Assessment of the Impact of Mining Activities on Water Quality in Kujama, Southern Kaduna - Nigeria

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A b s t r a c t

Geochemical Assessment of the impact of Rock Quarrying on Groundwater quality in Kujama area of Kaduna was carried out. The Quarry falls within the basement complex of North Central Nigeria underlined by the Migmatites gneiss complex. Outcrops of biotite granite and diorites were mapped as the main lithological units. Fourteen (14) water samples were collected from hand dug wells and boreholes within the study area using plastic bottles, thoroughly rinsed with the water to sampled. Physical parameters which include pH, temperature, TDS and FC were measured in-situ. The pH ranges from 6.2 – 9.3, Temperature $28^0C – 33^0C$, while EC is from 0.05 – 4.3 Us/m suggesting low mineralization of the groundwater. Hydrogeochemstry reveal average concentrations of Ca as 12.96, Mg 1.53, K 12.38mg/L and Na 27.4 mg/L. The relative high value of Na suggests dissolution of Sodic-rich feldspar by groundwater. Average concentration of Anions indicates CL (233.05 mg/L), Sulfate (13.18mg/L) Bicarbonate (HCO3) range 0.4 – 4.6 mg/L; while Nitrate is 0.448mg/L suggesting pollution free in terms of anion and human discharge. Heavy metals levels of Fe, Cd, Pb, Cr, Ni were found too potentially high. The Piper diagram classified the water as $Na^+ - K^+ - Cl^- - SO_4^2+$ type based on the major cations and anions. The overall quality of the groundwater in the area is considered to be poor based on the Environment Water Quality Index (CCME WQI) used in this study.

**Keywords:** *Geochemical Assessment and Mining activities*

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Background to the Study

In general, the natural environment is composed of land/soil, water, and air. The major challenge is the release of industrial waste into any one of these components or the excessive modification of one of these components of the environment resulting in pollution the presence of these pollutants affects the natural balance of the environment which in turn affects the functionality of the environment (air, land and water) thus affecting plants, animals and human life. The overall objective of this work is assessment of the impact of mining activities on water quality in Kujama, Kaduna State, using the physicochemical properties of the water samples and comparing these values with the acceptable standards in Nigeria and the world. The most significant impact of mining activities is its effect on the water quality and availability of water resources within the mining area. The degree of impact depends upon many factors, in particular the mining type and method, and the operation size. Mining activities in the past have generated uncontrolled waste and tailings deposit, and today they are a major source of acid mine drainage (Navarro-Torres, *et al* 2011).

Mining activity mainly disturbs and changes topography of land which ultimately affects the hydrogeological conditions (Baba and Gungor, 2002). Negative water impact could be described as those that lead to a decline in the quality of natural water to the extent that it is not suitable for use by man or other forms to live. The impacts degrade water by alteration of biological, physical and chemical properties of water (Magombedze, 2006). Previous research associates the presence of chemical pollutants in water to the extraction industry since the extraction of mineral ores affects the hydrology of the water catchment area. Research has documented a relationship between mining activities and water pollution (Aigbedion and Iyayi, 2007). It is argued that water pollution occurs when metals contained in the excavated rock comes into contact with water. Mining also affects water bodies when seepage from tailings and waste rock impoundments come into contact with the water bodies.

According to Miranda and Sauer (2010), water related impacts can arise at nearly every stage in the mining process and could have significant impact on groundwater resources with potential for generation of acid mine drainage. The mining process and activities such as drilling, extraction, beneficiation, dewatering of the subject area: leaching from the waste rock piles and tailing dams cause changes in the water quality and quantity. Water contamination also occurs when the pollutants are directly introduced to the water bodies by the miners. The discharge seeps through the waste rock piles, tailing dumps and country rocks, dissolving metals along its flow path, eventually finding its way to water bodies (Vermeulen and Bester, 2010).
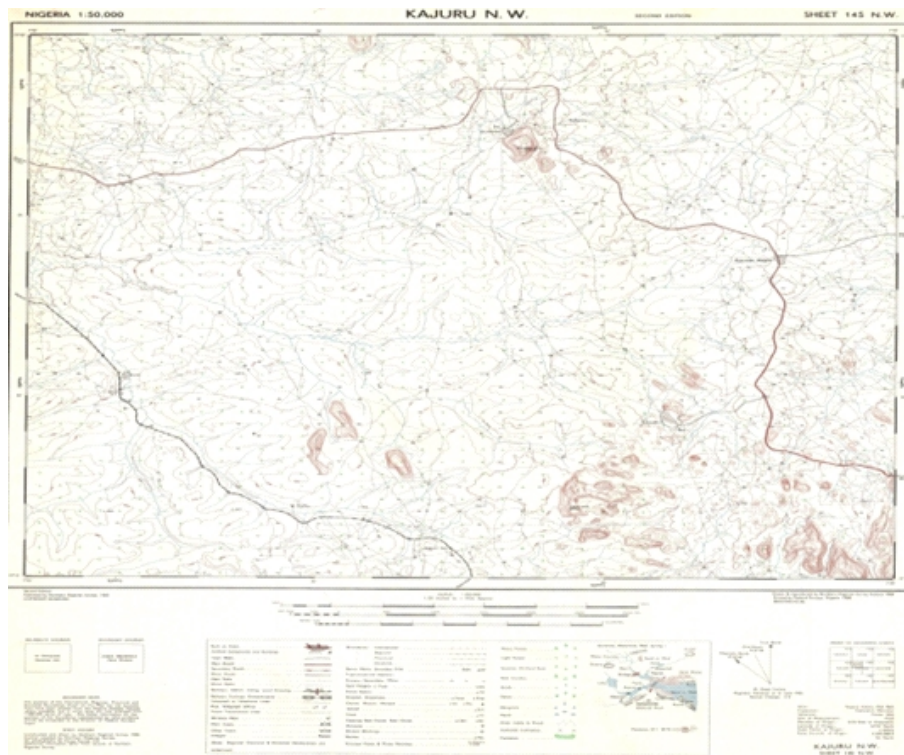
Figure 1: Topographical map showing Kaduna State (sheet 145 NW)

Location and Extent of Kaduna State

Kaduna State occupies almost the entire mid-central portion of the northern parts of Nigeria. The state is located globally between latitudes $9^0 03'N$ to $11^0 32'N$ and longitudes $6^0 05'E$ to $8^0 38'E$. The total land mass occupied by the state is estimated at 46,053sqkm which is about 5% of the total land area of Nigeria. It shares boundaries southward with the Federal capital Territory (FCT) and Nasarawa state, eastward and with Plateau states, and westward with Niger State, northward it shares with Kano state (Figure 1)

Literature

Though studies have been conducted on some aspects of the geology and hydrogeology of Kujama by several researchers, very little data are available on the quality of water within the study area. The previous work done is based on work carried out locally and abroad on the effect of quarrying on water quality. Natural water resources are subjected to pollution comprising of organic and inorganic constituents. The stone quarrying industry greatly contributes as a major source of water pollution which eventually becomes hazardous to various environmental attributes. The environmental impact of mining/quarry activities is very complex and it not only destroys the existing vegetation but also affects the surface and groundwater quality. The wastes from industry like dusts, solutions, and variety of minerals such as tailing containing trace and toxic elements pollute water environment.

