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Research Article
Polycyclic Aromatic Hydrocarbon Concentrations in *Clarias gariepinus* from Oluwa River, Ondo State, Nigeria

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Abstract
Background and Objective: Petroleum hydrocarbons are one of the major organic pollutants that consist of an extremely complex assemblage of chemicals coming from various sources and their fate on the environment is receiving attention in recent times. This research is designed to determine the concentration of polycyclic aromatic hydrocarbons in *Clarias gariepinus*, water and sediment of the Oluwa River. **Materials and Methods:** The concentrations of 16 environmentally significant Polycyclic Aromatic Hydrocarbons PAH, were investigated in the sediment and water samples as well as fish (*Clarias gariepinus*) from the Oluwa River using standard analytical methods. **Results:** The result revealed that all the 16 PAH investigated were present in all samples investigated at varying concentrations. The total of 16 PAH (Σ_{16} PAH) in the fish sample (*Clarias gariepinus*) was 4.90×10^{-3} mg kg^{-1} and that of sediment was 4.242×10^{-1} mg kg^{-1} while, that of the water sample from the river was 1.038×10^{-1} mg L^{-1}. The results followed the order *C. gariepinus*<water<sediment. **Conclusion:** Conclusively, the value of total PAH obtained from water samples from the Oluwa River when compared with the WHO standard regulatory limit of 0.001 mg L^{-1} strongly implicated the river to be polluted with PAHs. The presence of Polycyclic Hydrocarbons (PAH) in high concentrations, especially those of 2-3 rings and the occurrence of carcinogenic 5-ring PAH, Benzo(a)pyrene in both surface water and sediment of the river above WHO regulatory limit has grossly implicated the river as being polluted. Consumption of fish and water from the river should be discouraged.

Key words: Polycyclic aromatic hydrocarbons PAH, *Clarias gariepinus*, sediment, bitumen, Oluwa River, pollutants, carcinogenic

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Petroleum hydrocarbons are one of the major organic pollutants that consist of an extremely complex assemblage of chemicals coming from various sources and their fate on the environment is receiving attention due to their well-known carcinogenic, toxic and mutagenic properties. In the past decades, aliphatic hydrocarbons and other compounds in atmospheric aerosols and sediments in crude oil-producing areas have been studied to ascertain their terrestrial, marine or anthropogenic origins[1,2]. The sources of aliphatic hydrocarbon can either be anthropogenic or biogenic[3,4]. Fish and other aquatic foods are regarded in nutrition as highly desirable food due to their contribution of high-quality protein and often low fat. This has attracted consumers due to its health benefits in addition to its widespread and relatively low price. In Nigerian markets, catfishes are some of the most common aquatic animal types. Thus, any high-level pollutant detected in these aquatic food exhibits a considerable public health risk.

Contamination of aquatic ecosystems by PAHs has been recognised as a major public health risk[5,6]. Exposure to PAHs is harmful to health under some circumstances. Epidemiological studies on air pollution have shown that individuals exposed to mixtures of PAHs via different routes, including GIT (gastrointestinal tract) and dermal contact, for long periods can develop cancer. Also several of the PAHs, including benz[a] anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h] anthracene and indeno [1,2,3-c,d] pyrene, have caused tumours in laboratory animals when they are exposed to these substances via several exposure pathways[7,8].

The point sources of emissions of the reportable size of polycyclic aromatic hydrocarbons include petroleum refineries, sites dealing with the production of coal tar, coke, bitumen and asphalt, paper and wood products and aluminium, industrial machinery manufacture and power production from fossil fuels[9]. Non-point sources may include aerial fallout, inadvertent oil spills and marine oil spillage[10]. Once formed, PAHs can be transported into an aquatic environment by several pathways including fossil fuel distribution, petroleum spillage, stormwater and surface runoff, sewage and wastewater effluent[11,12]. Bitumen is one of the most abundant natural resources in Nigeria, similar to hydrocarbons in composition. Bitumen known as 'oil tar sand' occurs in the Southwestern part of Nigeria covering Ondo, Ogun, Edo and part of Lagos. The accidental discovery of bitumen as a black viscous tar oozing out of river valleys and farm Lands in areas of Ofosu, Agbabu, Mafowoku and Eregu has been dated back several decades[13].

The occurrence of PAHs in the aquatic ecosystem has been the subject of significant investigation across many industrialised countries[14-17]. In a related study, the highest concentration of PAHs in water in Canada was reported for water samples from ditches next to utility and railway lines near Vancouver. The highest mean concentrations were measured near utility points treated with creosote, with values estimated at 2000 ng L^{-1} for fluoranthene, 1800 ng L^{-1} for phenanthrene and 490 ng L^{-1} for naphthalene[18]. The research is aimed at evaluating the concentrations of polycyclic aromatic hydrocarbon in the sediment and water samples as well as *Clarias gariepinus* from bitumen and seep polluted Oluwa River.

