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HYDROCHEMICAL ASSESSMENT OF GROUNDWATER IN IKENYI AREA SOUTHEAST NIGERIA.

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Abstract

The most resilient and sustainable source of water supply in Ikenyi area is groundwater. Unfortunately, groundwater in the area is plagued by contaminants of geogenic origin which is suspected to be the cause of the frequent occurrence of water borne disease in the area. Hydrochemical analysis of water samples from the area was carried out to identify the key contaminants and their spatial distribution in the area. The work revealed that wells in the area which encountered aquifer between the depths of 16m to 22m are mostly contaminated with heavy metals. The heavy metals with concentration values higher than WHO recommended maximum allowable concentration are Iron, Lead, Zinc, Arsenic and Chromium. While anomalous concentration values for Arsenic and Chromium are recorded in less than 40% of the tested water samples, Iron, Zinc and Lead anomalous concentration values occur in 80% to100% of the samples. Heavy metal anomalies are predominantly in the Northeast of the study area. Water quality index based on the weighted arithmetic index method indicates that the tested groundwater is good to poor in the Southeast, mostly very poor in the west and unfit for consumption in the Northeast. The similarity of the Water quality index map derived from weighted arithmetic index and Heavy metal pollution index demonstrated that the water quality in the study area is driven by the heavy metal anomaly. Given the prevalent heavy metal contamination in the study area, it is imperative to consider a robust water treatment plan in any groundwater development project in the area.

Keywords: *Groundwater, Heavy metals, Water quality index, contaminants*

Introduction

The need for good water quality for domestic purposes cannot be over emphasized as it strongly influences the health of the inhabitants of the community that depends on that source of water (Ayejoto *et al.* 2022, Odikamnoro, *et al.* 2014). Sources of potable water could be rainfall, surface water bodies such as streams and groundwater. Based on Adedeji *et al*. 2018, the climate of Southeast of Nigeria covering Ikenyi is broadly defined by two seasons referred to as the dry and rainy season. The dry season spans from the month of November to April while the rainy season takes place from the month of May to October. During the rainy season, the source of water for domestic purposes could be from rainfall streams and groundwater. However, during the peak of the dry season typically occurring around February, the most common and unavoidable source of water supply in the area is groundwater due to the absence of rainfall and limited availability of surface water bodies.

Regrettably, there has been frequent occurrence of life-threatening water-borne diseases in Abakiliki province that are associated with the quality of the groundwater available to the inhabitants during the dry season. This has triggered intensive research on the evaluation and sources of groundwater contamination in the area (Adeolu 2019, Ani *et al.* 2015, Eyankware, 2021, Tyopine, 2024).

Generally, water contamination could be associated with natural causes often referred to as geogenic activities or anthropogenic activities. In geogenic cases the dissolution and leaching of minerals and matrix of the aquifer rocks during the groundwater flow could alter the chemical composition of the groundwater in the aquifer (Edet 1993, Etu-Efeotor 1998). Groundwater contaminations through anthropogenic activities include indiscriminate siting of refuse dumps and septic tanks, leaching of fertilizers used for agricultural practices, improper management of tailings from mines, involuntary agitation of rock matrix during mining (Gajoweic, 1993), aggressive withdrawal of groundwater which could pull in contaminants in less permeable layers (Zhang *et al.* 2019).

The study area is located in the Lower Benue trough characterized by the Albian deposits of the Asu River group and the Santonian tectonics (figure 1). Among the formations in the Asu River Group is Abakiliki Formation which underlies the study area with dominant lithologies of Shale, Limestone, silt and iron-stained pebbles. The Santonian tectonics, however, led to granite intrusions in the area and also facilitated the generation of epithermal minerals such as Lead and Zinc in the area. The occurrence of these economic minerals has attracted artisanal miners who rarely indulge in environmental impact assessment prior to their mining activities. Thus, groundwater contamination associated with the interaction of the epithermal minerals in the aquifer and indiscriminate disposal of mine tailings by the artisanal miners is imminent in the area and often considered as the root cause of most of the incessant water-borne diseases.

