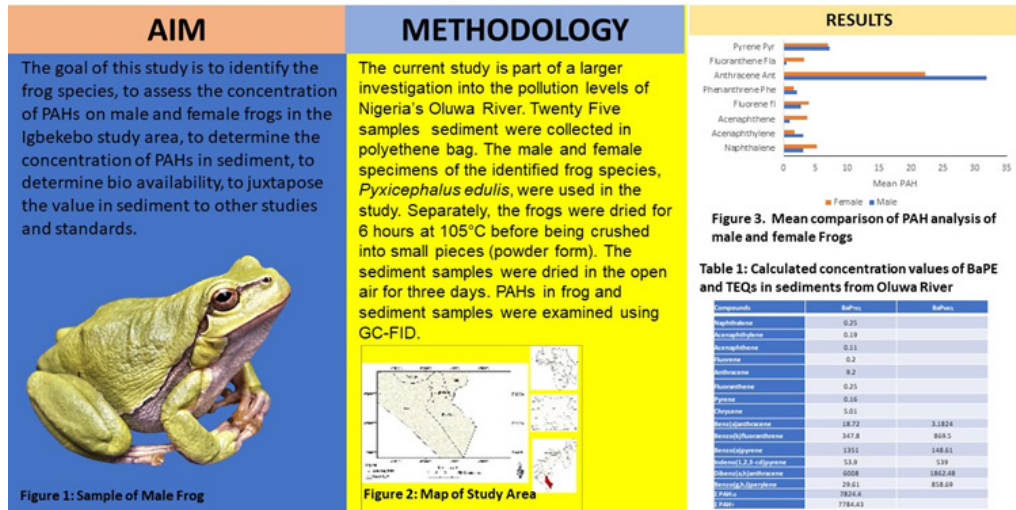


RESEARCH ARTICLE

The quantum of polycyclic aromatic hydrocarbon in *Pyxicephalus edulis* and sediments in Oluwa river, Igbekebo area, Ondo state, Nigeria

Thompson F. Ediagbonya^{1,*}, Felix A. Ikuesan² Akinsanmi M. Oyeyemi¹, Johnson A. Ogunjobi³ and Opeyemi E. Omoyugbo¹



Highlights

- The toxicity equivalent (TEQ) value of polycyclic aromatic hydrocarbons (PAHs) in sediments was determined with the help of Sediment Quality Guideline (SQG).
- Male frogs had significantly higher concentrations of total PAHs than females
- Male frogs had significantly lower concentrations of Nap, Ace, Flu, and Fln, while BaAnt, BbF, Bkf, BaP, InP, DahAnt and BghiP were reported only among males.

RESEARCH ARTICLE

The quantum of polycyclic aromatic hydrocarbon in *Pyxicephalus edulis* and sediments in Oluwa river, Igbekebo area, Ondo state, Nigeria

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Received: 27.04.2022 ; Accepted: 25.07.2023

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are organic compounds composed of two or more fused aromatic rings. PAHs can be found in a variety of foods and beverages, including drinking water, vegetables, fruits, cereals, oils, seafood, and meats. The current study investigated the pollution levels of the quantum of polycyclic aromatic hydrocarbon in *Pyxicephalus edulis* and river sediments. Twenty-five sediment samples and male and female specimens of *Pyxicephalus edulis* were collected from Oluwa River near Igbekebo, Ondo State Nigeria. The sediment samples were then dried in the open air for three days while the identified frog species were dried separately for 6 hours at 105°C before being powdered. The physicochemical parameters of sediment samples examined using standard physical and chemical analytical techniques and polycyclic aromatic hydrocarbons in frog and sediment samples were examined using gas chromatography-flame ionization analysis (GC-FID). The toxicity equivalent (TEQ) values of PAHs in sediment samples were determined by comparing the findings of this study to the Sediment Quality Guideline (SQG) with effects range from viz., low (ERL), median (ERM) and threshold-effects level (TEL)/probable-effects level (PEL) to assess the toxicity of PAHs to aquatic organisms living in sediments. Male frogs had significantly higher concentrations of Acenaphthylene, Phenanthrene, Anthracene, Pyrene, and total PAHs than females, and lower concentrations of Naphthalene, Acenaphthylene, Fluorene, and Fluoranthene. BaAnt, Benzo(b) fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-cd) pyrene, Dibenz(a,h)anthracene, Benzo(g,h,i) perylene were reported only among males. The cause of this variation is unknown, but it could be due to differences in the genetic make-up of male and female frogs.

