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DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SOME CHARCOAL ROASTED FOODS COMMONLY CONSUMED IN PORT HARCOURT, NIGERIA

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Abstract: *Sixteen (16) priority polycyclic aromatic hydrocarbons (PAHs) were investigated in commonly consumed charcoal roasted foods prepared by roadside vendors in Port Harcourt, Nigeria. Charcoal roasted fish (CR-FH), meat (CR-MT), plantain (CR-PN) and yam (CR-YM) were homogenized, extracted, fractionated and for PAH analysis, gas chromatography flame ionization detector (GC-FID) system was used. Eleven (11) PAHs were identified in CR-FH, 14 in CR-MT, 11 in CR-PN and 13 in CR-YM with total concentrations of 166.48 µg/kg, 91.46 µg/kg, 68.39 µg/kg and 70.36 µg/kg respectively. Fluoranthene was observed to be the most prominent PAH in all the charcoal roasted food samples, being the most abundant in CR-FH, CR-MT and CR-PN with the concentrations of 113.6 µg/kg (68.23%), 37.4 µg/kg (40.87%) and 39.8 µg/kg (58.21%) respectively and the next most abundant in CR-YM with a concentration of 17.8 µg/kg (25.36%). The compositions of PAHs in the charcoal roasted foods revealed the 4-6 ring high molecular weight (HMW), from 97.21 - 98.75%, were considerably dominant over the 2-3 ring low molecular weight (LMW), from 1.25 - 2.79%, which were only minor. Ratio values of PAH isomers for Phe/Ant 0.05; Fth/Pyr, from 2.00 - 4.89 and BaA/Chr, from 0.60 - 17.63, indicate PAHs in the charcoal roasted foods were pyrogenic and derived from the combustion of foods. From the results, charcoal roasting of fish, meat, plantain and yam prepared by roadside vendors and commonly consumed in Port Harcourt, Nigeria contaminated the foods with PAHs.*

Keywords: *charcoal roasted foods, PAHs, fluoranthene, abundance, 4-6 ring HMW, Port Harcourt.*

1. Introduction

The knowledge of the harmful effects of polycyclic aromatic hydrocarbons (PAHs) has increased the concern about their presence in the environment [1], [2]. Two major sources of PAHs in the environment are petrogenic and pyrogenic. Petrogenic sources include raw oil, while pyrogenic are from the incomplete combustion organic materials such as petroleum fuels (gasoline, kerosene, diesel and lubricating oil), coal, wood, tires, plastics, asphalt, incinerators and electronic waste [3-5]. More than 100 different PAHs are known, but the United States Environmental Protection Agency (USEPA) has classified sixteen (16) as priority pollutants because they are toxic, mutagenic and carcinogenic in humans [6], [7]. This group of PAHs consist of two to six aromatic rings fused together e.g. naphthalene, anthracene, benzo[a]anthracene, and benzo(a)pyrene. PAHs are chemically stable, highly lipophilic and persist in the environment [8].

Food is one of the major routes by which humans are exposed to PAHs. PAHs in foods originate from environmental deposits or pyrolysis of organic substances like fats, carbohydrates and proteins which are at temperatures above 200°C. Cooking techniques such as frying, drying, grilling, smoking and roasting generate and increase the level of PAHs in foods [9-12]. Investigation of various grilled and smoked foods (meat, chicken and vegetables) showed the presence of 16 priority PAHs with phenanthrene having the highest mean concentration of $54.9\ \mu g\cdot kg^{-1}$, which accounts for 37.1% of the total PAHs [13]. It was observed that conditions such as the type of heat source, duration of grilling and fat content influenced PAHs formation in the foods. In milk and meat/fish based baby foods available on the Italian market, 14 PAHs were found to frequently occur and their average concentrations were higher than the permissible EU limits [14]. However, in polystyrene food contact materials low-ring PAHs were detected while the high-ring PAHs (>4 rings) were not found. Eight low-ring PAHs were detected with phenanthrene and naphthalene having the highest average concentrations which collectively accounted for over 80% of the Σ_8PAH total concentrations in all the samples [15]. The concentrations of 16 PAHs in baked ready-to-eat cake, sausage roll, meat pie, burger and bread hawked in Nigeria, showed that baked foods were mainly contaminated with 2-, 3-, and 4-ring PAHs [16]. This study is aimed at identifying PAHs and their distributions in some commonly consumed foods (fish, meat, plantain and yam) in Port Harcourt, Nigeria, prepared by charcoal roasting method.

