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Determination of pollutions in the surface of water samples from Ogbajarajara river, Nigeria by spectrophotometer and atomic absorption spectrometry before evaluation of health risk assessment

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ABSTRACT

Determination of environmental pollution in the surface water is very important. So, in this study, determination, and health risk assessment were evaluated. The pollutions such as anions, cations, and heavy metals were analyzed in surface water by photometer spectrometry and atomic absorption spectrometry (AAS). Other parameters such as pH and TDS were determined. The results showed us, the electrical conductivity (EC) in this study falls between 100.68 ± 1.0 - 194.74 ±1.4 µs cm^{-1} in the dry and wet season. The pH value in this study for the two seasons varied from 5.57±0.22 to 5.73±0.28 which shows a little acidity. In the current study, TDS for wet and dry seasons goes from 122.17±1.74 mg L^{-1} to 63.80±0.86 mg L^{-1}. This may conceivably be a sign of typical pollution from the runoff of soils in the study area. The high phosphate levels in both wet and dry seasons are recorded from 60.74±0.61 to 60.27±0.38 mg L^{-1} in both seasons. Iron values observed range from 8.42±0.06 to 6.28±0.11 mg L^{-1} in the wet and dry season, Cu was recorded between 0.08±0.01 - 0.07±0.01 mg L^{-1}, Mn recorded from 0.07±0.01 to 0.06±0.01 mg L^{-1}, Zn recorded between 2.29±0.09 - 1.15±0.09 mg L^{-1}, and Pb recorded from 0.69±0.09 to 0.40±0.18 mg L^{-1} while Cd and Ni were not detected in the study. Water quality index (WQI) values were determined as 549 for wet and 328 for the dry season, the hazard indices for both seasons are below one. The outcomes in this present study showed that the level of Pb in the surface water could present a carcinogenic risk to both adults and children. All heavy metals results were validated by electrothermal atomic absorption spectrometry (ET-AAS).

1. Introduction

As a universal solvent, water exists as a solid, liquid, and gaseous state. Water is mostly used in a liquid state. Since water is crucial for all known types of life, ensuring our water is clean and preserved should be the most significant and head for this present generation and the next generation to come [1]. Water can be viewed as a chemical substance that is fundamental for all known types of life. So, the pollution in water must be analyzed

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by analytical methods [2]. For the most part, surface waters comprise streams, rivers, reservoirs, lakes, and wetlands. Stream is applied to epitomize other streaming surface waters, beginning from c/reeks to the huge rivers [3]. Water pollution is a serious biological and chemical hazard. At the point when water is polluted, it then represents an unsafe impact on all creatures and the wellbeing of humans. At the point when poisonous constituents break down in waterways of each kind like oceans, lakes, and rivers, the water becomes polluted. Poisons consistently defame the surface water, which stands a genuine risk to families that use the polluted water.

Recently. The researchers used supported liquid extraction (SLE), the micro solid-phase extraction (MSPE), liquid-liquid microextraction (LLME), (liquid-liquid extraction) LLE, Liquid-phase membrane extraction (LPME) for metal, pesticides, carboxylic acids, and phenol in water matrixes. Also, many metals and VOCs were determined by different ionic liquids and adsorbents. Cloud point extraction (CPE) has been utilized for the preconcentration of cobalt, mercury, and nickel, after the arrangement of a complex with 1-(2-thiazolylazo)-2-naphthol (TAN), and later examination by flame atomic absorption spectrometry utilizing octylphenoxypolyethoxyethanol (Triton X-114) as surfactant [3,4]. The inhabitants of this area depend on the Ogbajarajara River [Og] for their domestic and recreational purposes without proper knowledge of the river water quality and possible health implications. The introduction of surface water pollution in rural areas is due to different anthropogenic activities villagers do on the surface water and the washing away of surface soil directly to the surface water after manures are applied straightforwardly on the farmland. Quick urbanization leads to rigorous anthropogenic activities and the consumption of resources and energy in urban areas [4]. Individuals from these communities in Nwangele Local Government rely upon the surface water for their homegrown exercises with not much pipe-borne water around the communities which is situated in a further place for the residents to get to. This fact, therefore, propelled the necessity of this study to find out the quality of surface water from the Ogbajarajara river in the Nwangele local government area. It is therefore accepted that in the consumption of surface water, certain tests should have been completed before consumption in guidelines with the standards of the World Health Organization (WHO) and Federal Ministry of Environment (FMEv). [5], evaluated the water quality of the Nwangele River located in the Southeast area of Nigeria and concluded that the river is slightly polluted with heavy metals and the present river studied has a flow with Nwangele River. [6], researched the effectiveness of the water quality index in Izombe in the Imo state of Nigeria. The scientific research was done in areas where gas flaming is unremitting to build up pollution levels in rainwater and boreholes as they are viewed as the two significant establishments of water supply in the area. The grouping of pollution among the examined water assets was accomplished by contrasting the result of physicochemical tracers and that of WHO norms for drinking water. The Ogbajarajara is a well-known river in the Nwangele local government area of the Imo State Nigeria. The major occupation in this area includes farming with few traders. The farming activities have an important bearing on the ecology of the area. Daily activities in this river include; washing and fermentation of cassava. Other activities are washing clothes, motorcycles, and cars, kitchen utensils, bathing, fishing, and road construction near the rivers. Recently many technologies such as the spectrophotometer [7], atomic absorption spectrometry [8], HPLC [9], gas chromatography [10], and electrochemistry were used for the determining of pollutions. The sole aim of this work is the determination of pollution in surface waters and the evaluation of human risk assessment due to the presence of heavy metals in surface water sources in this area.

