

INCIDENCES OF POLYCYCLIC AROMATIC HYDROCARBONS IN ROASTED PLANTAINS OBTAINED WITHIN OSOGBO METROPOLIS, NIGERIA

ABIONA OLUSEYE OLADAPO¹, ADEGUNWA ABIODUN ODUNLAMI²,
AWOJIDE SHOLA HEZEKIAH², ANIFOWOSE ADEBANJO JACOB²,
TAYO ADENIYI SOLOMON²

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Abstract. *The present study was conducted to assess the carcinogenic and non-carcinogenic health risks of PAHs contamination in roasted plantain collected from three different locations within Osogbo metropolis, Nigeria. The PAHs were extracted using Soxhlet extraction technique with n-hexane and dichloromethane (3:1) as the extracting solvent. A column, packed with silica gel, was used for clean-up process and the levels of the targeted PAHs were determined by a gas chromatograph–flame ionization detector (GC-FID). The result revealed that the concentrations of total PAHs detected in the roasted samples at location A, B, C were 3.958 µg/kg, 3.654 µg/kg and 3.217 µg/kg. The HMW carcinogenic PAHs constitute about 32% of the total PAHs in the roasted plantain samples where benzo(a)pyrene, which is a marker for carcinogenicity, was found to be 9%. Comparing these results with the regulatory limits, all the analyzed roasted plantain samples were found below the maximum residual limit (MRL) of 5 µg/kg, but the calculated carcinogenic risk (CR) presented value greater than 1×10^{-4} , signifying health risk associated with the consumption of the roasted plantain. The major source of the PAHs using diagnostic ratios (Fla/Pyr and Ph/Ant) showed that the charcoal used in roasting is a major contributing factor to the high levels of PAHs detected in the roasted plantain samples.*

Keywords: *Roasting; Plantain; PAHs; health risk; GC-FID.*

1. INTRODUCTION

Plantain is one of the major sources of food in Nigeria which can be eaten in various forms. Plantain is eaten boiled, fried (*dodo*), roasted (*boli*), pounded alone or with yam or cassava flakes or made to flour for various delicacies and also for baby foods [1]. PAHs were ranked to be the ninth most threatening persistent organic pollutants (POPs) to human health in 2001 due to their carcinogenic and mutagenic properties. Thermal treatment of raw food materials has been rated to be the major exposure route to consumption of PAHs in food [2].

The presence of PAHs in food is usually a consequence of PAHs in the environment or their formation during cooking/manufacturing processes [3]. Electric plate grilling or frying would generate PAHs in cooked meat and fish, especially throughout the first cooking

¹ Osun State University, Department of Food Science. & Technology, Osogbo, Osun State, Nigeria. Email: oluseye.abiona@uniosun.edu.ng

² Osun State University, Department of Pure & Applied Chemistry, Osogbo, Osun State, Nigeria. Emails: abiiodun.adegunwa@uniosun.edu.ng; shola.awojide@uniosun.edu.ng; chemistbanjo@gmail.com; adeniyi.tayo@uniosun.edu.ng.

method which causes a rise in the formation of carcinogenic PAHs because of direct contact of foods with the heat source [4].

The PAHs are also deposited from smoke produced through incomplete combustion of different thermal agents. There has been considerable evidence which indicated that food stuffs processed by frying, boiling, barbecuing, roasting among others, produce traces of compounds like PAHs. High PAH concentrations have been reported in charcoal grilled/barbecued meat grilled under prolonged and severe conditions. Several PAHs such as benzo(a)pyrene are carcinogenic and mutagenic as well [5]. It can be concluded that PAHs have mutagenic or carcinogenic potential and they are widely believed to make a substantial contribution to the overall burden of cancer in humans [6-9].

The method of preparation of roasted plantain involves direct exposure of fresh plantain to charcoal heat on a grid /wire mesh. The presence of PAHs in roasted plantain poses risk to the health of people who depends on them as source of staple food. Smoke production which grilled the plantain is based on a process of incomplete combustion. When charcoal is completely combusted, only carbon dioxide, water and ash are produced but incomplete combustion via thermal pyrolysis produces polycyclic aromatic hydrocarbon (PAH) compounds [10].

