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Heavy Metal Pollution in the Marine Environment: A Study Contribution of Three Rivers to the Pollution at the Upper of the River Niger, Nigeria

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ABSTRACT

Water is not only essential for life, but also it is life. Safeguarding this resource from heavy metals is good for our well-being. This research investigated heavy metals content and their potential health problems in some rivers across Anambra, Nigeria. The mean concentration of Zn was recorded as 0.03 mg/L which was lower than the limits set by the World Helth Organization (WHO) (3 mg/L), USEPA (5 mg/L), and EU (3 mg/L). Cu (0.003 mg/L) was also lower than limits set by the WHO (2 mg/L), USEPA (1.3 mg/L), and EU (2 mg/L). Fe (1.177 mg/L) was found higher than limits prescribed by the WHO (0.3 mg/L), USEPA (0.3 mg/L), and EU (0.2 mg/L). Cd (0.001 mg/L) was lower than limits set by the WHO (0.003 mg/L), USEPA (0.005 mg/L), and EU (0.005 mg/L). Pb (0.001 mg/L) was lower than limits set by the WHO (0.01 mg/L), USEPA (0.015 mg/L), and EU (0.01 mg/L). Lastly, As (0.01 mg/L) was equal to limits set by the WHO (0.01 mg/L), USEPA (0.01 mg/L), and EU (0.01 mg/L). The values for validation parameters are low indicating minimal variability and uncertainty in our measurements, signifying high precision in measuring instruments and the tested samples. The *p*H measurement of all the samples proved acidic. Based on the elevated values of iron (Fe) and arsenic (As) recorded in this study, regular monitoring and treatment of drinking water sources are essential to ensure compliance with regulatory limits and to provide iron and arsenic-free as well as the other metal-free drinking water to the public within the investigated location.

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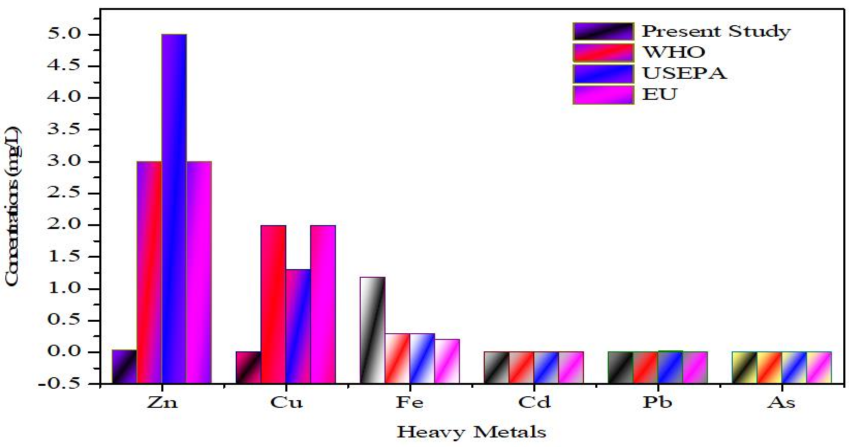
GRAPHICAL ABSTRACT



Introduction

Water is not just essential for life; it is life. Its unique properties and universal presence make it a precious resource that sustains ecosystems, supports human health, and drives the functioning of the natural world. Safeguarding and responsibly managing this invaluable resource are critical for the well-being of our planet and future generations [1-6]. River water is of paramount importance for various ecological, social, and economic reasons. Rivers provide critical habitats for diverse plant and animal species. Healthy river ecosystems support biodiversity and help maintain ecological balance. They are a major source of freshwater for drinking, agriculture, and industrial use. There essentiality in human survival and economic activities makes them crucial for used in irrigation to cultivate crops, ensuring food security and supporting agriculture [7-14].

