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Advance Indexed Model Analysis of Heavy Metals Pollution of River Ureje, Ado Ekiti, Nigeria

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Abstract

The results obtained from heavy metal pollution assessment of River Ureje using Heavy Pollution Index (HPI) and Contamination Index (C_d). HPI values at upstream and downstream point of the river, Cd, Pb, Cr had high pollution load that exceeded threshold value of 100 while Mn, Cu, Zn, Ni had low pollution index which are below threshold value. This indicated that high pollution status of Cd, Pb, Cr were observed because they compete with other essential metallic cations for binding sites and inhibits enzyme activity while there is no pollution presence of Zn, Mn, Ni, Cu. C_d value results in both upstream and downstream point revealed that Zn, Cd, Cu, Pb had a low contamination index below <1 contamination value and tends to show no effect on aquatic environment and drinking water quality. However, Cr, Ni had medium contamination compared to (C_d=1-3) C_d value, this indicates slight contamination of these heavy metals and have slight effect on drinking water quality and aquatic life present while Manganese had high C_d value compared to (C_d>3) C_d value which to tends have high effect on drinking water quality and aquatic system. In conclusions, this study revealed that High level of HPI above critical index value was observed for Cd, Cr, Pb while Mn shows high C_d far above contamination index value.

Keywords: Contamination Index (C_d); Heavy Metals; Heavy Pollution Index (HPI); Nigerian Standard for Drinking Water Quality (NSDWQ); River Ureje; Upstream and Downstream point

Highlights

The levels of heavy metals in the river water were established.

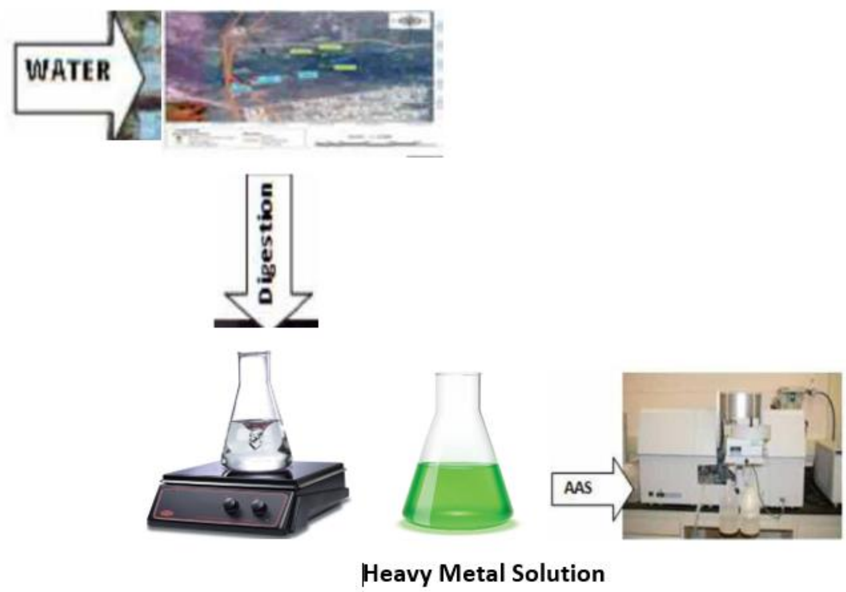
The degree of heavy metal pollution indices using the Heavy Pollution Index (HPI) and Contamination Index (C_d) of the river were established.

At both Upstream and Downstream point of the river, there is high pollution status, slight contamination, and high contamination pollution of some heavy metals.

The Ureje river water was considered not fit for human consumption.

High level of heavy metal pollution index (HPI) above critical index value was observed for Cd, Cr and Pb while only Mn shows high contamination index (C_d) far above contamination index value.

Graphic Abstract



Introduction

Heavy metal pollution of surface water by harmful substances has generated high level of discharge of significant heavy metals into waterways thereby generating high concentrations of toxicity to humans and aquatic habitats because of poor derogation, bioaccumulation ability and long biological shelf lives. These imperilments oblige applicable appropriate legislations in distinction to discharging of significant metals into the atmosphere and necessary solutions should be place in situ to combat removal of those significant metals from waterways or surface water embody bioremediation, chemical precipitation, adsorption, clotting, coagulation, flocculation, electrochemical removal, ion exchange, biosorption etc [2] or these techniques is combined together for optimum removal of significant metals. However, there square measure limitations or issues encountered by most of those techniques resulting in high generation of secondary pollutants, sludge generation, high energy consumption, low potency removal, high price of handling and high energy consumption, high level of cyanogenetic substances, sensitive operative conditions, and inadequate removal [3]. Researches and up to date development on significant metals aboard advance indexed watching in surface water became vital because of issues of high accumulation and cyanogenetic impacts to each aquatic organisms and humans through the organic phenomenon since contaminations at low concentration will persist for several years even in sediments wherever they hold the high potential to have an effect on affect human health and have prejudicious effect on the atmosphere [4]. Contamination of water by foreign matter or foreign bodies like microorganisms, chemicals and industrial waste discharge or sewages, different wastes, square measure are major causes of pollution and contamination that affects the standard of the water and renders it unsave for human uses. Contaminated water may be a international public inflicting tons of illness and diseases like looseness of the bowels, dysentery, and different malady in addition as chemical intoxication that ends up in untimely death [5]. Therefore, it is of nice vital to create the water safe for consumptions to confirm public health, environmental protection, and sustainable development [6, 7].

Human evolution activities square measure on high demands on the Ureje River, Ado-Ekiti, Nigeria and this has generated tons of untreated harmful substances been discharged into the river system and resulted into pollution across the water bodies and have vital effects on the water quality and have accumulated issues of adverse health outcomes once their contents exceed the permissible limit in portable water [8-10] 2007 investigated the pollution status of heavy metal (elemental) analyses on the three major rivers in Ado Ekiti, as found out that in river Ureje, Pb, Cr, and Cd were not detected on it while river Awedale revealed that Pb was above the WHO recommended value, but Mn fall below the permissible limit and Cr and Cd were not detected in the river. Meanwhile, river Oloogan only shows that both Pb and Cd were above WHO permissible limit as Cr and Mn fall below the recommended value. Meanwhile, [11] 2015 investigated the Water Quality Assessment of River Elemi and Ureje in Ado Ekiti, conducted assessment on quality of the river water based physicochemical parameter like BOD, COD, DO, pH and other water quality parameters but the pollution status of the heavy metal present was not considered, but in comparing the quality of water from the Elemi River and Ureje River, it can be concluded that Elemi River is better to use for domestic purposes than Ureje River.

