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HYDROCHEMICAL CHARACTERIZATION AND EVALUATION OF GROUNDWATER QUALITY OF ZAMFARA AREA, NORTHWEST, NIGERIA

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ABSTRACT

This study deals with hydrochemical assessment of groundwater within the lithological framework underlain Zamfara State, Northwestern Nigeria with the aim of ascertaining its suitability for human consumption. Groundwater samples were collected from boreholes tapping the aquifer of the area and analyzed for various physico-chemical parameters, such as total dissolve solids, electrical conductivity (Ec), pH, temperature, Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3, Cl^-, SO_4, NO_3, PO_4, and trace elements (Mn, Cu, Zn, Fe, Pb and Cr). The results obtained were subjected to multivariate statistical analysis, water quality index method, and hydrochemical variation plots for proper characterization. As far as suitability is concerned most of the studied physic-chemical parameters trace elements (iron, lead and chromium ions) revealed average concentrations lower than the permissible limit set for domestic water use by World Health Organization. However, the compiled overall water quality index for the studied groundwater shows 'very poor water quality'. Due to the fact that WQI rating reflect the composite influence of different water quality parameters. The result of the multivariate statistical analysis, as applied to the chemical data set of the studied groundwater provides an insight into the underlying controlling hydrochemical processes in the area. Four factors including factor-1 (total hardness, chloride, nitrate, manganese, bicarbonate and alkalinity), factor-2 (TDS, conductivity, total hardness, magnesium and calcium), factor-3 (Temperature, sodium, potassium, copper, zinc, iron and chromium), factor-4 (calcium, magnesium and nitrate) represents the signatures from dissolution of bedrock through which the groundwater passes, ionic mixing, leaching from the lateritic overburden, agricultural activities (fertilizer application) and effluent from waste dumpsites in the study area. The distribution of major ions in the groundwater shows relative abundance of cations: $\mathbf{Na^+}$+$\mathbf{K^+}$ > Ca^{2+} > Mg^{2+}; while the relative abundance of the anions is: $\mathbf{Cl^-}$ > HCO_3^- > SO_4^{2-}. Groundwater in the aquifer of the study area are majorly of evolved type with mixing of ionic concentrations. Alkali's are more in abundant to that of alkaline earth, while Cl and HCO_3 dominate SO_4 and NO_3 concentration. The water samples are basically 'Alkali waters' with 'Earth Alkaline' components that are predominantly HCO_3^- and Cl^-.The relative abundance of the three (3) dominant water types are as thus: **Na-$\mathbf{HCO_3}$-Cl** > Ca-Mg-HCO_3-Cl > Na-Ca-Cl. Simple mineral dissolution or mixing processes is mainly responsible for the variation in the hydrochemistry of the groundwater of the study area.

KEYWORDS: Hydrochemical classification, Water quality index, Multivariate statistical analysis, Groundwater, Zamfara State.

1.0 INTRODUCTION

Groundwater contains minerals carried in solution, the type and concentration of which depends upon several factors like soluble products of rock weathering and decomposition in addition to external polluting agencies and changes in space and time. As a result of chemical and biochemical interaction between groundwater and contaminants from urban, industrial and agricultural activities along with geological materials through which it flows, it contains a wide variety of dissolved inorganic chemical constituents in various concentrations. The character of groundwater in different aquifers over space and time proved to be an important technique in solving different geochemical problems (Srinivasamoorthy *et al*., 2005).

The importance of groundwater as an alternative water supply is increasingly recognized, in response to escalating decreasing quality of surface waters and low supply from various water vendors. It is often thought to be cleaner and easier to treat as compared to surface water and as a result, many wells have either been sunk or drilled (Rosenberry, 2003, Arabi *et al.,* 2012). Possible water quality issues and decreasing water

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levels increase the need for a comprehensive understanding of the groundwater system that would yield better management of the resources.

Clean, safe and adequate freshwater is of utmost importance to human existence and survival of living components in the ecosystem. Water quality issues are complex and diverse, deserving urgent global attention and action (Ige *et al.,* 2008). The decline in water quality has become a global issues of concern because of its inherent ability to hydrological cycle. The past decade has been remarkable impact of man on the environment due to unprecedented increase in population and rapid rate of urbanization as well as the intensification and expansion in agricultural practices. This has led to progressive and continued degradation of groundwater resources. Contamination of groundwater is an important vehicle for spread of diseases (Ezeigbo, 1989; Abubakar *et al.,* 2017).

More so, the need for water has resulted in an increasing withdrawal of groundwater in sensitive areas like crystalline environments, where aquifers may suffer from over abstraction, which consequently may result in deterioration of its quality (Akujieze *et al.,* 2007, Amadi and Olasehinde, 2008, Amadi, 2010, Kanade and Gaikwad, 2011, Akano, 2015, Shuaibu and Abdullahi, 2015, Abubakar *et al.,* 2017).

It is worthy to note that water quality has been evaluated in the last years owing to greater understanding of mineralization process and greater concern about its origin (Shane and Jerzy, 2003). Water quality shows water-rock interaction and indicates residence time and recharge zone confirmation (Sanchez and Trenolieres, 2003; Cronin *et al.,* 2005). Thus, water quality indicators must reflect mineralization process, integrate reservoir properties and groundwater recharge rate and flow direction (Adams *et al.,* 2001; Legout, 2005; Andre *et al.,* 2005; Grassi and Cortecci, 2005).

Consequently, water is a scarce resource in Zamfara State due to the climate and the nature of the dominant geologic framework as well as anthropogenic influences. Especially during dry season when the yields of open wells and boreholes falls and surface water from rivers, stream, and impounding reservoirs become dry. Groundwater is the major source of water for irrigation and also support domestic and industrial water supply. Due to rise in agriculture production and demographic change, groundwater has set a declining trend throughout the major aquifer of the study area. The current rate of groundwater abstraction so far has exceeded the rate of groundwater recharge. As pumping wells tapping the various aquifers of the region are unevenly distributed, the consequences of this unbalanced groundwater exploitation vary from one part of the study area to another (Garba and Schoeneich, 2005). The baseline problems from too little water and contamination noticed by this research in the entire Zamfara State call for proper assessment and management of the available groundwater resources.

Therefore, there is a need for a thorough assessment of the quality of water available for human, agricultural and industrial purposes. Moreover, water resources safeguard policy requires periodic assessment of both groundwater quantity and quality. The present study focuses on assessment of groundwater quality and its suitability for domestic purpose for the proper management.

1.1 STUDY AREA

This research covers the entire Zamfara State with total area coverage of 39,762Km^2, within the North Western Nigeria (Figure 1), with Longitude: 5^{0}1'27.638″E to 13^{0}10'45.537″N, and Latitude: 6˚18'13.709″E to 11˚49'4.152″N. Temperatures are generally extreme, with average daily minimum of 18°C, during cool months of December and January while in the hottest months of April to June, an average maximum of 38°C and minimum of 24°C temperatures are recorded (NiMET, 2020).

Rainfall is generally low; the average annual rainfall ranges from 600 to 1000mm across the entire State. Much of the rain, falls between the months of May to September, while the months of October to April experienced little or no rainfall. Evaporation is high, ranging from 80mm in July to 210mm in April to May (NiMET, 2020). A monthly average evapo-transpiration range of about 140mm represent 30 of monthly average precipitation into the catchment.

The study area belongs to the Sudan savannah region of Africa; an area most affected by droughts (Figure 1).