2. Experimental

2.1. Study Area

The research area is the Ogbajarajara River located

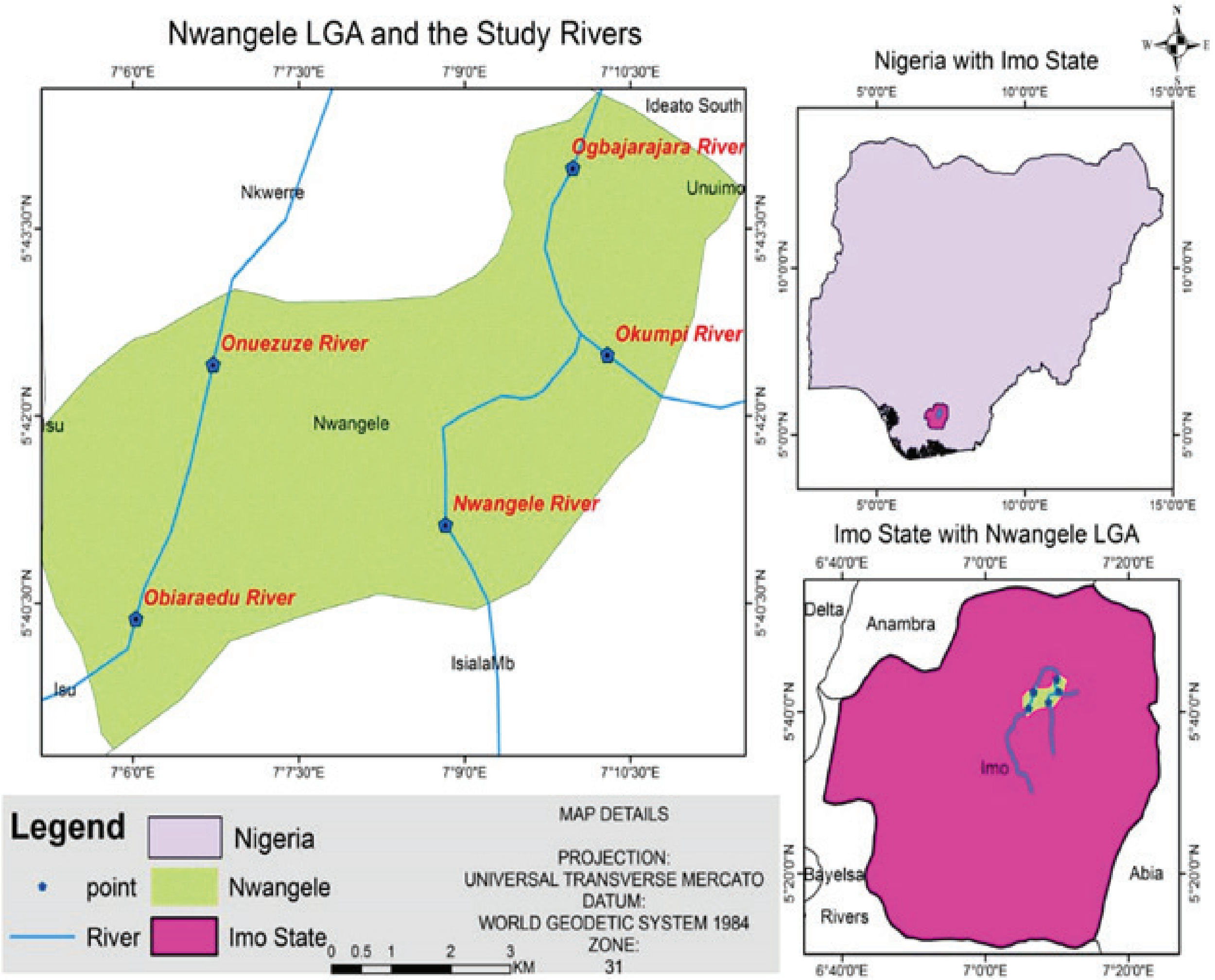


Fig. 1. Map of the Nwangele L.G.A. and its environs showing the Ogbajarajara River

in the Nwangele local government area of Imo state. The Nwangele is in the tropical rainforest region and it has two different seasons which are the dry and wet seasons. The wet season changes from April completely through October with top occurrence in June and September through the dry season starts in November entirely through March yearly. Nwangele has its headquarter in Amaigbo and an area of 63 km^2 (24 sq mi) and a populace of 128,472 as of the 2006 census (Fig.1). The geology of the Nwangele area includes plain soil which is about 0.05-2.0 mm in size and it is to some degree permeable, deep, and profoundly leached. Nwangele Local Government has numerous networks including Abba community, Isu Community, Umuozu community, Abajah community, and Amaigbo community. Topographically, the area falls between directions of latitude 5.7045779011-5.7111225452 and longitude of 7.13319502340-7.4222545475. The occupants of these areas are dominatingly Igbos and they are Christians with not very many conservatives and other religions. Their significant occupation is farming with not many traders. The farming exercises have a significant bearing on the ecology of the area. Daily exercises in this river incorporate; washing and aging of cassava. Different exercises are washing clothes, bikes, cars, cooking wares, bathing, and fishing.

2.2. Sample Collection

Ten surface water samples were collected randomly within the dry and wet seasons during the research period. Sampling was carried out for both dry and wet seasons and specified as Ogw and Ogd, where

Ogw will be for wet and Ogd will be for dry season respectively. The samples were collected using a clean plastic bottle from the surface waters. Five [5] samples were collected from the river to make up a composite sampling technique. The plastic bottles used for the collection of the surface water samples were appropriately marked and cleaned before sample collection by soaking it in 10% HCl for 48 hours, washed and cleaned with deionized water, and dried up [11,12].

2.3. Laboratory Analysis

The surface water samples were analyzed for the following: Electrical conductivity (EC), pH, Dissolved Oxygen (DO), Total dissolved solids (TDS), Temperature, and color. Also anions and cations such as, Calcium (Ca), Sodium (Na), Potassium (K), Phosphate (PO_4^{3-}), Nitrate (NO_3^{2-}), Sulphate (SO_4^{2-}), Lead (Pb), Copper (Cu), Iron (Fe), Nickel (Ni), Manganese (Mn), Zinc (Zn) and Cadmium (Cd) were determined

2.4. Instrumentation and reagents

The heavy metals concentrations were determined by a double beam flame atomic absorption spectrometer (FAAS, GBC 906, Aus.). The Air or N_2O-acetylene (C_2H_2), the deuterium lampas was used by FAAS. The Avanta system was used for calculating data. In addition, the electrothermal atomic absorption spectrophotometer ET-AAS, GBC, Aus.) was used for the validation of heavy metals in surface water samples. The current and wavelength of the HCL lamp were adjusted for each element. Chemical modifiers such as $Pd(NO_3)_2$ and Mg $(NO_3)_2$ were used for increasing the ashing point. The electrical conductivity was assessed using the HANNA HI8733 EC METER in µS cm^{-1} and the pH was assessed using JENWAY 3510 pH METER. The DO centralization of the surface water tests was set up using a JENWAY 9071 digital oxygen analyzer. The anion examination was done using multi-parameter bench photometer HI 82300 by HANNA instruments. TDS were done using Groline TDS meter by HANNA instruments. Also, many anions and cations such as calcium, sodium, potassium, iron, copper, cadmium, nickel, manganese, zinc, and lead, in the surface water during the dry and wet seasons were analyzed using atomic absorption spectrophotometer [13]. All reagents with AAS grade such as; metal solution, inorganic solutions (HNO_3, NaOH) were purchased from Sigma Aldrich (Germany). Metal standard solution (M) was diluted from the stock of 1000 mg L^{-1} solution in 2 % nitric acid for further studies. The standard solutions were diluted by distilled water (DW) from Millipore (USA). Reagents utilized all through the research were of high-quality analytical grade, which was bought from BDH Chemical Ltd, UK, and Sigma-Aldrich Chemie GmbH, Germany. Detergents and deionized water were utilized to wash the dish sets and sample bottles. They were splashed for the time being with a solution of 10% HNO_3 in a 1% HCl solution, trailed by washing with deionized water. Additionally, the reagents that were utilized for the assurance of anion focuses with the Hanna Hi 83,200 Instrument were gotten from Hanna Instruments. The instrument (GBC 903) utilized for the assurance of the groupings of metallic elements in the samples has high sensitivity—commonly (more than 0.9 absorbances) with an exactness (less than 0.5% RSD) from ten-second integrations for 5 mg L^{-1} metal standard.

