African Journal of Agriculture and Food Science
ISSN: 2689-5331
Volume 5, Issue 2, 2022 (pp. 24-31)
www.abjournals.org

MAPPING OF FUEL WOOD TYPES USED IN SMOKING FISH IN RELATION TO OCCURRENCE OF PAHs IN SMOKED FISH IN NIGERIA

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Cite this article:

Whenu O.O., Akintola S.L., Ajibade M.A. (2022), Mapping of Fuel Wood Types Used in Smoking Fish in Relation to Occurrence of PAHs in Smoked Fish in Nigeria. African Journal of Agriculture and Food Science 5(2), 24-31. DOI: 10.52589/AJAFS-AVRIFSV2.

Manuscript History

Received: 5 April 2022

Accepted: 20 April 2022

Published: 19 May 2022

ABSTRACT: *Polycyclic aromatic hydrocarbons (PAHs) are organic contaminants present in fuel woods which are hazardous to human health. The aim of the study is to determine the level of PAHs present in fuel woods used for smoking fish in Nigeria. Samples of fuels collected all over Nigeria were categorized into Hard, Soft and Starters. Four samples were extracted and analyzed using gas chromatography attached with a mass spectrophotometer. The result showed that all the fuelwoods have PAHs below maximum permissible level. Teak wood has high level of PAHs in Naphthalene 0.048 ± 0.000132, Acenaphthylene 0.0013 ± 0.00005, Fluorene 0.0105 ± SE-05, Pyrene 0.0105 ± SE-05, Fluoranthene 0.0119 ± 0.0001, Triphenylene 0.0011 ± 1E-04, Benz(a)anthrax 0.0008 ± SE-05. The order of increase of hazard (PAHs) for the fuel woods are Tectona spp > Azadirachta spp > Mangifera spp > Anacardium spp. When the four fuel woods were used to smoke the same fresh Clarias gariepinus with the same equipment, it was revealed that all were having a high level of PAHs above maximum permissible limit. Fish smoked with Anacardium spp of wood has the highest level of PAHs. Therefore, excess use of Anacardium spp of woods should be averted when smoking fish because of the lipophilic nature of PAHs.*

KEYWORDS: PAHs, lipophilic, *Anacadium* spp., Conventional, *Clarias gariepinus*.

Article DOI: 10.52589/AJAFS-AVRIFSV2
DOI URL: https://doi.org/10.52589/AJAFS-AVRIFSV2

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INTRODUCTION

One of the commonest and conventional methods of preserving fish in Africa is smoking with firewood, especially in Nigeria (Hassan *et al.*, 2013; Dalgaard *et al*., 2006). Wholesomeness and quality of smoked fish is very important. It is when people eat wholesome smoked fish that consumers can have good health. Fuel wood smoke contains a lot of carcinogenic compounds on food (Hassan *et al*., 2013). WHO (1989) and USEPA (1989) reported that PAHs are organic compounds formed as a result of burning fuel woods used for smoking fish. In Nigeria, these contaminants are believed to be responsible for most of the hazardous chemicals in smoked fish, hence causing a lot of diseases to human health, especially the consumers. The presence of these contaminants in the fuel woods whether low or high has impact on the health of consumers (Gram *et al.*, 1987). It is believed that incomplete combustion of fuel woods is known to lead to the production of these PAHs (Ndu, 2006). Our environment is already polluted and most of our soils in which plants grow and even plants themselves are full of causative agents of PAHs, which are responsible for their presence in the fuel woods because the trees which give us fuel woods get their nutrients from the soil.

The PAHs accumulate in the soil (Nwabeze *et al.*, 2013; Seisay *et al.*, 1997) as the solubility decreases with increase in molecular weights (Adekoya, 2004). From this stage, the nutrients are absorbed into the body system of the trees and consequently accumulate and become harmful before transforming into toxic materials in the fuel woods. Differences in smoking methods and processes, wood species, temperature of pyrolysis and even duration before evenly dried correspond with the number of PAHs available in each smoked fish product (Shimang, 2005). Wood species vary with their chemical composition, hence emit different PAHs (Otubusin, 2011). Among the latest equipment used for PAHs analysis are HPLC, GC/MS and they are effective in giving accurate results.

