World Journal of Public Health
2021; 6(1): 6-12
http://www.sciencepublishinggroup.com/j/wjph
doi: 10.11648/j.wjph.20210601.12
ISSN: 2637-6040 (Print); ISSN: 2637-6059 (Online)

Assessement of Water Quality and Risk of Polyaromatic Hydrocarbons in Lungfish (*Protopterus annectens*) from Freshwaters of Ogba/Egbema/Ndoni, Rivers State, Nigeria

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To cite this article:

Elechi Owhoeke, Julius Nkeonyeasua Ehiwario. Assessement of Water Quality and Risk of Polyaromatic Hydrocarbons in Lungfish (*Protopterus annectens*) from Freshwaters of Ogba/Egbema/Ndoni, Rivers State, Nigeria. *World Journal of Public Health*. Vol. 6, No. 1, 2021, pp. 6-12. doi: 10.11648/j.wjph.20210601.12

Received: December 1, 2020; **Accepted**: December 14, 2020; **Published**: March 10, 2021

Abstract: Water quality and health risk of polycyclic aromatic hydrocarbons in *P. annectens* from freshwaters of Egi, Egbema, and Omoku communities, in Ogba/Egbema/Ndoni local government area of Rivers State, Nigeria were examined. The PAHs were checked using gas chromatography coupled with flame ionization detector (GCFID), while the physicochemical parameters were done using standard methods. Summary of the results from the three communities indicates that TDS (Total Dissolved Solids) mean value was 98.1±16.88 mg/l, TSS (Total Suspended Solid) had an average value of 68.5±10.29 mg/l, turbidity and pH had averages of 1.6±0.011 Unit (NTU) and 7.4±1.05 respectively. The concentrations of tPAHs were 4.415±1.34 µg/kg, 4.634±0.59 µg/kg, and 4.859±0.69 µg/kg for Egi, Egbema, and Omoku communities. The major PAHs were Nap, Acn, and BbF. The cancer risk for children was 2.1E-3, 2.3E-3, and 9.5E-5 for Egi, Egbema, and Omoku while that for adults were 7.1E-4, 5.7E-4, and 2.6E-4 for Egi, Egbema, and Omoku respectively. The cPAHs with the most risk index were DbA, BaA, BaP, and BkF respectively. The risk indexes were higher than the USEPA criterion of 10^{-6}, indicating contamination of the fish species. It is recommended that monitoring of effluent should be done often and consumption of fish from polluted water sites should be avoided.

Keywords: Water Quality, Polycyclic Aromatic Hydrocarbons, Cancer Risk and Lungfish

1. Introduction

In the developed world, environmental protection agencies are more active and environmental regulations are followed strictly. The overall check on the quality of the environment and also specifically water quality should be carried out on a a schedule time or a routine assignment [1-4]. Therefore, if there is any unusual alteration in the environmental or water property, this can easily be seen and needed attention given to avoid an epidemic. This is quite different in the developing and underdeveloped countries of the world. Freshwaters are essential to inhabitants of the hinterland due to its resources especially for purposes like; recreation, source of income, and fishing port, etc. Human activities have greatly impacted the water bodies such as activities like crude oil and natural gas exploration in the oil producing communities of Nigeria [5]. There is always the release of obnoxious materials to the water bodies from their sources which could contain toxic chemicals; if absorbed by fishes could be transferred to man [6]. Aquatic organisms play a vital role as food due to their dietary composition which is good for the consumer [7]. The African Lungfish serve as food for many around sub-Saharan African, its contamination by chemicals is of major concern to researchers and scientists.

The aim of the study is to assess the physicochemical property of freshwater bodies and the health risk due to the presence of PAHs in Lungfish from Egi, Egbema, and Omoku all in Ogba/Egbema/Ndoni Local Government Council of Rivers State, Southern Nigeria.

2. Methodology

2.1. Study Area

The local government stretches from longitude 6°28' 13"E through longitude 6°47'34"E and latitude 5°9'42" N through 5°44'3"N. It is one of the oil-producing LGAs of the Southern region of Nigeria. It is surrounded on the West by the River Orashi and bordered on the East by the River Sombreiro. There are several fresh-waters in the area and oil fields within Onelga.