2.5. Data Analysis

The data were evaluated for their mean and standard deviation by SPSS software. The data obtained was subjected to pollution index models and contamination. Also, Spear-man's correlation coefficient, degree of contamination, Hierarchical Cluster Analysis (HCA), water quality index (WQI) analysis and, health risk assessment was carried out.

3. Results and Discussion

3.1. Physicochemical parameters of surface water

The physicochemical analysis of the surface water collected in the dry and rainy seasons is presented in Table 1. The obtained results were compared with WHO permissible limits.

Table 1. The mean levels of studied parameters linked with WHO in wet and dry season

Parameters	wet						dry						W.H.O
	Ogw_1	Ogw_2	Ogw_3	Ogw_4	Ogw_5	Mean±Std	Ogd_1	Ogd_2	Ogd_3	Ogd_4	Ogd_5	Mean±Std	
Temp. (^{O}C)	24.32	25.43	25.48	25.71	25.53	25.29±0.55	28.37	27.99	29.01	28.36	28.31	28.40±0.38	20-30
DO (mg^{-1})	8.87	8.92	8.65	9.02	8.9	8.87±0.13	5.49	5.29	5.36	5.41	5.59	5.42±0.12	10.0
EC	197.55	200.21	199.11	199.36	196.85	194.74±1.37	99.02	100.57	101.61	100.96	101.24	100.68±1.0	2500
pH	5.24	5.57	5.82	5.49	5.74	5.57±0.22	5.33	5.02	5.29	5.79	5.44	5.37±0.28	6.50-8.50
TDS	122.07	123.03	123.34	119.36	123.07	122.17±1.74	64.32	63.47	62.63	63.71	64.91	63.80±0.86	500
Color	11.00	12.00	11.00	13	12	11.8±0.83	12.00	13.00	13.00	14.00	13.00	13±0.00	15
NO_3^- (mg L^{-1})	22.4	21.32	22.94	21.32	21.54	21.9±0.73	21.33	21.41	22.31	20.59	21.32	21.39±0.61	50
PO_4^{2-}(mg L^{-1})	59.93	60.24	61.32	60.97	61.23	60.74±0.61	59.97	60.39	60.12	59.99	60.89	60.27±0.38	1.0
SO_4^{2-} (mg L^{-1})	0.57	0.52	0.51	0.58	0.52	0.54±0.03	0.42	0.47	0.44	0.41	0.45	0.43±0.02	250
Ca(mg L^{-1})	3.67	4.02	4.13	3.99	4.17	4.0±0.19	3..40	3.44	3.60	3.41	3.52	3.49±0.08	75
Na (mg L^{-1})	7.05	7.63	7.04	7.14	7.11	7.19±0.24	6.20	5.98	6.02	6.07	6.13	6.08±0.08	200
K(mg L^{-1})	5.88	5.39	5.47	5.71	5.69	5.63±0.19	5.09	5.12	5.42	5.15	5.17	5.19±0.13	20
Fe (mg L^{-1})	8.42	8.36	8.52	8.39	8.42	8.42±0.06	6.31	6.32	6.42	6.11	6.28	6.28±0.11	0.3
Cu(mg L^{-1})	0.06	0.07	0.07	0.06	0.07	0.07±0.01	0.08	0.09	0.08	0.07	0.09	0.08±0.01	2.00
Cd (mg L^{-1})	0.00	0.00	0.00	0..00	0.00	0.00±0.00	0.00	0..00	0.00	0.00	0.00	0.0±0.0	0.003
Ni (mg L^{-1})	0.00	0.00	0.00	0.00	0.00	0.00±0.00	0.00	0.00	0.00	0.00	0.00	0.0±0.0	0.02
Mn(mg L^{-1})	0.05	0.06	0.05	0.07	0.07	0.06±0.01	0.07	0.08	0.07	0.08	0.08	0.07±0.01	0.4
Zn(mg L^{-1})	2.22	2.16	2.39	2.35	2.33	2.29±0.09	1.11	1.31	1.09	1.13	1.13	1.15±0.09	3.00
Pb (mg L^{-1})	0.63	0.71	0.59	0.82	0.74	0.69±0.09	0.47	0.09	0.50	0.49	0.48	0.40±0.18	0.01

The temperature of water centers on its proposed usage. The temperature of surface water, conferring to the standards used falls within 20-30^{0}C. From this study and displayed in Table 1 above, the temperature of the assessed river was higher during the dry season and this could be attributed to the hot weather during the dry season. It can be seen that the season has an effect on the temperature of the river body. Nevertheless, the dry season in the study revealed a minor upsurge in temperature which possibly will be due to the current weather condition of the environment at the location of study. Decline and expansion in temperature level are some of the prominent significant highlights of seasonal variation and weather change. The slight increase in dissolved oxygen [DO] and pH during the wet season can be concentrated in accordance with the affectation by comparative anthropogenic exercises. Interrelated outcomes were seen for Nworie river [14]. The EC can critically affect the taste of water. The EC in this study falls between 100.68±1.0 - 194.74±1.37 µS cm^{-1} in the dry and wet seasons. The values obtained were contained by the WHO standard for risk-free drinking water. The pH value in this study for the two seasons varied from 5.57±0.22 to 5.73±0.28 µS cm^{-1} which shows a little acidity that was not in agreement with the standard pH (6.50-8.50) recorded by [11] guidelines for safe drinking water. The lower pH might be a result of daily anthropogenic activities on this river on daily basis by the community inhabitants. In the current study, TDS for wet and dry seasons goes from 122.17±1.74 mg L^{-1} and 63.80±0.86 mg L^{-1}. This may conceivably be a sign of typical pollution from the runoff of soils in the study area. Color in essence corresponds to the appearance, taste, and also general drinkability of water. The color of the water samples at all the sampling locations was lower than the permissible limit which has 13.00±0.00 – 11.0.38 PCU in the wet and dry season against 15 PCU used as the W.H.O standard. The nitrate in this present study for the wet season was all found to be below the standard of WHO standard for safe drinking water both for wet and dry seasons and they range from 8.72-2154 mg L^{-1} to 1.20-21.32 mg L^{-1}. Sulfate values observed in the current study 0.54±0.03 mg L^{-1} in the wet season and 0.43±0.02 mg L^{-1} in the dry season were all below WHO standard for good drinking water and for domestic water use. Similar findings were observed in sulfate values obtained from the study carried out in the Okumpi river [11]. One of the huge and crucial nutrients responsible for the richness and strength of fish ponds is phosphorous. Phosphate at a sensible sum is fitting for the development of plankton [16]. The phosphate level in both wet and dry seasons goes from 60.74±0.61 to 60.27±0.38 mg L^{-1} in both seasons. The high phosphate levels obtained from this current study; likely could be as a result of the existence of blue-green growth on the water surface in the study area in both seasons. This research perhaps will conclude that phosphate grounded fertilizer may possibly have been applied on farmlands near the rivers. Nitrate in all the points is below the WHO standards. Calcium, potassium, and sodium as found from the current study in the wet and dry seasons are below the standard used for this current study. This result is in agreement with the outcome of the result obtained from the Obiaraedu River [17] and the Okumpi River in Imo State [11].

