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Lead, Zinc and Iron Pollutants Load Assessment in Selected Rivers in Southern Nigeria: Implications for Domestic Uses

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Abstract

The aim of the study is to comparatively assess the concentrations of lead, zinc and iron in Rivers Ase, Warri and Ethiope, in Nigeria. Monthly water samples were collected from six randomly selected sites along the rivers course. 72 water samples were collected from each river at 0 - 15 cm depths. Samples were analysed based on the standard methods recommended by the WHO for testing lead, zinc and iron. The assessment of the water quality was done using the Water Quality Index (WQI) of the Canadian Council of Ministers of the Environment (CCME-WQI). While hypotheses were tested using ANOVA. Findings indicated that CCME-WQI values were 47.3, 66.52 and 78.7. This meant that the water quality of River Ase is impaired and departed from desirable levels, while that of Warri and Ethiope were considered to occasionally be impaired and depart from desirable levels. The ANOVA model showed that there is a significant variation in heavy metal load in the selected rivers at $P < 0.05$. River water was put to domestic uses such as drinking (20.5%) preparing food (17.8%), bathing (19.8%), washing clothes and dishes (21.3%), brushing teeth (13.3%), and catering for domestic animals (7.5%). Poverty (49.5%) was the major reason for the use of river water for domestic purposes. The locals highlighted that they usually suffer from cholera (26.8%), diarrhoea (25.8%), dysentery (24%) and typhoid (23.5%) as a result of using the river water. The study recommended routine monitoring of anthropogenic and geologic activities, testing of the water regularly amongst others.

Keywords

Assessment, Water-Quality-Index, Domestic, Heavy-Metals

1. Introduction

Water is one of the natural resources and a basic need of man. He uses water for his domestic needs such as, drinking, bathing, washing and other social economic activities [1]. A large proportion of the water exists as surface water on the earth surface [2], which is found in the oceans, seas, rivers, streams, lakes and ponds. This huge amount of water may not be suitable for human consumption, depending on the rates of natural or anthropogenic pollution [3]. Also, river water quality is questionable due to geologic and anthropogenic activities of man within the source of the supply and along the course of the water [4]. Thus, there is variation in the quality of the water in terms of the Physicochemical and biological characteristics. This presents the need to assess river water quality for domestic purposes in order to safeguard human health especially those who drink and cook with river water [5].

Surface water is prone to contamination from small and large scale industrial activities, release of wastewater from households and discharges of septic tank effluents [6], particularly in less developed countries [7]. Furthermore, dumping of human waste into the water bodies has posed a serious threat to the use of the water for domestic purposes [8]. The deterioration in water quality has become a major concern to users in recent times. Hence, the quality of surface water is of importance to man, to ensure that it is potable for drinking and other domestic uses at all times. As part of the measures to control the pollution loads in water, it is germane to determine the physicochemical and biological indices of the water, especially metals such as lead (Pb^+), zinc (Zn), and iron (Fe), as they are known to affect human health [9].

Surface water, especially rivers, on average contains between 3 to 30 ppb of lead [10]. However, when lead comes in contact with moist air its reactivity with water increases [11]. When oxygen and water are present, metallic lead is converted to lead hydroxide ($Pb(OH)_2$);

$$2Pb(s) + O_2(g) + 2H_2O(l) \rightarrow 2Pb(OH)_2(s) \quad (1)$$

Lead may, however, occur dissolved in water as $PbCO_3$ or $Pb(CO_3)_2^{2-}$. Lead frequently binds to sulphur in sulphide form (S^{2-}), or to phosphorus in phosphate form (PO_4^{3-}). In these forms, lead is extremely insoluble and is present as immobile compounds in the environment. Lead compounds are generally soluble in soft and slightly acidic water.

Lead is generally toxic and most harmful pollutant eco-toxicologically [12]. Lead salts are attributed to water hazard class 2, and are generally harmful. Lead and its compounds such as lead acetate, lead oxide, lead nitrate and lead carbonate are toxic pollutants [13]. The Safe Drinking Water Act (SDWA) has reduced the maximum allowable lead content that is considered "lead free" to be a weighted average of 0.25 percent calculated across the wetted surfaces of pipes, pipe fittings, plumbing fittings and fixtures and 0.2 percent for solder and flux [14]. However, the Environmental Protection Agency (EPA) has set the maximum contaminant level goal for lead in drinking water at zero because lead is a toxic metal that is harmful to human health, even at low exposure levels [15].

Zinc is used by living organisms for metabolic activities, however studies by Hatakeyama [16], Jensen, *et al.* [17] and Wada and Suzuki [18] found toxicological effects of zinc on aquatic organisms. This led to the enactment of an Environmental Quality Standards (EQS) in Japan in 2003, restricting the concentration of zinc in water to 0.03 mg/l. However the zinc concentration remains high, exceeding 0.03 mg/l in several prefectures [19]. Moreover, several studies by Gozzard, *et al.* [20], Chen, *et al.* [21] and Wang, *et al.* [22] revealed that zinc concentrations in water bodies vary with the seasons. It is discharged into water bodies by anthropogenic and geologic activities of man. In natural water, zinc can be found as hydrated ions, metal inorganic complexes or metal organic complexes [23]. In the process of hydrolysis, hydrated zinc cations may form zinc hydroxide or zinc oxide. Zinc enters the environment and water bodies from industrial waste and is a major component of sludge. Zinc causes health effect when found in doses in water. It is also toxic to plant at high levels [24].

Iron makes up at least five percent (5%) of the earth's crust and is one of the most abundant resources on the earth surface [25]. Although present in drinking water, it is seldom found at concentrations greater than 10 mg/l/10ppm. However as little as 0.3 mg/l can cause water to be reddish brown in colour. Iron occurs in two forms; first as soluble ferrous iron or as an insoluble ferric iron and is considered a secondary or aesthetic contaminant of water [26]. Dissolved ferrous iron gives water a disagreeable metallic taste [27]. Iron impacts a bitter astringent taste in water when consumed by man and a brownish colour to laundered clothes [28]. Iron occurs in surface water in the ferrous state and may be oxidized to ferric state [29]. Iron is mostly present in acidic water [30].

