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Pah Content of *Clarais gariepinus* Harvested from Ekulu River, Eastern Nigeria Contaminated with Effluents Generated from a Roofing Sheet Industry Risk Impact Assessment

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Authors' contributions

This work was carried out in collaboration among all authors. Author UCS designed the study, author NEJ wrote the protocol and half (50 percent) of the study, author AMV managed the analyses of the study, authors AAV and OES wrote the remaining part of the study, authors KRO and ET conducted the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Aim: This study evaluated PAH content and health risks associated with consuming *Clarais gariepinus* (cat fish) from Ekulu Rivers, in Enugu, Nigeria fed with roofing sheet company effluent.
Place and Duration of Study Design: Ekulu River, the largest body of water in the city of Enugu in Enugu State, south-eastern Nigeria, is a 25-kilometer long river (16mi) and it originates in the same city as well. The city is located on latitude 06^{o} 21^{o} N and 06^{o} 30^{o} and longitude 07^{o} 26^{o} E and 07^{o} 37 E^{o}.

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Methodology: This analysis was conducted with the use of Gas Chromatography – Mass Spectroscopy (GC-MS) machine equipped with Flame ionization detector (FID). The health risks were evaluated by the mathematical models stipulated by USEPA and WHO.
Results: The PAHs identified from the *Clarias gariepinus* samples were Acenaphthene, Acenaphthylene, Naphthalene, Fluorene, Phenanthrene, Anthracene, Flouranthene, Pyrene, Benzo(α)pyrene and Benzo (g-h-i)perylene. Benzo(α)pyrene and Benzo (g-h-i)perylene were predominant. The quantity of PAHs detected in all fish samples including the control ranged from below detectable limit (BDL) through 0.001 to 0.0786mg/kg. The LMW PAHs detected were 60 % while the HMW PAHs were 40 % of the total PAHs in isolated. The total PAH concentration observed from the different point locations were 0.1003 mg/kg, 0.0977 mg/kg, 0.1102 mg/kg and 0.0414 mg/kg for the downstream, upstream, POD and control respectively. The HQ and HI obtained in all point locations were < 1. The ILCR of all the PAHs detected were in the range of 10^{-5} to 10^{-9}. The benzo (α) pyrene in cat fish obtained from the POD has the most carcinogenic potency and also recorded the maximum limit (5E -03 mg/kg).
Conclusion: it is pertinent to enlighten the fish consumers and mongers on the dangers posed by the consumption of fish from Ekulu River and also caution industries with injudicious effluent disposal into water bodies.

Keywords: PAHs; pollution; effluents; risk assessment; effluents; clarias gariepinus.

1. INTRODUCTION

The population boom experienced by developing countries has given rise to a considerable spike in urbanization, industrial and agricultural land use. This phenomenon has increased the discharge of a wide range of pollutants into water bodies and has caused a detrimental impact on the aquatic life. In Nigeria, this disposal threatens the aquatic ecosystem in the estuarines and inland water bodies as well as its purity as they are also used for domiciliary purposes. These effluents generated is dependent on the type of industry within the environment altering the physicochemical properties as well as the biological properties bestowed on them by nature [1]. These effluents range from dyes, heavy metals, surfactants, hydrocarbons and solids which goes to negate the life supporting system of aquatic life forms. They impact on the biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids and suspended solids (TDS and TSS) and total organic carbon (TOC) levels as well as the acidity and alkalinity of these aquatic habitats [2]. These effluent have polluted the water bodies beyond sustainability [3]. The aquatic faunas have been exposed to these myriad of pollutants causing them to accumulate them (heavy metals as well as polycyclic aromatic hydrocarbons (PAHs)) within their tissues. Although the introduction of PAHs into the environment can be seen via the haphazard disposal of industrial effluents [4,5], PAHs have natural and anthropogenic sources into the environment, such as natural sources ranging from forest fires and volcanoes to combustion of petroleum and coal via the wide range of transport system is seen as the rout of the anthropogenic sources. They are divided into low molecular weight (LMW) and high molecular weight (HMW) PAHs and are termed persistent as a result of their poor biodegradability. The LMW contains 3 rings while the HMW are made of 4-6 aromatic rings [6]. The concern over the adverse effects of PAHs has been on the increase since their toxicity, carcinogenicity and teratogenicity has been acknowledged. Anthracene, benzo (α) pyrene, benzo (α) anthracene and phenanthrene are known for their carcinogenicity [7] as well as classified under HMW PAHs. Although the LMW PAHs may not be carcinogenic, they also constitute a threat to marine health and by extension humans.

