Effect of Mining Activities on Groundwater Quality in Ikwo Local Government Area of Ebonyi State, Nigeria

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Abstract:- The groundwater quality in Ikwo Local Government Area of Ebonyi State was assessed for a period of seven (7) months (November 2020 to June 2021) at seven (7) sampling locations (SLs) to determine the effects of mining activities on the quality status. Measurements were made on samples collected with 500ml sample bottles for ten (10) physical and chemical parameters according to standard methods. Water samples for six (6) heavy metals were collected in 250ml bottles and fixed with concentrated HNO3. Descriptive Statistics, Analysis of Variance (ANOVA), Principal Component Analysis (PCA), Pearson's Correlative Coefficient (r), and Water Quality Index were used to analyze data. Mean values of the parameters obtained were: Temperature 27.84 ±0.28°C, pH 6.57±0.15, EC 78.00±7.00µs/cm, TDS 29.84 ± 6.40mg/L, TSS 3.80 ±0.56mg/L, Turbidity 2.31 ± 0.3 1NTU, DO 6.05 ±0.57 mg/L, Alkalinity 9.90 ±0.72mg/L, COD9.25±0.97mg/L, BOD 2.76±0.40mg/L,Mg 0.93±0.14mg/L, Hardness 7.93±0.58mg/L, Pb 0.31±0.01mg/L, Zn 26.20±3.00mg/L, Cu 2.30 ± 0.36mg/L, Cd 0.71 ±0.23mg/L, and Cr 0.47±0.16mg/L. All the trace metals analyzed (Mg, Pb, Zn, Cu, Cd, and Cr) exceeded the permissible limits of WHO (2010). There significant spatial difference in the levels of Temperature, Alkalinity, and Total Hardness (Sig F= 0.06 to 0.174) and significant temporal difference in the levels of Temperature, EC, pH, and TDS between control and other locations at p<0.05. Six principal components (PCs) formed the extraction solution with a cumulative percentage variability of 83.435%. PCs 1, 2,3,4,5, and 6 were highly correlated with Zn (0.814), Cr (0.647), COD (-0.836), DO (0.724), and Temperature (0.830). Results of the Water Quality Index show that the groundwater of the studied area is not potable, as it is laden with trace metals; The study recommends proper treatment of the water before consumption.

***Keywords*:-** *Groundwater Quality, Heavy Metals, Water Quality Index and Trace Metals.*

I. INTRODUCTION

Water is essential for the sustenance of life. It occupies 71% of the entire earth's surface and biologically makes up a large percentage of the total body fluids of all living things (Obasi and Akudinobi, 2013). It is one of the prime elements responsible for life on earth. Water circulates through the land just as it does through the human body, transporting, dissolving, and replenishing nutrients and organic matter, while carrying away waste material. In the human body, water regulates the activities of fluids, tissues, cells, lymph, blood and glandular secretions (Jan, 2011).

The body of an average adult contains 42 liters of water and with just a small loss of 2.7 litres he or she can suffer from dehydration, displaying symptoms of irritability, fatigue, nervousness, dizziness, weakness, headaches and consequently reach a state of pathology (Nwali, *et al* 2016).

Apart from drinking it to survive, people have many other uses for water. These include: cooking: bathing, washing of cloth and cooking utensils (pots, saucepans, crockery and cutlery), keeping houses and communities clean, recreating (swimming pools), keeping plants alive in gardens and parks (Obasi, 2001).

Water is also essential for the healthy growth of farm crops and farm stock and is used in the manufacture of many products. The quality of water is determined by its physicochemical and biological makeup and the amount of trace contaminants it contains. The term 'water pollution' can be defined as the deterioration in the physical, chemical and biological properties of water resulting from human activities (Chatterjee, 2011).

Contamination of groundwater due to heavy metals is one of the most important concerns that have received attention at local, regional, and global levels because of their toxicological importance in ecosystems and impact on public health (Ding, 2016).

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Review of relevant literature reveals that, geogenic and anthropogenic processes both contribute to the degradation of natural water quality (Jan, 2011; Ayeni, *et al* 2009). According to relevant statistics, only about 61% of urban dwellers in developing countries have access to safe water supply sources (Igwenyi and Aja-Okorie, 2014). It is also estimated that 1.2 billion people around the world lack access to safe water, and close to 2.5 billion people are not provided with adequate sanitation (Bai, *et al* 2016). In Nigeria, 75-80% of the total population of about 160 million people live in rural areas, and less than 50% of that number have access to potable water (Obasi and Akudinobi, 2013). At present, there is an increasing trend that ground has become a major source pf water supply due to rapid population growth, urbanization and unsustainable consumption of surface water in industry and agriculture (Poyraz and Taspinar *2014;* Wongsasuluk, *et al 2016;* Bai, *et al 2016;* Ding, *et al 2016).* In developing countries, the problem is further aggravated due to the lack of proper management, unavailability of professionals and financial constraints (Sun, *et al 2017,* Liao, *et al 2018*). In January 2000, the Federal Government of Nigeria launched its National Policy on Water and Sanitation to all Nigerians. The International adoption of the Sustainable Development Goals (SDGs) in 2015 created a new framework for reducing deficiencies in the quantity and quality of water supply and sanitation. Specifically, Goal 6 of the 17 SDGs calls for clean water and sanitation and most importantly, reducing by half the number of people without sustainable access to safe drinking water. This gap is most accurate in Sub-Saharan Africa where only 58% of the population enjoys access to safe drinking water (Barnerjeo and Morella, 2011). The exploitation of groundwater both in urban and rural areas will go a long way to bridge this gap, only if human activities that contribute to its pollution are properly regulated. The involvement of the scientific community in the regular monitoring of groundwater resources will be an advantageous tool for mitigating pollution problems.

- *Study Area*

The area of study is Ikwo Local Government Area, situated on the eastern part of Ebonyi State. Ikwo is the largest Local Government Area in the State. It lies between Latitude 06^{O}10ˋ29.6ˋˋand Longitude 08^{O}08ˋ08.0.” in the derived Savannah Vegetation. Three communities of the Local Government namely Ndiagu-amagu, Enyibichiri, and Echara were selected for this study. The area experiences a bimodal pattern of rainfall (April–July) and (September–November) with a short dry spell in August normally called “August break”. The total mean annual rainfall is between 1700 and 2000mm. At the onset of rainfall, it is torrential and violent, sometimes lasting for 1–2 hours. The minimum and maximum temperatures are 27°C and 31°C, respectively, while relative humidity is in the range of 60–80% (ODNRI, 2009). The vegetation of the area is Parkland, characterized mainly by grasses and shrubs which are derived from savannah (Obiora *et al.*, 2016). The soil consists of dark sandy shales, with fine-grained micaceous sandstone and mudstone.

The lithology of the area comprises of rocks and shales belonging to the Asu River Group of the Albian Cretaceous sediments, while the sedimentary rocks are predominantly black calcareous shale with irregular intercalation of siltstone. The group is known to be associated with Pb–Zn mineralization with shales which are often calcareous and pyritic (Ezeh and Anike 2009). The rocks are extensively fractured, folded and faulted, while the geology and mineral resources are the main factors responsible for the availability of heavy metals (Nnabo 2015a). Surface drainage in the area is quite undulating and irregular with several ephemeral ponds, streams and rivers which always dry up with the advent of rainy season.

Ikwo LGA has a land mass approximated to 500km, and shares a border with Abakaliki and Ezza Local Government Areas of Ebonyi State. The soil in this area belongs to the order Ultisol (FDALR 1985). The relief of the area is undulating but with isolated hillocks that rise up to 200 m above sea level (Obiora *et al.*, 2016). Ikwo lies within the Cross River Drainage Basin. Major rivers in Ebonyi state are the Eastern and Western Ebonyi Rivers which are tributaries of Cross River. All other rivers and streams are tributaries of these two Ebonyi Rivers. The existence of groundwater in parts of the state varies and is seriously influenced by the local geology. While the greater part, which includes the Abakaliki Metropolis, Onueke, some parts of Afikpo North and their environs record reduced groundwater yield to hand dug well and boreholes due to the underlying aquiclude (Adelakan, 2007).