MATERIALS AND METHODS

Study area: River Oluwa in Agbabu is located on the Okitipupa South-East belt of the bituminous sands field at latitude 06°29"-06°45"North and 04°44"-05°00"East of the Greenwich Meridian. Agbabu bitumen belt is made of the main Agbabu village inhabited by about 1,600 people and other smaller farm settlements such as Temidire Village made up of about 600 people. Farmers in this area deal mainly in fishing along River Oluwa, which flows through the whole, land. Some of those living in the villages and hamlets live on the shallow surface water of the river as a source of potable water.

Description of sampling site: Two sampling sites A and B 1 km apart were selected on the Oluwa River. Site A is located upstream where there are high fishing activities and fewer domestic activities. Site B is located downstream where there are high domestic activities like fetching the river water for drinking, bathing and swimming activities as well as washing clothes. Samples were collected from April, 2019-March, 2020.

Polycyclic aromatic hydrocarbon analysis: The extraction method for the analysis of polyaromatic hydrocarbons profiles in sediment, fish and water samples was followed by employing the modified methods[18-20].

Extraction of PAHs from sediment samples: About 20.0 g of the solid sample was weighed into a 250 mL capacity beaker of borosilicate material and 100 mL of the ratio 3:1 redistilled hexane: Dichloromethane was added. The beaker and its content are placed in the sonicator to extract the hydrocarbon for about 2 hrs. The organic layer was filtered into the 250 mL capacity borosilicate beaker. The extract was dried by passing

Table 1: Gas chromatography condition of polyaromatic hydrocarbons

GC	HP 6890 powered with HP ChemStation Rev.A09.01 ([12]06) software
Column	HP-I
Column length	30 m
Column ID	0.25 μm
Column film	0.25 μm
	250°C
Injection temperature	320°C
Detector temperature	FID
Detector	60°C
Initial temperature	15°C/min for 14 min, maintained for 3 min
First rate	10°C/min for 5 min, maintained for 4 min
Second rate	Nitrogen
Mobile phase or carrier	30 psi
Nitrogen column pressure	28 psi
Hydrogen pressure	32 psi
Compressed air pressure	

the filtrate through the funnel containing the anhydrous sodium sulphate. The dried extract was concentrated with a stream of nitrogen gas.

Extraction of PAHs from fish (*Clarias gariepinus*): About 40 g of the fish sample was crushed in the mortar with the pestle. The crushed sample was placed in the flat borosilicate container and dried in the oven at 60°C. A total of 20.0 g of the dried sample was weighed into a 250 mL capacity beaker of borosilicate material for fat extraction, esterified and the esterifiable fat was removed by soxhlet extraction. The aliphatic and polyaromatic hydrocarbons were extracted with 100 mL of the ratio 3:1 redistilled hexane:dichloromethane in the beaker. The beaker and its content were placed in the sonicator to extract the hydrocarbon for about 2 hrs. The organic layer was filtered into the 250 mL capacity borosilicate beaker. The extract was dried by passing the filtrate through the funnel containing the anhydrous sodium sulphate. The dried extract was concentrated with a stream of nitrogen gas.

Extraction of PAHs from water sample: About 1000 mL of the water sample was transferred to a 2 L separatory funnel and 60 mL of the redistilled dichloromethane was added. The separatory funnel was shaken vigorously for about 2 min with periodic venting to release vapour pressure. The organic layer was allowed to separate for 10 min and was recovered into the 250 mL flasks. The aqueous layer was re-extracted twice with 60 mL of the extractant. The combined extract was dried by passing through the funnel containing the anhydrous sodium sulphate. The dried extract was concentrated with a stream of nitrogen gas.

PAH separation: The concentrated oil was separated into the aliphatic profiles and polyaromatic hydrocarbon profiles by packing the glass column with activated alumina, neutral and activity/grade. At 10 mL of the treated alumina was packed into the column and cleaned with redistilled hexane. The extract was poured onto the alumina and was allowed to run down with the aid of the redistilled hexane to remove the aliphatic profiles into a pre-cleaned 20 mL capacity glass container. The aromatic fraction was recovered by allowing the mixture of hexane and dichloromethane in a ratio of 3-1 and finally removed the most polar PAH by removing the dichloromethane into the pre-cleaned borosilicate beaker.

The mixture was concentrated to 1.0 mL by a stream of nitrogen gas before the gas chromatography analysis. The gas chromatography conditions are as stated in Table 1.

Statistical analysis: Analysis of Variance (ANOVA) and Duncan's Multiple Range Tests as well as bar and pie charts using the SPSS statistical package were used in the comparison of data where, values of $p<0.05$ were considered significant.