The increase in search of food has increased the search and hunt for marine food due to their protein content, vitamins and unsaturated essential fatty acids (EFA). Owing to its affordability and advantages, it has also been widely consumed by humans. They are lipophilic and as such accumulate within the fatty tissues of these fishes. This has informed researchers that fishes are potential route for human exposure to PAHs. The European Union (EU) stipulated that 1µg/g wet weight for benzo (a) pyrene in foodstuff is the maximum tolerable amount in fishes. Recently, studies have shown that dibenzo (a, 1) pyrene is about 100 times more carcinogenic than benzo (a) pyrene replacing the former as a standard reference [8]. These standards have been used to assess the

human health risks associated with consuming PAH infested sea foods. Ekulu River is the largest water body in Enugu city, located in Enugu east, Enugu Nigeria. It is also a major source of *Clarais gariepinus* (Commonly called cat fish) within the city. As a result of urbanization of the city, the river is exposed to all forms of effluents and contaminants and indirectly consumed by the aquatic life forms. This work is aimed at evaluating the PAH content and health risks associated with the consumption of cat fish obtained from Ekulu rivers in Enugu, Nigeria.

2. METHODS

2.1 Study Area

Ekulu River, the largest body of water in the city of Enugu in Enugu State, south-eastern Nigeria, is a 25-kilometer long river (16mi) and it originates in the same city as well. The city is located on latitude 06° 21 ° N and 06 ° 30 ° and longitude 07 ° 26 ° E and 07 ° 37E °. It has an estimated land area of about 72.8 square kilometres. Enugu as the state capital of Enugu State of Nigeria has a total land area of about 12,831 kilometre. The Ekulu River has Abakpa Rivers as one of its tributaries and empties itself into Emene Rivers.

2.2 Collection of Samples

Matured catfish (*Clarias gariepinus*) were captured from Ekulu river, Emene Enugu state, using a fishing hook and a harvesting buckets provided by the fisher men. They were collected from three different locations of the river. The first location was 20 m away from the point of discharge of the effluent generated from the roofing sheet industry, the second and third locations were from the upstream and downstream location of the river. The control was harvested from a hygienic fish pond. They were all wrapped individually in a clean aluminium foil, labelled and transported to the laboratory for analysis.

2.3 Determination of Polycyclic Aromatic Hydrocarbons in Cat Fish Samples

A total of 20g each of the harvested cat fish tissue samples were homogenized and placed into a 500ml beaker. Extraction of hydrocarbon compounds from samples was carried out using 300 ml of (1:1) hexane acetone for 24 hrs. The crude extract obtained after filtration using chromatographic paper were evaporated to dryness using a rotary vacuum evaporator at 40 degree celcius. The residue obtained was then transferred to 5 ml florisil column for clean-up. 10 ml each of the filtered samples were dissolved in 50 ml chloroform and transferred to a 100ml volumetric flask and diluted to mark. Most of the chloroform was evaporated at room temperature after which 1 ml of inter esterification reagent (20% vol benzene and 55% vol methanol) was added. After the esterification, the organic compound is extracted with hexane and water so that the final mixture of reagent, hexane and water is in the right proportion of 1:1:1 (i.e the addition of 1ml each of the hexane and water to the reaction mixture). The mixture was shaken for two minutes and about half of the top hexane phase was transferred to a small testube for injection into GC column for analysis.