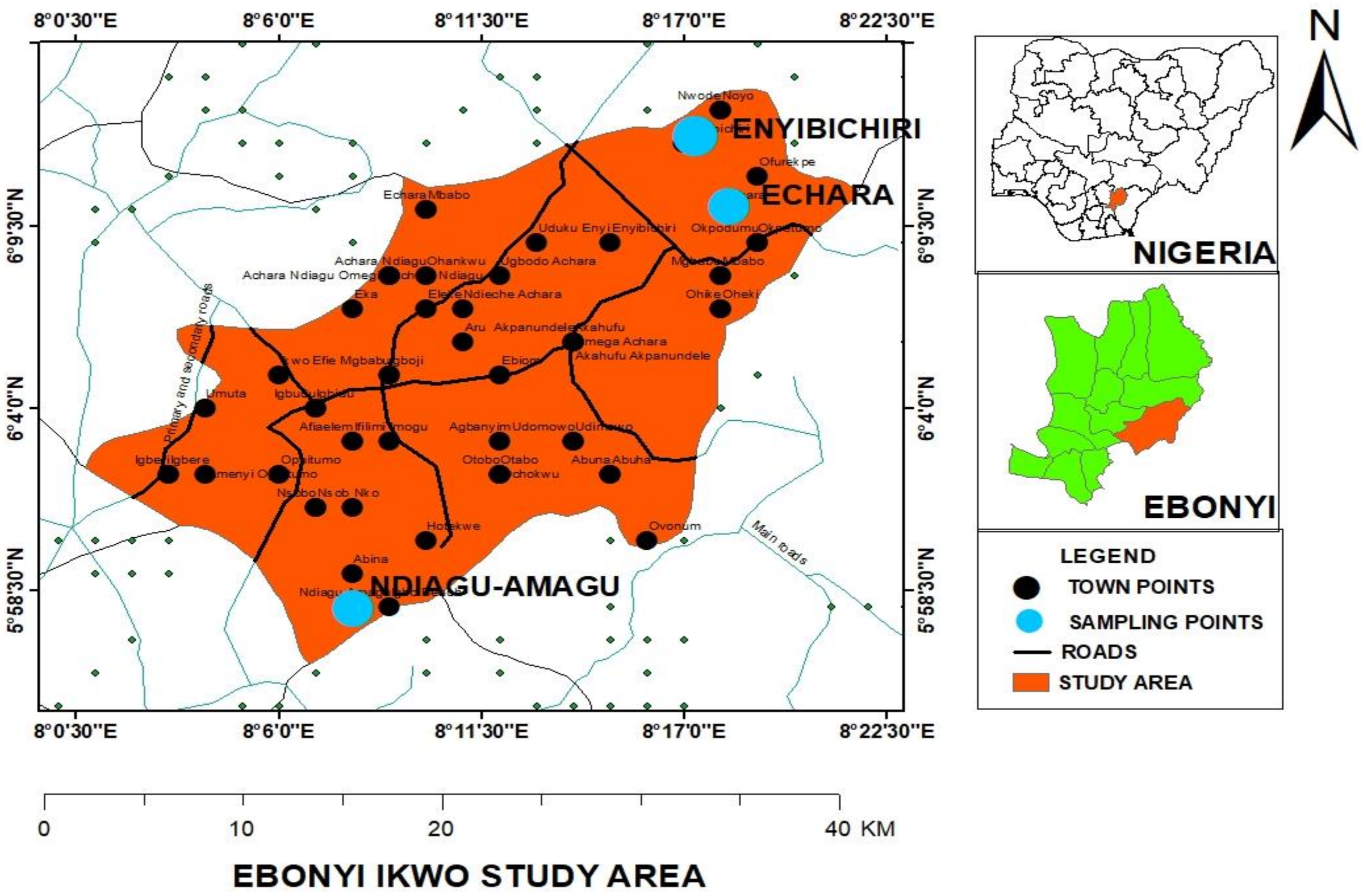

Fig 1 Map of the Study Area, Ikwo LGA in Ebonyi State Showing Ndiagu-Amagu, Enyibichiri, and Echara the Selected Communities.

II. METHODOLOGY

➢ *Sample Collection and Measurement*

Water samples were collected from the seven sampling boreholes located in the four communities (3 communities in the mining area and one from the control area) using conventional methods (WHO, 2011). These samples were collected under asceptic conditions using disposable sterile hand gloves. Bottles were rinsed with the borehole water before collection. The water taps were left to run for about 40seconds during pumping from the borehole, and samples collected directly from water coming out from groundwater.

Collected water samples were subjected to filtration. The standard reagents used in the analysis were prepared using double distilled water. Water samples for trace metals were collected in 250mls plastic bottles and fixed with concentrated H2SO4 in the ration of 2:500. Water samples for other parameters were collected in 500mls sterile plastic bottles. All were tightly closed and properly labeled; and stored in the icebox and promptly transported to Yamatech Laboratory Services, Aba for analysis. A total of fourteen (14) samples were collected from the seven sampling points from November 2020 to June 2021.

Borehole water Temperature, Electrical Conductivity, pH, Dissolved Oxygen (DO), Turbidity and Total Dissolved Solids (TDS) were determined electronically at the site (insitu) with the HANNAH HI 9828 VI PH/OR/EC/DOMeter. The meter was calibrated with standard HI 9828-25 calibration solution. The desired physicochemical parameters were read off the LCD.

➢ *Temperature and pH*

The temperatures and pH of the water samples were taken in situ using a simple thermometer calibrated in degree Celsius for the temperature, and a portable pH meter for pH. Known buffer solutions of pH 4, pH 7, and pH 10 were prepared and used to standardize the equipment, and the pH readings of the water samples were immediately taken. All field meters and equipment were checked and calibrated according to the manufacturer's specifications and instructions.

➢ *Total Dissolved Solid (TDS) and Electrical Conductivity (EC)*

TDS was determined by subtracting the values of the suspended solids from the corresponding total solids of the samples.

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EC was measured with the help of WTW LF330 conductivitymeter which measures the resistance offered by the water between two platinized electrodes. The instrument was standardized with known values of conductance observed with standard KCl solution.

- *Total Suspended Solids (TSS) and Turbidity*

Total suspended solid was determined by using Whatman filter paper rinsed in double distilled water and was dried in an oven at 105^0C for exactly one hour and cooled in desiccators. Its residue weight (W1) was determined using a digital balance. The sample of 100 ml of water was filtered through the resin paper and then evaporated at 105°C for one hour. This weight which represents W2 of the filter paper containing the residue was noted, and TSS was calculated using (W2 − W1) × 100mg/L. The turbidity of the water samples was determined in situ using turbidity meter (Turner designs Aquafluor 8000-001).

- *Dissolved Oxygen (DO) and Alkalinity*

The DO in the water samples is measured titrimetrically by Winkler's method after 5 days' incubation at 20^0C. The difference in initial and final DO gives the amount of oxygen consumed by the bacteria during this period. Alkalinity values are determined by titration methods. 50 ml of the water samples was taken in a clean 150mL conical flask, and three drops of the phenolphthalein indicator were added. After that, it was titrated with 0.05 M H_2SO_4 until colour disappeared. To the colourless solution, three drops of the methyl orange indicator were added and titrated further until colour changed from yellow to permanent reddish or orange red, and then titre values were recorded, and alkalinity was calculated. The procedure needed special BOD bottles which seal the inside environment from atmospheric oxygen.