There is always need for concerns for the inhabitants of an area served by rivers, as to the concentration of metals and pollutants such as lead, zinc, and iron in the water obtained from such rivers. This is because, these locals may depend heavily on these rivers for their domestic and other uses (to the neglect of its quality), based on its availability [31]. The deterioration of surface water quality due to high concentration of lead, zinc and iron has increased over the years in Nigeria due to industrial activities and open dumping of industrial wastes in river water. And this has become a major concern in recent times. In Southern Nigeria, increase in population, industrial activities, oil exploration and exploitation has posed a threat to the quality of surface water, hence there is the need to assess river water quality in the light of the concentration of lead, zinc and iron. River Ase, Warri and Ethiope, are major rivers to the south of Nigeria, which serves over one million (1 m) persons' domestic needs daily. It is possible that this waters are polluted but to no knowledge of the locals. This study is set out to assess the lead, zinc and iron load of rivers Ase, Warri and Ethiope using the Canadian Council of Ministers of the Environment (CCME) Water Quality Index (WQI) for domestic purposes.

Prevailing Trend

The increase in anthropogenic and geologic activities of man has a forceful impact on the quality of surface water. Anthropogenic activities along the bank of surface water sources impair the quality of the water. Also industrial effluents not only change the chemistry of the water but its physical characteristics. Furthermore, the river water suffers from contamination caused by the use of detergents, solid waste disposal, effluent discharge, industrial waste and sewer leakages from human activities. Due to theses impingements, high concentrations of lead, zinc and iron are prevalent in the surface water, resulting in adverse health effect when such water is consumed by man. Thus, over exposure to lead in water results in colic, skin pigmentation and paralysis. While in children, even low level of lead in the blood can cause behaviour and learning problems, lower IQ and hyperactivity, slowed growth, hearing problems and anaemia. While in adults, exposure to lead can result in cardiovascular effects, increased blood pressure, hypertension, decreased kidney function and reproductive problems.

Additionally, zinc inhalation and consuming polluted water may result in gastrointestinal diseases or modifications in gastrointestinal soft tissues [32]. While iron concentration as low as 0.3 mg/l will leave reddish brown stains on fixtures, table-wares and laundry that are very hard to remove [33]. Also, dissolved ferrous iron gives water a disagreeable taste [34]. Thus, vegetables cooked in water containing excessive iron may look dark and hazardous to human health [35].

In all, metals such as lead, zinc and iron found in high concentrations in drinking water poses health hazards to man [36]. Challenges related to metals in drinking water will magnify in the future due to an ever increasing population that needs to share in the already polluted and poorly managed water resources. There is therefore the need to assess these metals—lead, zinc, iron—in surface water using the CCME water quality index for the overall development and substance of man on the earth's surface, especially in Southern Nigeria. This underscores the need for this study.

2. Aim, Objectives and Hypothesis

The aim of the study is to comparatively assess the concentration of lead, zinc and iron in River Ase, Warri River and River Ethiope using the CCME WQI for domestic purposes in Southern Nigeria. Arising therefore, the specific objectives are:

1) Assess the mean values of the physicochemical characteristics of the analysed water samples for lead, zinc and iron in River Ase, Warri River and River Ethiope in Southern Nigeria.

2) Compare the variation in concentration of lead, zinc and iron using the CCME WQI in the water samples analysed of the three rivers—River Ase, Warri River and River Ethiope in Southern Nigeria.

3) Assess the implication of their uses (the river water) for domestic purposes in the study area.

4) Suggest ways of normalizing the river water quality; especially the concentration of lead, zinc and iron in the study area.

Hypothesis

Ho: There is no significant variation in the concentration of lead, zinc and iron in Rivers Ase, Warri and Ethiope in Delta State.

3. Materials and Method

3.1. Area of Study

The areas of study are River Ase, Warri River and River Ethiope in Southern Nigeria (See **Figure 1**). River Ase is located approximately on latitude 5˚17' and 5˚53' North of the Equator and longitude 6˚17' and 6˚31' East of the Greenwich Meridian (Federal Surveys, Nigeria, Sheet 78 (Kwale) (1970). River Ase is a tributary of the Forcados River, the western arm of the River Niger. The river is approximately 292 kilometres in length. Conversely, Warri River stretches within latitudes 5˚21' and 6˚00' north of the Equator and longitudes 5˚24' and 6˚21' east of the Greenwich Meridian. The river is about 150 kilometres long and occupies an area of about 255 square kilometres. While River Ethiope is located within latitudes 5˚40' and 6˚00' North of the equator and longitudes 5˚39' East and 6˚10' East of the Greenwich Meridian. River Ethiope is over 100 kilometres in length [37].