2. Matherials and Methods

2.1. Description of sampling area

The location of sampling is Port Harcourt, situated in Rivers State, Southern Nigeria. Rivers State has tropical rain forest vegetation greatly blessed with aquatic and agricultural resources thus, the natives are predominantly fishers and farmers. The riverine communities are well-known for fishing, while the upland communities are noted for farming of livestock, and crops such as palm oil, yam, cassava, plantain, melon, banana and vegetables. Port Harcourt is a city in Rivers State and a commercial nerve center. Notable markets in the city include Mile 1, Mile 3, Rumuokoro and Oil mill.

2.2. Sample collection and preparation

Foods used for this study are considered as ready-to-eat delicacies and are commonly consumed in Port Harcourt, Rivers State. They include fish, meat, plantain and yam. The foods were obtained from the popular Mile 3 market in Obio/Akpor Local Government area (L.G.A) of Port Harcourt. The food samples were each divided into two sets. The first set of samples were sent to roadside vendors within the campus of the Rivers State University of Science and Technology (RSUST), Port Harcourt, who prepared the foods in their usual way for consumption by charcoal roasting method. The second set was not prepared (raw) to serve as the control. The surface and near surface layers of the charcoal roasted fish (CR-FH), plantain (CR-PN) and yam (CR-YM) were cut off from the bulk, leaving the inner most parts, while the charcoal roasted meat (CR-MT) was not cut. All the food samples (charcoal roasted and raw) were air-dried for 4 days, homogenized, labelled appropriately and taken to laboratory for analysis.

2.3. Sample extraction and clean up

Five (5) grams of each homogenized food sample was weighed out into a conical flask. 20 ml of hexane/dichloromethane (1:3 v/v) was measured out, poured into the conical flask, stirred, and agitated with a mechanical vibrator for 30 minutes for efficient extraction. The mixture was filtered and the filtrate concentrated by evaporation under a gentle stream of dry nitrogen in a fume cupboard. Clean up of the concentrated extracts was achieved on a glass chromatographic column (25cm x 1cm) packed with activated silica gel (mesh 100-200) and 0.5g of sodium sulphate to absorb any moisture. Hexane was poured onto the top of the column to elute the saturate fraction and dichloromethane poured to elute the aromatic hydrocarbons. The aromatic hydrocarbon fraction, which contains the PAHs, was concentrated in a fume cupboard under a gentle stream of nitrogen.

2.4. Polycyclic aromatic hydrocarbon (PAH) analysis

Analysis of the 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). One microlitre (1µL) of each cleaned up extract was introduced into the GC capillary column with the aid of a G4513A automatic liquid sampler (ALS) using the 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 OPEN LAB CDS Edition.

3. Results and Discussion

3.1. Distribution of PAHs in the charcoal roasted foods

Gas chromatographic (GC) analysis of the charcoal roasted food samples revealed the presence of PAHs, which were absent in the raw samples. The distributions of the PAHs identified in the charcoal roasted food samples; fish (CR-FH), meat (CR-MT), plantain (CR-PN) and yam (CR-YM), are shown in figures 1-4 respectively.

Total PAHs identified in the food samples were 11 in CR-FH, 14 in CR-MT, 11 in CR-PN and 13 in CR-YM. The PAHs identified in the food samples are: CR-FH, from anthracene to benzo[*g,h,i*]perylene; CR-MT, acenaphthylene, acenaphthene and from phenanthrene to benzo[*g,h,i*]perylene; CR-PN, anthracene to benzo[*g,h,i*]perylene and CR-YM, acenaphthene, fluorene and from anthracene to benzo[*g,h,i*]perylene (figures 1-4). This result indicate the charcoal roasted food with the most PAHs identified is meat (CR-MT), followed by yam (CR-YM), with fish (CR-FH) and plantain (CR-PN) having same number.