Historically, rivers have been important trade and transportation routes. Even today, they play a role in shipping goods and people in many regions. Rivers offer recreational opportunities like fishing, boating, and tourism, contributing to local economies and quality of life. They are harnessed for hydropower generation, providing renewable energy [15-21]. Heavy metals, such as zinc, copper, iron, cadmium, lead, and arsenic can have adverse health effects when present in river water at elevated concentrations [22, 23].Excessive zinc intake can lead to gastrointestinal upset, including nausea and vomiting. High copper levels may cause gastrointestinal issues, liver and kidney damage, and in severe cases, Wilson's disease. Elevated iron concentrations in water usually result in aesthetic issues, like a metallic taste or staining of laundry and fixtures, rather than health concerns. Iron is an essential nutrient when consumed in reasonable amounts [24, 30].

Cadmium is highly toxic. Long-term exposure to cadmium in water or food can lead to kidney damage, lung cancer, and bone disorders. Lead exposure, especially in children, can result in developmental issues, cognitive impairment, anemia, and damage to various organs. Even low levels of lead are a concern. Arsenic is a potent carcinogen. Long-term exposure to high arsenic levels in water can cause skin lesions, cancers (e.g., skin, lung, and bladder), and other health problems [31-35]. It is crucial to regularly monitor and control heavy metal concentrations in river water to safeguard public health and the environment. Water treatment and strict regulatory standards are essential to ensure that heavy metal levels in drinking water are within acceptable limits. Efforts to reduce industrial pollution and promote sustainable land use practices are also crucial to protect river ecosystems and water quality [36-42].

This research investigated heavy metals content and their potential health problems in some river water across Anambra, Nigeria.

Experimental

Materials and Methods

Materials

The materials used for this study are glass beakers, glass conical flask, measuring cylinder, wash bottles, electronic weighing balance, hot plate, water bath, oven, rubber funnel, and Atomic Absorption Spectrometer.

Methods

Description and Location

This research work was conducted in Otuocha River which comprises of Omambala River, Otuako River, and Ezichi River located in the Anaku Fishing Community in Anambra State, Nigeria. The native names of the Anambra rivers are tributaries of the famous River Niger (North), Ezu River (South), Omor, and Umuerum communities (East). Anaku is a fishing community and the administrative headquarters of Ayamelum Local Government Area of Anambra State, South-East Nigeria [43]. The coordinates of the study area are presented in Table 1 and its map is displayed in Fig 1. The area falls within the tropical climate which accounts for the prevailing moist rainforest vegetation. The climate of the area is characterized by a dry season from November to March and a rainy season from April to October with mean annual rainfall of about 1805 mm. The river is the most important feeder of the river Niger which flows 210 kilometers (130 miles) into the Niger River before finally being released into the Atlantic Ocean through various outlets [43]. The crop farming and fishing activities in the community are of great economic importance as most of the dwellers are crop farmers and fisherfolks who cultivate mainly rice, as well as other crops (yam, cassava, vegetables, and cocoyam), and also engage actively in daily fishing activities, as depicted in Fig 2.

Collection and Preparation of Water Samples

Nine water samples were collected from sampling points of Omambala River, Otuako River, and Ezichi River of Anambra State, Nigeria. The sampling points were chosen along the water cause of the river, waste dump side, and normal site.

Table 1. Geographical coordinates of the study area

Location Names	Sample Code	Longitude (E)	Latitude (N)
Otuako River 1	A	6°52'53.82"	6°27'40.86"
Otuako River 2	B	6°52'21.92"	6°26'34.14"
Otuako River 3	C	6°51'47.85"	6°25'14.69"
Omambala River 1	A	6°53'34.78"	6°31'25.84"
Omambala River 2	B	6°54'13.37"	6°32'54.44"
Omambala River 3	C	6°52'54.08"	6°30'14.37"
Ezichi River 1	A	6°55'9.69"	6°35'31.47"
Ezichi River 2	B	6°55'11.84"	6°34'49.90"
Ezichi River 3	C	6°55'44.65"	6°36'17.92"