Smoked fish can also be exposed to PAHs through roadside pollution where fishes are sold. Other sources include industrial emissions nearest to production sites, cigarette smoking amongst fish sellers, and automobile discharges during carriage to the final consumers. However, precautions could limit the presence of PAHs in smoked fish by educating fish sellers to sell their products in closed shops, closed environments, or enclosed markets but the root cause of the PAHs may have started from the fuel woods used for smoking it. The International Agency for Research on Cancer (IARC) and the United Nations Environmental Protection Agency (USEPA) reported that most of the PAHs especially Pyrene, Naphthalene and Benzo-e-pyrene are possibly carcinogenic to humans since research showed evidence of cancer in animals introduced with these chemicals (Caddy, 1997; Adekoya *et al*., 2004). Animals inhaling these contaminants have developed blood, kidney and liver abnormalities (Osman *et al*., 2001). All contaminants are rich in PAHs (Huss, 1988); therefore, whatever we plant in the soil is prone to absorption and enrichment of these contaminants which eventually will affect the final consumers. Hence, nothing planted in the soil is free/safe from these contaminants (Edward *et al*., 2009). Research on soils revealed that bioremediation is an approach recently taken to remediate contaminated land through in situ and ex situ methods (Li *et al*., 2004; Lee *et al*., 2003). Therefore, the aim of the study is to determine the level of PAHs present in fuel woods used for smoking fish in Nigeria.

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MATERIALS AND METHODS

The PAHs used for standards are from reputable companies in Nigeria with 98% purity, purchased from SIGMA (Seelze, Germany). All the organic solvents used like Hexane and Acetone used for extractions and clean up were equally purchased by SIGMA/ALDRICH. Silica gel, used in column chromatography, was supplied from Germany. They are of HPLC analytical grade.

Sampling Sites: Fuel wood samples were collected from different parts of each of the six geopolitical zones of the federation, especially where small-scale fish smoking business is being practiced. The study areas comprise predominantly small scale smoked fish producers and smoked fish mongers (Figure 1). Samples were taken to the Biochemistry laboratory, Landmark University, Omu Aran, Kwara State of Nigeria for proper identification, categorization and analysis of PAHs.

