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Research Article

Effect of polynuclear aromatic hydrocarbons levels in suya and barbecue fish on cancer risk index in Warri Metropolis, Southern Nigeria

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ABSTRACT

This study examined the levels of polynuclear aromatic hydrocarbons (PAHs) in Suya (peppered meats) and barbecue (grilled seafood) and applied them as potential cancer risk indices. A total of 24 samples, comprising 12 Suya and 12 grilled fish, were analyzed for the 16 priority PAHs as defined by the Environmental Protection Agency (EPA). High-performance liquid chromatography coupled with flame ionization detection (HPLC-FID) was employed for the quantitative analysis. The analytical method had a limit of quantification (LOQ) of 1.00 x 10^{-3} mg/kg, with recovery rates ranging from 52.90% to 71.30%, ensuring reliable detection of PAHs. Concentrations of individual PAHs varied across the samples, with 2-PAHs ranging from below detection limit (Bdl) to 0.16 mg/kg, 4-PAHs from Bdl to 0.21 mg/kg, 8-PAHs from Bdl to 0.52 mg/kg, and the sum of the 16-PAHs from 0.03 to 2.48 mg/kg. In Suya samples, five of the 13 sampling stations recorded benzo[a]pyrene (BaP) concentrations exceeding the European Union (EU) limit of 2.00 x 10^{-3} mg/kg, with a peak value of 0.12 mg/kg. Additionally, seven of the 12 Suya samples had 4-PAH concentrations above the EU threshold of 0.01 mg/kg. Similarly, the grilled fish samples exhibited higher contamination levels, with seven sampling locations exceeding the BaP limit and nine samples surpassing the EU limit for 4-PAHs. Notably, the NPA sampling site recorded the highest BaP concentration of 0.27 mg/kg among all samples. The comparative analysis indicated a higher percentage of grilled fish exceeding regulatory limits than Suya, suggesting a greater potential health risk from grilled seafood consumption. Overall, 66.60% of Suya and 33.30% of grilled fish samples were within tolerable risk levels based on international standards. The findings highlight significant public health concerns for residents of Warri Metropolis, emphasizing the need for stringent monitoring and regulation of local cooking practices to mitigate PAH exposure.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are amongst the most prominent persistent organic pollutants based on their potential to cause cancer, classifying them as carcinogens. PAHs can further be categorized as mutagenic or teratogenic. Studies indicate that both parent and metabolized forms of various PAHs are associated with strong genotoxic effects, linking them to numerous cancer types (Nowakowski *et al.*, 2022). The ubiquitous nature of PAHs stems from incomplete combustion of organic materials, exemplified by coal, wood, diesel, fat, incense as well as fossil fuels. Anthropogenic activities and natural occurrences such as volcanic eruptions and forest fires also play critical roles in the environmental distribution of these pollutants (Radu *et al.* 2021).

Evidence from various studies shows that PAHs can form during food processing, particularly when food is exposed to high temperatures (Sampaio *et al.*, 2021). Elevated PAH levels have been detected in foods like meat and fish that are barbecued or grilled over charcoal or wood, where the direct heat source and the lipophilic nature of PAHs lead to their absorption in fatty tissues. This process can alter the structural integrity of cell membranes, affecting their functions in food items like meat and fish (Duan *et al.*, 2016). Additionally, the degree of proximity between the food and the heat source significantly impacts PAH formation (Singh *et al.*, 2020).

The anthropogenic health risks associated with PAHs have been widely recognized, with extensive research documenting their genotoxic, teratogenic, and carcinogenic properties. The European Food Safety Authority (EFSA) has identified 16 priority PAHs that can pose serious human health risks, including benzo [j]fluoranthene (BjFA), cyclopenta [cd]pyrene (CPP), dibenzo [a, e]pyrene (DBaeP), dibenzo [a,i]pyrene (DBaiP), dibenzo [a,h]pyrene (DBahP), 5-methylchrysene (MCH) as well as benzo [c]fluorene (BcFL) (Nowakowski *et al.*, 2022). Among these, benzo[a]pyrene (BaP) is routinely described as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC), which is indicative of clear evidence of its carcinogenic related activities in humans, as documented by agencies like the Food and Agriculture Organization (FAO) as well as the World Health Organization (WHO). Moreover, the European Commission (EC) has designated four PAH moieties: benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), and benzo[a]pyrene (BaP) as markers for assessing PAH contamination levels in foods, setting specific maximum concentration limits for BaP and 4-PAHs in smoked fish and meat products sold across all parts of Europe (European Commission 2011).

The United States Environmental Protection Agency (USEPA) has described the utilization of benzo(a)pyrene as a comparative reference to define the relative carcinogenicity of some PAH congeners utilizing the term "toxicity equivalency factors" (TEFs). Amongst other PAHs, some that can used as a comparative reference include; indeno(1,2,3-cd)pyrene, dibenzo (a,h)anthracene, benzo(a) anthracene and benzo(b) fluoranthene (Hussain *et al.*, 2015). TEF as a tool have been utilized to evaluate dietary exposure in this study.