RESULTS AND DISCUSSION

Total PAHs (Σ_{16} PAH) in the samples: The concentrations of 16 environmentally significant Polycyclic Aromatic Hydrocarbons PAH were investigated in the sediment and water samples as well as fish (*Clarias gariepinus*) from the Oluwa River. All the 16 PAH investigated were present in all samples investigated at varying concentrations. The result revealed that the total of the 16 PAH (Σ_{16} PAH) in the fish sample (*Clarias gariepinus*) was 4.900×10^{-3} mg kg^{-1} and that of sediment was 4.242×10^{-1} mg kg^{-1} while, that of the water sample from the river was 1.038×10^{-1} mg L^{-1} (Table 2). The results followed the order *C. gariepinus*

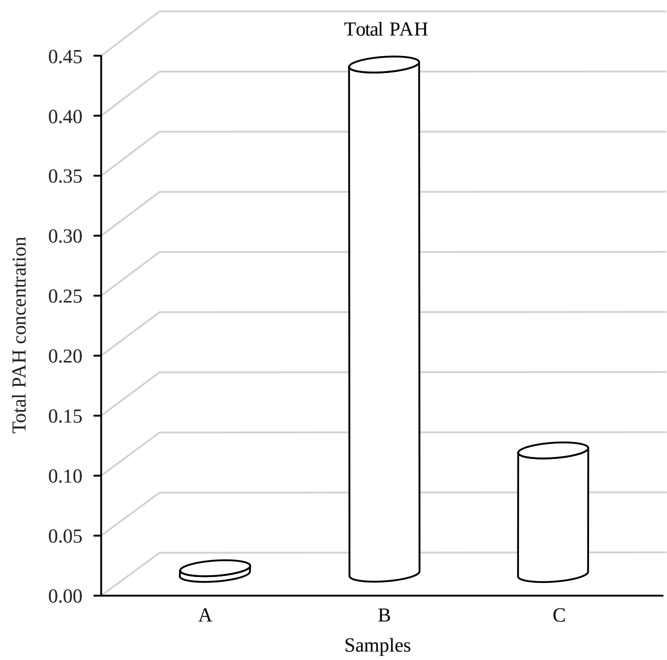

Fig. 1: Total concentrations of PAHs in the surface water, sediment and *Clarias gariepinus* from the Oluwa River
A: Fish (*Clarias gariepinus*), B: Sediment and C: Surface water

Table 2: Relative distribution pattern and percentage composition of individual PAHs in the surface water, sediment and *Clarias gariepinus* from Oluwa River

Sample	A		B		C	
PAH rings	*Clarias gariepinus* (mg kg^{-1})	(%)	Sediment (mg kg^{-1})	(%)	Surface water (mg L^{-1})	(%)
2	3.150×10^{-4}	6.40	1.607×10^{-1}	37.80	7.67×10^{-2}	73.90
3	2.308×10^{-3}	47.00	1.088×10^{-1}	25.60	9.756×10^{-3}	9.30
4	1.178×10^{-3}	24.00	0.996×10^{-1}	23.40	1.110×10^{-2}	10.60
5	1.096×10^{-3}	22.30	0.545×10^{-4}	12.80	6.22×10^{-5}	5.90
6	2.578×10^{-6}	0.05	4.456×10^{-4}	0.10	3.958×10^{-5}	0.04
Total PAH	4.900×10^{-3}		4.242×10^{-1}		1.038×10^{-1}	

A: Fish (*Clarias gariepinus*), B: Sediment and C: Surface water

(4.900×10^{-3} mg kg^{-1}) <water (1.038×10^{-1} mg L^{-1})< sediment (4.242×10^{-1} mg kg^{-1}) (Fig. 1). Table 3, revealed that the total of low molecular weight PAH (LPAH) in *C. gariepinus* (2 rings and 3 rings) was 2.623×10^{-3} mg kg^{-1} while, that of high molecular weight (HPAH) PAH was 2.272×10^{-3} mg kg^{-1} (4, 5 and 6 rings). The total LPAH in the sediment sample was 2.695×10^{-1} mg kg^{-1} while, that of HPAH was 1.545×10^{-1} mg kg^{-1}. The total of LPAH in the water sample was 8.65×10^{-2} mg L^{-1} while that of HPAH in the water sample was 1.735×10^{-2} mg L^{-1}. The result for LPAH follows the trend *C. gariepinus*<water <sediment. The result for HPAH also followed the trend *C. gariepinus*<water<sediment.

Percentage composition of PAHs in *Clarias gariepinus*: The average percentage composition of 2, 3, 4, 5 and 6 ring PAHs in the fish sample (*C. gariepinus*) were recorded to be 6.40, 47.00, 24.00, 22.30 and 0.05%, respectively as shown in Table 2. About 2-3 rings PAH, Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, phenanthrene and Anthracene had the highest percentage in the fish sample while 6 rings PAH, Benzo (g, h, i) perylene (BgP) had the least percentage composition of 0.05% (Fig. 2).