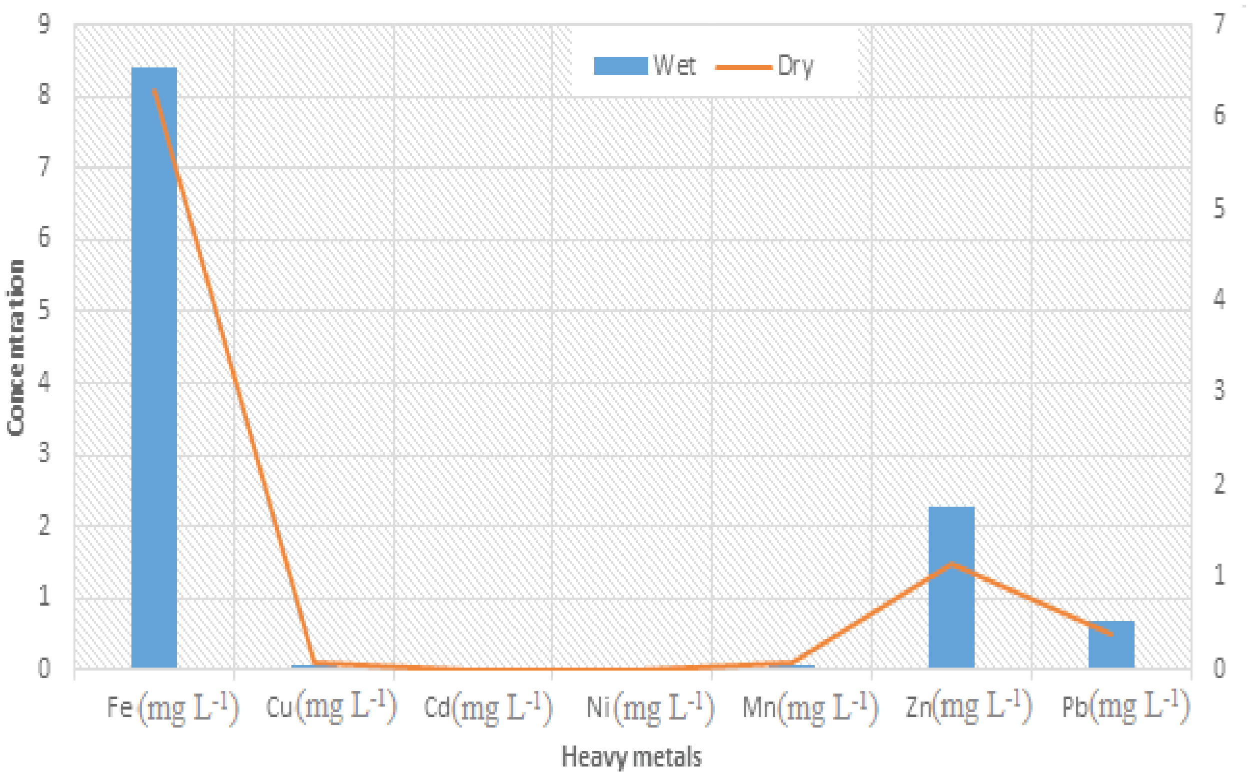


Fig. 2. Clustered column plots for the distribution of the heavy metal

Cadmium and nickel were not detected in the surface water from the Ogbajarajara River in both seasons, the plotted distribution of heavy metals are presented in Figures 2. Iron values observed in this current study ranges from 8.42±0.06 to 6.28±0.11 mg L^{-1} in wet and dry season are higher than WHO standards of 0.3 mg L^{-1}. Iron detected in every one of the samples in the wet season may be as a result of the utilization of iron coagulants [18]. This higher concentration of Fe observed during the wet than the dry season might be because most mineral residues on the soil may have a high level of iron, subsequently runoff from residue may taint the water, particularly during the rainy season. Copper is an imperative supplement, also drinking water impurity [19]. Cu amount for both wet and dry seasons in this current study was all underneath WHO standard for drinking water and domestic uses and they went from 0.08±0.01 to 0.07±0.01 mg L^{-1}. Running river is probably going to display a low level of copper [19]. The low level of copper in this current study is in line with the result observed in the Nwangele River [5] and in River Nworie [14]. Equivalent discoveries were likewise seen in a study done on River Uramurukwa in Imo State [20] and Obiaredu River [17]. Manganese goes from 0.07±0.01 to 0.06±0.01 mg/L through the wet and dry season. With respect to WHO standard and NSDWQ for household and drinking water value for Mn, all points for the wet season showed a low level of Mn. At high concentrations, Mn can comprise an aggravation with a particular metallic taste and staining properties [16]. Zinc observed both in wet and dry season between 2.29±0.09–1.15±0.09 mg L^{-1}; were observed to be below the WHO standard for water quality against the scheduled level of 3.0 mg L^{-1}. Zinc uncovered an unwanted harsh taste to water [15]. Pollution of lead in a river may conceivably be an outcome of the disbanding of lead from the soil and earth's external layer. Lead is in participation a harmful and superfluous metal that has no healthful significance to living creatures. Lead levels in every one of the samples are observed to be high, going from 0.69±0.09 to 0.40±0.18 mg L^{-1} in the wet and dry season which are higher than the WHO standard at 0.01 mg L^{-1}. No amount of Pb is viewed as protected in drinking water. A related study was observed in a study of the river Uramurukwa in Imo State [20].

3.2. Correlation coefficient matrix

A substantial positive correlation (r > 0.5) was observed between some of the metals, and anions parameters. Table 2 shows the coefficient of relationship for all the metals and anions. The metals showed a negative association/relationship with copper and cadmium. Nevertheless, significant positive relations during the wet season were exhibited between NO_3^-/Fe (0. 0.888), PO_4^{2-}/Ca (0.847), PO_4^{2-}/Fe (0.544), PO_4^{2-}/Zn (0.894), Ca/Cu (0.769) and Mn/Pb (0.934). Significant positive associations through the dry season were exhibited between NO_3^-/Fe (0. 888), PO_4^{2-}/Ca (0.847), PO_4^{2-}/Fe (0.544), PO_4^{2-}/Zn (0.894), SO_4^{2-}/K (0.746), Ca/Cu (0.769), Ca/Zn (0.524), Fe/Zn (0.691) and Mn/Pb (0.934). Once the correlation is seen positive, the establishment of tainting of the positively connected metals is indistinguishable while negative correlation suggests disparate/various bases of contamination. Notable pollution can be through the washing of engine cars, tricycles and, motorcycles at the river. Some of the relationship shown by the metals has been examined by [21].

