**Research Article**

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Studies on the Physicochemical Properties and Heavy Metals Concentration in Water and Sediment of Ezu River, Awka North Local Government Area of Anambra State, Nigeria

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A study on the physicochemical parameters and heavy metal concentration in water and sediment of Ezu River in Anambra State, Nigeria was carried out for a period of four (4) months (July to October, 2023) to determine their levels in this river. Three different stations tagged as SSI (Amansea), SSII (Ebenebe) and SSIII (Mgbakwu), were chosen along the course of the river. Samples were collected monthly using the best acceptable practices and were taken to laboratory for analysis. Physico-chemical parameters of water which include temperature, pH, turbidity, dissolved oxygen, total dissolved solids, transparency, alkalinity, turbidity, hardness, chlorine, phosphate, magnesium, and nitrate were taken and analyzed with standard laboratory methods. The fish and water samples were digested before being analyzed, using a Varian AA240 Fast Sequential Flame Atomic Absorption Spectrophotometer (AAS) machine to determine the levels of heavy metals. The results showed that there were no significant difference ($P > 0.05$) in some physicochemical parameters such as BOD, Temperature, Transparency, Turbidity, Hardness, phosphate across the sampling stations. In water, the heavy metal concentrations were found to be in the order, $Zn > Pb > Hg > Cd > As$, with the highest concentration (0.312 ± 0.013 ppm) obtained in Zn in station III (Mgbakwu) and lowest (0.003 ± 0.001 ppm) in As in station II (Ebenebe). In sediment, the heavy metal concentrations were found to be in the order, $Zn > Pb > Hg > Cd > As$, the highest concentration (1.370 ± 0.08 ppm) was obtained in Zn in station II (Ebenebe), and lowest (0.012 ± 0.00 ppm) in As in station I (Amansea). All the heavy metal determine were below the maximum permissible limit set by FEPA, FAO and WHO. However, Zn were found to be predominant in both sediment and water of Ezu River. There should be continuous monitoring of the pollution levels of the river to provide adequate information necessary for its effective management.

Keywords: Heavy metals, Pollution, Ecosystem, Rivers systems

Introduction

Rivers all over the world are used for a variety of purposes such as drinking, washing, bathing, recreation as well as numerous other varied industrial applications, the wholesomeness of these water bodies has become an issue of great concern. Rivers are the most important freshwater resource for man [1]. Unfortunately, river water is constantly being polluted by indiscriminate disposal of sewage, industrial waste and plethora of human activities, which adversely affects their physicochemical properties including heavy metals content [2]. It is a serious growing problem, as the increasing amount of industrial and municipal waste that are being discharged into rivers has led to various deteriorating effects on aquatic organism which accumulate pollutants directly from contaminated water and indirectly via food chain. Human feed on these aquatic animals hence the accumulated pollutants are transferred into the body system causing diseases and infections [3]. A river system can be severally contaminated by heavy metals as a result of domestic, industrial mining and related agricultural influence [4]. Contamination of rivers by heavy metals may have catastrophic effects on the ecology balance of aquatic life and the diversity of aquatic organisms which could be limited by the extent of the contamination [5].

Intensive urbanization and increase in industrial activities have caused increasing heavy metal pollution resulting from industrial, agricultural and geochemical wastes. Pollution of heavy metal in water bodies is a threat to public water supplies and also to consumer of fishery sources [6]. These heavy metals bioaccumulate in food chain and consequently pose great risks to humans after consumption due to the persistent nature in the environment [7]. The presence of pollutant such as metals in fresh water is known to disrupt the balance of the aquatic ecosystem and bioaccumulation and magnification is capable of leading to toxic level of these metals in fish, even when the exposure is low [8]. Fishes and other aquatic foods are capable of concentrating heavy metals in their muscles and for the fact that they play vital role in human nutrition, they need to be screened properly to ensure that unnecessary high level of some organic and inorganic pollutants is not being transferred to human through consumption [9,10]. Previous reports showed that industrial and domestic effluent constitute the largest sources of heavy metal which contribute to the increasing metallic pollutant in aquatic and terrestrial environment in most part of the world [10, 11].

