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Exploration of Heavy Metal Levels and their Possible Health Implications in Selected Rivers within Nasarawa West, Nigeria

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ABSTRACT

This research investigated heavy metals content and their potential health problems in some rivers across Nasarawa west, Nigeria. The mean concentration of Zn was recorded as 0.32 mg/L which was lower than the limits set by the World Health Organization (WHO), USEPA, and EU. Cu with mean of 0.03 mg/L was also lower than limits set by the WHO, USEPA, and EU. Fe with mean of 1.25 mg/L are found higher than limits prescribed by the WHO, USEPA, and EU. Cd with mean of 0.01 mg/L are lower than limits set by the WHO, USEPA, and EU. Pb with mean of 0.01 mg/L are lower than limits set by the WHO, USEPA, and EU. Lastly as with mean of 0.01 mg/L are equal to limits set by the WHO, USEPA, and EU. 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 pH 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 other metal-free drinking water to the public within the investigated location.

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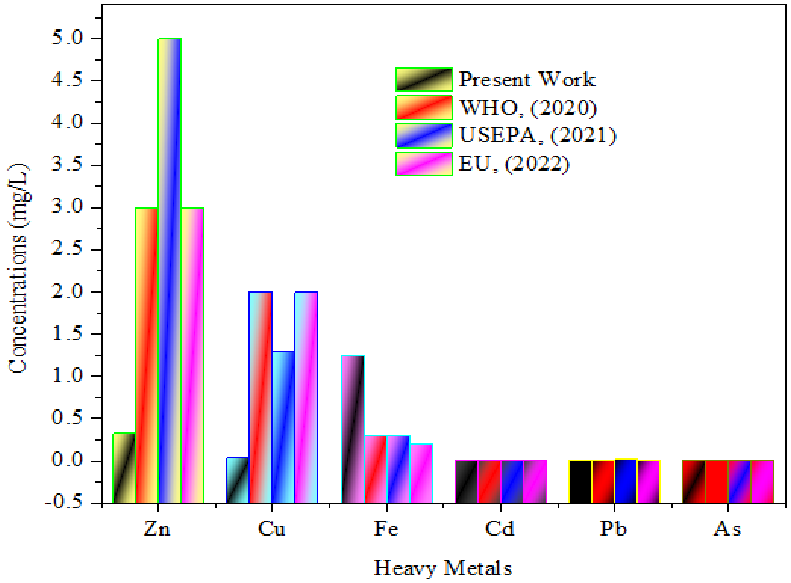
Graphical Abstract



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, 2].

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 [3-6].

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 [7, 8].

Heavy metals, such as zinc, copper, iron, cadmium, lead, and arsenic can have adverse health effects when present in river water at elevated concentrations [9, 10].

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 [11, 15].

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 [16, 17].

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 [18].

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

Experimental

Materials and methods

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.

Description and location

This research work was conducted in Antau river, Laminga river, Kotto river and Loko river all located in Nasarawa west in Nasarawa State, Nigeria. The coordinates of the study area are presented in Table 1. The map of Nasarawa state, showing Keffi and Nasarawa Local Government areas is depicted by Figure 1, while the map of Keffi and Nasarawa Local Government areas showing the sample locations is shown in Figure 2.

The study area lies in the tropical climate that accounts for the persuading moist rainforest vegetation. The area's climate is characterized by a sonny (dry season) from November to March and a wet (rainy) season from April to October with average annual rainfall of almost 1805 mm. The rivers are the most important feeder of the Benue River which flows 210 kilometers (130 miles) into the Benue River before lastly being allowed into the Atlantic Ocean through several outlets [19].

The fishing and crop farming activities in the community are of paramount economic importance as most of the dwellers are fisherfolks and crop farmers who cultivate mainly rice, as well as other crops (yam, cassava, vegetables corn, guinea corn, millet, melon, and cocoyam), and also engage actively in daily fishing activities.

Collection and preparation of water samples

From Antau River, Kotto River, and Loko River of Nasarawa State, Nigeria, nine (9) water samples were collected from sampling points. The sampling points were chosen along the water cause of the river, waste mining dump side, and normal site. Preliminary measures were taken following the standard guideline by the FAO (2020) [20] to avoid any possible contaminations. Samples collected 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 litre of the collected water samples were set into a pyrex flask and a 25 cm^3 of nitric acid (concentrated, 70% High Purity HNO, and specific gravity of 1.42 g/mL) against 75 cm^3 of hydrochloric acid (35% HCl concentrated and specific gravity of 1.18 g/mL) in the ratio of 1:3, was then figure up to disband the metals.