Profile of PAHs

Fluoranthene was observed to be the most prominent PAH in all the charcoal roasted food samples (figures 1-4). It is the most abundant PAH in CR-FH, CR-MT and CR-PN with concentrations of 113.6 µg/kg, 37.4 µg/kg and 39.8 µg/kg, which constitute 68.23%, 40.87% and 58.21% of total PAHs in the charcoal roasted food samples respectively.

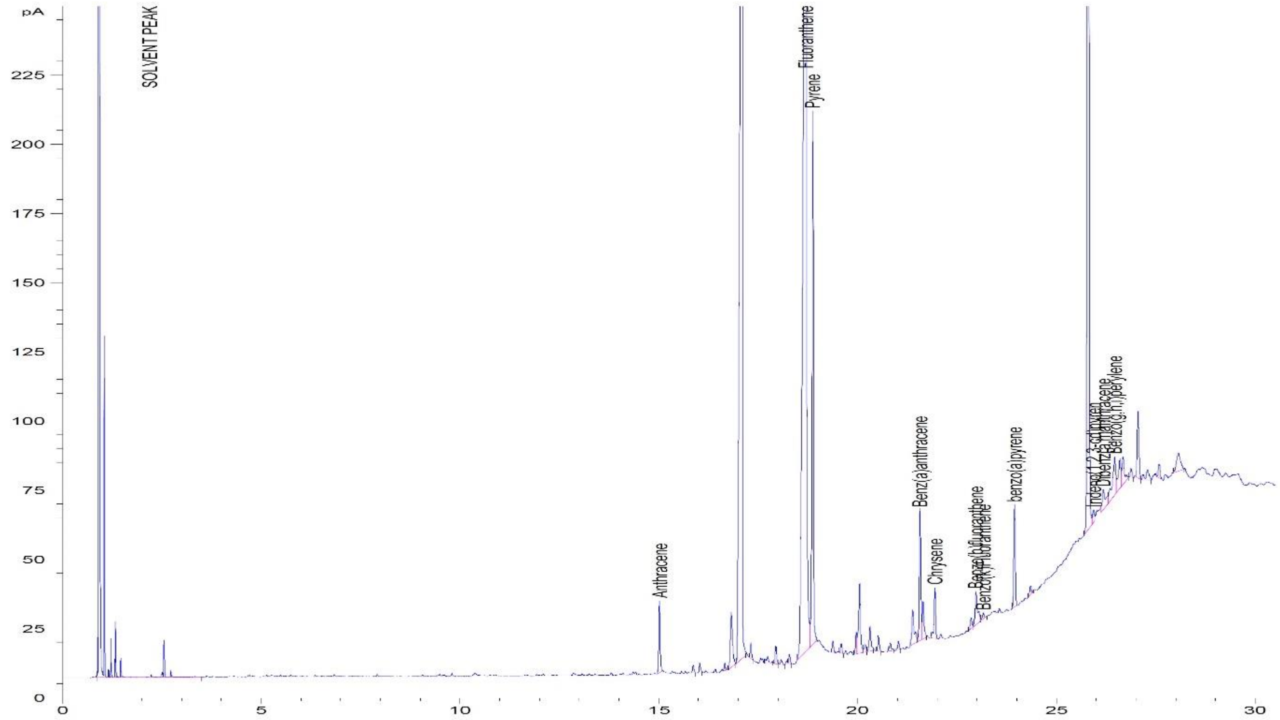

Fig. 1. Gas chromatogram showing the distribution of polycyclic aromatic hydrocarbons (PAHs) in charcoal roasted fish (CR-FH) sample.

