Polycyclic Aromatic Hydrocarbon Composition and Source in Food Snacks in University Community, Nigeria

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ABSTRACT
This study was carried out to assess PAH composition and source in raw and roasted food - Herring, Scubia and Sabida and plantain sold and consumed in Federal University of Petroleum Resources, Nigeria. The identification and concentration of PAHs were carried out by gas chromatography coupled with FID with the aid of 17 PAH standards. A total of seventeen PAHs were detected in the roasted herries and only 5 were detected in the raw herries, 8 detected in the roasted sarbida and 10 detected in the raw sarbida while 8 PAH was detected in the roasted scumbia and only 6 in the raw scambia. In the plantain sample, 10 PAHs was detected in the roasted plantain and only 6 detected in the raw plantain.

The levels of BaP found in roasted sarbida, herries and plantain with concentrations 0.016mg/kg, 0.023mg/kg and 0.017 mg/kg were far higher than the recommended maximum permissible concentration of 5.0 μg/ kg or 0.005 mg/kg. Source diagenesis of PAHs detected in the roasted fish samples reveal pyrogenic and combustion origin.

Key Words: Roasted fish, Plantain, benzo(a)Pyrene, Gas Chromatography

INTRODUCTION
Polycyclic aromatic hydrocarbons (PAHs), also known as the polynuclear aromatic hydrocarbons constitute a large class of organic compounds, containing 2 or more fused aromatic rings made up of carbon and hydrogen atoms. Food is one source of PAH [1]. When food particularly meat products and fish is smoked, roasted, barbecued, or grilled; PAHs are formed as a result of incomplete combustion or thermal decomposition of the organic materials [2]. Pyrolysis of the fats in the meat/fish generates PAH that become deposited on the meat/fish. PAH production by cooking over charcoal (barbecued, grilled) is a function of both the fat content of the meat/fish and the proximity of the food to the heat source [3, 4]. Several analyses of charcoal roasted/grilled common food items have proven the presence of PAHs such as benzo[a]pyrene, anthracene, chrysene, benzo[a]anthracene, indeno[1,2,3-c,d]pyrene [5, 6].

PAHs are produced in food when the fat from meat, poultry or fish drips onto hot coals or stones resulting in smoke and flare-ups which are carried back onto the grilled food. The amount and types of PAHs produced depend on the type of food, cooking method, temperature and cooking time. PAHs which formed in processed and cooked foods are very well known ecotoxictants (genotoxic substance) that are harmful to health. In mammalian cells PAH undergoes metabolic activation to diol epoxides that binds covalently to cellular macromolecules, including DNA, thereby causing errors in DNA replication and mutation that initiates the carcinogenic process. A number of PAHs have been found to have carcinogenic and mutagenic effects while some of them may act as synergists.

One of the major routes of human exposure to PAHs in non-smoking people is food. PAHs are also found in foods as a result of certain industrial food processing methods such as smoke curing, broiling, roasting and grilling over open fires or charcoal which permits the direct contact between food and combustion products [7]. Natural crude oil and coal deposits contain significant amounts of PAHs, arising from chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons. They are also found in processed fossil fuels, tar and various edible oils [8]. In a study evaluating the genotoxic and carcinogenic risks associated with the consumption of repeatedly heated coconut oil (RCO), one of the commonly consumed cooking and frying medium, it was concluded that dietary consumption of RCO can cause a genotoxic and preneoplastic change in the liver [9].

The detail mechanism of PAHs formation in food processing or cooking is still a subject of scientific investigation [10]. However, it is generally considered that incomplete combustion is involved [11, 12, 3]. Literature information has it that the formation of PAHs occurs through pyrolysis of fat at temperatures...
of above 200°C [10], and is favored at a temperature range of 500-900°C, especially above 700°C [11]. Knize et al., [13], also reported that pyrolysis of other organic matters such as proteins and carbohydrates might be involved in the formation of PAHs.

The carcinogenic nature of some PAHs is well established and their occurrence in foods is not a subject of debate. Methods of preparation or cooking have also been established to be sources of some PAHs found in cooked foods. Arising from these, there has been an increase in public interest in the occurrence of PAHs in both cooked and uncooked foods.