The present study was undertaken to examine the concentration and risk assessment of polycyclic aromatic hydrocarbons in roasted plantain obtained from major selling points within Osogbo metropolitan, Nigeria.

2. MATERIALS AND METHODS

2.1. MATERIALS

Samples of roasted plantain used for the study were collected randomly from selected sales spots in Osogbo metropolis, Nigeria. Osogbo is a fast-growing city within the tropic rainforest zone in Nigeria and has a total land area of 47 km² with an estimated population of 156,694 as at 2006 census [11]. It is located on latitude 7° 77'2" N and longitude 4° 56'36" E with an elevation of 336 m above sea level. The samples were collected from three sampling locations directly from the vendors using polyethylene bag. The samples were dried in a hot oven at temperature range of 40-60°C to remove free moisture. They were then preserved in the desiccator and stored in the dark until time of analysis.

2.2. METHODS

2.2.1. Extraction and sample preparation

Dried roasted plantain samples were homogenized in a mortar with about 10 g of Na₂SO₄ until a uniform size was obtained. The homogenized sample (10 g) was extracted with redistilled *n*-hexane and dichloromethane (3:1) using Soxhlet extraction techniques according to ASTM D3328 and ASTM3415 method with slight modification. The beaker and its content were placed in the sonicator to extract the hydrocarbons for about 2 h. The organic layer was filtered into the 250 mL capacity borosilicate beaker. The solvent mixture was removed from the extract by using a Fischer brand rotary evaporator [12].

2.2.2. PAH separation

The concentrated oil was separated into the aliphatic profiles and polycyclic aromatic hydrocarbons profiles by packing the glass column with activated alumina. 10 mL of the treated alumina was packed into the column and cleaned properly with redistilled hexane. The extract was poured onto the alumina and was allowed to run down with the aid of the redistilled hexane to remove the aliphatic profiles into a pre-cleaned 20 mL capacity glass container. The aromatic fraction was recovered using a mixture of hexane and dichloromethane in 3:1 ratio to finally remove the most polar PAHs through elution with the dichloromethane into the pre-cleaned borosilicate beaker. The mixture was concentrated to 1.0 mL by stream of the nitrogen gas before the gas chromatography analysis.

2.2.3. Stock solutions

Stock solutions was prepared from standard samples of PAHs in *n*-hexane and stored in volumetric flask (with glass stopper) at 4 °C and was then wrapped with aluminum foil to avoid possible light degradation. Working standard solutions were prepared from the stock solution.

2.2.4. Chromatographic method

The GC-FID system consists of a Hewlett Packard Model 5890 gas chromatograph equipped with a flame ionization detector (GC-FID) and a data processor. The gas chromatographic column used was HP-1932530, a non-polar, fused-silica capillary column (30 m length × 25 µm inner diameter × 0.25 µm film thickness). The carrier gas used was nitrogen gas at a flow rate of 1 mL/min (pressure of 30 psi). The injector and detector temperature were set at 250°C and 320 °C respectively. The column temperature was programmed as follow; hold at 60°C for 5min; a ramp to 260°C at 15°C/min for 14 min followed by 3mins hold time; and a final ramp to 320°C at 10°C/min with a 4 min hold time. Verification of peaks was carried out based on retention times compared to those of external PAHs.

2.2.5. Human Health Risk Assessment

The route of PAHs pollutants in the analyzed roasted plantain to human body is majorly through direct ingestion in which the health risk assessment can be calculated by equations (2), (3) and (4) derived from USEPA [13].

Carcinogenic risk (CR) was calculated from the equation (3):

$$EDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (2)$$

$$CR = EDI \times SF \quad (3)$$

where EDI - estimated daily intake (ng µL⁻¹day⁻¹); C - chemical concentration in the beverages (ng µL⁻¹); IR - beverage ingestion rate (0.6 L day⁻¹); EF - exposure frequency (365 days year⁻¹), ED - exposure duration (year) (for children: ED = 6; for adults: ED = 70); BW = body weight (for children: BW = 14 kg; for adults: BW = 70 kg); AT = average lifespan (for children: AT = 2190 days; for adults: AT = 25550 days); SF = slope factor (kg day⁻¹ mg⁻¹).