Keywords: PAHs; Male Frogs; Female Frogs; Sediment; GC-FID; Physicochemical parameters

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic chemicals composed of two or more fused benzene and/or pentacyclic rings arranged in a linear, angular or cluster configuration (Alomirah *et al.*, 2009; Iwegbue *et al.*, 2014; 2015a, 2015c, Ossai *et al.*, 2015; Iwegbue *et al.*, 2016a). Man-made activities and natural processes contribute

to PAH formation in the environment (Iwegbue *et al.*, 2014). PAHs are present in a wide range of foods and beverages, including seafood, and meat vegetables, fruits, cereals, water and atmospheric particles (Kazerouni *et al.*, 2001; Dost *et al.*, 2012; Ediagbonya *et al.*, 2012; 2013b; Ediabonya *et al.*, 2013a). Contamination from sediment, soil, atmosphere, water and manufacturing industry are the most likely sources of PAHs in food. PAHs are highly lipophilic and have a low water solubility (Llobet *et al.*, 2006). Owing to the lipophilicity of these compounds, they can easily cross lipid membranes and creating fatty tissues of a wide range of aquatic organisms (Ramalhosa *et al.*, 2009; Squadrone *et al.*, 2014). PAHs dispersed widely in the environment as a result of their mechanism of synthesis (Ossai *et al.*, 2015; Iwegbue *et al.*, 2015b, d) and are also notorious for their long-lasting, genotoxic, mutagenic and carcinogenic properties (Kishikawa *et al.*, 2003; Iwegbue *et al.*, 2015b; Ossai *et al.*, 2015; Iwegbue *et al.*, 2016b). PAHs are dispersed across the gas and particle phases of the atmosphere and undergo long-distance transport and deposition (Cabuk *et al.*, 2013). PAHs are almost all hydrophobic and biodegradable. As a result, they are thought to be easily absorbed by organisms and sediments (Das *et al.*, 2008; Guo *et al.*, 2010). PAHs are detrimental to animal, humans and other organisms near or far away from their origin (Naccari *et al.*, 2011). These compounds are of concern not only because they are among the most common types of environmental pollutants but because they are carcinogenic and mutagenic (Fernandez *et al.*, 2000; Xue & Warshawsky, 2005; Usenko *et al.*, 2007). The amount and constituents of PAHs found in sediments, air, organisms and water reveal source characteristics as well as the physicochemical properties of individual PAHs with significant impacts on the partitioning of various phases (Deb *et al.*, 2000; Colombo *et al.*, 2006; Ozaki *et al.*, 2006). Based on their frequency of occurrence and toxicological characteristics, the US Environmental Protection Agency (USEPA) has designated 16 PAHs as priority control

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pollutants, with seven of them known to cause human cancer (Qin *et al.* 2013; Zhao *et al.* 2014; Qin *et al.* 2014). Furthermore, ultraviolet light exposure can alter the carcinogenicity of PAHs, and 11 of the 16 USEPA priority PAHs have photo-mutagenic properties (Yang *et al.*, 2004). Apart from cigarette smoking and exposure to PAH in workplaces, consuming polluted food, particularly aquatic lives and plant are also possible sources of PAH exposure in humans (Phillips, 1999; Falcó *et al.*, 2005). PAHs cause growth retardation, endocrine disturbances, reproductive system failure, and DNA damage in marine creatures (Nkpaa *et al.*, 2013). Frogs are members of the vertebrate class known as amphibians (Omonona & Ekpenko, 2011). Warkentin *et al.* (2009) summarized alarming data on the number of Asian frogs taken for human consumption. Human interference in the environment has resulted in the decline of frogs (Cohen 2001; Hayes *et al.* 2006; Simon *et al.* 2012). Frogs are more vulnerable to environmental contaminants than other animals because their egg membranes and skins do not obstruct the passage of foreign substances (Snodgrass *et al.* 2003). Eggs and tadpoles have been used as bioindicators for pollution evaluation (Berzins and Bundy 2002; Haywood *et al.* 2004; Simon *et al.* 2012).

The goal of this study is to assess the concentration of PAHs in *Pyxicephalus edulis* (frogs) and sediments in the Igbekebo area of Oluwa River as well as determine bio availability in order to compare values in sediment to other studies and standards.

MATERIALS AND METHODS

Study Area

Igbekebo is the Administrative Headquarter of Ese – Odo Local Government Area in Ondo State, Nigeria. It is home to the Ijaw (Izon) ethnic subgroups of the Western Apoi

and the Arogbo tribes. It has a land area of 762 km² and a population of 154,978 people according to the 2006 census. Oluwa River stretches along Okitipupa, Ilaje and Ese- Odo Local Governments with Igbekebo being one of the communities along the river bank. The river is usually heavily polluted due to several anthropogenic activities such as oil spills which might lead to large amounts of PAHs in the river and sediments. The map of the sampling location (Ediagbonya *et al.* 2022a; 2022b) is shown in Figure 1.

