COMPARATIVE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBON (PAH) DISTRIBUTIONS IN SOME COMMONLY CONSUMED FOODS IN PORT HARCOURT (NIGERIA), PREPARED BY DIFFERENT METHODS

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ABSTRACT

The distribution and concentrations of 16 priority polycyclic aromatic hydrocarbons (PAHs) in grilled (GR) and roasted (RO) fish (FH), meat (MT), plantain (PN) and yam (YM), commonly consumed in Port Harcourt (Nigeria), were evaluated. Gas chromatography analyses detected PAHs in the grilled (13-16) and roasted (11-14) food samples with the total concentration in each food sample higher for the roasted than grilled. Nine PAHs were detected in all the food samples: anthracene (3 ring), fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i)perylene (4-6 ring). Total concentrations of the 4-6 ring high molecular weight (HMW) PAHs were more in the grilled food samples (28.88, 14.88, 32.84 and 21.56) and significantly more in the roasted food samples (54.87, 42.88, 34.85 and 78.86) than the 2-3 ring low molecular weight (LMW), which were generally minor constituents or absent, respectively. Fluoranthene and pyrene were most prominent in all the food samples with concentrations from 7.89 to 37.00 μg/kg and 3.04 to 13.53 μg/kg in the grilled, and 17.84 to 113.58 μg/kg and 8.93 to 23.23 μg/kg in the roasted, respectively. Ratio of fluoranthene and pyrene (Fth/Pyr) commonly employed as diagnostic of PAH formation processes range from 2.04 to 2.73 for the grilled and 2.00 to 4.89 for the roasted food samples. These results indicate that grilling and roasting of fish, meat, plantain and yam generated and incorporated PAHs, with comparable distributions and varying concentrations, into the food samples which are commonly consumed in Port Harcourt, Nigeria.

Keyword: - *Food, Nigeria, Polycyclic aromatic hydrocarbons (PAHs), Grill, Roast, Gas chromatography, Concentration, Distribution*

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1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds are composed of two or more aromatic (benzene) rings fused together. They are mostly derived from two sources; petrogenic, from petroleum and pyrogenic, from incomplete combustion of organic substances such as petroleum and its derivatives (gasoline, kerosene, diesel and lubricating oil), asphalt, coal, wood, tires, plastics, tobacco, garbages and electronic waste [1-4]. There are more than 100 known PAHs occurring in the environment as complex mixtures [5,6]. However, the United State Environmental Protection Agency (USEPA) has designated 16 PAHs as priority pollutants, based on their widespread occurrence and toxic characteristics in humans, by forming carcinogenic and mutagenic diols and epoxides that react with DNA, resulting in many health problems such as lung and skin cancer [7]. Among the 16 USEPA priority PAHs, benzo (a) anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene and dibenzo(a,h)anthracene are classified as probable human carcinogens [8].

Food is one of the major routes of human exposure to PAHs [9]. Several studies have reported PAHs in foods such as fruit, vegetable, fish, meat, milk, flour, cereals, baked ready-to-eat foods and seafood. PAHs in foods originate from environmental deposits or incomplete combustion of organic substances like fats, carbohydrates and proteins at temperatures above 200 ^oC with their formation enhanced by temperature between 500 - 900 ^oC [10-13]. It has been reported that thermal methods of preparation like frying, drying, baking, grilling, smoking and roasting generate PAHs in foods whereas boiling and steaming scarcely bring about PAHs formation [14-17]. For instance, about 130 µg/kg was observed in barbecued meat while for uncooked foods the average background values were between 0.01 to 1 µg/kg [18].

Assessment of the levels of PAHs in roasted plantain and fried plantain chips in Warri, Nigeria, using gas chromatography flame ionization detector (GC-FID) showed the total concentration of 16 EPA priority PAHs ranged from 6.9 to 18.3 µg/kg in roasted plantain and 3.8 to 10.5 µg/kg in fried plantain [19]. While evaluation of PAHs in meats and fishes sold in Abobo market in Côte d'Ivoire showed smoking produced more PAHs than frying or grilling with benzo(a)pyrene appearing in the majority of samples in quantities above the European Union fixed limit [20]. Investigation of grilled and smoked meat, chicken and vegetables by Alomirah et al., (2011) showed phenanthrene, a non-carcinogenic PAHs, had the highest mean concentration of 54.9 $\mu g \cdot kg^{-1}$, which accounted for 37.1% of the total PAHs, whereas chrysene and benz[*a*]anthracene (both genotoxic PAHs) had mean values 4.88 $\mu g\ kg^{-1}$ and 2.27 $\mu g\ kg^{-1}$, which accounted for 3.29% and 1.53%, respectively [21]. These researchers observed that conditions such as the type heat source, duration of grilling and fat content influenced PAHs formation in the foods. Due to the generation of harmful PAHs in foods by thermal preparation processes, we investigated the distributions and concentrations of 16 USEPA priority PAHs in some commonly consumed foods; plantain, yam, fish and meat, in Port Harcourt, Nigeria, prepared by roasting and grilling methods.