With reference to smoked fish and meat products in Europe, the EC's Regulation No. 835/2011 has mandated maximal permissible limits between 2012 and 2014. The limit for BaP was 5.00 µg/kg and 30.00 µg/kg for the sum of 4-PAHs; these limits were later reduced to 2.00 µg/kg for BaP and 12.00 µg/kg for the 4-PAHs total starting in 2014 (European Commission 2011). Despite extensive global studies, there is limited data specific to Africa, particularly in Nigeria, regarding PAH contamination from traditional cooking practices like grilling and roasting over charcoal. Some research in Nigeria, however, has shown that PAHs such as indeno[1,2,3-c,d]pyrene, chrysene, anthracene, benzo[a] anthracene as well as benzo[a]pyrene are present in roasted and grilled foods, such as Suya (peppered meats) and barbecue (grilled fishes) (Sese-Owie *et al.*, 2020; Adeyeye *et al.*, 2021; Adeyeye *et al.*, 2022, Olubunmi *et al.*, 2023; Iwu *et al.*, 2024).

This study addresses the gap by assessing the levels of PAHs in Suya and barbecue sold in Warri Metropolis, Delta State, Southern Nigeria. The investigation applies a Cancer Risk Index to evaluate the potential health risks and compares the concentration levels found in these local foods with European regulatory limits for BaP and 4-PAHs in smoked foods (European Commission 2011).

MATERIALS AND METHODS

Materials

Geographical area of study

Warri is the major commercial nerve centre of Delta State. This is justified by the myriad of oil and gas industries within the city. It is surrounded by a network of water body. Its different crude oil and natural gas reserve made it one of the most sought after city by oil exploration giants within South-South Nigeria. The current estimated metro area population of Warri muncipality in 2024 is 1,031,000, a 4.46% increment from the year 2023 (Macrotrends, 2024). There are different relaxation spots within the city wherein suya (peppered meat) and barbecue (grilled fishes) are prepared and sold. Samples were collected at 13 strategic locations in Warri (Enerhen road, Airport road, Opete, Jakpa, Refinery road, Water resources, Ovie Palace road, NPA, Orhuwhorun, Sedico, Ugbuomro, Okpaka and PTI road). The sampling areas were geo-referenced as observed in the map shown below (Figure 1). Business activities of this nature generally begin towards late evening when their customers would have closed from their works/jobs and settle down at these relaxation spots. Samples were collected at the aforementioned spots during the late hours of the day by direct purchase at these sales points.

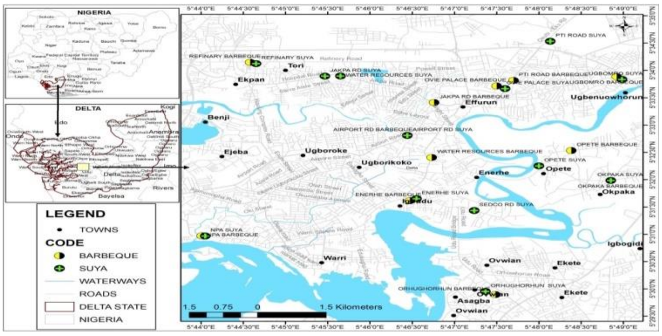

Figure 1: Map showing the sampling locations within Warri Metropolis

Chemicals

In the course of this work, reagents purchased and employed for analysis were either analytical or chromatographic grade. The chemical vendor from where we purchased dichloromethane was procured from is a registered supplier of that Sigma Aldrich (UK) reagents and chemicals. Hexane was acquired through a Fisher Scientific vendor. A PAH mix – Z - 014G with the subsequent 16 PAHs: benzo[a]anthracene (BaA), Chrysene (CHR), benzo[b] fluoranthene (BbF), benzo[k] fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3] pyrene (IP), dibenzo[a,h]anthracene (DbA), benzo[g,h,i] perylene (BPer) was procured from a United State based Organic Standards manufacturer called Accustandard. All glassware in the course of this work was subjected to thorough washing using chromic acid and detergent, followed by rinsing with re-distilled water. Furthermore, acetone was to rinse to ensure complete elimination of water. Before being used, they were ultimately dried at 90 ^{o}C.

Sample collection and storage

The respective food specimens were purchased at the sales point between the hours of 6.00 – 7.00pm (peak sales hours) into zip – lock bags, meticulously marked with consistent codes for easy identification and kept in a cooler filled with ice packs prior to being brought to the laboratory. Upon arrival, samples were kept in designated refrigerators for storage at temperature less than 4^{o}C until the next day before extraction.