The samples were weighed as the weight of fish gives clue on the age of the fish and the possible extent of PAHs accumulated on the fish, oven dried, homogenised and dissolved in several solvents for extraction and preparation for gas chromatography analysis of polycyclic aromatic hydrocarbon compounds present in the samples as well as their concentrations. Gas chromatograph equipped with flame ionization detector (FID) was used for the separation and quantification of the different polycyclic aromatic hydrocarbons present in the fish samples. Flame ionization detector was chosen over thermal conductivity detector due to its high sensitivity primarily to hydrocarbons. Generally, substances are identified (quantitatively) in the order in which they elute from the column and by the retention time of the analytes in the column. Homogenised tissue samples of the test-fish sample were taken to the laboratory which used a column chromatography equipped with flame ionization detector (FID) that used a helium carrier at 5psi for PAH analysis. To determine whether analyte detection was affected by the difference between diluent used for PAHs extraction and the experimental sample matrix, prepared standard curves were used to extrapolate the amount of added analyte in each case which denoted the spike recovered

2.4 The Reference Standard

The reference standard mix solutions of the United State Environmental Protection Agency's (USEPA) 16 priority PAHs, each at 100 µg/L in dichloromethane, were purchased from Sigma-

Aldrich (St. Louis, MO, USA). The surrogate standard was a mixture containing naphthalene-d8 (N-d8), acenaphthene-d10 (Ace-d10), phenanthrene-d10 (Phen-d10), chrysene-d12 (Ch-d12) and perylene-d12 (Per-d12), which was added to the samples before extraction and used as internal standards for quantification. Stock solutions were used to prepare working standard solutions for calibration and spiking experiments

2.5 Instrumental Processes

Temperature: The initial temperature was set at 60°C at an initial time of 00 s. The sample ramp rate was at 1:8°C /min to a final temperature of a temperature 300°C held for 10 minutes. The temperature of the injector was at 250°C while the detector's temperature was at 300°C.

2.6 Health Risk Assessment Studies on Cat Fish

This was investigated in order to access the possibility that there will be an adverse health effect from consuming these fish samples obtained from a roofing sheet effluent channelled river plausibly contaminated with PAHs. This was investigated using the modules stipulated by USEPA 1996 as well as adults for the study.

2.7 Estimation of the Daily Intake (EDI)

The EDI was calculated to determine the specific intake of PAHs from the fish sample with reference to the acceptable tolerable limits. This was calculated using the following Formula expressed in mg/person/day.

$$EDI = \frac{IRc \times Cpf}{WB} \quad (1)$$

Where,

EDI = represents the estimated daily intake or average daily dose (mg,kg/d) of the metal.
IRc = is the daily intake of cat fish (0.0685 g/ kg/day) [9].
Cpf = is the PAH concentration in the fish *Clarias gariepinus* (cat fish) (mg/kg).
WB = represent the average Nigerian adult weight (70 kg) [9].

2.8 Hazard Quotient for Non-carcinogenic Health Risk Assessment

This is used to evaluate the non-carcinogenic health adverse effects associated with the consumption of cat fish (*Clarias gariepinus*). This module entails dividing the quantity of consumed PAHs via fish by the stipulated reference dose. This was proposed by USEPA and a value above 1 suggests a threat to human health while when it is below 1 is termed safe over a life time [10].

$$\mathrm{THQ} = \frac{\mathrm{EDI}}{\mathrm{RFD}} \quad (2)$$

2.9 Hazard Index (HI)

The Hazard Index was determined in order to evaluate the overall risk of exposure to the sum total of PAHs present in the sample (*Clarias gariepinus*). It is also considered safe when the HI is less than 1, it is safe for consumption while it is unsafe when it is above 1 [10].

Table 1. Reference dose and carcinogenic slope factor for PAHs

PAHs	Reference dose Rf ding (Mg/kgday) [10]	Carcinogenic slope factor CSF (Mg/Kg bw- day-1)
Acenaphthene	0.06	NA
Acenaphthylene	NA	NA
Naphthalene	0.02	NA
Fluorene	0.04	NA
Phenanthrene	0.3	NA
Anthracene	0.3	NA
Fluoranthene	0.04	NA
Pyrene	0.03	NA
Benzo (α) pyrene	0.0004	7.3
Benzo (g-h-i) perylene		NA

NA: Not Available

$$\mathrm{THI} = \sum_{i=1}^{n} \mathrm{THQ} \quad (3)$$

Where,

n stands for the number of PAHs present.
i stands for the individual PAH.