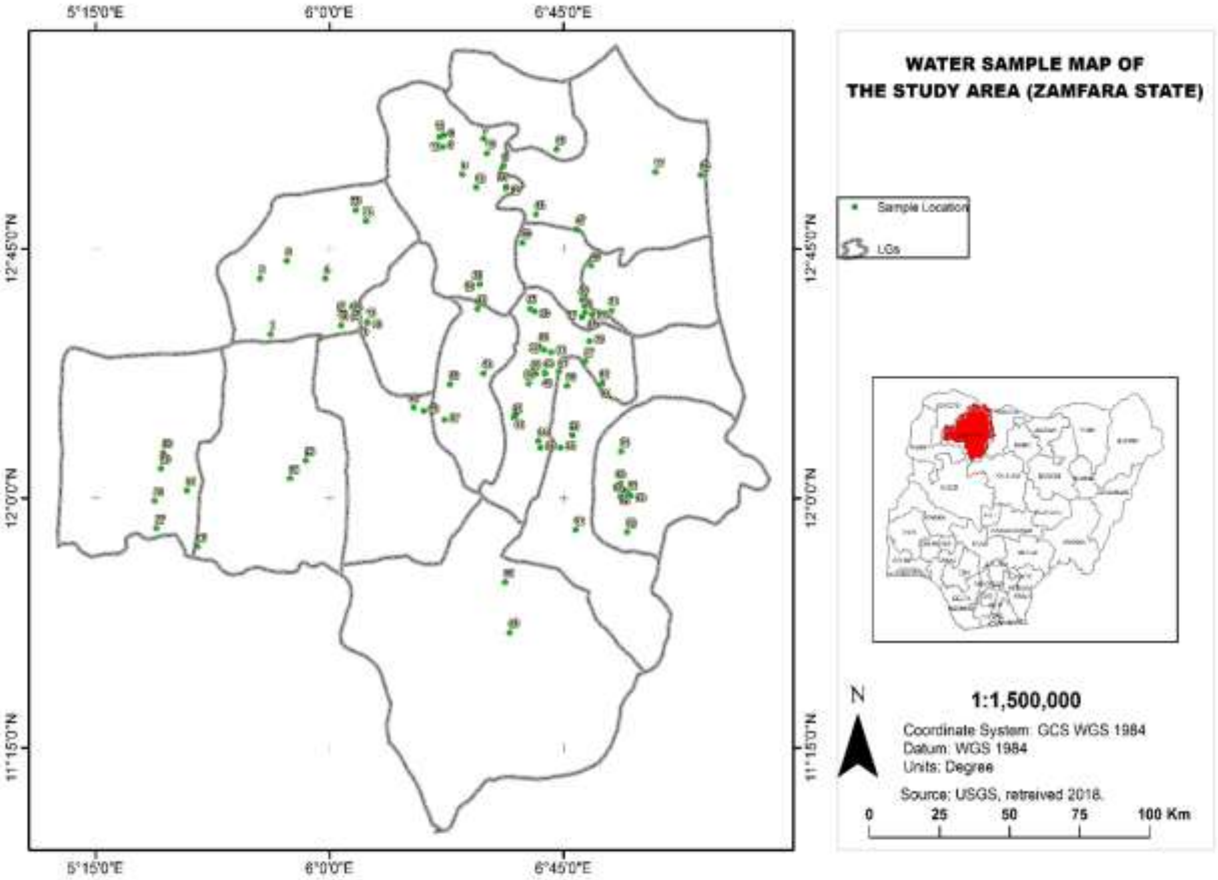

Figure 1: Map of the Study Area

2.0 GEOLOGICAL SETTING

About 90% of the State is underlain by a variety of crystalline rocks of the basement complex of north western Nigeria described by McCurry (1976) to be composed largely of gneiss, schist, migmatite, granite and granodiorite (Figure 2). The structural features commonly exhibited by the basement rocks include foliation, lineation, folds, rock-rock contacts, faults and joints. The rest of the state is underlain by the oldest sediments of the Sokoto (Illullemeden) basin described by Oteze (1976) and Kogbe (1976). Groundwater in the basement rocks of the study area are mainly sourced from fractures and joints (Yaya *et al*, 2001) and in the

About 10% of the study area is underlain by Gundumi formation which consists of clays, sandstones and pebble beds, thought to be lacustrine and fluviatile in origin (Figure 2). Its maximum thickness is reported to be up to 300m, near the Niger border. The base is marked by conglomeratic beds which are well preserved and exposed by the road side at Tureta and Ruwan Kalgo (Kogbe, 1976). These basal beds contain rounded quartz cobbles and pebbles and attain a thickness of about 3m. The formation is the oldest sedimentary rocks in the Northern parts of the Sokoto basin, it lies uncomfortably on the Basement Complex. The indication, from borehole sections, is that the basal conglomerates are overlain by beds which are more argillaceous from the bottom to the top (Ogilbee *et al.,* 1965). The intergrannular pores of fine to coarse (white or light grey) sand or gravel in Gundumi formation served as its aquiferous layer (Oteze, 1976).

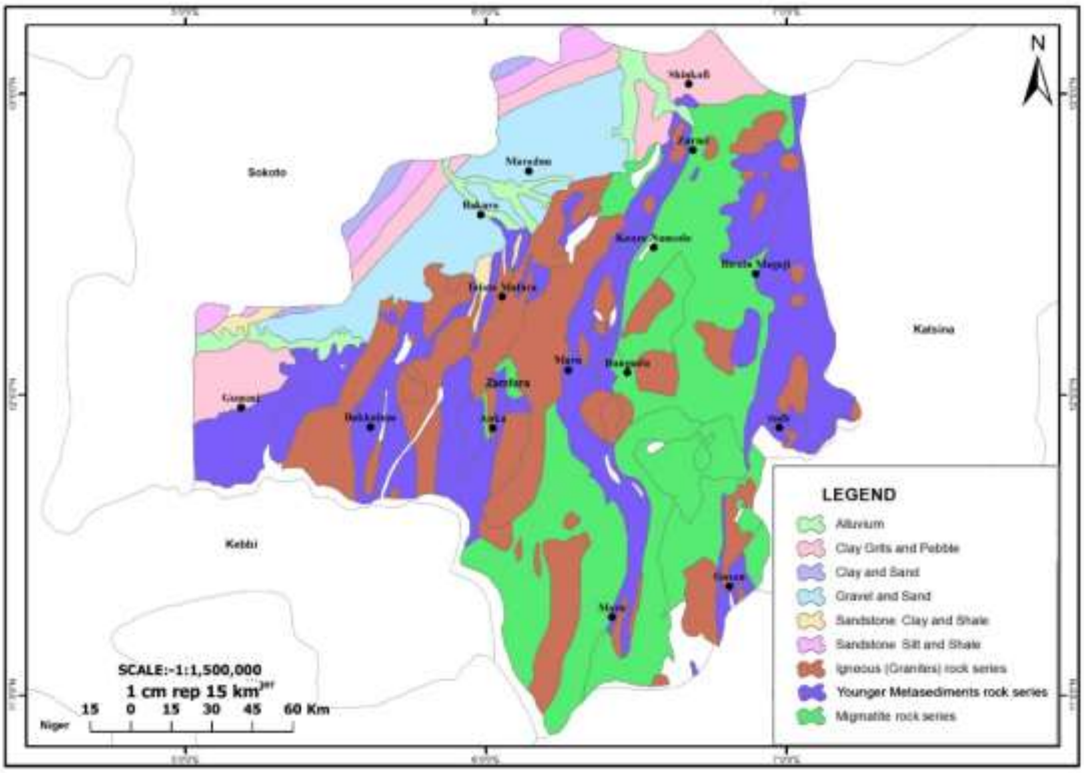

Figure 2: General Geological Map of Zamfara State, (Nigeria Geological Survey Agency, 2006).

3.0 MATERIAL AND METHODS

In this study, one hundred (100) groundwater samples were collected from boreholes, covering entire study area of Zamfara State, Northwestern Nigeria (Fig. 1), and the water samples were analyzed for major, minor and trace elements.

