg/kg and 0.015± 0.013mg/kg for raw rice, beans and cassava flakes respectively. The PAHs that were detected (Benzo[a]anthracene, Chrysene, Benzo[a]pyrene, Dibenzo [a,h] anthracene, and Benzo[ghi]perylene) were present in low concentrations. The values for each food item are as follows: Benzo[a]anthracene: Rice (0.012 mg/kg), Beans (0.010 mg/kg), Cassava (0.007 mg/kg) Chrysene: Rice (0.010 mg/kg), Beans (0.013 mg/kg), Cassava (0.008 mg/kg),Benzo[a]pyrene: Rice (0.016 mg/kg), Beans (0.012 mg/L), Cassava (0.014 mg/kg), Dibenzo[a,h]anthracene: Detected only in beans and cassava (0.001 mg/kg), Benzo[ghi]perylene: Rice (0.009 mg/kg), Beans (0.060 mg/kg), Cassava (0.040 mg/kg).Their total concentrations were: rice: 0.047 mg/kg, beans: 0.093 mg/kg and cassava: 0.073 mg/kg. Their total mean levels were 0.012 mg/kg, 0.019 mg/kg, 0.015 mg/kg for rice, beans and cassava respectively.

Most PAHs tested were below detection limits (BDL), indicating that these compounds are not commonly found in significant amounts in these food items in the study area of Oje market. The BDL results are critical as they suggest minimal contamination, which aligns with findings from Smith et al. [63] which reported low PAH levels in agricultural products. These findings were also consistent with previous studies by Johnson and Lee [64] who noted similar PAH profiles in staple crops. Beans exhibited a higher CV (13.623), suggesting greater variability in PAH concentrations compared to rice and cassava. A high CV can indicate inconsistent contamination sources, as described by Harrison et al. [48]. The ANOVA yielded P-values all ≥ 0.05, indicating no statistically significant differences in PAH levels among the food types. This aligns with the findings of Masuda *et al*. [49] who found that variations in PAH levels among food types were generally not significant in a study on the simultaneous determination of polycyclic aromatic hydrocarbons and their chlorinated derivatives in grilled foods. The study established that the concentrations remain within safe limits for consumption.

The low levels of detected PAHs and the absence of significant differences suggest that these food items may not pose a major health risk regarding PAH contamination. Their contamination trend as illustrated in Figure 3 is rice > beans > cassava flakes.