In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals [12]. Also, human exposure has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological applications [13]. Reported sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources. Environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations [14]. Although heavy metals are naturally

occurring elements that are found throughout the earth's crust, most environmental contamination and human exposure result from anthropogenic activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds [15]. Studies on bioaccumulation of pollutants in fish are important in determining different content of trace metal in fish species from bio-magnifications of food chains, metabolic capability and feeding habits [16]. This provides substantial information on the adverse effect of metal in aquatic ecosystem [17]. In Nigeria, surveys on heavy metals in fish have been reported by some researchers [18-20].

Moreover, water bodies possess diverse physicochemical properties influenced by factors like temperature, pH, dissolved oxygen, conductivity, turbidity, and nutrient levels, crucial for ecosystem health. Temperature affects gas solubility and organism metabolism, while pH influences chemical reactions and nutrient availability. Dissolved oxygen is vital for aquatic life, fluctuating due to various factors. Conductivity and turbidity reflect water clarity and ion content, affected by sedimentation and pollution. Nutrient levels, particularly nitrogen and phosphorus, impact plant growth and can lead to eutrophication [21]. Ezu River located in Anambra State, Nigeria has encountered numerous challenges in recent years, posing significant threats to its well-being [22]. One pressing issue revolves around pollution, with various sources contributing to the contamination of its waters. Waste from abattoirs, agricultural runoff, and sewage discharge have collectively compromised the river's water quality, prompting legitimate concerns about potential ramifications for public health [23]. Ensuring the physicochemical properties and heavy metal concentrations of the Ezu River fall within World Health Organization (WHO) limits is not just a matter of environmental preservation, but a crucial step towards safeguarding the health and well-being of the communities that rely on it. Exceeding these limits can trigger a cascade of consequences, endangering both aquatic life and human populations. This study therefore evaluates the physicochemical properties and heavy metal concentrations of Ezu River, Anambra State, Nigeria.

Materials and Methods

Site Description

The study was carried out in Ezu river, Awka North local government, Anambra State of Nigeria. The data were collected from three different stations tagged as Station I(Amansea), Station II (Ebenebe) and Station III (Mgbakwu). The choice of these different stations was based on the level of activities going on there.

Sampling Station 1(Amansea)

Amansea is a moderately populated area which is about 30 km from Awka capital territory, Anambra state of Nigeria. The town is located between Latitude: 6° 12' 45.68" N and Longitude: 7° 04' 19.16" E.

Sampling Station 2(Ebenebe)

Ebenebe is 25 km from Awka the capital city of Anambra State. The town is located between the latitude and longitude of $6^{\circ}20'02''\text{N } 7^{\circ}07'45''\text{E}$.

Sampling Station 3 (Mgbakwu)

Mgbakwu is one of the villages in Nigeria situated some 10 km northwest of Awka. The town is located between the Latitude: $6^{\circ}16'00''$ Longitude: $7^{\circ}03'00''$.

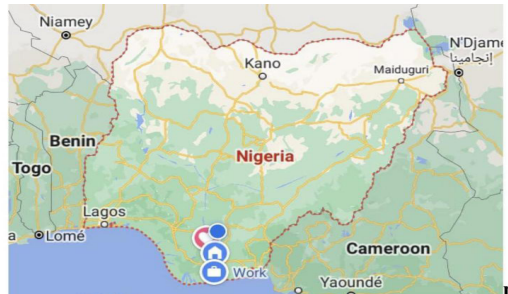


Figure 1: Map of Nigeria showing States.



Figure 2: Map of Anambra State showing Local Government Areas.

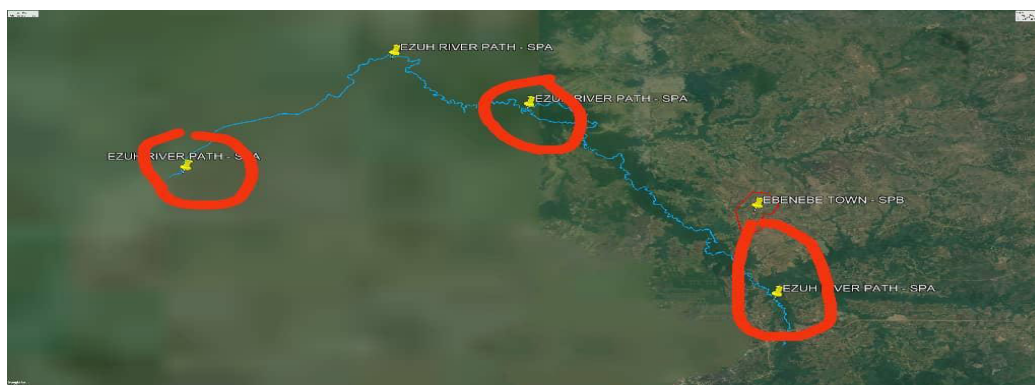


Figure 3: Map showing sampling stations at Amansea/Ebenebe/Mgbakwu Rivers.