Table 1. Geographical coordinates of the study area

Location Names	Sample Code	Longitude (E)	Latitude (N)
Antau River 1	A	7°53'15.42"	8°51'26.09"
Antau River 2	B	7°53'9.06"	8°51'7.36"
Antau River 3	C	7°53'24.09"	8°50'52.97"
Kotto River 1	A	7°42'7.70"	8°31'10.13"
Kotto River 2	B	7°42'26.11"	8°31'8.21"
Kotto River 3	C	7°42'44.54"	8°31'9.73"
Loko River 1	A	7°46'17.59"	8° 0'15.94"
Loko River 2	B	7°47'7.72"	8° 0'5.17"
Loko River 3	C	7°48'19.70"	7°59'54.85"

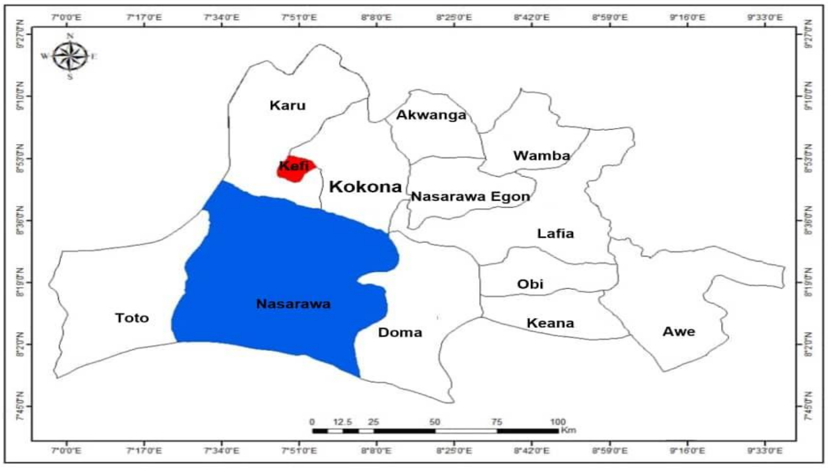


Figure 1. Map of Nasarawa State showing Keffi and Nasarawa local government area

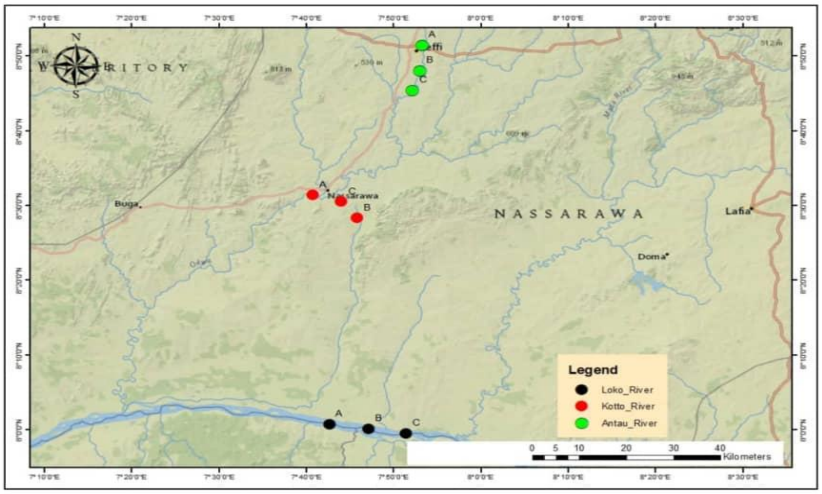


Figure 2. Map of Keffi and Nasarawa local government area showing sample points

A litre of the collected water samples were set into a pyrex flask and a 25 cm^3 of nitric acid (concentrated, 70% High Purity HNO, and specific gravity of 1.42 g/mL) against 75 cm^3 of hydrochloric acid (35% HCl concentrated and specific gravity of 1.18 g/mL) in the ratio of 1:3, was then figure up to disband the metals. The developed mixture was then set on a VM-300S hot-plate (with loading capacity (the maximum) of 50 mL and range of speed of 300 rmp) and allowed to cool. The evolved solution was later filtered with whatman filter paper no. 42 and completed up to a 50 mL mark with water (distilled) [21]. This was taken to Perkin Elmer Atomic Absorption Spectrophotometer AAnalyst 400 for the analysis of metal ion content [22].