3.1 SAMPLING TECHNIQUES

The samples were collected during the peak of rainy season (August, 2018). During the exercise, global positioning system was used to obtain the coordinates, one litre of plastic rubbers was used to collect the samples. The plastic rubbers were washed, dried and rinsed with the water before filling it to capacity and labelled accordingly. Prior to collection of water samples, the physical parameters were determined in the field using portable standard equipment (pH meter: PHS 125 REX, Conductivity meter: PCE-SM11).

After the sample collection, the samples were stored in a cool box and later transported to the Water Quality Laboratory, Federal University of Technology, Minna.

The Atomic Absorption Spectrophotometer (AAS) was used for the determination of the concentrations of Ca^{2+} and Mg^{2+} as well as the trace metal; Pb^{2+}, Cu^{2+}, Cr^{2+}, Mn^{2+}, Zn^{2+} and Fe^{2+} while flame analysis was used for the determination of the concentration of Na^+ and K^+. The colorimetric method was used to determine SO_4^{2-} and PO_4. The Ultra-Violet Spectrophotometer (UVS) was utilized in the determination of NO_3^- while the concentration of HCO_3^- and CO_2 were determined using titrimetric method.

The obtained chemical data set were subjected to water quality index analysis, multivariate statistical interpretation and hydrogeochemical graphical models for optimal characterization of the hydrogeochemical processes.

Multivariate Statistical Analysis: The data obtained from laboratory analyses were used as variable inputs for factor analyses (R-Mode). A factor analysis was performed using the SPSS package described by Nie *et al.* (1975). Before the analysis, the data were standardized to produce a normal distribution of all variables (Davis, 1973). This was followed by a preparation of a correlation matrix of the data from which initial factor solutions were extracted using the principal component analysis method. Factor extraction was done with a minimum acceptable eigenvalue of 1 (Kaiser, 1958; Harman, 1960). Orthogonal rotation of these initial factors to terminal factor solutions (Table 1) was done with Kaiser's varimax scheme (Kaiser, 1958). This method maximizes the variance of the loadings on the factors and hence adjusts them to be either +1, -1 or zero (Davis, 1973). Factor score coefficients are derived from factor loading. Factor scores are computed for each sample by a matrix multiplication of the factor score coefficient with the standardized data. The value of each factor score represents the importance of a given factor at the sample site. It should be noted that a factor score > +1 indicates intense influence by the process. Highly Negative values (< -1) reflects areas virtually unaffected by the process while zero score shows areas with only moderate effect of the process. The four factor scores represent the four types of elemental enrichment (Table 2).

WQI: Water Quality Index: Water quality index (WQI) is one of the most effective tools to communicate information on the quality of water to the concerned citizens and policy makers. It thus, becomes an important parameter for the assessment and management of surface water and groundwater. WQI is a scale used to estimate an overall quality of water based on the values of the water quality parameters

(Amadi, 2011). It is a rating reflecting the composite influence of different water quality parameters. WQI is calculated from the point view of the suitability of groundwater for human consumption (Lambarkis et al., 2004, Amadi, 2010).

Calculation of WQI: The Water Quality Index (WQI) was calculated using the Weighted Arithmetic Index method. The quality rating scale for each parameter qi was calculated by using this expression:

$$q_i = (C_i / S_i) \times 100 \quad (1)$$

A quality rating scale (q_i) for each parameter is assigned by dividing its concentration (C_i) in each water sample by its respective standard (S_i) and the result multiplied by 100. Relative weight (W_i) was calculated by a value inversely proportional to the recommended standard (Si) of the corresponding parameter:

$$W_i = 1/Si \quad (2)$$

The overall Water Quality Index (WQI) was calculated by aggregating the quality rating (Q_i) with unit weight (Wi) linearly.

$$WQI = \sum_{n=1}^{1=n} qiwi \qquad (3)$$

Where: qi: the quality of the ith parameter, wi: the unit weight of the ith parameter and n: the number of the parameter considered. Generally, WQI were discussed for a specific and in-tended use of water. In this study the WQI for drinking purposes is considered and permissible WQI for the drinking water is taken as 100.

All the physical and chemical parameters analyzed from the studied sampled water were used to calculate the WQI in accordance with the required procedures and the results contained in the table 5, subsequently this equation was applied $\left[\text{Overal WQI} = \frac{\sum q1w1}{\sum w1}\right]$ (4) to the entire water quality classification scheme.

4.0 RESULTS AND DISCUSSION

The descriptive statistical summary of the hydrochemical results is presented in Table 1.

Table 1: Statistical summary of the physical and chemical analyses of Groundwater samples

Parameters	Minimum	Maximum	Mean	Std. Deviation	Skewness	WHO (2017)
Temperature	27	33	30.16	1.19	-0.24	Ambient
pH	5.7	8.8	6.78	0.57	0.83	6.5 - 8.5
TDS	67.2	967.04	470.58	227.28	0.21	1000
Ec	105	1688	753.20	374.69	0.32	1500
Alkalinity	52	498	190.22	97.94	1.11	200
TH	17	296	99.34	68.90	1.03	200
Cl	6.6	234	68.36	52.67	1.34	250
HCO_3	0	429	82.17	75.37	2.17	600
SO_4	0	184.3	83.96	56.71	-0.07	250
PO_4	0.01	0.8	0.12	0.08	6.15	5
CO_2	1.14	131	10.37	13.32	7.71	
NO_3	0	99	3.07	12.29	6.28	50
Na	4.55	900	87.68	144.12	2.96	200
K	0.54	86	11.77	15.67	2.81	100
Mg	0.49	73.96	19.24	17.44	1.55	150
Ca	3.63	159.56	48.05	32.49	1.17	200
Mn	0	2.35	0.05	0.24	9.59	0.2
Cu	0	0.42	0.08	0.12	1.22	2
Zn	0.01	0.72	0.19	0.12	0.84	5
Fe	0	7.89	0.28	0.83	8.17	0.3
Pb	0	0.53	0.05	0.13	2.53	0.01
Cr	0	0.81	0.05	0.12	4.12	0.003

The pH values range between 5.7 to 8.8 with mean value of 6.78 while water temperature varies from 27^0C to 33^0C with mean value of 30.16^oC (Table 1). They are important water quality indicator and plays important role in the dissolution of chemical substances in water. The mean value of pH falls within the acceptable limit of 6.50 to 7.5 as recommended by WHO, (2017). Most often biochemical processes in groundwater are influenced by changes in pH and temperature, as chemical substances dissolve more readily in water under low pH and high temperature conditions.

Total dissolve solids (TDS) indicate the amount of substance dissolved in water. Its concentration in the studied water samples range between 67.2 to 967.04 mg/l with average value of 470.88mg/l. This value revealed that the groundwater is fresh. However, value of electrical conductivity (EC) varied between 105 to 1688 µs/cm with mean value of 753.2 µs/cm (Table 1) as against their respective maximum permissible limit of 1000mg/l and 1500 µs/cm respectively. This is an indication of moderate ionic dissolution in studied groundwater. The large variation in EC values is attributed to geochemical evolution of groundwater through rock-water interaction and possible anthropogenic influences.

The concentration of alkalinity of the studied water samples range between 52 to 498 mg/l with an average value of 190.22 mg/l. Its permissible limit is 200mg/l (WHO, 2017). This imply moderate dissolution of mineral substance from lithologic framework. Total hardness concentration varied between 17 and 296 mg/l with mean value of 99.34 mg/l (Table 1). The elevated concentration of Ca and Mg ions is believed to be responsible for the hardness of the studied groundwater. The mean concentrations of anions in the studied water samples (chloride, sulphate, bicarbonate, nitrate, and phosphate) is lower than their maximum recommended limit for domestic water use (WHO, 2017). Similarly, the average concentration of the major cations (Ca, Mg, Na and K) were equally below their respective recommended permissible limit (WHO, 2017, table 1). Nonetheless, result of Na^+ shows maximum concentrations of 900 mg/L which is above the threshold of WHO, (2017) standard for drinking water. This suggest decomposition of feldspathic minerals in a location of the particular sample.