In addition, [12] 2016 accessed Water quality of the Elemi River, Ado-Ekiti and shows that Pb, Cd, Cr and Cu were not detected in all the samples at the three locations of upstream, midstream, and downstream point but Zn falls below the permissible limit of WHO. Lastly, [13] 2017 investigated the water quality of the river Ureje reservoir during a dry season as found that the concentration of Pb, Mn and Cu were not detected in the river water. [14] 2020 considered the surface water vulnerability and public health risks of two urban rivers (River Ureje and River Awedale), Ado-Ekiti, this proved that Pb, Cd and Mn were above WHO permissible limit for drinking water quality in both river Ureje and Awedale while Zn, Cr, Ni and Cu fall below WHO recommended limits in both rivers while 2020, observed that heavy metals in surface water samples in River Ureje and Awedele revealed that all metals measured were within WHO specified limits, except Pb, Cd and Mn in surface water of both rivers which were above the recommended limits.

Heavy metals square measure serious environmental pollutants with elevated level of pollutant tendency, long shelves live and persistence within the environment [15] 2019 Heavy metal concentrations in aquatic habitats square measure sometimes monitored by activity their concentration levels in water. Many studies on significant metal contamination of water resources are done round the world [16-19] however, [20] 2016 rumored that it's not invariably simple to interpret or report the leads to water quality assessment once several parameters square measure in situ as a result of a number of these parameters square measure separately influenced or littered with different evolution sources whereas victimization solely fewer parameters on the opposite hand can have an effect on the quality of the assessment methodology [21, 22]. Some indices are developed for the aim of assessment of water quality, however quality indices square measure helpful in obtaining a composite influence of all parameters on overall pollution and this additionally makes the assessments into a duplicatable result and permits several of those pollution parameters to possess some easy accessibility.

During soil and water pollution investigation, the geoaccumulation index (Igeo) [23], single-factor index (SPI) [22] Nemerow comprehensive index (NCPI) potential ecological risk index (PERI) [23] and human health risk assessment methods have been commonly used for the evaluation of pollution.

Water quality index (WQI), variable statistics and heavy metal index (HMI) are utilised and located to be reliable tools for providing helpful insights towards property decision-making for water management. The single factor index approach and the systematic index method are the most common approaches for analyzing aquatic heavy metal contamination [24]. The first is a straightforward approach for comparing testing results to water quality requirements. The latter reflects a number of variables, including the grey correlation analysis method, fuzzy systematic assessment method, and principal feature analysis method, [25]. Most practiced indices for heavy metal contamination assessment are Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI), Degree of Contamination (DC) and Hazard Index (HI) which gives a composite influence of several metals on overall water quality. It summarizes the combined effects of several heavy metals considered harmful to conclude the overall contamination in an easier manner, For instance, [26-28] have incontestable in their numerous studies that the preceding approaches square measure appropriate tools for assessing pollution status of rivers, groundwater and leachate in numerous climes. The requirement of frequent water quality watching should not be neglected. It is important and supreme if public health and major water resources should be protected in Nigeria and elsewhere.

Heavy metal pollution index (HPI) and contamination index (C_d) are quality indices used in rating the composite influence of dissolved heavy metals in rivers [29-31]. It is calculated from the viewpoint of the suitability of water for human consumption concerning metals contamination [32]. The HPI is a method of assessment that shows the compound influence of individual heavy metal on the total quality of water while Cd is the Degree of contamination (C_d) is the sum of all the contamination factors (CF) for a given set of samples. Therefore, the main target of this current analysis was to gauge the chance potential of significant metal pollution in river Ureje, wherever stress on two indices particularly significant heavy metal pollution index (HPI) and contamination index (C_d) were used. The target of the study was to assess the water quality of Ureje River, Ado Ekiti, Nigeria using heavy metal pollution indices and therefore the contributions of every significant metal to the river pollution load for portable water purpose and compare this pollution index parameters of River Ureje to limits prescribed by the World Health Organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ). Therefore, since many communities located on the course of the river rely heavily on that for his or her daily moveable, recreational, and agricultural desires, therefore, it is terribly pertinent to determine the extent of pollution of the river and advocate the right purification and management measures to be adopted.

Materials and Methods

Description of the Study Area

The study area was in Ado-Ekiti, Ekiti State, a rapidly growing urban city. Ado-Ekiti is located on the southwestern upland area of Nigeria and the topography of the area revealed that most area in the town lies between 1200 meters and 2200 meters above mean sea level, with the North tops taking the heights. The rivers and streams in Ado-Ekiti include Ureje, Awedale and Ologan. The town lies between the latitude 70 331 and 70 421 North of the equator and the longitude 50 111 and 50 201 East on a low-land surrounded by many isolated hills and inselbergs, [33] and 456m elevation about the Sea level. Geologically, the study area region lies entirely within the pre-Cambrian basement complex rock group, which underlies much of Ekiti State [34]. The study was carried out in River Ureje in Ado Local Government Area, Ekiti State. River Ureje is located between longitudes 005^{0}18’25.87”E and latitudes 07^{0}36’ 23.82”N. It flows from Ikere Ekiti in Ikere Local Government to Ado in Ado Local Government Area from there it flows to Ilokun in Ifelodun Local Government.

The residents around the study area conduct different activities which may have impacts on the river. Some of the activities around the river include agricultural activities, an oil palm mill, sawmill industry, construction of residential buildings, especially a recent project of construction of a recreational centre at the bank of the river, which serve as refuse and sewage deposition sites as all these impose hazardous threats on the quality of the water body.

Image1: Map of the Ado Ekiti showing the geographical location of the study Area

Cleaning Procedures of Sampling Materials

All sampling materials (such as plastic bottles and plastic scoops) were thoroughly washed with phosphate free detergent and then with distilled water before soaking in 10% nitric acid. Finally, all containers were rinsed with de-ionized water before used for sampling. In the field, the sampling bottles and caps were rinsed three times with water that will be sampled prior to sampling.

Sample Collection, Preservation, and Transportation Procedures

The geo-reference coordinate of the sampling points was taken at the point of collection during the dry season of the year. 2Liters polyethylene plastic bottle was used to collect samples from two points (Upstream and Downstream) of river with wide distance range from each other. Sampling for the study was done in two different stations, the upstream (station A) and downstream (station B). Activities going on in station A are bathing, washing, and building constructions while in station B; dumping of refuse, sewage and agricultural practices are the activities around the place. Samples from the river were obtained directly by immersion of plastic containers into the river and the fetched water sample were poured immediately into the polyethylene plastic sample containers. Then, each container of the sample was labelled with water sample description detailing the sample condition. Finally, all the collected samples from the study area were labelled, preserved in ice box at temperature of 4 to 10°C to avoid any contamination, and transported to the laboratory for analysis. Standard methods [72] was used for sample collection, handling, and preservation to ensure data quality and consistency. The water sample in the plastic bottle were analyzed using UV-visible spectrophotometer (Lambda, CE1021) [35].

Data Analysis

Data collected were presented and Descriptive analysis of water quality variables was presented as Mean ± Standard Deviation and subjected to T-test. Statistical significance was set at α 0.05. All the results were statistically analysed using IBM Statistical Package for Social Science (SPSS, version 16.0) and T-test was performed to determine the location of significant difference.