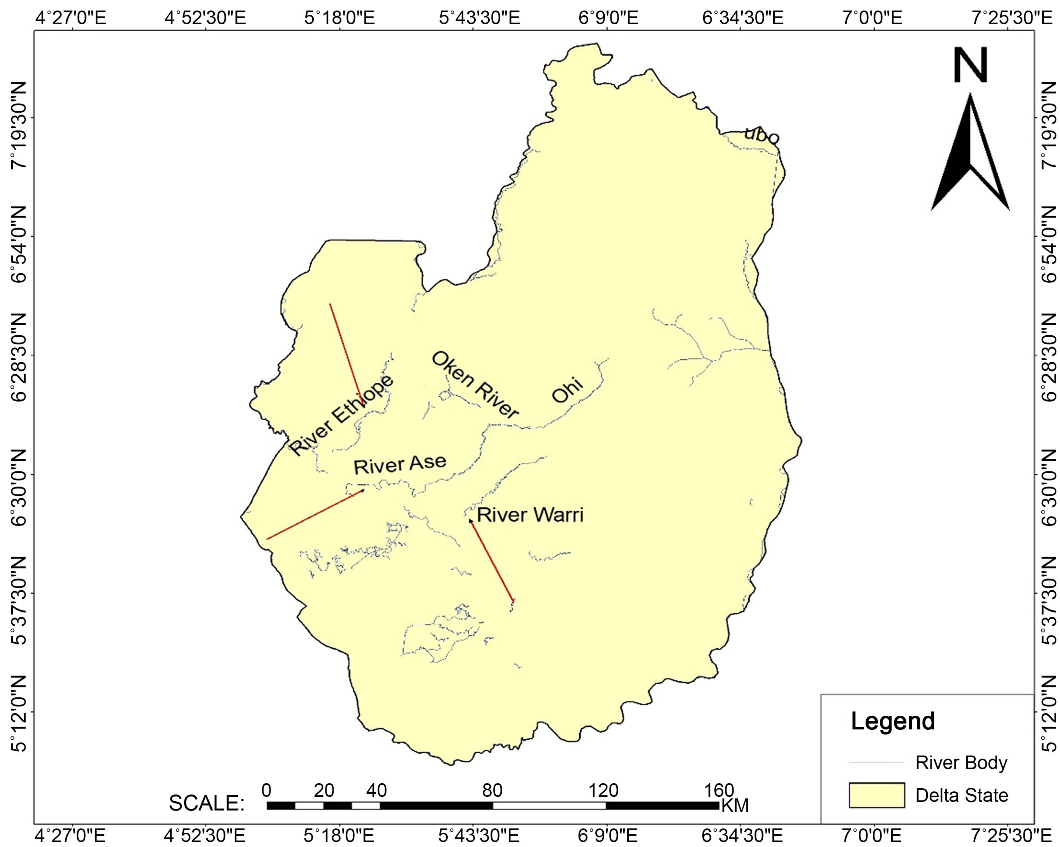

Figure 1. Map of the Delta State showing the rivers studied in this research.

The study is an empirical research that adopted the experimental research design as also deployed by Ushurhe, *et al.* [38]. This involves field survey, collection of water samples and laboratory analysis of the samples collected. The systematic random sampling technique was used for the collection of the water samples, while the simple random sampling technique was used for selecting six sites each along the course of the rivers. These chosen sites were studied from January to December 2021. A total of two hundred and sixteen (216) water samples were collected. This represents seventy-two (72) samples each for one river and three samples each for one month for the said period.

3.2. Sample Collection

The method of water samples collection was through direct field collection from the surface and sub-surface of the river *i.e.* 0 - 15 cm depth. The samples were collected early in the morning between the hours of 6 am to 8 am to reduce the effect of temperature on the collected samples [39]. The water samples were collected using sterilized 2-litre plastic cans fitted with information tag for identification. The plastic cans with water were securely corked and stored in ice-packed containers before transporting them to the laboratory for analysis [40]. This was done within six hours of collection as advised by Davidson, *et al.* [41].

3.3. Digestion of the Samples

Water samples were conveyed into instruments (beakers) in preparatory for laboratory. The water samples were digested using concentrated nitric-acid. For the measurements to be adequate and replicable, 10 milliliters (ml) of nitric acid was mixed with 50 ml of water (H_2O). This was done in a 250 milliliter (ml) conical flask. This solution was evaporated until it was half the original volume using hot plate. When it cooled down, it was then filtered.

3.4. Preparation of Standard

A 1000 milligram per litre (mg/L) solution of metals were prepared. This was achieved when 24.62, 1.63, 1.60 grams (g) of associated salt was dissolved in five percent (5%) nitric-acid into a one litre flask. This mixture was thereafter mixed vigorously and filed to the brim to 1litre with nitric-acid for the individual metal. Solutions of aimed metal ions were made ready based on the typical standard using serial dilution.

3.5. Sample Analysis

The processed water tests were analysed for the concentrations of lead, zinc and iron utilizing the 210 VGP atomic absorption spectrophotometer (AAS). The calibration plot strategy was utilized for the investigation. Air-acetylene was the fire utilized and cathode light of the comparing components was the reverberation line source. The wave lengths for the assurance of the components were 283.31 nm, 219.92 nm and 213.856 nm for lead, zinc and iron. The processed tests were analysed duplicating the normal concentration of metals shown in mg/L by the instrument after extrapolation from the standard curve. An AAS, Model 180-30 Hitachi, was deployed to ascertain the heavy metal concentrations (Zinc, Iron and Lead) [32] [38].

These materials and methods used for the analysis were based on the analytical equipment recommended and validated by the World Health Organization, United States Public Health Services, Canadian Public Health Association, American Society for Testing and Materials and the Nigerian Federal Ministry of Environment for Testing Water Quality. The analysis of variance (ANOVA) test was deployed to test the posited hypothesis; while the Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) was used to calculate the water quality of the rivers. The CCME WQI is a well-accepted and universally applicable model for evaluating water quality standard and compares observation to a benchmark or a water quality standard [42]-[47]. Robert and Pirro [48] used this model in their evaluation of water quality in parts of Albania, and they achieved significant results, hence the application of this model in this study.

Furthermore, the study needed to find out from the local the uses to which they put the river water and the challenges they face while using the water. To achieve this, the researchers used questionnaire. The Taro Yamane equation (see Equation (1)) was used to determine a sizable amount of respondents (400) from a total of 1.062 m persons who lived on the river catchment and use the rivers water for their domestic needs.

$$n = N / \left(1 + Ne^2\right) \quad (2)$$

where n = Represents total sample size,

N = the total population size,

e = sampling error (0.05),

1 = is a constant.

With the help of a psychometrician face content validation was employed to validate the questionnaire. The reliability of the questionnaire was achieved using the re-retest techniques. This involved distributing 10% of the questionnaire to same group of respondents (40) twice in an interval of three weeks. Then, the outcomes were compared using Pearson's Product Moment Correlation coefficient (PPMC) to relate the two outcomes and the result was r = 0.93. This technique has been used by Famous & Adekunle [49].