Hire Khan et al., (2002) studied the groundwater quality of iron-ore mining area in Gao and reported that the groundwater in mining area has low pH due to pyretic rocks at the bottom. In few cases of accumulation of water in the pits, the water becomes turbid leading to the contamination of groundwater. Offodile (1992) did a case study of Nigeria and reported that tropical countries like Nigeria, high temperature partially account for the water dissolving more minerals. Elements like lead, copper, cadmium, chromium are regarded as toxic elements. Therefore, their presence in water above permissible limits stipulated by WHO (2021) and NAFDAC which are peculiar to Nigeria can affect the central nervous system.

Barnes and clarke (1964), in their work on the geochemistry of groundwater in mine drainage problems concluded that mines can produce a variety of groundwater pollution problems. Enrich and Merritt (1969), worked on the effects of mine drainage on groundwater while et al (972), worked on effects of early day mining operations on present day water quality. They all concluded that the pollution depends on the material being extracted and the milling process; coal, uranium and phospate mines are major contributors, while metallic ores for production of iron, copper, zinc and lead are also important.

Klusman and Edward (1977) observed that groundwater moving through mineralized rock may have a higher concentration of certain heavy metals than groundwater movement through non-mineralized districts. Kashef (1986), in his book 'Groundwater Engineering" said changes in groundwater quality are due to varying quality of the infiltrated precipitation, the reaction of groundwater to its environment, the length of the flow path, the residence time of water in a certain location, vegetation types and human- determined features. He presented changes in chemical quality to be more intense in shallow aquifers than in deeper ones because shallow aquifers are more easily affected by seasonal variations and human activities.

Idris et al (2014) worked on the environmental impact on surface and groundwater pollution from mining activities in Ikpeshi, Edo state, Nigeria. It was observed that pollutants found their way to the ground and surface water system through path ways such as fracture zones and pore spaces into the aquifer zone, through run-off, infiltration and percolations thereby contaminating the potable water.

Materials and Method
Materials
The field equipment used during geological field work and sampling programme include; geological hammer, geological compass, sampling bags, masking tape, permanent marker, water sampling bottles (polyethylene), Global Positioning System (GPS), and water kit technology (for measuring water physical parameters).

Sampling and Analytic Method
Fourteen (14) water samples were collected from different optimum sampling locations for analysis of heavy metals in the groundwater in the study area. Measurements of physical water parameters including pH, temperature, Total Dissolved Solids (TDS), and electrical

conductivity (EC) were carried out in-situ on each sample. In addition, sampling procedure described in Willis (2008) and Todd (1959) were adopted for the collection of water samples in the area. Apart from the heavy metal analysis, major cations (Mg^{2+}, Ca^{2+}, Na^+, and K^+) and anions (SO_4^{2-}, Cl^- and HCO_3^-) that constitute the bulk chemistry of the water were also determined in order to characterize the groundwater based on the water-rock interaction. The heavy metals analysed for each sample include iron (Fe), manganese (Mn), chromium (Cr), cadmium (Cd), zinc (Zn), lead (Pb), and nickel (Ni).

Water samples were collected from hand pump and motorized boreholes after minutes of constant pumping and hand dug wells using bailers. Plastic polyethylene bottles used were thoroughly rinsed with the water to be sampled. Each sampling bottled was labeled and precise sampling point was recorded using global positioning system (GPS) for reference purposes. The samples were carefully stored in the sampling container and transported to the laboratory while ensuring that they were not contaminated. The standard procedure for the chemical analysis using AAS and Flame Photometry were adhered in the conduct of elemental determination in the Chemical Laboratory at Center for Energy Research, Zaria.

Rock sampling was done based on the outcrop exposures and freshness of the individual rock unit following sampling procedure prescribed by Angela (2010). The geological map of the area was developed based on the rock samples collected from the field. QGIS version 3.28.8 was used for modeling of the derived data into the various illustrations provided in the work such as spatial hadrochemical map of each heavy metal concentration and geological map of the area. A specialized excel template was used to generate a Piper and Gibb's diagrams.