Digestion and Heavy Metal Analysis in the Water Samples

The heavy metals determined are as follows; Iron (Fe), Magnesium (Mg), Zinc (Zn), Manganese (Mn), Calcium (Ca), Cadmium (Cd) Nickel (Ni), Chromium (Cr), Copper (Cu), Lead (Pb), Arsenic (As). Digestions were conducted to remove organics pollutants from the wastewater and release metals bound to organic matter [96] by dispensing 2 mL of each water sample from station A (Upstream) and B (Downstream) into two different 15 mL of concentrated analytical grade nitric acid (HNO3) in a 250 mL conical flask. The mixture was heated over an electric hot plate at a temperature of between 200 °C and 250 °C under a hood until the volume will be reduced to 5 mL. The digest was allowed to cool, filtered using Whatman number 41 filter paper, and then and transferred into a 100 mL volumetric flask and made up to mark by adding distilled water. Blank samples were prepared using the same quantity of nitric acid. The metals were analyzed using an atomic absorption spectrophotometer (AAS) (Solar 969 Unicam series). Acetylene flame was used as the oxidant and the source of radiation was a hollow cathode lamp. The Atomic Absorption Spectrophotometer (AAS) was calibrated for all the metal samples. The standard solutions of each metal salt and blank samples were conducted with each set of experimental digests.

Results and Discussion

Table1: Results of Physiochemical Analysis for Upstream and Downstream water samples of Ureje River in Ado Ekiti

Heavy Metals	Upstream Concentration (mg/L)	Downstream Concentration (mg/L)	Mean Concentration (mg/L)	WHO permissible Limit (mg/L)	NSDWQ permissible Limit (mg/L)
Zn	0.9	1.65	1.275	1	3
Mn	2.75	1.4	2.075	0.3	0.2
Cd	0.001	0.002	0.0015	0.003	0.003
Ni	1.5	1.8	1.65	<1.000	<1.000
Cr	0.2	0.15	0.175	0.1	0.05

Cu	0.03	0.05	0.04	0.5	1
Pb	0.016	0.018	0.025	0.01	0.01

Table2: The mean values and Standard Deviation of heavy metals parameters in Ureje River

Heavy Metals	Mean ± Std	SEM = Std. Error Mean	NSDWQ t (P-Value = 0.05)	WHO t (P-Value = 0.05)	NSDWQ Level of Significant
Zn	1.2750 ± 0.5303	0.375	3 (0.136)	1 (0.597)	0.136
Mn	2.0750 ± 0.9545	0.675	0.20 (0.220)	0.3 (0.231)	0.22
Cd	0.0015 ± 0.0007	0.0005	0.003 (0.205)	0.003 (0.205)	0.205
Ni	1.6500 ± 0.2121	0.15	0.99 (0.142)	0.99 (0.142)	0.142
Cr	0.1750 ± 0.0353	0	0.05 (0.0000)*	0.10 (0.000)*	0.000*
Cu	0.0400 ± 0.0141	0.01	0.10 (0.007)*	0.50 (0.014)*	0.007*
Pb	0.0170 ± 0.0014	0.001	0.01 (0.090)	0.01 (0.090)	0.09

Note: significant Different at the 0.05 level (2- tailed)

* = p<0.05

SEM = Standard Error of Mean

Heavy Metals Analysis

From the result in Table 1, Zinc, Chromium, Lead, Copper, Nickel, Cadmium, and Manganese were detected in upstream and downstream point of the river water samples. The concentration of the analysed heavy metals in mg/L was in the order of Mn > Ni > Zn > Cr > Cu >Pb > Cd. Spatially, the downstream points were higher than the upstream point in concentration of Zinc, Cadmium, Nickel, Copper, and Lead while Manganese and Chromium shown that the upstream point have high concentration than the downstream point. High Manganese content in the river water both in the upstream (Control) with the value of 2.750 mg/L and downstream point of value 1.40 mg/L with a mean value of 2.075 ± 0.9545 mg/L which is above both World Health Organisation (WHO) and National Standard of Drinking Water Quality (NSDWQ) permissible limit of 0.2 - 0.3 mg/L can cause brown coloration and impact unaesthetic and cosmetic effects; because it has been discovered that at concentrations above 0.15 mg/L, manganese stains plumbing fixtures and laundry and produces undesirable tastes in beverages and also cause high accumulation of microbial load and can form coatings on in the water pipes to generates black precipitates in the water system. On the other hand, [36] [14] [12] and found the same when assessing of water quality in River Oloogan, Awedale River, Elemi River and River Ofin in Ado Ekiti metropolis.

From Table 2, The presence of high concentration of Chromium metals in the river whose both upstream point with a concentration of 0.2 mg/Land downstream point of 0.15 mg/L concentration with a mean value of 0.175 ± 0.0353 mg/L which exceeded the permissible limit for WHO and NSDWQ, which further substantiate the argument that the some effluents are discharge into the river which contributes immensely to its pollution as this metal is good associates to some manufacturing process chemicals which are been run off into the river. Similar observation was reported on the study of heavy metals by [37, 38]. Chromium a toxic pollutant due to its harmful effects on human health, especially in its hexavalent (VI) form [39].

High concentration chromium above permissible limit of WHO / NSDWQ can bioaccumulate and biomagnified into the food chain and causes a lot of diseases in human body and This ranges from dermal, renal, neurological, and gastro-intestinal diseases which can leads to several cancers including lungs, larynx, bladder, kidneys, testicles, bone, and thyroid [40, 41].

From Table 2 above, the concentration of Zinc was 0.90 mg/L for the upstream point and 1.650 mg/L downstream point with a mean value of 1.275 ± 0.5303 mg/L which was within the permissible limit for National Standard of Drinking Water Quality (NSDWQ). Zn is considered an essential element in our diet, but too much Zinc can cause damaging to health such as damage to pancreas, anaemia, vomiting and nausea specially in children [42, 43]. It is also a major component of insulin and is essential in the formation of protein. But in considering WHO permissible limits, it is slightly higher in the downstream part of the river due to high contamination from dumping of refuse and other anthropogenic activities which will likely increase the acidity of the river water and likely cause health problems, hence harmful to the human body [44]. Similar observation was observed and when evaluating selected heavy metals status in river systems.

Likewise, Copper is an important micronutrient associated with several metalloenzymes especially cytochrome-c oxidase. Cytochrome-c oxidase plays an essential role in oxidative metabolism. On this basis, this river can support aquatic life if other conditions are favourable, hence may not pose any danger to the community but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. Cadmium classified as toxic metal tend to accumulate with age in some organs such as the kidney and it is considered as an agent to cause tumor and cardiovascular diseases [45]. It was also observed that the concentration of both Cadmium and Copper for both upstream (Cd: 0.001 mg/L and Cu 0.03 mg/L) and downstream (Cd: 0.002 mg/L and Cu 0.05 mg/L) with mean value of 0.0015 ± 0.0007 mg/L for cadmium and 0.040 ± 0.0141 mg/L for Copper in the river water were lower than the maximum recommended limit values recommended by NSDWQ and WHO and agrees with the report of Cu is not magnified in the body or bioaccumulated in the food chain and its solubility is drastically increased at pH 5.5, which is rather close to the ideal farmland pH of 6.0–6.5 while Presence of Cd in contaminated water could disturb the necessary mechanisms in the body, possibly resulting in short-term or long-term disorders [46, 47].