The water samples were obtained from three different locations along the Ezu River. Strategic sampling was carried out before collection to obtain a true representation of the area under study. The aesthetic (non-health related) parameters like, colour,

and temperature (using a thermometer) were performed on-site at the sample collection point along the Ezu River. Afterwards, the collected water sample was then transferred to a plastic container which had been previously washed, rinsed with deionised water,

and labelled properly for easy identification. Furthermore, the physicochemical properties of the sample were conducted within 24 hours of collection. The collected sample was transported to Docchy Analytical Laboratories and Environmental Services Limited Anambra State, Awka, Anambra State, Nigeria, where relevant physicochemical analyses were conducted as promptly as possible. Meanwhile, the samples meant for heavy metal analysis (which could not commence immediately) were stored at 4°C or relevant preservatives were added depending on the parameter to be determined and the duration of preservation.

Evaluation of Physico-chemical Parameters of Water

Temperature was determined using the mercury-in-glass thermometer, which was inserted in water and the temperature (°C) reading was taken after four minutes. pH was measured pH Meter Hanna model HI991300 [24]. while the values of electrical conductivity, turbidity, total dissolved solids, water hardness, nitrate, phosphate, dissolved oxygen, alkalinity, BOD, and chloride were determined using standard laboratory methods described by APHA, [24]. The current meter was used to determined water current. It was deployed at different depths of the river, it was left for a few seconds and then the velocity and direction of the water movement was taken and recorded afterwards in determining the transparency of the river a Secchi disk was lowered into the water, and the disk deeply disappeared into the water. Determining transparency in water is often done using a Secchi disk. Lower the disk into the water until it disappears, then measure the depth. A deeper disappearance indicates clearer water, while a shallower depth suggests lower transparency.

Collection of Sediment Samples

Samples for Sediment were collected from the two sample locations by means of bottom grab sampler. They were placed in plastic bags earlier drenched in nitric acid and cleaned in distilled water. Sediment samples air- dried at a temperature of 60 °C in a moisture extraction oven to constant weight. They were stored in labelled packs prior to digestion and analysis.

Digestion of Samples

Water Samples

The frozen water samples were allowed to defrost at room temperature (27 °C) and digested using pre-concentrated Nitric

acid method [25]. Blanks will be prepared with acids.

Sediment

The oven-dried sediment samples were filtered through a 200m mesh size screen. The samples were weighed and 1g of each sample was placed into a 250ml flask and digested with hydrochloric acid (10ml). The mixture was heated until a milky precipitate appears indicating complete digestion. The precipitate was then allowed to cool and made up to mark with distilled water. Blanks were prepared using the same quantity of hydrochloric acid.

Analysis of Heavy Metals

The following heavy metals in water and sediment was analyzed; Lead (Pb), Copper (Cu), Chromium (Cr) at Docchy Analytical Laboratories and Environmental Services Limited Anambra State, Awka, Anambra State, Nigeria, Heavy metals analyses was carried out using Atomic Absorption Spectrophotometer (AAS) Buck scientific machine, Model 210VGP.

Data Analysis

The presentation of Data was achieved by using means and standard deviations. Means were subjected to one-way analysis of variance (ANOVA) using 9.0 statistical package for scientist and social sciences (SPSS) (2012) to determine significant differences at 5% level of probability. Significant means will be subjected to Duncan Multiple Range Test (DMRT).