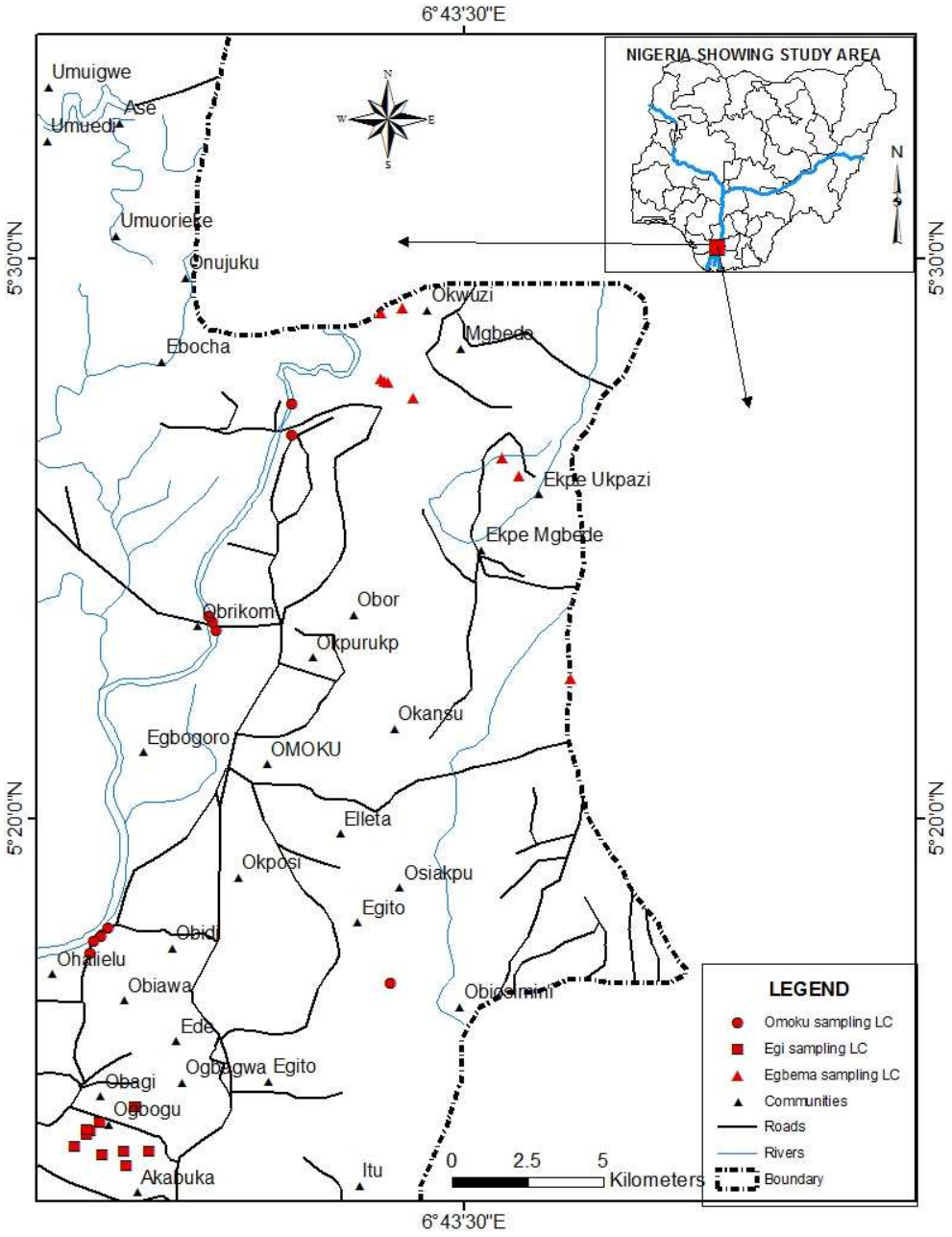

Figure 1. *Map of the locations.*

2.2. Samples Collection

The water sampling involved thirty (30) locations across the three sub-areas of from Egi, Omoku, and Egbema communities respectively. Before the samples were collected, the glass bottles were washed and dried in the sun; the glass bottles were rinsed twice with the same water samples they are to contain. In each case, samples were taken at 15cm deepness below the water surface employing amber-colored 1 liter capacity glass bottles [8]. The collected samples in the bottles were instantly covered, adequately labeled, and positioned in cooler containing an ice chest with ice for more treatment and examination in the research laboratory.