Results and Discussion
Geology
The result of geological mapping reveals that biotite granite and diorite are the main lithological units in the area (figure). The biotite granite dominates the area and occurs in different forms such as inselberg, whaleback and boulders. The outcrop exposures are mostly weathered and eroded. Outcrops of diorite occur mostly as intrusions within the biotite granites. Both rocks exhibited fractures, pegmatites and quartz veins in various degrees. The measurements of strike and dip from joints and other structural features indicated a general trend of NNW-SSE direction which points to the possible trend of mineralization in the study area (figure).
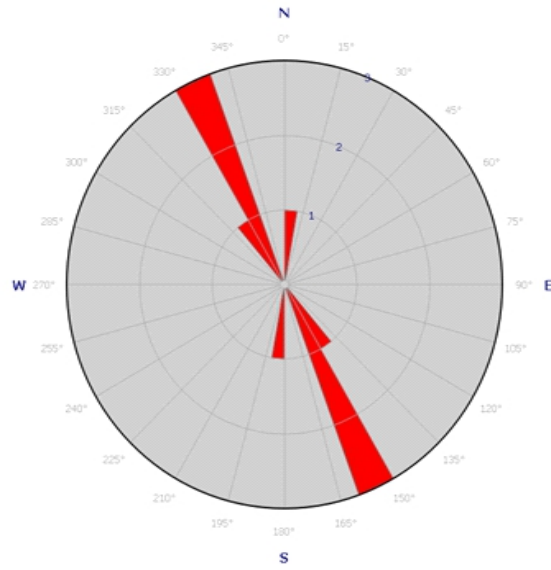
Figure 2: Rose diagram of joints showing NNE-SSW as the dominant orientation
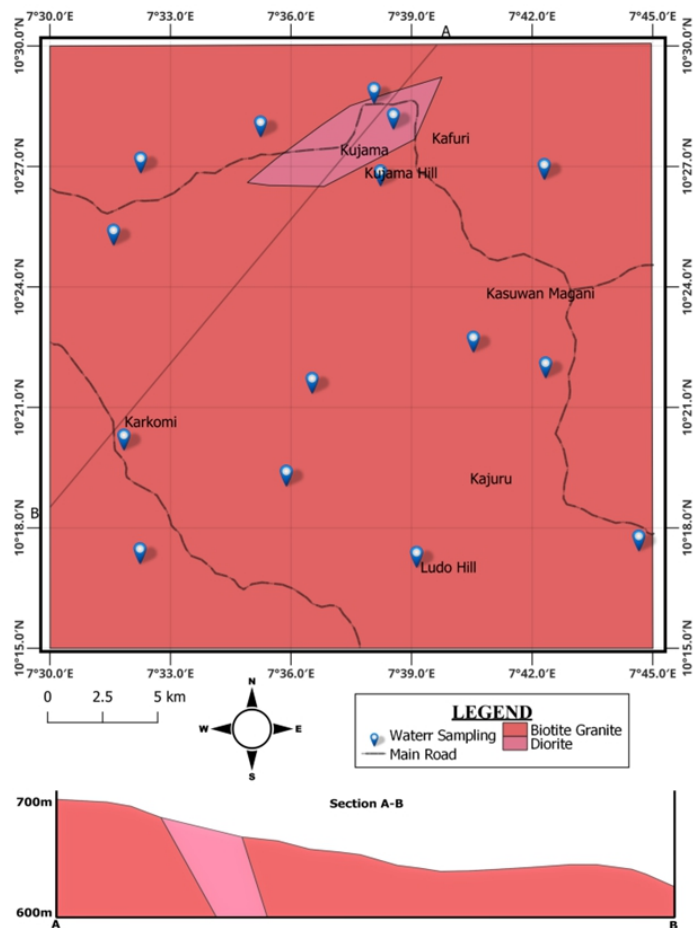
Figure 3: Geological map of the study area showing water sampling points

Groundwater Composition
Physical Parameters
Table 1 presents the results of the physico-chemical parameters of the water samples collected from the study area. The pH values range from 6.2 to 9.3 with a mean of 7.19 indicating slightly both acidic and basic character (Todd, 1959). Measured values for temperature in all the water samples vary from 28.2° to 33.1° with an average of 29.97°. The electrical conductivity of the water samples appears to be infinitesimal which range from 0.05 to 4.3 with an average of 0.66µs/cm. This, however, suggests low mineralization of the groundwater in the area. Although total dissolved solids (TDS) are closely related to electrical conductivity (EC) because both parameters point to the dissolved substances in water but TDS values (1029 to 1 with a mean of 258.2 mg/l) of the water samples from the study area appeared to be higher compared to the values of EC.

Cation Chemistry
The chemical components composed of cations are presented in table 1. The results show highest concentration of calcium of about 73.902 to a minimum of 0.048 with an average value of 12.96 mg/l. The ranges of Magnesium are 2.745 to 0.29 averaging about 1.53 mg/l. Potassium values are varied and range from 35 to 2.4 with a mean value of 12.38 mg/l. Sodium, on the other hand, varied from 136 to 2.9 recording average value of 27.4 mg/l. In particular, based on the average values of the major cations present in the water samples, sodium appears to be the dominant ion which indicates the dissolution of sodic-rich feldspar by groundwater.

Table 1: Analytical values of groundwater samples in the study area.

Sample ID	Physical Parameters				Major Cations				Major Anions			
	pH	Temp (°C)	EC (µs/cm)	TDS (mg/l)	Ca^{+2} (mg/l)	Mg^{+2} (mg/l)	K^+ (mg/l)	Na^+ (mg/l)	SO_4^{-2} (mg/l)	Cl^- (mg/l)	HCO_3^- (mg/l)	NO_3^- (mg/l)
SA	8.3	29.4	1.38	1029	49.86	2.607	12.8	42.6	10.344	488.874	1.8	0.448
SB	8.7	28.1	4.3	1	73.902	2.745	24.1	136	7.523	1523.303	0.6	0.294
SC	9.3	30	0.48	345	13.09	2.35	9.3	26.5	3.997	170.043175	2.4	0.084
SD	6.5	28.8	0.05	53	0.048	1.44	7	10.6	4.467	17.71283073	1.4	0.112
SE	6.8	28.2	0.32	231	3.369	1.651	11	15.4	3.527	113.3621167	0.8	0.098
SF	6.3	29.3	0.05	46	1.186	0.301	35	2.9	4.702	17.71283073	2.2	0.098
SG	6.6	30.1	0.15	112	0.175	0.884	4	12.5	4.467	53.1384922	1	0.098
SH	6.2	29.1	0.13	100	0.776	0.881	2.4	9.4	5.878	46.0533599	0.4	0.154
SI	8.2	33.1	0.88	633	26.119	2.661	32.5	35	4.467	311.7458209	4.6	0.154
SJ	7	29.6	0.19	138	0.713	0.644	5	19.6	3.291	67.30875678	0.6	0.112
SK	6.6	28.8	0.11	84	1.347	0.29	4.2	11.1	3.056	38.96822761	1.4	0.28
SL	6.8	29.3	0.74	528	9.4	2.395	15	40.2	3.291	262.1498948	1	0.126
SM	6.3	32.7	0.19	138	0.646	0.582	6.5	15.1	61.361	67.30875678	1	0.238
SN	7.1	33.1	0.24	177	0.777	2.036	4.5	12.8	64.182	85.02158751	2	0.273

Anion Chemistry
The major anions analyzed in this work are presented in the table above and consist of sulfate, chloride, nitrate, and bicarbonate. Of these ions, chloride constitutes the highest concentration which varies from 1523.303 to 17.713 with an average value of 233.05 mg/l. Sulfate values varied from 64.182 to 3.056 mg/l (with average of 13.18 mg/l). Bicarbonate (HCO_3) ranges from 4.6 to 0.4 mg/l. Nitrate concentrations are less with about 0.448 mg/l

being the highest recorded in sample SA and the lowest concentration of about 0.098 observed in three samples (SE, SF, and SG). This indicates that the groundwater in the study area is pollution-free in terms of animal excrements and plant debris (Todd, 1959). On the average, chloride concentration dominates the rest of the anions.

