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Investigating the Level and Health Risk of Polycycic Aromatic Hydrocarbons (PAHS) in Fish (*Scomber Scombrus*) from South-West Nigeria

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Abstract

As food supply essential nutrient to the body, it can also cause problem to the body system. This study evaluates the level and health risk associated to polycyclic aromatic hydrocarbons in *Scomber scombrus* smoked fish samples consumed in south-west Nigeria. Fish samples (*Scomber scombrus*) was collected from various locations from difference state which then undergo GC-MS analysis using standard method. Risk assessment of Hazard index, Hazard quotient and cancer risk were determined using standard methods. Twenty-two PAHs congeners was determined but Indeno[1,2,3-cd]pyrene recorded the highest PAHs for both raw and smoked fish while smoked fish has the highest PAHs concentration. ΣPAHs level in smoked fish has high concentration. Seventeen PAHs congeners was observed for average daily dose and 10 congeners exceed the permissible limit. Indeno[1,2,3-cd]pyrene and Naphthalene has the highest concentration for both raw and smoked samples which can cause advance effect. Benzo[a]pyrene shows high concentration level for cancer risk. The result from this study indicates that possible exposure to this PAHs can cause carcinogenic effect through consumption.

Keyword: PAHs, Cancer risk, human health risk, smoked fish.

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1. Introduction

The regular intake of food is an activity to keep the body healthy. Smoked fish serve as protein in most diets. Smoke fish serve as means of preservation in the developing countries due to drying out and bactericidal properties and also give the fish unique taste and smell (Palm et al 2011). Significantly, smoked especially coal or wood smoked contains PAHs, in which many are carcinogenic (Silva et al 2011). Smoking is one of the most widely recognized technique utilized in preserving fish in developing countries. Smoked fish are one of the most accessible type of fish product for human consumption due to lack to electricity in the country to preserve fish from been spoiled.

Polycyclic aromatic hydrocarbons (PAHs), consist of organic chemicals fused together with aromatic rings of carbon and hydrogen atoms. As PAH rings number increases, lipid solubility, mutagenicity and carcinogenicity are relatively increases. (Tian and Zheng, 2004).

PAHs can penetrate into the environment through incineration evaporation of industrial solvent and combustion of coal and wood, spillage of oil and other organic substances (Taiwo et al., 2020). PAH congener can be introduced into foodstuff during processing such as smoking, curing, roasting, drying, curing, barbecuing, grilling and refining. These foodstuff processing increase and create the degree of PAH congener in the food (SCF, 2002).

According to Environmental Protection Agency (USEPA, 2008), several PAHs has been classified as potent carcinogens which can cause respiratory Effects, Neurological diseases, cancer of lung, oral cancer (USEPA, 2008). People exposed to PAH congener can experience lung cancer, bladder cancer, skin cancer and gastrointestinal (IDPH, 2019).

In developed and underdeveloped countries, cancer diseases are rated the second common causes of deaths (Bray et al., 2018)., This study tends to examine the level of PAHs concentration in smoke fish from selected environs in southwestern Nigeria.

2. Materials and Methods

Sample Collection

Samples of frozen and smoked fish of *scomber scombrus* (popularly known as Atlantic mackerel or Titus) were randomly collected from three different markets (Abeokuta, Lagos and Oyo market) around July 2019. Smoked samples obtained, was wrapped with aluminum foil and was packed in a plastic container and labeled while the frozen sample was stored using ice chest prior to analysis.

PAHs analysis

PAHs was extracted using Wang et al., (1999) methods. Exactly 15g of the homogenized tissue samples alongside 10g of anhydrous Na_2SO_4 was thoroughly mixed until completely dehydrated and homogenized. Exactly 40ml of Hexane: Dichloromethane (1:1) was used as extraction solvent. The homogenized samples were then placed in an extraction bottle, and then it was vortexed at 80°C for 45 minutes. Organic layer was poured into a conical flask and was then dried with Na_2SO_4. Florisil clean-up method was used for cleanup (EPA, 2014). 4ml of hexane was introduced to 1g of Florisil cartridge and was submerge for 6 min then 1ml of the sample was then added and poured into the chromatography column. The cartridge was then filled-up with 90% of hexane and 10% acetone (ratio 90:10) and the solution was collected into 25ml conical flask, then concentrated to 2ml using yamato rotary evaporator. PAHs determination was determined with (GC–MS).