2.10 Carcinogenic Risk

This was determined by multiplying the cancer slope factor by the estimated daily intake (EDI). The cancer slope factor (CSF) of benzo (α) pyrene is 7.3 mg/kg/day. The cancer slope factor of other PAHs are determined from that of benzo (α) pyrene. This is done by multiplying 7.3 with the toxicity equivalency factors (TEF). The life time probability cancer can be calculated by the equation below. Cancer risks in the range of 1.0 × 10^{-6} to 1.0 × 10^{-4} are within the acceptable limit [11]. The summation of ILCR is used to ascertain the limit otherwise known as the risk index (RI)

CR = Estimated Daily Intake (mg/kg/day) x Ingestion Carcinogenic Slope Factor (mg/kg/day)-1.

$$\mathrm{RI} = \sum_{i=1}^{n} \mathrm{ILCR} \quad (4)$$

Where,

n stands for the number of PAHs present.
i stands for the individual PAH.

2.11 Carcinogenic Potency

This was ascertained by multiplying the concentration of individual PAH by its toxicity equivalency factor (TEF). This toxicity equivalency factor is an estimation of the rate at which the giving PAH will cause cancer when compared to Benzo (α) pyrene [12]. Cancer risks in the range of 1.0 × 10^{-6} to 1.0 × 10^{-4} are within the acceptable limit [13]

$$\text{B (α) Pteq} = C_i \times \text{TEF}_i \quad (5)$$

Where,

B(α)Pteq is the carcinogenic potency of the PAHs.
C*i* is the individual PAH concentration.
TEF*i* is the toxicity equivalency factor of each PAH.

2.12 The Toxic Equivalency Quotient (TEQ)

This is obtained by the multiplication of toxicity equivalency factors by the individual concentration of each PAHs found within the tissue and totalling them [12].

$$TEQ = \Sigma [C_i \times TEF_i] \quad (6)$$

Where,

TEQ- the toxic equivalency quotient.
Σ- Summation.
C*i*- is the individual PAH concentration.
TEF*i*- is the toxicity equivalency factor of each PAH.

2.13 Statistical Analysis

One-way ANOVA test were used to estimate the significant difference in the concentration of the various investigated polycyclic aromatic hydrocarbons with respect to the cat fish from. A probability at level of 0.05 or less was considered significant. Standard errors were also estimated.

3. RESULTS AND DISCUSSION

The aquatic ecosystems have been continuously threatened by the irresponsible disposal of wastes generated from industrialization and mechanization. These wastes range from heavy metals, agrochemicals and PAHs. Some of these contaminants such as PAHs also pollute these water bodies via crude oil spillage, runoffs from contaminated sites and industries [14]. They bioaccumulate within the tissues because they are fat soluble, causing detrimental effects to these organisms and humans at large. From the results above, the total number of PAHs identified in Clarais *gariepinus* isolated from Ekulu River (from the downstream, upstream and POD) were 10 in number including the HMW and LMW PAHs. They were comprised of acenaphthene, acenaphthylene, naphthalene, fluorine, phenanthrene, anthtracene, flouranthene, pyrene, benzo (α) pyrene and benzo (g-h-i) perylene as seen in Table 3. Of all the point of location fishes were isolated, the point of discharge of the effluent recorded the highest quantity of PAHs in *Clarias gariepinus*. It recorded anthracene as the PAH with the most dominant concentration 0.0787 mg/kg. The quantity of PAHs detected in all fish samples including the control ranged from below detectable limit (BDL) through 0.001 to 0.0786mg/kg. The LMW PAHs detected were 60 % while the HMW PAHs detected were 40 % of the total PAHs in *Clarias gariepinus* isolated from Ekulu River as shown in Table 4. The total PAH concentration observed from the different point locations were 0.1003 mg/kg, 0.0977 mg/kg, 0.1102 mg/kg and 0.0414 mg/kg for the downstream, upstream, POD and control.