Likewise, from Table 2, the mean concentration of Lead (Pb) was 0.025 mg/L and 0.016 mg/L in upstream point and 0.018 mg/L in downstream point respectively with a mean value of 0.0170 ± 0.0014 mg/L, which was higher than the National Standard of Drinking Water Quality (NSDWQ) and World Health Organisation (WHO) acceptable limits (0.01 mg/L). The high concentrations of Pb recorded in this study may be because of the direct disposal of domestic waste containing Pb from human activities at the riverbank and vehicular exhausts from automobile car wash services and some individuals' personnel washing their cars and motorcycle near the river. Pb has been implicated in the ethiology of functional diseases such as microcytic anaemia, inhibitory effects on delta-aminolevulinic acid dehydratase and in neurological damage in young children. It is therefore important for rivers to be treated and managed so that the Pb level meets these standards before it could be safe for drinking and use for domestic activities [48].

Also, the mean concentration of Nickel (Ni) was 1.500 mg/L in upstream point and 1.800 mg/L in downstream point respectively with a mean value of 1.6500 ± 0.2121 mg/L, which was higher than the National Standard of Drinking Water Quality (NSDWQ) and World Health Organisation (WHO) acceptable limits (< 1.0 mg/L). Thus, the possible source of Nickel in the area may be from municipal waste dumps which are scattered virtually all around the study area and possible anthropogenic sources such as a burning fuel which when use for drinking and domestic purposes at high concentration, Nickel can cause carcinogenic diseases [82].

WHO and NSDWQ Comparison of Heavy Metal Concentration with Previous studies on River Ureje

Comparison of the concentrations of the analysed metals in the river Ureje with permissible guideline values for WHO revealed that Zn, Mn, Pb, Cr, Ni were above recommended permissible limits while Cd, and Cu were below the WHO recommended permissible limits. But it can be deduced that there is no significant difference when comparing WHO and NSDWQ standards with the heavy metals concentrations accessed in the water except Chromium (Cr) ($p=0.000$) and Copper (Cu) ($p=0.007$) which showed high significant difference comparing with WHO and NSDWQ permissible limits as stated in Table 2. Looking at other previous studies on Ureje River from stated that Zn, Mn, Pb were far above WHO recommended limit and Cd, Cr, Ni and Cu were within permissible limits; [13] 2017 revealed that Zn, Mn, Pb were also far above WHO permissible limits with only Cu and Cd are within the permissible limits while 2007 showed that Zn, Ni, Pb and Cr were above WHO permissible limits and Cd, Mn are lower than the permissible limit. This study further proved that Zn, Mn, Pb and Ni have consistently higher concentrations in the river which were above WHO permissible limits while Cu, Cr and Ni metal ions have low concentrations in the river and within WHO permissible limits. On the other hand, with previous research from 2007 and this study further affirmed that River Ureje has high concentration of Mn, Pb and Cr which were higher than the recommended limits of National Standard of Drinking Water Quality (NSDWQ) and lower concentration of Zn, Cd and Cu, they are recommended safe for NSDWQ [90 ; 39]. The safe limits of different metals recommended to fresh water are Pb < 0.010 mg/L, Cd < 0.003 mg/L, Cu < 1.00 mg/L, Cr < 0.1 mg/L, Ni < 1.0 mg/L, Mn < 0.3 mg/L and Zn < 3 mg/L [91].

Heavy Metal Pollution Index and Contamination Index Parameter

Pollution Evaluation Indices

The assessment methods used this study was the Heavy metal pollution index (HPI) proposed by the Contamination index (C_d) developed by [49].

Heavy Metal Pollution Index

Based on weighted arithmetic mean method, HPI indicates the total quality of water with respect to heavy metals. To compute HPI, unit weightage (W_i) is considered as a value inversely proportional to the recommended standard (S_i) of the relevant parameter. HPI was calculated as:

$$HPI = \frac{\sum q_i x W_i}{\sum W_i}$$

Where, qi is the sub-index of ith parameter. Wi is the unit weightage of ith parameter and n is the number of parameters considered.

$$qi = 100x\frac{C_i}{S_i}$$

The sub-index (q_i) of each parameter is defined by where C_i is the measured value of ith parameter, while S_i is the recommended standard value of ith parameter. The critical value of HPI for drinking purposes as given by [9] is 100. In computing the HPI for the present study, seven (7) heavy metals (Mn, Cu, Pb, Zn, Cd, Cr and Ni) were considered and the weightage (Wi) was taken as the inverse of standard permissible value which is the Nigerian Standard for Drinking Water Quality [93].

Table3: Heavy metal Pollution Index Parameter for Upstream and Downstream Points of River Ureje

HPI Parameter for Up Stream point of the River					HPI Parameter for Down Stream Point of the River			
Heavy Metals	qi = 100 X Ci/Si	Wi = 1/Si	HPI = Sqi X / Wi Swi	Pollution Index Status	qi = 100 X Ci/Si	Wi = 1/Si	HPI = Sqi X Wi/Swi	Pollution Index Status
Zn	30	0.33	1.65	Low	55	0.33	1.62	Low
Mn	1375	5	25.02	Low	700	5	24.64	Low
Cd	33.33	333.33	1668.12	High	666.66	333.33	1642.99	High
Ni	300	0.2	1	Low	360	0.2	0.98	Low
Cr	400	20	100.08	High	300	20	98.58	Low

Cu	3	1	5	Low	5	1	4.92	Low
Pb	160	100	500.44	High	180	100	492	High
	ɛQi = 2301.33	**ɛ**Wi = 459.86			**ɛ**Qi = 2266.66	**ɛ**Wi = 459.86		

Table4: Contamination Index Parameter for Upstream and Downstream Points of River Ureje.