However, Fe^{+2} concentration range between 0 to 7.89 mg/L with mean value of 0.28 mg/L against its permissible limit of 0.3 mg/L by WHO, (2017). This shows that some locations within the area of study have elevated iron concentration which is majorly sourced from superficial material (clay mineral) as shown in figure 3.

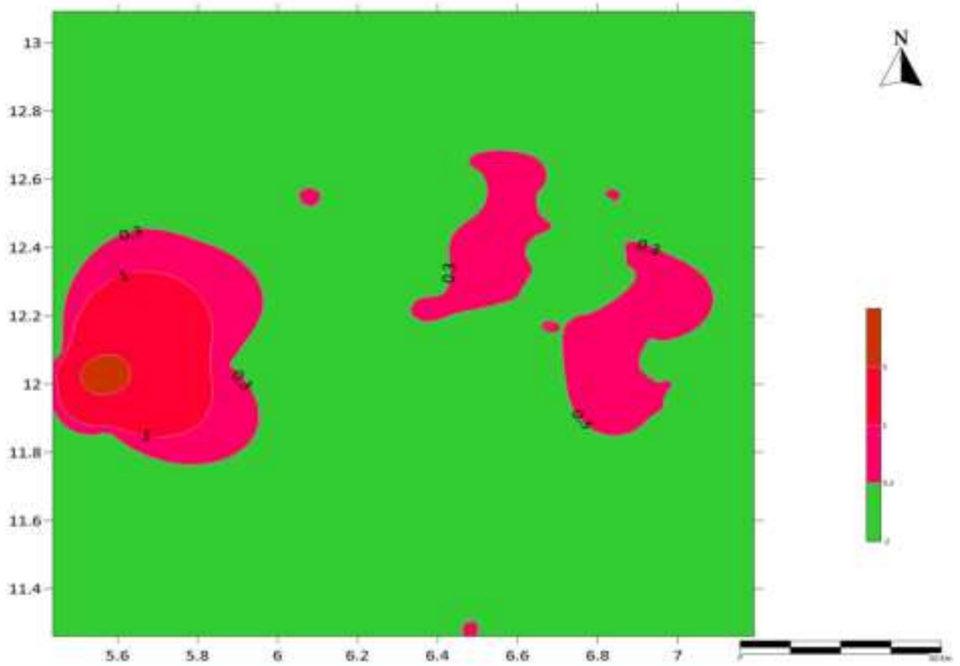

Figure 3: Plot of Fe^{+2} in the studied water samples against its WHO permissible limit

Concentration of lead (Pb^{+2}) in the water samples shows mean value that is higher to its permissible standard limit for drinking water, however, many locations depict concentration below the WHO, (2017) standard limit for drinking water as shown in figure 4.

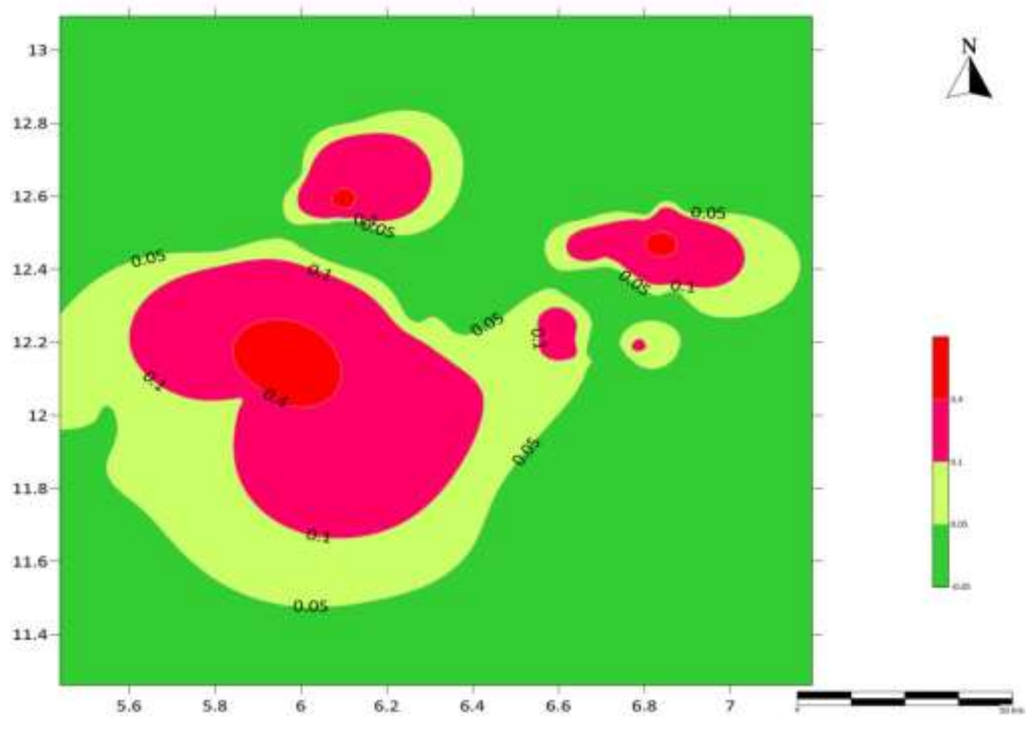

Figure 4: Plot of Pb^{+2} in the studied water samples against its WHO permissible limit

Furthermore, the concentration of chromium ion in groundwater samples range between 0 and 0.81 with mean value of 0.05 which is above its permissible limit for drinking purposes (WHO, 2017, table 1), nonetheless, many localities shows concentration of chromium ion below the threshold of WHO, (2017) (Figure 5).

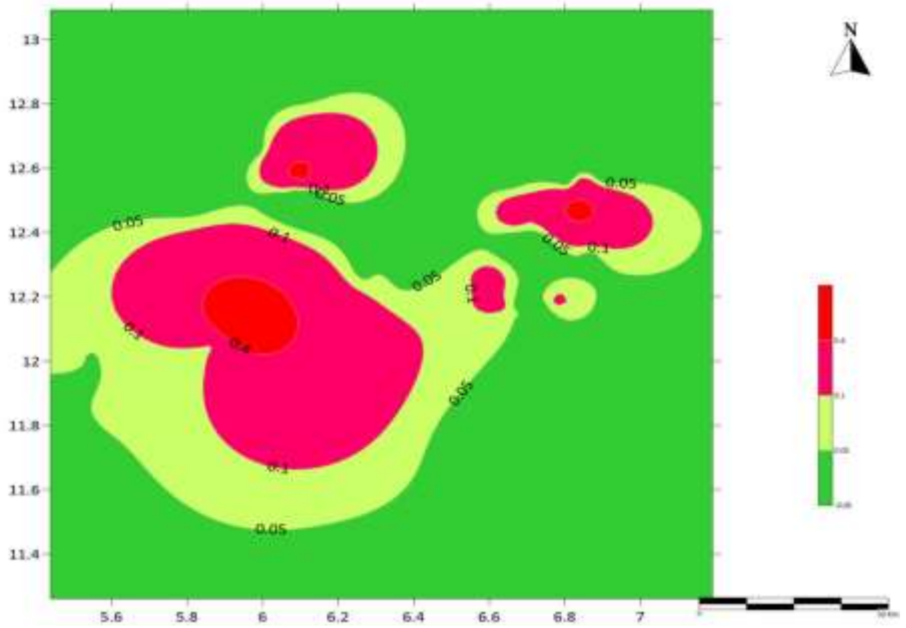

Figure 5: Plot of Cr^{+2} in the studied water samples against its WHO permissible limit

Naturally, trace elements occur in varying quantities in rocks depending on the geochemical composition of the geological formation. As a result of the mobility of these elements in soil, they flow from the surface to the water-bearing formation below. Also, these elements can also result from anthropogenic sources such as improper waste disposal and the application of insecticides. The low concentration noticed in majority of water samples (95%) collected from the study area could be as a result of the depth to the aquifer, which prevented the water-bearing formation from every form of an external pollutant that could influence the purity of the groundwater.