Table 2. Toxicity Equivalency Factors (TEFs) for individual PAHs [15]

Compound	TEF
Dibenzo[a,h]anthracene	5
Benzo[a]pyrene	1
Benzo[a]anthracene	0.1
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Indeno[l23-c,d]pyrene	0.1
Anthracene	0.01
Benzo[g,h,i]perylene	0.01
Chrysene	0.1
Acenaphthene	0.001
Acenaphthylene	0.001
Fhroranthene	0.001
Fluorene	0.001
2-Methylnaphthalene	0.001
Naphthalene	0.001
Phenanthrene	0.001
Pyrene	0.001

The total number of PAHs identified in CLARAIS *GARIEPINUS* isolated from Ekulu River (from the downstream, upstream and POD) were higher when compared to the control. The concentration of the individual PAHs assayed for in fishes were also higher than the control Olaiyinka et al. [16]. The concentration of PAHs detected downstream of the river ranged from anthracene > naphthalene > acenaphthalene > phenanthrene > fluoranthene and Benzo (g-h-i) perylene > benzo (α) pyrene > acenaphthene while fluorene and pyrene were not detected. The PAHs detected upstream ranged from anthracene > benzo (g-h-i) perylene > acenaphthylene > pyrene > fluorene > fluoranthene with naphthalene and benzo (α) pyrene below the detectable limit. The PAHs identified at the POD also ranged from anthracene > pyrene > Benzo (g-h-i) perylene > fluorine > acenaphthylene > benzo (α) pyrene, naphthalene was not detected. The PAHs detected in the control sample ranged from anthracene > acenaphthylene and Benzo (g-h-i) perylene > fluorene and the remaining 6 PAHs were below detectable limit. Some PAHs were also detected in the control samples which were acenaphthylene, fluorine, anthracene, xylene and benzo (g-h-i) perylene. The spotted PAHs in the control could be as a result of translocation and soil runoffs. The detected PAHs in Clarais *Gariepinus* were more of the LMW PAHs which are less carcinogenic and they include acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, fluoranthene and naphthalene. This result is in tandem with the work done by Olaji et al. [17] who investigated the total hydrocarbon concentration in four fish species of Degele community, Nigeria and their dietary intake in the populace.

Forensic diagnosis of PAHs was estimated using the priority pollutant ratio to determine if the source were pyrogenic (Combustion) or petrogenic (oil-based). This involved determining the phenanthrene/anthracene (Ph/An) and fluoranthene/pyrene (Fl/Py) quotient. If the phenanthrene/anthracene > 10, it implies a possible petrogenic origin while phenanthrene/anthracene < 10 suggests a probable pyrogenic origin. In the case of fluoranthene/pyrene (Fl/Py), if the value is > 1, it is considered to be pyrogenic while if it is < 1 it is considered to be petrogenic. The values obtained from Ph/An as seen in downstream, upstream and point of discharge (POD) were 0.011, 0.0038 and 0.0038 respectively while Fl/Py values were 1.2 and 0.58 for upstream and POD. Using the Fl/Py methodology, it suggested that they were petrogenic for the upstream and pyrogenic for the PAHs that accumulated in *Clarais Gariepinus* at the POD. The results obtained by Olayinka et al. [16] also suggested that the PAHs detected in fishes were of both petrogenic and pyrogenic. The petrogenic sources of PAHs observed in Clarais *gariepinus* obtained from the upstream can be as a result of runoffs from oil contaminated effluents from the industry while the pyrogenic sources at the POD can be assigned to the combustion that occurs in the roofing sheet industry nearby. This being said, the prevalence of the LMW PAHs (60%) in the fish samples can also be attributed to

pyrogenicity. The sources in the downstream were not assayed for because pyrene was not detected.

The health risk assessment was investigated with the aid of the estimated daily intake (EDI). It was used to obtain the carcinogenic and non-carcinogenic (hazard quotients, HQ and index, HI) impacts of daily consumption of PAHs in Cat fish obtained from the different points of Ekulu River. The non-carcinogenic risk was ascertained with HQ and HI models. A hazard quotient or index < 1 is considered safe while when it is > 1 there is every possibility of non-carcinogenic health risks as informed by USEPA [18]. The HQ and HI obtained in all point of Ekulu river < 1. This result proposes a safe non carcinogenic health risk from consuming *Clarias gariepinus* from Ekulu River. This result conforms to the study done by Benson et al. [19] who studied PAHs in imported Sardinops *Sagax*. The sequence of the hazard index of PAHs investigated in *Clarais Gariepinus* different locations are as follows 0.0286 (POD) > 0.013 (downstream) > 0.00317 (upstream).