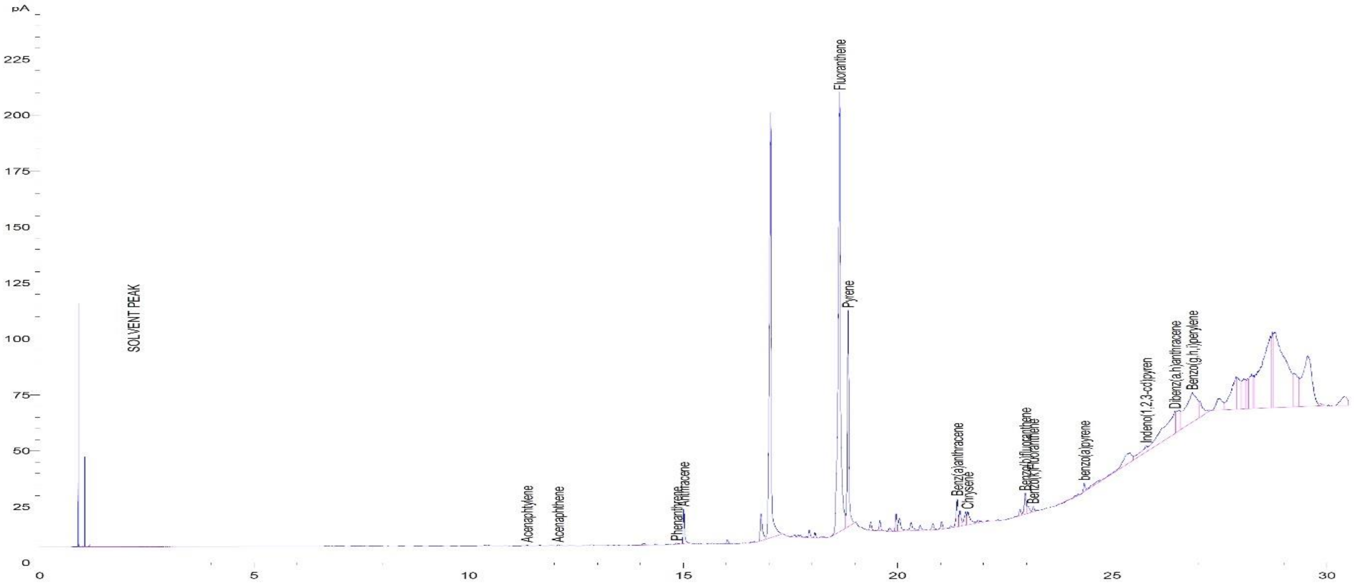

Fig. 2. Gas chromatogram showing the distribution of polycyclic aromatic hydrocarbons (PAHs) in charcoal roasted meat (CR-MT) sample.