For the estimation of the non-carcinogenic risk, hazard quotient (HQ) was calculated using the equation (4):

$$HQ = \frac{EDI}{RfD} \quad (4)$$

where RfD ($\text{mg kg}^{-1} \text{ day}^{-1}$) is the reference dose of the contaminant via oral exposure route. The values of SF and RfD for OCPs are obtained from the USEPA Integrated Risk Information System [13].

2.2.6. Statistical analysis

The PAH analysis was carried out for each sample in triplicate ($n = 3$). The obtained results were statistically analyzed using SPSS (version 20.0) windows software and the result was expressed as mean and standard deviation (SD). The significant statistical level was set at $p < 0.05$. The result was subjected to one way ANOVA and the means were compared using Duncan's multiple range test.

3. RESULTS AND DISCUSSION

3.1. CONCENTRATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

Table 1 shows the results of PAHs concentrations of the analyzed roasted plantain collected from different locations within Oshogbo metropolis. All the 16 targeted PAHs were detected in reasonably quantity in the roasted plantain. The result of the roasted plantain analyzed revealed that the sum of the average PAH concentrations of the roasted plantain of the three investigated locations were within 2-5 $\mu\text{g}/\text{kg}$ set by European commission as tolerable limit: A ($3.958 \pm 0.005 \mu\text{g}/\text{kg}$), B ($3.654 \pm 0.002 \mu\text{g}/\text{kg}$) and C ($3.217 \pm 0.010 \mu\text{g}/\text{kg}$). The mean total concentration of PAH in the roasted plantain ranges between 0.201 and 0.247 $\mu\text{g}/\text{kg}$. The maximum PAHs concentration detected in the analyzed roasted plantain in all the three locations under investigations was phenanthrene ($0.49 \mu\text{g}/\text{kg}$) while the PAH with minimum concentration was indeno(1,2,3-cd)pyrene ($0.01 \mu\text{g}/\text{kg}$).

In this study, the sum of the average concentrations of the low molecular weight PAHs having 2 to 4 aromatic rings such as naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene were found higher ($1.94 \mu\text{g}/\text{kg}$) than the high molecular weight PAHs ($1.15 \mu\text{g}/\text{kg}$) with 4 to 6 aromatic rings such as benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene benzo(g,h,i)perylene, chrysene and indeno(1,2,3-cd)pyrene in the analyzed roasted plantain samples. It was also observed that all the seven PAHs classified as probable human carcinogens were detected but with relatively low concentrations in the samples.

Reports from previous publications also revealed that PAHs with higher molecular weight (HMW) shows high carcinogenic potency than the lower molecular weight (LMW) PAHs [2]. In this study, the HMW carcinogenic PAHs constitute about 32% of the total PAHs in the roasted plantain. Out of this, Benzo(a)pyrene which is the most studied PAHs used as a marker for carcinogenicity was 9%.

Table 1. Concentration of the individual PAH in the roasted plantain samples [$\mu\text{g}/\text{kg}$]

PAH	Abbrev	A	B	C
Naphthalene	Nap	0.353 \pm 0.010	0.135 \pm 0.050	0.282 \pm 0.010
Acenaphthylene	Acy	0.058 \pm 0.001	0.196 \pm 0.002	0.306 \pm 0.005
Acenaphthene	Ace	0.533 \pm 0.002	0.619 \pm 0.030	0.288 \pm 0.001
Fluorene	Flu	0.399 \pm 0.001	0.472 \pm 0.100	0.692 \pm 0.002
Phenanthrene	Phe	0.713 \pm 0.050	0.653 \pm 0.001	0.102 \pm 0.001
Anthracene	Ant	0.265 \pm 0.010	0.311 \pm 0.005	0.099 \pm 0.025
Fluoranthene	Fla	0.310 \pm 0.002	0.326 \pm 0.001	0.249 \pm 0.004
Pyrene	Pyr	0.259 \pm 0.010	0.308 \pm 0.050	0.342 \pm 0.020
Benzo(a)anthracene	BaA	0.638 \pm 0.002	0.144 \pm 0.021	0.069 \pm 0.001
Chrysene	Chr	0.066 \pm 0.005	0.077 \pm 0.001	0.086 \pm 0.001
Benzo(b)fluoranthene	BbF	0.030 \pm 0.001	0.035 \pm 0.002	0.045 \pm 0.005
Benzo(k)fluoranthene	BkF	0.037 \pm 0.001	0.042 \pm 0.001	0.059 \pm 0.030
Benzo(a)pyrene	BaP	0.253 \pm 0.002	0.285 \pm 0.005	0.486 \pm 0.001
Indeno(1,2,3-cd)pyrene	IcdP	0.005 \pm 0.001	0.006 \pm 0.001	0.013 \pm 0.001
Dibenzo(a,h)anthracene	DahA	0.019 \pm 0.001	0.023 \pm 0.001	0.047 \pm 0.002
Benzo(g,h,i)perylene	BghiP	0.020 \pm 0.001	0.022 \pm 0.001	0.052 \pm 0.001
Total PAHs		3.958\pm0.005	3.654\pm0.002	3.217\pm0.010