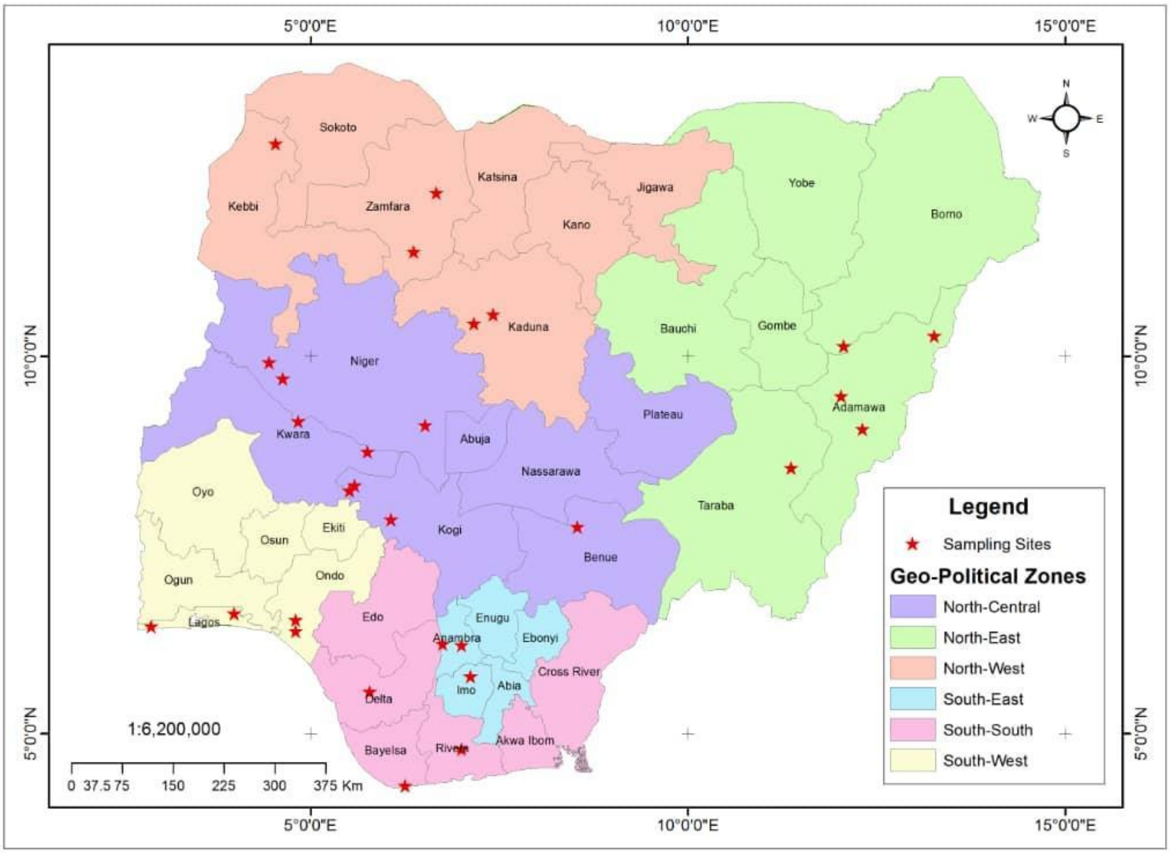

Figure 1: Map of the 6 geopolitical zones of Nigeria showing the sites where samples were collected

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Identification

Useful plants of West Africa by Burkili (1985) was used to identify all the fuel woods one after the other up to genus and species levels while *Clarias gariepinus* was the only common smoked fish among the smoked fish collected.

Categorization

The woods were first categorized on a zonal basis because they were so many (arranged according to how they were collected from each zone). Frequency distribution tool was used to know the commonest ones in each zone and only four species common to all the six zones were chosen. These are A*zadirachta* species, *Anacadium* species, *Tectona* species and *Mangifera* species. All these fuel woods were first turned into powder form before analysis using GC/MS equipment to know the presence and level of PAHs in each of them. 10gm of each sample was put in an extraction flask and organic solvent chloroform/methanol was added to make half of the flask of the soxhlet extractor and was extracted seven times for 24 hours. Each sample was treated likewise before readings.

RESULTS

Four samples that cut across the six zones were chosen and PAHs in them were analyzed.

AN *Anacadium* spp. (Cashew)

AZ *Azadirachta* .spp. (Neem)

TE *Tectona* spp. (Teak)

MA *Mangifera* spp. (Mango)

Figure 2 shows the level of PAHs in the four raw fuel woods (Teak, Neem, Mango and Cashew). Teak contained the highest level of PAHs while Mango had the least PAHs content. Among all the PAHs detected in the fuel woods, Acenaphthene had the highest level which was the only one found in Teak. Specifically, Teak contained the peak level and Acenaphthene (0.0176ug/l,), the peak PAHs in Mango was Acenaphthylene (0.00283ug/l), Cashew contained its highest PAHs in Benz(a)anthracene (0.00225ug/l) while the maximum PAH in Neem was Acenaphthylene (0.0013ug/l). On the other hand, Acenaphthene, Fluoranthene, Fluoerene, Pyrene and Triphenylene were detected in Mango, Neem, and Cashew. More so, Acenaphthalene and Triphenylene were not detected in Cashew and Mango respectively.