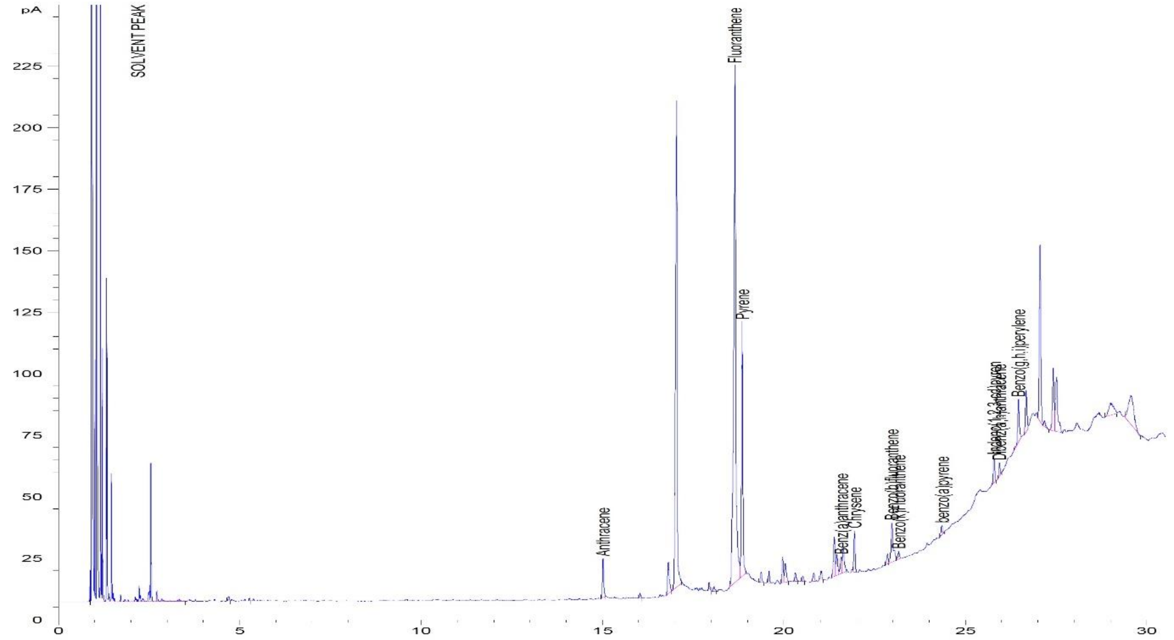

Fig. 3. Gas chromatogram showing the distribution of polycyclic aromatic hydrocarbons (PAHs) in charcoal roasted plantain (CR-PN) sample.

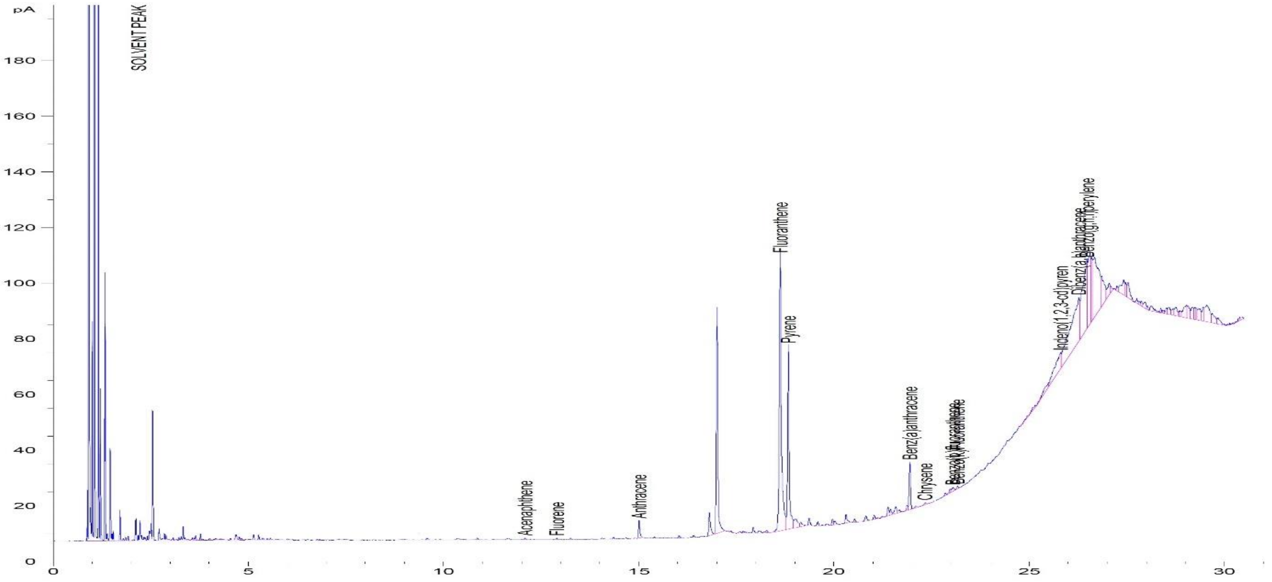

Fig. 4. Gas chromatogram showing the distribution of polycyclic aromatic hydrocarbons (PAHs) in charcoal roasted yam (CR-YM) sample.

In CR-YM, dibenzo[a,h]anthrancene was the most abundant PAH with a concentration of 19.4 µg/kg (27.52%) followed by fluoranthene with 17.8 µg/kg (25.36%). The total concentrations of PAHs in the charcoal roasted food samples are shown in the figure 5.

The total concentration of the 11 PAHs identified in CR-FH was 166.48 µg/kg, 14 PAHs identified in CR-MT was 91.46

µg/kg, 11 PAHs identified in CR-PN was 68.39 µg/kg and 13 PAHs identified in CR-YM was 70.36 µg/kg. The total PAH concentrations decreased in the order CR-FH > CR-MT > CR-YM > CR-PN. When organic substances in foods are in contact with flame, pyrolysis generates PAHs. But the highest concentrations of PAHs are linked to the pyrolysis of fats, which melts, drips onto the heat source and the PAHs generated deposits on the food being roasted as the smoke goes up [17]. Consequently, the total PAH concentration was highest in the charcoal roasted fish sample which is consistent with the pyrolysis of its fats and oil content.