Cd Parameter for Up Stream point of the River					Cd Parameter for Down Stream Point of the River			
Heavy Metals	CAi	CNi	CFi = (CAi/CNI)-1	Contamination Index: Cd < 1 = low Cd between 1-3 = Medium Cd > 3 = High	CAi	CNi	CFi = (CAi/CNI)-1	Contamination Index: Cd < 1 = low Cd between 1- 3 = Medium Cd > 3 = High
Zn	0.9	3	-0.7	Low Contamination	1.65	3	-0.45	Low Contamination
Mn	2.75	0.2	12.75	High Contamination	1.4	0.2	6	High Contamination
Cd	0.001	0.03	-0.96	Low Contamination	0.002	0.03	-0.93	Low Contamination
Ni	1.5	0.5	2	Medium Contamination	1.8	0.5	2.6	Medium Contamination
Cr	0.2	0.05	3	Medium Contamination	0.15	0.05	2	Medium Contamination
Cu	0.03	1	-0.97	Low Contamination	0.05	1	-0.95	Low Contamination
Pb	0.016	0.01	0.6	Low Contamination	0.018	0.01	0.8	Low Contamination

Contamination Index

Contamination index calculates the relative contamination of different metals separately and present the sum of generated components as a representative [49]. Contamination index is calculated via the following equation:

$$C_d = \sum_{t=0}^{n} C_{fi}$$

$$Cf_i = (\frac{CA_i}{CN_i}) - 1$$

Cf_i = contamination factor for i-th component.

CA_i = analytical value for i-th component.

CN_i = upper permissible concentration of i-th component. (N denotes the” normative value”)

The low, medium, and high contamination levels are referred to C_d values of less than 1, between 1 and 3 and greater than 3, respectively. CN_i is considered as the standard permissible value (S_i) used in the calculation of HPI. These methods have been widely used by the various scientists.

From Table 4 above, the low, medium, and high contamination levels are referred to Cd values of less than 1, between 1 and 3 and greater than 3, respectively. CNi is considered as the standard permissible value (Si) used in the calculation of HPI. The various scientists have widely used these methods. [50].

The convergence of both indices (Heavy Metal Pollution Index and Contamination Index) in this study was of interest, reflecting the effects of geogenic and anthropogenic activities. Heavy metal Pollution index was applied to assess the quality of surface water of river Ureje with respect to heavy metal contents. From Table 3, The calculated HPI of the studied heavy metals in water of River Ureje River in both upstream and downstream point had high and low pollution index among the heavy metals. At upstream point of the river, Zn, Mn, Ni, Cu had low pollution Index while Cd, Cr, Pb had high heavy metal pollution Index. However, For Low heavy metal pollution at upstream point, the ordered were as follows ; Mn > Cu > Zn > Ni while that of high heavy metal pollution index at upstream point show that Cd > Pb > Cr. Likewise, at downstream point of the river, Zn, Mn, Ni, Cr, Cu had low pollution Index while Cd, and Pb had high heavy metal pollution Index. Also, For Low heavy metal pollution at downstream point, the ordered were as follows ; Cr > Mn > Cu > Zn > Ni while that of high heavy metal pollution index at downstream point show that Cd > Pb. Nickel had the least contamination at both upstream and downstream because it easily absorbed by the active transport together with facilitated diffusion.

For heavy metal pollution Index at upstream point, the HPI values of Cadmium (Cd) (HPI=1668,12), Lead (Pb) (HPI=500.44) and Chromium (Cr) (HPI=100.08) had high pollution load that exceeded the threshold value of 100 while Manganese (Mn) (HPI=25.02), Copper (Cu) (HPI=5.00), Zinc (Zn) (HPI=1.65) and Nickel (Ni) (HPI=1.00) had low pollution index which are below the threshold value. This indicated that at upstream point of the river, high pollution status of , Cd, Pb and Cr were observed while there is no pollution presence of Zn, Mn, Ni and Cu as the presence of these heavy metals were not observed [51]. At the same time, for heavy metal pollution Index at downstream point, the HPI values of Cadmium (Cd) (HPI=1642.99),

Lead (Pb) (HPI=492.90) had high pollution load that exceeded the threshold value of 100 while Chromium (Cr) (HPI=98.58), Manganese (Mn) (HPI=24.64), Copper (Cu) (HPI=4.92), Zinc (Zn) (HPI=1.62) and Nickel (Ni) (HPI=0.98) had low pollution index which are below the threshold value. This proved that at downstream point of the river, both Cadmium and Lead had high heavy metal pollution status because they compete with other essential metallic cations for binding sites, inhibiting enzyme activity, or altering the transport of essential cations such as calcium while no heavy metal pollution of Zinc, Manganese, Nickel, Chromium, and Copper observed as the presence of these heavy metals was not observed [51].

Comparing the heavy metal pollution index at upstream and downstream point of the river, there is high pollution observed in the upstream point than the downstream point because there is high discharge of untreated waste and high level of anthropogenic activities at this upstream point which leads to high accumulation and toxic effects of these heavy metals while this multifarious activity was not observed at the downstream point. The Contamination Index (C_d) values of the results in both upstream and downstream point of the river from Table 4 indicated that heavy metals such as Zn, Cd, Cu and Pb had low contamination index at both upstream and downstream point as their order shows Pb > Zn > Cd > Cu but heavy metal contamination was very low comparing to that of downstream point except for Pb that had low contamination at upstream than the downstream because of high Pb content discharge at the upstream. Likewise, Ni and Cr had medium contamination in both upstream and downstream point of the river as their order of contamination shows that Cr > Ni at upstream point and Ni > Cr at downstream point, but Cr contamination level is above Ni at the upstream point and vice versa for the downstream point.

This indicated that there is high transport of Ni from upstream point to downstream point and so also low transport of Cr was observed from upstream to downstream point because of high solubility and high oxidation rate of Chromium while high contamination was observed in Mn at both upstream and downstream due to low concentration of iron that present in the river water which tends to increase uptake of manganese but upstream contamination rate is more than downstream point because Mn have low capacity active transport mechanism.

In addition, Table 4 revealed that for contamination pollution Index at upstream point, the Cd values of Lead (Pb) (C_d =0.60), Zinc (Zn) (C_d = - 0.7) and Cadmium (Cd) (C_d = - 0.96) and Copper (Cu) (Cd = - 0.97) and at downstream point, the Cd values of Lead (Pb) (C_d =0.80), Zinc (Zn) (C_d = - 0.45) and Cadmium (Cd) (C_d = - 0.93) and Copper (Cu) (Cd = - 0.95) had a low contamination index that is below < 1 contamination value respectively. But the contamination index of Cd, Zn and Cu were extremely low compared to Pb at both upstream and downstream point of the river. This indicated that there was low contamination of heavy metal such as Zn, Cd, Cu, Pb and tends to show no effect on the aquatic environment at both sampled point of the river. However, Chromium (Cr) and Nickel (Ni) had medium contamination index value of Chromium (Cr) (C_d =3.00) and Nickel (Ni) (C_d = 2.00) for upstream point; Chromium (Cd) (C_d =2.00) and Nickel (Ni) (C_d = 2.60) for downstream point compared to (C_d = 1 - 3) contamination Index value. This revealed that Cr and Ni shows slight contamination of these heavy metals and will have slight effect on aquatic life present in both upstream and downstream point of the river. Manganese had high contamination index value in both upstream and downstream point. Manganese (Mn) (Cd = 12.75) for upstream point and Manganese (Mn) (C_d = 12.75) (C_d =6.00) for downstream point compared to (C_d > 3) contamination Index value. This infers that manganese have high contamination pollution in the upstream and downstream of the river water and will have high effect on aquatic life present in the river.