Results

The results of the physicochemical composition of the Ezu River are presented in Table 1. The result in Table 1 shows that the mean values of DO, Turbidity, Chlorine, and Phosphate values were above the WHO-recommended standard. However, the mean Temperature, conductivity, BOD etc were below the recommended standard by WHO. The result of the concentration of Heavy metals in water collected from the Amansea, Ebenebe, and Mgbakwu rivers is presented in Table 2. It shows the ascending order of heavy metal concentration. The result of the concentration of Heavy metals in water collected from the Amansea, Ebenebe, and Mgbakwu rivers is presented in Table 3. From the analysis of the sediment collected from the river it was observed that Zinc (Zn) is above the WHO recommended standard, however, the Mercury (Hg), Lead (Pb), Arsenic (As), cadmium(cd) is below the WHO recommended standard

Table 1: Physicochemical properties of Ezu River, Anambra State, Nigeria.

Parameters	Sampling Stations			WHO Limit [26]
	SSI	SSII	SSIII	
Temperature (°C)	27.97 ± 1.32 ^a	28.10 ± 0.19 ^a	27.90 ± 0.23 ^a	25-50
Conductivity ys/cm	112.87 ± 6.31 ^a	115.05 ± 1.69 ^b	117.97 ± 2.65 ^b	400
Dissolved oxygen mg/L	8.02 ± 0.12 ^a	7.40 ± 0.22 ^b	7.56 ± 0.32 ^b	4-6.0
BOD mg/L	5.40 ± 0.22 ^a	5.41 ± 1.60 ^a	5.33 ± 0.53 ^a	<50
Total dissolved solid mg/L	23.90 ± 1.30 ^a	24.55 ± 1.24 ^b	25.00 ± 0.79 ^b	<450

Transparency cm/L	44.95 ± 0.30 ^a	44.98 ± 0.28 ^a	44.68 ± 0.72 ^a	-
Alkalinity mg/L	98.40 ± 1.14 ^a	96.98 ± 1.34 ^b	97.31 ± 0.78 ^b	-
Turbidity	7.54 ± 0.04 ⁿ	7.65 ± 0.17 ⁿ	4.33 ± 0.17 ^a	<5
Hardness	88.75 ± 0.27 ^a	88.60 ± 0.83 ^a	88.90 ± 0.54 ^a	500
pH	6.80 ± 0.02 ^a	6.73 ± 0.07 ^a	6.50 ± 0.02 ^a	6.5-8.5
H ₂ O Current (cm/s)	18.61 ± 1.87 ^a	19.79 ± 1.24 ^b	19.93 ± 0.55 ^b	-
Chlorine	135.66 ± 1.29 ^a	137.33 ± 0.47 ^b	136.33 ± 1.25 ^b	5
Phosphate mg/L	6.77 ± 0.21 ^a	6.81 ± 0.42 ^a	6.67 ± 0.24 ^a	4
Magnesium mg/L	3.00 ± 0.19 ^b	2.64 ± 0.39 ^a	2.80 ± 0.47 ^a	0.1
Nitrate mg/L	1.54 ± 0.20 ^a	1.55 ± 0.15 ^a	1.55 ± 0.31 ^a	50

Means within the same column with different superscripts are significantly different (P<0.05)

Table 2: Mean Heavy metals concentration in water in Ezu River, Anambra State, Nigeria.

Parameters	Sampling Stations			WHO [27]	FME [28]
	SSI	SSII	SSIII		
Mercury (Hg)	0.029 ± 0.008 ^a	0.024 ± 0.001 ^a	0.021 ± 0.001 ^a	0.001	0.002
Lead (Pb)	0.030 ± 0.001 ^b	0.032 ± 0.004 ^b	0.026 ± 0.001 ^a	0.01	0.015
Zinc (Zn)	0.295 ± 0.070 ^a	0.303 ± 0.006 ^b	0.312 ± 0.013 ^b	5	5
Arsenic (As)	0.005 ± 0.001 ^a	0.003 ± 0.002 ^a	0.004 ± 0.009 ^a	0.01	0.01
Cadium (Cd)	0.013 ± 0.016 ^a	0.010 ± 0.001 ^a	0.012 ± 0.002 ^a	0.001-0.005	0.005

Means within the same column with different superscripts are significantly different (P<0.05)

Table 3: Heavy metals concentrations in the sediment of Ezu River, Anambra State, Nigeria.