- *Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD)*

Determination of COD was done as per the method described in standard methods. 50 ml of the water sample was taken in a reflux flask, and 10 mL of potassium dichromate solution with 1g mercuric sulphate was thoroughly mixed. Antibumping beads were added to control boiling of the solution. To this, 10 mL of concentrated sulphuric acid containing silver sulphate was added through the open end of the condenser carefully and mixed by swirling motion. The reflux apparatus was operated for around 1 hour and allowed to cool. The flask was removed, and its content was diluted to 150 mL with distilled water. To the resulting solution, three drops of the ferroin indicator were added, its sample was titrated with standard ferrous ammonium sulphate to an end point where blue-green colour just changed to reddish-brown.

Chemical oxygen demand (COD) of the blank sample was then calculated.

Biochemical oxygen demand was determined using azide modification of Winkler's method. BOD bottle was prepared and incubated at 20° C for 5 days in the dark. After five days, incubated BOD bottle was poured with mixing 2 mL of orthophosphoric acid; it was shaken gently and titrated with sodium thiosulphate to the end point where there was change in color, the titer value represents dissolve oxygen on day five. BOD was then calculated as the difference between dissolve oxygen on day one and that on day five.

- *Magnesium And Hardness*

Magnesium was determined by complex metric titration with standard solution of EDTA using Eriochrome black T as indicator under the buffer conditions of pH 10.0. The buffer solution is made from Ammonium Chloride and Ammonium Hydroxide. The solution resists the pH variations during titration. The hardness of the water samples was determined by ethylenediaminetetracetic acid (EDTA) titrimetric method. This was done by taking 100ml of the samples and added to 2ml buffer solution, and by also adding 2 - 3 drops of Black T. Titration was done with standard EDTA solution (with continuous stirring) until the last reddish colour disappears. At the end point the solution turns blue. The volume used was note down.

- And the total hardness calculated as follows:

Hardness (in mg/L as CaCO3) = (V × N × 50 ×1000) / (SV).

Where: V = volume of titrant (mL); N = normality of EDTA; 50 = equivalent weight of $CaCO_3$; SV = sample volume (mL).

- *Heavy Metals (Pb, Zn, Cu, Cd and Cr)*

- Lead (Pb) was determined by Sulphide Method as described by Vogel (1965).
- Zinc (Zn) was determined by EDTA Titration Method as described by Jackson (1969).
- Copper (Cu) was determined by Ferrocyanide Method as described by Alexeyev (1969).
- Cadmium (Cd) was determined using Xylenol Orange Indicator as described by Vogel (1965). Chromium (Cr) was determined by Bicarbonate Method using Starch Indicator as described by Alexeyev (1969).

- *Calculation Of Water Quality Index (WQI)*

Calculation of water quality index, sixteen important parameters were chosen. The WQI has been calculated by using the standards of drinking water quality recommended by the World Health Organization (WHO). The weighted arithmetic index method has been used for the calculation of WQI of the water samples. Further, quality rating or sub index (q_n) was calculated using the following expression.

$$q_n = 100[V_n - V_{io}] / [S_n - V_{io}] \qquad \text{Eq. 1}$$

- Let there be n water quality parameters and quality rating or sub index (q_n) corresponding to n^{th}parameter is a number reflecting the relative value of this parameter in the polluted water with respect to its standard permissible value.

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- q n =Quality rating for the nth Water quality parameter Vn =Estimated value of the nth parameter at a given sampling station.
- Sn =Standard permissible value of the nth parameter.
- V io = Ideal value of nth parameter in pure water. (i.e., 0 for all other parameters except the parameter pH and Dissolved oxygen (7.0 and 14.6 mg/L respectively)
- Unit weight was calculated by a value inversely proportional to the recommended standard value Sn of the corresponding parameter.

$$W_n = K/ S_n \qquad \text{Eq. 2}$$

- W_n= unit weight for the nth parameters.
- S_n= Standard value for nth parameters
- K= Constant for proportionality.
- The overall Water Quality Index was calculated by aggregating the quality rating with the unit weight linearly.

$$WQI=\sum q_n W_n/ \sum W_n \qquad \text{Eq. 3}$$

Table 1 Water Quality Index (WQI) and Status of Water Quality (Chatterji and Raziuddin 2002)

Water Quality Index Level	Water Quality Status	Grading
0-25	Excellent Water Quality	A
26-50	Good Water Quality	B
51-75	Poor Water Quality	C
76-100	Very Poor Water Quality	D
>100	Unsuitable for Drinking	E

III. DATA ANALYSES

The statistical analysis was done using MS Excel embedded XLStat as the Statistical tool for data analyses. Data collected were analyzed using descriptive statistical methods to explore the minimum and maximum values as well as ranges, means and standard errors of the data set. Data were also presented in tables, graphs and charts.

The relationships between physical and chemical parameters were explored with the use of Pearson's Correlation Coefficient (r). Test of homogeneity in mean variance of groundwater quality parameters was explored with a one-way analysis of variance (ANOVA) factor analysis procedure using Principal Component Analysis (PCA) method of extraction for data reduction was used to remove highly correlated variables from the set with a smaller number of uncorrelated variables. Water Quality Index (WQI) was calculated with the use of a model (Chatterji and Raziuddin 2002).

IV. RESULTS

Table 2 Descriptive Statistics of the Physicochemical Parameters of Borehole Water Quality

Parameters	Minimum	Maximum	Mean	SE	NSDWQ	WHO (2010)
Temperature (°C)	25.40	30.10	27.84	0.28	20-30	28-30
pH	5.70	8.70	6.57	0.15	6.0-9.0	6.5-8.5
EC (µs/cm)	36.00	142.00	78.00	7.00	1	0.25
TDS (mg/L)	3.00	95.00	29.84	6.40	600	500-1500
TSS (mg/L)	0.10	8.50	3.80	0.56	500	-
Turbidity (NTU)	0.40	4.90	2.31	0.31	5.00	5.00-10.00
DO (mg/L)	2.40	12.60	6.05	0.57	7.50	10-20
Alkalinity (mg/L)	1.40	15.90	9.90	0.72	200	200
COD (mg/L)	3.50	18.60	9.25	0.97	8-10	10
BOD (mg/L)	0.80	5.90	2.76	0.40	10	10-20
Mg (mg/L)	0.30	2.40	0.93	0.14	-	0.05
Hardness (mg/L)	1.10	12.70	7.93	0.58	150	100-200
Pb (mg/L)	0.00	0.14	0.31	0.01	0.01	0.01
Zn (mg/L)	2.30	47.40	26.20	3.00	3.0	5.0
Cu (mg/L)	0.00	5.37	2.30	0.36	-	1.00-2.00
Cd (mg/L)	0.00	3.12	0.71	0.23	-	0.003
Cr (mg/L)	0.00	2.31	0.47	0.16	0.05	0.05

* EC = Electrical Conductivity, TDS = Total Dissolved Solids, TSS = Total Suspended Solids, DO = Dissolved Oxygen, COD = Chemical Oxygen Demand, BOD = Biological Oxygen Demand.

- Water Temperature, pH, Electrical Conductivity (EC), and Total Dissolved Solids (TDS) varied from 25.40 – 30.10 (27.84 ± 0.28) °C, 5.70 – 8.70 (6.57 ± 0.15) mg/L, 36.0 – 142.0 (78.0 ± 7.0) µs/cm and 3.00 – 95.00 (29.84 ± 6.40) mg/L respectively (Table 4.1).