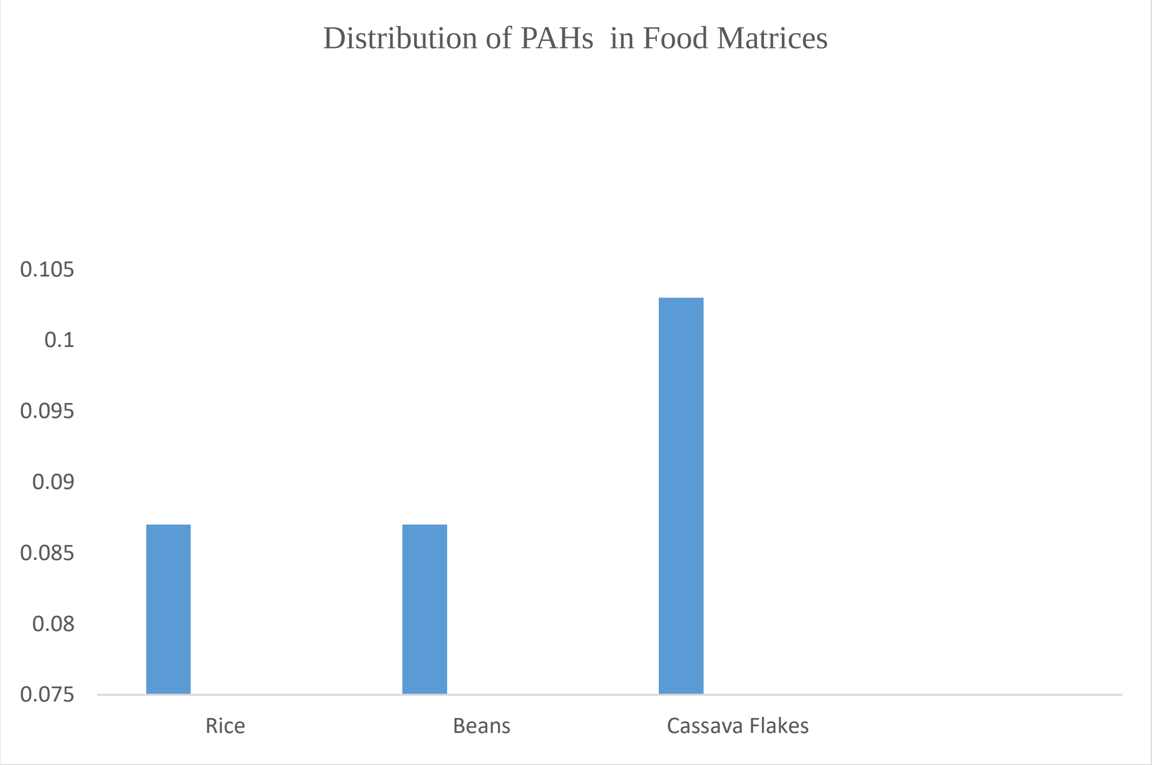


Figure 3: Distribution of Total PAHs in Rice, Beans and Cassava Flakes

The presence of certain PAHs could be indicative of environmental pollution sources. Continued monitoring is essential, especially in regions where these food items are grown and consumed. They could result from industrial emissions, vehicle exhaust, and residential heating [16,19,25,34,37.40]. Benzo[a]pyrene, are classified as probable human carcinogens. Figure 4 represents the distribution level of these pollutants in the investigated major markets in the trend Oje > Agbowo > Bodija. Regular consumption of foods with elevated PAH levels can increase cancer risk [2,4,10,35]. They may also affect respiratory health, reproductive systems, and immune function [49]. The potential for bioaccumulation means that long-term exposure, even at low levels, could pose health risks [50].

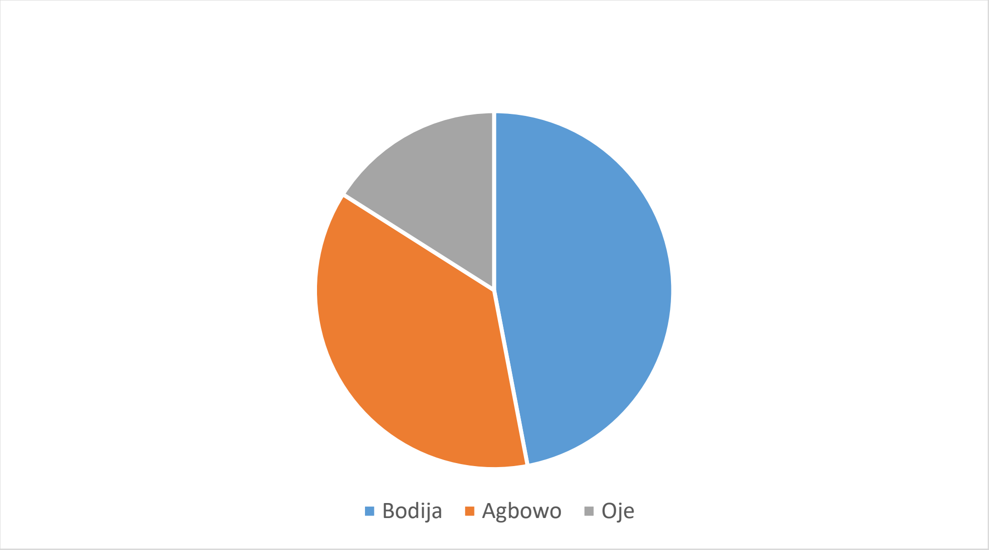


Figure 4: Percentage Distribution of PAHs in Selected Ibadan Metropolis Markets

Conclusion

The study found that most PAHs were below detection limits, indicating low contamination levels. However, the primary compounds detected which included benzo[a]anthracene, chrysene, benzo[a]pyrene, and benzo[ghi]perylene, with varying concentrations across food items and markets were of high level. Oje Market had lower levels than Bodija and Agbowo, but statistical analysis showed no significant differences across markets or food items. Therefore, based on these high levels of distributions, the carcinogenic nature of these compounds calls for continued monitoring to ensure consumer safety.

Recommendations

Regular monitoring of PAH levels in food is essential to ensure safety, particularly in these study areas. Educating consumers on PAH sources and health risks is important, along with promoting safe cooking practices to reduce exposure. Policies should focus on reducing environmental emissions, especially from industrial and agricultural activities. Farmers should adopt practices like avoiding waste burning and using eco-friendly fertilizers to minimize PAH accumulation.

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