Hydrochemical Facies

The major cations and anions discussed above constitute about 99% composition of natural waters and can be used to understand the hydrochemical facies of water by portraying their composition on a Piper (1994) diagram. The chemistry of natural water is best displayed on a piper diagram because multiple samples can be shown. Both cations and anions are presented on either triangle at the base and their combination is displayed on the diamond plot at the center. In general, water can be classified as: (1) Ca^{2+}–Mg^{2+}–Cl^--$SO4^{2-}$, (2) Na^+–K^+–Cl^-–SO_4^{2-}, (3) Na^+–K^+–HCO_3^-, and (4) Ca^{2+}–Mg^{2+}–HCO_3^-. The results of the chemical constituents of the water samples are portrayed in the Piper diagram (figure).
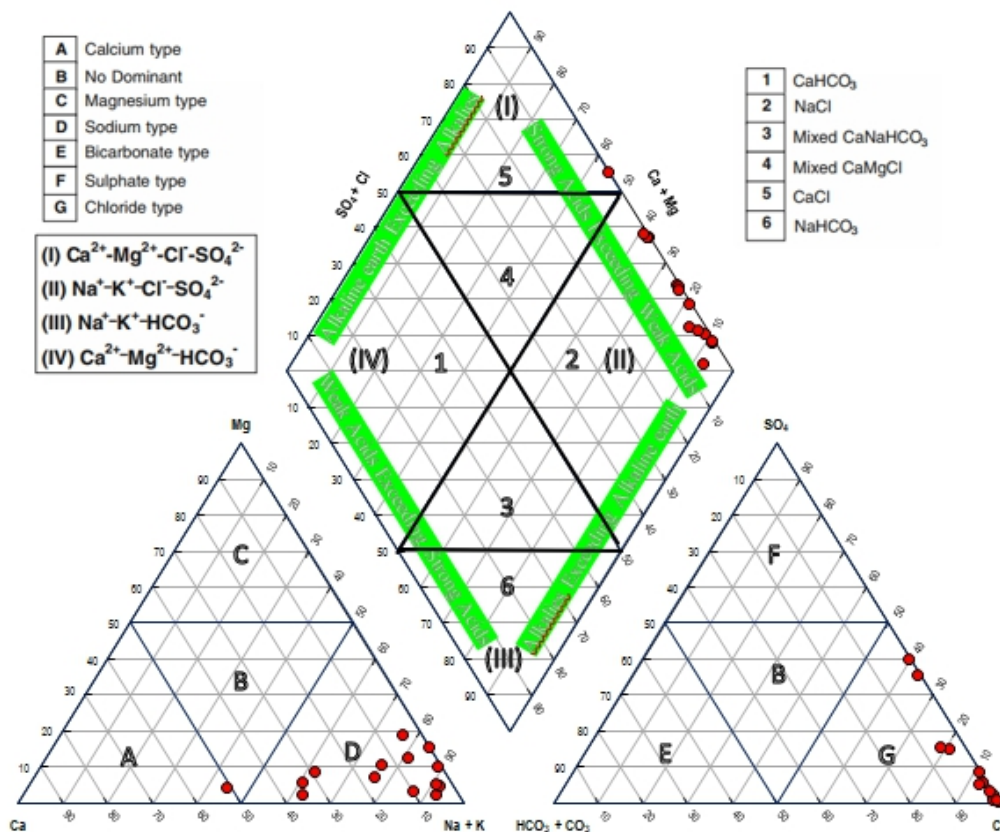

Figure 4: Piper diagram for water samples

Figure (piper) shows all the water samples collected from the study area. As can be seen, majority of the water samples fall within sodium and chloride (NaCl) type based on the

dominant ions. Furthermore, the water belongs to Na^+–K^+–Cl^-–SO_4^{2-} group with the exception of one sample (SB) which belongs to Ca^{2+}–Mg^{2+}–Cl^--$SO4^{2-}$. The table below further explains the water specie based on the illustration in the Piper diagram.

Table 2: Characterization of the water samples in the study area based on hydrochemical facies displayed on the Piper plot

Segments of the Diamond	Character of the water type and Hadrochemical Facies	Number of Samples
1	Alkaline earth exceeds alkalies.	1
2	Alkalies exceed alkaline earths	13
3	Weak acids (CO_3 + HCO_3) exceed strong	0
4	Strong acids exceed weak acids	14
5	Magnesium type	0
6	Calcium type	1
7	Sodium + potassium dominance	13
8	Sulfate type	0
9	Bicarbonate type	0
10	Chloride type	14
11	No dominant	0
12	Ca^{2+}–Mg^{2+}–Cl^--SO_4^{2-}	1
13	Na^+–K^+–Cl^-–SO_4^{2-}	13
14	Na^+–K^+–HCO_3^-	0
15	Ca^{2+}–Mg^{2+}–HCO_3^-	0

Mechanism Controlling Groundwater Chemistry

Gibbs (1970) developed a diagram displaying three formative mechanisms controlling the chemistry of groundwater. This can be achieved by determining the ratio of both cations [(Na+K)/(Na+K+Ca)] and anions [Cl/(Cl+ HCO_3)] to that of total dissolved solids (TDS). The three mechanisms include precipitation dominance, rock dominance, and evaporation dominance. The results of the groundwater samples are displayed on the diagram below where majority of the samples belong to rock dominance type. However, three samples (SA, SI, and SL) fall within precipitation dominance class and one sample (SB) displays a precipitation dominance.
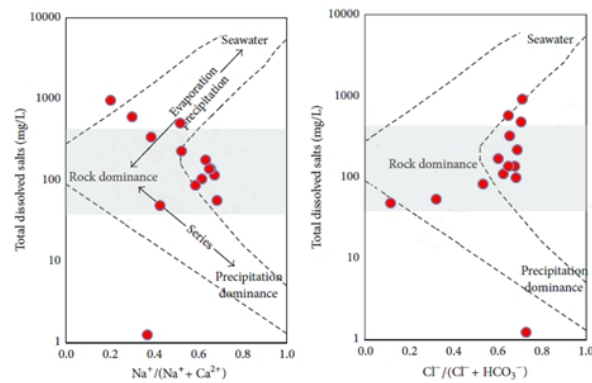
Figure 5: Gibbs diagrams indicating the groundwater natural evolution mechanisms (a): TDS vs. Na/(Na+ Ca); (b): TDS vs. Cl/(Cl+ HCO$_3$)

Heavy Metal Analysis

The analytical values of heavy metal concentrations in groundwater collected from the study area are listed in table 3. Although concentration of heavy metals in groundwater seldom exceeds 1%, mostly appears in extremely unquantifiable concentrations, their presence can significantly alter the quality of water when exceeding permissible limits (AbdurRashid *et al.,* 2023; Edmunds and Smedley, 1996).