- Total suspended solids (TSS) varied from 0.10 – 8.50 (3.80 ± 0.50) mg/L, Turbidity varied from 0.40 – 4.90 (2.31 ± 0.31) NTU, Dissolved Oxygen (DO) varied from varied from 2.40 – 12.60 (6.05 ± 0.50) mg/L, and Total Alkalinity varied from 1.40 – 15.90 (9.90 ± 0.72) mg/L.
- Chemical Oxygen Demand (COD) varied from 3.50 – 18.60 (9.25 ± 0.97) mg/L, Biological Oxygen Demand varied from 0.80 – 5.90 (2.76 ± 0.40) mg/L, Magnesium varied from 0.30 – 2.40 (0.93 ± 0.14) mg/L, Hardness varied from 1.10 – 12.70 (7.93 ± 0.58) mg/L.
- Lead (Pb), Zinc (Zn), Copper (Cu), Cadmium (Cd) and Chromium (Cr) varied from 0.00 – 0.14 (0.31 ± 0.01) mg/L, 2.30 – 47.40 (26.20 ± 3.00) mg/L, 0.00 – 5.37 (2.30 ± 0.36) mg/L, 0.00 – 3.12 (0.71 ± 0.23) mg/L and 0.00 – 2.31 (0.47 ± 0.16) mg/L respectively.

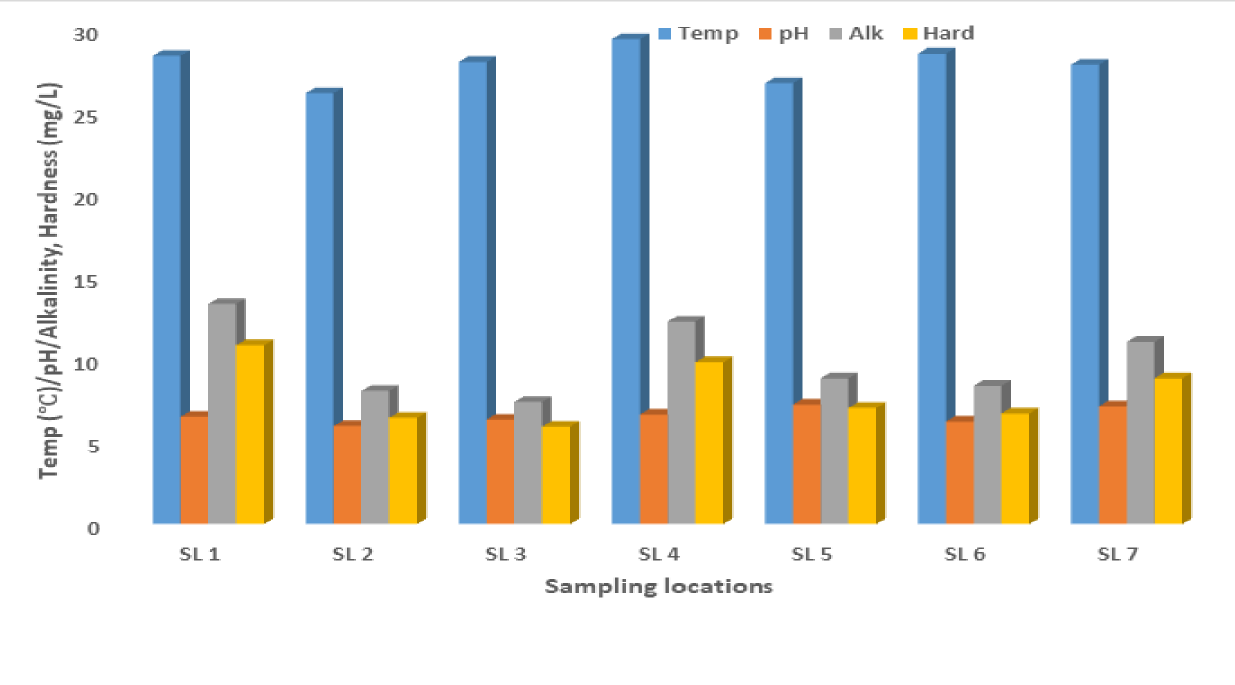

Fig 2 Mean Spatial Variations in Water Temperature, Ph, Alkalinity and Hardness of Water Samples in the Study Area

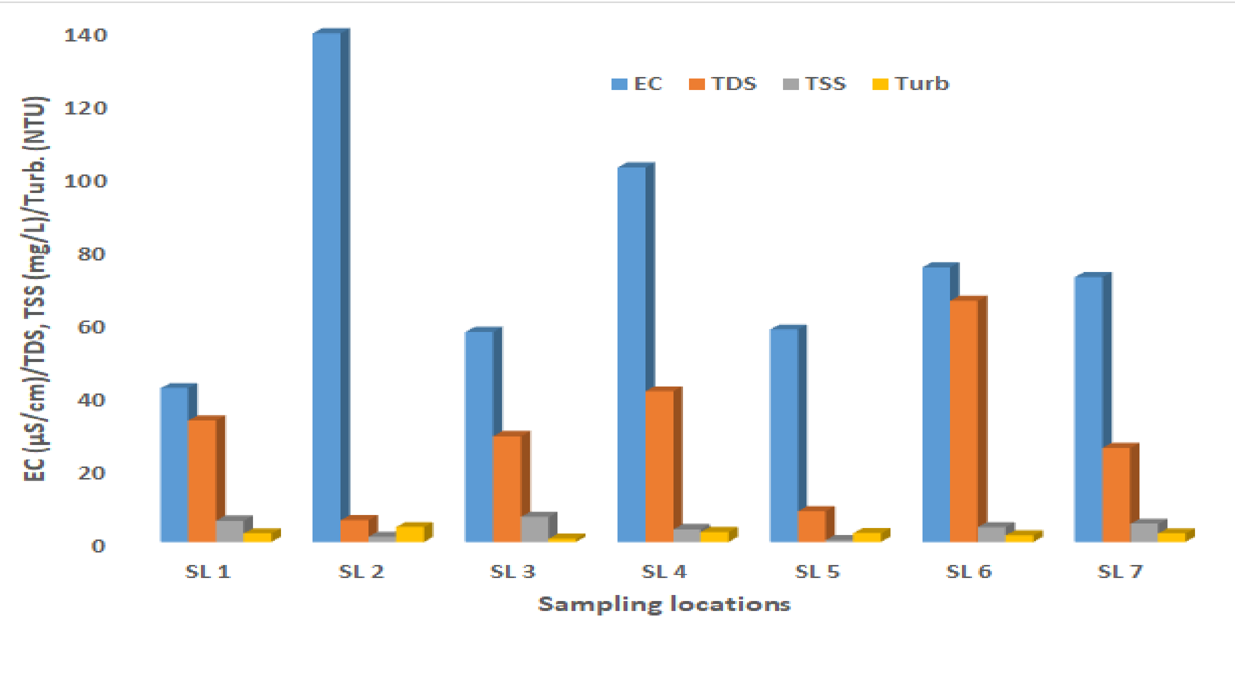

Fig 3 Mean Spatial Variations in Electrical Conductivity, Total Dissolved and Suspended Solids, and Turbidity of Water Samples in the Study Area