2. MATERIALS AND METHODS

2.1 Sample Collection

The foods selected for this study are commonly consumed and sometimes as ready-to-eat delicacies in the city of Port Harcourt, Rivers State, situated in southern Nigeria. The commonly consumed foods include fish, meat, plantain and yam. They were obtained from the popular Mile-3 market in Port Harcourt and each shared into three (3) sets with each of the first and second food sample sets further divided into four portions.

2.2 Sample Preparation

The four portions of the first food sample set were grilled separately using an electric Halogen multi-cooker with temperature set at 200 ^oC. Plantain was grilled for 30 minutes, meat for 35 minutes, yam for 40 minutes and fish for 55 minutes, making all cooked and ready for consumption. The four portions of the second food sample set were sent to roadside vendors, within Port Harcourt, who separately roasted the foods, in their usual way for consumption, using charcoal. The third set of each food samples were not prepared (raw) to serve as the control. All the prepared food samples (grilled and roasted) were air-dried for 4 days (with the carbon black layer of the charcoal roasted food samples removed), homogenized and the four portions of each food sample set mixed together.

2.3 Sample Extraction and Clean up

Five (5) grams of each homogenized and mixed food sample was weighed into a conical flask. 20 ml of hexane/dichloromethane (1:3 v/v) was measured and poured into the conical flask. The mixture was stirred, agitated with a mechanical vibrator for 30 minutes, filtered and then concentrated under a gentle stream of dry nitrogen. A glass chromatographic column (25 cm x 1 cm) packed with activated silica gel (mesh 100-200) and 0.5g of sodium sulphate, to absorb any moisture, was used for sample clean-up. Each concentrated sample was transferred onto the top of the glass chromatographic column. 20 ml of hexane was poured into the column, to elute the saturated hydrocarbons, then 20 ml of dichloromethane was poured to elute the aromatic hydrocarbons, which contain the PAHs, and the aromatic fraction eluent concentrated under a gentle stream of nitrogen.

2.4 Analysis of Polycyclic Aromatic Hydrocarbons (PAHs)

Analysis of the 16 USEPA polycyclic aromatic hydrocarbons in the food samples was achieved with an Agilent 7890B gas chromatography (GC) system fitted with a HP-5 silica capillary column (30 m x 320 µm id and 0.25 µm film thickness) and coupled to a flame ionization detector (FID). The concentrated aromatic fraction of each food sample was dissolved in hexane, transferred into labelled glass vials and with the aid of a G4513A automatic liquid sampler (ALS) one microlitre (1µL) was injected into the GC system operated in a splitless injection mode. Helium was used as the carrier gas and oven temperature for the analysis was programmed from 35 ^{o}C to 325^{o}C at 10^{o}C/min with 2 mins hold at 35^{o}C and 10 mins hold at 325^{o}C. PAHs were identified by comparing their retention times with internal standard. Quantification of each identified peak was acquired by area integration and processed by Chemstation software OPEN LAB CDS Edition.

3. RESULTS AND DISCUSSION

GC analyses showed PAHs were present in the grilled fish (GR-FH), meat (GR-MT), plantain (GR-PN) and yam (GR-YM) as well as the roasted fish (RO-FH), meat (RO-MT), plantain (RO-PN) and yam (RO-YM), but absent in the control food samples. This indicate both food preparation methods generated and incorporated PAHs into the food samples. The total PAH concentrations in the grilled and roasted food samples are presented in figure 1.