Percentage composition of PAHs in sediment: The average percentage composition of 2, 3, 4, 5 and 6-ring PAH in the sediment sample was recorded to be 37.80, 25.60, 23.40, 12.80 and 0.10%, respectively as shown in Table 2. The 2-ring PAH Naphthalene had the highest percentage composition (37.80%) while 6-ring PAH also had the least percentage composition of 0.10% (Fig. 3).

Percentage composition of PAHs in water: The average percentage composition of 2, 3, 4, 5 and 6 rings of PAH in the water sample was recorded to be 73.90, 9.30, 10.60, 5.90 and

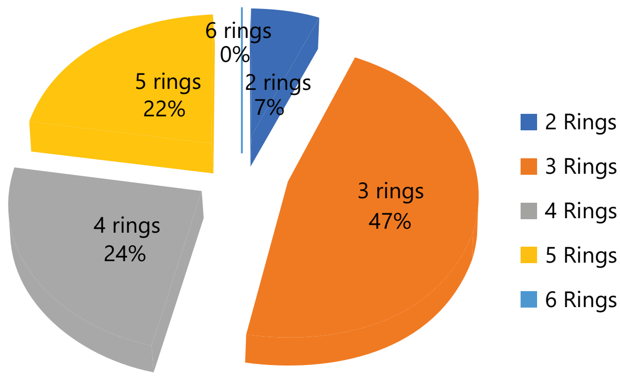

Fig. 2: Spatial distribution of PAHs based on the number of the ring size in *Clarias gariepinus* from the Oluwa River

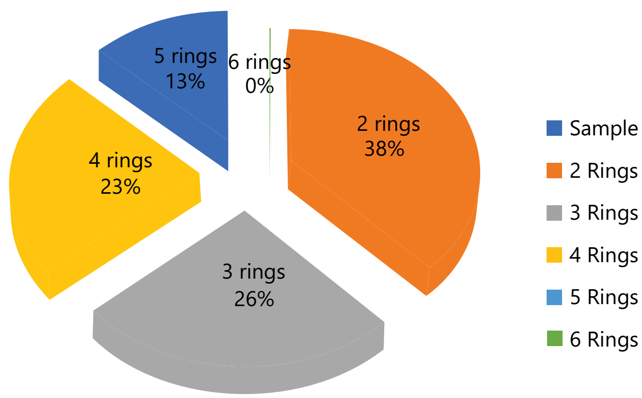

Fig. 3: Spatial distribution of PAHs based on the number of the ring size in a sediment sample from the Oluwa River

Table 3: Concentrations of PAHs in surface water, sediment and *Clarias gariepinus* from Oluwa River

PAH	Sample A (mg kg^{-1})	Sample B (mg kg^{-1})	Sample C (m L^{-1})
Naphthalene	3.150×10^{-4}	1.607×10^{-1}	7.675×10^{-2}
Acenaphthylene	2.288×10^{-4}	6.258×10^{-3}	4.753×10^{-3}
Acenaphthene	4.566×10^{-4}	7.548×10^{-2}	2.589×10^{-3}
Fluorene	2.144×10^{-4}	6.252×10^{-3}	5.915×10^{-4}
Phenanthrene	6.023×10^{-4}	4.754×10^{-3}	6.141×10^{-4}
Anthracene	8.061×10^{-4}	1.611×10^{-2}	1.209×10^{-3}
Total (LPAH)	2.623×10^{-3}	2.695×10^{-1}	8.650×10^{-2}
Fluoranthene	7.833×10^{-4}	7.943×10^{-3}	6.728×10^{-4}
Pyrene	9.624×10^{-5}	2.925×10^{-2}	3.297×10^{-3}
Benzo(A)Anthracene	2.028×10^{-4}	2.675×10^{-2}	3.255×10^{-3}
Chrysene	9.609×10^{-5}	3.575×10^{-2}	3.885×10^{-3}
Benzo(B)Fluoranthene	2.167×10^{-4}	3.834×10^{-2}	1.540×10^{-3}
Benzo(K)Fluoranthene	4.593×10^{-4}	8.662×10^{-3}	3.253×10^{-3}
Benzo(A)Pyrene	1.761×10^{-4}	3.191×10^{-3}	5.517×10^{-4}
Indeno(1,2,3-Cd)Pyrene	1.073×10^{-4}	2.261×10^{-3}	4.573×10^{-4}
Dibenzo(A,H)Anthracene	1.372×10^{-4}	2.129×10^{-3}	4.197×10^{-4}
Benzo(G,H,I)Perylene	2.578×10^{-6}	4.456×10^{-4}	3.958×10^{-5}
Total (HPAH)	2.277×10^{-3}	1.545×10^{-1}	1.735×10^{-2}

Sample A: Fish (*Clarias gariepinus*), Sample B: Sediment and Sample C: Surface water

0.04%, respectively as represented in Table 2. The 2 ring PAH Naphthalene had the highest percentage composition of 73.90 in the water sample while 6-ring PAH (BgP) also had the least percentage composition in water 0.04% (Fig. 4).