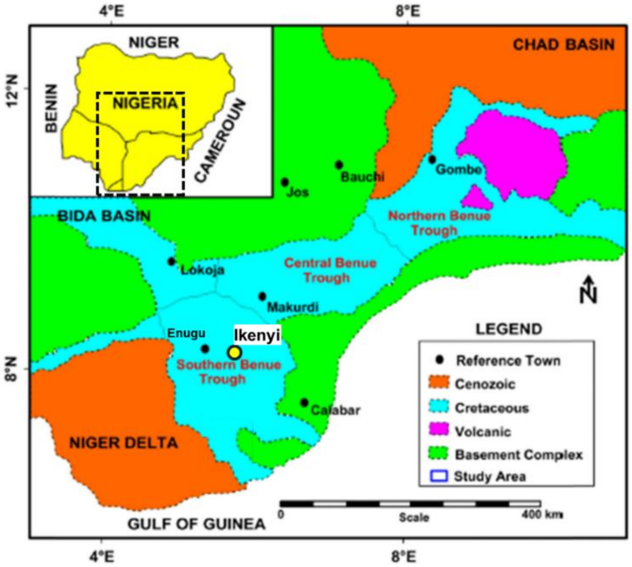


Figure -1: Location of the study area with respect to the Benue trough (adapted from Eldosouky et al. 2022)

Based on geology and prevalent human activities in the study area, groundwater contamination through both geogenic activities and anthropogenic activities in the area are evident (Adeolu 2019, Ayejoto *et al.* 2022). This work is therefore focused on water quality assessment in Ikenyi and environs with the aim of mapping low risk contamination areas and high-risk contamination zone using the trend deduced from the water quality distribution map.

Materials and Methods

The study area is defined by WGS 1984 UTM zone 32N coordinate reference system with Northwestern origin at X: 406300, Y: 704500. The topographic map of the study area in figure 2 shows increase in elevation from West to East . Water samples were taken from 16 boreholes with good geographical spread in Ikenyi and environs. The borehole depth ranges from 16m to 22m. The workflow implemented for the study is as shown in figure 2.