Methods

Sample extraction and clean-up

The collected samples peppered meat (suya) and grilled fish (barbecue) were meticulously thawed into tiny shreds, afterwards; five grams (5.00 g) of Na_2SO4 and ten grams (10.00 g) of portion were thoroughly mixed in clean, 250 ml beaker capacity. Following that, the samples were submerged in an ultrasonic bath along with 100 milliliters of recently made 1:1, v/v acetone and dichloromethane solution. The beaker – containing submerged samples with both solvents were sonicated for about 55 minutes. These samples were then vortexed for 5 min afterwards, the upper phase were then carefully decanted and even more refined. The samples were introduced into the gel permeation chromatography (GPC) system using a purification column (80 mm × 6 mm, styrene divinylbenzene copolymer gels, Bio-Beads S-X3) after the upper segment was put into a 5 mL vial. The mobile phase, a 1:1 v/v mixture of acetone and dichloromethane, was used at a column flow rate of 3 mL/min. The extracts were then concentrated to about 4 mL using a rotary evaporator (Rotavapor R-300, Buchi, Flawil, Switzerland).

The eluents were capped into amber bottles that had already been thoroughly cleaned with chromic acid and distill water, and then allowed to evaporate through the passage of a gentle stream of nitrogen (> 99% purity) to a final volume of 1 ml. Injection into an Agilent 6890 Gas Chromatography flame ionization detection (GC/FID) system with an automated sampler was used to perform the analysis.

Operating Conditions for Gas Chromatography

Gas Chromatography flame ionization detection (HP 6890 series) operating in splitless mode enabled efficient separation of the target analytes on an HP-5, 30 m x 0.25 mm column. Because of its inert properties and economic feasibility, nitrogen is the preferred carrier gas, with a pressure of 10.2 psi and a flow rate of 1.5 mL/min. Injector and detector operating temperatures were 250 °C and 320 °C, respectively. The oven was set to start at 80 degrees, which was held for one minute, then ramped up to 280 degrees at a rate of 20 degrees per minute. After that, it was ramped up to 300 degrees at a rate of 2.5 degrees per minute, and it was held for a final ten minutes. This oven programme was to guarantee effective split-up of desired analytes. The operating software used in the course of this work was Agilent ChemStation which had the ability to confirm peak detection and integration. Seven (7) point external calibration standards of known concentration were ran on the GC FID to adequately and robustly account for target analyte identification and quantification.

The following equation was used to determine each target PAH analyte's concentration:

$$Conc.of\ analyte\ \left(\frac{up}{kp}\right)=\frac{Ax.vt-D}{wd-CF}\ldots\ldots\ldots..(1)$$

Where:

A_x = Area of the analyte measured in area count
V_t = Total volume of extract measured in µL
D = Dilution factor, dimensionless
W_d = Dry weight of samples extracted measured in grams (g)
CF = Mean calibration factor for target PAH analyte

Data analysis and quality assurance

The Laboratory control samples were tagged along the real life samples and analyzed in between different runs particularly after each analytical batch. This made it possible for both matrixes to be run under the same conditions to eliminate systematic error and to unearth any likelihood of contamination with respect to additional peaks elution. Any PAH detected in these laboratory control samples were abstracted from what was extracted from the sample. Peak detection in the calibration standard was carried out using a window retention time of ±0.05 min. Surrogate standards were used in matrix spike techniques to evaluate the overall analytical method's accuracy. For every recovery standard, the average recovery varied from 84 to 113%. The evaluation of the Limit of Quantification was done to verify a signal-to-noise ratio of 10. PAH quantification had a limit of 0.001 mg/kg. In order to assess sample recovery, three distinct concentrations (1.0, 5.0, and 10.0 mg/kg) were spiked into Ottawa sand and used as laboratory control samples. The European Union (EU) Regulation 836/2011, which stated that recoveries should be between 50% and 120%, was in line with the average recoveries, which varied from 52.9 to 71.3%.

$$\%\ \text{Recovery}=\frac{extracted\ concentration}{spiked\ concentration}\ x\ 100\ldots\ldots\ldots\ldots(2)$$

Samples were subjected to triplicate analysis for account for precision. Statistical tool for interpretation of the mean, standard deviation, ANOVA of data were made feasible by using SigmaPlot® and Excel. Using the equation, the total toxicity equivalent concentration (TTEC) was assessed.

$$TTEC = \Sigma Cn\ TEFn \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3)$$

Where Cn is the concentration of a specific congener n in the PAH mixture, TEFn is the toxicity equivalency factor of each member congener n.

The PAH levels of twenty-four samples - twelve (12) peppered meat (suya) and 12 grilled fish (barbecue) in Warri metropolis were sampled, analyzed and evaluated for risk assessment based on the 16 – PAHs. To indicate the relative carcinogenic risk of 16 PAHs, benzo(a)pyrene was used as the fundamental PAH for the toxicity equivalent factors (TEFs). Utilizing these toxicity equivalent factors, the relative carcinogenic risk of 16 PAHs was described. TEF for Ace, Flt, Phe, Nap, Pyr, and Flo were assigned 0.001; BaA, IcdP, BkF, and BbF were 0.10; Chr, BghiP, and Ant were 0.01 while DBahA and BaP had 1 inputed for them. The examined twenty – four (24) samples were subjected to risk assessment based on the aforementioned. The BaPeq of suya and barbecue were calculated according to Equation (3).

