

## RISK ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SMOKE-DRIED EUROPEAN HAKE FISH (*MERLUCCIUS MERLUCCIUS* LINNEAUS, 1758) FROM SELECTED MARKETS IN BENIN CITY, NIGERIA

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### ABSTRACT

*Polycyclic aromatic hydrocarbons (PAHs) are recognized in the scientific community for their carcinogenicity, mutagenicity and teratogenicity. The paucity of ecotoxicological data on the PAH content of smoke-dried European Hake fish (*Merluccius merluccius*) from selected markets in Benin City, Nigeria, warranted this research which was achieved using a gas chromatograph with a mass selective detector. The summary statistics for the mean concentrations of PAH congeners in *M. merluccius* ranged from 0.005 µg/kg Benzo[b]fluoranthene (BBF) to 2.408 µg/kg Naphthalene, with a total PAH burden of 2.840 µg/kg. The mean concentrations of PAH congeners in *M. merluccius* by market point ranged from 0.004 ± 0.005 µg/kg for BBF at Oba market to 3.391 ± 0.675 µg/kg for Naphthalene at Oluku market, with no observed significant difference ( $p > 0.05$ ) in the mean concentrations of BBF and Benzo[a]anthracene (BAA) in *M. merluccius* between markets. The hazard quotient (HQ) for PAHs in *M. merluccius* ranged from 0.001 for BBF to 0.482 for Naphthalene, while the toxic equivalency (TEQ) for PAH in *M. merluccius* was 0.030. The cancer risk factor (CRF) for PAHs ranged from  $2.55 \times 10^{-8}$  for BAA to  $1.25 \times 10^{-6}$  for BBF with a risk specific dose ranging from 19.44 mg/kg/day for BAA to 40.23 mg/kg/day for BBF. Overall, *M. merluccius* was considered safe for human consumption as PAHs levels in the fish species fell below internationally established acceptable limits.*

**Keywords:** Smoked-dried fish, Polycyclic aromatic hydrocarbons, Hazard quotient, Cancer risk factor

### INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a well known group of persistent organic pollutants produced via the incomplete combustion of organic matter. They are especially recognized in the scientific and

medical community for their carcinogenicity, mutagenicity and teratogenicity. In aquatic ecosystems, it has been observed that the accumulation of PAHs is dependent on the living habits and feeding behavior of fish and that benthic organism have a very high potential for the accumulation of PAHs making such aquatic

resources a potential risk to humans (Xie *et al.*, 2023). PAHs have been classified into pyrolytic and petrogenic groups based on their mode of formation and origin. The former is produced via the combustion of organic matter, while the latter is directly linked with the petroleum industry. Sources of PAHs in the environment include volcanic eruptions, forest fires and biogenic formations (El-Maradny *et al.*, 2023).

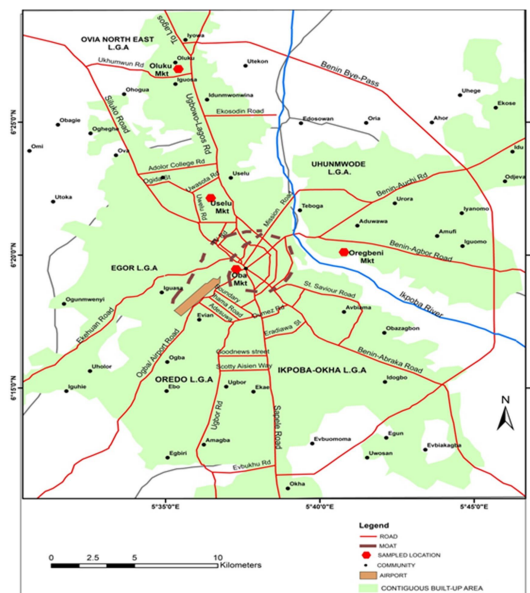
In addition, on the basis of their molecular structure, PAHs can be classified into two categories, namely the low-molecular-weight (LMW) PAHs which contain four or fewer aromatic rings and the high-molecular-weight (HMW) PAHs which contain five or more aromatic rings (Wang *et al.*, 2022). Apart from the natural contamination of food by PAHs, food preparation and processing methods which apply very high temperatures such as frying, grilling, baking and smoke-drying have been observed to contribute to the PAH burden in food including fish (FSA, 2018). In Benin City, Nigeria, several fish species of commercial appeal are sold smoke-dried including the European Hake fish (*Merluccius merluccius* Linnaeus, 1758 Gadiformes: Merlucciidae). Smoke-drying has been recognized to be a widely adopted method of preserving fish especially in sub-Saharan Africa as fish are notoriously prone to spoilage upon harvesting (Erhabor *et al.*, 2018). From available literature, there is currently a paucity of risk assessment research on PAHs in *M. merluccius* from open markets in Benin City, Nigeria. However, there is a systematic review on PAHs in both fresh and dried fish from selected parts of Nigeria and their potential public health impact (Emoyoma *et al.*, 2023).