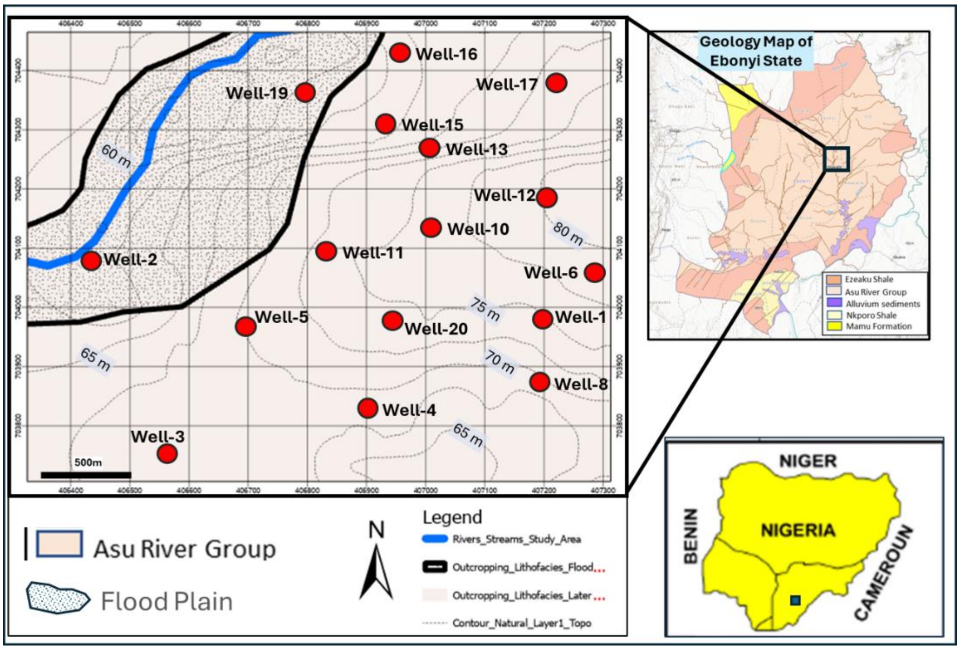


Figure 2: Geology map of the study area

Procedure developed by United States Geological Survey National field manual (*USGS NFM*) for the collection of water-quality data was adopted for the water sample collection. Based on the USGS National field manual, two types of water sample collection procedure were deployed for 2 groups of sample analysis. They are sampling for unpreserved classical chemistry constituents and physical characteristics such as Chlorides, Nitrates, Sulfates, Acidity, Conductivity and Total Dissolved Solids; and sampling for metals such as Arsenic, Lead, Zinc, Chromium and Magnesium. In the former the samples are collected with plastic or glass bottles, preserved at temperatures $\leq 4^oC$ and analyzed within 72 hours after collection while in the latter samples are collected with plastic bottles, preserved with nitric acid to lower pH to 2 and could be held for up to 28 days before analysis. Purging of the borehole is done prior to collecting water samples from the borehole. This ensures that water samples representing the true state and quality of the groundwater at that point are taken. A duplicate of each of the samples were collected for redundancy and quality assurance.

The analysis of the water samples for the determination of the physical characteristics and concentration of each of the elements and properties of interest were done using the procedure described in the *APHA (2017) Standard Methods for the Examination of Water and Wastewater. 23rd Edition, APHA, Washington DC.*

The results of the analysis were plotted in their respective geographical locations and interpolated to generate a 2D map of the distribution of the concentration of elements of interest as well as the physical properties of the water.

To determine the water quality the water sample is benchmarked with the maximum allowable concentration of the elements recommended by reference authorities like WHO. The benchmarked elements and properties in each water sample are harmonized with different statistical methods to obtain a value that will be used to rank the water sample. Some of the statistical methods that were used in this study are water quality index (WQI) based on the weighted arithmetic index method by Brown et al., 1972 and Heavy metal pollution Index (HPI) as implemented by Mohan *et al.* 1996.

To determine the general water quality with all indices available such as water physical properties and concentration of certain elements, the water quality index (WQI) based on the weighted arithmetic index method proposed by Brown *et al.* 1972 was used. WQI based on the weighted arithmetic index method is expressed with the equation 1 below:

$$WQI = \frac{\sum W_n Q_n}{\sum W_n} \qquad (1)$$

Where Wn is weighting factor defined by equation 2 $\quad W_n = \frac{K}{S_n} \qquad (2)$

Where $\quad K = \frac{1}{{}^{1}/_{S_1} + {}^{1}/_{S_2} + {}^{1}/_{S_3} + \cdots + {}^{1}/_{S_n}} = \frac{1}{\sum \frac{1}{S_n}} \qquad (3)$

S is Standard desirable value of the nth parameters $\quad Q_n = \frac{(V_n - V_o)}{(S_n - V_o)} * 100 \qquad (4)$

Where Vn is the mean concentration of the nth parameters

Sn is the standard desirable value of the nth parameters

Vo is actual values of the parameters in Pure water (generally Vo = 0 for most parameters except for pH).

The ranking of water quality using Water Quality Index (WQI) based on Weighted arithmetic index is summarized in Table I.

Table I Water quality ranking based on the WQI with Weighted Arithmetic Index Method

Water Quality Index	Water Quality Status
0 - 25	Excellent
26 - 50	Good
51 - 75	Poor
76 - 100	Very Poor
>100	Unfit for Consumption