RESULTS AND DISCUSSION

Table 1a. revealed a profile of the means, minimal as well as maximal concentrations of 16 - PAHs (BaA, Chr, BbF, BaP, BkF, DBahA, BghiP, and IcdP) include Ap, Acy, Ace, Flo, Phe, Ant, Flt, Pyr, and categorised into genotoxic 2 - PAHs, 4 - PAHs, and 8 - PAHs) in the suya and barbeque samples. The most abundance PAH is pyrene with concentration of 0.99mg/kg in peppered meat (suya) at Ugbomro while the most abundance PAHs concentrations observed for barbecue was naphthalene and Acenaphthene with 2.47mg/kg and 0.95mg/kg both at Airport road respectively. As observed in Table 1a., in the category of lower molecular weight polycyclic aromatic hydrocarbons, naphthalene had the highest mean concentration (0.20 mg/kg), accounting for 27.10% of the total mean PAHs concentration. Conversely, aside from acenaphthylene, other moieties that were not detected because they were below the detection limit of the equipment were benzo(a)anthracene, dibenzo(a,h)anthracene, and benzo(g,h,l)perylene. Chrysene showed the lowest mean value of 0.003 mg/kg representing 0.40% of the total mean PAH value. A profile of the genotoxic PAHs in order of relative abundance showed (8 - PAHs), IcdP (0.43 mg/kg, 37.40%) and BaP (0.12 mg/kg, 10.70%) as the highest values. Noticeably, BaP ranged between below detection limit and 0.12mg/kg while the bulk of 8 - PAHs were also below detection limit.

The concentrations of 2 and 4 – PAHs and 8 – PAHs ranged from BDL to 0.21 and 0.52 mg/kg respectively, and the levels of 16 – PAHs and 8 – PAHs varied from 0.03 to 2.48 mg/kg. In the stations where peppered meat (suya) were collected, five (5) sampling stations had BaP concentrations above the EU limit of 0.002mg/kg with the highest concentration of 0.12mg/kg (Figure 2a). Also, out of the twelve (12) samples, seven (7) had concentrations of 4 - PAHs that exceeded the EU limit of 0.01 mg/kg (Figure 2b). Comparatively, sampling stations for barbecue showed that seven (7) locations had BaP values above the EU limit of 0.002mg/kg (Figure 3a & 3b). NPA sampling location had the highest concentration of BaP – 0.27mg/kg. Furthermore, out of the twelve (12) samples, nine (9) contained levels of 4 - PAHs higher than the EU limit of 0.01 mg/kg (Figure 5). A greater percentage of barbecue exceeded the BaP and 4 - PAHs limits compared to that of the peppered meat.

With reference to the sampling locations, for barbecue, the highest BaP contamination was observed in PTI (0.27 mg/kg), succeeded by Ovie palace road (0.21 mg/kg), Ugbomro (0.20 mg/kg), while the least contaminated was at water resources (0.07 mg/kg). For peppered meat (suya), the highest BaP contamination was observed at Ugbomro (0.12 mg/kg), accompanied by Okpaka (0.06 mg/kg) while the least contaminated was at Enerhen road (0.04mg/kg) (Tables 1b & 2). The total concentrations of 2 - PAHs, 4 - PAHs, 8 - PAHs, and 16 - PAHs in peppered meat (suya) were highest at Ugbomro (2.48 mg/kg) while for barbecue, highest concentration was at airport road (4.29mg/kg). On the other hand lowest concentrations of 2 - PAHs, 4 - PAHs, 8 - PAHs, and 16 - PAHs were at Orhuwhorun (0.03 mg/kg) an Enerhen road (0.12 mg/kg) for peppered meat and barbecue respectively. The relative distribution of BaP and 4 PAHs in all the twelve sampling locations for peppered meat and barbecue are shown in Figure 2a. – 3b. The most prevalent PAH congener in both peppered meat (suya) and grilled fish (barbecue) is acenaphthene. This belonged to the class of low molecular weight polynuclear hydrocarbons. It had a mean value of 0.06 mg/kg and total concentration of 0.74 mg/kg in suya which was lower than grilled fish with mean value of 0.20 mg/kg and total concentration of 2.39 mg/kg in all the sampling locations. Benzo (g,h,i) perylene was not detected in suya and barbecue throughout the sampling station.