In a study carried out by Vaessen et al., [14] showed that the quality and quantity of PAHs produced are closely related to the reaction conditions, temperature and amount of air. A number of PAHs are carcinogenic and/or mutagenic, which may have a significant contribution to human cancer. Toxicity tends to increase with the number of rings. For instance, PAHs containing four fused rings, such as benzo(a)anthracene and chrysene, are weakly carcinogenic. Five- or six-fused ring polycyclic hydrocarbons, such as benzo(b)fluoranthene, benzo(a)-pyrene, and indo(1,2,3-cd)pyrene are very potent carcinogens. Researchers has it that high consumption of fried, or barbecued food (meats) was associated with increased risks of colorectal [15], pancreatic [16], and prostate [17] cancer.

There are many snacks sold in Nigeria including university communities, which are prepared through direct or indirect exposure to fire from biomass materials. The Federal University of Petroleum Resources Effurun (FUPRE) is Nigerian premier and only specialized university in the oil and gas sector. The university is at its infancy stage (barely seven years old) and as a result there is near absence of decent eateries and restaurants. Besides that, the university is located in the suburb of Effurun City, making it difficult for members of the university community to access eateries and restaurants in the City. Therefore, the preferred eatery is the make shift “roasted fish and plantain joint” which both members of staff and students patronize. Given the public health significance of PAHs, this study investigated the composition and source of polycyclic aromatic hydrocarbon present in roasted fish and plantain sold within the university community.

MATERIALS AND METHOD

Collection of Food items

Samples of frozen and roasted Herring, Scubia and Sabida and plantain (Musa paradiasa) used for the study were obtained from the only roasted fish and plantain sales spot in Federal University of Petroleum Resources, Effurun, Nigeria.

Extraction of Food Samples for PAH Determination

2g of each of the homogenized food samples was thoroughly mixed with anhydrous Na₂SO₄ salt to absorb moisture and then extracted with unspecified quantity of analytical grade dichloromethane (CH₂Cl₂). The dichloromethane extract was cleaned up by passing through a column packed with anhydrous Na₂SO₄ salt. The resulting extract was concentrated on a rotary evaporator to give an oily residue; which was again dissolved in 1ml CH₂Cl₂ and 1µL was injected into the GC for analysis. The gas chromatography used was Hewlett Packard 5890 series II, coupled with flame ionization detector (FID) (Hewlett Packard, Wilmington, DE, USA). The identification of PAHs was based on comparison of the retention times of the peaks with those obtained from standard mixture of PAHs (standards supplied by instrument manufacturer). Quantification was based on external calibrations curves prepared from the standard solution of each of the PAHs.

RESULTS AND DISCUSSION

The results of analysis of PAH from the various samples are as presented in Tables 1 and figure 1 below:

In Table 1, the total PAH concentrations (mg/Kg) in fish samples are as follows. Sarbida recorded 0.667mg/Kg and 0.822mg/Kg for raw and roasted respectively while that of raw and roasted Scumbia was 0.180mg/Kg and 0.448mg/Kg respectively. Herries raw fish sample recorded 0.278mg/Kg while that of roasted sample recorded 0.799mg/Kg.

PAH Distribution

In the fish samples, 17 PAHs was detected in the roasted herries and only 5 was detected in the raw herries, 8 detected in the roasted sarbida and 10 detected in the raw sarbida, while 8 PAH was detected in the roasted scumbia and only 6 in the raw scumbia. In the plantain sample, 10 PAHs was detected in the roasted plantain and only 6 detected in the raw plantain.