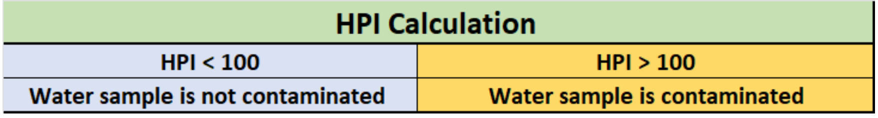
Based on geology of the study area, one of the key anticipated groundwater contaminants are heavy metals which are associated with the intense mineralization in the area. The impact of the heavy metal concentration on the water quality was assessed with Heavy Metal Pollution index (HPI) methodology. Heavy Metal Pollution index (HPI) is a water quality assessment methodology anchored on the severity of the integrated effect of the constituent heavy metals with respect to the maximum allowable concentration recommended by reference authorities like WHO. The calculation of Heavy Metal Pollution Index can be carried out with equation 5

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \qquad 5$$

Where HPI is Heavy Metal Pollution Index, W_i is the unit weight of the i^th^ parameter, Q_i is sub-index value of the i^th^ parameter.

The Heavy Metal Pollution Index ranking for water sample is as shown in Table II.

Table II Water quality ranking based on Heavy Metal Pollution Index



HPI Calculation	
HPI < 100	HPI > 100
Water sample is not contaminated	Water sample is contaminated

Results

The water properties and elements evaluated are pH, Total Hardness, Total dissolved solids, Bicarbonates, Sulphates, Nitrates, Chlorides, Barium, Chromium, Lead, Zinc, Arsenic and Iron. The result of the physical properties and concentration of certain elements of the water samples in comparison with the maximum allowable concentration of the elements recommended by WHO are as shown in Table III.

Table III Comparison of the WHO Water Maximum allowable concentration values with values derived from the study area water samples

	X	Y	pH	Bicarbonate (mg/l)	Chloride (mg/l)	Total Hardness (mg/l)	TDS (mg/l)	Sulphate (mg/l)	Nitrate (mg/l)	Lead (mg/l)	Zinc (mg/l)	Barium (mg/l)	Chromium (mg/l)	Arsenic (mg/l)	Iron (mg/l)
WHO (Max. Allowable Conc.)			6.5-8.5	400	250	500	1000	400	10	0.05	5	1.3	0.05	0.05	0.3
Sample 1	407212	703970	8.16	100	78	180	144	112.2	8.12	0.043	16.425	0.027	0.003	0.018	0.7099
Sample 2	406429	704087	8.13	35	84	192	85	104.2	7.892	0.048	7.067	0.034	0.022	0.022	1.584
Sample 3	406561	703750	7.92	70	82	512	95	64.5	7.145	0.082	6.872	0.056	0.045	0.047	0.7075
Sample 4	406895	703860	7.02	90	89	340	119	64.8	6.048	0.015	5.112	0.076	0.007	0.019	0.3094
Sample 6	407262	704074	8.14	52.5	92	340	57	41.28	7.658	0.021	25.084	0.027	0.013	0.025	1.4446
Sample 12	407202	704193	8.1	52.5	92	446	194	50.5	7.166	0.126	9.609	0.025	0.056	0.105	0.4507
Sample 13	407036	704261	8.1	57.5	92	660	109	54.72	7.433	0.072	6.676	0.055	0.014	0.079	0.2698
Sample 15	406929	704294	8.06	62.5	76	460	186	42	7.771	0.086	25.056	0.086	0.023	0.044	1.0464
Sample 16	407004	704458	7.92	35	71	342	73	65.06	7.187	0.119	6.257	0.048	0.034	0.034	0.2762
Sample 19	406816	704354	7.92	32.5	71	80	135	65.78	7.321	0.02	9.693	0.045	0.054	0.105	0.4109
Sample 5	406775	704034	7.69	65	85	348	99.67	77.83	7.028	0.055	6.35	0.055	0.025	0.0205	0.867
Sample 8	407075	703873	7.62	86.5	84	973	131.6	78.72	7.03	0.0485	10.67	0.054	0.015	0.023	0.5086
Sample 10	407032	704135	8.05	57.2	89	532	144.85	54.47	7.329	0.089	13.51	0.04	0.03	0.072	0.4827
Sample 11	406830	704139	7.95	61.7	84	489	131.56	58.18	7.388	0.069	12.69	0.06	0.021	0.0565	0.7277
Sample 17	407234	704380	8.04	48.3	85	483	125.3	56.76	7.262	0.1056	11.9	0.043	0.034	0.076	0.3322
Sample 20	406949	703980	7.67	69.6	86	453	131.8	59.15	6.922	0.0576	10.44	0.059	0.019	0.032	0.5066