4. Results and Discussion

Calculation of Water Quality Index

The CCME WQI consists of three variables—Scope (F_1), Frequency (F_2) and Amplitude (F_3). The scope represents the percentage of variables that met the approved standards; while frequency represents the percentage of individual tests that did not meet the standard and amplitude represents the amount by which failed test values do not meet their standard. These variables combine together to produce a value between 0 and 100 that shows the overall water quality of that area [43]. These values are further ranked as shown in **Table 1**.

The detailed calculation of the CCME WQI is as follows:

$$\text{CCME-WQI} = 100 - \frac{\sqrt{F_1^2 - F_2^2 - F_3^2}}{1.732} \tag{3}$$

where the divisor normalizes the resultant values to a range between 0 - 100

$$F_1 = \frac{\text{number of failed variables}}{\text{total number of variables}} \times 100 \tag{4}$$

$$F_2 = \frac{\text{number of failed tests}}{\text{total number of tests}} \times 100 \tag{5}$$

Thus F_3 is calculated in three steps as follows:

$$\text{Excursion}_i = \frac{\text{failed test values } i}{\text{standard } j} - 1 \tag{6}$$

where excursion is the number of times by which an individual concentration is greater than or less than the standard.

The collective amount by which individual tests are out of compliance is calculated by summing the excursions of individuals as normalized sum of excursions as:

$$\text{Thus} \quad \text{nSe} = \frac{\sum_{i=1}^{n} \text{excursion } i}{\sum \text{of tests}} \tag{7}$$

F_3 is then calculated to get a range between 0 and 100 as:

$$F_3 = \frac{\text{nSe}}{0.01\text{nSe} + 0.01} \tag{8}$$

Thus, **Table 2** shows the data from the analysed water samples from River Ase, Warri River and River Ethiope used for the calculation of the CCME WQI in the area.

Table 1. CCME WQI categorization scheme.

RANK	WQI VALUE	DESCRIPTION
Excellent	95 - 100	Water quality very close to natural or pristine levels.
Very Good	89 - 94	Water quality close to natural pristine levels.
Good	80 - 88	Water quality condition rarely departs from natural or pristine levels.
Fair	65 - 79	Water quality sometimes departs from natural or desirable levels.
Marginal	45 - 64	Water quality conditions often depart from natural or desirable levels.
Poor	0 - 44	Water quality conditions usually depart from natural or desirable levels.

Source: Khan, Paterson & Khan, 2004.

Table 2. Calculated values of WQI in the three rivers.

S/N	Terms of index	Values			Rating of water Quality
		River Ase	Warri River	River Ethiope	
1.	Scope = F_1	33.3	33.3	33.3	Water quality in River Ase is marginal and impaired and departs from desirable levels. While River Ethiope and Warri River, the water quality is fair but occasionally impaired and sometimes depart from desirable levels.
2.	Frequency = F_2	33.3	27.7	11.1	
3.	nSe	3.6	0.628	0.13	
4.	Amplitude = F_3	78.26	38.57	11.5	
5.	WQI	47.3	66.52	78.7	

Source: Field work, 2021.

Thus the CCME WQI for River Ase is as follows:

Failed Parameters = 1

Total tests = 3

Failed tests = 12

Total parameters = 36

$$F_1 = \frac{\text{Fp}}{\text{Tp}} \times \frac{100}{1} = \frac{1}{3} \times \frac{100}{1}$$

$$F_1 = 33.3$$

$$F_2 = \frac{\text{Ft}}{\text{Tt}} \times \frac{100}{1} = \frac{12}{36} \times \frac{100}{1}$$

$$F_2 = 33.3$$

$$\text{Excursion}_\text{i} = \frac{4.56}{0.30} - 1 = 14.2$$

ii. $\frac{4.05}{0.30} - 1 = 12.5$

iii. $\frac{4.08}{0.30} - 1 = 12.6$

iv. $\frac{4.74}{0.30} - 1 = 14.8$

v. $\frac{4.43}{0.30} - 1 = 13.76$

vi. $\frac{4.33}{0.30} - 1 = 13.4$

vii. $\frac{4.09}{0.30} - 1 = 12.63$

viii. $\frac{3.65}{0.30} - 1 = 11.16$

ix. $\frac{2.57}{0.30} - 1 = 7.56$

x. $\frac{2.35}{0.30} - 1 = 6.83$

xi. $\frac{2.27}{0.30} - 1 = 6.56$

xii. $\frac{2.09}{0.30} - 1 = 5.96$

$$\text{Total Excursion} = 131.96$$

$$\text{nSe} = \frac{131.96}{36}$$

$$\text{nSe} = 3.6$$

$$F_3 = \frac{\text{nSe}}{0.01\text{nSe} + 0.01}$$

$$F_3 = \frac{3.6}{0.01 \times 3.6 + 0.01}$$

$$F_3 = \frac{3.6}{0.046}$$

$$F_3 = 78.26$$

$$\text{WQI} = 100 - \frac{\sqrt{F_1^2 - F_2^2 - F_3^2}}{1.732}$$

$$\text{WQI} = 100 - \frac{\sqrt{33.3^2 + 33.3^2 + 78.26^2}}{1.732}$$

$$\text{WQI} = 100 - \frac{\sqrt{1108.89 + 1108.89 + 6115.24}}{1.732}$$

$$\text{WQI} = 100 - \frac{\sqrt{8333.02}}{1.732}$$

$$\text{WQI} = 100 - \frac{91.286}{1.732}$$

$$\text{WQI} = 100 - 52.7$$

$$\text{WQI} = 47.3$$

For Warri River, the CCME WQI is calculated thus:

Failed Parameters = 1

Total tests = 3

Failed tests = 10

Total parameters = 36

$$F_1 = \frac{\text{Fp}}{\text{Tp}} \times \frac{100}{1} = \frac{1}{3} \times \frac{100}{1}$$

$$F_1 = 33.3$$

$$F_2 = \frac{\text{Ft}}{\text{Tt}} \times \frac{100}{1} = \frac{12}{36} \times \frac{100}{1}$$

$$F_2 = 27.7$$

$$\text{Excursion}_i = \frac{0.96}{0.30} - 1 = 2.2$$

ii. $\frac{0.92}{0.30} - 1 = 2.06$

iii. $\frac{0.62}{0.30} - 1 = 1.06$

iv. $\frac{1.02}{0.30} - 1 = 2.4$

v. $\frac{2.01}{0.30} - 1 = 5.7$

vi. $\frac{1.04}{0.30} - 1 = 2.46$

vii. $\frac{0.94}{0.30}-1=2.1$

viii. $\frac{0.76}{0.30}-1=1.53$

ix. $\frac{0.82}{0.30}-1=1.73$

x. $\frac{0.72}{0.30}-1=1.4$

Total Excursion = 22.64

$$\text{nSe}=\frac{22.64}{36}$$

$$\text{nSe}=0.628$$

$$F_3=\frac{\text{nSe}}{0.01\text{nSe}+0.01}$$

$$F_3=\frac{0.628}{0.01\times 0.628+0.01}$$

$$F_3=\frac{0.628}{0.01628}$$

$$F_3=38.57$$

$$\text{WQI}=100-\frac{\sqrt{F_1^2-F_2^2-F_3^2}}{1.732}$$

$$\text{WQI}=100-\frac{\sqrt{33.3^2+27.7^2+38.57^2}}{1.732}$$

$$\text{WQI}=100-\frac{\sqrt{1108.89+767.29+1487.6449}}{1.732}$$

$$\text{WQI}=100-\frac{\sqrt{3363.8249}}{1.732}$$

$$\text{WQI}=100-\frac{57.998}{1.732}$$

$$\text{WQI}=100-33.48$$

$$\text{WQI}=66.52$$

While in River Ethiope, the calculated CCME WQI is as follows:

Failed Parameters = 1

Total tests = 3

Failed tests = 4

Total parameters = 36

$$\text{Excursion}_1=\frac{0.96}{0.30}-1=2.2$$

ii. $\frac{0.2}{0.01}-1=1$

iii. $\frac{0.027}{0.01}-1=1.7$

iv. $\frac{0.02}{0.01}-1=1$

Total Excursion = 4.7

$$\text{nSe}=\frac{4.7}{36}$$

$$nSe = 0.13$$

$$F_3 = \frac{nSe}{0.01nSe + 0.01}$$

$$F_3 = \frac{0.13}{0.01 \times 0.13 + 0.01}$$

$$F_3 = \frac{0.13}{0.0113}$$

$$F_3 = 11.3$$

$$WQI = 100 - \frac{\sqrt{F_1^2 - F_2^2 - F_3^2}}{1.732}$$

$$WQI = 100 - \frac{\sqrt{33.3^2 + 11.1^2 + 11.5^2}}{1.732}$$

$$WQI = 100 - \frac{\sqrt{1108.9 + 123.21 + 132.25}}{1.732}$$

$$WQI = 100 - \frac{\sqrt{1364.35}}{1.732}$$

$$WQI = 100 - \frac{36.937}{1.732}$$

$$WQI = 100 - 21.3$$

$$WQI = 78.7$$

The calculated WQI values of River Ase, Warri River and River Ethiope are shown in Table 2.

The results of the analysed water samples for lead, zinc and iron in River Ase, Warri River and River Ethiope are shown in Table 3 and discussed.

Table 3. Mean values of analysed Lead, Zinc and Iron from January-December, 2021 in River Ase, Warri River and River Ethiope.

Months of the year	River-Ase			Warri River			River Ethiope		
	Pb (PPM)	Zn (PPM)	Fe (PPM)	Pb (PPM)	Zn (PPM)	Fe (PPM)	Pb (PPM)	Zn (PPM)	Fe (PPM)
Jan.	<0.01	1.61	4.56*	0.001	1.21	0.96*	0.001	0.04	0.01
Feb.	<0.01	1.87	4.05*	0.001	1.01	0.92*	0.002	0.21	0.01
Mar.	<0.01	1.72	4.08*	0.002	0.96	0.62*	0.007	0.36	0.01
Apr.	<0.01	0.67	4.74*	<0.001	0.46	0.28	0.001	0.46	0.02
May	<0.01	0.66	4.43*	<0.001	0.16	0.24	0.02*	0.51	0.05
June	<0.01	0.76	4.33*	<0.001	0.56	1.02*	0.001	0.41	0.04
July	<0.01	0.77	4.09*	0.002	0.42	2.01*	0.027*	0.41	0.00
Aug.	<0.01	0.67	3.65*	0.001	0.24	1.04*	0.001	0.36	0.07
Sep.	<0.01	0.84	2.57*	0.002	0.16	0.94*	0.01	0.01	0.01
Oct.	<0.01	0.96	2.36*	0.001	1.31	0.76*	0.01	0.01	0.03
Nov.	<0.01	0.92	2.27*	0.002	1.42	0.82*	0.02*	0.01	0.01
Dec.	<0.01	0.92	2.09*	0.001	1.26	0.72*	0.02*	0.02	0.02
RANGE	<0.01	1.21	2.65	0.002	1.26	1.77	0.009	0.50	0.06
X	<0.01	1.03	3.60	0.001	0.76	0.85	0.01	0.23	0.02
WHO	0.01	3.00	0.30	0.01	3.00	0.30	0.01	3.00	0.30

Source: Fieldwork, 2021. *Failed Test Values.

In River Ase, lead concentration in the water samples in all the sampled stations were less than 0.001 (<0.001 ppm) (See **Figure 2**). This implies that there was a complete absence of lead poisoning in the area as no trace of lead was found in the water samples. This can best be attributed to the low industrial and mining activities in the area. This value is less than 0.01 ppm recommended by the WHO. In Warri River, lead values range from 0.001 ppm in May/June to 0.002 ppm in March/July/September/November. In River Ethiope, mean lead values range from 0.001 ppm in January/April/June/August to 0.027 ppm in July.