Data analysis

Data was analyzed using descriptive statistics (mean ±standard deviation) using SPSS version 23

Risk Assessments

Health risk of PAH congener were determined for average daily dose (ADD), hazard index (HI), hazard quotient (HQ and cancer risk (CR) (USEPA 2001, 2002).

$$ADD = \frac{C \times IR \times EF \times ED}{BW \times AT}$$

Where C = The Concentration of PAHs in fish sample
IR = Ingestion rate of fish sample (24.7 g/day) (FAO, 2008),
ED = Exposure Duration for 30 years for carcinogenic effects on adults
EF = Exposure frequency for 350 days/year (Li et al., 2009),
AT=Averaging time =54 years (WHO, 2015)
AT=ED (AT = 54×365 days for carcinogenic effects for adult
BW = 60 kg for an adult.
HI = $\sum_{i=1}^{n} HQ$

i=1…n

Hazard quotient (HQ) = $\frac{ADD}{RfD}$

Where,
RfD=Reference dose (mg/kg/day)
N = observed elements

Hazard quotient less than 1.0 indicate no significant effect of noncarcinogenic while HQ greater than 1.0 indicate advance effect or risk of non-carcinogenic.

Cancer Risk=ADD × SF

SF=Slope factor

3. Result and Discussion

The mean concentrations and standard deviation of individual PAH congeners of the fish sample were presented in Table 1 below. Total mean concentrations of PAHs obtained for smoked fish is 75.80 mg/kg and 45.66 mg/kg for raw fish. High PAHs concentration was measured in smoked sample. Indeno[1,2,3-cd]pyrene having the most noteworthy focus for both the raw and smoked fish of 44.05 and 73.17. The smoked fish sample was contaminated with 18 PAH congeners, where Indeno[1,2,3-cd]pyrene offered 90% of the total PAHs. High concentration of this may be attributed to the difference types of smoking process adopted during fish preparation. Benzo[a]pyrene (BaP) for both raw and smoked fish ranges between 0.02 and 0.04 respectively. Smoked sample for (BaP) has the highest PAHs of 0.04 which is greater than the threshold value of 0.002mg/kg by (EFSA 2008). The total mean concentrations of PAHs value for both raw and smoked fish were above the permissible limit of EFSA (2008). Isioma et al., (2016) reported high PAHs concentration in different types of smoked fish (9.51×10^{-1}, 3.58×10^{1}, 6.94×10^{-1} and 7.15×10^{-1}) in T. *zilli*, S *scombrus*, E. *fimbriata* and C. *gariepinus* and respectively but the observed mean concentration in this study were above reported PAHs concentration. High increase in PAHs can be ascribed to the utilization of local method of smoking in the preservation and preparation of fish. Taiwo et al., (2019) also recorded high value of PAHs which is a major worry to general wellbeing, which can cause possible carcinogenic effect. Fish smoking need healthier method of preservation to curtail or reduce the level of high PAHs concentration.

Table 1: Mean concentrations of PAHs congeners of raw and smoked Fish samples

mg/kg	Raw Fish (N=3)				Smoked Fish (N=3)			
	Mean	Std.	Min.	Max.	Mean	Std	Min.	Max.
Naphthalene	1.17	0.35	0.72	1.55	1.04	0.40	0.47	1.34
Fluorene	0.02	0.05	< 0.0001	0.09	0.18	0.22	< 0.0001	0.43
Acenaphthene	0.09	0.04	0.06	0.15	0.17	0.21	< 0.0001	0.42
Anthracene	< 0.0001		< 0.0001	< 0.0001	0.02	0.02	< 0.0001	0.03
Pyrene	< 0.0001		< 0.0001	< 0.0001	0.02	0.04	< 0.0001	0.07
Chrysene	< 0.0001		< 0.0001	< 0.0001	0.01	0.03	< 0.0001	0.05
Fluoranthene	< 0.0001		< 0.0001	< 0.0001	0.01	0.01	< 0.0001	0.03
Acenaphthylene	0.09	0.02	0.07	0.10	0.17	0.17	< 0.0001	0.39
Indeno[1,2,3-cd]pyrene	44.05	21.44	0.31	99.86	73.17	21.84	0.51	104.06