Table 2. PAH isomer ratios of sampled roasted Plantain

Sample/ Isomer ratio	Phen/Ant	Fla/Pyr	An/(An+Phe)	Flu/(Flu+Phe)	Nap/Phe
A	2.691	1.197	0.274	0.359	0.495
B	2.100	1.058	0.323	0.420	0.207
C	1.031	1.000	0.493	0.872	2.765
Total	5.822	3.255	1.090	1.651	3.467

3.2. SOURCES OF PAHs DETECTED IN SAMPLES

Diagnostic isomer ratios are indices associating different isomer ratios of PAHs to possible sources [14]. Some sets of PAHs have been identified as markers for various sources such as petrogenic, fuel combustion, wood and coal combustion or mixed origin [15].

The ratios of fluoranthene to pyrene (Fla/Pyr) and phenanthrene to anthracene (Phe/Ant) have been used by different authors [16]. Ratio of fluoranthene to pyrene greater than one (Fla/Pyr > 1) is attributed to pyrolytic source, while Fla/Pyr < 1 is attributed to petroleum hydrocarbon source. Also, ratio of phenanthrene to anthracene less than ten (Ph/Ant < 10) indicates combustion source and Ph/Ant > 10 is apportioned petrogenic source [17,18]. This present study showed Ph/Ant < 10 (1.031 to 2.691) and Fla/Pyr < 1 (0.100 to 1.197). Charcoal, being the source of heat used for grilling the plantain samples used in this study, plausibly contributed to the levels of PAHs found in the roasted plantain [14]. The presence of BaP in relatively appreciable concentrations in the samples also gives credence to this suggestion with a clear indication that the source of PAHs detected from the roasted plantain originated from the roasting process.

3.3. COMPARISON OF THE PAHs CONCENTRATIONS WITH SIMILAR STUDIES

The average PAH concentrations of the investigated roasted plantain in this study were compared with similar studies as presented in Table 4. The identified PAHs in this study are all greater than the ones reported in the roasted plantain obtained from Lagos and Abia, Nigeria [19] and [20].

Table 4. Comparison of the PAHs concentrations of this study with similar studies

PAH	Abbrev	This Study	[19]	[20]
Naphthalene	Nap	0.257±0.001	ND	0.038±0.001
Acenaphthylene	Acy	0.187±0.005	0.009±0.001	0.000±0.000
Acenaphthene	Ace	0.480±0.010	ND	0.058±0.002
Fluorene	Flu	0.521±0.025	0.002±0.001	0.000±0.000
Phenanthrene	Phe	0.489±0.002	0.007±0.001	0.000±0.000
Anthracene	Ant	0.225±0.005	0.007±0.001	0.011±0.001
Fluoranthene	Fla	0.295±0.010	0.007±0.001	0.064±0.010
Pyrene	Pyr	0.303±0.001	0.019±0.002	0.000±0.000
Benzo(a)anthracene	BaA	0.284±0.002	ND	0.013±0.001
Chrysene	Chr	0.076±0.001	ND	0.000±0.000
Benzo(b)fluoranthene	BbF	0.037±0.001	0.067±0.001	0.000±0.000
Benzo(k)fluoranthene	BkF	0.046±0.002	0.237±0.004	0.000±0.000
Benzo(a)pyrene	BaP	0.341±0.001	ND	0.000±0.000
Indeno(1,2,3-cd)pyrene	IcdP	0.010±0.001	ND	0.000±0.000
Dibenzo(a,h)anthracene	DahA	0.030±0.001	ND	0.000±0.000
Benzo(g,h,i)perylene	BghiP	0.031±0.005	ND	0.000±0.000
Total PAHs		3.612±0.003	0.355±0.001	0.184±0.001