In the overall assessment, 3-ring PAH was the most abundant in the fish sample (*C. gariepinus*) with the least being 6-ring in the fish sample. Some suspected carcinogenic 5-ring PAHs were detected in a high proportion of the fish

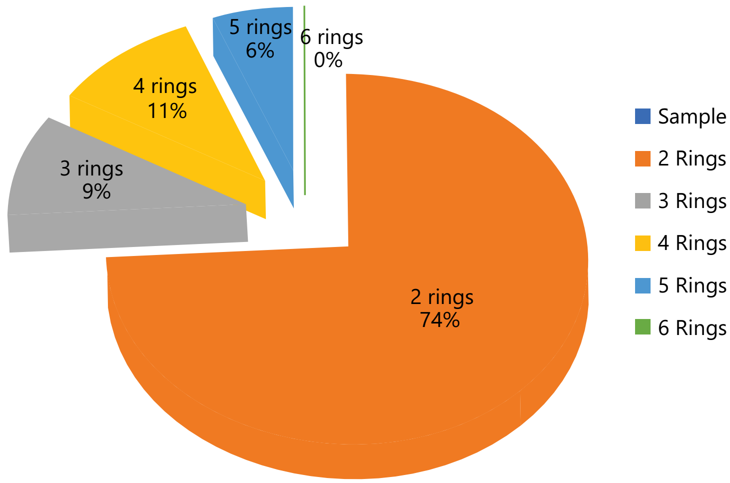

Fig. 4: Spatial distribution of PAHs based on the number of the ring size in a water sample from the Oluwa River

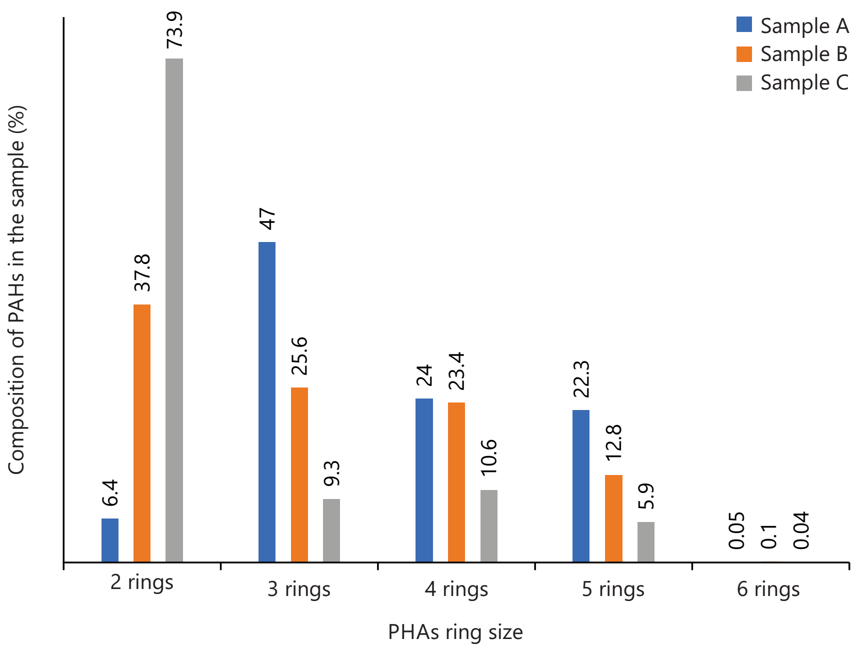

Fig. 5: Percentage composition of PAHs based on ring size in *Clarias gariepinus*, sediment and water samples from Oluwa River

sample (Fig. 5). For the sediment sample 2-ring PAH (Naphthalene) was the most abundant with the least being 6-ring. Carcinogenic 5-ring PAHs were also detected. High molecular weight PAH (4-5 rings) like Fluoranthene, pyrene, Benzo(a)Anthracene and Chrysene Benzo(a)Pyrene were also detected in high proportion in the sediment sample.

Results obtained for the water sample also revealed that 2-ring PAH (Naphthalene) was the most abundant while the least was 6-ring PAH. Carcinogenic 5-ring PAH was also detected in the water sample. In sample A (*C. gariepinus*) the resulting base on ring size of PAH followed the trend 3-ring > 4-ring >5-ring>2-ring>6-ring while for sample B (sediment) it followed the trend 2-ring>3-ring>4-ring>5-ring>6-ring and for sample C (water) the result followed the trend 2-ring>3-ring>4-ring>5-ring>6-ring. The result obtained for the percentage composition of PAH in all the samples investigated followed the trend 2-ring>3-ring>4-ring>5-ring>6-ring.