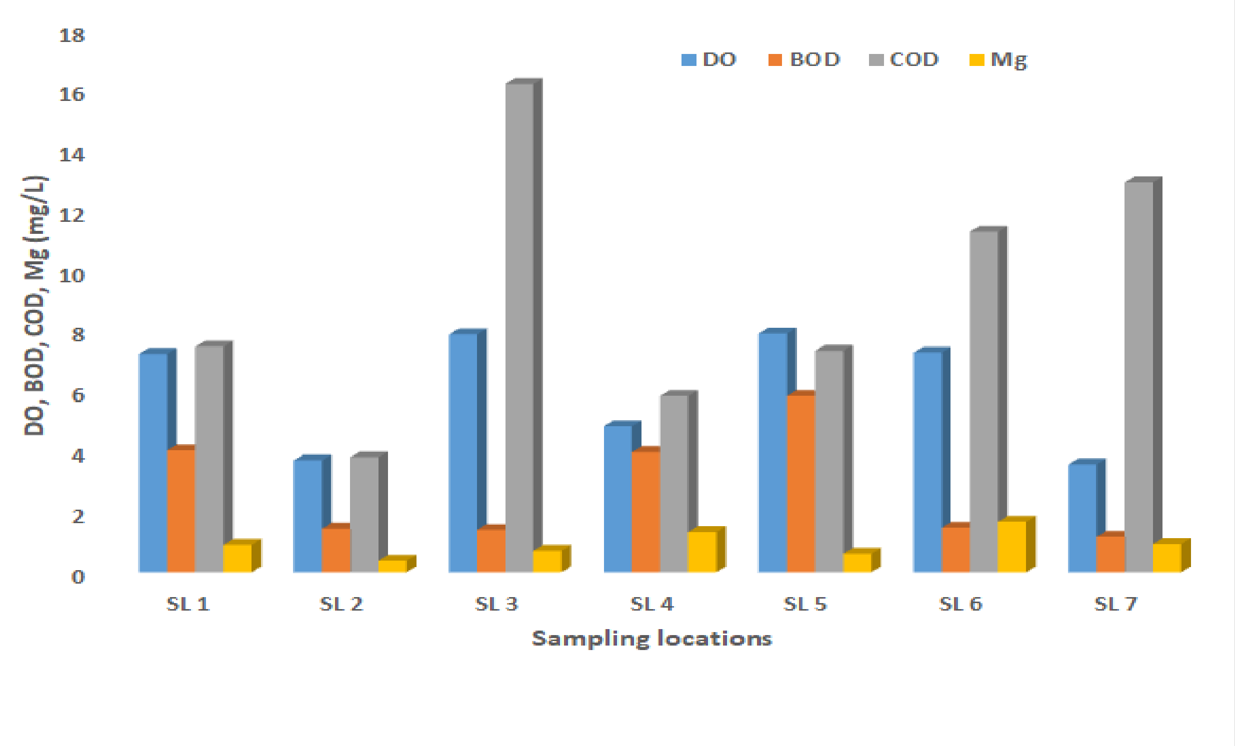

Fig 4 Mean Spatial Variations in Dissolved Oxygen, Biological and Chemical Oxygen Demands, and Mg Ion Concentrations of Water Samples in the Study Area

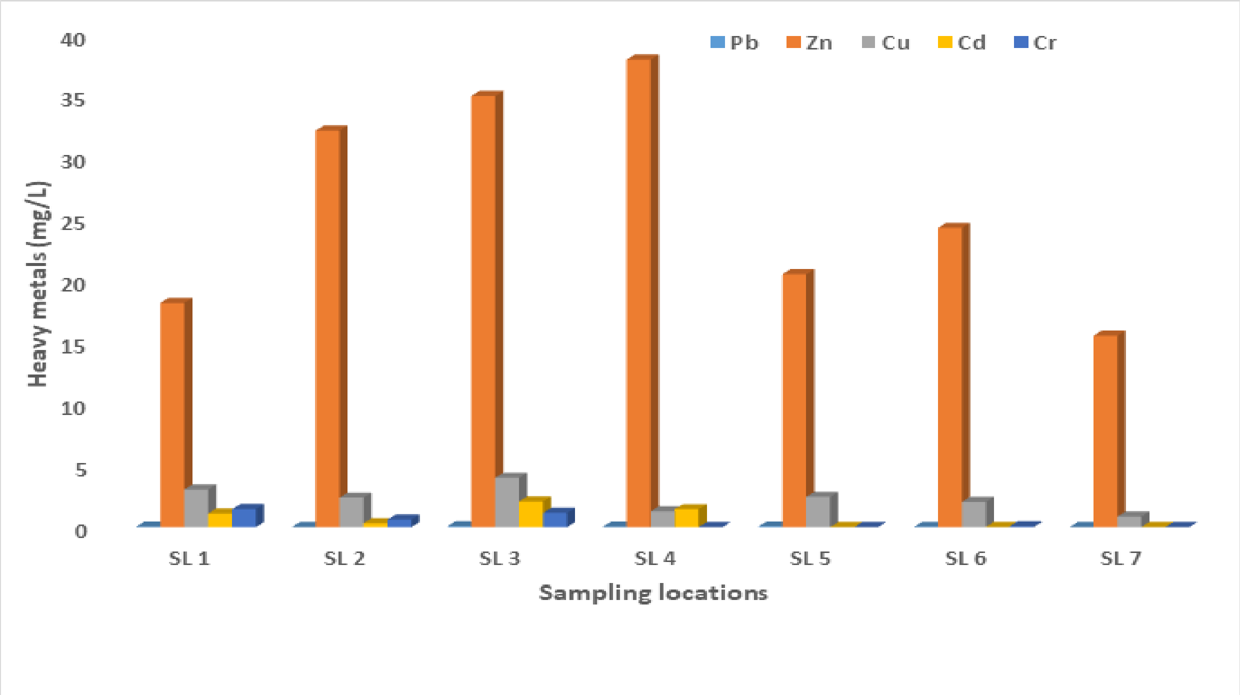

Fig 5 Mean Spatial Variations in Heavy Metals (Pb, Zn, Cu, Cd, Cr) in Water Samples of the Study Area

- Spatial variations were also observed in the levels of physicochemical parameters measured during the study period.
- Mean Water Temperature, pH, Total Alkalinity, and Total Hardness were 28.37 ± 0.87°C, 6.50 ± 0.40, 13.33 ± 1.03mg/L, and 10.83 ± 0.73mg/L respectively at sampling location (SL1), 26.10°C, 5.93, 8.07mg/L and 6.43mg/L at SL2, 28.00°C, 6.33, 7.40mg/L and 5.90mg/L at SL3 and 29.37°C, 6.63, 12.27mg/L and 9.80mg/L at SL4 (Fig 4.1).
- However, their respective mean values were 26.70°C, 7.23, 8.83mg/L and 7.03mg/L at SL5, 28.50°C, 6.20, 8.37mg/L and 6.70mg/L at SL6 and 27.83°C, 7.13, 11.03mg/L and 8.83mg/L at SL7, the control location.

Table 3 Mean Seperation of the Physicochemical Parameters of Borehole Water Samples using Duncan Multiple Range Test (P<0.05)

Parameters	SL1	SL2	SL3	SL4	SL5	SL6	SL7	NSDWQ	WHO(2010)
Temperature (°C)	28.37^{c}	26.10^{a}	28.00^{bc}	29.37^{c}	26.70^{ab}	28.50^{c}	27.83^{bc}	20-30	28-30
pH	6.50^{ab}	5.93^{a}	6.33^{ab}	6.63^{ab}	7.23^{b}	6.20^{ab}	7.13^{b}	6.0-9.0	6.5-8.5
EC (µs/cm)	42.00^{a}	139.00^{c}	57.33^{ab}	102.33^{d}	58.00^{ab}	75.00^{c}	72.33^{bc}	1	0.25
TDS (mg/L)	33.13^{ab}	5.90^{a}	28.83^{ab}	41.13^{ab}	8.37^{a}	65.83^{b}	25.67^{ab}	600	500-1500
TSS (mg/L)	5.77^{cd}	1.33^{ab}	6.77^{d}	3.40^{bc}	0.40^{a}	4.00^{bcd}	4.90^{cd}	500	-
Turbidity (NTU)	2.30^{ab}	4.03^{b}	0.80^{a}	2.67^{ab}	2.37^{ab}	1.73^{ab}	2.30^{ab}	5.00	5.00-10.00
DO (mg/L)	7.23^{ab}	3.70^{ab}	7.87^{b}	4.83^{ab}	7.90^{b}	7.27^{ab}	3.57^{a}	7.50	10-20
Alkalinity (mg/L)	13.33^{b}	8.07^{ab}	7.40^{a}	12.27^{ab}	8.83^{ab}	8.37^{ab}	11.03^{ab}	200	200
COD (mg/L)	7.47^{b}	3.80^{a}	16.17^{d}	5.83^{ab}	7.33^{b}	11.27^{c}	12.90^{cd}	8-10	10
BOD (mg/L)	4.03^{b}	1.44^{a}	1.40^{a}	3.97^{b}	5.83^{c}	1.47^{a}	1.17^{a}	10	1.0-2.0
Mg (mg/L)	0.90^{ab}	0.37^{a}	0.70^{ab}	1.33^{ab}	0.60^{ab}	1.67^{b}	0.93^{ab}	-	0.05
Hardness (mg/L)	10.83^{b}	6.43^{ab}	5.90^{a}	9.80^{ab}	7.03^{ab}	6.70^{ab}	8.83^{ab}	150	100-200
Pb (mg/L)	0.43^{a}	0.00^{a}	0.06^{a}	0.03^{a}	0.05^{a}	0.02^{a}	0.00^{a}	0.01	0.01
Zn (mg/L)	18.17^{a}	32.17^{a}	34.93^{a}	37.90^{a}	20.50^{a}	24.27^{a}	15.50^{a}	3.0	5.0
Cu (mg/L)	3.05^{ab}	2.39^{ab}	4.01^{b}	1.29^{ab}	2.46^{ab}	2.05^{ab}	0.85^{a}	-	1.00-2.00
Cd (mg/L)	1.11^{ab}	0.32^{a}	2.08^{b}	1.45^{ab}	0.00^{a}	0.13^{a}	0.00^{a}	-	0.003
Cr (mg/L)	1.46^{b}	0.60^{ab}	1.15^{b}	0.00^{a}	0.00^{a}	0.07^{a}	0.00^{a}	0.05	0.05