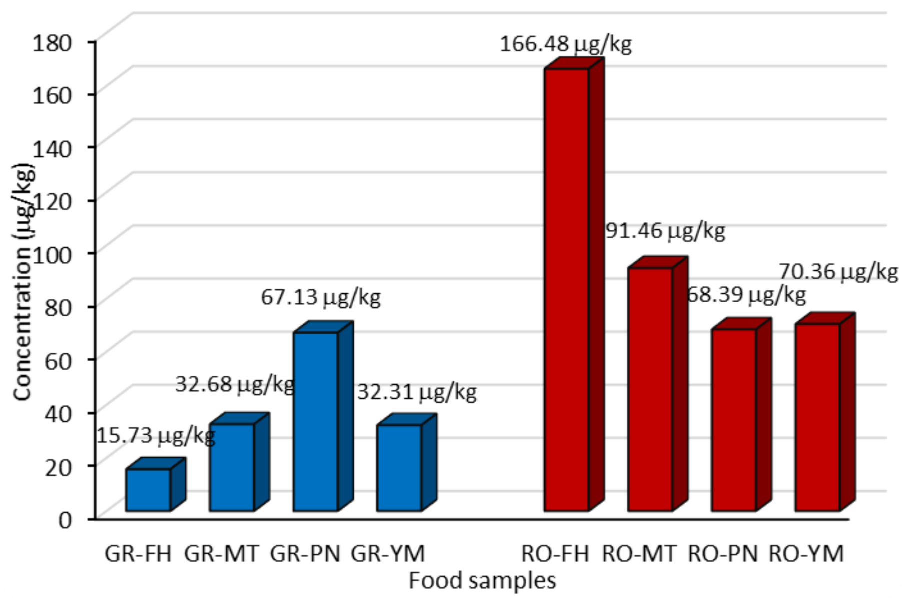

Fig. 1: Total PAH concentrations in the grilled and roasted food samples

Total PAH concentrations ranged from 15.73 to 67.13 µg/kg in the grilled food samples and 68.39 to 166.48 µg/kg in the roasted food samples (fig. 1). For each food sample, it was observed that the total PAH concentrations was higher in the roasted than the grilled. The temperature of roasting are usually higher than that used for grilling of the food samples (200 ^{o}C). This suggest that the higher the temperature used for food preparation, the higher the concentration of PAHs in that food. It was also observed that the total PAH concentration in plantain, meat, yam and fish, which were grilled for 30, 35, 40 and 55 minutes, decreased, respectively. This suggest increase grilling time decreases the total concentration of PAHs in the food samples.

The distributions and concentrations PAHs detected in the grilled and roasted food samples are shown in figures 2 and 3, respectively.