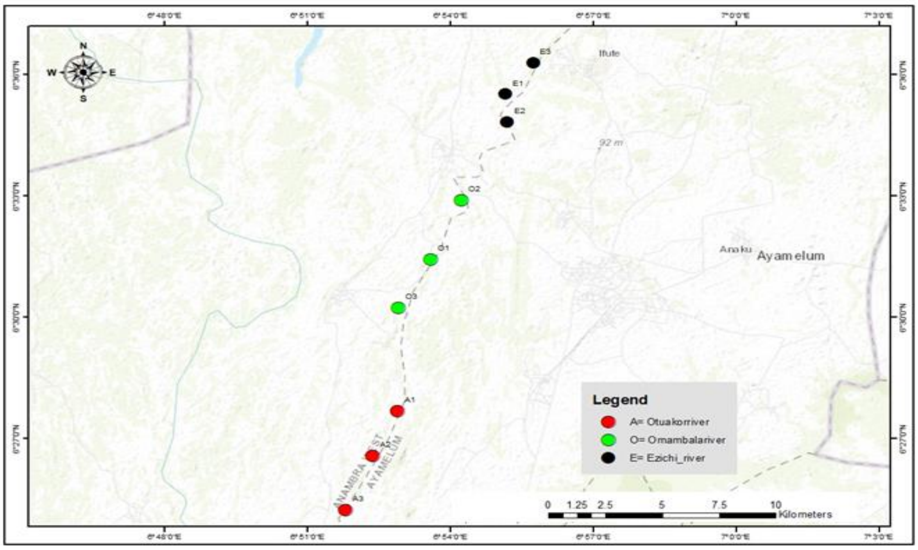


Fig1. Map of the study area showing sample locations

Fig2. Omambala river in Anambra State, Nigeria

Preliminary measures were taken following the standard guideline by the FAO (2020) [44] to avoid any possible contaminations. The collected samples were transported to the laboratory for extraction, digestion, and analysis of heavy metals analysis. The samples were collected in both rainy and dry season using the same method of collections. A liter of the collected water samples were laid into a Pyrex flask and a 25 cm^3 of nitric acid (concentrated ,70% High Purity HNO_3) (with specific gravity of 1.42 g/mL) against 75 cm^3 of hydrochloric acid (35% Hcl concentrated) (with specific gravity of 1.18 g/mL) been in the ratio of 1:3, was then added to dissolve the metals [45]. The resulting mixture was then laid on a VM-300S hot-plate (with maximum loading capacity of 50 mL and speed range of 300 rmp) and left to be cool. The obtained solution was later filtered via whatman filter paper no. 42 and filled up to a 50 mL mark with water (distilled).

This was taken to Perkin Elmer Atomic Absorption Spectrophotometer AAnalyst 400 for metal ion content analysis [46]. The AAS Aanalyst 400 model was utilized for the determination of heavy metal content in previously digested soil samples. The setup process involved fixing the nitrous oxide, acetylene gas, and compressor. The compressor was then activated, and the liquid trap was purged to eliminate any trapped liquid. Following this, both the Extractor and the AAS control were switched on [46]. To ensure the precision of the analysis, meticulous cleaning procedures were performed. The slender tube and nebulizer piece were thoroughly cleansed using a purifying wire, and the burner's opening was cleaned using an arrangement card. Subsequently, the AAS programming worksheet on the connected PC was opened, and the empty cathode light was inserted into the light holder. The light source was turned on, and the cathode beam was carefully adjusted to precisely target the arrangement card, ensuring optimal light throughput. Once this was achieved, the machine was ignited [47].

In preparation for analysis, a fine amount of the sample was placed in a 10 ml graduated cylinder containing deionized water, and the aspiration rate was measured. An analytical blank was meticulously prepared, followed by the creation of a series of calibration solutions with known quantities of the analyte element (standards). These standards, along with the blank, were atomized sequentially, and their respective responses were recorded. Calibration curves were constructed for each standard solution, enabling the subsequent atomization and measurement of the sample solutions.

Finally, the concentrations of various metals within the sample solution were determined by referencing the absorbance values obtained for the unknown sample against the calibration curves. This methodology allowed for the accurate quantification of heavy metal concentrations in the soil samples [47].