4.1 MULTIVARIATE STATISTICAL ANALYSIS OF HYDROCHEMICAL COMPONENTS

Results of the factor analysis (R-Mode) of the groundwater chemistry data (n=100) indicates four factors (Table 2).

Table 2: Varimax rotated factor loading matrix for groundwater chemistry

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Communalities
Temperature_°C	0.452	-0.236	0.513	0.074	0.528
pH	-0.144	-0.118	-0.466	0.261	0.32
Total Dissolve Solids	-0.238	0.682	-0.407	-0.349	0.809
Conductivity µs/cm	-0.254	0.698	-0.352	-0.342	0.793
Total Hardness	0.539	0.522	0.274	-0.275	0.714
Alkalinity	0.733	0.308	0.211	-0.222	0.725
Cl^-	0.784	0.169	0.133	-0.252	0.725
HCO_3	0.737	0.35	0.152	-0.201	0.729
SO_4	-0.267	-0.042	-0.408	-0.589	0.587
PO_4	-0.223	0.249	-0.706	0.127	0.626
CO_2	0.342	0.191	0.395	-0.286	0.391
NO_3	0.669	0.395	-0.05	0.446	0.805
Na^+	-0.642	0.453	0.345	0.065	0.74
K^+	-0.5	0.138	0.336	0.316	0.482
Mg^2	0.388	0.502	-0.282	0.491	0.722
Ca^{2+}	0.104	0.72	-0.133	0.503	0.8
Mn^2	0.562	0.419	0.115	0.156	0.529
Cu^2	-0.775	0.377	0.369	0.022	0.879
Zn^2	-0.528	0.3	0.322	0.017	0.472
Fe^2	0.019	-0.259	0.305	0.21	0.205
Pb^2	-0.715	0.424	0.379	-0.091	0.844
Cr^2	-0.607	0.231	0.333	0.019	0.533
Eigen Value	5.916	3.499	2.682	1.86	
Cum. Eigen	5.916	9.415	12.097	13.957	
% Variance	26.892	15.906	12.192	8.455	
Cum. Variance	26.892	42.798	54.989	63.44	

Extraction Method: Principal Component Analysis.

Factor 1: account for 26.89% total data variance as shown in table 2 and presents significant and positive loading of total hardness, chloride, nitrate, manganese, bicarbonate, and alkalinity (Table 2). This factor is the most significant factor because it explain more than one third of the total variance. It has been demonstrated by high positive loading (0.733, 0.784 and 0.737) for alkalinity, chloride and bicarbonate ions. Natural water alkalinity is determined by the soil and bedrock through which it passes, which could contain carbonate, bicarbonate, and hydroxide compound including silicate minerals. The high positive factor loading of bicarbonate and alkalinity suggest rainwater as the major source of recharge of the aquifer. And lithological framework as the source of groundwater chemical enrichment. The total hardness show positive loading which signifies moderate to high mineralization of the groundwater within the study and this could be from the dissolution of silicate minerals from crystalline basement rock units that underlain approximately 80% of the study area.

Consequently, chloride and nitrate positive loading signify groundwater enrichment from anthropogenic sources through leachate flow from agricultural activities (use of inorganic fertilizers and dumpsites).

Factor 2: reveal 15.91% of the total variance explain (Table 2) with high positive loading of total dissolve solid, electrical conductivity, total hardness, magnesium and calcium concentrations. The TDS and the conductivity are as a result of the dissolution of ions in the water through natural means in the course of groundwater movement or anthropogenic means via leachate migration from soak away, pit-latrine, dumpsites and industrial wastes. It equally revealed much of ionic mixing as a major process of the groundwater evolution against ionic exchange. Consequently, this result revealed that calcium and magnesium ions are essential contributor to the hardness of groundwater in the study area.

Factor 3: account for 12.19% total variance explain (Table 2) with significant loading of temperature, sodium, potassium, copper, zinc, iron and chromium ions (Table 2). The positive loading of Na^+ and K^+ suggest dissolution of silicate minerals (weathering of feldspathic minerals) into the groundwater body, most especially during the wet season of the year. The positive loading of heavy metals could either be both of natural or anthropogenic (discharge from mining and agricultural activities).

High temperature in the study area encourages rapid chemical weathering, which leads to the formation of lateritic soils in the area. They are characterized by the presence of iron and aluminum oxides or hydroxides, particularly those of iron, which give the reddish-brown or yellow colour to the soil. The iron in groundwater is leached from thick lateritic overburden in the area through the porous and permeable formation into the shallow water table below it. Leachate of metallic object from dumpsites also migrates through the unconfined highly permeable sandy formation to the water table. Iron may also be present in drinking water as a result of the use of iron coagulants or the corrosion of steel and cast iron pipes during water distribution as well as weathering process of minerals. Iron is one of the most abundant metals in the earth's crust and an essential element in human nutrition. Estimates of minimum daily requirement for iron depend on age, sex, physiological status and iron bioavailability. Excessive iron in the body does not present any health hazard, only the turbidity, taste and appearance of the drinking water will usually be affected.

Positive loading of heavy metals such as copper, zinc, and chromium ions suggest dissolution of a mineralized ore body hosted by younger metasediments rock units.

Factor 4: account for 8.46 % of the total variance (Table 2) with high positive loading of calcium, magnesium and nitrate (Table 2). This affirmed the divergent source of the studied groundwater as being from both geogenic (dissolution of mineral matter from underlain lithologic units) and the anthropogenic source (leachate flow from inorganic fertilizer as well as indiscriminate waste dump across the study area).

4.2 CORRELATION MATRIX FOR HYDROCHEMICAL COMPONENTS

Table 3 shows the results of correlation analysis of major, minor and trace elements. The data illustrate that major ions (Mg^{2+}, Ca^{2+}) with TDS, EC, total hardness and alkalinity are significantly correlated. This suggest similar source of enrichment which is mostly natural dissolution of rock forming minerals. However, Mg^{+2} and Ca^{+2} show significant correlation with pH, nitrate and chloride ions of the groundwater of the study area, thus suggesting chemical weathering of the bedrock (source of mineral enrichment) and rainfall as the major source of the groundwater recharge (Table 3). However, the positive correlation of nitrate against manganese and calcium indicated enrichment from anthropogenic sources

Alkaline ions show broad affinity with trace elements in the studied groundwater samples as they depict positive correlation with Na, K, Mg, and Ca. This indicate an enrichment from both natural and anthropogenic sources. It equally suggest anionic mixing during wet season and majorly rock-water interactions. Though positive correlation of total hardness and Nitrate ion illustrate an impact ofs leachate flow from organic matter.