PAH Composition

Analysis showed that Naphthalene and 2- methyl naphthalene, were less than 0.001mg/kg in both fish and plantain samples except for the roasted herries fish. Acenaphthalene and Acenaphthene were also less than 0.001mg/kg in the sarbida, scumbia fish and the roasted plantain. These PAHs are classified as low molecular weight PAHs (LMW PAHs), and they are relatively unstable. The non-detection of LMW PAHs in
these samples may be due to instrument sensitivity or their relative low stability. Thermal decomposition of this group of PAHs is a possibility because the samples were exposed to direct heat during grilling [2]. Similar result was obtained in the levels of Polycyclic Aromatic Hydrocarbons in Grilled/Roasted Maize and Plantain Sold in Ogbomosho, Nigeria [18]. In a previous research work carried out at Amassoma, Nigeria, 15 PAHs were detected in reasonable quantity in the roasted fish and only 3 were found in suya beef; but none was detected in the raw food items and roasted plantain [19]. This is in agreement with other research work that raw foods do not normally contain high levels of PAHs but they are formed during processing, roasting, baking, smoking or frying [20, 21, 18]. However appreciable amounts of PAHs were observed in both raw and roasted plantain in this study which is in agreement with a recent study carried out by [22].

As shown in Table 1, the sum of all PAHs concentration present in the roasted fish which include herries, sarbida, and scumbia ranged from 0.009-0.443mg/kg, 0.003-0.443mg/kg and 0.009-0.233mg/kg respectively. In Fig.1 the concentration of the various PAH compounds are widely distributed among the high molecular weight PAH and the low molecular weight PAH. In the roasted plantain sample the highest PAH concentration is 0.051mg/kg which is chrysene that happens to be among low molecular weight PAH while the raw plantain has its highest PAH concentration as indeno (1,2,3) pyrene (0.134mg/kg) which is a high molecular weight PAH. The raw and roasted scumbia fish had its highest PAH concentration as 0.102mg/kg and 0.233mg/kg respectively which is benzo (k) fluoranthene; a high molecular weight PAH. The roasted sarbida fish and raw sarbida fish had fluoranthene (0.433mg/kg) has its highest PAHs concentration which is detected to be a low molecular weight PAH. In both raw and roasted herries fish, benzo(g,h,i)perylene (0.059mg/kg) and dibenzo(a,h)anthracene (0.175mg/kg) were recorded as the highest PAHs concentrations respectively. Both PAHs are high molecular weight compounds. Toxicity tends to increase with the number of rings. PAHs containing four fused rings, such as benzo (a)anthracene and chrysene, are weakly carcinogenic. Five- or six fused ring polycyclic hydrocarbons, such as benzo(b)fluoranthene, benzo(a-) pyrene, and indo(1,2,3-cd) pyrene are very potent carcinogens [18]. However, from these results high molecular weight PAH compounds recorded highest concentration in both roasted and raw fish sample as well as raw plantain while in the roasted plantain low molecular weight PAH compound dominates. Reports from previous publications have revealed that PAHs with higher molecular weight (HMW) are more carcinogenic and mutagenic than the lower molecular weight (LMW) PAHs [23, 24].

The sum average PAHs concentration present in the raw fish (1.393mg/kg) is lower than that of the roasted fish (1.801mg/kg) samples. The observed higher levels in the roasted fish samples may be attributed to the strong correlation that exists between fish lipids and PAH compounds, and also the close proximity of the fish to the heat source. Akpan et al., [25] reported that strong correlation exists between fish lipids and PAH compounds; since PAH compounds are stored in fatty fish tissue. The sum average PAHs concentration level present in the roasted plantain, 0.202mg/kg is higher than the raw plantain 0.155mg/kg as a result of the fat content present in the plantain and its proximity to the heat source. High levels of PAHs have been reported to be associated with the dark colorations in intensively heated products. Several analyses of charcoal roasted/grilled common food items have proven the presence of PAH such as benzo(a)pyrene, anthracene, chrysene, benzo(a)anthracene, and indeno(1,2,3-c,d)pyrene [26, 25, 27, 5].