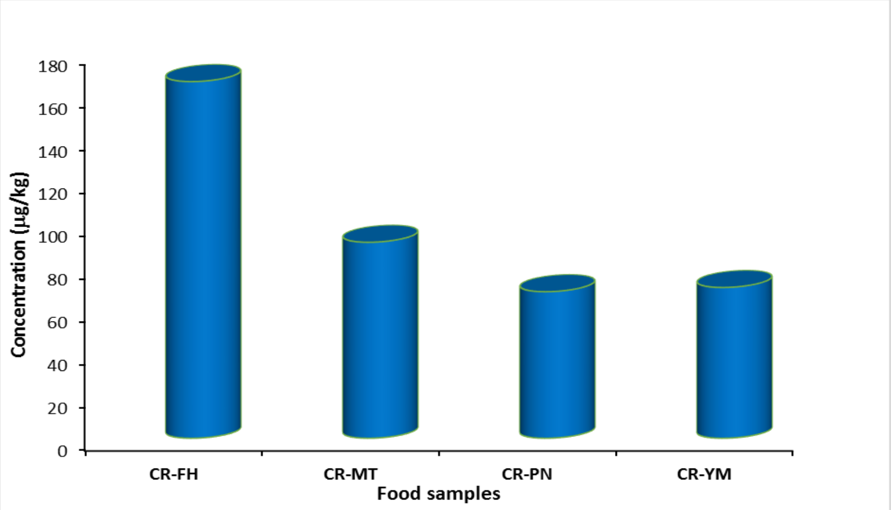

Fig. 5. Profiles of total PAH concentrations of in the charcoal roasted food samples.
CR-FH, charcoal roasted fish; CR-MT, charcoal roasted meat, CR-PN, charcoal roasted plantain; and CR-YM, charcoal roasted yam.

Source of PAHs in the charcoal roasted foods

PAHs derived from different sources have characteristic composition which is used for source identification and differentiation in environment forensic [18]. Compositions of PAHs dominated by the low molecular weight (LMW) 2-3 ring are usually of raw oil source with the high molecular weight (HMW) 4-6 ring being minor components, but dominant in products from combustion (pyrolysis) of organic materials [19],[20]. In CR-FH, the LMW 2-3 ring PAHs identified was anthracene; in CR-MT, acenaphthylene, acenaphthene, phenanthrene and anthracene; in CR-PN, anthracene and in CR-YM acenaphthene, fluorene and anthracene. However, ten (10) HMW 4-6 ring PAHs from fluoranthene to benzo[*g,h,i*]perylene were identified in CR-FH, CR-MT and CR-PN, with only benzo[*a*]pyrene absent in CR-YM. Total LMW PAH concentrations were 2.98 µg/kg, 2.08 µg/kg, 1.91 µg/kg and 0.88 µg/kg in CR-FH, CR-MT, CR-PN and CR-YM respectively. These LMW PAH concentrations were significantly lower than the total HMW concentrations of 163.50 µg/kg, 89.38 µg/kg, 66.48 µg/kg, and 69.48 µg/kg respectively. Abundance of LMW over HMW (>1) signifies a probable petrogenic (petroleum) origin for PAHs, while the abundance of HMW are generally considered to indicate combustion source [20]. The PAH concentrations in the charcoal roasted foods revealed the HMW 4-6 ring PAHs, with compositions of 98.21%, 97.72%, 97.21%, and 98.75% were considerably dominant over the LMW 2-3 ring PAHs, which were only minor components with compositions of 1.79%, 2.28%, 2.79% and 1.25% respectively. This indicates that PAHs in all the charcoal roasted foods were derived from combustion source.

Ratios of PAH isomers, phenanthrene (Phe) and anthracene (Ant), 3 rings; fluoranthene (Fth), pyrene (Pyr), benzo[*a*]anthracene (BaA) and chrysene (Chr), 4 rings, are employed as source type diagnostic parameters for environmental samples. Calculated diagnostic ratios of the PAH isomers are shown in the table 1.