Fresh Lungfish (*Protopterus annectens*) samples were obtained from freshwaters like the Orashi and Sombreiro rivers, creeks, lakes, and swamps in Egi, Omoku, and Egbema clans in Ogba/Egbema/Ndoni LGA, Rivers State. The fishes were transferred into a sterilized cellophane bag and taken for identification by experts at the Department of

Animal and Environmental Biology, University of Port Harcourt.

2.3. Determination of Physicochemical Parameters of the Freshwaters

The pH, turbidity, total dissolved solids (TDS), and total suspended solids (TSS) were carried out using standard procedures as described by APHA, 1992 [9].

2.4. Sample Preparation

The fresh fish samples obtained were sun-dried, and then later oven-dried in the laboratory to constant weight at 33°C for hours till completely dried. The whole fish sample (without the bones) was then grounded with a blender and preserved in a container that is impermeable to air, before the extraction process.

2.5. Extraction of the Sample

The extraction involved 6 g of the powdered extract been moved to the extraction casing and placed in the extraction compartment of the Soxhlet extractor, which made up of a 250 ml round bottom flask, condenser, and extraction tube, well held in the heating mantle with a wide temperature range. N-hexane and dichloromethane (3:1 v/v) was the extraction solvent which was carried out at 50°C for 6 h as described by USEPA 3540 Method [10]. The extract was concentrated in a rotary evaporator at 60°C to a concentration of 2 ml. This same procedure was carried out for other samples.

2.6. Clean up of the Extracts/Gas Chromatography Analysis

5ml n-hexane was used to dissolve the concentrated extract. Activated alumina of 2.5 g was used to adsorb the resulting extract, and the mixture was dried under a high vacuum dryer. A glass column (10 mm id ×40 mm length) was packed with activated alumina adsorbent (7.5 g) and the adsorbed extract was packed on the top. In series, 50 mL of the n-hexane, and 50 mL of a mixture of the n-hexane: DCM (95:5%) was used to elute the saturate and PAHs fractions from the adsorbed extract. The collected saturate fraction was subjected to further analysis. The PAHs fraction was reduced to a concentration of 1 ml in an evaporator, and was transferred into a sample vial and refrigerated till further usage [11]. The procedure was repeated for all the samples.

PAHs concentration evaluation was carried out following the recommended procedures as described by Essumang *et al.*, (2009) [12]. The sample in the vial was injected into the gas chromatography coupled with a flame ionization detector (FID). This was carried out on an HP 5890 series II GC with th following properties; fused silica capillary (HP5) of 30 m length, internal diameter of 0.32 mm, and 0.25 µm film diameter was 0.25 µm and the rate was 6°C /min. The oven temperature was programmed from an initial temperature of 110°C (2 min hold) to 250°C at the rate of 6°C /min and was constant at 250°C for 25 minutes. Injector and detector temperature were kept at 285°C and 305°C respectively. The carrier gas was helium.

2.7. Human Health Risk Assessment

Calculated daily doses (mg/kg/day) were estimated for adults (as the overall population) and children (as a vulnerable group) to estimated human contact through direct consumption of the fish (Eq. 1)

$$CDI=(Ef \times Ed \times Fir \times Cf \times Cff \times Cpahs)/(BW \times AT) \quad (1)$$

$$\text{Cancer Risk}=CDI \times SF \quad (2)$$

Where Cpahs=metal concentration in fish, [13], Ed is the exposure duration=65 years for an adult and 15 years for children, Ef is the exposure frequency=365 days/year, Fir is fresh fish ingestion=48 g/person/day, Cf is the conversion factor for fresh to dry weight for fish=0.208, Cff=0.001 conversion factor from µg to kg, BW is average body weight=15 kg and 60 kg for children and adults, AT is the average exposure time=Ed × Ef. day, IdP=0.73 mg/kg-day, BaA=0.73 mg/kg-day, Chr=0.073 mg/kg-day, and DbA=7.3 mg/kg-day [14].