Collection of samples

Sediment and frog (male and female) samples were taken from the Igbekebo area of Oluwa River. Plastic bottles were used to collect samples from five (5) separate locations at a depth of 10 cm. Samples A and B were assigned to the frog samples. Ten (10) equal-sized samples of male and female frogs were taken, as were 25 samples of silt. Figure 1 shows the sampling locations and Table 1 contains the coordinates of the locations.

Table 1: Location and coordinates of sample collection points.

Location	Latitude	Longitude
A	6° 21' 00" N	4° 52' 00" E
B	6° 21' 02" N	4° 54' 05" E
C	6° 21' 05" N	4° 54' 05" E
D	6° 23' 07" N	4° 54' 07" E
E	6° 23' 07" N	4° 56' 08" E

Preparation of sample

The frogs were dried for 6 hours at 105°C and then crushed into fine powder for analysis. The sediment samples were air- dried for three days before being prepared for analysis.

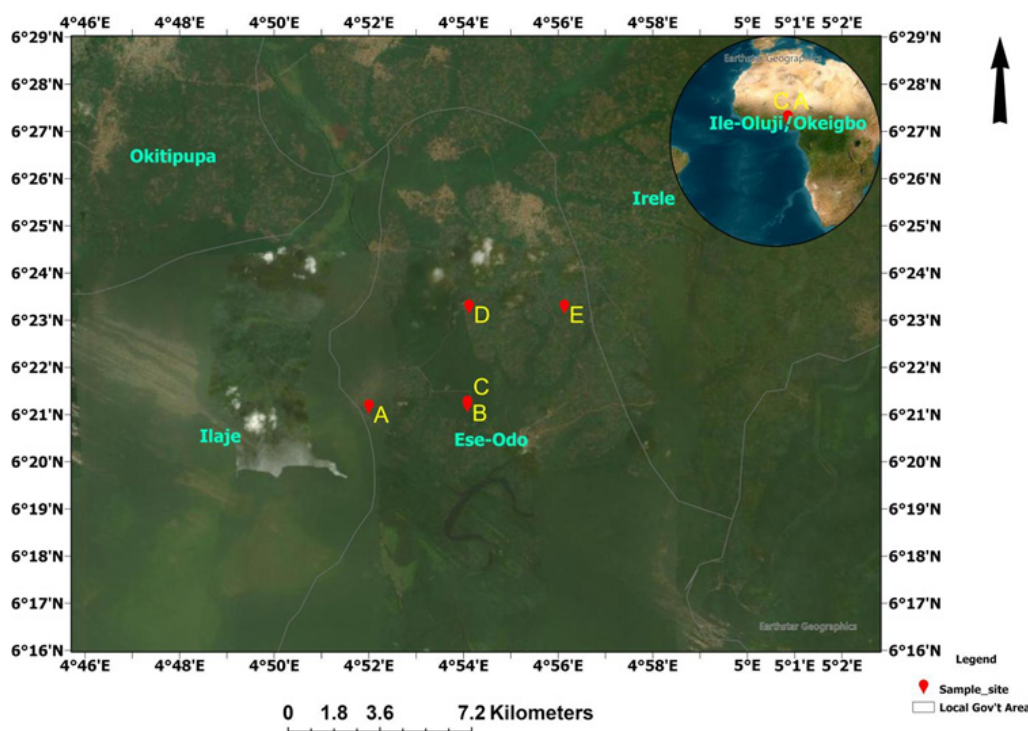


Figure 1: A map showing the study area, Oluwa River near Igbekebo, Ondo State Nigeria.

Sample analyses

GC-FID 5890 series paired with a Flame ionization detector was used for the GC/FID analysis. The GC had a Helium gas carrier with a split less inlet mode and a linear velocity of 30cm/sec. The GC separation was performed on a capillary column HP-5 (cross linked PH ME siloxane) 19091J-413 (30 m 0.32 mm 0.25 m, phase ratio 320). The following temperature programs were used for the analysis: initial temperature of 100°C, initial time of 1 minute with rate 1: 4°C/minute, final temperature of 310°C, and detector temperature of 300°C. A flame Ionization Detector holding 35ml/minute of hydrogen and 350ml/minute of air (EPA, 1984; NIOSH 1994; Cai *et al.* 2009).

Statistical Analysis

The data was analyzed using the Statistical Package for Social Sciences (SPSS) version 26.0 for Windows. The data was described using means and standard deviation. The independent t-test was used to compare mean differences between frog types (water and land) and sexes, while spatial variation was compared using One Way Analysis of Variance (ANOVA) with Scheffé post hoc. The relationship between physicochemical parameters and PAHs was investigated using Pearson's correlation. The distribution of physicochemical characteristics was represented using box plots.