3.3. Hierarchical Cluster Analysis (HCA)

Additionally, we performed Hierarchical Cluster Analysis (HCA) to identify groupings of physicochemical characteristics based on their Square Euclidian Distance (SED) [21]. The cluster plots for physicochemical parameters in the water in dry and wet seasons are presented in Figure 3. In the dry season, three groups were identified. In group 1, the combination included all parameters except for pH, Phosphate, and, EC in another group and then TDS in the third group. Similarly, in the wet season, the combination includes all parameters except for DO and temperature in group 2 while TDS and EC in group 3. The clustering of all metals in similar indicates that their source(s) are common. The HCA results agree with correlation analysis.

Table 2. Correlation coefficient matrix heavy metals and anions from surface water samples in wet/dry season (mg L^{-1})

	NO_3^-	PO_4^{2-}	SO_4^{2-}	Ca	Na	K	Fe	Cu	Cd	Ni	Mn	Zn	Pb
Wet													
NO_3^-	1												
PO_4^{2-}	0.098	1											
SO_4^{2-}	-0.217	-0.402	1										
Ca	-0.168	0.847	-0.702	1									
Na	-0.586	-0.398	-0.277	0.115	1								
K	0.051	-0.260	0.746	-0.635	-0.642	1							
Fe	0.888	0.544	-0.384	0.256	-0.671	-0.083	1						
Cu	0.054	0.424	-0.986	0.769	0.365	-0.772	0.257	1					
Cd	0	0	0	0	0	0	0	0	1				
Ni	0	0	0	0	0	0	0	0	0	1			
Mn	-0.848	0.383	0.154	0.457	0.161	0.063	-0.540	-9.312	0	0	1		
Zn	0.338	0.894	-0.072	0.524	-0.721	0.064	0.691	0.047	0	0	0.181	1	
Pb	-0.900	0.155	0.424	0.203	0.235	0.134	-0.693	-0.271	0	0	0.934	0.040	1
Dry													
NO_3-	1												
PO_4^{2-}	0.098	1											
SO_4^{2-}	-0.217	-0.402	1										
Ca	-0.168	0.847	-0.705	1									
Na	-0.586	-0.398	-0.277	0.115	1								
K	0.051	-0.260	0.746	-0.635	-0.642	1							
Fe	0.888	0.544	-0.384	0.256	-0.671	-0.083	1						
Cu	0.054	0.424	-0.986	0.769	0.365	-0.772	0.257	1					
Cd	0	0	0	0	0	0	0	0	1				
Ni	0	0	0	0	0	0	0	0	0	1			
Mn	-0.844	0.383	0.154	0.457	0.161	0.063	-0.540	-9.344	0	0	1		
Zn	0.338	0.894	-0.072	0.524	-0.721	0.064	0.691	0.047	0	0	0.181	1	
Pb	-0.900	0.155	0.424	0.203	0.239	0.134	-0.693	-0.271	0	0	0.934	0.040	1

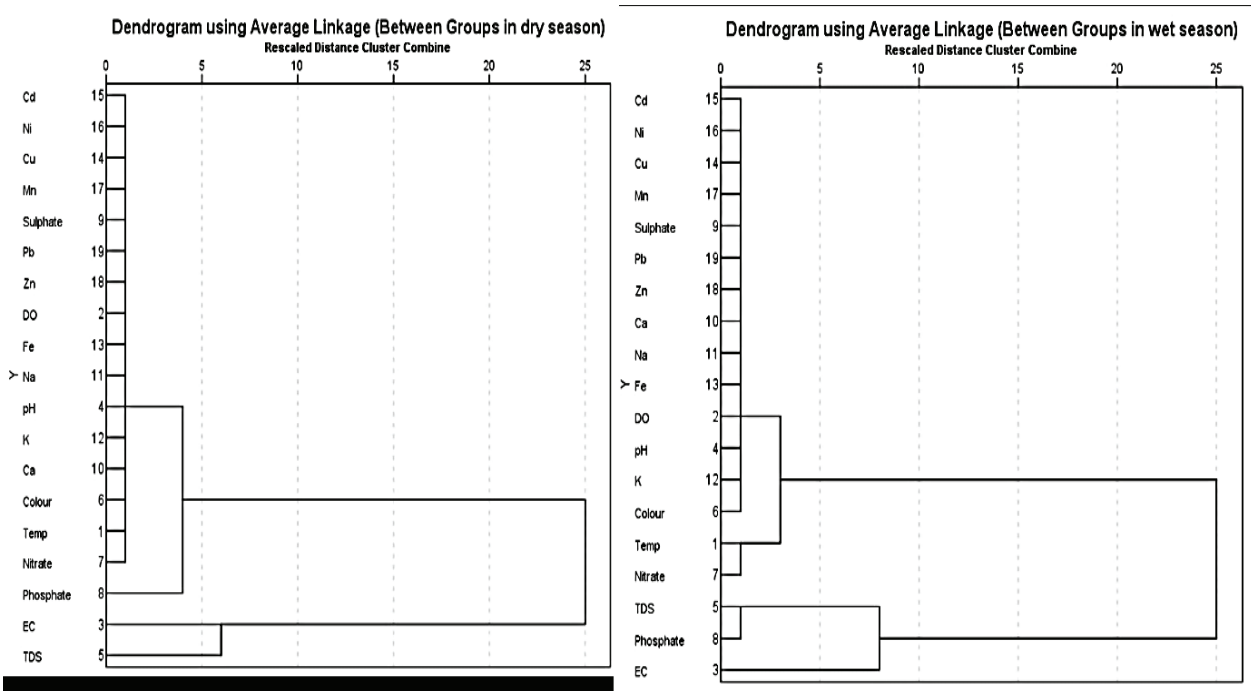


Fig. 3. Hierarchical cluster analysis for physicochemical properties in the dry and wet season

3.4. Chemometric Analysis

3.4.1. Contamination factor

The contamination factor was employed to check the rate of individual metal contamination in the water samples. Contamination factors were calculated with equation I.

$$Cf = \frac{cmetal}{C_{background}} \qquad \text{(Eq. I)}$$

Where Cf connote contamination factor, C metal address the grouping of heavy metal and $C_{\text{background}}$ means the foundation worth of metal. WHO suggestions for safe drinking water are taken as the foundation esteems for a water sample. Contamination factor ranking followed by Table 3.