This research is expected to ascertain if PAHs levels in *M. merluccius* are suitable for human consumption or otherwise. *M. merluccius* is usually found between 70 M and 370 M depth, but may also occur within a wider depth range, from inshore waters ranging from 30 M to 1000 M. The fish species lives close to the bottom during day-time, but moves away from the bottom at night. Females grow faster than males and the Mediterranean stock is known to grow slower. Adults feed mainly on fish, such as small hakes, anchovies, sardines and gadoid

species. The young individuals feed on crustaceans especially euphausiids and amphipods. The fish species can reach a maximum total length of 140 cm (though total lengths of 30 – 60 cm are common) and attain a maximum weight of 15 kg. The main fishing grounds are the areas north and west of Scotland, west and South of Ireland. The species is marketed fresh, frozen, dried, salted and canned (FAO, 2020). *M. merluccius* is imported into Nigeria from Europe in its frozen state.

## MATERIALS AND METHODS

**Description of Study Area:** This research was carried out in Benin City (Latitude 6°20' 00"N and Longitude of 5 37' 20" E) in Edo State, Nigeria (Figure 1).



**Figure 1: Map of Benin City showing the sampled markets (Source: Department of Geography, University of Benin, Nigeria)**

The City is located within the tropical rainforest ecological zone of south-south Nigeria. Further details of the study area have been published by Wangboje and Momoh (2023). After a comprehensive reconnaissance, four markets were purposely selected for this research viz; Oluku market (GPS: Latitude 6°27'0"N and Longitude 5°36'0"E), Uselu market (GPS: Latitude 6.3744°N and Longitude 5.6134°E),

Oba market (GPS: Latitude 6.3348°N and Longitude 5.6201°E) and Oregbeni market (GPS: Latitude 6.2056°N and Longitude 5.3933°E).

**Collection of Fish Samples:** Smoke-dried fish samples were purchased from the aforementioned markets between February and May 2022. Both wet and dry months were accommodated in order to ascertain the possible existence of temporal variations in the levels of PAHs in samples of smoke-dried fish. Samples were placed in labeled zip-lock bags and conveyed to the laboratory within 24 hours for further studies.

**Laboratory Assay of PAHs:** Samples of smoke-dried fish were milled using an electric blender. Extraction of PAHs from milled samples was done in accordance with the method of Dean and Xiong (2000). Blanks were prepared following the same procedures without adding the dried and milled fish sample. All extracts were separated and activated copper was applied to the combined extract for the desulphurization process. After subsequent drying over anhydrous sodium sulphate and concentrated to 1.0 mL using a rotary evaporator, an internal standard mixture solution was added to the extract. Final analysis for PAHs was achieved using an Agilent Gas Chromatograph (HP 5890 Series II) with mass selective detector (MSD), after following conditioning procedures. The standard PAHs used for the research had 98% purity (SIGMA, Germany) while the organic solvents used for extractions and clean up were also manufactured by SIGMA, Germany. All reagents used were of analytical grade. The PAH values in analyzed samples were expressed in  $\mu\text{g}/\text{kg}$ .

**Hazard Quotient (HQ) for PAHs:** The HQ measures the possibility of a contaminant being of ecological risk or a contaminant of potential ecological concern (Purchase, 2000). The HQ is expressed as follows:  $\text{HQ} = \text{Measured concentration of contaminant} \div \text{Toxicity reference value or selected screening benchmark}$ .  $\text{HQ} \geq 1 =$  Possibility of ecological

risk indicated or a contaminant of potential ecological concern (COPEC).