Parameter	Temp	pH	TDS	Ec	Alkalinity	TH	Cl	HCO3	SO4	PO4	CO2	NO3	Na	K	Mg	Ca	Mn	Cu	Zn	Fe	Pb	Cr
Temp	1																					
pH	.227*	1																				
TDS	-0.138	0.167	1																			
Ec	-0.128	0.172	.981**	1																		
Alkalinity	-0.032	0.07	.446**	.455**	1																	
TH	-0.032	0.077	.312**	.318**	.573**	1																
Cl	0.165	0.039	0.167	0.154	.218*	.212*	1															
HCO3	-0.019	0.141	-0.047	-0.054	0.163	0.178	-0.048	1														
SO4	0.05	-0.08	.208*	.232*	-0.06	0.057	.206*	-.460**	1													
PO4	-.258**	-0.012	.275**	.258**	-0.069	-0.167	-0.019	-0.169	.245*	1												
CO2	-0.011	-0.068	-0.029	-0.036	-0.086	-0.044	.212*	0.03	0.088	-0.027	1											
NO3	-0.019	-0.092	-0.022	-0.015	.202*	.295**	.251*	0.038	0.056	-0.006	-0.002	1										
Na	-.271**	-.263**	0.043	0.065	-0.065	-0.109	-0.193	-0.175	.234*	0.104	-0.065	0.015	1									
K	-0.104	0.069	0.033	0.053	-0.12	-0.167	-0.136	0.027	-0.027	0.013	0.02	-0.1	.383**	1								
Mg	.320**	.266**	.363**	.372**	.208*	0.055	.438**	0.011	0.183	0.016	-0.023	-0.08	-.330**	-0.087	1							
Ca	0.15	0.15	.376**	.393**	.232*	0.187	.346**	-0.1	.240*	.249*	-0.061	.294**	0.086	-0.058	.631**	1						
Mn	0.07	-0.045	0.002	0.014	.290**	.319**	.267**	0.095	0.065	-0.069	0.017	.795**	0.029	-0.065	-0.039	0.19	1					
Cu	-.359**	-0.195	0.156	0.186	-0.136	-0.144	-0.136	-.202*	.221*	0.091	-0.098	-0.17	.672**	.347**	-0.064	0.12	-0.11	1				
Zn	0.022	0.147	0.067	0.112	-0.058	-0.059	-0.062	0.123	-0.114	-0.087	0	-.295**	-0.048	0.093	.272**	0.09	-0.11	.265**	1			
Fe	0.096	0.016	-0.115	-0.117	-0.053	-0.02	-0.077	-0.032	0.003	-0.152	-0.001	0.172	0.116	.241*	-0.154	-0.13	0.056	-0.068	-0.12	1		
Pb	-.267**	-.251*	0.059	0.091	-0.062	-0.113	-0.196	-.221*	.282**	0.077	-0.062	-0.09	.860**	.319**	-.282**	0.05	-0.06	.762**	0.043	0.019	1	
Cr	-0.151	-0.135	0.014	0.043	-0.161	-0.17	-0.16	-.213*	.210*	0.038	-0.027	-0.1	.520**	.398**	-0.194	0	-0.06	.529**	0.052	0.033	.744**	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

4.3 WATER QUALITY INDEX (WQI) OF THE STUDY AREA

The computed overall WQI value using equation (4) is 92.05 which is in the class of "very poor water quality" as shown in table 5.

Table 4: Standard water quality classification scheme based on WQI value

Parameters	C	S	q_1	w_1	q_1w_1
Temp	30.16	25	120.64	0.04	4.83
pH	6.78	7.5	90.39	0.13	12.05
TDS	470.58	500	94.12	0.002	0.18
Ec	753.20	1000	75.32	0.001	0.08
Alkalinity	190.22	200	95.11	0.005	0.48
TH	99.34	200	49.67	0.005	0.25
Cl	68.36	250	27.34	0.004	0.11
HCO3	82.17	100	82.17	0.01	0.82
SO4	83.96	100	83.96	0.01	0.84
PO4	0.12	5	2.39	0.2	0.48
NO3	3.07	50	6.15	0.02	0.12
Na	87.68	200	43.84	0.005	0.22
K	11.77	100	11.77	0.01	0.12
Mg	19.24	150	12.83	0.007	0.09
Ca	48.05	200	24.03	0.005	0.12
Mn	0.05	0.2	22.5	5	112.5
Cu	0.09	1	8.48	1	8.48
Zn	0.19	3	6.64	0.333	2.21
Fe	0.29	0.3	95.3	3.333	317.67
Pb	0.05	0.05	103.2	20	2064
Cr	0.05	0.05	104.4	20	2088

Table 5: Computed WQI values for the study area

WQI Value	Rating of Water Quality	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
Above 100	Unsuitable for drinking purpose	E

4.4 HYDROCHEMICAL EVOLUTION OF THE GROUNDWATER IN THE STUDY AREA

The results of groundwater chemistry were analyzed to decipher chemical alteration and to mask of natural or meteoric characteristics of groundwater. Gibbs (1970) plot was used to determine major processes controlling the groundwater chemistry. The groundwater samples points on the Gibbs diagram suggest that the groundwater chemistry is controlled principally by rock-water interaction (weathering) (Figure 6). This is expected as possible recharge from rainfall increase the amount of chemical weathering within the aquifer system, during the wet season.

The Gibb's diagram highlights the supremacy of weathering of rocks in controlling the geochemistry of the water samples in the study area. It should be noted that no data point plotted above and below the boomerang, where water composition is dominated by evaporation-crystallization and atmospheric precipitation respectively.

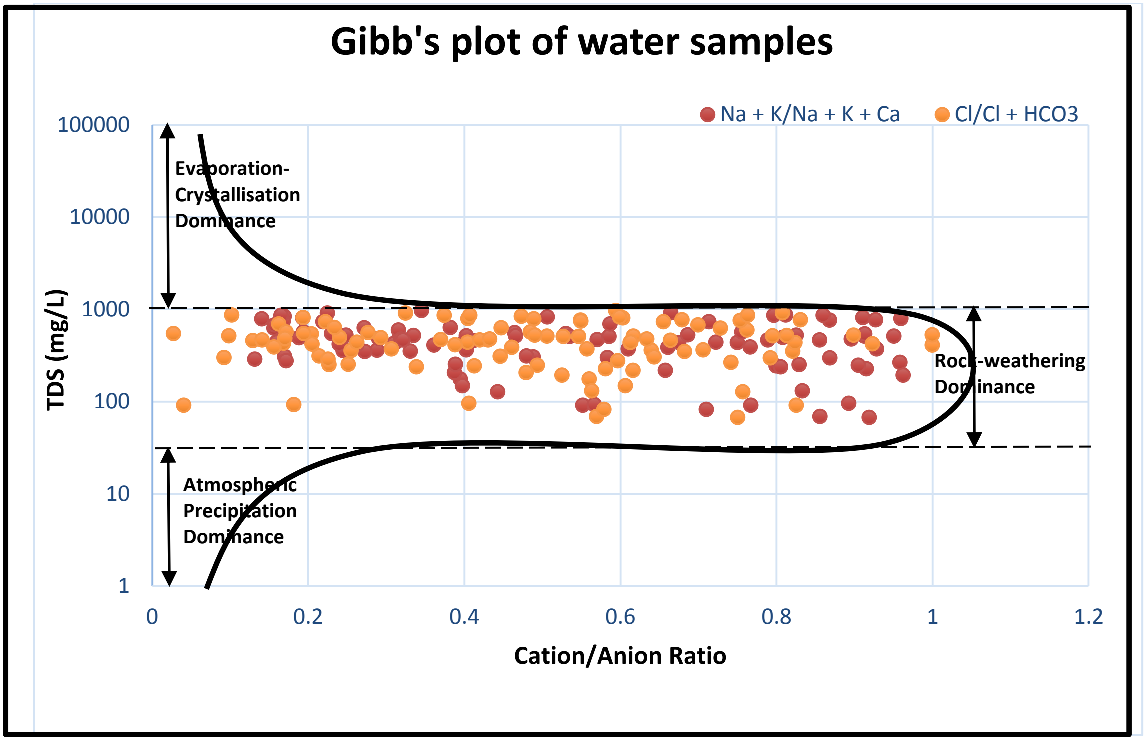

Figure 6: Gibbs plot showing major processes controlling groundwater chemistry

Ionic concentration of major elements present in groundwater were analyzed for relative abundances and ionic affinity. Schoeller plot was used to decipher the relative abundance of ionic concentration in the groundwater which is in the order of (relative abundance of cations is: **Na^++K^+** > Ca^{2+} > Mg^{2+}; while the relative abundance of the anions is: **Cl^-** > HCO_3^- > SO_4^{2-}) as shown in figure 7. This suggest enrichment of ions from dissolution of diverse lithologic framework underlain the study area, compared to ionic exchange phenomenon.