3. Result and Discussions

3.1. Physico-Chemical Parameters of Freshwater

The result of the physicochemical parameters obtained from the Egi, Omoku, and Egbema communities are shown in Table 1.

Table 1. *Summary of Physico-chemical Properties with Permissible Limit.*

Area	TDS (mg/l)	TSS (mg/l)	Turbidity (NTU)	pH
Egi	119.9±14.53	68.3±7.54	3.7±0.00	7.2±1.08
Omoku	61.4±12.40	66.4±11.40	0.2±0.00	7.4±0.96
Egbema	113.0±23.70	70.8±11.93	0.8±0.00	7.5±1.05
Mean	98.1±16.88	68.5±10.29	1.6±0.00	7.4±1.05
WHO (2006)	1000	100	5	6.5-8.5
India (EPR, 1993)	500	100	10	6.5-8.5
Nigeria (FMENV, 1992)	1000	500	5	6.5-8.5

TDS was 98.1±16.88 mg/l as the mean for the three areas which was lower than the limit. Alabaster and Lloyd [15], submitted that extreme concentration of suspended and dissolved solid influence the toxicity of the water to aquatic organisms, this is because it reduces the quality of the water, affects processes that leads to photosynthesis, and increases the amount of sediment/depth of water. The mean of total suspended solids for the three areas were Egi; 68.3±7.54

mg/l, Omoku; 66.4±11.40 mg/l, and Egbema area; 70.8±11.93 mg/l. The TSS is low compared with the Federal Ministry of Environment (FMENV) and WHO's standard of 2006. These values were higher than reports by Ewa *et al.,* (2011) [16] on the Omoku creek (22.3 mg/l).

The mean Turbidity value was 1.6±0.00 which was lower than WHO's standard of 5 NTU. This is also relatively lower than work by Ewa *et al*. (2011), where they reported 29.30 NTU on Omoku creek. This could be attributed to the water current from the flooding which washed away most of the organic particles on the surface of these water bodies. The mean of pH were within the range recommended by WHO (2006) [17] for drinking water. Although the values reveal that the surface water samples are slightly basic, it is in agreement with what was reported by other researchers in a similar study [18]. Chinedu *et al.,* (2011) [19], (6.0±0.52 to 7.2±0.52) on surface water around Ota, southwest Nigeria. This result recorded for the surface water is agreeable to the fact that ONELGA is an oil and gas production area that is characterized by industries that discharge effluents made of organic matter.

3.2. Polycyclic Aromatic Hydrocarbons in Lungfish

The table below revealed the result of PAHs presence in the lungfish from the study area.

Table 2. *Summary measurements of PAHs in Protopterus annecteens samples (µg/kg).*

PAHs	Location		
	Egi	Egbema	Omoku
Nap	0.967±0.12	Nd	0.789±0.07
Ace	0.286±0.03	0.124±0.02	0.349±0.03
Acn.	Nd	0.774±0.07	0.677±0.05
Flo	0.467±0.14	Nd	0.420±0.09
Ant	0.151±0.11	0.180±0.09	0.256±0.08
Phe	0.823±0.21	Nd	0.017±0.00
Flu	Nd	0.895±0.08	0.020±0.00
Pyr	Nd	0.246±0.03	Nd
BaA	Nd	Nd	0.867±0.06
Chr	Nd	Nd	Nd
BbF	0.321±0.23	0.987±0.15	Nd
BkF	0.216±0.05	0.261±0.00	0.754±0.13
BaP	0.201±0.09	0.067±0.01	0.033±0.01
IdP	0.456±0.19	0.423±0.04	Nd
DbA	0.290±0.11	0.241±0.06	0.026±0.01
BgP	0.237±0.06	0.375±0.04	0.651±0.16
tPAHs	4.415±1.34	4.634±0.59	4.859±0.69