Table 1.

Diagnostic ratios of polycyclic aromatic hydrocarbons employed for oil spill study

	LMW	HMW	Phe/Ant	Fth/Pyr	BaA/Chr
CR-FH	2.98	163.50	n.d.	4.89	2.59
CR-MT	2.08	89.38	0.05	3.11	1.38
CR-PN	1.91	66.48	n.d.	3.23	0.60
CR-YM	0.88	69.48	n.d.	2.00	17.63

n.d. - not determined

Phe/Ant ratios for CR-FH, CR-PN and CR-YM were not determined because of the absence of phenanthrene in these samples (figs. 1, 3 and 4), while the ratio for CR-MT was 0.05. Fth/Pyr ratio for the charcoal roasted food samples ranged from 2.00 - 4.89 and BaA/Chr ratio ranged from 0.60 – 17.63 (table 2). These results reveal Ant, Fth and BaA were dominant over their isomers, Phe, Pyr and Chr. Phe, Pyr and Chr are petroleum characteristic compounds derived from crude oil in which they are the dominant isomers, while Ant, Fth and BaA are preferentially generated during combustion of organic materials [21]. Phe/Ant ratio >10 suggest crude oil (petrogenic) source for PAHs, with degraded crude oils having ratios <10 and combustion (pyrogenic) products having ratios <1. Fth/Pyr ratios <1 suggest petrogenic origin and ratios >1 indicate pyrogenic processes, while BaA/Chr ratios for crude oils are < 0.02 with higher values indicating pyrogenic input from combustion of organic material [22].

From the ratios, the high abundance of the pyrogenic PAHs (Ant, Fth and BaA) in all the food samples indicated combustion process via charcoal roasting contaminated the foods with PAHs.

4. Conclusion

Gas chromatographic (GC) analysis of charcoal roasted fish (CR-FH), meat (CR-MT), plantain (CR-PN) and yam (CR-YM) commonly consumed in Port Harcourt, Rivers State, Nigeria, showed the presence of polycyclic aromatic hydrocarbons (PAHs) in foods. The United States Environmental Protection Agency (US EPA) priority analyzed PAHs in the charcoal roasted foods and 11 were identified in CR-FH, 14 in CR-MT, 11 in CR-PN and 13 in CR-YM. The total PAH concentrations decreased in the following order: CR-FH > CR-MT > CR-YM > CR-PN. Fluoranthene was observed to be the most prominent PAH in all the charcoal roasted food samples.

The compositions of the HMW 4-6 ring PAHs (≥ 97.21%) were considerably dominant over the LMW 2-3 rings PAHs (≤ 2.79%), which were only minor components. This indicates that PAHs in all the charcoal roasted food samples were derived from combustion source. PAH isomer ratios of Phe/Ant, Fth/Pyr and BaA/Chr, indicated pyrogenic source for PAHs from the combustion of foods.

5. References

[1].AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY (ATSDR), Toxicology profile for polycyclic aromatic hydrocarbons. Public Health Service, U. S. Department of health and human services, Atlanta, Georgia, (1995) Assessed from https//www.atsdr.cdc.gov [November 7, 2016.]

[2].BANSAL, V., KIM, K., Review of PAH contamination in food products and their health hazards Environment International 84: 26-38, (2015).

[3].KHALILI, N.R., SCHEFF, P.A., HOLSEN, T.M., PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmospheric and Environment*, 29: 533-542, (1995).

[4].HSU, W.T., LIU, M.C., HUNG, P.C., CHANG, S.H., CHANG, M.B., PAH emissions from coal combustion and waste incineration. *Journal of Hazardous Materials*, 318: 32-40, (2016).

[5].ONYEMA, M.O., OBASI, C.M., OKOYE, N.H. AND OSUJI, L.C., Distribution of Polycyclic Aromatic Hydrocarbons in Soils within Vicinity of an Electronic Waste Open Burning Workshop in Aba, South East Nigeria. *International Journal of Sciences: Basic and Applied Research (IJSBAR)*, 35(1): 286-293, (2017).