* Values with same superscripts along same row are not significantly different at P<0.05.
* EC = Electrical Conductivity, TDS = Total Dissolved Solids, TSS = Total Suspended Solids, DO = Dissolved Oxygen, COD = Chemical Oxygen Demand, BOD =Biological Oxygen Demand

A post-hock mean separation using the Ducan Multiple Range Test revealed that the observed difference in Water Temperature was between SL1=SL3=SL4=SL6=SL7 AND SL2 (Table 3). The spatial difference in pH was between SL2 and the rest location in EC; was between SL1 and SL2 and SL4 and SL6; in TDS was between SL2 and SL6; and in TSS was between SL5 and SL1 and SL3 and SL4 and SL6 and SL7. The observed difference in Turbidity was between SL3 and the rest locations; in DO was between SL7 and SL5=SL3; and in Total Alkalinity was between SL3 and the rest locations.

However, the observed difference in COD was between SL2 and SL1 and SL3 and SL6; in BOD it was between SL2=SL3=SL6=SL7 and SL1 and SL5; that in Mg ion was between SL2 and SL6; that in Total Hardness was between SL3 and the rest of the location.

For the heavy metals, the observed spatial difference in Cu was between SL7 and the rest of the location, In Cd was between SL2=SL7 and the rest of the location and in Cr was between SL1=SL3 and the rest of the location.

Table 4 Extraction Sums of Squared Loading in Total Variance Explained of the PCA.

Components	Total	% of Variance	Cumulative %
1	3.987	23.454	23.454
2	2.716	15.974	39.428
3	2.502	14.720	54.148
4	2.168	12.751	66.899
5	1.674	9.848	76.747
6	1.137	6.687	83.435

- The rotation maintained the cumulative percentage of variation explained by the extracted components.

Table 5 Rotation Sums of Squared Loading in Total Variance Explained of the PCA.

Components	Total	% of Variance	Cumulative %
1	2.633	15.489	15.489
2	2.580	15.179	30.668
3	2.327	13.688	44.356
4	2.309	13.585	57.942
5	2.302	13.542	71.484
6	2.032	11.951	83.435

The first six Principle Components (PCs) formed the extraction solution. The cumulative percentage (%) revealed that the extracted component explained about 83.44% of the variabilities in the original 17 variables (Table 4). This reduces the complexity of the data set by using these components with only about 16.56% loss of information.

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PC1 contributed about 15.49% variability, PC2 contributed about 15.18% variability, PC3 contributed about 13.69% variability, PC4 contributed about 13.58% variability, PC5 contributed about 13.54% variability, while PC6 contributed 11.95% variability to the cumulative percentage.

Table 6 Correlative (r) Matrix Between Physicochemical Parameters in Borehole Water Samples

	Temperature	pH	EC	TDS	TSS	Turbidity	DO	Alkalinity	COD	BOD	Mg	Hardness	Pb	Zn	Cu	Cd	Cr
Temperature		-0.102	-0.275	0.481*	0.481*	-0.230	-0.148	0.295	0.249	-0.022	0.613**	0.292	-0.250	-0.261	-0.201	0.366	0.081
pH			-0.282	-0.20	-0.130	0.039	0.067	0.142	0.067	0.371	-0.300	0.147	0.176	-0.302	-0/061	-0.445*	-0.388
EC				-0.182	-0.378	0.587**	-0.537*	-0.34	-0.480*	-0.297	-0.121	-0.47	-0.001	0.125	0.013	0.370	0.103
TDS					0.139	-0.562**	-0.139	0.185	0.139	0.23	0.015	0.197	-0.259	0.195	0.191	-0.093	-0.323
TSS						-0.176	0.094	0.372	0.631**	-0.407	0.274	0.373	-0.282	-0.456*	-0.326	-0.460*	-0.011
Turbidity							-0.211	0.220	-0.523*	-0.57	0.156	0.208	0.454*	-0.340	-0.391	0.199	0.324
DO								-0.386	0.077	0.264	0.119	-0.376	0.101	-0.299	-0.092	-0.180	-0.040
Alkalinity									-0.064	0.261	0.034	1.000**	-0.023	-0.067	-0.072	-0.045	-0.018
COD										-0.462*	0.130	-0.069	-0.212	-0.211	-0.185	-0.460*	-0.342
BOD											-0.255	0.267	0.277	0.140	0.301	0.094	0.118
Mg												0.022	-0.037	-0.294	-0.73*	-0.147	0.038
Hardness													-0.030	-0.064	-0.64	-0.047	-0.018
Pb														0.017	0.006	0.439*	0.355
Zn															0.574**	0.569**	-0.070
Cu																0.443*	0.262
Cd																	0.502*
Cr																	

- The relationships existing between the physicochemical parameters as explored with the Pearson's Correlation Coefficient (r) are shown in Table 6
- At $P<0.05$, Water Temperature correlated positively with TDS (r=0.481) and TSS (r=0.481) while pH correlated negatively with Cd (r= -0.445). EC correlated negatively with DO (r= -0.537) and COD (r= -0.480), while TSS correlated negatively with Zn (r= -0.456), and Cd (r= -0.467). Turbidity correlated positively with Pb (r= 0.454), and negatively with COD (r= -0.523). COD correlated negatively with BOD (r= -0.463) and Cd (r= -0.460) while Mg ion correlated negatively with Cu (r= -0.473). Pb correlated positively with Cd (r= -0.439), Cu correlated positively with Cd (r= 0.443) while Cd correlated positively with Cr (r= 0.502).
- At $P<0.01$ Water Temperature correlated positively with Mg ion (r= 0.613), EC correlated with Turbidity (r= 0.587) while TDS correlated negatively with Turbidity (r= 0.562).
- TSS correlated positively with COD (r= 0.631), Total Alkalinity correlated positively with Total Hardness (r= 1.000) while Zn correlated positively with Cu ions (r= 0.574).

Table 7 Water Quality Index

	SAMPLING LOCATIONS						
	SL1	**SL2**	**SL3**	**SL4**	**SL5**	**SL6**	**SL7**
POLLUTION INDEX	58	44	43	42	61	43	35

- The overall Water Quality Index shows that the groundwater in the area is not potable, and must be properly treated before use.
- The Water Quality Index calculated in the groundwater of Ikwo LGA of Ebonyi State during the study period in the selected Sampling Location (SL).
- SL1 was 58, SL2 was 44, SL3 was 43, while SL4, SL5, SL6 and SL7 had 42, 61, 43, and 35 respectively.