In conclusion, this study revealed the impact of anthropogenic sources on the heavy metal pollution load of the water in the river. The heavy metal pollution index (HPI) of this Ureje River was found to be above the critical index value 100, due to impermissible values of Cd, Cr and Pb in the water. The contamination index (C_d) of Mn was also found to be above contamination index value and Ni and Cr show medium contamination which tend to accumulate to high contamination if there are continuous and intense anthropogenic and farming activities around the river. Based on this indication, the Ureje river water was considered not fit for human consumption and adequate measures must be taken to regulate anthropogenic and farming activities and its associated impact on the heavy metal content of the river.

Comparison with Previous Studies

[13] 2017 investigated the water quality of the river Ureje reservoir during a dry season, showed that the mean value of Zinc was 0.87 ± 0.62mg/L in surface water, The mean values are lower compared to the WHO standard recommended limit of 5.00mg/L but this present study proved that mean value of Zn 1.275 ± 0.5303 mg/L was higher at both Upstream and Downstream point than results from [13] 2017 and they were within the permissible limit for National Standard of Drinking Water Quality (NSDWQ) but, in considering WHO permissible limits it is slightly higher in the downstream part of the river due to high contamination from dumping of refuse and other anthropogenic activities which will likely increase the acidity of the river water and there is no significant different when comparing WHO and NSDWQ to the pollution status of Zinc component present in the river while Lead, copper and manganese were not detected in the surface water samples.

2007 investigated the pollution status of heavy metal (elemental) analyses on the three major rivers in Ado Ekiti, and found out that in river Ureje, Lead (Pb), Chromium (Cr), Cadmium (Cd) were below detection limit in the river but Copper (Cu) (0.25+0.07) and Manganese (Mn) (0.25+0.00) values were below the limits recommended for drinking water but Zinc (Zn), (4.25+0.49) and Nickel (Ni) (0.05+0.07) appeared higher than the WHO and NSDWQ recommended limits but this study showed that the mean value Pb (0.0170 +0.0014), Cr (0.1750 +0.0353), Ni (1.6500 ± 0.2121), Mn (2.0750 ± 0.9545) were above the permissible limits of WHO and NSDWQ while Zn, Cd, and Cu with a mean value 1.2750 ± 0.5303 , 0.0015 ± 0.0007 and 0.0400 ±0.0141 which were below permissible limit of WHO and NSDWQ. Meanwhile Zn, Cu, Ni, and Mn were significantly different when subjected to t-Test (P < 0.05 (Duncan Multiple Range Test) while in this study Cu (p= 0.007) and Cr (p=0.000) were significantly different when subjected to t-Test comparing to WHO and NSDWQ permissible limit. This study gives a similar report with on quality amount of Cu present in the river water.

Likewise, when comparing this study with accessed water quality for physicochemical, heavy metals and microbiological qualities of the river water of the Elemi River, which was another major river like River Ureje which was located along Iworoko road, Ado Ekiti showed that three locations namely, upstream (US), midstream (MS) and downstream (DS) have been selected along the river course for quality examination. The concentrations of the heavy metals Cu, Pb, Cd and Cr were all at normal and acceptable limits of WHO. A tolerable and acceptable copper concentration of 0.01 mg/L was observed at Upstream point while no trace of Cu was detected in both Middle Stream point and Down Stream point. Similarly, Pb, Cd and Cr were not detected in all the samples at the three locations, indicating that toxic metals would not constitute any hazard while this present revealed that mean value of Zn (1.2750 ± 0.5303), Cu (0.1750 ± 0.0353), Cd (0.0015 ± 0.0007) were below WHO permissible limit at both upstream point and downstream point of river Ureje but mean concentration of Pb (0.0170 ± 0.0014), Cr (0.1750 ± 0.0353), Mn (2.0750 ± 0.9545), Ni (1.6500 ± 0.2121) were detected at both sampling point of the river and they are far above the WHO permissible limit which tends to constitute appreciable hazard. This showed that this study was similar when considering amount of Cu and Cd present in the river water.

In addition, study assessed the relationship between disrupted watershed, drinking water quality and health risks of two urban rivers: Ureje and Awedele, Ado-Ekiti (Nigeria). It was concluded that when comparing the results of this study with [14] for Ureje, the mean concentration of only Pb (0.02 ± 0.001) was above both WHO and NASREA permissible limit, while the same results was obtained for Pb (0.0170 ± 0.0014), Mn (2.0750 ± 0.9545), Cr (0.1750 ± 0.0353) and Ni (1.6500 ± 0.2121) on this study, were above both WHO and NSDWQ. Meanwhile, Zn (0.59 ± 0.01), Cd (0.004 ± 0.001), Mn (0.54 ± 0.08) were above WHO permissible limit but below NASREA recommended limit as stated by [14] while this present revealed that only Zn (1.2750 ± 0.5303) was above WHO limit but below NSDWQ recommended limit. Lastly, [14] showed that the mean concentration of Cr, Ni, Cu (0.002 ± 0.001; 0.01 ± 0.00; 0.12 ± 0.01) were below both WHO and NASREA permissible limit, and this study show that both Cd and Cu mean concentration (0.0015 ± 0.0007; 0.0400 ± 0.0141) were below WHO and NSDWQ recommended permissible limit. This can be concluded that the same results were obtained from [14] and this present study for Pb, Zn, and Cu when comparing with the WHO, NASREA and NSDWQ regulation standard.

Many heavy metal pollution indices have been used to determine river pollution load for drinking water purposes. Enrichment factor, geoaccumulation index, pollution load index [52-54]; modified degree of contamination (mC_d) (2015), Nemerow pollution index (PN) [55] and potential Ecological Risk Index (RI) [52] have been used by many researchers. 2022 used pollution indices (heavy metal pollution index and contamination index) and health risk assessment for non-carcinogenic were used to check the water's suitability for human consumption in Ikwu River Umuahia, Nigeria. Five (Mn, Pb, Fe, Cd, and Cr) out of Eight heavy metals accessed showed high pollution levels with exceeded the threshold value (100), ranging between 503.56 and 746.80, high contamination potential ranged between 10.74 and 17.12 that exceeded unity (1), and high mean heavy metal concentrations that were exceeded acceptable limits with standard methods when compared with the Nigerian Drinking Water Quality Standard. Comparing the results of this study to the above study, they show similar results as three of the heavy metals (Cd, Pb, Cr) have high heavy metal pollution rate with exceeded the threshold value (100), ranging between 1668.12, 500.44 and 100.08 at upstream point and 1642.99 and 492.90 for downstream point of the river while Mn had high contaminations index potential ranged of 12.75 at upstream point and 6.00 for downstream point that exceeded unity (1). However, two of this heavy metal (Ni and Cr) had medium contamination index between range of 2 and 3 at both upstream and downstream point which was not found in comparison to study from [25]