3.4.2. Pollution load index (PLI)

The proposed pollution load record through Tomlinson for distinguishing pollution levels in soil was applied to the water tests to recognize the convergence of contamination of heavy metal in the different areas. The PLI appraises the metal fixation status and gives a thought of the different moves that can be made to control the issue [22]. Scientists have assessed the pollution load index utilizing equation II.

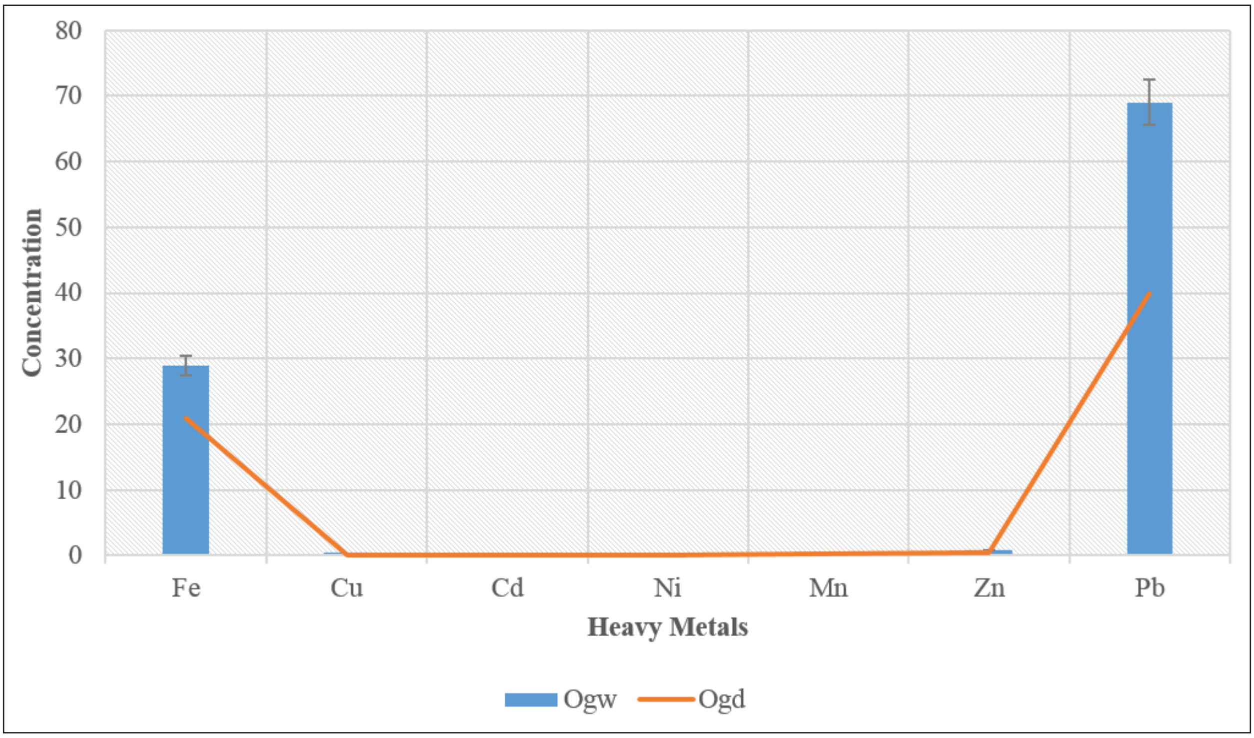
$$PLI = \sqrt[n]{C_{f1} \times C_{f2} \times C_{f3} \times \ldots C_{fn}} \qquad \text{(Eq. II)}$$

A PLI value > 1 point toward an instantaneous intervention to ameliorate pollution; a PLI value < 1 specifies that extreme rectification procedures are not needed.

High contamination factor was recorded for lead

Table 3. Contamination factor ranking

Cf values	Contamination factor level
$C_f < 1$	Low contamination
$1 \le C_f < 3$	Moderate contamination
$3 \le C_f < 6$	Considerable contamination
$6 \le C_f$	Very high contamination



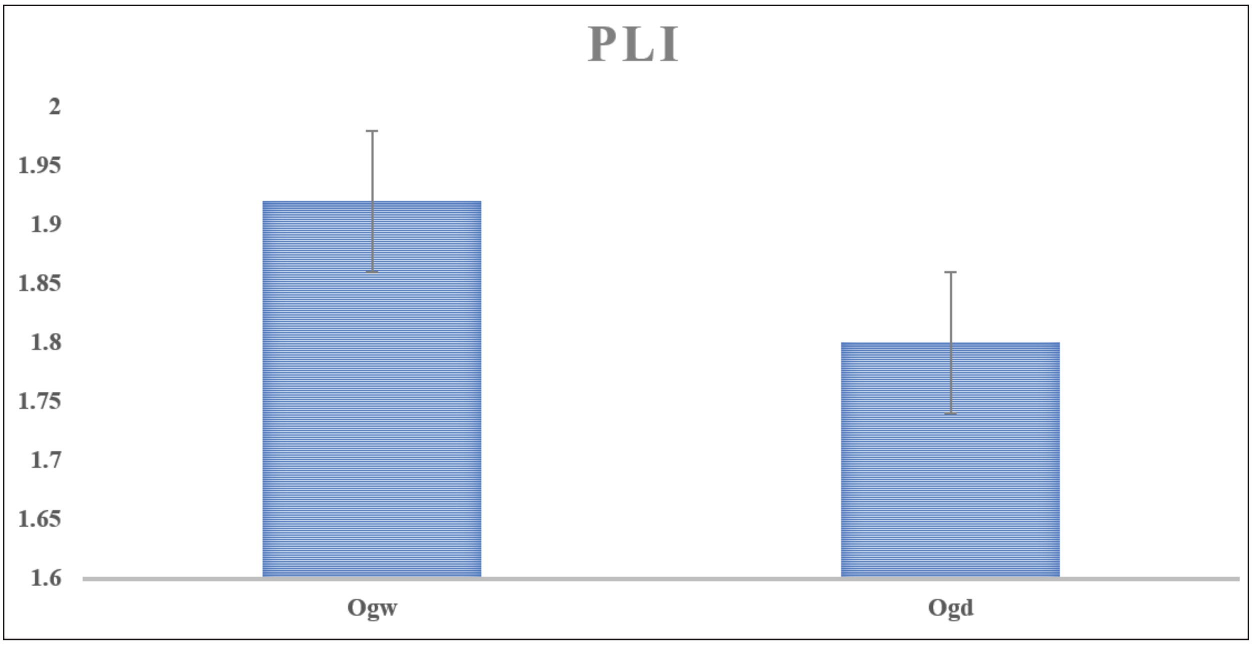


Fig. 4. Contamination factor and PLI for heavy metals and anions in the wet season

and iron in this present study both in wet and dry seasons. The contamination was higher during the wet seasons and this may be due to runoff during the wet season which comes directly from the farmlands surrounding the river. The contamination factor was recorded accordingly Pb>Fe>n>Mn>Cu>Cd and Ni in both wet and dry seasons. The river has shown a high pollution load index of 1.192 in wet and 1.8 in the dry season as shown in Figure 4 above. However, there is a need to constantly evaluate the water source in this location.