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V. DISCUSSION

Temperature was highest in SL4 (29.37) followed by SL6 (28.50), SL1 (28.37), SL3 (28.00), SL7 (27.83), SL5 (26.70) and lowest in SL2 (26.10) as shown in Table 4.2. The standard recommendation of temperature in water is 20-30 for NSDWQ and 28-30°C by WHO. There was no significant difference ($P<0.05$) in the temperature of water samples collected from the sampling locations.

The difference in temperatures observed across the locations studied could be due to variations in ambient at the time of sampling and analysis (Ayandele *et al*, 2015). The high temperature values obtained in SL4 maybe as a result of developmental, industrial and agricultural activities going on in the area

pH was highest in SL5 (7.23) followed by SL7 (7.13), SL4 (6.63), SL1 (6.50), SL3 (6.33), SL6 (6.20) and lowest in SL2 (5.93). There was no significant difference ($P<0.05$) in pH values of the samples. The standard recommendation of pH in water is 6.0-9.0 for NSDWQ (Nigerian Standard for Drinking Water Quality, NSDWQ 2007) and 6.50-8.50 by WHO (2011).

Disparities in pH values can be attributed to changes in living and non-living processes like respiration, photosynthesis, temperature exposure to air, industrial waste disposal, Geology and mineral content of a catchment area, acid mine drainage, Agricultural runoff, carbon dioxide concentration in the atmosphere and accumulation and decomposition of organic debris in the water producing weak carbonic acids (Sibanda *et al* 2014). The samples in the study area had a pH within the recommended limits of NSDWQ and WHO for human use. This finding is in agreement with Iroha *et al* (2020), Odikamnoro *et al* (2020).

With the pH of the water samples within acceptable limit, the water may pose no serious health risk to users who use the water for recreational, agricultural and domestic uses.

Electrical conductivity was highest in SL2 (139.00) followed by SL4 (102.33), SL6 (75.00), SL7 (72.33), SL5 (58.00), SL3 (57.33). The lowest is SL1 (42.00) as shown in Table 3. The standard recommendation limit of electrical conductivity in water is 1ms/L as given by NSDWQ (2007) and 0.25ms/L by WHO (Yasin *et al*, 2015). The electrical conductivity of the samples analyzed showed no significant difference ($p<0.05$). The difference in water conductivity may be due to varying climatic factors, high use of agrochemicals, the general make-up of the water and vegetative factors. The conductivity of water increases as the concentrations of ions in water bodies increases. Malla *et al*, (2015) stated that conductivity can be vital in the measurement of the ionic condition of water which is greatly affected by temperature, concentration of impurities and mobility of ions. Water samples with high conductivity increases corrosive nature of water (Patil, 2012).

Total Dissolved Solids was highest in SL6 (65.83), followed by SL4 (41.13), SL1 (33.13), SL3 (28.83), SL7 (25.67), SL5 (8.37) and the least is SL2 (5.90) as shown in Table 3. There was a significant difference ($p<0.05$) in the Total Dissolved solid of water samples during the study period. The standard recommended limit of Total Dissolved Solid in water is $600mgL^{-1}$ as given by NSDWQ (2007) and $500mgL^{-1}$ by WHO. Total Dissolved Solids affect the taste and acceptability of water if present at levels beyond the standard recommended limits. The use of water with a high Total Dissolved Solids could result to the deposit of unwanted dissolved mineral in the body and on Agricultural farms after evaporation.

High Total Dissolved Solids affect the clarity, color and taste of water thereby indicating the presence of toxic minerals and micro-organisms (USEPA, 1999). However, the Total Dissolved Solids found in the water samples could be considered to fall within the standard recommended by NSDWQ and WHO for drinking water.

Total Suspended Solid, there was a significant difference ($p<0.05$) in the level of Total Suspended Solids during the study area period. The Suspended Solid was highest in SL3 (6.77), followed by SL1 (5.77), SL7 (4.90), SL6 (4.00), SL4 (3.40), SL2 (1.33) and SL5 (0.40). The standard recommended limit of TSS in water as given by NSDWQ is 500; hence, a part from SL3 (6.77) and SL1 (5.77) that exceeded the standard recommended limit, SL7, SL6, SL4, SL2, and SL5 did not exceed the recommended level and so accepted. Harrison, (2007) stated that higher TSS reduces water clarity which could contribute to reduced photosynthetic activities and possibly lead to increase in water temperature. It plays a major role in pathogen transmissions (Iroha *et al*, 2020).

Turbidity was highest in SL2 (4.03), followed by SL4 (2.67), SL5 (2.37), SL1 and SL7 both have values of 2.30. The least are SL6 and SL3 with values of 1.73 and 0.80 respectively as shown in Table 3. The standard recommended limit of Turbidity in water is 5.00 by NSDWQ and 5.00-10.00 by WHO. The Turbidity profile of the analyzed water samples did not vary significantly ($p<0.05$) throughout the study duration. Water samples with high Turbidity cloudy appearance and is usually not suitable for drinking purposes. A higher value of Turbidity reduces the aquatic lives. This situation can also affect disinfection and provides medium for microbial growth and causes symptoms such as nausea, cramps, diarrhea and associated headache (Akoto *et al*, 2007). However, the values of the water samples all fell within the limits provided by NSDWQ and WHO for Turbidity in drinking water.

Dissolved Oxygen was highest in SL5 (7.90), followed by SL3 (7.87), SL6 (7.27), SL1 (7.23), SL4 (4.83), SL2 (3.70) and SL7 (3.57). There was no significant difference in Dissolved Oxygen concentration among the water samples. The standard regulatory limit for DO in water is 7.50 and 1.00-2.00 as given by NSDWQ and WHO respectively. Apart from SL5 (7.90) and SL3 (7.87); the water samples in the other locations met the NSDWQ

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standard for DO in water. Whereas, based on the limit set by WHO (1.00-2.00), all the water samples did not meet the safe limit for DO in water samples. Dissolved Oxygen is known to affect such attributes as growth, survival, distribution, behavior and physiology of aquatic organisms.

Alkalinity was highest in SL1 (13.33), followed by SL4 (12.27), SL7 (11.03), SL5 (8.83), SL6 (8.37), SL2 (8.07) with the least been SL3 (7.40) as shown in Table 4.2. The results showed no significant difference ($p<0.05$) throughout the study period. The standard recommended limits for Alkalinity in water as given by NSDWQ and WHO is 200mgL^{-1} respectively. Water with high Alkalinity could cause corrosion, highly Alkaline water is foul-tasting and leads to scale formation (Shrestha *et al*, 2018). The use of water with high Alkalinity level could result in diseases like Gastro intestinal illness such as stomach cramps, abdominal distress and diarrhea (Iroha *et al*. 2020). However, the water samples collected from different locations are within the recommended safe limits given by NSDWQ and WHO (2010).

Chemical Oxygen Demand was in the following order: SL3 (16.17) > SL7 (12.90) > SL6 (11.27) > SL1 (7.47) > SL5 (7.33) > SL4 (5.83) > SL2 (3.80) as shown in Table 4.2. The standard recommended limit of COD in water is 8-10mgL^{-1} given by NSDWQ (2007) and 10mgL^{-1} by WHO, (2011). There was no significant difference in the values obtained. The value of COD in the samples collected from SL5 (7.33), SL1 (7.47), SL4 (5.83) and SL2 (3.80) all fall within the regulatory limit provided by NSDWQ and WHO, whereas SL3 (16.17), SL7 (12.90) and SL6 (11.27) were all above the regulatory safe limit for COD as given by NSDWQ and WHO. High levels of COD are an indication of lack of oxygen and can result to death of aquatic organisms and poor growth of aquatic plants.