Method of Determination of Validation Parameters

The Limit of Blank (LOB), Limit of Detection (LOD), and Limit of Quantitation (LOQ) were evaluated which are important parameters in analytical chemistry, particularly in the context of analytical method validation. These parameters help determine the sensitivity and reliability of an analytical method as pointed out by Muhammad *et al.* (2011) [48].

The formulas for calculating these limits vary depending on the specific method and statistical approach used, but here are common approaches for each:

Limit of Blank (LOB) as in Equation (1), represents the highest apparent analyte concentration that is expected to be indistinguishable from the background signal (blank) with a certain level of confidence. It is typically calculated according to Muhammad *et al.* (2011) [48] as follow:

$$LOB = Mean\ signal\ of\ blank + k \times (SD\ of\ blank) \quad (1)$$

Limit of Detection (LOD), as in Equation (2), represents the lowest concentration of an analyte that can be reliably detected but not necessarily quantified. It is typically calculated according to Muhammad *et al.* (2011) [48] as follow:

$$LOD = LOB + k \times (SD\ of\ low\ concentration) \quad (2)$$

Where, k is a constant that depends on the desired level of confidence. Common values for k include 1.645 for a 95% confidence level and 2.33 for a 99% confidence level when assuming a normal distribution. Repeatability and reproducibility are important measures of the precision or variability of an analytical method. These measures help assess how consistent the results are when the same analyst repeats the analysis (repeatability) or when different analysts or laboratories perform the analysis (reproducibility). They are often expressed as standard deviations or coefficients of variation. Here are the formulas for calculating repeatability and reproducibility:

Repeatability (R), as in Equation (3), also known as intra-laboratory precision, assesses the precision of results obtained within the same laboratory by the same analyst or instrument on different days or under different conditions. It is typically calculated according to Muhammad *et al.* (2011) [48] as the standard deviation (SD) or coefficient of variation (CV) of a series of replicate measurements on the same sample:

$$R = \sqrt{\left[\frac{\Sigma(x_i - \bar{x})^2}{(n-1)}\right]} \quad (3)$$

Reproducibility (Rp), as in Equation (4), also known as inter-laboratory precision, assesses the precision of results obtained by different analysts or different laboratories using the same method. It is typically calculated similarly to repeatability according to Muhammad *et al.* (2011) [48], but it involves measurements from multiple laboratories or analysts. The formula for reproducibility standard deviation (RSDR) is similar to repeatability:

$$R_P = \sqrt{\left[\frac{\Sigma(x_i - \bar{x})^2}{(m-1)}\right]} \quad (4)$$

Where, x_i equals each individual measurement, $\bar{x}$ equals the mean of the measurements n is the number of replicates and m is the number of laboratories or analysts. These formulas as reported by Muhammad *et al.* (2011) [48] provide quantitative measures of the precision within a single laboratory (repeatability) and the precision between different laboratories or analysts (reproducibility). The choice of whether to use standard deviation or coefficient of variation depends on your preference and the reporting requirements of your analytical method validation or quality control procedures.

Results and Discussion

The results of heavy metals concentrations in Otuako River, Omambala River, and Ezichi River from different locations (A, B, and C) are listed in Table 2. Otuako River has the mean concentration values of 0.25 mg/L for zinc (Zn), 0.001 mg/L for copper (Cu), cadmium (Cd) and lead (Pb), 2.357 mg/L for iron (Fe), and 0.01 mg/L for arsenic (As). It is possible to see that Otuako River A has iron (Fe) with value of 2.807 mg/L as the highest, followed by zinc (Zn) with 0.044 mg/L, and then arsenic (As) with 0.01 mg/L, and lastly copper (Cu), cadmium (Cd) and lead (Pb) with the least

Table 2. Heavy metals concentrations in Otuako river, Omambala river, and Ezichi river