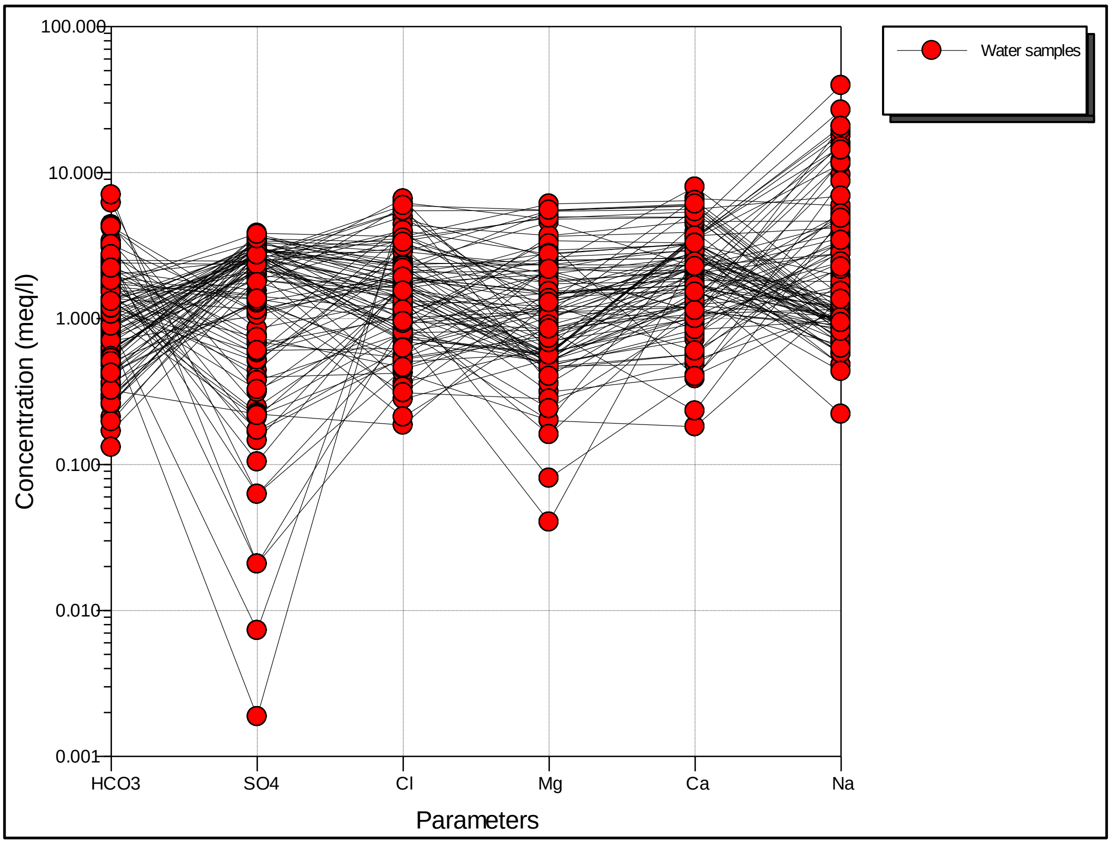

Figure 7: Scholler's classification for the hydrochemical components

Simple mineral dissolution or ionic mixing processes is mainly responsible for the variation in the hydrochemistry of the water samples in the study area as it depicted by the cluster of the data points plotting majorly in the simple dissolution or mixing rectangle (Figure 8) which depicts a high rate of dissolution of chemical constituents usually experienced at the peak of the rainy season. However, few of the samples plotted within the 'Ion Exchange' and 'Reverse Ion Exchange' fields, indicating that the water in the study area has undergone partial mixing. The cluster of data groundwater sample points represents samples with similar composition of anions and cations (Figure 8).

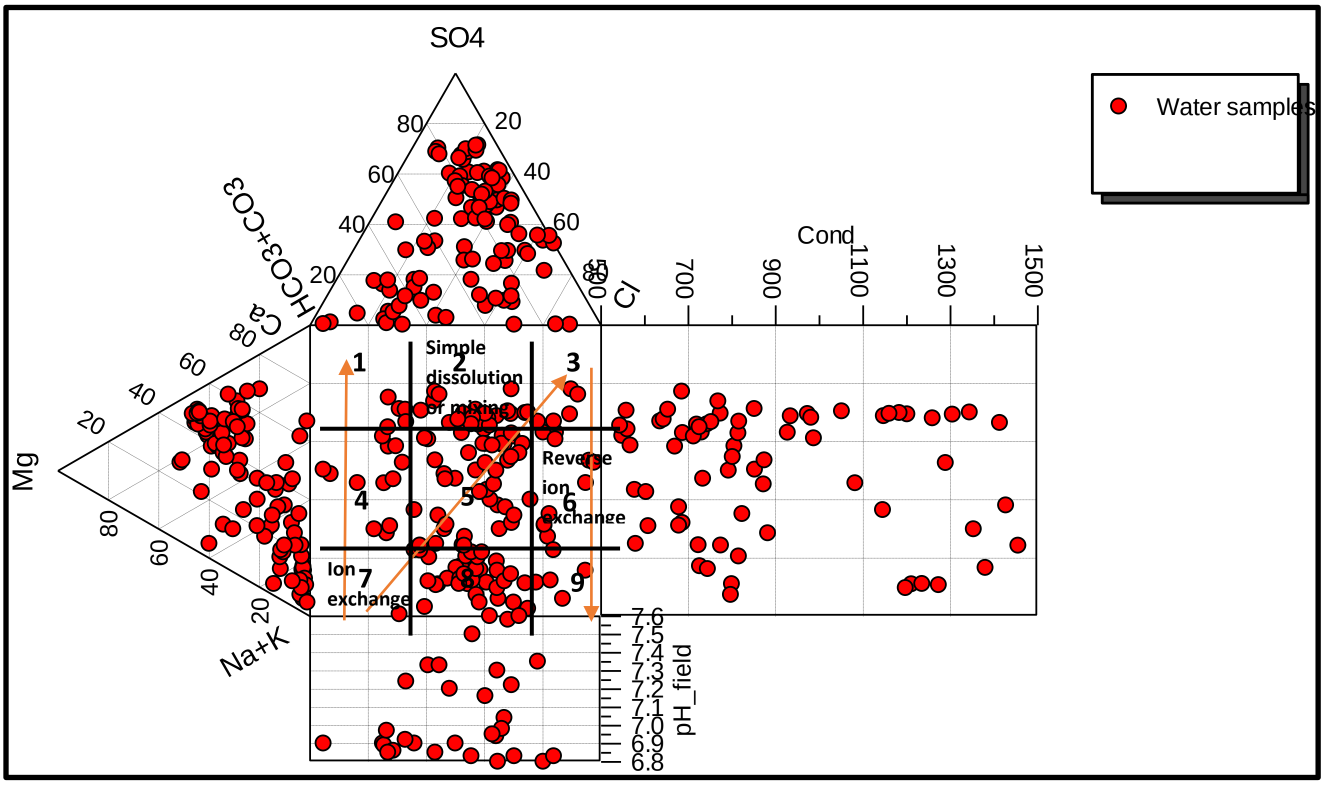

Figure 8: Durov's Plot of the Studied Water Samples

4.5 HYDROCHEMICAL CLASSIFICATION

The classification of groundwater facies was done using Piper's diagram (Piper 1944). The ternary diagrams (Figure 9) show the water samples in the study area are basically 'Alkali waters' with 'Earth Alkaline' components that are predominantly HCO_3^- and Cl^-. The relative abundance of the three (3) dominant water types are: **Na-HCO$_3$-Cl** > Ca-Mg-HCO$_3$-Cl > Na-Ca-Cl. The plots of desirable data on the diamond-shaped field classify the groundwater types into three groups (Figure 9).

Majority of sample (85 %) falls in groups I and II which show evolved groundwater type where unique chemical masking is achieved through rock-water interaction, ion exchange within unsaturated zones; increased resident time; and anthropogenic influences.