**Toxic Equivalency (TEQ) for PAHs:**

According to the United States Environmental Protection Agency (USEPA), the TEQ estimates the individual PAH potencies relative to that of Benzo[a]pyrene, (BAP) in order to obtain a BAP equivalent (USEPA, 2019).  $\text{TEQ} = \sum \text{Ti} \times \text{TEF}$ , where: TEQ = Toxic equivalency,  $\text{Ti}$  = Concentration of PAH congener in sample and TEF = TEQ Factor. BAP has a TEF value of 1 and it serves as an index PAH for other PAH compounds. Dibenz[a,h]anthracene also has a TEF value of 1, while Benzo[a]anthracene (BAA), Benzo[k]flouranthene, Benzo[b]flouranthene and Indeno[1,2,3-cd]pyrene have TEF values of 0.1. Chrysene however has a TEF value of 0.001.

**Estimated Annual Intake (EAI) and Estimated Daily Intake (EDI) of PAHs:**

$\text{EAI (mg/person/year)} = \text{Concentration of PAH in fish} \times \text{Per capita figure} \div \text{Adult body weight (assumed to be 70 kg)}$ , where per capita figure is 13.3 kg/person/year for Nigeria (World Fish Center, 2023).  $\text{EDI (mg/person/day)} = \text{EAI} \div 365 \text{ days}$ .

**Cancer Risk Factor (CRF):** The general equation for estimating human exposure to cancer through the consumption of fish is stated thus:  $\text{ECR} = \text{EI} \times \text{ED} \times \text{CSF} \div \text{BW} \times \text{AT}$ , where ECR = Excess Cancer Risk; EI = Estimated Intake; ED = Exposure Duration (30 years for adults); CSF = Oral Cancer Slope Factor (ranging from 0.0073 to 0.73) BW = Body Weight (assumed to be 60 kg); AT = Average Time for carcinogens (70 years for adults) (USEPA, 1989; Wangboje and Opobo, 2019). The cancer risk guideline value for comparison is  $1.0 \times 10^{-6}$

**Risk Specific Dose (RSD):** An RSD is the concentration associated with a specified cancer risk on the assumptions of a 70 kg body weight, consumption of water 2 L/day over a lifetime (70 years), and a cancer potency estimate for the compound derived from carcinogenicity dose-response data using a linearized multistage model, which is a conservative model

(Nowel and Resek, 1994; Hamilton *et al.*, 2003).  $RSD = 70 \text{ kg body weight} \times \text{Risk level} \div 2(L/day) \times q$ , where Risk level is usually specified e.g.  $10^{-6}$  or 1 in a million and  $q = \text{Cancer potency factor}$ . In dealing with fish however, the modified RSD is stated thus:  $RSD = 70 \text{ kg body weight} \times \text{Risk level} \div EDI \times q$  (Wangboje and Opobo, 2019), where,  $EDI = \text{Estimated daily intake value for PAHs}$ , Risk level is usually specified e.g.  $10^{-6}$  or 1 in a million and  $q = \text{Cancer potency factor}$ .

### **Carcinogenic PAH (cPAH) Relative Potency**

**Evaluation:** The easiest way to add the potencies of individual cPAH in an environmental sample is to convert the potency of each cPAH into a unitless relative potency factor (RPF). The concentration of each cPAH multiplied by its RPF can then be considered as a concentration of the index cPAH. BAP is the conventional index PAH and relative potencies of individual cPAHs are determined relative to the potency of BAP. As a result, cPAHs that are more potent than BAP have RPFs greater than 1 and vice versa (MDH, 2016). Concentration of the index cPAH = Concentration of cPAH  $\times$  RPF.

**Statistical Procedure:** Statistical software (GENSTAT Version 12.1 for Windows) was used for analyzing generated data. One-way analysis of variance (ANOVA) was used to test for significant differences ( $p < 0.05$ ) between mean values of PAH congeners, while the New Duncan Multiple Range Test was used to separate significant means. Microsoft Excel for Windows 2010 was used for designing Tables and Figures.