In this study, the sum of the average amounts of the low molecular weight PAHs (those containing 2 to 4 aromatic rings) such as naphthalene, acenaphthene, and pyrene, were found higher (1.424mg/kg) than the high molecular weight PAHs (0.347mg/Kg ), those having 4 to 6 aromatic rings such as benzo(a)anthracene, benzo(a)pyrene [BaP], indeno(1,2,3,c,d)pyrene in roasted fish samples(scumbia, sarbida, herries). However, in the raw fish samples, the sum average amount of the low molecular weight PAHs (2-4 aromatic rings) was found lower (0.538mg/kg) than the high molecular weight PAHs(0.585mg/kg). Similar results were obtained by Borokovcovova et al., [28], who determine the levels of PAHs in samples of the food basket of the Czech Republic. In the study, the sum average amount of the low molecular weight PAHs (2-4 aromatic rings) were found lower (0.098mg/kg) than high molecular weight PAHs (0.104mg/kg) in the roasted plantain. Similarly, the sum average amount of the low molecular weight PAHs (2-4 aromatic rings) were found (0.01mg/kg) lower than the high molecular weight PAHs (0.145mg/kg) in the raw plantain.

Reports from previous publications have revealed that PAHs with higher molecular weight (HMW) are more carcinogenic than the lower molecular weight (LMW) PAHs [23, 24]. In this study, the HMW carcinogenic and LMW PAHs constitute about 16.29% and 66.88% of the total PAH in the roasted fish, 52% and 47.82% of the total PAH in the raw fish, 51.48% and 48.51% of the total PAH in the roasted plantain, 93.55% and 6.45% of the total PAH in the raw plantain respectively. In roasted fish, 1.94% and
29.16% was accounted to contain benzo (a) pyrene in the sarbida and herries respectively while 8.41% was accounted to be present in the roasted plantain sample. Benzo(a)pyrene was not detected in roasted scumbia and the raw fish and plantain samples. The levels of BaP found in roasted sarbida, herries and plantain with concentrations 0.016mg/kg, 0.023mg/kg and 0.017 mg/kg were far higher than the recommended maximum permissible concentration of 5.0 μg/kg or 0.005 mg/kg fixed for BaP in smoked meat, fish and smoked meat and fishery products [29]. Therefore the observed %BaP recorded in both the roasted sarbida and herries may illicit carcinogenic effect on humans. In a related study, Akpambang et al., [30] reported BaP at levels ranging from 2.4 to 31.2 μg/kg wet weights in smoked fish and meat samples. Benzo(a)pyrene is the most studied PAHs, and it is often used as a marker for PAHs in foods. According to EU Scientific Committee on Food [10], BaP can be used as an indicator of occurrence, concentration and effect of the carcinogenic HMW PAHs in foods.

**SOURCES OF PAHs DETECTED IN SAMPLES**

The Ratios of Fluoranthene (Fla) to Pyrene (Pyr) are often used to verify the sources of the PAHs detected in the fish samples. Ratio of Fluoranthene to pyrene greater than one (Fla/Pyr> 1) is attributed to be a Pyrogenic source while Fla/Pyr<1 is attributed to Petrogenic source [31]. Similarly, ratio of Phenanthrene (Ph) to Anthracene (An) is also used to verify the sources of PAHs detected in food samples. Ph/An<10 (is attributed to a combustion source), Ph/An>10 (is attributed to petrogenic source) [32]. In this study, the ratio of Fla/Pyr obtained from the roasted fish are in the range of 2.97- 8.054. This suggests that the PAHs detected from the roasted fish originated from roasting process (pyrogenic sources). The ratio of Ph/An obtained from plantain samples are <0.001. This suggests that the PAHs were originated from combustion source.

**Health Implications**

Ziegler [32] reported that eating a charcoal-broiled food may expose one to the same quantity of PAHs as one would receive from smoking 600 cigarettes. Similarly, epidemiological studies carried out by Bababunmi et al., (1982), Fritz and Soos (1980), Emerole (1980) and Kazerooni et al., [33, 34, 35, 4] indicated a statistical correlation between the increased occurrence of cancer of the intestinal tract and frequent intake of roasted food. Health effects from chronic or long-term exposure to PAHs may include catactas, kidney and liver damage and jaundice. Repeated contact with skin may induce redness and skin inflammation. Naphthalene, a specific PAH, can cause the breakdown of red blood cells if inhaled or ingested in large amounts. Alonge, [24] reported that PAHs are common and may constitute health hazards in Nigeria. The roasted fish and roasted plantain as presently consumed by the university community (Federal University of Petroleum Resources Effurun, Nigeria) may therefore create high health risk.