Table 1a: Occurrence and contamination levels of PAHs in suya within Warri Metropolis

COMPONENT	ENERHEN ROAD	AIRPORT ROAD	REFINERY ROAD	ORUWHORUN	OKPAKA (FISH)	PTI ROAD	OPETE	JAKPA ROAD	WATER RESOURCES	OVIE PALACE ROAD	NPA	UGBOMRO
Naphthalene	0.15	Bdl	0.21	Bdl	0.19	0.18	0.21	0.23	0.065	0.18	0.18	0.78
Acenaphthalene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Acenaphthene	0.09	0.04	0.08	0.03	0.07	0.08	0.06	0.07	Bdl	0.06	0.06	0.08
Flourene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.04	0.08	0.034	0.06	0.07	0.18
Anthracene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.03	Bdl	Bdl	Bdl	0.05
Phenathrene	0.04	Bdl	0.05	Bdl	0.06	0.06	Bdl	Bdl	Bdl	Bdl	Bdl	0.09
Fluoranthene	0.11	0.07	Bdl	Bdl	0.57	Bdl	0.10	0.18	0.049	0.13	0.12	0.04
Pyrene	Bdl	Bdl	Bdl	Bdl	0.02	Bdl	0.31	0.24	0.255	0.24	0.27	0.99
Benzo(a)anthracene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	BDL
Chrysene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.03
Benzo(b)Fluoranthene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.04	0.05	Bdl	0.04	0.03	0.05
Benzo(k)Fluoranthene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.05	0.04	Bdl	Bdl	Bdl	0.05
Benzo(a)pyrene	0.04	Bdl	Bdl	Bdl	0.06	Bdl	Bdl	0.06	Bdl	0.05	Bdl	0.12
Dibenzo(a,h)anthracene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Indeno(1,2,3-cd)pyrene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.43	Bdl	Bdl	Bdl	Bdl	Bdl
Benzo(g,h,l)perylene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Genotoxic 2 PAHs	0.04	Bdl	Bdl	Bdl	0.06	Bdl	Bdl	0.06	Bdl	0.05	Bdl	0.16
Genotoxic 4 PAHs	0.04	Bdl	Bdl	Bdl	0.06	Bdl	0.04	0.11	Bdl	0.09	0.03	0.21
Genotoxic 8 PAHs	0.04	Bdl	Bdl	Bdl	0.06	Bdl	0.52	0.15	Bdl	0.09	0.03	0.26
Total PAHs (mg/kg)	0.42	0.10	0.34	0.03	0.97	0.32	1.23	0.99	0.403	0.76	0.72	2.48

Table 1b: Occurrence and contamination levels of PAHs in barbeque within Warri Metropolis

Naphthalene	0.15	Bdl	0.21	Bdl	0.19	0.18	0.21	0.23	0.07	0.18	0.18	0.78
Acenaphthalene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Acenaphthene	0.09	0.04	0.08	0.03	0.07	0.08	0.06	0.08	Bdl	0.06	0.06	0.08
Flourene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.04	0.08	0.03	0.06	0.07	0.18
Anthracene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.03	Bdl	Bdl	Bdl	0.05
Phenathrene	0.04	Bdl	0.05	Bdl	0.06	0.06	Bdl	Bdl	Bdl	Bdl	Bdl	0.09
Fluoranthene	0.11	0.07	Bdl	Bdl	0.57	Bdl	0.10	0.18	0.05	0.13	0.12	0.04
Pyrene	Bdl	Bdl	Bdl	Bdl	0.02	Bdl	0.31	0.24	0.26	0.24	0.27	0.99
Benzo(a)anthracene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Chrysene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.03
Benzo(b)Fluoranthene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.04	0.05	Bdl	0.04	0.03	0.05
Benzo(k)Fluoranthene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.05	0.04	Bdl	Bdl	Bdl	0.05
Benzo(a)pyrene	0.04	Bdl	Bdl	Bdl	0.06	Bdl	Bdl	0.06	Bdl	0.05	Bdl	0.12
Dibenzo(a,h)anthracene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Indeno(1,2,3-cd)pyrene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.43	Bdl	Bdl	Bdl	Bdl	Bdl
Benzo(g,h,l)perylene	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Genotoxic 2 PAHs	Bdl	Bdl	0.09	Bdl	Bdl	Bdl	0.19	0.14	0.07	0.21	0.27	0.20
Genotoxic 4 PAHs	Bdl	0.08	0.16	0.05	Bdl	Bdl	0.29	0.22	0.12	0.26	0.31	0.26
Genotoxic 8 PAHs	Bdl	0.16	0.24	0.05	0.04	Bdl	0.59	0.28	0.16	0.60	0.39	0.40
Total PAHs (mg/kg)	0.42	0.10	0.34	0.03	0.97	0.32	1.23	0.99	0.40	0.76	0.72	2.48

Genotoxic 2 PAHs is summation of chrysene and benzo[a]pyrene. Genotoxic 4 PAHs is summation of chrysene, benz[a]anthracene, benzo[a]pyrene and benzo[b]fluoranthene. Genotoxic 8 PAHs is summation of benzo[k]fluoranthene, benz[a]anthracene, chrysene, indeno[1,2,3- cd]pyrene, benzo[b] fluoranthene, benzo[a]pyrene, dibenz[a,h] anthracene, and benzo[g,h,i]perylene.