H/M	Season	A	B	C	Mean	A	B	C	Mean	A	B	C	Mean
		Otuako River (mg/L)				Omambala River (mg/L)				Ezichi River (mg/L)			
Zn	Rainy	0.044	0.005	0.027	**0.025**	0.014	0.036	0.080	**0.043**	0.134	0.049	0.005	**0.063**
	Dry	0.001	0.001	0.001	**0.001**	0.014	0.036	0.080	**0.043**	0.001	0.001	0.001	**0.001**
Cu	Rainy	0.001	0.001	0.001	**0.001**	0.001	0.001	0.001	**0.001**	0.001	0.001	0.001	**0.001**
	Dry	0.008	0.001	0.013	**0.007**	0.003	0.001	0.001	**0.002**	0.007	0.001	0.001	**0.003**
Fe	Rainy	2.807	2.254	2.010	**2.357**	0.653	0.633	0.787	**0.691**	2.476	2.651	2.390	**2.506**
	Dry	0.278	0.195	1.676	**0.716**	0.322	1.335	0.134	**0.597**	0.213	0.178	0.201	**0.197**
Cd	Rainy	0.001	0.001	0.001	**0.001**	0.001	0.001	0.001	**0.001**	0.001	0.001	0.001	**0.001**
	Dry	0.001	0.001	0.001	**0.001**	0.001	0.001	0.001	**0.001**	0.004	0.001	0.001	**0.002**
Pb	Rainy	0.001	0.001	0.001	**0.001**	0.001	0.001	0.001	**0.001**	0.001	0.001	0.001	**0.001**
	Dry	0.001	0.001	0.001	**0.001**	0.001	0.001	0.001	**0.001**	0.001	0.001	0.001	**0.001**
As	Rainy	0.010	0.010	0.010	**0.010**	0.010	0.010	0.010	**0.010**	0.010	0.010	0.010	**0.010**
	Dry	0.010	0.010	0.010	**0.010**	0.010	0.010	0.010	**0.010**	0.010	0.010	0.010	**0.010**

value of 0.001 mg/L. Otuako River B was the same trend with iron (Fe) with the highest value of 2.254 mg/L, followed by zinc (Zn) with 0.005 mg/L, and then arsenic (As) with 0.01 mg/L and copper (Cu), cadmium (Cd), and lead (Pb) with the least value of 0.001 mg/L. Similar trend was equally observed in Otuako river C, where iron (Fe) has the highest value of 2.010 mg/L, followed by zinc (Zn) with 0.027 mg/L, and then arsenic (As) with 0.01 mg/L and copper (Cu), cadmium (Cd), and lead (Pb) with the least value of 0.001 mg/L.

For Omambala Town River, the mean concentration values are 0.043 mg/L for zinc (Zn), 0.001 mg/L for copper (Cu), cadmium (Cd), and lead (Pb), 0.691 mg/L for iron (Fe) and 0.01 mg/L for arsenic (As). It is equally worthy of notice that Omambala River A has the highest value of 0.653 mg/L in iron (Fe), followed by zinc (Zn) with 0.014 mg/L, and then arsenic (As) with 0.01 mg/L, and then copper (Cu), cadmium (Cd), and lead (Pb) with the least value of 0.001 mg/L. Omambala River B was the same trend with iron (Fe) having the highest value of 0.633 mg/L, followed by zinc (Zn) with 0.036 mg/L, and then arsenic (As) with 0.01 mg/L and copper (Cu), cadmium (Cd), and lead (Pb) with the least value of 0.001 mg/L. Similar trend was equally observed in Omambala River C, where iron (Fe) has the highest value of 0.787 mg/L, followed by zinc (Zn) with 0.08 mg/L, and then arsenic (As) with 0.01 mg/L and copper (Cu), cadmium (Cd), and lead (Pb) with the least value of 0.001 mg/L.