3.4.3. Water quality index (WQI)

WQI is a number-arithmetic articulation used to change the enormous number of adjustable data into a solitary number, which implies the water quality level. The WQI is created from the accompanying formula presented to equation III [23].

$$Wi = \frac{w_i}{\sum_{i=1}^{n} wi} \qquad \text{(Eq. III)}$$

Where: Wi is equal to the comparative weight, wi is equal to the mass of every single parameter and n is confer to the parameters. Water quality evaluation may be developed conferring to equation VI [24, 25].

$$qi = \frac{C_I}{S_I} \times 100 \qquad \text{(Eq. IV)}$$

Where qi is the quality positioning, Ci is the concentration of every chemical boundary in each and every water sample in mg L^{-1}, and Si is the WHO drinking water quality standard. To work out the WQI, the SI was set up for every chemical boundary, which is then used to decide the WQI utilizing Equation V and VI.

$$SI_i = W_i \times q_i \qquad \text{(Eq. V)}$$

$$WQI = \sum SI \qquad \text{(Eq.VI)}$$

SIi is the sub-index of ith (mathematics Occurring at position [i] in the sequence) parameter, qi is the rating dependent on the concentration of ith parameter and n is the number of parameters. The benchmark esteems were procured from World Health Organization (WHO) standard for drinking water, 2007. The accompanying point of arrangement of (WQI) and the nature of water WQI showed in Table 4 [27].

The examined samples from this study are severely polluted with physicochemical tracers given the value of 549 for wet and 328 for a dry season as reported in Figure 5 below, which makes the water unsuitable for drinking. Various activities around the sampling point might have contaminated the rivers in an intense way, while the wet season recorded more concentration from this present study.

Table 4. Water Quality Index Values

Cf Value	Water Quality
WQI < 50	Excellent water quality
50 < WQI ≤ 100	Good water quality
100 < WQI ≤ 200	Poor water quality
200 < WQI ≤ 300	Very poor water quality
WQI > 300	Unsuitable for drinking

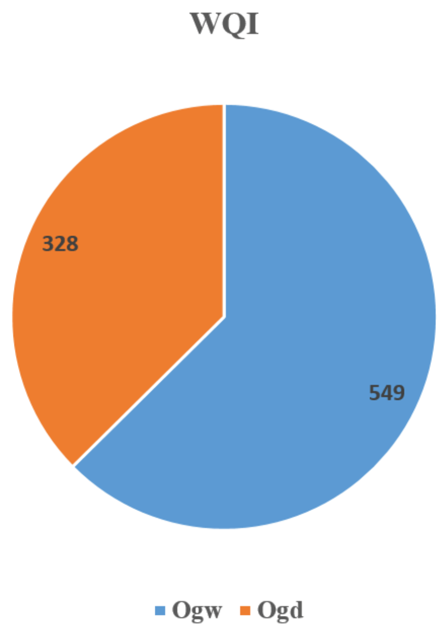


Fig. 5. WQI values of the sampling points in the wet season

3.5. Assessment of health risk after determination

3.5.1.Dermal and ingestion exposure, Hazard quotient (HQ), Hazard Indices (HI)

Health risk through human exposure to these metals contamination can be either by means of dermal ingestion, inhalation, or absorption, which are the normal contact passageways to the water. Thusly all the rivers studied in this research are constantly utilized by individuals generally for their domestic exercises and sporting exercises. The calculation of health risk was calculated using equations VII and VIII according to the USEPA risk estimation method [30-32].

$$Exp_{ing} = \frac{C_{WATER} \times IR \times EF \times ED}{BW \times AT} \quad \text{(Eq. VII)}$$

$$Exp_{derm} = \frac{C_{water} \times SA \times KP \times ET \times EF \times ED \times CF}{BW \times AT} \quad \text{(Eq. VIII)}$$

Exp_{ing} denotes the exposure dose through ingestion of water (mg kg^{-1} per day); Exp_{derm} addresses the exposure dose by means of dermal absorption (mg kg^{-1} per day); C_{water}: show the normal level of the assessed metals in water (µg L^{-1}); IR shows the ingestion level in this study (2.2 L per day for adults; 1.8 L per day for children); EF shows the exposure equation frequency (365 days/year); ED shows the exposure duration (70 years for adults; and 6 years for children); BW show the normal body weight (70 kg for adults; 15 kg for children); AT shows the averaging time (365 days/year × 70 years for a grown-up; 365 days per year × 6 years for a children); SA shows the uncovered skin area (18,000 cm^2 for adults; 6600 cm^2 for children); Kp shows the dermal permeability coefficient in water, (cm/h), 0.001 for Cu, Mn, Fe and Cd, though 0.0006 for Zn; 0.0001 for Ni; and 0.004 for Pb; ET shows the exposure time (0.58 h per day for adults; 1 h per day for children) and CF shows the unit conversion factor (0.001 L cm-^{3}) [29]. Potential non-cancer-causing chances in line for exposure of heavy metals were set up by assessing the determined toxin exposures from every exposure path (ingestion and dermal) with the proposal dose [29] utilizing equation IX.

$$HQ_{ing/derm} = \frac{Exp_{ing/derm}}{RfD_{ing/derm}} \quad \text{(Eq. IX)}$$

Where $RfD_{ing/derm}$ addresses the ingestion and dermal toxicity suggestion dose (mg kg^{-1} day^{-1}). The RfD_{derm} and RfD_{ing} esteem were gotten from the literature [30, 31]. An HQ under 1 is presumed to be safe and taken as substantial non-carcinogenic as equation X [29].

$$HI = \sum_{i=1}^{n} HQ_{ing/derm} \quad \text{(Eq. X)}$$

Where $HI_{ing/derm}$ is hazard index through dermal contact or ingestion.

The dermal and ingestion exposure determined in Table 5 were utilized to decide the hazard quotient in Table 6. The hazard quotient (HQ) was resolved and both HQ_{derm} and HQ_{ing} in the two seasons for all the trace metals checked in the examination were lower one (1) as seen in Table 6 for adults and children. This shows there is basically no adversative health sway expected to be ordered by any of these metals when the surface water is used. The HQ $_{ing}$ and HQ $_{derm}$ decreased in the request for lead > iron > zinc > manganese > copper > nickel > and cadmium, lead > manganese> iron > copper > zinc > nickel and cadmium, for the two children and adults in wet season, individually. HQ_{ing} and HQ_{derm} decreased in the request for nickel > lead > manganese > copper > zinc > iron and lead >zinc > nickel > copper > manganese > iron > for the both children and adults in dry season, individually. It has been suggested that the calculated HQ results for metals > 1 for children ought not to be ignored [32], presumably in light of the fact that, children are limitlessly disposed to pollutants [33]. The significant source of non-cancer-causing health risk in the two ways were Pb and Ni. The assessed absolute HQ esteems were less than one as found in Table 6.