Note: Nd=Not Detected, Nap.=Naphthalene, Ace.=Acenaphthylene, Acn=Acenaphthene, Flo.=Fluorene, Ant.=Anthracene, Phe.=Phenanthrene, Flu.=Fluoranthene, Pyr.=Pyrene, BaA=Benz (a) Anthracene, Chr.=Chrysene, BbF=Benzo (b) Fluoranthene, BkF=Benzo (k) Fluoranthene, BaP=Benzo (a) Pyrene, IdP=Indeno (1,2,3-cd) Pyrene, DbA=Dibenz (a, h) Anthracene, BgP=Benzo (g, h, i) Perylene.

The distribution of PAHs in *P. annectens* sampled from different sites is given in Table 2. The total PAHs detected for the different sites were 4.415±1.34 µg/kg, 4.634±0.59 µg/kg, 4.859±0.69 µg/kg, for Egi, Egbema, and Omoku respectively. The values ranged from 0.00 to 0.987 µg/kg. The prominent PAHs were Nap (0.967±0.12 µg/kg) and Phe (0.823±0.21 µg/kg) for Egi sites, BbF (0.987±0.15 µg/kg) and Flu (0.895±0.08 µg/kg) for Egbema sites, and BaA (0.867±0.06 µg/kg) and Nap (0.789±0.07 µg/kg) for Omoku sites. Chr was not detected in all the sites. This result was lower than reports by Mihalca *et al.,* (2011) [20] (77.3 µg/kg) on smoked fishes. Mirsadeghi *et al.,* (2011) [21] reported a higher value of 3.34±0.77 to 46.85±5.50 µg/kg in *A. granosa.* Though reports by Olabemiwo *et al.,* (2011), [22] (0.814 µg/kg) on *T. guineensis* was lower. The range of values indicates human activities have impacted the freshwater bodies.

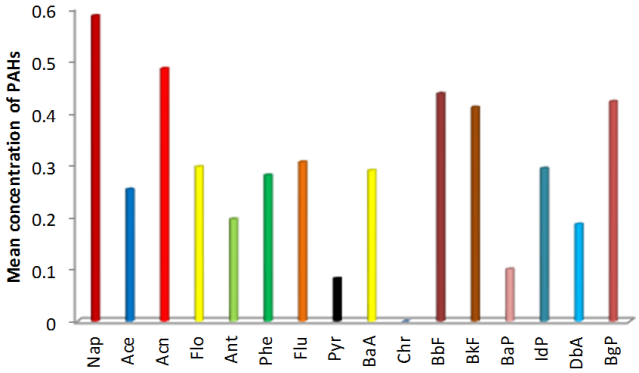

Figure 2. *Mean concentration of PAHs across the study area.*

The mean of PAHs reveals that the PAHs with the highest concentrations were Nap, Acn, BbF, and BgP respectively. The result also shows that the non-carcinogenic PAHs were of higher concentration than the cPAHs.

Table 3. *Calculated daily intake (CDI) and cancer risk of PAHs estimate for children.*

	Egi	Egbema	Omoku
		CDI value	
Chr	-	-	-
BaA	-	-	5.8E-4
BbF	2.1E-4	6.6E-4	-
BkF	1.4E-4	1.7E-4	5.0E-4
BaP	1.3E-4	4.5E-5	2.2E-5
IdP	3.0E-4	2.8E-4	-
DbA	1.9E-4	1.6E-4	1.7E-5
		Cancer Risk	
Chr	-	-	-
BaA	-	-	4.2E-4
BbF	1.5E-4	4.8E-4	-
BkF	1.0E-4	1.2E-4	3.6E-4
BaP	2.2E-4	3.3E-4	1.6E-4
IdP	2.2E-4	2.0E-4	-
DbA	1.4E-3	1.2E-3	1.2E-5
tPAHs	2.1E-3	2.3E-3	9.5E-4