After *Clarias gariepinus* were smoked with Mango (A1), Cashew (B2), (C3) and (D4) (Figure 2), the results showed that *Clarias gariepinus* smoked with Cashew contained Benzo (c,g,h,j), perylene (82ug/l), Acenaphthene (27.88ug/l), Acenaphthylene (4ug/l), Chrysene (4.0ug/l), Benzo(b)fluoranthene (700ug/l) and Benzo(k)fluoranthene (5ug/l). *Clarias gariepinus* smoked with Mango (A1) contained Benzo(g,h,i)perylene=(70ug/l and Chrysene (12ug/l). Tectonal spp=(C3) contained Acenaphthylene (5.45ug/l), Acenaphthene (20ug/l) and Benzo(b)fluoranthene (7.68ug/l). On the other hand, *Clarias gariepinus* smoked with *Azadirachta* spp. (D4) contained Naphthalene (5.57ug/l), Acenaphthalene (4ug/l),

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Acenaphthene (25ug/l), Benzo(b)fluoranthene (6ug/l) and Benzo(a)pyrene (25.98ug/l), as shown in Figure 2 below.

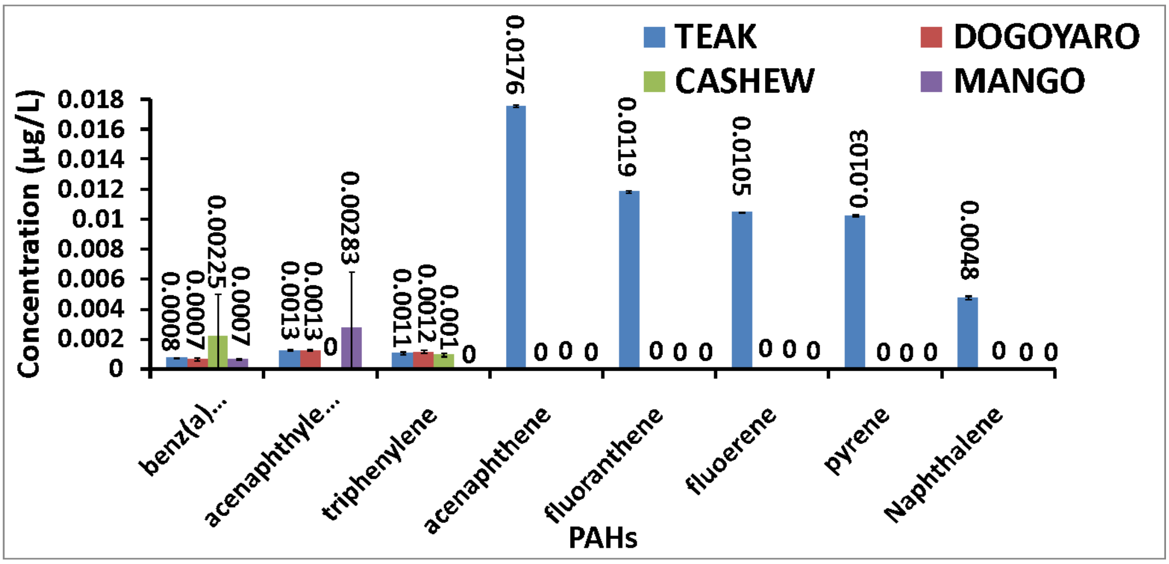

Figure 2: PAHs of selected four fuel woods before using them for smoking fish.

After smoking species of *Clarias gariepinus with* the four species of fuel woods, the results of PAHs recorded in these smoked fish were obtained as shown below:

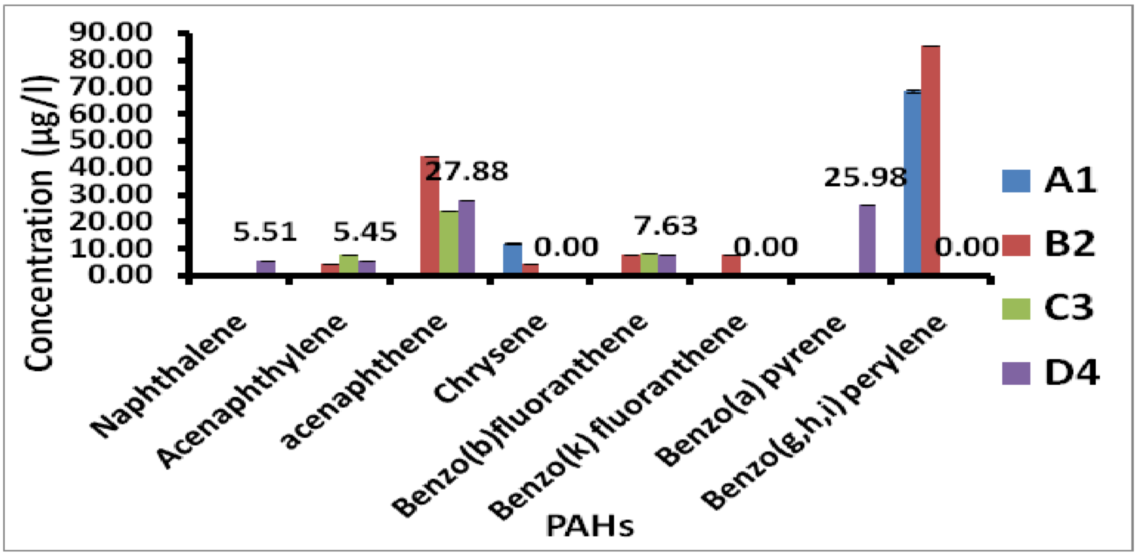

Figure 3: Shows the level of PAHs in *Clarias gariepinus* smoked with *Mangifera* spp *(A1), Anacadium* spp (B2)

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DISCUSSION

Different fuel woods emit different concentrations and levels of PAHs which shows that PAHs are found in the four selected common fuel woods before using them for smoking fish. The PAHs detected were in minute level in relation to USEPA 1989 maximum permissible limit for human health. Acenaphthylene is present in all the woods. Triphenylene is common to *Anacadium* spp, *Azadirachta* spp. and *Tectona* spp, while Benz(a)Anthracene is also common to *Anacadium* spp and *Azadirachta* spp. Acenaphthylene, Fluorene, Pyrene, Fluoranthene and Ben(a)anthracene are common to *Tectona* spp only.

In figure 3, the PAHs level of Pyrene is higher, so also Benzo-e-pyrene after analysis of the smoked fish smoked with *Anacadium* spp. The order of arrangement is *Anacadium* spp. > *Mangifera* spp. > *Tectona* spp. > *Dogoyaro* spp. Their PAHs of especially *Indeno{1;2;3;cd}perylene PAHs* is $68.41_{ug/l}$ in *Mangifera* spp, $85–15_{ug/l}$ in *Anacadium* spp, and $0_{ug/l}$ in both *Tectona* spp. and *Dogoyaro* spp.

From the results, in Figure 3 again, all the PAHs analyzed from the four samples are higher and greater than the maximum permissible limits recommended by W.H.O. But *Anacadium* spp. when used to smoke has the highest level of PAHs. Therefore, *Anacadium* spp. of wood is not advisable to be used for smoking fish, being hazardous. Also in the same Figure 3, the numbers and the levels of PAHs in *Anacadium* spp. of wood increased drastically and higher than all other three woods. While we recorded eighty five to eighty nine of Benzo{ghi}perylene for *Anacadium* spp., Pyrene is as low as 4.3ug, which is the least. The number and levels of PAHs in *Anacadium* and *Mangifera* spp. of woods in the value collected make them to be more hazardous for smoking fish than others.

CONCLUSION

Certain fuel woods release chemicals during smoking and these are hazardous to human health. These fuel woods have higher concentrations and levels of PAHs quantitatively which are above the maximum permissible levels recommended by WHO 1989. The species of woods to be used for smoking fish is very important and should be checked to reduce contamination. These hazardous chemicals, if not checked, could be dangerous to the consumers being the end users.

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