The AAnalyst 400 offers a wide dynamic range, allowing for the analysis of heavy metals at various concentration levels. It covers a broad range of wavelengths, enabling the measurement of multiple elements. This instrument offers exceptional sensitivity, making it suitable for trace-level analysis [23]. The AAnalyst 400 provides both flame and furnace atomization capabilities, offering versatility in sample introduction methods. It features advanced data handling software for accurate and efficient data processing [24].

The instrument is rigorously calibrated using certified standards of known concentrations of heavy metals. Calibration curves are generated, which establish the relationship between the instrument's response and the concentration of the analytes. This step is crucial to ensure accurate quantification of heavy metals in water samples [25]. The AAnalyst 400 operates on the principle of atomic absorption spectroscopy. In this technique, a light source emits a specific wavelength of light through a sample containing the heavy metal of interest [26]. The atoms of the metal absorb the light at their characteristic absorption wavelengths, and the instrument measures the extent of this absorption. The degree of absorption is directly proportional to the concentration of the metal in the sample [27].

The AAnalyst 400 is known for its reliability and accuracy in heavy metal analysis. It offers high precision in measurements due to its stable design and precise control of experimental conditions. The instrument's robust construction and advanced technology ensure that results are consistent and dependable, making it a trusted tool for environmental monitoring and water quality analysis [28].

With the utilization of AAS Aanalyst 400 model, heavy metal content in previously digested water samples was determined. The process for the setup encompasses fixing the nitrous oxide, acetylene gas, and compressor. Activation of the compressor was done, and the liquid trap was purged to quench any trapped liquid. Accordingly, both the AAS control and the extractor were switched on [29].

To make sure we have higher precision of the analysis, scrupulous cleaning plan of action were performed. The slender tube and nebulizer piece were utterly cleansed using a purifying wire, and the burner's opening was cleaned using an arrangement card [30]. Thereafter, the AAS programming worksheet on the attached PC was opened, and the null cathode light was inserted into the light holder [31]. The light source was turned on, and the cathode beam was attentively modified to precisely target the arrangement card, guaranteeing optimal light bandwidth. Immediately this was realized, the machine was ignited [32].

In the course of preparing for analysis, a little amount of the sample was set in a 10 ml calibrated cylinder containing deionized water, and the aspiration rate was measured. An analytical blank was punctiliously prepared, then by the initiation of a series of calibration solutions with known quantities of the analyte element (standards). These standards, along with the blank, were atomized successively and their corresponding responses were recorded. Calibration curves were constructed for each standard solution, enabling the later atomization and measurement of the sample solutions.

Eventually, the various metals concentrations within the sample solution were gotten by referencing the absorbance values acquired for the unknown sample against the calibration curves. This methodology permit for the accurate heavy metal concentrations quantification in the water samples [33, 34].

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 David and Terry in 2018, Mohammad *et al.* in 2023b, Mohammad *et al.* (2023c) and Mohammad *et al.* (2023d) [35-38] and are given by Equations (1) to (4), respectively.

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.

$$\mathrm{LOB} = \text{Mean signal of blank} + \mathrm{k} \times (\text{Standard Deviation of blank}) \qquad (1)$$

Limit of Detection (LOD), as in Equation (2), represents the lowest concentration of an analyte that can be reliably detected but not necessarily quantified.

$$\mathrm{LOD} = \mathrm{LOB} + \mathrm{k} \times (\text{Standard Deviation of low concentration sample}) \qquad (2)$$

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 as the standard deviation (SD) or coefficient of variation (CV) of a series of replicate measurements on the same sample:

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

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, but involves measurements from multiple laboratories or analysts. The formula for reproducibility standard deviation (RSDR) is similar to repeatability:

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

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 David and Terry in 2018, Mohammad *et al.* in 2023b, Mohammad *et al.* (2023c), and Mohammad *et al.* (2023d) [35-38] 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 Antau River, Kotto River, and Loko River from different locations (A, B, and C) were listed in Table 2. Antau River has the mean concentration values for both rainy and dry seasons as 0.52 and 0.32 mg/L for zinc (Zn), 0.01 and 0.07 mg/L for copper (Cu), 0.01 and 0.01 mg/L for cadmium (Cd), lead (Pb) and arsenic (As), and 2.24 and 1.16 mg/L for iron (Fe), respectively.