Quality Control

A method blank, a method blank spike, a Diesel/Lube standard, a sample duplicate, and a sample matrix spike were all prepared in order for exactness and precision of the PAHs determination process in this investigation. The quality control standard was done by using the method blank with only reagents (hexane: acetone 1:1) and treating it in the same manner as the sample. Using reagents (hexane: acetone 1:1) and spiked with 200L (150,000 ppm) of Diesel/Lube standard, a technique blank spike was created. It was processed in the same way as the sample. With each analysis, a sample duplicate (SD) and a sample matrix spike (SS) were also prepared. The SD is the same sample made exactly, while the SS is prepared exactly and then spiked with 200L of Diesel/Lube.

Toxicity equivalency factors

The toxic equivalent factor (TEF) and mutagenic factor (MF) were used to assess the carcinogenic and mutagenic potential of PAHs (MEF). The total of the products of the amounts of each individual PAH and their associated poisonous equivalent factors or mutagenic factors, yields the carcinogenic and mutagenic equivalents respectively.

$$BaP_{TEQ} = \sum (BaP_{TEQ(i)}) = \sum (C_{PAH(i)} \times TEF_{PAH(i)})$$

The BaP_{eq} was calculated using the toxic equivalent factor value for each PAH according to Nistbet and Lagoy (1992) while the mutagenic factor value for 7 PAH was according to Durant *et al.*, (1999) and used for the calculation of the mutagenic potency (BaP_{MEQ}) of the individual PAH. The TEF values (Chaber & Gworek, 2020; Ediagbonya *et al.*, 2022b).

The mutagenic and carcinogenic equivalents can be

calculated by multiplying the levels of each PAH and their corresponding toxic equivalent factors or mutagenic factors,

$$\text{Total TEQ} = \sum_i C_i \times TEF_i$$

Where C_i was the concentration of individual PAHs (ng/g d.w.) and TEF_i was its corresponding toxic equivalency factor.

RESULTS AND DISCUSSION

The mean comparisons of PAHs of male and female frogs are given in Table 2. The results revealed that the PAH parameters ranged $0.41 \pm 0.02 - 47.85 \pm 0.00$ (ng/g⁻¹) for the male frogs and $1.56 \pm 0.00 - 22.15 \pm 0.30$ (ng/g⁻¹) for the female frogs. Dibenzo(a)anthracene (47.85 ± 0.00 ng/g⁻¹) and Anthracene (22.15 ± 0.30 ng/g⁻¹) were highest for male and female frogs respectively. Also, except for Fluoranthene, Acenaphthene and Fluorene, all the PAHs were higher in the male frogs than the females. The order of concentrations of the PAHs in frogs were; DahA > Ant > BghiP > Bap > Pry > InP > Acy > Nap > Fl > Phe > BaA > BkF > Ace > BbF > Chr > Fla. The detection of PAHs in frogs suggests their accumulation in the aquatic animal. Result of this study corroborates the assertion that aquatic animals are known bio-indicators and they accumulate heavy metals and persistent organic pollutants (Iwebue *et al.* 2016b; Ediagbonya *et al.* 2019; 2020b; 2022a). However, the concentration of the following Chr BaA, BbF, BkF, Bap, InP, DahA and BghiP were detected in the male frogs but all values were below the detection levels in female frogs.

The variation in PAH concentrations might be due to their genetic compositions, ecological or biological factors. PAHs are known carcinogens. PAHs and especially their metabolic products are therefore of great concern. Savinov *et al.* (2003) reported that BaA, BaP, BbF, BkF, DahA, and InP are some of the potentially carcinogenic PAHs (CPAHs). Total CPAH concentrations in Jialu River sediments ranged from 192.8 to 856.0 ng/g d.w., with an average of 489.1 ng/g, accounting for 20.07–51.58 percent of total PAH concentrations.

The concentration of the PAHs in sediment for Nap in location C 253.46 ± 0.30 has the highest mean concentration (253.46 ± 0.30) while location B had the lowest (250.85 ± 0.00). Locations A, D, E were approximately the same 252.36 ± 2.14 , 252.25 ± 1.97 , 252.21 ± 2.35 respectively. Acy in location C has the highest mean concentration (197.81 ± 0.00), locations A, B, D, E, are spatially the same 192.56 ± 7.42 , 192.56 ± 7.37 , 192.57 ± 7.41 , 192.54 ± 7.40 , for Ace Location A, C, D, E, were higher than location B 100.11 ± 0.00 . The concentration of Fl ranged $213.09 \pm 0.00 - 213.68 \pm 0.83$ for all the locations with location B having the least value (213.09 ± 0.00).