Benzo[b]fluoranthene	0.03	0.03	< 0.0001	0.06	0.36	0.42	< 0.0001	0.87
Benz[a]anthracene	< 0.0001		< 0.0001	< 0.0001	0.02	0.04	< 0.0001	0.07
Benzo[e]pyrene	0.09	0.12	< 0.0001	0.26	0.15	0.12	< 0.0001	0.25
Benzo[k]fluoranthene	0.07	0.10	< 0.0001	0.21	0.14	0.18	< 0.0001	0.40
Benzo[ghi]perylene	< 0.0001		< 0.0001	< 0.0001	< 0.0001		< 0.0001	< 0.0001
3-Methylcholanthrene	< 0.0001		< 0.0001	< 0.0001	0.08	0.11	< 0.0001	0.24
Benzo[c]phenanthrene	< 0.0001		< 0.0001	< 0.0001	0.05	0.11	< 0.0001	0.22
Dibenz[a,h]anthracene	0.03	0.05	< 0.0001	0.10	0.15	0.15	0.005	0.34
Benzo[a]pyrene	0.02	0.004	0.02	0.03	0.04	0.04	0.01	0.09
Dibenzo(a,i)pyrene	< 0.0001		< 0.0001	< 0.0001	< 0.0001		< 0.0001	< 0.0001
Dibenzo[a,h]pyrene	< 0.0001		< 0.0001	< 0.0001	< 0.0001		< 0.0001	< 0.0001
Dibenzo(a,l)pyrene	< 0.0001		< 0.0001	< 0.0001	< 0.0001		< 0.0001	< 0.0001
Phenanthrene	< 0.0001		< 0.0001	< 0.0001	0.03	0.03	< 0.0001	0.07
∑PAHs	45.66	22.20	1.18	102.41	75.80	24.14	1.00	109.37

The ∑PAHs of the fish sample for smoked fish were generally higher than raw fish. The smoked fish was 75.80mg/kg which is three times higher than raw fish of 45.66mg/kg. The high level of PAHs concentration can also be attributed to the following factors which include, exposure of fish sample to incomplete combustion of wood and fossil fuel, air pollution contaminants during point of sale and different methods in fish processing (Taiwo et al., 2019). The PAHs concentration in this study were greater than the reported value made by other researcher in the world, such as Malaysia (573.66×10^{-6}mg/kg) (Nasher et al., 2016), China (6.65×10^{-6}mg/kg) (Duan et al., 2016) which could be due to the method of smoking the fishes that involves the use of coal that could result in incomplete combustion.

Health risk assessment

Mean concentration for average daily dose was presented in table 2 below. These was determined based on the body weight of 60kg assuming the adult consumes 24.7g of the fish samples for 350 days^{-1} year. Base on the result, there is indication that Indeno[1,2,3-cd]pyrene and Naphthalene have the highest ADD of PAHs for both the raw and smoked fish (1.93×10^{-2} and 3.20×10^{-2}, 5.14×10^{-4} and 4.54×10^{-4}) respectively. However Indeno[1,2,3-cd]pyrene have the highest concentration of 1.93×10^{-2} in raw fish and Naphthalene have the highest concentration of 4.54×10^{-4} in smoked fish. Benzo [b] fluoranthene, Benzo [e] pyrene, Benzo [c] phenanthrene, Benzo [k] fluoranthene, Dibenz [a,h] anthracene, Benzo [a] pyrene and Indeno [1,2,3-cd]pyrene (1.57×10^{-4}, 6.51×10^{-5}, 2.40×10^{-5}, 6.35×10^{-5}, 6.42×10^{-5}, 1.62×10^{-5} and 3.20×10^{-2}. exceed the permissible limit of 10×10^{-6} in smoke fish. (JECFA 2005). This can cause a high health risk threats to consumer of smoked fish due to carcinogenic and mutagenic properties of BaP.

Table 2: ADD values of PAHs

mg/kg/day	**Raw Fish**		**Smoked Fish**	
	Mean	SD	Mean	SD
Naphthalene	5.14E-04	1.55E-04	4.54E-04	1.77E-04
Acenaphthene	4.10E-06	1.68E-05	7.52E-05	9.09E-05
Acenaphthylene	4.01E-06	8.13E-06	7.27E- 05	7.34E- 05
Fluoranthene			3.30E- 06	6.54E- 06