For Kotto River, the mean concentration values for both rainy and dry seasons are 0.23 and 0.15 mg/L for zinc (Zn), 0.01 and 0.02 mg/L for copper (Cu), 0.01 and 0.01 mg/L for cadmium (Cd), lead (Pb) and arsenic (As), and 0.68 and 0.6 mg/L for iron (Fe), respectively.

And lastly, for Loko River, the mean values for both rainy and dry seasons are 0.46 and 0.21 mg/L for zinc (Zn), 0.01 and 0.03 mg/L for copper (Cu), 2.62 and 0.21 mg/L for iron (Fe), 0.01 and 0.02 mg/L for cadmium (Cd), and 0.01 and 0.01 mg/L for lead (Pb) and arsenic (As), respectively.

Table 2. Heavy metals concentrations in Antau River, Kotto River, and Loko River

H/M	Season	Antau River (mg/L)	Kotto River (mg/L)	Loko River (mg/L)
Zn	Rainy	0.52	0.23	0.46
	Dry	0.32	0.15	0.21
Cu	Rainy	0.01	0.01	0.01
	Dry	0.07	0.02	0.03
Fe	Rainy	2.24	0.68	2.62
	Dry	1.16	0.60	0.21
Cd	Rainy	0.01	0.01	0.01
	Dry	0.01	0.01	0.02
Pb	Rainy	0.01	0.01	0.01
	Dry	0.01	0.01	0.01
As	Rainy	0.01	0.01	0.01
	Dry	0.01	0.01	0.01

Also, comparing the data for rainy season with those of dry season, as presented in Table 2, it could be observed in all the rivers (Antau River, Kotto River, and Loko River) that, the concentration of zinc (Zn) is higher in rainy season than that in dry season, unlike that of copper (Cu) which exhibited high concentration in dry season compared to that of rainy season. It was found in the same rivers that, the concentration of iron (Fe) is higher in rainy season than that in dry season while the remaining metals like cadmium (Cd), lead (Pb), and arsenic (As) have similar concentration values in both dry and rainy season. This could be as a result of high deposition during the rainy season. The high value of copper in dry season compared to rainy season in Antau River showed that, due to the high density of copper, it could settle at the bottom of the river even after the river dried. There was also a higher deposition of iron (Fe) and zinc (Zn) in the rainy season than observed in dry season at Antau River which could be attributed to fact that the river carries iron and zinc scraps from the anthropogenic activities going on in the towns and villages around the study areas and flow along with them during the rainy season.

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

H/M	Seasons	Antau	Kotto	Loko	Mean	WHO	USEPA	EU
Zn	Rainy & Dry	0.42	0.19	0.34	0.32	3.000	5.000	3.000
Cu	Rainy & Dry	0.04	0.02	0.02	0.03	2.000	1.300	2.000
Fe	Rainy & Dry	1.70	0.64	1.42	1.25	0.300	0.300	0.200
Cd	Rainy & Dry	0.01	0.01	0.02	0.01	0.003	0.005	0.005
Pb	Rainy & Dry	0.01	0.01	0.01	0.01	0.010	0.015	0.010
As	Rainy & Dry	0.01	0.01	0.01	0.01	0.010	0.010	0.010