Parameters	Sampling Stations			WHO [27]
	SSI	SSII	SSIII	
Mercury (Hg)	0.053±0.0082 ^a	0.055±0.0080 ^b	0.052±0.0225 ^a	-
Lead (Pb)	0.081±0.0002 ^a	0.079±0.0008 ^b	0.080±0.0183 ^a	2.00
Zinc (Zn)	1.363±0.0854 ^a	1.370±0.0840 ^a	1.444±0.1118 ^b	5
Arsenic (As)	0.012±0.00020 ^a	0.015±0.0020 ^b	0.015±0.0022 ^b	2.00
Cadium (Cd)	0.021±0.0030 ^a	0.021±0.0023 ^a	0.020±0.0007 ^a	0.1

Means within the same column with different superscripts are significantly different (P<0.05)

Discussion

In the three study sites, the physicochemical parameters were recorded during the period of four months of sample collection and were compared with the World Health Organization standard [27, 29]. The mean variation in water temperature of 27.99°C observed in Ezu river lies within the optimum temperature range of 25 to 30°C by WHO [27, 28], required for the survival of tropical aquatic organisms. The temperature values in the three sampling sites were relatively high, this could be because most of the temperature readings were taken in the afternoon (13hrs -15hrs) in these locations. The similarity in temperature values of the Ezu River may significantly favour the biological activities of various life forms in the aquatic ecosystem. Life cycles and population densities of many

river organisms are very temperature dependent and alteration of the average river temperature by a few degrees could alter the flora and fauna of the river. Water temperature was within the optimum range (23-32 mg/l) ideal for fish survival and growth throughout the study period as recommended by federal ministry for environment [29]. Environmental temperature has been found to influence breeding and reproductive behaviour in aquatic animals thus it plays a major role overtime [29]. In Nigeria, water temperature is usually high as a result of during the dry periods [30], which hampers the spawning of fish. Report on the range for water temperature required for spawning vary between 21 °C and 30 °C. Spawning activity can decrease rapidly at temperatures below 21 °C or above 30 °C, the water must be 24 °C -30 °C for successful hatching [31].

Temperature is also known to have strong influence on heavy metal dilution, enzyme reaction, growth efficiency, reproduction and immune response in fish [32]. The dissolved oxygen range throughout the study period was slightly higher than the optimum range (6-8 mg/l) recommended by the federal ministry for environment [23] best for fish survival. The best range of dissolved oxygen for growth and reproduction is from 5 mg/l-8 mg/l [34]. In this study, the slightly higher value of DO in Amansea River than Ebenebe and Mgbakwu may be attributed to the higher transparency of Amansea River, thus causing photosynthetic activity to be higher, leading to the release of more oxygen into the water body. One major factor responsible for low DO levels in tropical rivers is the influx of discharge effluents from the surroundings into the streams. These effluents contain high organic matter. Generally, when an organism is subjected to chemical, physical, or biological (i.e. pathogen infection) stress, sudden shortage of dissolved oxygen causes abnormal oxidative reactions in the aerobic metabolic pathways, resulting in the formation of excessive amounts of singlet oxygen and free radicals [35]. Water pH was also within safe range recommended by [36] throughout the study period. Total dissolved solid values was within safe limit throughout the study period. High values of total dissolved solids tend to affect heavy metal availability since this will also affect the level of sedimentation in the river water. High TDS values have aquatic plant growth, which also causes high turbidity in river water [37].

Turbidity is a measure of the ability of water to receive light and is caused by small particles in the various measures of turbidity that exist. The mean value (7.50mg/l) of Ezu rivers falls above the range considered suitable by WHO [27,29] for fish growth. However, the Amansea River had a higher light extinction value, thus penetration of sunlight is more likely and sunlight energy is important in photosynthesis. The pH of water in Ezu River has a mean value of (6.68) thus, these waters are good for the survival of aquatic organisms since (Wetzel) reported waters with a pH range of 5.5 to 9.0 as most suitable for aquatic organisms. Also, when compared with the WHO [27,29] standard pH range of 6.5 - 8.5, it is suitable for aquatic ecosystems. The BOD values of Ezu River ranged from 5.40mg/l, 5.41mg/l, and 5.33mg/l respectively which did not fall within the recommended range of 5.0mg/l by WHO [27,29]. Thus, it is unsuitable for aquatic life. The BOD was generally high during the study. Waters with BOD levels less than 4mg/l are termed reasonably clean and unpolluted while waters with levels greater than 10mg/l are considered polluted since they contain large amounts of degradable organic materials. In the research conducted by [38] in Anambra River. The BOD was in the range of 3.1 to 4.3 mg/l which was said to support low organic enrichment of the river. The Alkalinity of water may mean any water with a pH value above 7.0, but often it means the total of alkaline substances present in association with bicarbonates, carbonates, and hydroxides. Low alkalinity was recorded at the three study sites compared to the high values at downstream locations of the three study sites. [39] were of the view that low alkalinity in the upstream could be explained mainly in terms of the absence of carbonate and bicarbonates, and the increasing values downstream due to a greater presence of both ions. Also, increasing