WHO reference values 🟦 **Within or equal to WHO reference values** 🟩 **Above WHO reference values** 🟥

According to Table III some of the water samples showed anomalous values of Total Hardness, Lead, Zinc, Chromium, Arsenic and Iron when compared with the maximum allowable concentration by WHO. Map of the study area showing the anomalous water properties in each of the water samples is shown in figure 3.

Values of hydrochemical parameters considered to be anomalous based on the water sample test were interpolated in order to obtain the spatial distribution of the parameters in the study area as shown in Figure 4.

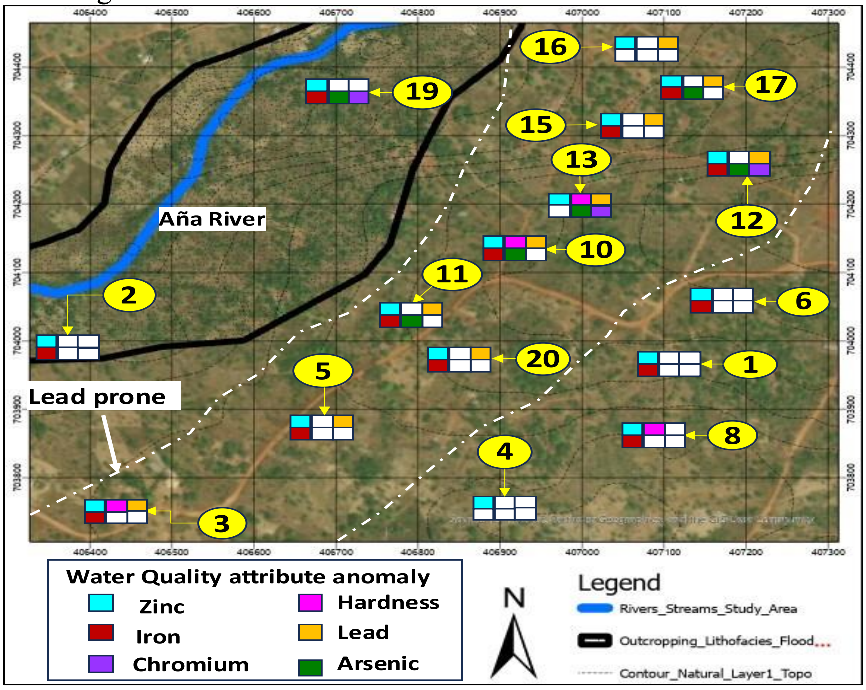


Figure 3 Water Sample location map highlighting hydrochemical parameters above WHO standards