## **RESULTS**

As shown in Table 1, the summary statistics for the concentrations of PAH congeners ( $\mu\text{g/kg}$ ) in *M. merluccius* ranged from 0.005 (Benzo[b]fluoranthene, BBF) to 2.408 (Naphthalene) with a total PAH burden of 2.840  $\mu\text{g/kg}$ . The mean concentration ( $\mu\text{g/kg}$ ) of PAH congeners in *M. merluccius* by month ranged from  $0.003 \pm 0.005$  for BBF in May to  $3.267 \pm 0.381$  for Naphthalene in March, with no significant difference ( $p > 0.05$ ) in the mean concentrations

of BBF in fish between months (Table 2), while the mean concentration ( $\mu\text{g/kg}$ ) of PAH congeners in *M. merluccius* by market point ranged from  $0.004 \pm 0.005$  for BBF at Oba market to  $3.391 \pm 0.675$  for Naphthalene at Oluku market, with no significant difference ( $p > 0.05$ ) in the mean concentrations of BBF and BAA in fish between markets (Table 3). The HQ for PAHs in *M. merluccius* ranged from  $9.2 \times 10^{-4}$  for BBF to 0.482 for Naphthalene (Figure 2), while the TEQ for PAH in *M. merluccius* was 0.030 with Fluoranthene presenting the highest sub-TEQ value of 0.025 as shown in Figure 3. The EAI values ( $\text{mg/person/year}$ ) for the PAH congeners ranged from  $10 \times 8.7^{-4}$  (BBF) to 0.458 (Naphthalene), while the EDI values ( $\text{mg/person/year}$ ) for the PAH congeners ranged from  $2.4 \times 10^{-6}$  (BBF) to  $1.3 \times 10^{-3}$  (Naphthalene) as shown in Figures 4 and 5 respectively. The CRF for PAHs ranged from  $2.55 \times 10^{-8}$  for BAA to  $1.25 \times 10^{-6}$  for BBF (Table 4), while the RSD ( $\text{mg/kg/day}$ ) for PAHs ranged from 19.44 for BAA to 40.23 for BBF (Table 5). The index carcinogenic PAH (ICP) values ranged from 0.002 for BAA to 0.025 for Fluoranthene (Table 6) while the percent quota for PAH congeners in *M. merluccius* ranged from 0.16% for BBF to 84.79% for Naphthalene as presented in Figure 6. As presented in Table 7, the mean concentrations of PAHs in smoke-dried fish species ranged from 0.00  $\text{mg/kg}$  for BBF in *Clarias gariepinus* to 3.824  $\mu\text{g/kg}$  for BBF in *Scomber scombrus* while Naphthalene in *M. merluccius* had the highest mean value of 2.408  $\mu\text{g/kg}$  compared to the other smoke-dried fish species.

## **DISCUSSION**

Risk assessments with regard to the PAH content of fish food has been on the front burner of eco-toxicological research around the world (Khalili *et al.*, 2023). In this research, Naphthalene was the dominant PAH congener in *M. merluccius* accounting for over 80% of the total PAH load in this fish species. Not surprisingly, the congener also had the highest mean concentration in the fish species. This observation may be linked to the fact that Naphthalene was easily and readily taken up by

**Table 1: Summary statistics for polycyclic aromatic hydrocarbons ( $\mu\text{g}/\text{kg}$ ) in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria**

| PAH congener              | Mean $\pm$ SD     | Maximum | Minimum | *Threshold                  |
|---------------------------|-------------------|---------|---------|-----------------------------|
| Naphthalene               | 2.408 $\pm$ 0.523 | 4.800   | 0.800   |                             |
| Phenanthrene              | 0.051 $\pm$ 0.005 | 0.080   | 0.024   | 5.0 $\mu\text{g}/\text{kg}$ |
| Anthracene                | 0.045 $\pm$ 0.008 | 0.080   | 0.027   |                             |
| Fluoranthene              | 0.314 $\pm$ 0.062 | 0.460   | 0.138   |                             |
| Benzo[a]anthracene        | 0.009 $\pm$ 0.001 | 0.020   | 0.000   |                             |
| Benzo[b]fluoranthene      | 0.005 $\pm$ 0.002 | 0.010   | 0.000   |                             |
| $\Sigma$ PAH <sup>6</sup> | 2.840             |         |         |                             |

\*EC (2006)

**Table 2: Mean concentration ( $\mu\text{g}/\text{kg}$ ) of polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria by month**