However, the above findings on River Ase contradict the results of Aisien, *et al.* [50] who carried out similar studies along River Ethiope in the Niger Delta of Nigeria and got values that ranged between 0.001 ppm - 2.12 ppm from sampled stations in their analysis. However, the findings along Warri River and River Ethiope agree with the findings of Aisien, *et al.* [50]. These high values were attributed to industrial fallouts, gasoline and plumbing activities around the sampled stations [50]. Egborge [51] also got similar results in his analysis of the biodiversity and chemistry of Warri River in Southern Nigeria.

There is generally low zinc concentration along the course of River Ase in the area (See **Figure 3**). This can best be attributed to low industrial waste generation in the area. However, zinc concentration along River Ase in varies from a mean value of 0.66 ppm in May to 1.87 ppm in February. In Warri River, zinc concentration varies from 0.16 ppm in May/September to 1.42 ppm in November. While, in River Ethiope, mean values vary from 0.01 ppm in September/October/November to 0.51 ppm in May. These mean values are, however, lower than the 3.00 ppm WHO permissible value for drinking water quality.

These low values of zinc concentration in the analysed water samples are in agreement with the findings of Aisien, *et al.* [50] and Egborge [51] in similar studies along the course of River Ethiope and Warri River respectively.

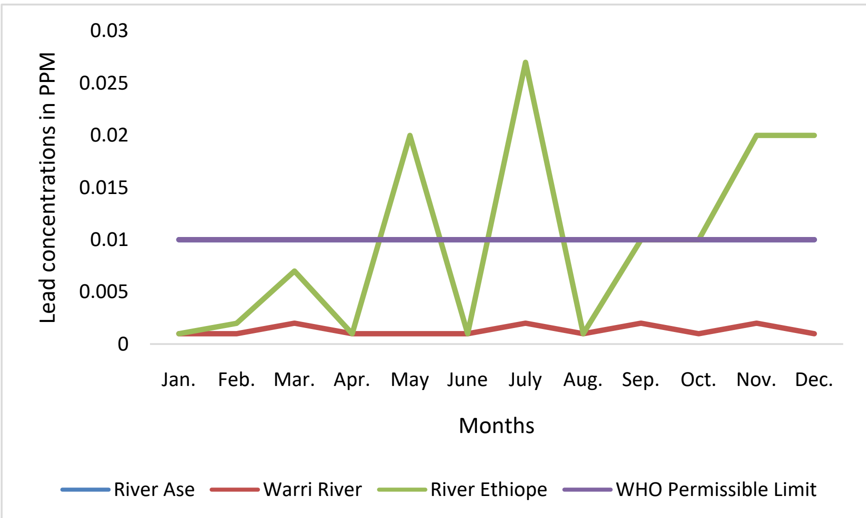

Figure 2. Mean lead concentration in water samples.

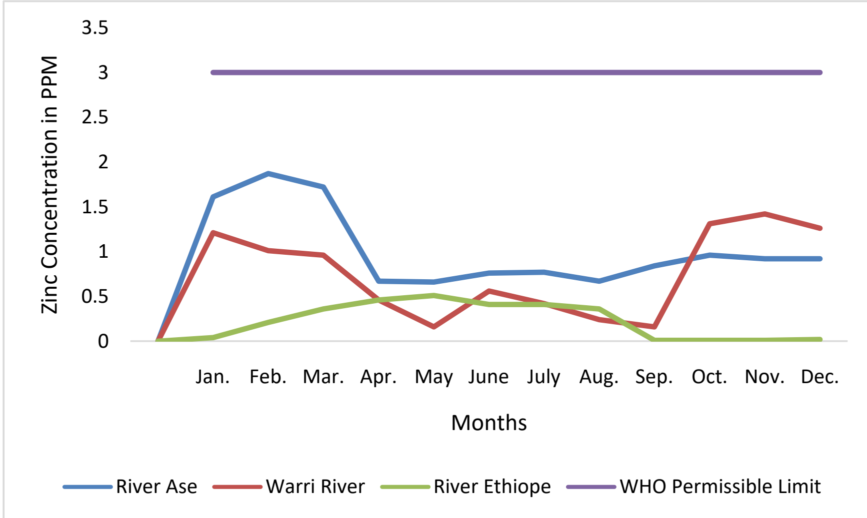

Figure 3. Mean Zinc concentration in water samples.

The iron content in the water samples range between 2.09 ppm in December to 4.74 ppm in April along River Ase, while that of Warri River, ranges from 0.24 ppm in May to 2.01 in July (see **Figure 4**). In River Ethiope, the values ranges from <0.001 ppm in January/February/July to 0.07 ppm in August. Some of these values are above the permissible value of 0.30 ppm of WHO. These low values recorded in some of these sites are in line with the findings of Parker [52] along the course of River Ethiope and River Ovwuvwe in Southern Nigeria. These high mean values are also in line with the findings of Aisien, *et al.* [50] along River Ethiope in the Niger Delta, where heavy metal concentration such as iron, ranged from 0.04 ppm - 5.12 ppm. These values also corroborate the findings of Egborge [51] along the Warri River.

The concentration of Zinc, Lead and Iron in the river water were tested among the selected rivers to see if the concentrations varied spatially in concentration amounts. This was achieved in **Tables 4-9**. In **Table 4**, the variation in Lead load among the rivers (Ase, Ethiope and Warri) was tested using ANOVA. The model was significant at $P < 0.05$ ($F = 64.728$; Sig-0.000). **Table 5** revealed where the difference in the Lead load lies.

In **Table 5**, the Duncan statistics proved that there are two categories when it comes to the lead load of the rivers. Whereas Warri River recorded the lowest amount of lead, Ethiope and Ase rivers recorded higher lead values.