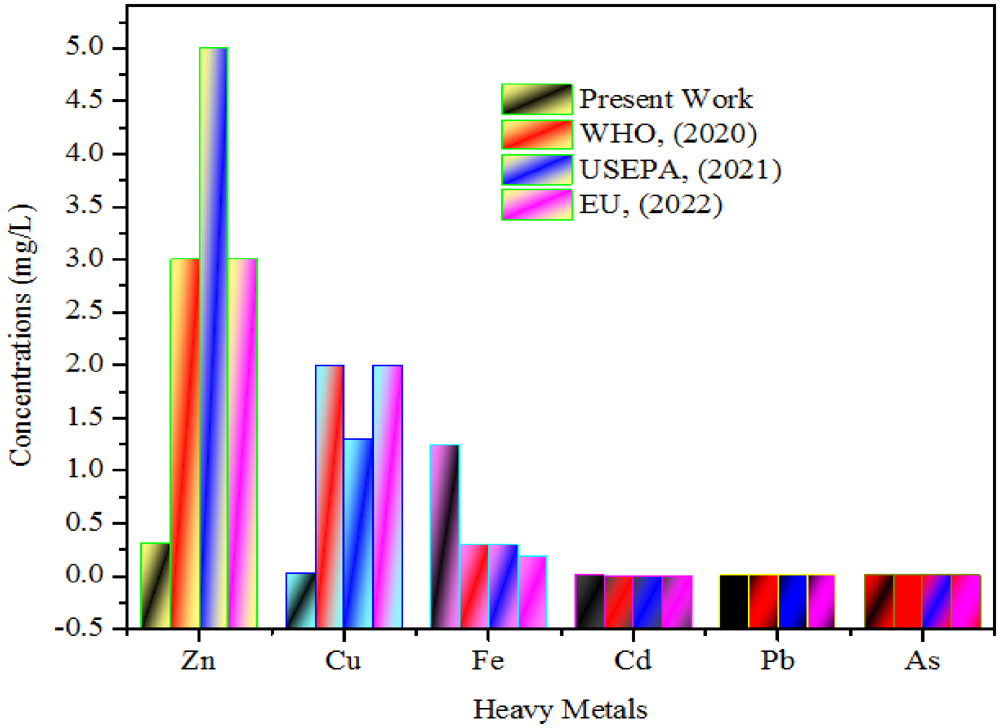


Figure 3. Comparison of mean concentrations in the present work with the WHO, USEPA, and EU

The comparison of results of mean heavy metals concentrations in Antau River, Kotto River, and Loko 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 Figure 3. Exceeding the established limits for zinc in drinking water can lead to adverse health effects, including gastrointestinal disturbances, nausea, and other health concerns [39, 40]. The mean concentration of zinc (Zn) in all rivers from this study (Antau River (0.423 mg/L), Kotto River (0.19 mg/L), and Loko (0.34 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 States Environmental Protection Agency (5 mg/L), and European Union (3 mg/L)). The mean concentration of zinc (Zn) obtained in the present study (0.32 mg/L) is lower than that reported by Mohammad *et al.* (2023) [40].

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 [40]. The mean concentration of copper (Cu) in all rivers from this study (Antau River (0.04 mg/L), Kotto River (0.02 mg/L), and Loko (0.02 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 States Environmental Protection Agency (1.3 mg/L), and European Union (2 mg/L)). The mean concentration of copper (Cu) obtained in the present study (0.03 mg/L) is lower than that reported by Tripathi *et al.* (1999) [41].

Excess consumption of iron in drinking water may pose aesthetic issues, such as discolored water, as well as potential health concerns, particularly for individuals with certain medical conditions [42]. The mean concentration of iron (Fe) in all rivers from this study (Antau River (1.7 mg/L), Kotto river (0.64 mg/L), and Loko (1.42 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 (1.25 mg/L) is higher than that reported by Nejati *et al.* (2022) [42].

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 [43]. The mean concentration of cadmium (Cd) in all rivers from this study (Antau River (0.01 mg/L), Kotto River (0.01 mg/L), and Loko (0.02 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 States 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 (0.01 mg/L) is lower than that reported by Emmanuel *et al.* (2023) [43].

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 [44]. The mean concentration of lead (Pb) in all rivers from this study (Antau River (0.01 mg/L), Kotto River (0.01 mg/L), and Loko (0.01 mg/L) are lower than all the three (3) regulatory bodies used for comparison in this work (the World Health Organization (0.01 mg/L), United States 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 (0.01 mg/L) is lower than that reported by Reza *et al.* (2020) [44].

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 [44]. The mean concentration of arsenic (As) in all rivers from this study (Antau River (0.01 mg/L), Kotto River (0.01 mg/L), and Loko (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 Reza *et al.* (2020) [44].

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 presented 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 pH measurement of all the samples collected from different samples across Anambra rivers (Antau River, Kotto River, and Loko 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 pH values measured from the point of sample collection

Locations	A	B	C
Antau River	5.74	5.89	5.97
Kotto River	5.39	4.63	5.42
Loko River	6.22	6.16	6.24

Conclusion

The current study has underscored the significant presence of heavy metals in Antau River, Kotto River, and Loko 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 pH 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 States

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.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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