And lastly, for Ezichi Town River, the mean values are 0.063 mg/L for zinc (Zn), 0.001 mg/L for copper (Cu), cadmium (Cd), and lead (Pb), 2.506 mg/L for iron (Fe) and 0.01 mg/L for arsenic (As). It is obviously noted that, in Ezichi River A, iron (Fe) has the highest value of 2.476 mg/L, followed by zinc (Zn) with 0.134 mg/L, and then arsenic (As) with 0.01 mg/L followed by copper (Cu), cadmium (Cd), and lead (Pb) with the least value of 0.001 mg/L. Ezichi River B, was the same trend with iron (Fe) having the highest value of 2.651 mg/L, followed by zinc (Zn) with 0.049 mg/L, and then arsenic (As) with 0.01 mg/L and copper (Cu), cadmium (Cd), and lead (Pb) with the least value of 0.001 mg/L. Similar trend was equally observed in Ezichi River C, where iron (Fe) has the highest value of 2.390 mg/L, followed by zinc (Zn) with 0.005 mg/L, then arsenic (As) with 0.01 mg/L and copper (Cu), cadmium (Cd), and lead (Pb) with the least value of 0.001 mg/L. In addition, comparing the data for rainy season with those of dry season, as presented in Table 1, it could be observed that the concentration of copper (Cu) in Otuako River (A), Otuako River (C), Omambala River (A), and Ezichi River (A) are higher in dry season than those of rainy season. This could be as a result of high deposition during the rainy season. There was also a higher deposition of iron (Fe) in the dry season than observed in rainy season at Omambala River (B) which could be attributed to same reason. The zinc (Zn) concentrations in Otuako River (A, B and C) and Ezichi River (A, B, and C) are noted to be higher in dry season than in the rainy season. It was the same trend for iron (Fe) concentration in Otuako River (A, B, and C), Omambala River (A and C) and Ezichi River (A, B, and C). This justified the fact that, when there is much flow of water in a river, it flows along with a lot of contaminants with it. All other metals apart from the above-mentioned ones have the same concentrations during the rainy and dry seasons.

The comparison of results of mean heavy metals concentrations in Otuako River, Omambala River, and Ezichi River with regulatory bodies like the World Health Organization (WHO), United State Environmental Protection Agency (USEPA), and European Union (EU) are presented in Table 3 and Fig. 3.

Table 3. Comparison of mean concentrations in the present work with the WHO, USEPA, and EU

H/M	Seasons	Otuako	Omambala	Ezichi	Mean	WHO	USEPA	EU
Zn	Rainy & Dry	0.013	0.043	0.032	0.030	3.000	5.000	3.000
Cu	Rainy & Dry	0.004	0.002	0.002	0.003	2.000	1.300	2.000
Fe	Rainy & Dry	1.537	0.644	1.352	1.177	0.300	0.300	0.200
Cd	Rainy & Dry	0.001	0.001	0.002	0.001	0.003	0.005	0.005
Pb	Rainy & Dry	0.001	0.001	0.001	0.001	0.010	0.015	0.010
As	Rainy & Dry	0.010	0.010	0.010	0.010	0.010	0.010	0.010