Table 2: Toxicity equivalent concentrations (mg/kg) of peppered meat (suya) PAHs

	TOXICITY EQUIVALENT CONCENTRATION (mg/kg)												
PAHs	ENERHEN ROAD	AIRPORT ROAD	REFINERY ROAD	ORUWHORUN	OKPAKA	PTI ROAD	OPETE	JAKPA ROAD	WATER RESOURCES	OVIE PALACE ROAD	NPA	UGBOMRO	***TEF**
Naphthalene	1.5E-04	-	2.1E-04	-	1.9E-0.4	1.8E-04	2.1E-04	2.3E-04	7.0E-05	1.8E-04	1.8E-04	7.8E-04	0.001
Acenaphthalene	-	-	-	-	-	-	-	-	-	-	-	-	0.001
Acenaphthene	9.0E-04	4.0E-05	8.0E-05	3.0E-05	7.0E-0.5	8.0E-	6.0E-0.5	8.0E-05	-	6.0E-0.5	6.0E-	8.0E-05	0.001
Flourene	-	-	-	-	-	-	4.0E-0.5	8.0E-05	3.0E-05	6.0E-0.5	7.0E-	1.8E-04	0.001
Anthracene	-	-	-	-	-	-	-	3.0E-05	-	-	-	5.0E-05	0.001
Phenathrene	3.5E-04	-	4.7E-04	-	6.0E-0.5	5.9E-04	-	-	-	-	-	9.1E-04	0.01
Fluoranthene	1.1E-04	7.0E-0.5	-	-	6.0E-0.5	-	1.0E-0.4	1.8E-04	5.0E-0.5	1.3E-04	1.1E-04	4.0E-0.5	0.001
Pyrene	-	-	-	-	2.0E-0.5	-	3.0E-0.5	2.4E-0.4	2.6E-0.4	2.4E-0.4	2.7E-	9.9E-0.4	0.001
Benzo(a)anthracene	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Chrysene	-	-	-	-	-	-	-	-	-	-	-	3.4E-0.4	0.01
Benzo(b)Fluoranthene	1.0E-03	-	-	-	-	-	-	4.0E-03	4.8E-04	-	4.3E-	3.0E-0.4	0.1
Benzo(k)Fluoranthene	-	-	-	-	-	-	4.9E-04	4.3E-0.4	-	-	-	5.2E-0.4	1
Benzo(a)pyrene	3.8E-0.4	-	-	-	5.8E-04	-	-	5.7E-04	-	5.0E-04	-	1.2E-03	0.1
Dibenzo(a,h)anthracen	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Indeno(1,2,3-cd)pyrene	-	-	-	-	-	-	4.3E-04	-	-	-	-	-	1
Benzo(g,h,l)perylene	-	-	-	-	-	-	-	-	-	-	-	-	0.1
ΣPAHs	2.1E-03	1.0E-04	7.6E-04	3.0E-04	6.2E-04	8.4E-04	3.5E-03	5,9E-03	8.8E-04	5.7E-04	5.0E-04	5.4E-03	

* Toxicity Equivalency Factor

Table 3: Toxicity equivalent concentrations (mg/kg) of grilled fish (barbeque) PAHs