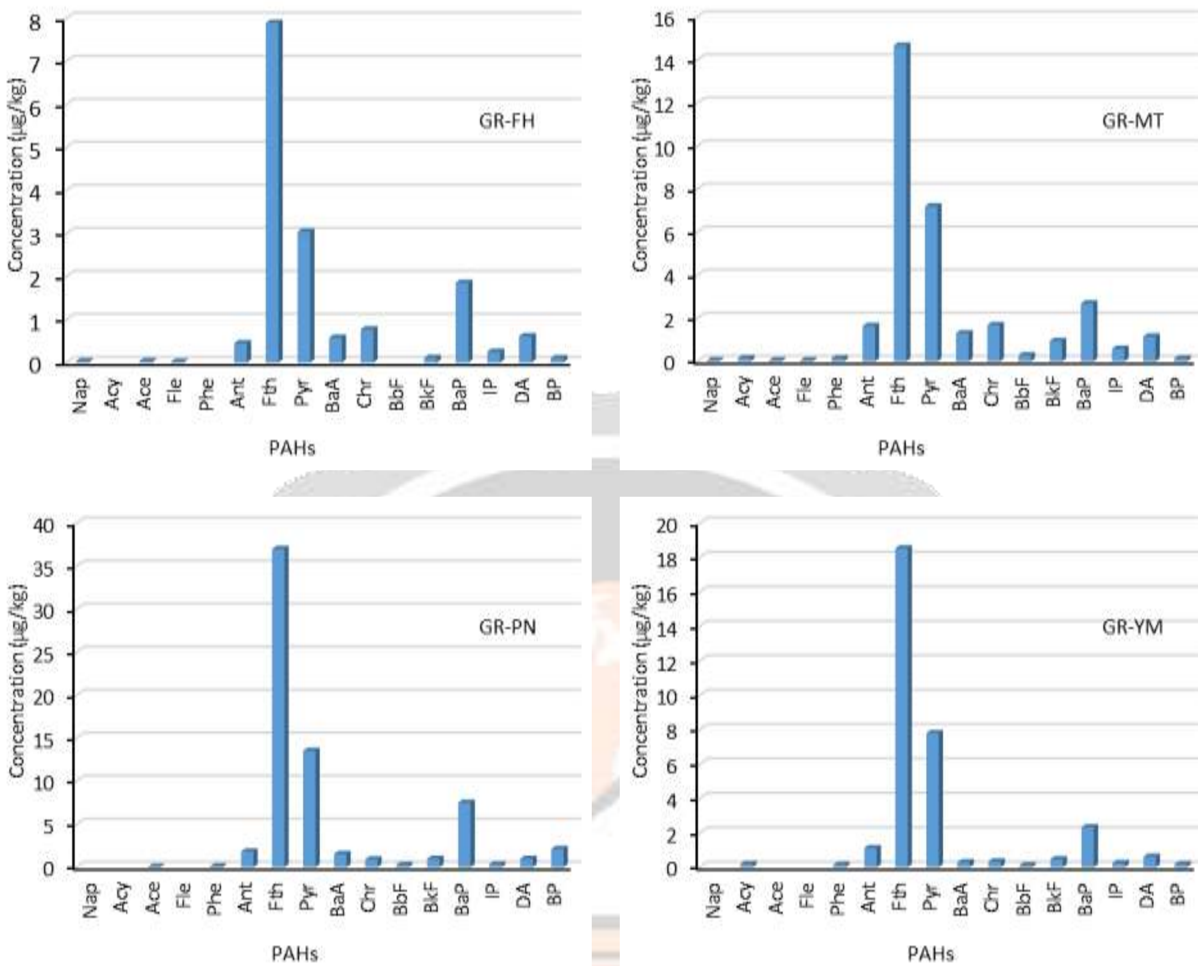

Fig. 2: Distributions and concentrations of polycyclic aromatic hydrocarbons (PAHs) in the grilled food samples

Nap; Naphthalene, Acy; Acenaphthylene, Ace; Acenaphthene, Fle; Fluorene, Phe; Phenanthrene, Ant; Anthracene, Fth; Fluoranthene, Pyr; Pyrene, BaA; Benzo(a)anthracene, Chr; Chrysene, BbF; Benzo(b)fluoranthene, BkF; Benzo(k)fluoranthene, BaP; Benzo(a)pyrene, IP; Indeno(1,2,3-*cd*)pyrene, DA; Dibenzo(*a*,*h*)anthracene, BP; Benzo(*g*,*h*,*i*)perylene.