Table 3: Analytical values of heavy metals in the groundwater

| Sample ID	Fe (mg/l)	Mn (mg/l)	Cr (mg/l)	Cd (mg/l)	Zn (mg/l)	Pb (mg/l)	Ni (mg/l)
SA	0.026	0.078	0.001	0.081	0.014	0.34	0.185
SB	0.068	0.035	0.003	0.076	0.015	0.331	0.233
SC	0.056	0.065	0	0.026	0.013	0.405	0.185
SD	0.15	0.053	0.014	0.045	0.016	0.536	0.386
SE	0.083	0.063	0.016	0.036	0.031	0.529	0.334
SF	0.131	0.051	0.01	0.04	0.016	0.627	0.385
SG	0.07	0.066	0.043	0.033	0.035	0.664	0.368
SH	0.1	0.062	0.025	0.037	0.034	0.715	0.384
SI	0.105	0.061	0.037	0.001	0.027	0.819	0.459
SJ	0.235	0.064	0.036	0.043	0.029	0.873	0.494
SK	0.225	0.052	0.063	0.05	0.03	0.868	0.551
SL	0.187	0.022	0.086	0.041	0.049	0.995	0.633
SM	0.224	0.013	0.083	0.053	0.037	1.04	0.662
SN	0.249	0.024	0.076	0.044	0.045	1.043	0.723
Mean	0.136	0.0506	0.035	0.043	0.0279	0.699	0.427
NSDWQ (2015) Permissible limit (mg/l)	0.3	0.2	0.05	0.003	3	0.01	0.02

Iron

Iron concentrations were between 0.249 to 0.026 with an average of 0.136 mg/l. Even at higher concentrations iron might not be toxic but a provisional limit of 0.3 mg/l has been set by the Nigerian Standard for Drinking Water Quality (NSDWQ, 2015). In basement terrain the source of iron in groundwater is often associated with igneous rocks whose iron content is relatively high which include gabbro, diorites, granites and their volcanic counterparts (Hem, 1985).

Manganese
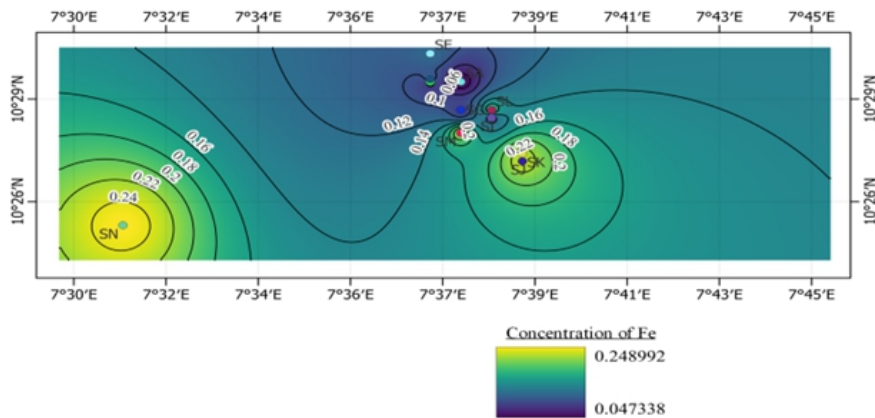
Manganese is often considered as undesirable impurity in water, mainly owing to the fact that it is unpalatable in terms of taste, odor, staining of laundry and to some extent discoloration of food (Ayedun, *et al.,* 2015). Groundwater enriched in manganese is associated with igneous and metamorphic minerals such as olivine, pyroxenes, and amphiboles. The values of Mn in the water samples varied from 0.013 to 0.078 mg/l with a mean of 0.2 mg/l. The recommended upper limit for manganese in public water supplies in Nigeria is 0.2 mg/l (NSDWQ, 2015).
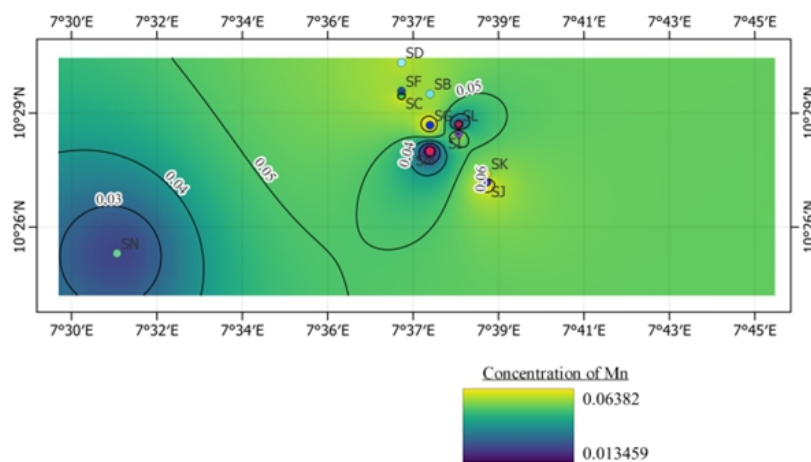

Chromium

Chromium concentrations between 0 and 0.086 mg/l were observed in the samples collected

from the study area. This could be attributed to the dissolution of chromite in the area. The maximum permissible limit for manganese in water is 0.05 mg/l as recommended by NSDWQ (2015).

Concentration of Cr
0.085245
0.001406
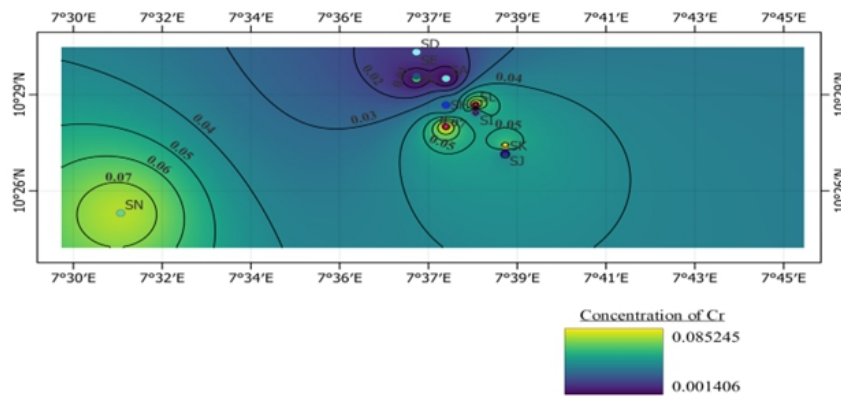
Cadmium

Cadmium occurrence in groundwater could be from both natural and anthropogenic sources (Gayatri *et al.,* 2012). Human sources are linked to industrial operations such as paint, plastic, and glass manufacturing. "Cadmium is an acute toxin, producing symptoms such as giddiness, vomiting, respiratory difficulties, cramps and loss of consciousness at high doses" (Edmunds and Smedley, 1996). The NSDWQ (2015) limit for Cd in drinking water is 0.003 mg/l but the average value for cadmium observed in the samples collected from the study area is 0.043 mg/l.