	TOXICITY EQUIVALENT CONCENTRATION (mg/kg)												
PAHs	ENERHEN ROAD	AIRPORT ROAD	REFINERY ROAD	ORUWHORUN	OKPAKA	PTI ROAD	OPETE	JAKPA ROAD	WATER RESOURCES	OVIE PALACE ROAD	NPA	UGBOMRO	***TEF**
Naphthalene	9.0E-05	2.0E-05	1.1E-04	4.3E-04	-	3.1E-04	1.4E-04	1.2E-04	2.7E-04	7.5E-04	9.6E-04	1.0E-03	0.001
Acenaphthalene	-	4.0E-05	6.0E-05	-	-	-	-	-	-	-	-	-	0.001
Acenaphthene	3.0E-05	1.0E-05	4.8E-04	1.2E-04	-	1.4E-04	1.5E-04	1.6E-04	9.0E-05	7.0E-05	1.0E-04	9.0E-05	0.001
Flourene	-	3.6E-04	2.0E-04	7.0E-05	5.0E-05	5.0E-05	4.1E-04	3.4E-04	1.0E-04	1.9E-04	1.7E-04	4.0E-05	0.001
Anthracene	-	1.0E-05	5.0E-05	1.2E-04	-	9.0E-05	6.0E-05	6.0E-05	-	5.0E-05	7.0E-05	5.0E-05	0.001
Phenathrene	-	1.0E-04	1.0E-03	-	-	-	1.7E-04	1.2E-03	3.7E-04	7.2E-04	6.3E-04	5.0E-04	0.01
Fluoranthene	-	5.0E-05	6.0E-05	-	-	-	6.0E-05	5.0E-05	2.1E-04	6.0E-05	7.0E-05	8.0E-05	0.001
Pyrene	-	1.2E-04	1.3E-04	4.0E-05	7.0E-05	2.0E-05	2.8E-04	5.0E-05	2.8E-04	3.5E-04	3.9E-03	3.7E-04	0.001
Benzo(a)anthracene	-	-	-	5.1E-04	-	-	6.5E-04	-	-	-	-	-	0.1
Chrysene	-	-	-	-	-	-	6.9E-04	-	-	-	-	-	0.01
Benzo(b)Fluoranthe	1.0E-04	-	7.8E-04	7.4E-04	-	-	-	4.0E-04	8.2E-04	4.5E-04	5.0E-04	4.1E-04	0.1
Benzo(k)Fluoranthe	-	8.0E-05	7.4E-04	-	-	-	1.0E-03	6.1E-04	4.1E-04	1.4E-04	8.5E-04	8.1E-04	1
Benzo(a)pyrene	-	-	8.6E-04	-	-	-	1.2E-03	1.4E-03	7.0E-03	2.1E-04	2.7E-03	2.0E-03	0.1
Dibenzo(a,h)anthrac	-	-	-	-	3.5E-04	-	2.0E-03	-	-	2.1E-04	-	-	0.1
Indeno(1,2,3-	-	-	-	-	-	-	-	-	-	-	-	5.9E-04	1
Benzo(g,h,l)perylen	-	-	-	-	-	-	-	-	-	-	-	-	0.1
ΣPAHs	2.2E-04	9.1E-04	4.5E-03	2.0E-03	4.7E-04	6.1E-04	6.8E-03	4.2E-03	9.6E-03	3.2E-03	6.4E-03	5.9E-03	

* Toxicity Equivalency Factor

Figures 2a – 3b showed that the distribution of BaP and 4 – PAHs were highest in barbecue compared to the peppered meat. This could be attributed to the lipophilic nature of polynuclear aromatic hydrocarbons since grilled fish (barbecue) are associated with high fatty content. According to recent research, cooked meat and fish can contain polycyclic aromatic hydrocarbons (PAH) (Zachara *et al.* 2017; Hasyimah *et al.* 2020; Oz 2021). The total concentrations of the various components of PAHs 4 and 8 are displayed in Tables 1a and 1b. During the most recent assessment of the toxicity of PAHs in food, the panel suggested computing the total of either four or eight PAHs. Rather than B(a)P, the CONTAM Panel suggested that the two sums serve as the most reliable markers of the presence of PAHs in food. Total concentration of 4 – PAHs in grilled fish was 1.74mg/kg and peppered meat – 0.57mg/kg. These were far higher than 0.16mg/kg for smoked fish and 0.06mg/kg for smoked meat obtained from the local market in Abijan, Côte d'Ivoire. The origin of the contamination was identified with the aid of the respective ratios of the various PAH congeners. These sources may come from heat-based (pyrolytic) or fossil-based (petrogenic) processes. BaA/(BaA + Chr), Ant/(Ant + Phe), Chr/BaA, Flu/(Flu + Pyr), Phe/Ant,and BaP/(BaP + Chr) are the ratios that are most frequently used for this problem. The grilled fish had a total phenanthrene/anthracene ratio of 1.17 and the peppered meat had a ratio of 3.40. Both values were below 10, suggesting that these hydrocarbons may have pyrolytic origins. A combustion source was indicated by anthracene/(Anthracene + Phenanthrene) ratio greater than 0.1, whereas a petroleum source was indicated by a ratio less than 0.1. BaA/(BaA + Chr) could be used to describe the type of possible sources of PAH emissions. Using coal, grass, and wood is strongly indicated by a BaA/(BaA + Chr) > 0.5 ratio (Dong *et al.*, 2021).

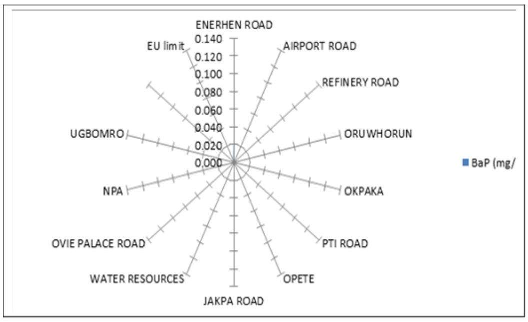

Figure 2a: Comparative distribution of BaP in twelve peppered meat sampling stations

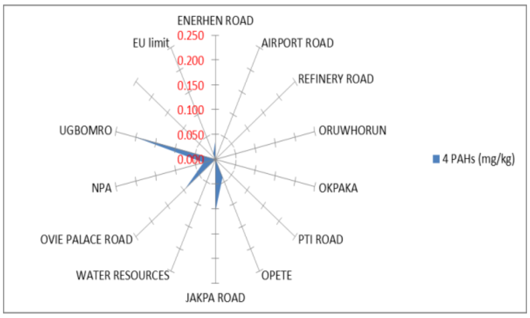

Figure 2b: Comparative distribution of 4 - PAHs in twelve peppered meat sampling stations