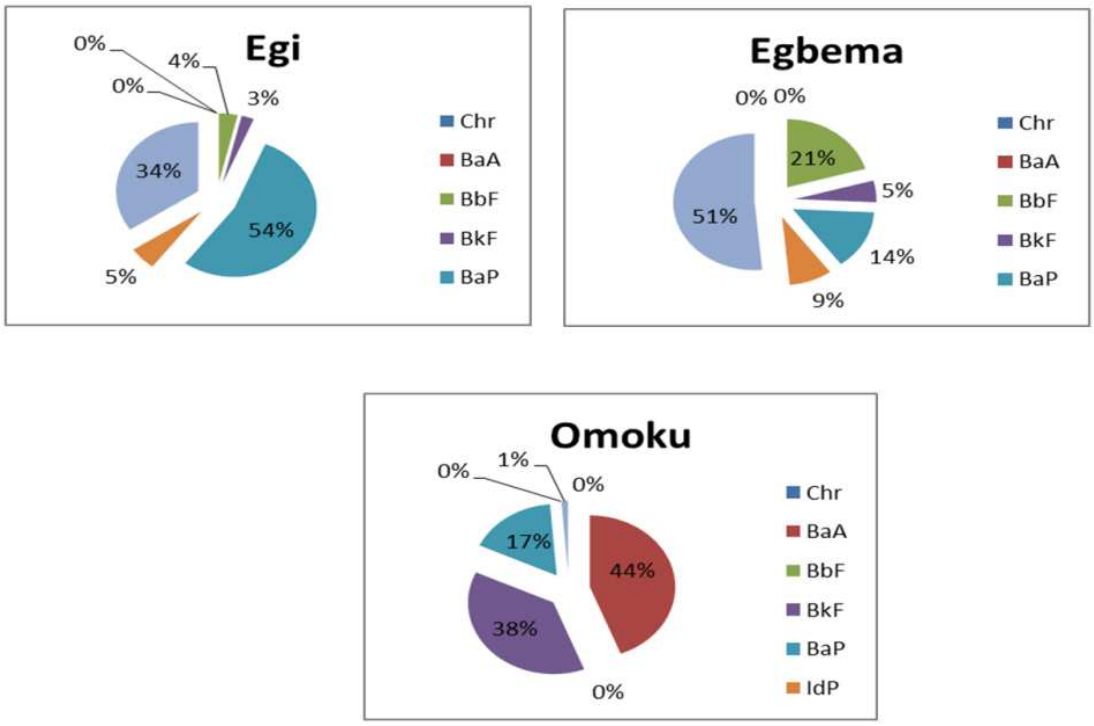

Figure 3. *Percentage representation of the cancer risk of individual cPAHs in children.*

The risk of PAHs in lungfish for children was high across the three communities studied with values at 10^{-3} to 10^{-4}. The total cPAHs CR values were 2.1E-3, 2.3E-3, and 9.5E-4 for Egi, Egbema, and Omoku. The Egi samples had the highest risk for BaP, Egbema was DbA, while Omoku was for BaA. It was lower than reports by Mirsadeghi *et al.,* (2011) [22] (2.67 x 10^{-2}). These values are higher than the USEPA risk management criterion. The risk management range of USEPA for greater cancer risk is 1 x 10^{-6}, which indicates the greater cancer risk signifying to one additional cancer in a populace of one million people.

This standard predicts that, for every 1,000,000 population eating fish or shellfish containing certain cPAHs at a certain ingestion rate estimated in g/day for 70 years, it will amount to only one additional case of cancer.