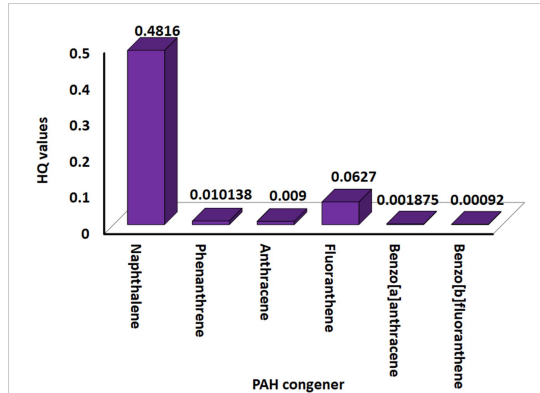
| PAHs congener        | Months   | Mean $\pm$ SD                   |
|----------------------|----------|---------------------------------|
| Naphthalene          | February | 2.988 $\pm$ 0.932 <sup>b</sup>  |
|                      | March    | 3.267 $\pm$ 0.381 <sup>b</sup>  |
|                      | April    | 1.438 $\pm$ 0.734 <sup>a</sup>  |
|                      | May      | 1.942 $\pm$ 0.858 <sup>a</sup>  |
| Phenanthrene         | February | 0.058 $\pm$ 0.011 <sup>b</sup>  |
|                      | March    | 0.059 $\pm$ 0.011 <sup>b</sup>  |
|                      | April    | 0.042 $\pm$ 0.013 <sup>a</sup>  |
|                      | May      | 0.044 $\pm$ 0.013 <sup>a</sup>  |
| Anthracene           | February | 0.046 $\pm$ 0.010 <sup>b</sup>  |
|                      | March    | 0.049 $\pm$ 0.012 <sup>b</sup>  |
|                      | April    | 0.051 $\pm$ 0.015 <sup>b</sup>  |
|                      | May      | 0.036 $\pm$ 0.007 <sup>a</sup>  |
| Fluoranthene         | February | 0.293 $\pm$ 0.104 <sup>ab</sup> |
|                      | March    | 0.332 $\pm$ 0.092 <sup>bc</sup> |
|                      | April    | 0.388 $\pm$ 0.052 <sup>c</sup>  |
|                      | May      | 0.243 $\pm$ 0.072 <sup>a</sup>  |
| Benzo[a]anthracene   | February | 0.015 $\pm$ 0.005 <sup>c</sup>  |
|                      | March    | 0.011 $\pm$ 0.007 <sup>bc</sup> |
|                      | April    | 0.007 $\pm$ 0.005 <sup>ab</sup> |
|                      | May      | 0.005 $\pm$ 0.005 <sup>a</sup>  |
| Benzo[b]fluoranthene | February | 0.005 $\pm$ 0.005 <sup>a</sup>  |
|                      | March    | 0.005 $\pm$ 0.005 <sup>a</sup>  |
|                      | April    | 0.005 $\pm$ 0.005 <sup>a</sup>  |
|                      | May      | 0.003 $\pm$ 0.005 <sup>a</sup>  |

Mean values with the same letter are not significantly different ( $p > 0.05$ ) for the monthly distribution of each PAH**Table 3: Mean concentration ( $\mu\text{g}/\text{kg}$ ) of polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* by selected markets in Benin City, Nigeria**

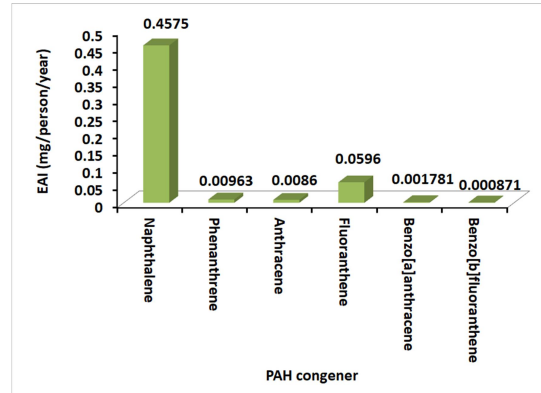
| PAHs congener | Market   | Mean $\pm$ SD                   |
|---------------|----------|---------------------------------|
| Naphthalene   | Oba      | 2.231 $\pm$ 0.823 <sup>a</sup>  |
|               | Oluku    | 3.391 $\pm$ 0.675 <sup>b</sup>  |
|               | Oregbeni | 1.658 $\pm$ 0.848 <sup>a</sup>  |
|               | Urelu    | 2.325 $\pm$ 1.127 <sup>a</sup>  |
| Phenanthrene  | Oba      | 0.056 $\pm$ 0.008 <sup>c</sup>  |
|               | Oluku    | 0.063 $\pm$ 0.010 <sup>c</sup>  |
|               | Oregbeni | 0.035 $\pm$ 0.009 <sup>a</sup>  |
|               | Urelu    | 0.048 $\pm$ 0.011 <sup>b</sup>  |
| Anthracene    | Oba      | 0.035 $\pm$ 0.009 <sup>a</sup>  |
|               | Oluku    | 0.058 $\pm$ 0.014 <sup>c</sup>  |
|               | Oregbeni | 0.042 $\pm$ 0.009 <sup>ab</sup> |
|               | Urelu    | 0.046 $\pm$ 0.004 <sup>b</sup>  |
| Fluoranthene  | Oba      | 0.236 $\pm$ 0.129 <sup>a</sup>  |
|               | Oluku    | 0.368 $\pm$ 0.088 <sup>b</sup>  |