3.4. HUMAN HEALTH RISK ASSESSMENT

Tables 5 and 6 presented the human health risk assessments of the analyzed PAHs in the roasted plantain upon consumption. According to USEPA guidelines for carcinogen risk assessment, the oral reference dose and slope factor values of some PAHs are yet to be documented and due to this, only the PAHs with reported reference values were investigated for their carcinogenic and non-carcinogenic health risk [21]. Hazard quotient (HQ) was applied for evaluation of the non-carcinogenic health risk through ingestion as reported by USEPA. $HQ < 1$ indicates little or no associated adverse impacts on human health, while $HQ > 1$ is an indication of significant negative impacts on human health [21].

Table 5. Non-Carcinogenic Risk Assessment of PAHs in roasted plantain on consumption (Adult)

PAH	Abbrev.	EDI	RfD	THQ
Naphthalene	Nap	0.0022	0.02	0.110
Acenaphthene	Ace	0.0046	0.06	0.077
Fluorene	Flu	0.0034	0.04	0.085
Anthracene	Ant	0.0022	0.30	0.007
Fluoranthene	Fla	0.0027	0.04	0.068
Pyrene	Pyr	0.0022	0.03	0.073
Benzo(a)pyrene	BaP	0.0022	0.0003	7.333

EDI = estimated daily intake, *RfD* = oral reference dose and *THQ* = target hazard quotient

Table 6. Carcinogenic Risk Assessment of PAHs in roasted plantain on consumption (Adult)

PAH	Abbrev.	EDI	SF	CR
Benzo(a)anthracene	BaA	0.0055	0.1	0.00055
Chrysene	Chr	0.00056	0.001	0.00000056
Benzo(b)fluoranthene	BbF	0.00026	0.1	0.000026
Benzo(k)fluoranthene	BkF	0.00032	0.01	0.0000032
Benzo(a)pyrene	BaP	0.0022	1.0	0.0022
Indeno(1,2,3-cd)pyrene	IcdP	4.286e-5	0.1	0.00000043
Dibenzo(a,h)anthracene	DahA	0.00016	1.0	0.00016

EDI = estimated daily intake, *SF* = slope factor and *CR* = Carcinogenic risk

The results of this investigation on computed targeted HQ values for the analyzed PAHs on ingestion were less than 1 except Benzo(a)pyrene (7.33). The low HQ for most of the PAHs is an indication that there is relatively little or no adverse health effect on the local consumers. Also, the acceptable values of CR are in the range of 1×10^{-6} – 1×10^{-4} . But the result of this investigation showed some CR values greater than 1×10^{-4} which indicates an exposure to carcinogenic PAHs through the consumption of the roasted plantains by individuals who depend on them as staple food.

4. CONCLUSIONS

The result of this study revealed the presence of polycyclic aromatic hydrocarbons in the analyzed roasted plantain samples sold from different locations within Osogbo metropolis, Nigeria. All the 16 priority PAHs detected in the analyzed roasted plantain were at relatively high concentration in all the samples as compared to some similar studies reported at some other locations around the world. The HMW carcinogenic PAHs constitute about 32% of the total PAHs in the roasted plantain and out of this, Benzo(a)pyrene which is the most studied PAHs used as a marker for carcinogenicity constitute 9%. Source of the PAHs using the diagnostic ratios (Fla/Pyr and Ph/Ant) showed that the charcoal used in roasting the plantain contributed to the levels of PAHs in the roasted plantain samples. The result of the carcinogenic and non-carcinogenic health risk revealed that there is little or no adverse impacts on the consumption of the food item as indicated by the value of the HQ which is less than 1, while average CR was greater than 1×10^{-4} with an indication of exposure to carcinogenic risk. Consequently, people who depend on this food as source of meal may likely be taking PAH-contaminated food which could have adverse health effect due to the high CR and HQ values for benzo(a)pyrene.

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