In **Table 6**, the variation in Zinc load among the rivers (Ase, Ethiope and Warri) was tested using ANOVA. The model was significant at $P < 0.05$ ($F = 82.349$; Sig-0.000). **Table 8** revealed where the difference in the zinc load lies.

In **Table 7**, the Duncan statistics proved that there are three categories when it comes to the zinc load of the rivers. Whereas Ethiope River recorded the lowest amount of zinc, Warri and Ase rivers recorded higher lead values of zinc.

In **Table 8**, the variation in iron load among the rivers (Ase, Ethiope and Warri) was tested using ANOVA. The model was significant at $P < 0.05$ ($F =$

689.768; Sig-0.000). Table 10 revealed where the difference in the zinc load lies.

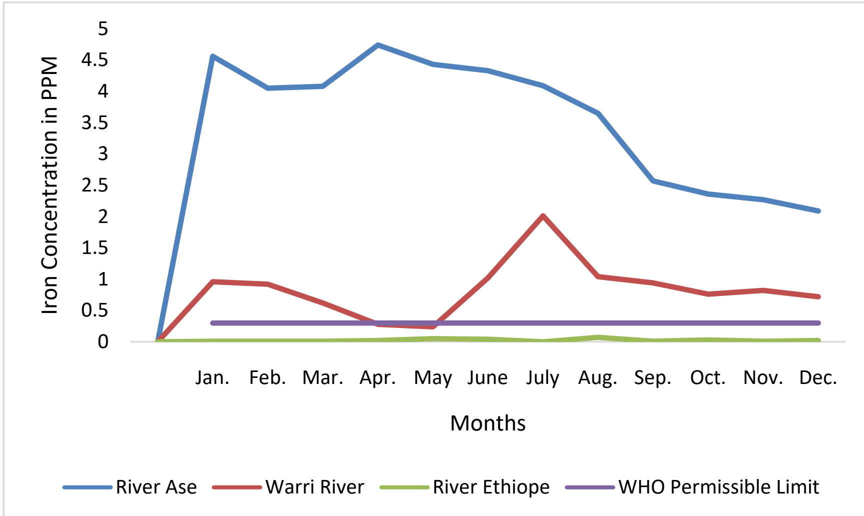

Figure 4. Mean Iron concentration in water samples.

Table 4. ANOVA summary of variation in Lead pollution in the selected rivers in the study area.

ANOVA					
Lead_pollution					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.004	2	0.002	64.728	0.000
Within Groups	0.006	213	0.000		
Total	0.010	215			

Table 5. Duncan statistics showing where the variation in Lead pollution among the rivers lie.

Lead_pollution			
Duncan			
Identifiers	N	Subset for alpha = 0.05	
		1	2
Warri River	72	0.0013	
River Ase	72		0.0100
Ethiope River	72		0.0100
Sig.		1.000	1.000

Means for groups in homogeneous subsets are displayed. a. Uses Harmonic Mean Sample Size = 72.000.

Table 6. ANOVA summary of variation in Zinc pollution in the selected rivers in the study area.

ANOVA					
Zinc_pollution					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	23.681	2	11.840	82.349	0.000
Within Groups	30.626	213	0.144		
Total	54.306	215			

Table 7. Duncan statistics showing where the variation in Zinc pollution among the rivers lie.

Zinc_pollution				
Duncan				
Identifiers	N	Subset for alpha = 0.05		
		1	2	3
Ethiope River	72	0.2342		
Warri River	72		0.7642	
River Ase	72			1.0308
Sig.		1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed. a. Uses Harmonic Mean Sample Size = 72.000.

Table 8. ANOVA Summary of variation in Iron pollution in the selected rivers in the study area.

ANOVA					
Iron_pollution					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	504.433	2	252.217	689.768	0.000
Within Groups	77.884	213	0.366		
Total	582.317	215			

Table 9. Duncan statistics showing where the variation in Iron pollution among the rivers lie.

Iron_pollution				
Duncan				
Identifiers	N	Subset for alpha = 0.05		
		1	2	3
Ethiope River	72	0.0233		
Warri River	72		0.8608	
River Ase	72			3.6017
Sig.		1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed. a. Uses Harmonic Mean Sample Size = 72.000.

Table 10. Domestic uses of river water in the study area.

Uses	Frequency	Percentage (%)
Drinking	82	20.5
Preparing food	71	17.8
Bathing	79	19.8
Washing clothes and dishes	85	21.3
Brushing your teeth	53	13.3
Cater for domestic animals	30	7.5
Total	400	100

In **Table 9**, the Duncan statistics proved that there are three categories when it comes to the iron load of the rivers. Whereas Ethiope River recorded the lowest amount of zinc, Warri and Ase rivers recorded higher lead values of iron.

There was need in this study, to find out the opinion of the locals about the uses to which they put the river water to. Also, the researchers wanted to identify the challenges (if any), the locals experience in the course of using the river water. Therefore, **Tables 10-12** were used to achieve this task. In **Table 10**, the domestic uses to which the river water is put have been listed. Drinking (20.5%) preparing food (17.8%), bathing (19.8%), washing clothes and dishes (21.3%), brushing teeth (13.3%), and catering for domestic animals (7.5%) were the domestic uses to which the locals indicated that the river water was put to. This finding corroborated the findings of Wutich [53]. However, it is important to note that the domestic uses to which the river water is put in 2023, does not indicate any visible development. In this area the water table is relatively very high, and the cost of sinking a water-well is quite cheap. Therefore, that the locals are still drinking untreated water at this age and time is greatly condemned in this study. However, **Table 11**, showed the reasons the locals are still depending on the river water for domestic purposes at this time. It is interesting to note that the locals identified poverty (49.5%) as the leading cause of their dependence on river water for domestic purposes.