|                             |          |                             |
|-----------------------------|----------|-----------------------------|
|                             | Oregbeni | 0.348 ± 0.053 <sup>b</sup>  |
| <b>Benzo[a]anthracene</b>   | Uselu    | 0.303 ± 0.030 <sup>ab</sup> |
|                             | Oba      | 0.009 ± 0.007 <sup>a</sup>  |
|                             | Oluku    | 0.012 ± 0.007 <sup>a</sup>  |
|                             | Oregbeni | 0.008 ± 0.006 <sup>a</sup>  |
| <b>Benzo[b]fluoranthene</b> | Uselu    | 0.008 ± 0.007 <sup>a</sup>  |
|                             | Oba      | 0.004 ± 0.005 <sup>a</sup>  |
|                             | Oluku    | 0.005 ± 0.005 <sup>a</sup>  |
|                             | Oregbeni | 0.005 ± 0.005 <sup>a</sup>  |
|                             | Uselu    | 0.004 ± 0.005 <sup>a</sup>  |

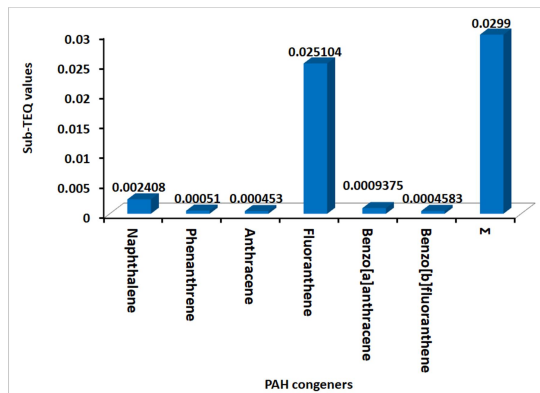
Mean values with the same letter are not significantly different ( $p > 0.05$ ) for the market distribution of each PAH



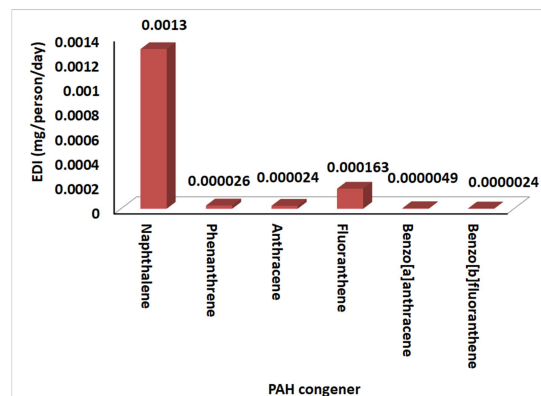
**Figure 2: Hazard quotient (HQ) values for polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria**



**Figure 4: Estimated annual intake (EAI) values for polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria**



**Figure 3: Toxic equivalency (TEQ) value for polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria**



**Figure 5: Estimated daily intake (EDI) values for polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria**

fish flesh to a greater level when compared directly to the other detected PAHs. It may also mean that the energy source or sources utilized in the smoke-drying process emitted more of Naphthalene than the other PAH congeners. Besides, PAHs being organic contaminants would logically have a greater affinity for adhering to organic matter such as fish flesh which can explain their presence in smoked fish.

It has been observed that during the smoking process, PAHs and its carcinogenic derivatives are usually produced (Erhabor *et al.*, 2018). However, in the marine environment, PAHs are bio-accumulated by fish from water, sediment and ingested food especially arising from combustion and ship emissions (Liu *et al.*, 2023).