Likewise, carried out comparative research on contamination factor and pollution load index of selected heavy metals (Pb, Cd, Zn, Mn and Fe) in Burullus and Edku lakes in Egypt. The results shows that both lakes have high concentration of Fe, Mn, Zn Pb which were above WHO and NSDWQ. The pollution indices showed that both lake's is highly contaminated based on heavy metal pollution Index (HPI) and Contamination Index (Cd) as their results are greater than (100 and 1), but Burullus lake (HPI= 195) have high heavy metal pollution index than Edku lake (165.20) for all the heavy metals but vice versa when considering the Contamination Index of both lakes as Edku lake show an average contamination of (C_d = 43.58) >> (C_d=38.59) of average contamination in Burullus lake. This indicated that examined water samples have very high contamination of both lakes water by the heavy metals studied in (Pb, Cd, Zn, Mn and Fe). The study revealed that both lakes had high heavy metal pollution Index (HPI) of Cadmium (Cd) and Iron (Fe) with high Contamination Index (Cd) of Manganese (Mn), Zinc (Zn) and Lead (Pb) of the study area. Comparing the results of this study to the above study, they show similar results as heavy metals like Cd, Pb, Cr have high heavy metal Pollution Index rate but Cd show a significant pollution index compared to other metals at upstream and downstream point of collection in the river and when comparing with the heavy metal pollution index of Cd in both lakes of the above study to this study, it shows that the Cd pollution index (HPI= 1668. 12 and 1642.99) at upstream and downstream point from this study is far greater than Cd pollution index rate of both lake Burullus and Edku lake (HPI= 195 and 165.20). Also, Contamination Index (Cd) rate observed in this study and study above were exceeded WHO permissible limits intakes in water bodies. Mn shows appreciable results as it had high Contamination Index in this study {Mn; C_d = 12.75 and 6.00) for both upstream and downstream point and study above {Mn; C_d = 43.58 and 38.59) in both lakes, this suggest that the above study had a high contamination than this study while medium contamination index was found in Ni and Cr for this study, and this was not observed in the study above. It can be concluded that both lakes are not safe for drinking water for human consumption and tend to have negatives impacts on human health if consumed.

Evaluate the distribution and status of heavy metal contamination of surface water in Nijhum Dweep Island of Hatiya Upazila under the Noakhali district of Bangladesh using ten surface water samples and analyzed for determination of heavy metals concentration and Heavy metal pollution Index Indices, the mean concentrations of the selected heavy metals were ranked in descending order of Fe > Mn > Pb > Co > Zn > Ni > Cu > Cd> Cr. All the metals except Cd, Pb, and Ni were found uncontaminated, as they fall within the permissible levels of Bureau of Indian standards [72] and these three metals influenced the values of heavy metal pollution indices. The heavy metal pollution index (HPI) revealed that mean value of HPI was 760.538 and ranged between 5.497 and 3462.89. According to [77], 40% of the samples were within the limit of low-class (HPI <15), 10% were within the range of medium-class (HPI 15-30), and the rest of the samples (50%) were within the high-class rank (HPI >30). Again, comparing the critical value of 100 proposed by [9], 40% of the samples exceeded the critical limit due to the higher concentration of Cd in those sampling stations. In general, the surface water was not polluted or contaminated by other metals except Cd. Localized Cd in surface water increased the overall HPI values of these sampling stations. Comparing the results above to the present study, the mean value of HPI of Cadmium (Cd) and Lead (Pb) was (HPI = 1655.55 and 496.67) which exceeded the threshold value (100), with standard methods when compared with their national Drinking Water Quality Standard. It shows similar results as only Cd among other heavy metals stated in above study and Cd and Pb in this study have high heavy metal pollution index rate while all other such as Fe, Mn, Pb, Co, Zn, Ni, Cu and Cr have low pollution index levels. It can be concluded that the surface water for individual metals analyzed for other heavy metals does not pose any non- carcinogenic health risk except Cadmium (Cd) which can possessed a lot of serious threat to human health, living organisms, and natural ecosystems [53]. [54] accessing heavy metals concentration and pollution index (HPI) in drinking water along the southwest coast of Ghana during wet and dry season, the result shows that there is increase in heavy metals concentration during wet season than dry season as all the heavy metals accessed (As, Pb, Se, Zn and Hg) were below WHO standards limits except Pb which exceeded the limit. The level of heavy metals concentration in water samples analyzed in the study area above increases in the order of Hg < Se < As < Zn < Cu < Pb. The mean concentration values of heavy metal analyzed during the wet and dry seasons were used to calculate the heavy metal pollution index (HPI) of the water samples and this revealed that HPI for all the heavy metals in both seasons fall within the category of high mean heavy metal pollution (HPI wet = 130) and (HPI dry = 143) according to [55]. This could be attributed to the presence of high concentrations of lead in the water. The HPI in the dry season were higher than the wet season indicating the effect of water supply in water quality in the region. Comparing the results of this study to the above study, they show similar results as three of the mean heavy metals (Cd and Pb) have high heavy metal pollution rate with exceeded the threshold value (100), ranging between 1655.55 and 496.67 and and show high heavy metal pollution index than the results above, the mean heavy metals pollution index of Pb at upstream and downstream of the river (HPI = 496.67) in this study is more than the mean heavy metals pollution index of Pb in wet season (HPI wet = 476.70) as this study sampling were taken during wet season but was below that of the dry season (HPI dry = 530.6) of results above. It was confirmed that increase in the heavy metals pollution index in one causes the other metal to decrease. Likewise, the HPI results in this study are in line with other findings from [56] from an index approach to heavy metal pollution assessment of Eme River, Umuahia, Nigeria, but contrary to the finding of [57-61] who reported HPI value less than 100 of underground water from North Kurdufan State, India, Bangladesh, southwest Iran, and southeast Iraq respectively.