Concentration of Cd
0.078489
0.001176
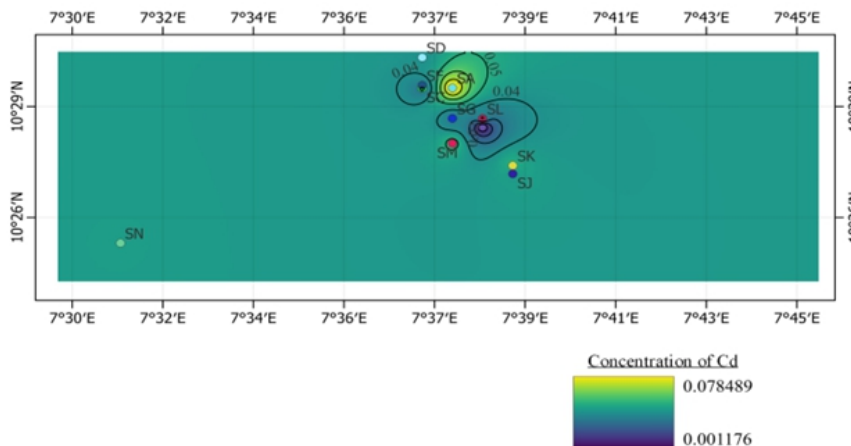
Lead/Zinc

Lead is a cumulative poison, mainly owing to the fact that human exposure to lead can initiate tiredness, irritability, anemia, behavioral changes, and impairment in intellectual functions and convulsions especially in children (Kabiru *et al.,* 2013). The concentrations of lead and

zinc in the water samples range from 1.043 to 0.331 and 0.013 to 0.049 mg/l, respectively. The NSDWQ (2015) maximum recommended concentration for Pb and Zn is 0.01 and 3 mg/l, respectively.
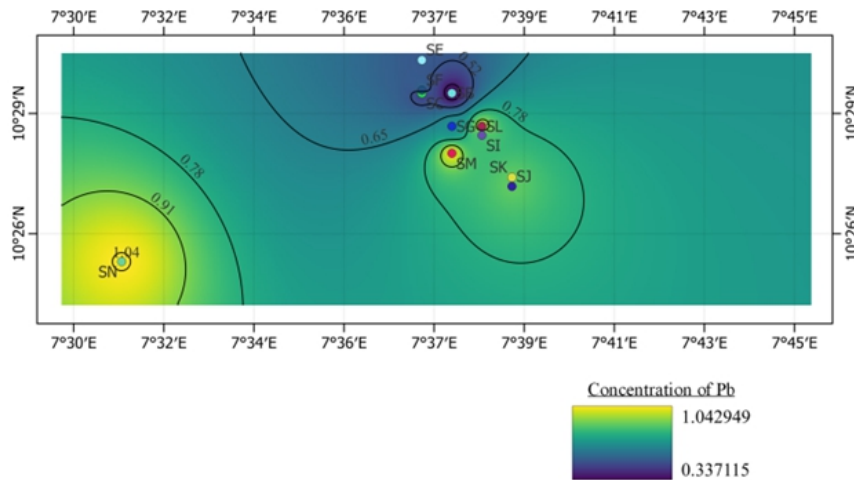
Nickel

Data in table 3 show ranges of nickel from 0.185 to 0.723 mg/l with a mean of 0.427 mg/l. The NSDWQ (2015) recommended limit for Ni in drinking water is 0.2 mg/l. Food is the dominant source of nickel exposure in the non-smoking, non-occupationally exposed population; water is generally a minor contributor to the total daily oral intake.
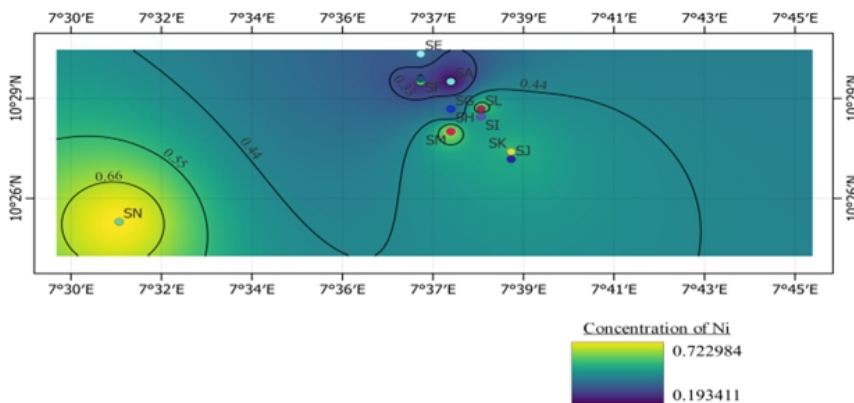
Water Quality Index (WQI)

Water quality index is a tool for simplifying the reporting of water quality data. WQI helps in transforming the analytical water quality by summarizing and simplifying the raw data into a single value. Water quality index of any assessment is based on the guideline and standard limit prescribed by a regulatory body. In this study, The Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) was employed to determine the overall quality of the water samples based on the analyzed parameters. Analyzed values for pH,

Electrical Conductivity, Total Dissolved Solids, Magnesium, Sodium, Iron, Manganese, Chromium, Cadmium, Zinc, Lead, Nickel, Nitrate, Sulfate, and Chloride from samples collected from different locations in the study area were used to compute CCME WQI. The Nigerian Standard for Drinking Water Quality (NSDWQ, 2015) was used as the standard (guideline) for the entire parameters analyzed. Table () presents the categorization of water quality based on the CCME WQI.

CCME WQI Computation (CCME, 2001)
The CCME WQI consists of three factors in its formulation. These factors include; scope (F_1), frequency (F_2), and amplitude (F_3). The objectives of variables in the CCME WQI refer to a standard or guideline of each parameter analyzed in the water samples and in this study The Nigerian Standard for Drinking Water Quality (2015) was employed to serve as a guideline.