**Table 1: PAH concentration in fish and plantain samples**

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>RSF</th>
<th>ROSF</th>
<th>RSCF</th>
<th>ROSCF</th>
<th>RHF</th>
<th>ROHF</th>
<th>RPT</th>
<th>ROPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.009</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.019</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.003</td>
<td>0.009</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>0.013</td>
<td>0.002</td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.010</td>
<td>0.019</td>
<td>0.011</td>
<td>0.016</td>
<td>&lt;0.001</td>
<td>0.014</td>
<td>&lt;0.001</td>
<td>0.010</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.006</td>
<td>0.003</td>
<td>&lt;0.001</td>
<td>0.009</td>
<td>&lt;0.001</td>
<td>0.009</td>
<td>0.001</td>
<td>0.015</td>
</tr>
<tr>
<td>Anthracene</td>
<td>&lt;0.001</td>
<td>0.016</td>
<td>0.012</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.014</td>
<td>0.004</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Fluoranthrene</td>
<td>0.418</td>
<td>0.433</td>
<td>&lt;0.001</td>
<td>0.107</td>
<td>&lt;0.001</td>
<td>0.443</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.079</td>
<td>&lt;0.001</td>
<td>0.014</td>
<td>0.036</td>
<td>&lt;0.001</td>
<td>0.055</td>
<td>&lt;0.001</td>
<td>0.022</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>0.043</td>
<td>&lt;0.001</td>
<td>0.012</td>
<td>0.014</td>
<td>0.086</td>
<td>0.042</td>
<td>0.011</td>
<td>0.029</td>
</tr>
<tr>
<td>Cryene</td>
<td>&lt;0.001</td>
<td>0.294</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.007</td>
<td>&lt;0.001</td>
<td>0.051</td>
</tr>
<tr>
<td>Benzo(b)flouranthrene</td>
<td>0.035</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.012</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>&lt;0.001</td>
<td>0.016</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.023</td>
<td>&lt;0.001</td>
<td>0.017</td>
</tr>
<tr>
<td>Benzo(k)fluoranthrene</td>
<td>0.020</td>
<td>0.012</td>
<td>0.102</td>
<td>0.233</td>
<td>&lt;0.001</td>
<td>0.009</td>
<td>&lt;0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>Indeno(1,2,3)pyrene</td>
<td>0.005</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.007</td>
<td>&lt;0.001</td>
<td>0.016</td>
<td>0.134</td>
<td>0.015</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>0.041</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.175</td>
<td>0.016</td>
<td>&lt;0.001</td>
<td>0.012</td>
</tr>
<tr>
<td>Benzo(g,h,i)pyrene</td>
<td>0.010</td>
<td>0.029</td>
<td>0.029</td>
<td>0.026</td>
<td>0.013</td>
<td>0.059</td>
<td>&lt;0.001</td>
<td>0.024</td>
</tr>
<tr>
<td>Total PAH (mg/kg)</td>
<td>0.667</td>
<td>0.822</td>
<td>0.180</td>
<td>0.448</td>
<td>0.278</td>
<td>0.799</td>
<td>0.155</td>
<td>0.202</td>
</tr>
</tbody>
</table>

Roasted Herring Fish (ROHF), Raw Herring Fish (RHF), Roasted Scubia Fish (ROSCF), Raw Scubia Fish (RSCF), Roasted Sabida Fish (ROSF), Raw Sabida Fish(RSF), Roasted Plantain(ROPT) and Raw Plantain(RPT).
CONCLUSION
This study was carried out to evaluate polycyclic aromatic hydrocarbon composition and source in roasted fish and plantain sold in Africa’s premier petroleum university - Federal University of Petroleum Resources, Effurun, Nigeria. The results reveal that levels of PAHs in the food snacks sold in the university exceeded permissible limits and therefore may create high health risk.

REFERENCES