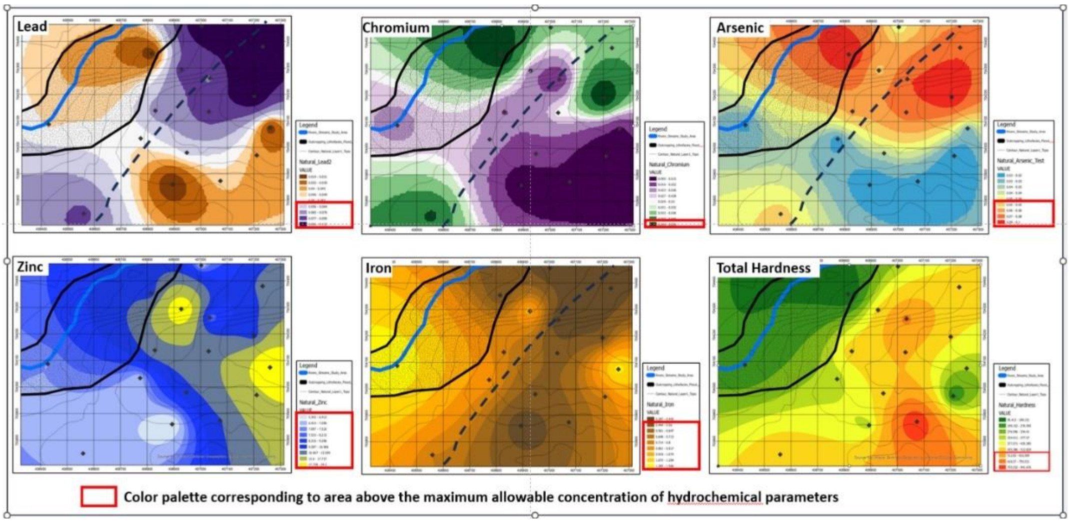


Figure 4 Spatial distribution of the Hydrochemical parameters above the WHO threshold in some parts of the study area.

The water quality index based on weighted arithmetic index method was computed with the measured hydrochemical parameters of the water sample. The result of the WQI-WAI analysis of water samples taken from the study area are as presented in Table IV. WQI ranges from 187 in sample 12 with water quality status “unfit for consumption” to 33 in sample 4 with water quality status “Good”.

Table IV: WQI-WAI analysis of water samples taken from the study area

	X	Y	Water Quality Index	Water Quality status
Sample 1	407212	703970	53	Poor
Sample 2	406429	704087	85	Very Poor
Sample 3	406561	703750	109	Unfit for consumption
Sample 4	406895	703860	33	Good
Sample 6	407262	704074	63	Poor
Sample 12	407202	704193	187	Unfit for consumption
Sample 13	407036	704261	108	Unfit for consumption
Sample 15	406929	704294	115	Unfit for consumption
Sample 16	407004	704458	121	Unfit for consumption
Sample 19	406816	704354	119	Unfit for consumption
Sample 5	406775	704034	78	Very Poor
Sample 8	407075	703873	63	Poor
Sample 10	407032	704135	128	Unfit for consumption
Sample 11	406830	704139	105	Unfit for consumption
Sample 17	407234	704380	141	Unfit for consumption
Sample 20	406949	703980	77	Very Poor

Interpolation of the computed WQI-WAI values as shown in figure 5 provides information on the spatial distribution of the groundwater quality ranking in the area.

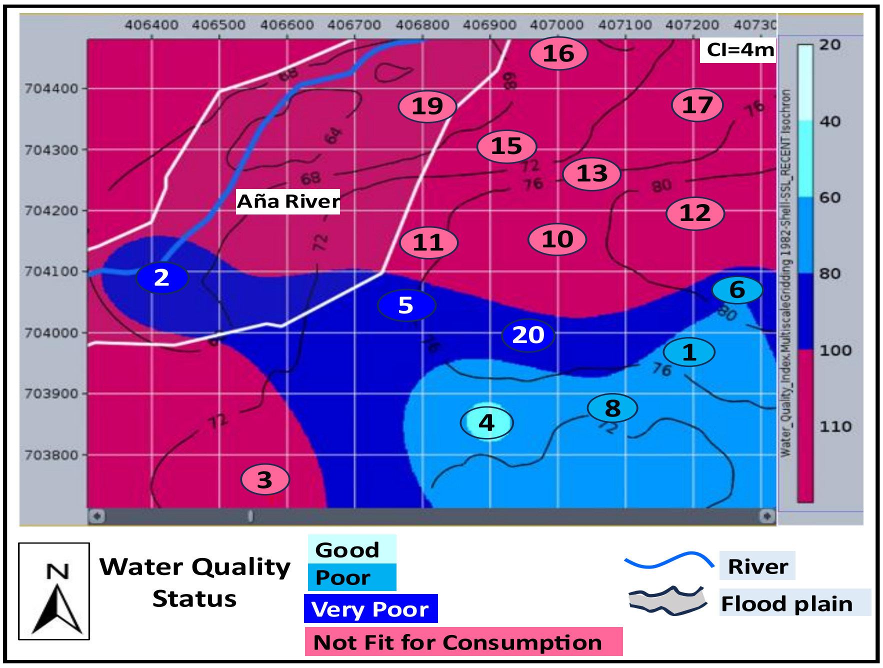


Figure 5 Classification of Water quality from the study area using an aspect of WQI -WAI