Analysis for sources of PAHs: Some ratios of selected PAH compounds could be used to assess the possible origins of PAHs., For example, the abundance ratio of 2-3 ring hydrocarbons to 4-6-ring hydrocarbon (Low Molecular

Table 4: Molecular indices of PAHs in the surface water, sediment and *Clarias gariepinus* from Oluwa River

PAH ratio sample	Phen/Ant	Fl/Pyr	BaP/Chr	NaPh/Phen	Ant/(Ant+Phen)	Fl/(Fl+Pyr)	BaA/(BaA+Chr)	InP/(InP+BgP)
A	0.747	8.14	1.83	00.52	0.57	0.89	0.68	0.97
B	0.3	0.28	0.08	33.8	0.78	0.2	0.43	0.84
C	0.51	0.2	0.14	124.97	0.66	0.169	0.46	0.92
	<10 = PY	>1 = PY	<10 = PY	<1 = PY	>0.1 = PY	>0.5 = PY	>1 = PY	>1 = PY
	>10 = PT	<1 = PT	>10 = PT	>1 = PT	<0.1 = PT	<0.4 = PT	<1 = PT	<1 = PT

Phen/Ant: Phenanthrene to Anthracene ratio, Fl/Pyr: Fluoranthene to Pyrene ratio, BaP/Chr: Benzo(a)Pyrene to Chrysene ratio, NaPh/Phen: Naphthalene/Phenanthrene ratio, Ant/(Ant+Phen): Anthraceneto (Anthracene+Phenanthrene) ratio, Fl/(Fl+Pyr): Fluoranthene to (Fluoranthene+Pyrene) ratio, BaA/(BaA+Chr): Benzo(a) Anthraceneto(Benzo(a)Anthracene+Chrysene) ratio, InP/(InP+BgP): Indeno(1,2,3,-Cd) Pyrene to [(indeno(1, 2, 3,-Cd) Pyrene]+ Benzo (g, h, i) Perylene ratio, PT: Petrogenic source and PY: Pyrolytic source

Weight/High Molecular Weight LMW/HMN) Ant/(Ant+Phen), Phen/Ant, Fl/Pyr, Fl/(Fl+Pyr), InP/(InP+BgP) can be applied to help distinguish the petrogenic and pyrolytic sources[21].

Phen/Ant ratios lower than 10 are seen to be characteristics of the combustion process (Pyrolytic) whereas values higher than 10 are seen in petroleum input (Petrogenic)[22,23]. The Fl/Pyr ratio below 1 is attributed to a petrogenic source, while above 1 is related to pyrolytic origins[24,25]. The Fl/(Fl+Pyr) ratio with 0.4 being defined as the petroleum/combustion transition points, the ratio less than 0.4 corresponded to petroleum pollution and values higher than 0.5 is characteristic of grass, wood or coal combustion, whereas between 0.4 and 0.5 being more related to liquid fossil fuel combustion such as vehicle and crude oil[26].

InP/(InP+BgP) ratio of <1 is suggested the discharge of petroleum input (petrogenic) and a ratio >1 indicated wood and coal combustion (Pyrolytic). Naph/Phen ratio greater than unity (1) assumed the presence of fresh and unweathered petroleum and bitumen[27].

To determine the sources of PAHs in fish (*C. gariepinus*), sediment and water samples from the Oluwa River, eight different molecular ratios were used (Table 4). Phen/Ant ratio in all the samples (*C. gariepinus,* water and sediment) ranged from 0.30-0.75, which suggested a pyrolytic origin. Fl/Pyr ratio ranged from 0.20-8.14 which indicated both pyrolytic and petrogenic origin. Naph/Phen ratio ranged between 0.5-124.97 which showed both pyrolytic and petrogenic origin. Ant/(Ant+Phen) ratio ranged from 0.57-0.78 which indicated pyrolytic origin. The Fl/(Fl+Pyr) ratio ranged between 0.17–0.89 which showed both pyrolytic and petrogenic origin. BaA/(BaA+Chr) ratio ranged from 0.43-0.68 which suggested petrogenic origin. Similarly, InP/(Inp+BgP) ratio ranged between 0.84-0.97 and also indicated petrogenic origin. The result obtained in this study was similar to those of[21-23,28-33], where they reported both petrogenic and pyrogenic sources of PAHs in water, sediment and soil samples investigation.

Total PAHs (Σ_{16} PAH) in the samples: With the development of environmental geochemistry, some criteria, such as Phen/Ant and Fl/Pry ratios have been developed for fingerprinting the sources of PAH, in environmental samples[34,35]. The sources of PAHs are formed mainly via two mechanisms, fuel combustion (Pyrolytic) and discharge of crude oil-related materials (Petrogenic) and may be identified by ratios of individual PAH compounds based on peculiarities in PAH compound and distribution patterns as a function of the emission sources[36,37].

A higher concentration of total PAHs observed in sediment samples compared to those of *C. gariepinus* and water could be associated with long term accumulation resulting from surface runoffs from nearby farms where, bush burning and burning of wood to make charcoal as well as bitumen seepage directly into the water body[38]. On the banks of the Oluwa River, farmers and hunters practice bush burning to clear the farm and hunt for animals. They also practice burning timbers to make charcoal. These anthropogenic activities could be the pyrolytic source of PAHs in the sediment of the Oluwa River. Furthermore, seepage of bitumen into the river could be the petrogenic source of PAHs observed in the sediment of the Oluwa River[7].