**Table 4: Cancer Risk Factor for polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria**

| PAH congener         | EI                    | ED | *CSF | BW | AT | ECR                   |
|----------------------|-----------------------|----|------|----|----|-----------------------|
| Benzo[a]anthracene   | $4.9 \times 10^{-6}$  | 30 | 0.73 | 60 | 70 | $2.55 \times 10^{-8}$ |
| Benzo[b]fluoranthene | $2.39 \times 10^{-5}$ | 30 | 0.73 | 60 | 70 | $1.25 \times 10^{-8}$ |

Guideline value =  $1.0 \times 10^{-6}$  \*Not available for the other detected PAH congeners

**Table 5: Risk specific dose (RSD) for polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria**

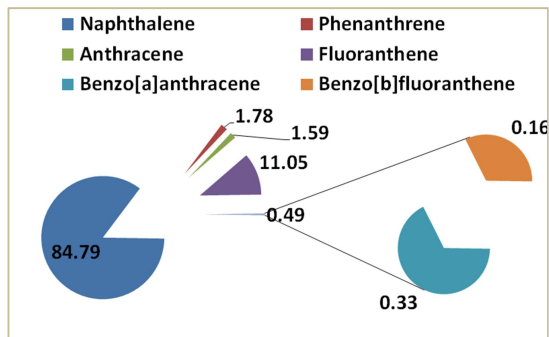
| PAH congener         | BW | Risk Level           | EDI                   | *CSF | RSD   |
|----------------------|----|----------------------|-----------------------|------|-------|
| Benzo[a]anthracene   | 70 | $1.0 \times 10^{-6}$ | $4.90 \times 10^{-6}$ | 0.73 | 19.44 |
| Benzo[b]fluoranthene | 70 | $1.0 \times 10^{-6}$ | $2.39 \times 10^{-5}$ | 0.73 | 40.23 |

\*Not available for the other detected PAH congeners

**Table 6: Evaluation of Index carcinogenic (ICP) for polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria**

| PAH congener         | Mean $\pm$ SD ( $\mu\text{g}/\text{kg}$ ) | RPF  | ICP   | Rank |
|----------------------|---|------|-------|------|
| Naphthalene          | $2.408 \pm 0.523$                         | N/A  | N/A   | N/A  |
| Phenanthrene         | $0.051 \pm 0.005$                         | N/A  | N/A   | N/A  |
| Anthracene           | $0.045 \pm 0.008$                         | 0.4  | 0.018 | 2    |
| Fluoranthene         | $0.314 \pm 0.062$                         | 0.08 | 0.025 | 1    |
| Benzo[a]anthracene   | $0.009 \pm 0.001$                         | 0.2  | 0.002 | 4    |
| Benzo[b]fluoranthene | $0.005 \pm 0.002$                         | 0.8  | 0.004 | 3    |

N/A = Not available



**Figure 6: Percent (%) quota for polycyclic aromatic hydrocarbons in smoke-dried *Merluccius merluccius* from selected markets in Benin City, Nigeria**

A total PAH burden of 2.840  $\mu\text{g}/\text{kg}$  was recorded in *M. merluccius* which was far less than the total of 419  $\mu\text{g}/\text{kg}$  observed for smoke-dried Atlantic bonito (*Sarda sarda*) by Sei *et al.* (2021). There were no significant differences ( $p > 0.05$ ) in the mean concentration of BBF in *M. merluccius* between months, an indication that the level of this particular congener was relatively stable and negligible in fish all through the research period. There were significant differences ( $p < 0.05$ ) in the mean concentration of all the detected PAH congeners with the exception of BBF and BAA in *M. merluccius* between markets, an indication that the smoke-dried *M. merluccius* may have been produced by