The groundwater quality assessment based on the Heavy Metal Pollution Index (HPI) was carried out with the heavy metal hydrochemical parameters measured from the water samples in the area. The heavy metal parameters used for the HPI calculation were Iron, Chromium, Arsenic, Lead and Zinc. The results of the HPI analysis are shown in Table V. The HPI value is divided into two categories denoted by values greater thank 100 and Values less than 100. Water samples with HPI values less than 100 indicates water samples not contaminated while water samples with HPI values greater 100 are contaminated.

Table V Ranking of water sample from the study area using HPI

	X	Y	Heavy Metal Polution Index	Water Quality status
Sample 1	407212	703970	53.75036	**Water Sample is not contaminated**
Sample 2	406429	704087	86.07059	**Water Sample is not contaminated**
Sample 3	406561	703750	109.9826	**Water sample is contaminated**
Sample 4	406895	703860	31.546	**Water Sample is not contaminated**
Sample 6	407262	704074	64.0097	**Water Sample is not contaminated**
Sample 12	407202	704193	189.1826	**Water sample is contaminated**
Sample 13	407036	704261	109.022	**Water sample is contaminated**
Sample 15	406929	704294	116.21	**Water sample is contaminated**
Sample 16	407004	704458	122.95	**Water sample is contaminated**
Sample 19	406816	704354	120.49	**Water sample is contaminated**
Sample 5	406775	704034	78.83	**Water Sample is not contaminated**
Sample 8	407075	703873	64.029	**Water Sample is not contaminated**
Sample 10	407032	704135	129.54	**Water sample is contaminated**
Sample 11	406830	704139	105.76	**Water sample is contaminated**
Sample 17	407234	704380	142.3	**Water samples is contaminated**
Sample 20	406949	703980	77.894	**Water Samples is not contaminated**

Interpolation of the computed HPI values as shown in figure 6 provides information on the spatial distribution of the groundwater quality based on the degree of heavy metal contamination in the area.