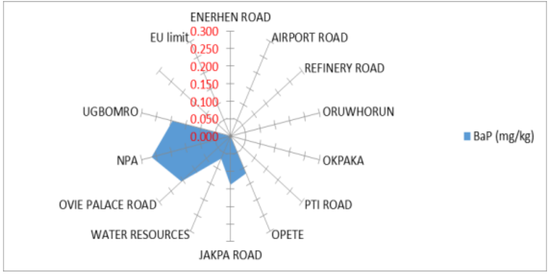

Figure 3a: Comparative distribution of BaP in twelve barbeque sampling stations

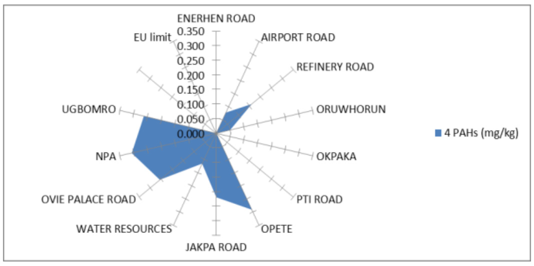

Figure 3b: Comparative distribution of 4 PAHs in twelve barbeque sampling stations

PAH to PAH ratios

BaP/(BaP + Chr), Anthracene/178 ratio [Anthracene/(Anthracene + Phenanthrene)] and (BaA + Chr) have also been used to explain the nature of PAH production within the environment (Marzye *et al*. 2023). Peppered meat gave 1.29 and grilled fish 1.70 both higher than 0.1 which showed ratios Anthracene/178 > 0.1, clearly an indication of the prevalence of combustion related activities associated with the liberation PAHs in the studied locations. These observed ratios were similar to results previously described by Ejeomo *et al.* (2023).

Risk Exposure

The incremental lifetime cancer risk was used to characterize the concentrations of the analyzed peppered meat and grilled fish in relation to their risks of exposure to 16 PAHs. According to the US EPA, ILCR values less than 1.00×10^{-6} are negligible, and ILCR data greater than 1.00×10^{-4} are probably harmful to anthropogenic health. Additionally, ILCR values between 1.00×10^{-6} and 1.00×10^{-4} are adjudged as a region of tolerable risk. Data presented in Table 2 showed that the peppered meat (suya) had ILCR values which varied from 1.00×10^{-4} and 5.90×10^{-3} which is an indication that 66.60% of these locations are within tolerable risk. Peppered meat samples collected from Enerhen, Opete, Ugbomro and Jakpa sampling locations were above tolerable risk. And for the assessment of grilled fish (barbecue) with respect to the sampling locations, the results showed ILCR values ranged between 2.2×10^{-4} and 9.6×10^{-3} (Table 3) which was indicative that 33.3% of these locations were within tolerable risk. A greater part of the sampling locations are above tolerable risk with maximal risk exposure recorded for Water Resources road. The ranking of ILCR values based on peppered meat (suya) and grilled fish (barbecue) showed that of the latter accounted for higher risk exposure, consequently a serious potential carcinogenic risk.

PAH concentrations detected in Drepane africana (fillet) samples sourced from the Atlas Cove jetty within Lagos area were higher than the approximated 0.02 mg/kg reported by Olayinka *et al*. (2019). Benzo(a)pyrene (BaP) in grilled fish (barbecue) was ascertained as utmost toxicity equivalent concentration obtained - 7.03×10^{-3}. On the other hand, highest toxicity equivalent concentration in peppered meat (suya) was 4.04×10^{-3} for benzo (b) fluoranthene.

CONCLUSION

The findings from this study revealed varying levels of PAH contamination in grilled fish and peppered meat (Suya), with grilled fish exhibiting maximal PAH contamination levels. Specifically, seven barbecue samples had BaP concentrations exceeding the EU limit of 0.002 mg/kg, while five Suya sampling stations also surpassed this threshold. The diagnostic ratios suggest pyrolysis as the predominant pathway for the formation of these persistent organic pollutants (PAHs). These results align with existing literature that associates elevated PAH levels with grilled foodstuffs. The study showed the potential carcinogenic risk posed to consumers from frequent consumption of these popular local delicacies. The presence of PAHs, whether in their parent or metabolized forms, correlates with intense genotoxic effects, which contribute to various cancer types. This trend would highlight the urgent need for further research to monitor and mitigate PAH contamination in food. The data provided critical insights into the extent of PAH contamination in suya and grilled fish sampled from different locations in Warri Metropolis, Delta State, Nigeria, emphasizing the need for regulatory interventions and public awareness to reduce health risks associated with these foods.

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