different food processors. The HQ values for all the detected PAH congeners were all below unity suggesting that potential consumers of smoke-dried *M. merluccius* will not be faced with oncological risk (Tongo *et al.*, 2017). The TEQ value of 0.030 was dominated by Fluoranthene which had a sub-TEQ value of 0.025, suggesting a greater potency of the congener compared to the other detected PAHs. The EAI and EDI values all peaked for Naphthalene and were the lowest for BBF, owing to the fact that Naphthalene and BBF had the highest and lowest mean concentrations in smoke-dried *M. merluccius*. The aforementioned dietary figures would mean that potential consumers of smoke-dried *M. merluccius* would be ingesting more of Naphthalene and less of BBF. The CRF for BAA and BBF were all below the Guideline value of  $1.0 \times 10^{-6}$  once again buttressing the absence of risk. However, the RSD of 19.44 and 40.23 mg/person/day were established for BAA and BBF respectively. An RSD is the concentration associated with a specified cancer risk taking into consideration a 70-kg body weight, the EDI of a congener over a lifetime (i.e. 70 years), and a cancer potency estimate for the congener (Wangboje and Opobo, 2019). The ICP, were established for Anthracene, Fluoranthene, BAA and BBF as they all have published relative potency factors.

**Table 7: Comparison of polycyclic aromatic hydrocarbons levels in smoke-dried *Merluccius merluccius* to selected smoke-dried fish**

| PAH congener         | <i>Merluccius merluccius</i><br>(This research)                   | <i>Clarias gariepinus</i><br>(Erhabor <i>et al.</i> , 2018) |
|----------------------|---|---|
| Naphthalene          | 2.408 µg/kg   | 0.004 mg/kg   |
| Phenanthrene         | 0.051 µg/kg   | 0.005 mg/kg   |
| Anthracene           | 0.045 µg/kg   | 0.008 mg/kg   |
| Fluoranthene         | 0.314 µg/kg   | 0.144 mg/kg   |
| Benzo[a]anthracene   | 0.010 µg/kg   | 0.001 mg/kg   |
| Benzo[b]fluoranthene | 0.005 µg/kg   | 0.000 g/kg  |
|                      | <i>Micropogonias undulantes</i><br>(Erhabor <i>et al.</i> , 2018) | <i>Scomber scombrus</i><br>(Wangboje and Okpobo, 2019)      |
| Naphthalene          | 0.005 mg/kg   | 1.969 µg/kg   |
| Phenanthrene         | 0.002 mg/kg   | 0.175 µg/kg   |
| Anthracene           | 0.000 mg/kg   | 0.096 µg/kg   |
| Fluoranthene         | 0.001 mg/kg   | 0.146 µg/kg   |
| Benzo[a]anthracene   | 0.000 mg/kg   | 0.043 µg/kg   |
| Benzo[b]fluoranthene | 0.002 mg/kg   | 3.824 µg/kg   |
|                      | <i>Gadus morhua</i><br>(Omodara <i>et al.</i> , 2019)             | <i>Sardinella fimbriata</i><br>(Diop <i>et al.</i> , 2023)  |
| Naphthalene          | ND  | ND  |
| Phenanthrene         | 0.110 mg/kg   | ND  |
| Anthracene           | 1.610 mg/kg   | ND  |
| Fluoranthene         | 0.830 mg/kg   | ND  |
| Benzo[a]anthracene   | 0.260 mg/kg   | 1.200 µg/kg   |
| Benzo[b]fluoranthene | 1.380 mg/kg   | 1.700 µg/kg   |

ND = Not detected

The ICPs are the estimated values of BAP which is the most toxic of all known PAH congeners. The estimated means of BAP in smoke-dried *M. merluccius* ranged from 0.002 to 0.025 µg/kg. The values of the individual PAH congeners as well as the total of mean values, did not exceed the 5.0 µg/kg threshold established by the EC (2006) for PAH levels in smoked fish, implying that smoke-dried *M. merluccius* is suitable for human consumption. The mean concentrations of PAH congeners in smoke-dried *M. merluccius* compared well to the PAH content in smoke-dried fish from some selected researches (Erhabor *et al.*, 2018; Omodara *et al.*, 2019; Wangboje and Okpobo, 2019; Diop *et al.*, 2023).

**Conclusion:** The paucity of ecotoxicological data for the PAH content in smoke-dried European Hake fish (*M. merluccius*) from selected markets in Benin City, Nigeria, warranted this research which was achieved via Gas Chromatographic technique. Essentially, the research revealed that the PAH levels in smoke-dried *M. merluccius* were below International threshold levels, implying the suitability of this

fish species for human consumption. In order to ensure that safety levels are not surpassed which could impact negatively on the health of potential consumers in the long run, it is suggested that a continuous monitoring programme should be implemented in addition to tests that would continue to ensure the prevention of hazardous levels of PAHs in smoke-dried *M. merluccius*.

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