Chrysene			5.83E- 06	1.20E- 05
Anthracene			7.40E- 06	8.50E- 06
Phenanthrene			1.40E- 07	1.51E- 07
Fluorene	1.01E-07	2.04E -07	8.00E- 07	9.57E- 07
Pyrene			7.68E- 06	1.54E- 05
Benz [a] anthracene			7.83E- 06	1.60E- 05
Benzo [b] fluoranthene	1.10E-05	1.28E -05	1.57E- 04	1.83E- 04
Benzo [e] pyrene	3.92E-05	5.44E -05	6.51E- 05	5.56E- 06
Benzo [c] phenanthrene			2.40E- 05	4.80E- 06
Benzo [k] fluoranthene	3.11E-05	4.34E -06	6.35E- 05	7.80E- 06
Dibenz [a,h] anthracene	1.15E-05	2.09E -06	6.42E- 05	6.59E- 06
Benzo [a] pyrene	9.64E-06	1.79E -06	1.62E- 05	1.55E- 05
Indeno [1,2,3-cd]pyrene	1.93E-02	3.14E -02	3.20E- 02	3.15E- 02

Hazard quotient and hazard index were represented in table 3 below, for the PAHs for raw and smoked fish. Base on the value above, it shows that hazard index and hazard quotient of the fish sample are less than 1.0 except Indeno[1,2,3-cd]pyrene, in smoked fish which indicated non-carcinogenic adverse health effects such as neurobehavioral effect, adverse birth outcome.

The cancer risk was presented in table 4 below. Indeno[1,2,3-cd]pyrene and BaP shows high concentration level cancer risk of (7.75×10^{-3} and 1.22×10^{-5}) for raw fish and (1.29×10^{-2} and 2.05×10^{-5}) for smoked fish which are higher than USEPA permissible limit of 1.0×10^{-6}. The high rate of cancer risk in the fish samples can indicate at most two persons out of hundred can develop cancer if the volume of this fish sample especially smoked fish is consumed as suggested in this research.

Table 3: Non-carcinogenic HQ and HI of PAH in fish

		Raw Fish		Smoked Fish	
	RfD (mg/kg/day)	Mean.	Std.	Mean	Std.
Naphthalene	0.02	2.56E- 02	7.75E- 03	2.27E- 02	8.87E- 03
Acenaphthene	0.06	6.78E- 04	2.84E- 04	1.30E- 03	1.62E- 03
Acenaphthylene	0.06	6.42E- 04	1.39E- 04	1.24E- 03	1.20E- 03
Pyrene	0.03			2.56E- 04	5.14E- 04
Fluorene	0.04	2.52E- 04	5.04E- 04	2.01E- 03	2.40E- 03
Benzo [a] pyrene	0.0003	3.21E- 02	5.96E- 03	5.41E- 02	5.17E- 02
Benzo [e] pyrene	0.03	1.30E- 03	1.80E- 03	2.20E- 03	1.82E- 03
Indeno [1,2,3-cd] pyrene	0.03	6.43E- 01	1.04E+ 00	1.07E+ 00	1.05E+ 00
HI		0.70	1.06	1.15	1.12

Table 4: Cancer Risk values of PAHs in fish samples

	Raw Fish		Smoked Fish	
	Mean	SD	Mean	SD
Benz [a] anthracene			3.17×10^{-6}	6.29×10^{-6}
Benzo [a] pyrene	1.22×10^{-5}	2.27×10^{-6}	2.07×10^{-5}	2.01×10^{-5}
Chrysene			2.34×10^{-8}	4.69×10^{-8}
Indeno [1,2,3-cd] pyrene	7.75×10^{-3}	1.27×10^{-2}	1.29×10^{-2}	1.30×10^{-2}
Benzo [k] fluoranthene	1.26×10^{-6}	1.73×10^{-6}	2.55×10^{-6}	3.12×10^{-6}
∑CR	7.77×10^{-3}	1.27×10^{-2}	1.30×10^{-2}	1.27×10^{-2}

4. Conclusion

In this study, we investigated the level of PAHs in smoked fish samples. The study shows that smoked fish has high concentration of PAHs. High PAHs in the fish samples can be through wood combustion, incomplete combustion of unburned fuel. There is strong relationship between smoked fish and Indeno[1,2,3-cd]pyrene, making Indeno [1,2,3-cd] pyrene having the highest PAH for both the raw and smoked fish. Non-carcinogenic health risk of hazard index (HI) for the fish samples are less than 1.0. The ADD value for BaP in the smoked fish were above the threshold of 10×10^{-6} mg $BaP^{-1}kg^{-1}day$. The (HI) for the fish samples is less than 1.0 except Indeno[1,2,3-cd]pyrene, in smoked fish. The availability of PAHs in our body system above the permissible limit is harmful to our body system which can cause respiratory effect and Neurological effect. High concentration of PAHs can lead to carcinogenic health effect. Therefore, consumption of smoke fishes should be reduced, in other to reduce the level of PAHs in our body system.

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