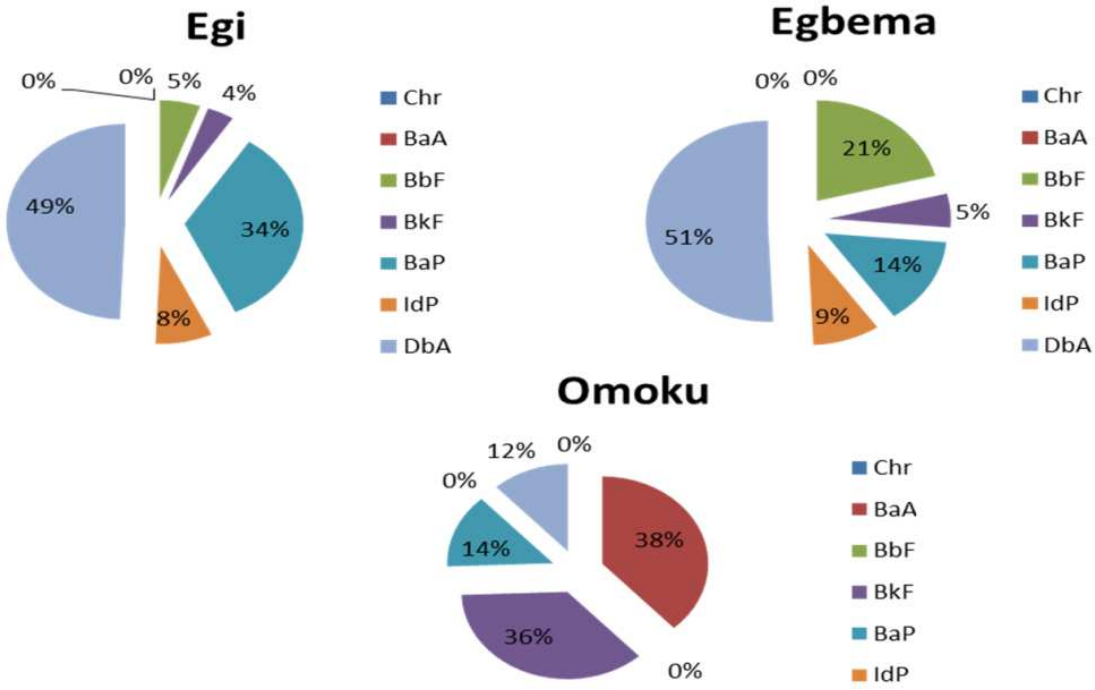

Figure 4. *Percentage representation of the cancer risk of individual cPAHs in Adults.*

Table 4. *Calculated daily intake (CDI) and cancer risk of PAHs estimate for Adults.*

	Egi	Egbema	Omoku
		CDI value	
Chr	-	-	-
BaA	-	-	1.4E-4
BbF	5.3E-5	1.6E-4	-
BkF	3.6E-5	4.3E-5	1.3E-4
BaP	3.3E-5	1.1E-5	5.0E-6
IdP	7.6E-5	7.0E-5	-
DbA	4.8E-5	14.0E-5	4.3E-6
		Cancer Risk	
Chr	-	-	-
BaA	-	-	1.0E-4
BbF	3.9E-5	1.2E-4	-
BkF	2.6E-5	3.1E-5	9.5E-5
BaP	2.4E-4	8.0E-5	3.6E-5
IdP	5.5E-5	5.1E-5	-
DbA	3.5E-4	2.9E-4	3.1E-5
tPAHs	7.1E-4	5.7E-4	2.6E-4

The cancer risk of tPAHs in lungfish for adults was 7.1E-4 for Egi, 5.7E-4 for Egbema, and 2.6E-4 for Omoku respectively. The PAHs of prominence in risk were DbA, BaA, BaP, and BkF. These risk values were above the USEPA management criterion levels which indicate risk of cancer for 1 person in every 1 million persons for adults. Though there may be a concern for consumers of such fishes since the probability of consuming it on daily basis is low, then such risk may be minimal. There is a need for actions from stakeholders to check, reduce, and eliminate possible sources of water contamination within the study area.

4. Conclusions

It could be concluded from the above findings, that the samples of *P.annectens* were contaminated by individual PAHs to certain concentrations. These levels could be attributed to human activities which are dominated by oil and gas exploration. Also, that the concentrations detected might be of possible cancer risk if consumed regularly by the locals of the study area. Therefore monitoring the presence and concentrations of PAHs in freshwaters and fishes within the study area should be considered important, in order to check the possible danger that may emanate in the near future. It is recommended that adequate attention should be paid to the consumption of fresh fish from polluted water bodies in the study area.

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