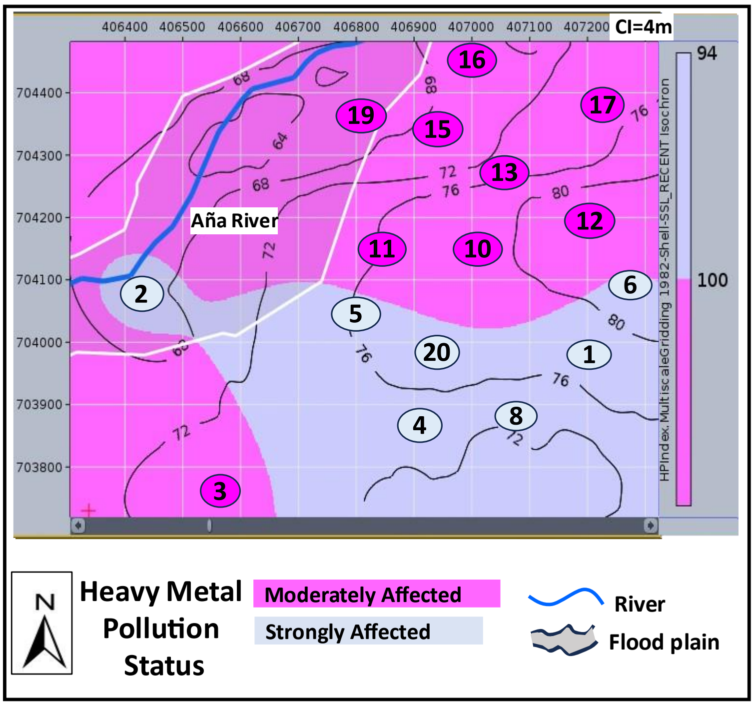


Figure 6 Spatial distribution of Heavy Metal Pollution Index in the study area

Discussion

The hydrochemical properties that exhibited concentrations higher than WHO maximum allowable limits in the water samples were Total Hardness, Lead, Zinc, Chromium, Arsenic and Iron as shown in Table III. Zinc concentration in the water samples collected was as high as 25mg/l and they are all above the WHO recommended maximum allowable concentration of 5mg/l which implies persistent Zinc contamination in the area. Samples with Lead concentration that are up to 0.1mg/l which is above the WHO maximum allowable limits of 0.05mg/l were recorded as shown in Table III. Evaluation of the spatial distribution of the Lead concentration in the groundwater sample suggests high Lead concentration in a Northeast Southwest corridor of the study area as shown in Figure 3. This Lead concentration trend is also evident in the map of Lead distribution in the area Figure 4.

81% of the water samples had iron concentration above the WHO maximum allowable limits of 0.3mg/l. The map of the iron concentration as deduced from the water samples indicates high iron concentration in the West and East in contrast with the high Lead concentration trend. 38% and 12% of the water samples had Arsenic and Chromium concentrations which are higher than the WHO maximum allowable limits of 0.05mg/l. They have both indicated high concentration above WHO maximum allowable limits of 0.05mg/l in the Northeast area.
The maps of the hydrochemical properties with groundwater samples higher than WHO recommended values generally have high concentration of heavy metals in the Northeast region of the study area as shown in Figure 4.

WQI-WAI map in Figure 5 revealed that the groundwater in the area is unfit for consumption in the Northeast, very poor in the West and poor in the Southeast. HPI map in Figure 6 shows that with the exception of Southeast and part of the West, the groundwater in the area is generally contaminated.

The similarity between the WQI-WAI and HPI shows that the water quality in the area is mostly influenced by the heavy metal concentration in the area.

The high Lead and Zinc mineral content of the water samples corroborates the presence of the Benue trough mineralization corridor defined by Cratchley and Jones 1965. The origin of the water contamination by heavy metals is therefore considered to be geogenic. This implies that the contamination is linked to the natural occurrence of these minerals.

Given the strong dependence on groundwater during the dry season in the area, the water-borne diseases and health epidemic that frequently occur in the study area are therefore not unrelated to this poor groundwater quality.

Conclusion

At Ikenyi area, the aquifer located between the depth interval of 16m to 22m produces water that has very high heavy metal contamination risk. Amongst the heavy metals identified with anomalous concentration in the groundwater were Arsenic, Chromium, Iron, Zinc and Lead. Even though anomalous concentration of Arsenic and Chromium were observed in some of the groundwater samples, the anomalous concentration and spatial distribution of Iron, Zinc and Lead were predominant. This anomalous concentration of Lead, Zinc and Iron is certainly impacting on the health of the inhabitants of the study area and could be associated with the frequent occurrence of water-borne diseases in the area. Based on the understanding of geology and field mapping exercise in the area, the source of the heavy metal contaminant is principally geogenic. The groundwater samples from the Northeast of the study area generally shows anomalous concentration of heavy metals while groundwater samples from the SE generally show lower heavy metal concentration. Moreso, the Northeast-Southwest orientation of the Lead concentration anomaly corridor suggests the presence of a Lead mineral deposit in the area. This indicates that subsurface structure may have a very strong influence on the occurrence of these heavy metals and their corresponding anomaly distribution. It is therefore imperative that additional studies on the impact of the geologic subsurface structure on the spatial distribution of the anomalies are carried out with subsurface imaging methods such as electrical imaging tomography ERT and Magnetic methods. Investigation of the subsurface structure and lithology with geophysical methods would help to evaluate the heavy metal risk potential at depths exceeding 22m and would also provide insight on the groundwater potential at such depth. Given the result of the hydrochemical analysis of the groundwater samples, it is imperative that the groundwater from the study area is subjected to extensive treatment to eliminate the contaminants before consumption.

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