Factor 1: Scope (F_1) The scope (F_1) represents the percentage and extent of variables that do not comply or meet their objectives over the period of interest commonly referred to as "failed variables" relative to the total number of variables measured. It is mathematically expressed below:

$$F1 = \frac{Number\ of\ failed\ variables}{Total\ number\ of\ variables}\ x\ 100$$

Factor 2: Frequency (F_2)
This represents the percentage of individual tests that do not meet objectives ("failed tests"):

$$F2 = \frac{Number\ of\ failed\ tests}{Total\ number\ of\ tests}\ x\ 100$$

Factor 3: Amplitude (F_3) represents the amount by which failed test values do not meet their objectives. F_3 is calculated in three steps:

Step - 1
The number of times by which an individual concentration is greater than (or less than, when the objective is a minimum) the objective is termed an "excursion" and is expressed as follows. When the test value must not exceed the objective:

$$Excursion = \frac{Failed\ test\ value}{Objectives} - 1$$

Step - 2
The collective amount by which individual tests are out of compliance is calculated by summing the excursions of individual tests from their objectives and dividing by the total number of tests (both those meeting objectives and those not meeting objectives). This variable, referred to as the normalized sum of excursions, or nse, is calculated as:

$$nse = \frac{\sum_{i=1}^{n} excursion}{Total\ number\ of\ tests} - 1$$

Step - 3

F_3 is then calculated by an asymptotic function that scales the normalized sum of the excursions from objectives (nse) to yield a range between 0 and 100.

$$F3 = \frac{nse}{0.01nse + 0.01}$$

The CCME WQI is then calculated as:

$$CCME\ WQI = 100 - \left[\frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732}\right]$$

The factor of 1.732 arises because each of the three individual index factors can range as high as 100.

Table 4: CCME WQI based water quality categorization

CCME WQI	Ranking	Water Quality Characteristics
95 -100	Excellent	Water quality is protected with a virtual absence of threat or impairment; conditions very close to natural or pristine levels.
80 – 94	Good	Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels.
65 - 79	Fair	Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels.
45 – 64	Marginal	Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels.
0 – 44	Poor	Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels.

Table 5: Computed CCME WQI of water Samples Collected from the Study Area.

CCME WQI Element	Samples Analyzed During Dry Season
Number of failed variables	7
Total number of variables studied	15
Total number of test	15
Total number of failed test	54
Excursion	1448.268605
Nse	96.55124031
F1	46.66666667
F2	360
F3	98.97489771
CCME Water Quality Index	-117.2418885
Category	Poor

The table above shows 15 numbers of total studied variables and 15 number of tests with 54 number of failed tests in the analytical data. Based on the computation of the analyzed data obtained from the water samples as presented in table 5, the overall quality of water during dry season in the study area is poor (-117.2). Hence, the poor quality is obvious from the analytical values of heavy metals such as lead (Pb), nickel (Ni), cadmium (Cd), and chromium (Cr) whose values exceed the permissible limits of the Nigerian Standard for Drinking Water Quality (NSDWQ).

Bulk Rock Geochemistry
The analytical data obtained from the geochemical analysis of the main rock in the study area is presented in table. The silica content is low (< 45 wt%), high alumina concentration (about 11 wt %), potassium feldspar is relatively high (3.72 wt %) with an elevated magnesium and iron contents of 2.64 wt % and 3.6238 wt %, respectively. The high aluminum concentration relative to sodium, potassium, and calcium makes the rock to be peraluminous ($Al_2O_3 >$ $Na_2O_3 + k_2O + CaO$). Based on the values of the oxides in table (), the rock appears to be dioritic in composition.

Table 6: Geochemical result of the XRF analysis for the rock sample

| Oxides	Weight percent (%)
Fe_2O_3	3.6238 %
SiO_2	44.490 %
Al_2O_3	11.227 %
MgO	2.64 %
P_2O_5	0.2582 %
SO_3	0.0795 %
TiO_2	0.6454 %
MnO	0.2776 %
CaO	1.8524 %
K_2O	3.792 %
CuO	0.00334 %
ZnO	0.02090 %
Cr_2O_3	0.00283 %
V_2O_5	0.01102 %
As_2O_3	0 %
PbO	0.00747 %
Rb_2O	0.01263 %
Ga_2O_3	0.00313 %
NiO	0 %
Cl	0.01199 %
ZrO_2	0.0558 %
Ta_2O_5	0.00465 %
Br	0 %
SrO	1.089 %
Nb_2O_5	0.1329 %
Bi_2O_3	0.04501 %
Sb_2O_3	0.512 %
Co_3O_4	0 %
CdO	0 %
HfO_2	0.000941 %
Ag_2O	0 %
CeO_2	0.0410 %
BaO	0.4789 %
Au	0 %
WO_3	[-0.06000] %
MoO_3	[-0] %
La_2O_3	0 %
ThO_2	[0.00073] %
SnO_2	0 %

Petrographic Analysis

The petrographic analysis of two rock samples collected from the study area is shown in figure and figure 2. Based on observations made with the petrographic microscope, the major rock units in the area are diorite and biotite granite.
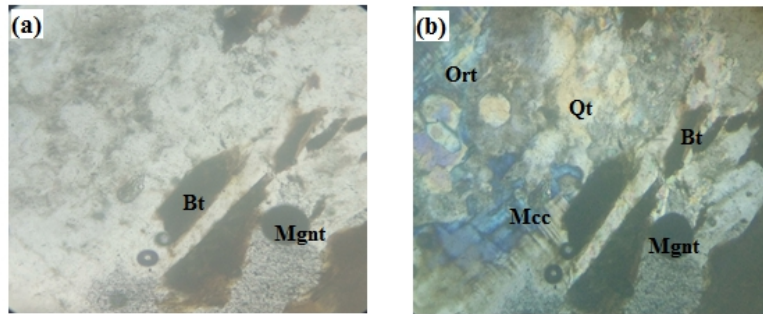
Plate I: Photomicrograph of biotite granite (L-2) under (a) Plane polarized light (PPL) and (b) Crossed polarized light (XPL) showing Qz=Quartz, Bt=Biotite, Mcc =Microcline, Ort=Orthoclase and Mag =Magnetite, Mag. =X40