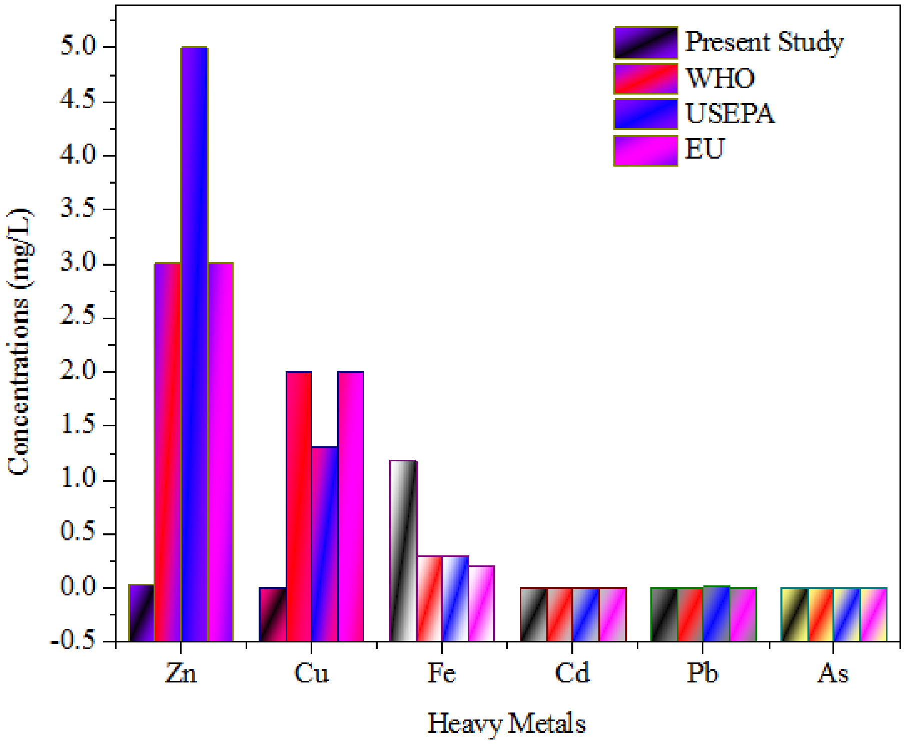


Fig3. Comparison of mean concentrations in the present work with the WHO, USEPA, and EU

Exceeding the established limits for zinc in drinking water can lead to adverse health effects, including gastrointestinal disturbances, nausea, and other health concerns. The mean concentration of zinc (Zn) in all rivers from this study (Otuako River (0.013 mg/L), Omambala River (0.043 mg/L), and Ezichi River (0.032 mg/L) are lower than all the three (3) regulatory bodies use for comparison in this work (the World Health Organization (3 mg/L), United State Environmental Protection Agency (5 mg/L), and European Union (3 mg/L)). The mean concentration of zinc (Zn) obtained in the present study (0.03 mg/L) is lower than that reported by Tripathi *et al.* (1999) [49]. When the established limits for copper in drinking water is exceeded, adverse health effects may arise, which include gastrointestinal disturbances and potential long-term health concerns. The mean concentration of copper (Cu) in all rivers from this study (Otuako River (0.004 mg/L), Omambala River (0.002 mg/L), and Ezichi River (0.002 mg/L) are lower than all the three (3) regulatory bodies use for comparison in this work (the World Health Organization (2 mg/L), United State Environmental Protection Agency (1.3 mg/L), and

European Union (2 mg/L)). The mean concentration of copper (Cu) obtained in the present study (0.003 mg/L) is lower than that reported by Tripathi *et al.* (1999) [49]. Excess consumption of iron in drinking water may pose aesthetic issues, such as discolored water and potential health concerns, particularly for individuals with certain medical conditions. The mean concentration of iron (Fe) in all rivers from this study (Otuako River (1.537 mg/L), Omambala River (0.644 mg/L) and Ezichi River (1.352 mg/L) are higher than all the three (3) regulatory bodies use for comparison in this work (the World Health Organization (0.3 mg/L), United State Environmental Protection Agency (0.3 mg/L), and European Union (0.2 mg/L)). The mean concentration of iron (Fe) obtained in the present study (1.177 mg/L) is higher than that reported by Tripathi *et al.* (1999) [49].