Another possible reason for the highest concentration of total PAH (Σ_{16} PAH) in the sediment of the Oluwa River could be a result of high-water content which could increase the surface area of sediment and improve organic matter adsorption ability onto the sediment. The concentrations of PAHs in sediments can also be affected by the chemical compositions of organic matter and clay content[39].

Total PAHs concentration of 0.1038 mg L^{-1} in the water samples from the Oluwa River was very high compared to 0.001, 0.002 and 0.003 mg L^{-1} recommended as freshwater guidelines by previous studies[7,40,41], respectively. This calls for serious environmental pollution concerns. Reports from other works within the vicinity of Agbabu and other South-Western places in Nigeria are in agreement with the result obtained in this study. Authors like Fagbote and Olanipekun[29] submitted that the concentration of PAHs such as Naphthalene and Benzo(a)pyrene (BaP) obtained from the sediment of the Oluwa River were higher than recommended limits. Gbadebo[13], submitted that exceptionally high concentrations of both total hydrocarbon and polynuclear aromatic hydrocarbon were predominantly higher in the sediment than in the soil with the least in the water samples (sediment>soil> water sample) from bitumen seep polluted parts of Ogun State South Western Nigeria when compared with standard values. This is also in agreement with the result obtained in this study for the concentration of Total PAH in sediment, water sample and *C. gariepinus* which followed the trend sediment>water>*C. gariepinus*.

Another possible reason for the result obtained for total PAH being the highest in the sediment among all the samples investigated could be due to the hydrophobicity of PAHs which may rapidly become associated with suspended particles and aggregated in sediments and finally enter into the aquatic environment.

However, although the least concentration of total PAHs was observed in the fish species (*C. gariepinus*) understudy, consumption of this fish species from the Oluwa River could pose great health concerns. It has been well established that certain PAH especially 4-6 rings are carcinogenic and mutagenic[29].

Percentage composition of Σ_{16} PAHs in *Clarias gariepinus*: Furthermore, the highest average percentage composition of Σ_{16} PAHs (the total of 16 PAHs investigated) recorded for 3 ring PAH (low molecular weight) in the fish species under study also calls for health concerns.

Although, PAHs do not show extremely high acute toxicity to aquatic organisms, the lower molecular mass PAHs (2-3 rings) tend to exhibit higher lethal toxicity to aquatic organisms than the larger PAHs[42]. Moreover, lethal concentration (LC_{50}) down to less than 10 µg $^{-}L^{1}$ has been reported for various organisms.

Percentage composition of PAHs in water L: The highest percentage composition of 73.9% 2-ring PAH (Naphthalene) in a water sample from the Oluwa River could be a result of the solubility of 2 and 3-ring PAH in water. Naphthalene often constitutes a significant fraction of crude oils, hence might be used to detect PAH input from these sources[25,43]. The result obtained in this study for the percentage composition of 2-ring PAH of Σ_{16} PAH investigated agrees with the submission of where they reported that 2-ring Naphthalene was the most abundant and makes up to 85% of the total PAHs in suspended particulate matter in Daliao River watershed, China. The author also concluded that molecular weight (2-3 rings) predominates polluted Daliao River water and suspended particulate matter. Ogunbisi *et al.*[44], also submitted that the concentration of 2-3 rings PAHs was relatively greater in samples collected in the surface water than those from the bottom water of Lagos Lagoon, Nigeria. However, another possible reason could be the roles played by microorganisms in the degradation of PAHs in water bodies. A wide array of microorganisms including fungi, algae and bacteria are known to degrade PAHs. However, bacteria play by far the most important role in complete mineralization. Lower molecular weight PAHs such as naphthalene and phenanthrene are degraded rapidly in sediments but higher molecular weight PAHs such as pyrene, fluoranthene, benzo(a)anthracene and benzo(a)pyrene are more recalcitrant[45].

Percentage composition of PAHs in sediment: The 2-ring PAHs were also abundant in the sediment this could be a result of the high seepage of bitumen into the river since Naphthalene often constitutes a significant fraction of crude oils, bitumen and petroleum products with higher fractions[45]. However, a high concentration of 3-5 ring PAHs was also present in the sediment. It has been well established that 4-6 rings of PAHs are present in the sediments, probably because heavier PAHs are rapidly adsorbed or condensed unto particles when deposited on surface waters, the dissolved fraction is capable of polluting the water bodies, while the relatively more hydrophobic 4-6 rings are embedded in bottom sediments[46]. In addition, the degradation reactions at the bottom are likely to be very slow as a result of low exposure of PAHs to Oxygen which is required for the cleavage of the aromatic ring[47].