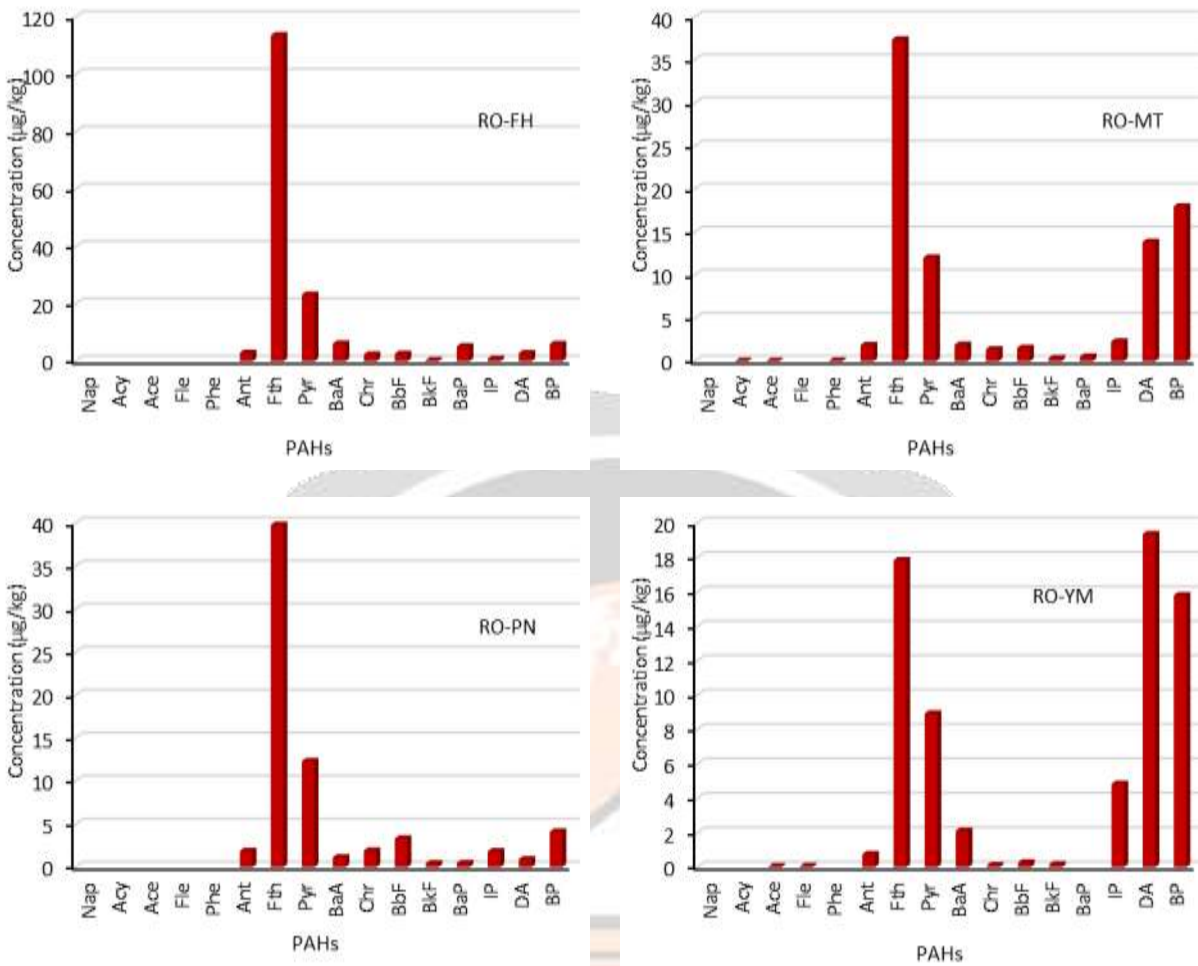

Fig. 3: Distributions and concentrations of polycyclic aromatic hydrocarbons (PAHs) in the roasted food samples

For the grilled food samples, 13 PAHs were detected in GR-FH, 16 in GR-MT, 13 in GR-PN and 13 in GR-YM (fig. 2), while for the roasted food samples 11 PAHs were detected in RO-FH, 14 in RO-MT, 11 in RO-PN and 13 in RO-YM (fig. 3). From these results, the total number of PAHs detected in each food sample was generally more in the grilled than the roasted with both preparation methods observed to generate the most PAHs in meat.

Among the PAHs detected, nine (9) were observed to be present in both the grilled and roasted food samples (figs. 2 and 3). They are Ant, Fth, Pyr, BaA, Chr, BkF, IP, BP. Of these PAHs, Fth and Pyr were prominent in all the food samples (figs. 2 and 3). In the grilled food samples, their concentrations ranged from 7.89 to 37.00 μg/kg and 3.04 to 13.53 μg/kg, while in the roasted food samples, their concentrations ranged from 17.84 to 113.58 μg/kg and 8.93 to 23.23 μg/kg, respectively. Also noticeable in all the grilled food samples is BaP and in the roasted food samples are DA and BP, particularly in RO-MT and RO-YM. Fluoranthene, pyrene, benzo(a)pyrene, dibenzo(*a*,*h*)anthracene, and benzo(*g*,*h*,*i*)perylene are 4-6 ring PAHs. Total concentrations of the 4-6 ring HMW were more than the 2-3 ring LMW in GR-FH (28.88), GR-MT (14.88), GR-PN (32.84) and GR-YM (21.56), and significantly more in RO-FH (54.87), RO-MT (42.88) RO-PN (34.85) and RO-YM (78.86). This concentration results indicate the 4-6 ring high molecular weight (HMW) PAHs were more abundant in the food samples than the 2-3 ring low molecular weight (LMW), which were generally minor constituents or absent.

Fluoranthene and pyrene are 4-ring PAH isomers. Their composition is an effective diagnostic index of PAH formation processes. Values of Fth/Pyr ratios < 1 indicate PAHs are petroleum-derived (petrogenic) and ratios > 1 are attributed to combustion (pyrogenic) of organic materials [22,23]. The relative abundance of fluoranthene to pyrene range from 2.04 to 2.73 for the grilled food samples and from 2.00 to 4.89 for the roasted food samples. This indicate PAHs in the food samples were from combustion source and revealed grilling and roasting of the foods; plantain, meat, yam and fish, generated PAHs which contaminated the foods.

4. CONCLUSIONS

The distribution and concentrations of polycyclic aromatic hydrocarbons (PAHs) in grilled and roasted food samples: fish, meat, plantain and yam, commonly consumed in Port Harcourt, Nigeria, were evaluated with gas chromatography analyses, which detected 13-16 PAHs in the grilled and 11-14 in the roasted food samples. Total PAH concentrations were higher in each roasted food sample than the grilled. Nine PAHs were detected in all the food samples with fluoranthene and pyrene being prominent in all. Ratio of fluoranthene to pyrene as well as the concentration of 4-6 ring high molecular weight PAHs being more in the grilled food samples, and significantly more in the roasted food samples, than the 2-3 ring low molecular weight, which were generally minor constituents or absent, indicate that grilling and roasting of fish, meat, plantain and yam generated and incorporated PAHs, with comparable distributions and varying concentrations, into the food samples which are commonly consumed in Port Harcourt, Nigeria.

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