Furthermore, the locals also indicated that they are traditionally attracted to the use of the river water (31.3%). This is expected as these rivers have existed for generations. It is possible for the locals to be tied to the river water use [54]. Furthermore, it is important to educate the locals on the increasing dangers inherent with the use of such river waters and ways to minimize them. This awareness seems to be lacking as reported by Okumagba & Ozabor, [5]. Till date the locals claim that it is traditional to use such river water. Okumagba & Ozabor, [55] already reported that inhabitants of the settlements that traverse the rivers catchment had some superstitious sentiments attached to the use of the river water. However, the continuous use of the river water is causing some health challenges for the locals, of which they can't explain the reasons (**Table 12**). Some of the diseases they listed were plaguing them include cholera (26.8%),

Table 11. Reasons for using river water for domestic purposes in the study area.

Reasons	Frequency	Percentage (%)
Poverty	198	49.5
Traditional	125	31.3
Preference	77	19.3
Total	400	100

Table 12. Health challenges encountered by locals for using the river water for domestic purposes.

Health challenges	Frequency	Percentage (%)
Cholera	107	26.8
Diarrhoea	103	25.8
Dysentery	96	24
Hepatitis A	0	0
Typhoid	94	23.5
Total	400	100

diarrhoea (25.8%), dysentery (24%) and typhoid (23.5%). This indicates that there is need for enlightenment of the locals on why they should take certain precautions before using surface (river) water for their domestic needs. Gyawali, *et al.* [56] reported that the indiscriminate use of surface water in Africa accounted for large number of infant mortality. The settlement of industries along the river banks and their discharge of wastes in the river indiscriminately, will continue to increase the heavy metals and thus could increase susceptibility of the locals to gastrointestinal and kidney issues, nervous system breakdown, skin problems, vascular damage, immune system dysfunction, birth defects, or even cancer [57].

5. Summary of Findings

The analysis of water samples for the concentration of lead, zinc and iron in River Ase, Warri River and River Ethiope using the CCME WQI for domestic purposes revealed that:

1) The quality of water from River Ase is marginal (at CCME WQI of 47.3), while that of Warri River (CCME WQI of 66.52) and River Ethiope (CCME WQI of 78.7) is fair. This implies that the concentration of lead, zinc and iron in River Ase, Warri River and River Ethiope do not pose a threat to domestic users.

2) The study discovered that anthropogenic and geologic activities such as oil exploration and exploitation, mining, wastewater generation among other factors were responsible for the concentration of lead, zinc and iron found in the surface water.

3) The study also discovered that there is significant variation in the concen-

tration of lead, zinc and iron at 0.05 level of significance in the three rivers. This implies that the concentration of these heavy metals in the rivers do not adversely affect their use for domestic purposes.

4) The study, further revealed that the concentration of lead and zinc in River Ase and Warri River are within permissible standard of WHO drinking water quality, except for iron concentration in the two rivers; while lead, zinc and iron concentrations in River Ethiope are within the WHO standard, except for the months of May, June, November and December in the case of lead.

5) The water quality from River Ase from the findings indicate that the water is impaired and departs from desirable level; while that of Warri River and River Ethiope are occasionally impaired and sometimes depart from desirable levels.

6. Recommendations

The following are recommendations made towards increasing or decreasing the concentrations of lead, zinc and iron in River Ase, Warri River and River Ethiope for domestic purposes in the area.

1) Surface water for domestic uses should be tested from time to time in order to identify increases or decreases in heavy metal concentration and other physicochemical parameters of water.

2) Anthropogenic activities of man along the bank and catchment area of the rivers should be monitored from time to time to address those ones responsible for the impairment of the water quality.

3) Risk assessment of water resources should be carried out, taking into consideration the hydrogeology and hydraulic loading of contaminants in the area.

4) The water from the river should be purified before usage, especially before drinking.

7. Conclusion

The study comparatively assessed the concentration of lead, zinc and iron in River Ase, Warri River and River Ethiope, using the CCME WQI for domestic purposes in southern Nigeria. A thorough examination of the water samples collected, showed that there is a significant variation in the concentrations of these heavy metals in the rivers. However, the calculation of the WQI showed that the quality is marginal at River Ase (47.3) to be fair at Warri River (66.52) and River Ethiope (78.7). The water quality, is influenced by geologic and anthropogenic activities of man. However, with improved monitoring, testing and control of surface water in Nigeria, (especially Rivers Ase, Warri and Ethiope) surface water pollution can be checked, thus making them more purposeful for domestic use.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Appendix A

RESEARCH QUESTIONNAIRE

This questionnaire consists of two parts, which are tailored to ascertain the uses to which your local river is put domestically; and to find out if there are challenges you face when you use the water. The questionnaire is purely designed for academic purposes. Therefore, whatever information you supply shall be treated with utmost confidentiality.

Answer each question carefully. There is no right or wrong answer. For each question, please indicate the response option you feel best represents your opinion.

Dr. Ushurhe *et al.*

Section A

Part A. Demographic and basic information of respondents

1. Name of respondent ________________________________

2. Identify the river closest to your community. a) Ase ☐ b) Ethiope ☐ c) Warri river ☐

3. For how long have you lived in this area? ______________________________

4. Your gender. a) Male ☐ b) Female ☐ c) I prefer not to say ☐

5. How old are you? a) 18 to 25 years ☐ b) 26 to 35 years ☐ c) 36 to 45 years ☐ d) 46 years and above ☐

6. Are you familiar with the river closest to you? a) yes ☐ b) no ☐

7. What is your occupation? _______________________________

Section B

8. What is your source of domestic water supply? _______________________

9. Do you know about the closest river to your house? a) Yes ☐ b) no ☐

10. If yes, do you use the river water for domestic purposes? Yes ☐ b) no ☐

11. If yes in 10 above, kindly list the uses to which you put the river water.
____
____
____

12. Kindly list the reasons you use river water for domestic purposes.
____
____
____

13. Do you know about water pollution? a) Yes ☐ b) no ☐

14. Do you think the river water is polluted? a) Yes ☐ b) no ☐

15. Are there health challenges you encounter from using river water for domestic purposes? a) Yes ☐ b) no ☐

16. If yes in 15 above, kindly list the health challenges you have faced by using the river water for domestic purposes.
____
____
____