Image2: Comparison of metal concentrations in the River upstream and downstream

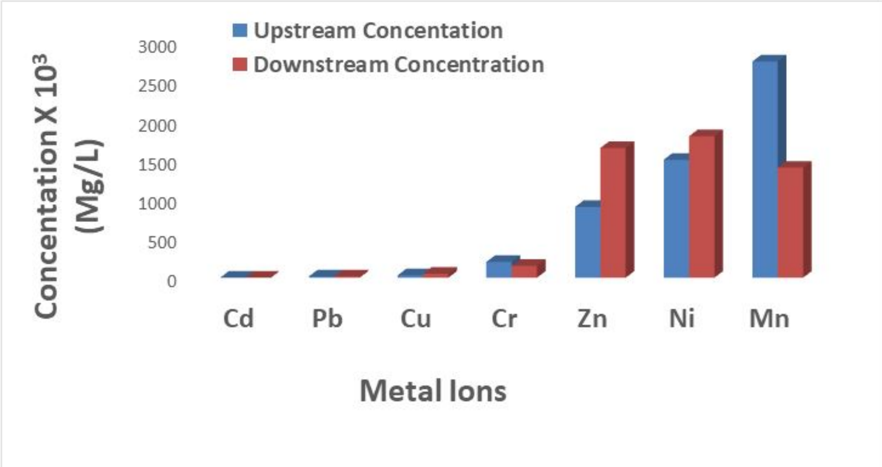


Image3: Comparative line and bar graph of Metal Ions and NSDWQ Standards

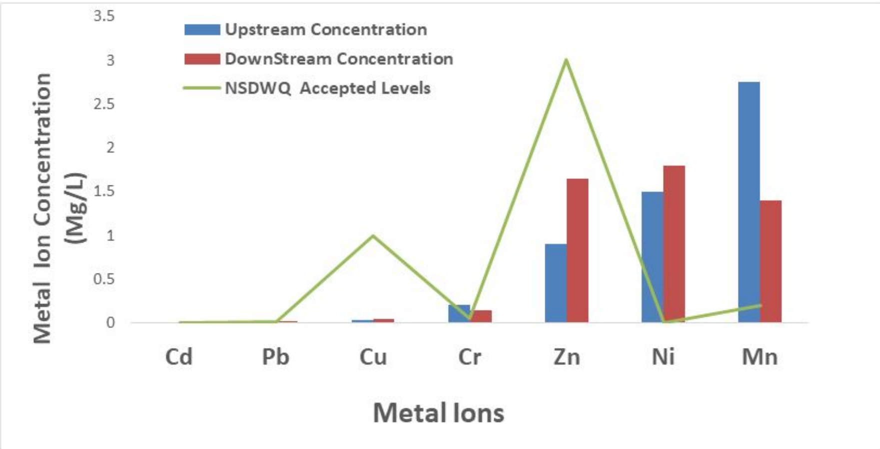


Image4: The values of the HPI recorded in Up Stream Against Down Stream Point of Ureje River

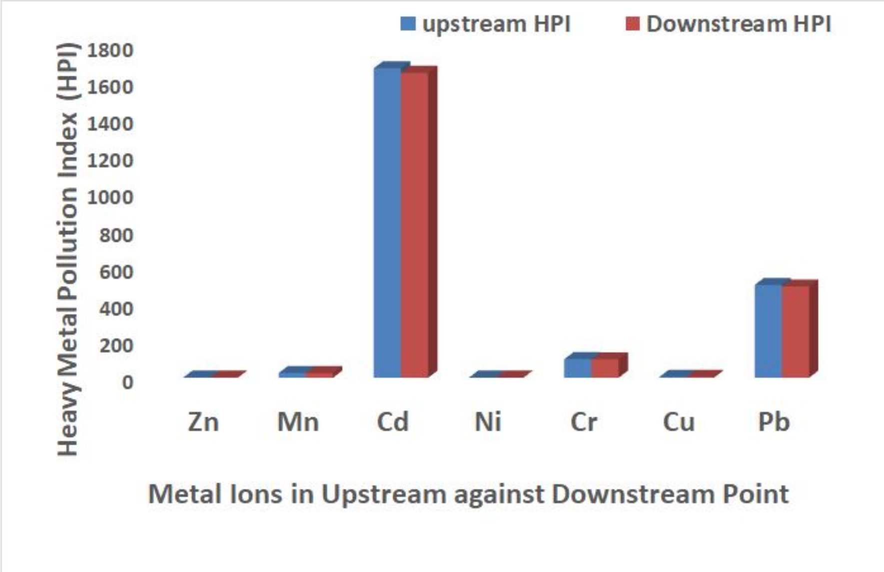
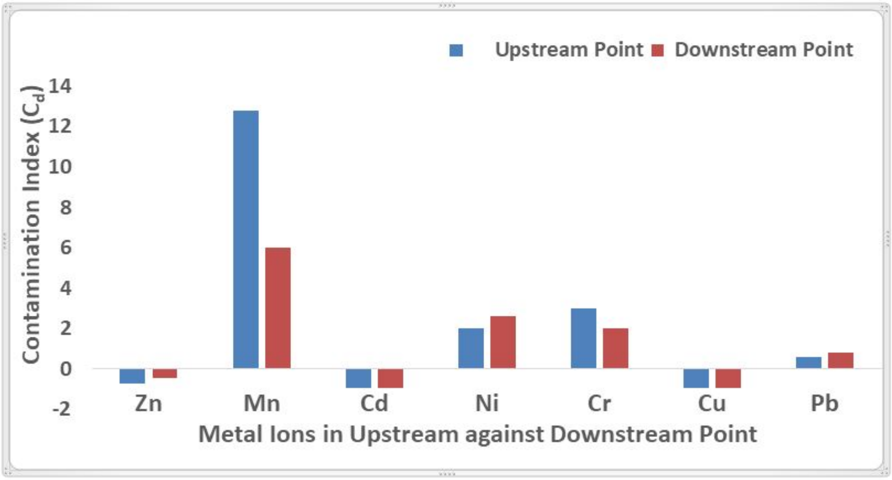


Image5: The values of the Cd recorded in Up Stream Against Down Stream Point of Ureje River.



Conclusion

Results of studies conducted on the water quality of Ureje River in Ado Ekiti for upstream and downstream points to assess its suitability for human consumption and compare it to National Standard of Drinking Water Quality (NSDWQ) and World Health Organisation (WHO), indicated variation in the quality of water emanating from human activities with respect to some heavy metals concentration that were above recommended limits. The average concentrations of different investigated heavy metals in the river water examined, heavy metals contents such as Manganese, Nickel, Chromium and Lead were above the permissible limits of NSDWQ and WHO while Zinc, Cadmium and Copper were below the permissible limits. This suggests that human activities within the study area posed a serious threat on the quality of water of the river system. A few chemical contaminants have been shown to cause adverse health effects in humans because of prolonged exposure through drinking water.

Furthermore, for heavy metal pollution index and contamination index parameter, it was shown that Lead Cadmium and Chromium had high pollution index load that exceeded the threshold value of 100 while Manganese, Copper, Nickel and Zinc had low pollution index which are below the threshold value. Also, Contamination Index parameter of the water quality, Manganese had high contamination index value, Chromium and Nickel had medium contamination index value while Zinc, Cadmium, Copper, and Lead had a low contamination index value. This revealed that the degree of Pollution Indices in river Ureje water is highly contaminated based on HPI and $C_{d,}$ and this indicated the river water is suffering from serious environmental pollution as they receive impact of anthropogenic sources, farming activities, agricultural drainage, open refuse, untreated waste, as well as domestic wastewaters directly without any treatments which brings about heavy metal pollution and contamination load of the water in the river. However, it is recommended that extreme precautions should be taken for preventing the sources of drinking water pollution in the study area.

Conflicts of Interest

"There are no conflicts to declare".

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