Table 3 shows that for Benzo(a)pyrene, Acenaphthylene, Fluoranthene Acenaphthene, recorded maximum values at location B, while Naphthalene, Chrysene, Benzo(k), fluoranthrene recorded maximum values at location C, Fluorene, Benzo(g,h,i) perylene reported maximum values

Table 2. Mean comparison of PAH (ng/g^{-1}) analysis of male and female Frogs samples.

	Male	Female	T	P
Naphthalene	3.02±0.00	5.19±0.04	-96.655	0.000
Acenaphthylene	3.09±0.01	1.68±0.11	22.680	0.000
Acenaphthene	0.98±0.01	3.65±0.03	-149.257	0.000
Fluorene (flu)	2.68±0.06	3.92±0.11	-17.467	0.000
Phenanthrene (Phe)	2.06±0.02	1.56±0.02	26.386	0.000
Anthracene (Ant)	31.84±0.37	22.15±0.30	35.033	0.000
Fluoranthene (Fla)	0.41±0.02	3.19±0.01	-209.181	0.000
Pyrene (Pyr)	7.14±0.01	6.96±0.02	14.140	0.000
Chrysene (Chr)	0.53±0.01	NC	NC	NC
Benz(a)anthracene (BaA)	1.80±0.01	NC	NC	NC
Benzo(b)fluoranthene (BbF)	0.69±0.00	NC	NC	NC
Benzo(k)fluoranthene (BkF)	1.38±0.00	NC	NC	NC
Benzo(a)pyrene (BaP)	21.37±0.05	NC	NC	NC
Indeno(1,2,3-cd) pyrene (InP)	3.60±0.01	NC	NC	NC
Dibenz(ah)anthracene (DahA)	47.85±0.00	NC	NC	NC
Benzo(ghi)perylene (BghiP)	29.82±0.01	NC	NC	NC
\sum PAHs ^a	158.26±0.37	48.30±0.45	324.613	0.000

NC, Not Computed; ^a \sum PAHs total concentration of 16 PAHs

at location D, while acenaphthene reported maximum value at location E. At location A, minimum concentrations of fluoranthene, dibenz(a,h)anthracene, and benz(a)anthracene were recorded. Fluorene, Chrysene, Benzo(k)fluoranthene, Benzo(g,h,i)perylene, and Acenaphthene all had minimal values at location B. At location D, the minimum values for total PAH, naphthalene pyrene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, and pyrene were reported. At location E, acenaphthylene and anthracene recorded their minimum levels. The Table also shows that there is no significant ($p>0.05$) spatial variation in the mean PAHs.

Table 4 above shows that Naphthalene, Indeno (1,2,3-cd) pyrene, Dibenz (a,h) anthracene, Acenaphthene, Fluorene, Benzo(g,h,i)perylene, Pyrene, Benz(a)anthracene, Benzo(b)fluoranthene, Benzo(a)pyrene, Phenanthrene and Total PAH shows negative relationship with pH, while the other PAHs showed positive relationship with pH. Also, Naphthalene, Phenanthrene, Pyrene, Acenaphthene, Fluorene, Benz(a)anthracene, Benzo(b)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-cd) pyrene, Dibenz (a, h) anthracene, Benzo(g,h,i)perylene, and Total PAH show positive relationship with EC, while the other PAHs parameters show negative relationship with EC. However, none of the relationships is statistically significant ($P > 0.05$). PAH concentrations in surface sediments collected from the Oluwa water body are compared to those reported in other studies (Table 5). The PAH levels found in the surface sediments are similar to those seen in India's River Gomti (Tripathi *et al.*, 2009) and the Yellow River in China (Xu *et al.*, 2007) but higher than those reported in Yalujiang River in China (Wu *et al.*, 2003), Taiwan's Gao-Ping River (Doong and Lin, 2004), China's Daliao River