values of alkalinity with decreasing distance from the seas have been reported in Southeastern streams and rivers, Minimum and maximum alkalinity values recorded upstream and downstream respectively also support the findings of [40].

The heavy metals (Cd, As, Zn, Pb, Hg) encountered in water occurred in the order of (SSI: As < Cd < Pb < Hg < Zn, SSII: As < Cd < Hg < Pb < Zn, SSIII: As < Cd < Hg < Pb < Zn) The trend of concentration of heavy metals in sediment is (As<Cd<Hg<Pb<Zn). The dominance of zinc over all other metals in the study shows a high accumulation of the metal in water and sediment samples. The mean concentration of zinc in water obtained in this study is lower than 10 mg/l which Haliru [41] recorded in Yola River. The mean concentration recorded in water was within the WHO acceptable standard while the sediments' mean value was above the WHO allowable limit. Zinc is an essential trace element that is easily bioaccumulated by aquatic life. However, it is toxic at levels above permissible limits. Heavy metals can enter the river through various anthropogenic activities, including industrial discharge, agricultural runoff, and urban pollution compromising water quality and aquatic biodiversity. Overfishing, sand mining, and unsustainable water extraction practices further exacerbate pressure on the river ecosystem, depleting fish stocks and disrupting natural hydrological processes. Uncontrolled logging and land clearing for agriculture result in soil erosion and habitat destruction along the riverbanks, leading to sedimentation and loss of biodiversity [42].

Heavy metals concentrations in water and sediments from Ezu River shows heavy metals concentration were higher in sediments compare to water during the study period. The mean concentration of heavy metals variations in water and sediment varied based on the three sampling locations upstream and downstream. The result showed that more of the metals are concentrated in the sediment compared to water, the maximum mean concentration recorded for Zn was observed in the sediment in SSIII while the least value was noted for as in SSI. The maximum value recorded for water was observed in Zn while the least value was recorded for as in SSII. These variation in values may be attributed to the large volume of effluents discharge from domestic waste and runoff from pesticide, fertilizer and diesel products which has accumulated overtime [43]. Heavy metals concentration in this study were generally lower during the study in both water and sediment. This finding similar to report by Wagboje and Ekundayo [44] for Ikpoba Reservoir. In this study, the levels of heavy metals in the sediment were generally higher than that of water. This may due high level of sedimentation occurring downstream compare to upstream. This is in agreement with the report of Uka, and Ekpo [45] who reported that there is high concentration of heavy metals in sediments when compare to water in Selected Rivers in Southeastern, Nigeria. Higher concentration of heavy metals in sediments may be due to sediments acting as sink to heavy metals and inability of the metals to dissolve in water thus got deposited in the sediment [46].

Conclusion and Recommendations

The study provides comprehensive data on the physicochemical

properties and heavy metal concentrations in Ezu river. The results indicated that the water quality in certain parameters exceeds WHO recommended standards, posing potential risks to human health and the environment. The results obtained from this study also confirmed the occurrence and intensities of heavy metals concentration in this order Zn > Pb > Hg > Cd > As in both water and sediments of the river. The levels of these metals in the water and sediment studied were below the WHO and FME recommended limits in quality drinking water and sediment. However, there is need for continuous monitoring of River Donga waters. In order to avoid serious environmental risks, there is need to establish effective water pollution control measures and management of this River. Additionally, presence of heavy metals in both water and sediment samples highlight the presence of anthropogenic pollutants in the river ecosystem. Therefore, urgent intervention measures are warranted to address water pollution and safeguard public health and environmental integrity in the study area.

Acknowledgement

None.

Conflicts of Interests

None.

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