Table 5. Dermal and ingestion exposure (mg kg^{-1} per day) for adults and children both in wet and dry season

			Wet				Dry			
Metals	RfD_{derm}	RfD_{ing}	EXP_{derm} (Adult)	EXP_{derm} (Children)	D_{ing} (Adult)	D_{ing} (Children)	EXP_{derm} (Adult)	EXP_{derm} (Children)	D_{ing} (Adult)	D_{ing} (Children)
Fe	140	700	1.25E-2	3.7E-3	2.26E0	`1.01E0	9.36E-3	2.76E-3	1.97E0	7.53E-1
Cu	8	40	1.04E-4	3.08E-5	2.2E-2	8.0E-3	1.19E-4	3.52E-5	2.5E-2	9.0E-3
Cd	0.5	0.025	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	5.4	20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.96	24	8.94E-5	2.64E-5	1.8E-2	7.0E-3	1.04E-4	3.08E-5	2.22E-2	8.0E-3
Zn	120	300	2.04E-3	6.04E-4	7.19E-1	2.74E-1	1.02E-3	3.03E-4	3.61E-1	1.38E-1
Pb	0.42	1.4	4.11E-3	1.21E-3	2.16E-1	8.2E-2	2.38E-3	7.04E-4	1.25E-1	4.8E-2

Table 6. Hazard quotient for potential non-carcinogenic risk (HQ) and cumulative hazard indices (HI) for each heavy metal present in wet and dry season for Adult and Children

	Wet				Dry			
Metals	HQ_{derm} (Adult)	HQ_{derm} (children)	HQ_{ing} (Adult)	HQ_{ing} (children)	HQ_{derm} (Adult)	HQ_{derm} (children)	HQ_{ing} (Adult)	HQ_{ing} (children)
Fe	1.78E-4	2.64E-5	3.22E-3	1.44E-3	6.68E-5	1.79E-5	2.71E-3	1.07E-3
Cu	1.3E-5	3.85E-6	5.5E-4	2.0E-4	1.48E-5	4.4E-6	6.25E-4	2.25E-4
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	1.02E-4	275E-5	7.5E-4	2.91E-4	1.08E-4	3.2E-5	9.25E-4	3.33E-4
Zn	1.7E-5	5.03E-6	2.39E-3	9.0E-4	8.5E-6	2.52E-6	1.2E-3	4.6E-4
Pb	9.78E-3	2.88E-3	1.52E-1	5.85E-2	5.66E-3	1.67E-3	8.92E-2	3.42E-2
HI	1.01E-2	2.94E3	1.61E-1	6.13E-2	5.85E-3	1.73E-3	9.46E-2	3.63EE-2

3.5.2. Chronic daily intake (CDI) and Carcinogenic risk (CR)

The carcinogenic risk (CR_{ing}) shows a gradual possibility that an individual will foster cancer during his lifetime inferable from disclosure under portrayed conditions were registered for the selected metals in this current study [30]. The chronic daily consumption of heavy metals through ingestion was computed using equation XI.

$$CDI = C_{water} \times \frac{DI}{BW} \quad \text{(Eq. XI)}$$

Where C_{water} addresses the centralization of trace metal in water in (mg L^{-1}), DI infer the; normal everyday admission of water which is referred to as daily intake (2.2 L each day for adults; 1.8 L each day for children) and BW shows the entire body weight (70 kg for adults; 15 kg for children), correspondingly [34]. The cancer risk (CR) was calculated using the formula in equation XII.

$$CR_{ing} = \frac{D_{ing}}{SF_{ing}} \quad \text{(Eq. XII)}$$

whereas SF_{ing} represent the cancer slop factor. The SF_{ing} for Pb is 8.5 mg kg^{-1} per day [26].

The CDI indices for heavy metals during the experimental time frame for the two ages were discovered to be in the request for Fe > Pb > Zn > Cu > Mn > Ni > Cd in wet season; and Fe > Zn > Pb > Mn > Cu > Ni > Cd in dry season as seen in Table 7. This proposes that the surface water expects less health dangers to the two adults and children by means of the pathways, except for Fe during the wet season for children which appears to be more than one. Table 8 present the carcinogenic risk of Pb for this present study for both adults and children in wet and dry season, for the reason that the value of carcinogenic slope factor for different metals couldn't be followed in literature, only lead was determined. Under extreme regulatory program the carcinogenic risk esteems within the range of 10^{-6} and 10^{-4} could present possible risk to an individual, subsequently, the outcomes in this present study showed that the level of Pb in the surface water could present a carcinogenic risk to both adults and children.

Table 7. Chronic risk assessment (CDI_{ing}) of heavy metals in adults and children

	wet		dry	
Metals	CDI (Adult)	CDI (children)	CDI (Adult)	CDI (children)
Fe	2.64E-1	1.01E-0	1.97E-1	7.53E-1
Cu	2.19E-3	8.4E-2	2.51E-3	9.6E-3
Cd	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00
Mn	1.88E-3	5.0E-1	219E-3	8.E-3
Zn	7.19E-2	2.74E-1	3.6E-1	1.38E-1
Pb	2.16E-2	8.28E2	1.25E-2	4.8E-2

Table 8. Carcinogenic risk assessment (CR_{ing}) of Pb for wet and dry season for both adults and children

Metal	**Wet**		**Dry**	
	Adult	Children	Adult	Children
Pb	2.54E-3	9.74E-3	1.47E-3	5.64E-3

4. Conclusion

The current study has shown that some actual appearances of pollution from surface water from the study area during the wet and dry seasons are not in line with WHO guidelines. The heavy metals; and cations were analyzed in surface water by photometer spectrometry and flame atomic absorption spectrometry (F-AAS). The results for metal analysis were validated by electrothermal atomic absorption spectrometry (ET-AAS). The study has shown additionally that the pH of all the sampling points is acidic. Phosphate apparently is high in all the sampling points at the various season and this can be related to the high utilization of more phosphate grounded fertilizer on farmlands surrounding the Rivers. The current study has uncovered also that the surface waters are profoundly contaminated with Fe, Zn and Pb, also this current study has shown that the surface water isn't appropriate for drinking purposes as shown by the high water quality index (> 300).

5. Recommendation

With regard to the results of the present study, the succeeding references are made after pollution analysis.

- The water resources observed in the Nwangele Local Government area should be done routinely to survey pollution levels (instrumental analysis) to check the spread of water-related complexities, particularly in the study area.
- In a circumstance of uncertain water quality, treatment is recommended through filtration, boiling, and the utilization of added substances (alum, liming, chlorine), accordingly lessening the danger of water-related issues.

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