(Guo *et al.*, 2007), Serbia's Sava River (Crnkovic *et al.*, 2008) and China's Luan River (Bai *et al.*, 2008). Therefore, the levels were lower than those found in the United States' Passaic River (Huntley *et al.*, 1995), the Czech Republic's Morava River (Huntley *et al.*, 1995; Vondracek *et al.* 2001) and the China's Zhujiang River (Mai *et al.*, 2002). Table 6 summarizes the 16 PAH concentrations in surface sediments. The total concentrations of the 16 USEPA priority PAHs ranged from 100.1 to 6,008.89 ng/g dry weight, with a mean concentration of 1147.4 ng/g. Wang *et al.* (2002) used semipermeable membrane devices (SPMD) to analyze the normalized concentrations of 13 PAHs (without Acy, Inp, and BghiP) in sediment samples from Xinyang City and Huainan City in the Huaihe River. They found that the total concentrations of 13 PAHs were 7.7 and 9.7 ng/mg organic carbon (OC), respectively, with a mean concentration of 8.7 ng/m. This is significantly lower than the pollution levels observed in our study (424.3–4185.6 ng/OC), and the use of SPMD may have influenced the analyzed results. Huang *et al.* (2004) looked at PAHs in surface sediments in the Jiangsu section of the Huaihe River and found that total concentrations of 12 PAHs (without Nap, Acy, BaA, and BbF) were 690–6,630 ng/g d.w., with a mean concentration of 3,740 ng/g, which is higher than our observation.

The PAH concentrations in surface sediments from the Jialu River were similar to those found in the River Gomti in India (Tripathi *et al.* 2009) and the Yellow River in China (Xu *et al.*, 2007), and higher than those found in the Yalujiang River in China (Wu *et al.*, 2003), the Sava River in Serbia (Crnkovic' *et al.*, 2008), the Luan River in China Bai (Doong & Lin 2004). The levels were, however, lower than those reported in the Zhujiang River in China

Table 3: Concentration of the PAHs in sediments collected from Igbekebo River

	A	B	C	D	E	F	p
Naphthalene	252.36±2.14	250.85±0.00	253.46±0.30	252.25±1.97	252.21±2.35	0.854	0.548
Acenaphthylene	192.56±7.42	197.81±0.00	192.56±7.37	192.57±7.41	192.54±7.40	0.016	0.999
Acenaphthene	114.25±20.00	100.11±0.00	114.34±19.82	114.24±19.98	114.46±19.71	0.311	0.860
Fluorene	213.66±0.81	213.09±0.00	213.67±0.86	213.68±0.83	213.65±0.83	0.559	0.703
Anthracene	963.15±24.80	980.68±0.00	963.16±24.76	963.16±24.78	963.14±24.78	0.747	0.600
Fluoranthene	256.68±24.44	273.96±0.00	256.82±24.21	256.88±24.15	256.69±24.44	0.647	0.653
pyrene	165.33±2.53	167.12±0.00	165.38±2.55	165.33±2.53	165.35±2.56	0.750	0.598
Chrysene	503.32±1.98	501.92±0.00	503.37±1.96	503.36±2.03	503.33±1.97	0.750	0.598
Benz(a)anthracene	187.92±0.13	188.01±0.00	187.97±0.14	187.95±0.09	187.95±0.17	0.750	0.598
Benzo(k)fluoranthrene	3478.95±3.89	3476.20±0.00	3479.10±3.39	3478.75±3.61	3479.05±3.75	0.750	0.598
Benzo(a)pyrene	1351.19±0.49	1351.53±0.00	1351.23±0.49	1351.19±0.48	1351.21±0.52	0.750	0.598
Indeno(1,2,3-cd)pyrene	539.46±0.66	539.92±0.00	539.47±0.72	539.15±1.09	539.48±0.69	0.750	0.598
Dibenz(a,h)anthracene	6008.85±0.70	6009.34±0.00	6008.88±0.70	6008.89±0.64	6008.86±0.72	0.750	0.598
Benzo(g,h,i)perylene	2961.20±0.68	2960.72±0.00	2961.20±0.65	2961.23±0.71	2961.21±0.66	0.261	0.891
Total PAH	17211.97±1.02	17211.25±0.00	17211.96±0.95	17212.05±1.12	17211.97±1.03	0.256	0.895

(Mai *et al.*, 2002), the Passaic River in the United States (Huntley *et al.*, 1995), and the Morava River in the Czech Republic (Huntley *et al.*, 1995; Vondracek *et al.*, 2001). The harm of contaminants in sediments is determined by measuring the biological effects on organisms and animals, which frequently includes the application of sediment quality guidelines (SQGs). (Long *et al.*, 1995; Wenning *et al.*, 2002; Apitz *et al.*, 2005) assessed the toxicity of PAHs to aquatic organisms living in the sediment of the Akaki River, Lake Awassa, and Lake Ziway in Ethiopia using SQGs based on effects range–low (ERL)/effects range–median (ERM) and threshold-effects level (TEL)/probable-effects level (PEL). As a result, the potential toxicity of PAHs in the sediments of the Oluwa River to sediment dwelling organisms was assessed using the SQGs and the ERL and ERM target values. The comparisons of PAH levels with SQGs in the current study are shown in the Table 6 above. The ERL and ERM values for a chemical define three concentration ranges, including those that were rarely used (below the ERL). A biological effect is unlikely to occur at concentrations lower than the ERL.