Table 3. PAH analysis of cat fish samples collected in Ekulu river, Emene in (mg/kg)

PAH compounds	Down stream	Upstream	POD	Control
Acenaphthene	0.0002	0.0001	0.0003	BDL
Acenaphthylene	0.0026	0.0071	0.0055	0.0008
Naphthalene	0.0033	BDL	BDL	BDL
Fluorene	BDL	0.0006	0.0056	0.0004
Phenanthrene	0.0008	0.0003	0.0003	BDL
Anthracene	0.0696	0.0786	0.0787	0.0374
Fluoranthene	0.0005	0.0005	0.0005	BDL
Pyrene	BDL	0.0010	0.0097	BDL
Benzo (α) pyrene	0.0004	BDL	0.0050	BDL
Benzo (g-h-i) perylene	0.0005	0.0095	0.0095	0.0008
Total - 10	0.1003	0.0977	0.1102	0.0414

Table 4. The percentage composition of rings present in the fish sample obtained from Ekulu river

Number of rings	Percentage found in sample
2 rings	10 %
3 rings	50 %
4 rings	20 %
5 rings	10 %
6 rings	10%

Table 5. Estimated daily intake, non carcinogenic and carcinogenic risks of PAHs as well as their carcinogenic potencies of the Individual PAHs isolated from different downstream of river Ekulu

PAH compounds	EDI	Non carcinogenic risk. (HQ)	(B(A)Pteq)	ILCR
Acenaphthene	1.96E-06	3.27E - 05	2.0E -07	1.43E -08
Acenaphthylene	2.54E-04	NA	2.6E -06	1.85E -06
Naphthalene	3.23E-05	1.62E - 03	3.3E - 06	2.36E -07
Fluorene	BDL	-	-	
Phenanthrene	7.83E-06	2.61E - 05	BDL	5.72E -08
Anthracene	6.81E-04	2.27E - 03	8E -07	4.97E -06
Fluoranthene	4.89E-06	1.22E - 04	5E -07	3.57E -08
Pyrene	BDL	-	-	-
Benzo (α) pyrene	3.91E-06	9.78E - 03	4E -04	2.85E -05
Benzo (g-h-i) perylene	4.89E-06	NA	5E- 06	3.57E -08
Total - 10		1.3E -02	4.124E -04	3.56E -05

Table 6.. Estimated daily intake, non carcinogenic and carcinogenic risks of PAHs as well as their carcinogenic potencies of the Individual PAHs isolated from different upstream of river Ekulu

PAH compounds	EDI	Non carcinogenic HQ	(B(A)Pteq)	ILCR
Acenaphthene	9.77E -07	1.63E -06	1E -07	7.13E -09
Acenaphthylene	6.95E -05	NA	7.1E -06	5.07E -07
Naphthalene	BDL	---	-----	
Fluorene	5.87E -06	1.48E -04	6E -07	4.29E -08
Phenanthrene	2.94E -06	9.8E -06	3E -07	2.15E -08
Anthracene	7.69E -04	2.56E -03	7.86E -04	5.61E -06
Fluoranthene	4.89E -06	1.22E -04	5E -07	3.57E -08
Pyrene	9.79E -06	3.26E -04	-	7.15E -08
Benzo (α) pyrene	BDL	----	------	
Benzo (g-h-i) perylene	9.30E -05	NA	9.5E- 05	6.79E -06
Total - 10		3.17E -03	8.896E -04	1.26E -05

Table 7. Estimated daily intake, non carcinogenic and carcinogenic risks of PAHs as well as their carcinogenic potencies of the Individual PAHs isolated from POD of river Ekulu