Analysis of sources of PAHs in *C. gariepinus*: Based on some established ratios of PAHs compounds[30], used in assessing the source of PAH in this study, it was discovered that Phen/Ant, Fl/Pyr, BaP/Chr, Naph/Phen, Ant/(Ant+Phen) and Flu/(Flu+Pyr) suggested that the sources of PAH in the fish species (*C. gariepinus*) understudy was pyrogenic. This could be as a result of bush burning practised by farmers when clearing farmLand near the river or bush burning by hunters, these activities could lead to partial or incomplete combustion of bitumen impregnated soil around the river which is in turn washed down into the river during runoffs.

However, the other two ratios BaA/(BaA+Chr) and InP/(InP+BgP) suggested that PAHs sources of the fish species could be from the petrogenic sources. This could be as a result of bitumen seeping directly into the river bed and could also be as a result of vehicular emissions from cars, trucks and motorboats used during bitumen exploration at Agbabu vicinity and during transportation of timbers on the river course. These emissions found their way as runoffs into the water body. This could also be attributed to the oil or fuel leakages from barges or transportation media along water course[27].

PAH sources in water sample: Fl/Pyr, Naph/Phen, Fl(Fl+Pyr), BaA/ (BaA+Chr) and InP/(InP+BgP) ratio employed suggested that PAH sources in the water sample are more of petrogenic origin. The high ratio Naph/Phen ratio further revealed the likely presence of fresh and unweathered petroleum and bitumen because the Naph/Phen ratio obtained (124.97) is far above unity as recommended previously[27]. However, Phen/Ant, BaA/Chr and Ant/(Ant+Phen) ratios suggested that the PAH could also be from a pyrolytic source. This result conforms with the submission of Olajire *et al.*[25] which recorded both pyrolytic and petrogenic sources for PAH in surface soil and water from the vicinity of the Agbabu bitumen field in South-Western, Nigeria.

PAH source in sediment sample: Fl/Pyr, Naph/Phen, Fl(Fl+Pyr), BaA/(BaA+Chr) and InP/(InP+BgP) ratio used also suggested that PAH sources in the sediment sample are more of petrogenic origin. However, Phen/Ant, BaP/Chr and Ant/ (Ant+Phen) ratio also suggested that the PAH could be from a pyrolytic source[23,30,31].

The total PAH distribution profile in the Oluwa River indicated the highest level in the sediment of the river. In addition, non-point sources, in particular, petrogenic inputs and bitumen fuel combustion were dominant sources in the river. The main concern about the occurrence of PAHs in the environment comes from the fact that they are mostly carcinogenic both in humans and other animals, whereas, some PAHs have also been classified to be mutagenic e.g., Benzo(a)pyrene (BaP) and Benzo(g,h, i)perylene. The value of total PAH obtained for water samples from the Oluwa River when compared with the previous study by Okafor and Opuene[5] the standard regulatory limit strongly implicated the river to be polluted with PAHs. Also, a high level of 3-ring PAH found in the fish species implicated the fish not being fit for human consumption.

The results obtained from this study revealed that the fish species are not fit for human consumption and consumption of fish and water from the Oluwa River could pose a serious health risk and should be discouraged.

This study also becomes additional data and information to already existing literature information on some Nigerian waters with high pollution rates and pollutants.

CONCLUSION

The total PAH distribution profile in the Oluwa River indicated the highest level in the sediment of the river. In addition, non-point sources, in particular, petrogenic inputs and bitumen fuel combustion were dominant sources in the river. The main concern about the occurrence of PAHs in the environment comes from the fact that they are mostly carcinogenic both in humans and other animals, whereas some PAHs have also been classified to be mutagenic e.g., Benzo(a)pyrene (BaP) and Benzo(g,h, i)perylene. The value of total PAH obtained for water samples from the Oluwa River when compared with the world health organisation standard regulatory limit, strongly implicated the river to be polluted with PAHs. Also, a high level of 3-ring PAH found in the fish species implicated the fish not being fit for human consumption. The results obtained from this study revealed that the fish species are not fit for human consumption. Consumption of fish and water from the Oluwa River could pose a serious health risk and it should be discouraged.

SIGNIFICANCE STATEMENT

This study revealed that the presence of polycyclic hydrocarbons (PAH) in high concentrations, especially those of 2-3 rings and the occurrence of carcinogenic 5-ring PAH, Benzo(a)pyrene in both surface water and sediment of the river above WHO regulatory limit has grossly implicated the river as being polluted. A high level of 3-ring PAH found in the fish species also implicated the fish not being fit for human consumption. The results obtained from this study revealed that the fish species are not fit for human consumption and consumption of fish and water from the Oluwa River could pose a serious health risk and should be discouraged. This study also becomes additional data and information to already existing literature information on some Nigerian waters with high pollution rates and pollutants. However further research could be conducted on the toxicological effects of Polycyclic aromatic hydrocarbon on the fish species using molecular tools.

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