In contrast, concentrations greater or equal to ERL and less than or equal to ERM, a biological effect occurs on occasion, at concentrations greater or equal to ERM, a negative

biological effect occurs on a regular basis, and sediments were expected to be toxic (Nasher *et al.*, 2013; Yuan *et al.*, 2013; Ediagbonya & Ayedun 2018a; Ediagbonya & Gbolahan 2018b; Ediagbonya & Balogun 2020). Table 6 shows the mean concentration of each PAH in sediments from the river sample. Some sampling sites had concentrations lower than the ERL while others had concentrations higher than the ERL. Except for Fl_n, Pyr, and BAnt, which recorded average values between the ERL and ERM, the levels of PAHs quantified in all sediment samples from the river were higher than the ERL. Except for Fl_n, Pyr, and BAnt, these values showed that the PAHs in the Oluwa River sediment samples have no adverse biological effects. These may occasionally impose negative toxic effects, but not acute effects. Therefore, all individual PAHs in sediment samples from the Oluwa River were below the ERM, indicating that biological activities are unlikely to occur in this study area and that the sediments are not toxic. Only Bkf, DahAnt, and BghiP are greater than ERM, suggesting that biological activities may occur.

A number of approaches have been developed to set numerical sediment quality guidelines (SQGs) based on the available ecotoxicology data on PAHs (Chapman 1989). Sediment assessors may find it difficult to select the most appropriate SQGs for specific applications.

Table 4. Relationship between physicochemical parameters (pH and Electrical Conductivity) of river water and PAHs in sediments

PAHs	pH		EC	
	r	p	R	P
Acenaphthylene	0.147	0.684	-0.073	0.841
Naphthalene	-0.283	0.428	0.327	0.356
Anthracene	0.102	0.780	-0.171	0.636
Fluorene	-0.059	0.872	0.095	0.793
Acenaphthene	-0.317	0.373	0.232	0.519
Fluoranthene	0.220	0.542	-0.256	0.476
Pyrene	-0.087	0.812	0.162	0.656
Benz(a)anthracene	-0.088	0.808	0.162	0.654
Chrysene	0.089	0.806	-0.164	0.650
Benzo(k)fluoranthrene	0.089	0.807	-0.163	0.653
Benzo(a)pyrene	-0.089	0.807	0.163	0.653
Indeno(1,2,3-cd) pyrene	-0.089	0.807	0.163	0.653
Dibenz(a,h) anthracene	-0.089	0.807	0.163	0.653
Benzo(g,h,i) perylene	-0.218	0.546	0.125	0.730
∑ PAHs ^a	-0.193	0.594	0.105	0.773

EC electrical conductivity; ^a∑ PAHs total concentration of 16 PAHs

Table 5: Mean, Range comparison between sediment sample concentrations recorded by other studies (ng/g⁻¹).

Location	Concentration ranged	Mean	Reference
Nigeria	100.11-6008.89	1147.4	This study
Gao-Ping River, Taiwan	8-356	81	Doong and Lin (2004)
Buffalo River, South Africa	33.49-7792	489	Adeniji <i>et al.</i> (2019)
Daliao River, China	61.9–840.5	287.3	Guo <i>et al.</i> (2007)
Yalujiang River, China	68-1500	290	Wu <i>et al.</i> (2003)
Luan River, China	6.7-1585.7	342.9	Bia <i>et al.</i> (2008)
Sava River, Serbia	416.2-592.3	501.6	Crnkovic <i>et al.</i> (2008)
River Gomti, India	68-3153	1182	Tripathi <i>et al.</i> (2009)
Yellow River, China	464-2621	1414	Xu <i>et al.</i> (2007)
Zhujiang River, China	1434-10811	4892	Mai <i>et al.</i> (2002)
Morava River, Czech Republic	636-13205	4997	Vondracek <i>et al.</i> (2001)
Passaic River, USA	220-8000000	145000	Huntley <i>et al.</i> (1995)

Long *et al.* (1995) developed two guideline values to assess sediment quality, an effects range low (ERL) and an effects range median (ERM), with a ranking of low to high impact values.

Chemical concentration ranges that are rarely, occasionally, or frequently associated with adverse biological effects are defined by the ERL and ERM values. The ERL and ERM values were compared to the PAH concentrations found in Oluwa River (Table 6). The total PAH concentrations at all locations in this study were below the ERL. Furthermore, while individual PAHs did not exceed ERM at any of the sites, there was at least one PAH that could cause biological impairment on occasion (with concentration higher than ERL). The findings suggested that while individual PAHs may cause biological impairment in some samples, no

samples contained constituents that caused biological impairment on a regular basis (with concentration higher than ERM).