The petrographic examination of the biotite granite (Plate I) unveiled a diverse mineral composition, encompassing orthoclase (41%), quartz (29%), biotite (16%), microcline (9%), and magnetite (5%). Quartz crystals manifested small to medium-sized subhedral forms with moderate relief, low birefringence, and undulose extinction. In cross-polarized light, alteration features, denoted by small dotted mafic minerals, were discerned. Biotite exhibited a brown hue under plain-polarized light, showcasing platy crystals with moderate relief and ranging from brownish to dark brown under cross-polarized light. It displayed subhedral shapes, preferential extinction, and pronounced pleochroism. Microcline, observed as light grey to colorless in cross-polarized light, demonstrated moderate relief, subhedral crystals with rectangular boundaries, and well-developed cross-hatched twinning. It also exhibited intergrowths with quartz crystals and the inclusion of mafic minerals. Orthoclase displayed subhedral crystals with interference colors ranging from grey to black, revealing Carlsbad twinning under cross-polarized light and irregular crystal extinction, interlocking with quartz crystals. The accessory mineral identified is magnetite.
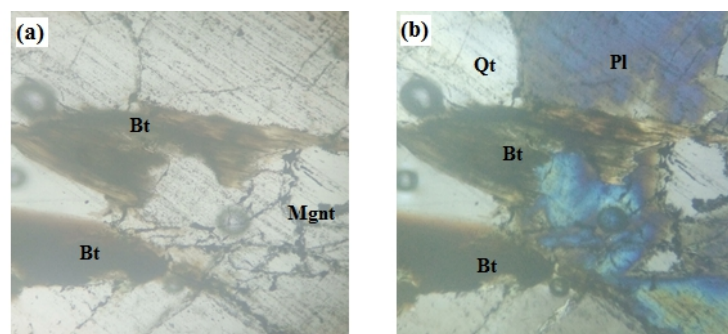
Plate II: Photomicrograph of diorite (L-1B) under (a) Plane polarized light (PPL) and (b) Crossed polarized light (XPL) showing Qz=Quartz, Bt=Biotite, Pl =Plagioclase, Ort=Orthoclase and Mag =Magnetite, Mag. =X40

The petrographic examination of the granitic gneiss uncovered a mineral composition featuring orthoclase (43%), quartz (27%), biotite (14%), plagioclase (12%), and magnetite (4%) (Plate II). Quartz crystals exhibited a colorless appearance with moderate relief and a medium-grain crystal structure, showcasing a subhedral habit. Biotite displayed crystal shapes with preferential orientation, low relief, bladed extinction, and pleochroic haloes, hinting at potential alteration. In cross-polarized light, orthoclase appeared gray with low birefringence and oblique extinction, presenting subhedral crystals and moderate relief in plane-polarized light. Plagioclase showcased small large (phenocryst) crystals with pale gray and light colors in cross-polarized light, suggesting alteration into green hues and potential weathering into seriate minerals with a brown color. Plagioclase exhibited typical polysynthetic twinning, straight extinction, and low birefringence in cross-polarized light. Furthermore, magnetite was identified as the sole accessory mineral in the sample.

Discussion

The study area is underlain by biotite granite and diorite. These rocks exhibited fractures, pegmatites, and quartz veins in various degrees. The geometrical measurements of dip and strike of joints indicated a trend of mineralization to be predominantly in the NNW-SSW direction. The geochemical analysis of the rock sample obtained from the study area show a strong depletion is silica and enrichment in alumina and alkali. The rock was found to be peraluminous with high iron content. Petrographic description also showed the bulk mineralogical composition of the rock samples collected from the study area. The results of pH of all the water samples were within the Nigerian Standard for Drinking Water Quality (NSDWQ) except for two samples (SB with 8.7 and SC with 9.3) which were slightly above the standard of 8.5. The levels of Electrical Conductivity in the study area were within the prescribed limit (NSDWQ: 1000μs/cm) which makes the water portable for both domestic and irrigational purposes. In this investigation, TDS values of the majority of the water samples were within the permissible limit with the exception of sample SA (1000), SI (633), and SL (528) which were found to be above the guideline (NSDWQ: 500mg/l). When TDS values are high it is an indication of strong interaction between the groundwater and its host lithology, therefore the residence time is high and the dissolution of constituent minerals by the groundwater must have taken place.

In particular, the major cations and anions that invariably make about 99% of the natural composition of groundwater were found conform to the permissible limit of NSDWQ. However, chloride values reported from three samples (SA, SB, SI, and SL) were observed to be above the permissible limit. When chloride concentration exceeds 100mg/l in water a salty taste will result and values above 100mg/l are not only desired by industries but affect physiological damage (Todd, 1980). In terms of pollution, the concentration of nitrate in all the water samples were below 50mg/l which makes the water pollution-free and can be safely used even by infants.

Based on the hydrogeochemical facies as portrayed on the Piper diagram (figure 1), the dominant water type is $Na^+–K^+–Cl^-–SO_4^{2-}$ and the major mechanism driving the chemistry of the groundwater in the area is rock dominance (figure 2). Of particular concern in this work is

the level of heavy metal concentrations observed in all the water samples in the study area. The levels of lead (Pb), nickel (Ni), cadmium (Cd), and chromium (Cr) were found to be potentially high, far exceeding the permissible limits of not only NSDWQ but virtually all drinking water guidelines worldwide.

Certain health problems such as poisoning, tiredness, irritability, anemia, behavioral changes, and impairment in intellectual functions and convulsions to mention a few associated with the exposure of water with high concentrations of lead have been reported in areas where sulfide-bearing minerals are mined and in numerous communities practicing inappropriate waste disposal. The concentrations of iron (Fe) and manganese (Mn) were all found to be within the standard of domestic water utility.

The Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) was employed to determine the overall quality of the water samples based on the analyzed parameters. Based on the computation of the CCME WQI, the overall quality of the water in the study area is very poor, displaying a negative value of about -117.

Conclusion

Based on the average pH values, the groundwater in the area was found to be slightly acidic and basic which makes it suitable for most uses. The response of the groundwater to electrical conductance was very low as indicated from the values of electrical conductivity. Thus, this is further corroborated by the average values of the total dissolved solids (TDS) which also point to the low mineralization and a residence time. The Piper diagram classified the water as $Na^+-K^+-Cl^--SO_4^{2-}$ type based on the major cations and anions. The ratios for both cations and anions to the total dissolved solids (TDS) as presented in the Gibb's diagram indicates that rock dominace is the main mechanism controlling groundwater chemistry, having moderate concentration of TDS values.

The concentration of most heavy metals analysed in the groundwater samples was found to be above the standard of the Nigerian Standard for Drinking Water Quality (NSDWQ, 2015). Although, even at higher concentrations iron tends not to be harmful to human health, the concentrations of iron in the groundwater were within the permissible limit of NSDWQ. The levels of lead (Pb), nickel (Ni), cadmium (Cd), and chromium (Cr) were found to be potentially high, far exceeding the permissible limits of not only NSDWQ but virtually all drinking water guidelines worldwide. Certain health problems such as poisoning, tiredness, irritability, anemia, behavioral changes, and impairment in intellectual functions and convulsions to mention a few associated with the exposure of water with high concentrations of lead have been reported in areas where sulfide-bearing minerals are mined and in numerous communities practicing inappropriate waste disposal.

To determine the overall quality of groundwater, the Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) was used an index in this study. Based on the computation of the CCME WQI, the overall quality of the water in the study area is very poor, displaying a negative value of about -117.

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