[6].UNITED STATE ENVIRONMENTAL PROTECTION AGENCY (US EPA), Polycyclic aromatic hydrocarbons (PAHs) - fact sheet. National Center for Environmental Assessment, Office of Research and Development, United State Environmental Protection Agency, Washington DC, (2008) Assessed from http://www.epa.gov/osw/hazard/wastemin/minimize/factshts/pahs.pdf [August 12, 2015].

[7].SILVA, B.O., ADETUNDE, O.T., OLUSEYI, T.O., OLAYINKA, K.O., ALO, B.I., Effects of the methods of smoking on the levels of polycyclic aromatic hydrocarbons (PAHs) in some locally consumed fishes in Nigeria. *African journal of foods science*, 5(7): 384-391, (2011).

[8].ABDEL-SHAFY, H.I., MANSOUR, M.S.M., A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, 25: 107-123, (2016).

[9].KNIZE M.G., SALMON C.P., PAIS P., FELTON J.S., Impact of processing on food safety. *Advances in Experimental Medicine and Biology*, 459: 179-193, (1999).

[10]. OGBUAGU, D.H., AYOADE A.A., Presence and levels of common polynuclear aromatic hydrocarbons (PAHs) in staple foods of Nigerians. *Food and Public Health*, 2(1): 50 – 54, (2012).

[11]. MANDA P., DANO D.S., EHILE E.S., KOFFI M., AMAN N., ASS Y.A., Evaluation of polycyclic aromatic hydrocarbons (PAHs) content in foods sold in Abobo market, Abidjan, Côted' Ivoire. *Journal of Toxicology and Enviromental Health Sciences*, 4(6): 99 - 105, (2012).

[12]. SINGH, L., VARSHNEY J.G., AGARWAL T., Polycyclic aromatic hydrocarbons' formation and occurrence in processed food. *Food Chemistry*, 199: 768-781, (2016).

[13]. ALOMIRAH, H., AL-ZENKI, S., AL-HOOTI, S., ZAGHLOUL, S., SAWAYA, W., AHMED, N., KANNAN, K., Concentrations and dietary exposure to polycyclic aromatic hydrocarbons (PAHs) from grilled and smoked foods. *Food Control*, 22(12): 2028-2035, (2011).

[14]. SANTONICOLA, S., ALBRIZIO, S., MURRU, N., FERRANTE, M.C., MERCOGLIANO, R., Study on the occurrence of polycyclic aromatic hydrocarbons in milk and meat/fish based baby food available in Italy. *Chemosphere*, 184: 467-472, (2017).

[15]. LI, S., NI, H., ZENG H., PAHs in polystyrene food contact materials: An unintended consequence. *Science of the Total Environment*, 609: 1126-1131, (2017).

[16]. IWEGBUE, C.M.A. Concentrations and Hazards of Polycyclic Aromatic Hydrocarbons in Hawked Baked Ready-to-Eat Foods in Nigeria. *Acta Alimentaria*, 45(2): 175-181, (2015).

[17]. CENTER FOR FOOD AND SAFETY (CFS), Chemical hazard evaluation. *Food and Environmental Hygiene*. 2004. Assessed from: https://www.cfs.gov.hk [January 31, 2017].

[18]. ZEMO, D.A. 2009. Use of Parent polycyclic aromatic hydrocarbon (PAH) proportions to attribute PAH sources in sediments: A case study from the Pacific Northwest *Environmental Forensics*, 10(3): 229-239.

[19]. CHEN, B., XUAN, X., ZHU, L., WANG, J., GAO, Y., YANG, K., SHEN, X., LOU, B. 2004. Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou city, China. *Water Resource*. 38: 3558–3568.

[20]. WANG, Z. 2009. Oil weathering and chemical fingerprinting of spilled or discharged petroleum in the environment. *IOC/WESTPAC Workshop, Qingdao, China.*

[21]. PETERS, K., WALTERS, C., MOLDOWAN, J., The biomarker guide: biomarkers and isotopes in petroleum systems and earth history. Vol. 2, 2nd edition, Cambridge university press, New York, (2005).

[22]. WANG, Z., FINGAS, M., PAGE, D.S., Oil spill identification - a review. *Journal of Chromatography. A*, 843: 369 - 411, (1999).