TEQ was used to calculate the toxicity of PAHs in the sampled sediment and expressed as BaP equivalent (BaP_{eq}) (Table 7). Total TEQ values for sediment samples ranged from 0.11 µgg⁻¹ to 6008 µgg⁻¹, according to calculations. Overall TEQ for the sediment samples was calculated to be 7824.43 µgg⁻¹. The total TEQ values for the carcinogenic PAHs was calculated to be 7784.43 µgg⁻¹, the contribution of these seven carcinogenic PAHs to the overall toxicity of PAHs in sediment sample was 99.5%. Ace had the lowest value of 0.11 µgg⁻¹ while DahA had the highest TEQ value of 6008 µgg⁻¹. DahHBaP_{eq} value had significant difference to other BaP_{eq} values of the sediment sample.

Table 6: PAH levels in sediments from Oluwa River, Ondo State compared with sediment quality guidelines (SQGs).

	SQG values(ng/g ¹ dm)			This study PAH concentration ng/g ¹ (Oluwa River)	
	ERL	ERM	MEAN	MIN	MAX
Nap	160	2100	252.25	0	253.46
Acy	44	640	193.6	0	197.81
Ace	16	500	111.5	0	114.46
Flu	19	540	213.7	0	213.68
Phe	240	1500	NA	0	NA
Ant	853	1100	916.4	0	980.68
Fln	600	5100	259.4	0	273.96
Pyr	665	2600	165.4	0	167.12
Chr	384	2800	502.6	0	503.37
Bant	261	1600	187.2	0	188.01
BbF	320	1880	NA	0	NA
Bkf	280	1620	3478	0	3479.1
BaP	430	1600	1351	0	1351.53
InP	NA	NA	539	0	539.9
DahAnt	63.4	260	6008	0	6009.34
BghiP	430	1600	2961	0	2961.23

ERL, Effects range low; ERM, Effects range median

Table 7: Calculated concentration values of BaPE and TEQs in sediments from Oluwa River, Nigeria

Compounds	TEF	MEF	BaP _{TEQ}	BaP _{MEQ}
Naphthalene	0.001		0.25	
Acenaphthylene	0.001		0.19	
Acenaphthene	0.001		0.11	
Fluorene	0.001		0.2	
Phenanthrene	0.001			
Anthracene	0.01		9.2	
Fluoranthene	0.001	NC	0.25	NC
Pyrene	0.001	NC	0.16	NC
Chrysene	0.01	NC	5.01	NC
Benz(a)anthracene	0.1	0.017	18.72	3.1824
Benzo(b)fluoranthene	0.1	0.082	NC	NC
Benzo(k)fluoranthene	0.1	0.250	347.8	869.5
Benzo(a)pyrene	1	0.110	1351	148.61
Indeno(1,2,3-cd) pyrene	0.1	1.000	53.9	539
Dibenz(a,h)anthracene	1	0.310	6008	1862.48
Benzo(g,h,i)perylene	0.01	0.290	29.61	858.69
Σ PAH ₁₆			7824.4	
Σ PAH ₇			7784.43	

TEF: Toxic Equivalency Factors; MEF: Mutagenic Equivalency Factor; TEQ; Toxicity Equivalent; MEQ; Mutagenic Equivalency; NC: Not calculated

PAHs in sediment samples have been used to assess risk all over the world. (Nasher *et al.*, 2013; Zhang *et al.*, 2018) However, there is no data on the quantitative risk assessment of PAHs. According to Yang *et al.*, (2014), soils with BaPE values less than 0.1 mg/kg are considered uncontaminated, soils with values between 0.1 and 1.0 mg/kg BaPE are considered slightly contaminated, and soils with 1 to 10 mg/kg BaPE are considered significantly contaminated. The value of the DahHBaP_{eq} (6008 μ gg⁻¹) in this study was very low compared to this range which indicated that toxicity level of the area was low and does not pose a significant risk to human.

CONCLUSION

The results conclude that the concentrations of PAHs in male and female frogs were significantly higher than the WHO limits, thus confirming that frogs from this study area to be harmful for consumption. PAHs that are produced by human activities such as burning of coal, oil, gas, wood, garbage, and tobacco industrial food processes could impose major impacts on the wildlife, and eventually on human health. In particular, oil spills may have contributed to the presence of polycyclic aromatic hydrocarbons in high concentrations in rivers.

ACKNOWLEDGEMENT

The authors are grateful to the authority of Olusegun Agagu University of Science and Technology, Okitipupa, Nigeria for providing the necessary conducive environment for the conduct of this research.

DECLARATION OF CONFLICT OF INTEREST

The authors declare no conflict of interest

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