Cadmium is a toxic heavy metal and exposure to elevated levels of cadmium can have serious health effects, including damage to the kidneys, bones, and respiratory system. The mean concentration of cadmium (Cd) in all rivers from this study (Otuako River (0.001 mg/L), Omambala River (0.001 mg/L), and Ezichi River (0.002 mg/L) are lower than all the three (3) regulatory bodies use for comparison in this work (the World Health Organization (0.003 mg/L), United State Environmental Protection Agency (0.005 mg/L), and European Union (0.005 mg/L)). The mean concentration of cadmium (Cd) obtained in the present study (0.001 mg/L) is lower than that reported by Tripathi *et al.* (1999) [49]. Exposure to elevated levels of lead in drinking water can have serious health effects, particularly in children, and can lead to developmental and neurological problems. The mean concentration of lead (Pb) in all rivers from this study (Otuako River (0.001 mg/L), Omambala River (0.001 mg/L), and Ezichi River (0.001 mg/L) are lower than all the three (3) regulatory bodies use for comparison in this work (the World Health Organization (0.01 mg/L), United State Environmental Protection Agency (0.015 mg/L), and European Union (0.01 mg/L)). The mean concentration of lead (Pb) obtained in the present study (0.001 mg/L) is lower than that reported by Tripathi *et al.* (1999) [69]. Arsenic is a highly toxic substance, and long-term exposure to high levels of arsenic in drinking water can lead to serious health problems, including cancer, skin lesions, and various other health concerns. The mean concentration of arsenic (As) in all rivers from this study (Otuako River (0.01 mg/L), Omambala River (0.01 mg/L), and Ezinchi River (0.01 mg/L) are lower than all the three (3) regulatory bodies use for comparison in this work (the World Health Organization (0.01 mg/L), United State Environmental Protection Agency (0.01 mg/L) and European Union (0.01 mg/L)). The mean concentration of arsenic (As) obtained in the present study (0.01 mg/L) is equal to that reported by Tripathi *et al.* (1999) [49]. Based on the elevated values of iron (Fe) and arsenic (As) recorded in this study, regular monitoring and treatment of drinking water sources are essential to ensure compliance with regulatory limits and to provide iron and arsenic-free as well as other metal-free drinking water to the public within the investigated location. Based on the validation parameters provided in Table 4, the values for the limit of blank, limit of detection, repeatability, and reproducibility are lower. The low values of these parameters in our study indicate minimal variability and uncertainty our measurements, signifying a high level of precision in both the measuring instruments and the tested samples. Based on Table 5, the *p*H measurement of all the samples collected from different samples across Anambra Rivers (Otuako River, Omanbala River, and Ezichi River) proved to be acidic.

Table 4. Validation parameters

Heavy Metal	LOB	LOD	R	Rp
Zn	0.036	3.0×10^{-3}	0.0022	0.0022
Cu	0.080	3.0×10^{-5}	0.0045	0.0045
Fe	0.001	3.0×10^{-7}	0.0002	0.0002
Cd	0.005	9.0×10^{-6}	0.0001	0.0001
Pb	0.016	5.2×10^{-6}	0.0012	0.0010
As	0.026	4.1×10^{-6}	0.0021	0.0020

LOB = Limit of blank; LOD = Limit of detection; R = Repeatability; and Rp = Reproducibility

Table 5. Water sample's *p*H values measured from the point of sample collection

Locations	A	B	C
Otuako	5.74	5.89	5.97
Omambala	5.39	4.63	5.42
Ezinchi	6.22	6.16	6.24

Conclusion

The current study has underscored the significant presence of heavy metals in Otuako River, Omambala River, and Ezenchi River. Notably, iron (Fe) exhibited a notable high concentration in all rivers under consideration, arsenic (As) proved closely high concentration in the entire rivers while other metals such as zinc (Zn), cadmium (Cd), copper (Cu), and lead (Pb) displayed inferior concentration levels in all locations under investigation. All samples proved acidic based on the *p*H values recorded. These findings raise concerns regarding the manufacturing processes employed in the iron industry, which may be the cause of high iron (Fe) contamination in these rivers. Importantly, the risk of heavy metal intoxication, specifically iron (Fe) and arsenic (As), remains unresolved, as all samples contained concentrations exceeding the maximum permissible limits recommended by the World Health Organization (WHO), United State Environmental Protection Agency (USEPA), and the European Union (EU).

Assessing the analytical validation parameters, including the limits of blank (LOB), limits of detection (LOD), repeatability (R), and reproducibility (Rp) presented in this study, we observed minimal variability and uncertainty in our measurements. This suggests a commendable level of precision in our measuring instruments and sample analysis. Consequently, we can cautiously assert the safety of water consumption within the investigated area. However, to ensure the broader safety of river water in the area, we strongly recommend ongoing research of this nature in other regions of the state to encompass the entirety of our jurisdiction. This proactive approach will uphold public health and safety standards in water consumption across the state.

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