PAH compounds	EDI	Non carcinogenic HQ	(B(A)Pteq)	ILCR
Acenaphthene	2.93E -06	1.62E -05	3E -07	2.14E -08
Acenaphthylene	5.38E -05	NA	5.5E -06	3.93E -07
Naphthalene	BDL	------	------	
Fluorene	5.48E -05	1.37E -03	5.6E -06	4.00E -07
Phenanthrene	2.94E -06	9.8E -06	3E -07	2.15E -08
Anthracene	7.70E -04	2.56E -03	7.87E -04	5.62E -06
Fluoranthene	4.89E -06	1.93E -02	5E -07	3.57E -08
Pyrene	9.49E -05	3.16E -03	------	6.93E -07
Benzo (α) pyrene	4.89E -05	2.15E -03	5E -03	3.57E -07
Benzo (g-h-i) perylene	9.30E -05	NA	9.5E- 05	6.79E -07
Total - 10		2.86E -02	5.89E -03	8.22E -06

This proposes that if there were to be a development of non-carcinogenic health risk from the consumption of consuming *Clarias gariepinus* from the River, it will stem from the point of discharge (POD) of effluents from the roofing sheet industry. This was greatly influenced by the evaluated HQ (1.93E -02) of fluoranthene. The environmental protection agency had suggested that incremental lifetime cancer risk in the range of 1.0×10^{-6} to 1.0×10^{-4} are within the acceptable limit, it poses a very negligible risk of one in ten thousand to a million. A threat is conceivable when it is within the range of 10^{-3} to 10^{-1}. [18, 20] The ILCR obtained for the downstream fluctuated from 1.43E -08 to 2.85E -05, 7.13E -09 to 6.79E -06 for upstream location and 2.14E -08 to 6.79E -07 at the point of discharge. The ILCR as seen above were in the range of 10^{-5} to 10^{-9}. This range are termed the inconsequential lifetime cancer risk because they are safe from a plausible life time consumption. The studies carried out by Tongo et al. [21] disagrees with this result.

The Toxicity equivalency quotient (TEQ) is obtained by the summation of the individual carcinogenic potency (B (α) Pteq) of the PAHs. This potency was determined with the aid of the toxic equivalency factor (TEF). The TEF is a calculated value of how toxic an individual PAH is when compared to benzo (α) pyrene which is considered as the most carcinogenic. It tells the impact of the total PAHs identified in the samples. The TEQ of the PAHs obtained from downstream, upstream and POD were 4.124E -04 mg/kg, 8.896E -04 mg/kg and 5.89E -03 mg/kg respectively suggesting that there will be no non carcinogenic toxicity from the consumption of cat fish from Ekulu river.

The carcinogenic potency of the individual PAHs varied within the different points of location in

Ekulu river. Benzo (α) pyrene has been used as the yard stick for carcinogenic PAHs in foods. In consequence, the benzo (α) pyrene in cat fish obtained from the POD has the most carcinogenic potency (B (α) Pteq) and also recorded the maximum limit (5E -03 mg/kg) as informed by the European Union [21]. Benzo (α) pyrene obtained from downstream gave 4E -04 mg/kg and none was recorded for cat fish obtained from upstream since it was not detected. The Benzo (g-h-i) perylene which is also a carcinogenic PAH was recorded to be 5E -06 mg/kg and the same (9.5E -05 mg/kg) for upstream and POD and this were all considered to be in the safe region of PAH consumption. The carcinogenic toxicity equivalents evaluates the carcinogenicity of individual PAHs. The quotient is a model used to evaluate the sum total of the carcinogenicity of these PAHs. From the results obtained from this study, the benzo (α) pyrene consumed from the POD location in the Ekulu River is likely to cause cancer with the value 5.89E -03. These values are far less when compared to the toxicity equivalency quotient recorded in the work that evaluated PAHs in roasted fish in southern Nigeria [22].

4. CONCLUSION

The present study observed the level of PAHs recorded in *Clarias gariepinus* obtained from different point location Ekulu River in Enugu State, Nigeria. From the findings of this study, it proposes that it is only the fishes obtained from the location of point of discharge from the roofing sheet industry that are likely to be unsafe. This is because the evaluated carcinogenic potency was at the maximum stipulated by USEPA. This calls for an urgent need for awareness to the fish consumers and mongers about the impact of consuming fishes from this location. Cautioning industries and factories that are frequent with irresponsible effluent disposal into water bodies becomes crucial.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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