Biological Oxygen Demand (BOD) was highest in SL5 (5.83) followed by SL1 (4.03), SL4 (3.97), SL5 (1.47), SL2 (1.44), SL3 (1.40) and SL7 (1.17). There was no significant difference ($p<0.05$) in BOD levels among the water samples at the different locations during the study duration. The standard regulatory limit as given by NSDWQ and WHO is 10mgL^{-1} and 1.0 2.0mgL^{-1} respectively. High BOD in water is an indication of pollution and contamination. Water samples with the BOD less than 4.0mg/L^{-1} are considered clean (Rajini *et al*, 2010).

Total Hardness was highest in SL1 (10.83), followed by SL4 (9.80), SL7 (8.83), SL5 (7.03), SL6 (6.70), SL2 (6.42) and SL3 (5.90). There was a significant difference ($p<0.05$) in Total Hardness of the samples analyzed. The standard recommended limits of Total Hardness in water are 150mg/L as given by NSDWQ and 100-250mgL^{-1} by WHO. High Total Hardness is due to the concentration of Calcium and Magnesium ions which are the principal cations impacting hardness. Water with a high level of hardness could cause serious problems in domestic, agricultural and industrial settings (Perkin 2016). From the result, it could be observed that the values fell within the regulatory safe limit.

Lead (Pb) was highest in SL1 (0.43) followed by SL3 (0.06), SL5 (0.05), SL4 (0.03), SL6 (0.02) and 0.00 in SL2 and SL7 respectively. The standard recommended limit of Pb in water is 0.01mgL^{-1} as given by NSDWQ and WHO. Lead is among the prevalent heavy metals contaminants. Apart from SL2 and SL7 with values 0.00, every other sample exceeded the standard recommended limit for Pb given by NSDWQ and WHO.

Zinc (Zn) was highest in SL4 (37.90) followed by SL3 (34.93), SL2 (32.17), SL6 (24.27), SL5 (20.50), SL1 (18.17), and SL7 (15.50) as shown in Table 4. No significant difference ($p<0.05$) was observed in the concentration of Zinc in water samples from the study locations. The standard recommended limit of Zinc in water is 3.0mgL^{-1} as given by NSDWQ and 5.0mgL^{-1} by WHO. High concentration of Zinc can cause a bitter, undesirable taste and forms an opalescent and greasy film especially when hot (WHO 2006). The presence of these Heavy metals in excess indicates danger and drinking such water without treatment may lead to liver and kidney damages, asthma and permanent disabilities (Iroha *et al*, 2020). Accordingly, the values of Zinc concentration obtained in the various locations exceeded the standard regulatory limits for drinking water as given by NSDWQ and WHO.

Copper (Cu) was highest in water samples from SL3 (4.01) followed by SL1 (3.05), SL5 (2.46), SL2 (2.39), SL6 (2.05), SL4 (1.29) and SL7 (0.85) as shown in Table 4.2. Aside in SL4 and SL7, none of the values for Copper are within the safe limit as recommended by WHO.

Cu is a potential health hazard that causes various health problems when exposed to it at levels above the permissible value. Short periods of exposure can cause gastro intestinal disturbance including nausea, diarrhea, dizziness and vomiting while use of water whose copper exceeds the maximum limit over many years causes liver or kidney damage (World Health Organization 2004, Chinwe *et al*, 2010, Zaira *et al*, 2011).

Cadmium (Cd), the levels of Cadmium in the water samples collected from the various locations and in the following order: SL3 (2.08) > SL4 (1.45) > SL1 (1.11) > SL2 (0.23) > SL6 (0.15), SL5 and SL7 have 0.00 Cd levels; as shown in Table 4.2. The standard recommended limit of Cd in water is 0.03mgL^{-1} as given by WHO. This shows that the water samples in the study locations contain high and unacceptable level of Cd. Cadmium find their way into the water through industrial and agricultural discharges. Exposure to high levels of Cadmium produces harmful effects on the cellular architectures and metabolism in a variety of body tissues including testes, liver, pancreas, kidney and bone (Al Motabagani, 2002, Jarup and Alfven 2004; Udu Ibiam *et al*, 2013).

Chromium (Cr) was highest in SL1 (1.46) followed by SL3 (1.15), SL2 (0.60), SL6 (0.07) and 0.00 for SL4, SL5 and SL7 as shown in Table 4.2. The value of Cr in the study locations show no significant difference among the water

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samples collected. The standard regulatory limit as given by NSDWQ and WHO is 0.05mgL^{-1}

Seasonal variations in the physicochemical parameters, this highlights the variations of the different water quality parameters of the samples analyzed. The spatial variations were observed; the temperature values ranged between 27.36 ± 0.39°c in wet season to 28.37 ± 0.33°c in dry season. The pH values ranges between 6.51 ± 0.12 in wet season to 6.63 ± 0.28 in dry season.

Electrical Conductivity (EC) values showed 80.45 ± 11.75 in wet season to 75.30 ± 7.61 in dry season while Total Dissolved Solids (TDS) showed 29.25 ± 6.99 in wet season and 30.48 ± 11.45 in dry season. All the variables except EC showed a slight increase in the values from wet to dry season. On the other hand, EC shows a slight decrease in value from wet to dry season. All studied parameters showed significant temporal difference and partial spatial variability. The seasonal changes in the water quality could be as a result of torpidity, organic pollution, mining activities, oxide related processes, erosion as well as other anthropogenic activities.

➢ *Water Quality Index*

The Water Quality Pollution Index in the study area location is as follows: SL1 (58), SL2 (44), SL3 (43), SL4 (42), SL5 (61), SL6 (43), and SL7 (35) as shown in Table 4.6. This shows that the area with the highest level of water pollution is SL5 (61) followed by SL1 (58), SL2 (44), SL3 (43), SL4 (42), the area with the lowest level of water pollution is SL7 (35). The overall Water Quality Index is not potable, and must be properly treated before use.

VI. CONCLUSION

The study investigates the concentrations of the physicochemical parameters and heavy metals in the groundwater in some selected communities in close proximity of the mining sites in Ikwo LGA of Ebonyi State-Nigeria.

➢ *From the Study, it was Concluded that:*

- The physicochemical parameters; Temperature, pH, TDS, TSS, Turbidity, DO, Alkalinity, COD, BOD and Total Hardness were all within the recommended limits as established by NSDWQ and WHO. This indicates that the above physicochemical parameters are not the major source of groundwater contaminants in the selected communities studied in Ikwo LGA;
- The heavy metals Pb, Zn, Cu, Cd, and Cr analyzed in the water samples collected from the various locations were of values higher than the recommended safe limits as established by NSDWQ and WHO. This implies that the water samples in the various locations were all contaminated by the heavy metals analyzed as it poses significant risk to human and animal health. This indicates that mining activities are strong source of contaminants to groundwater in Ikwo LGA;
- Some parameters studied showed significant spatial and temporal variability/changes in water quality;
- Results of the Water Quality Index shows that the overall groundwater quality is not potable as it contains high levels of trace metals.

RECOMMENDATIONS

➢ *Based on the Results of the Study, the Following Recommendations are Considered:*

- Drinking water in the vicinity or the area around the mining site should be properly treated before consumption and other uses. The treatment process could either be by boiling or sedimentation for proper removal of major trace metals contained in the water;
- Adequate monitoring of heavy metals and other possible potential toxic contaminants in groundwater in the study location is strongly advocated as this will help local authorities set new guidelines for various contaminants that affect water quality;
- Educative and awareness programs should be organized by the Government agencies and researchers to create awareness on the potential danger associated with consumption of affected water;
- Mining sites should not be located within the proximity of residential areas, or where the raw materials are domicile at a certain location, of which the populace should be informed of the inherent danger of living in such area, and if need be residents should be relocated from such area;
- It is also necessary to monitor the quality of water and strict quality control measures should be strengthened to ensure the effective treatment of drinking water

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