The group III water types representing meteoric signatures or fresh recharged water constitutes only 5 % of the total samples. The location of the samples collected varies widely both vertically and spatially within the study area, suggesting precipitation as the major source groundwater recharge.

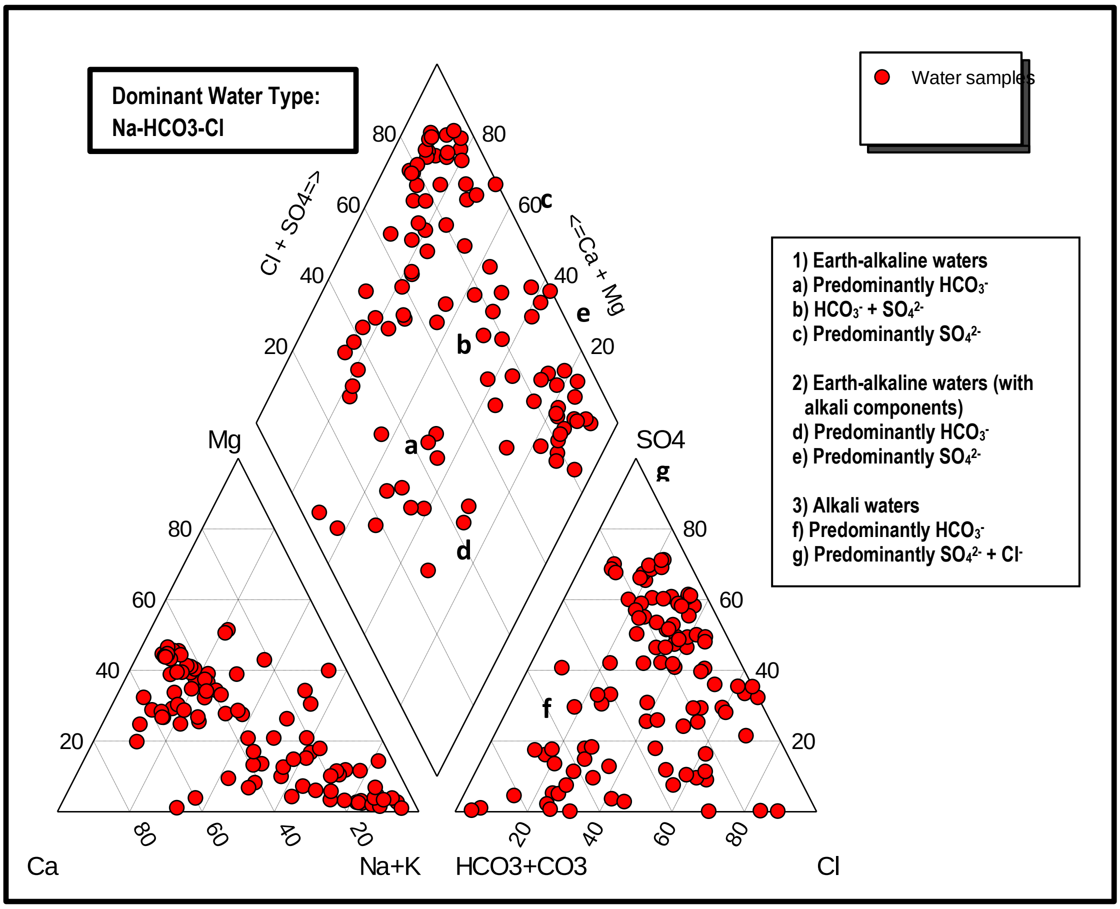

Figure 9: Piper's trilinear plot showing the different hydrochemical facies

The sodium hazard of the groundwater samples in the study area ranges from 'Low' to 'Very High', with most of the samples plotting within the 'Low' field; while the salinity hazard ranged from 'Low' to 'High' as shown in figure 10. This indicate that the groundwater of the area can be used for plants having good salt tolerance and also indicate that it suitable for irrigation purposes, in case of tube wells development.

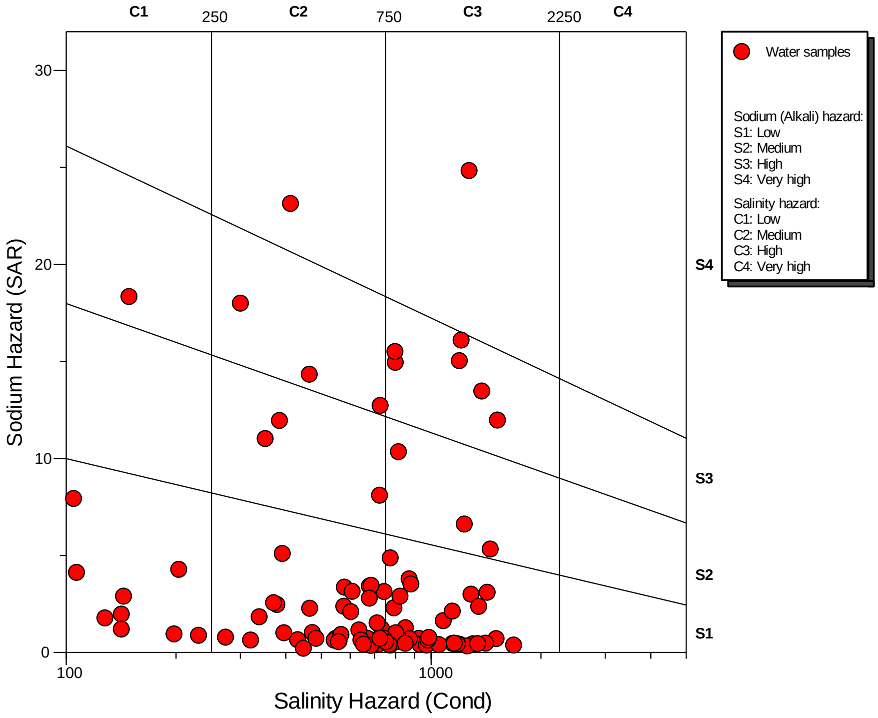

Figure 10: Wilcox plot of water samples

5.0 CONCLUSION

As far as suitability is concerned virtually all the studied cations and anions revealed average concentration lower than the maximum permissible limit for drinking water by WHO, (2017). Though the compiled overall water quality index for the studied groundwater shows 'very poor water quality'. These are due to the fact that WQI rating reflect the composite influence of different water quality parameters. Heavy metals such as iron, lead and chromium show average concentrations that is above the threshold of world health organization's standard for drinking water. Though the slight contamination of those heavy metals does not call for alarm, but constant monitoring is required to safeguard further contamination of those metals.

The result of the multivariate statistical analysis, as applied to the chemical data set of groundwater in the Zamfara underlain aquifer, provides an insight into the underlying controlling Hydrochemical processes in the area. Five factors including factor-1 (total hardness, chloride, nitrate, manganese, bicarbonate and alkalinity), factor-2 (TDS, conductivity, total hardness, magnesium and calcium), factor-3 (Temperature, sodium, potassium, copper, zinc, iron and chromium), factor-4 (calcium, magnesium and nitrate) were extracted from the data-set represents the signatures from dissolution of bedrock through which the groundwater passes, ionic mixing, leaching from the lateritic overburden, agricultural activities (fertilizer application) and effluent from waste dumpsites in the area. Out of 86.43% of the total variance in the dataset, ionic enrichment coming from natural means accounts for 69.63%. The porosity and permeability of the aquifer system in the area allows for groundwater movement of contaminant from one point to another. The remaining 16.80% is attributed to manmade factors like farming activities and poor land-use system prominent in the area.

The distribution of major ions in the groundwater is as follows: relative abundance of cations is: **Na^++K^+** > Ca^{2+} > Mg^{2+}; while the relative abundance of the anions is: **Cl^-** > HCO_3^- > SO_4^{2-}. Groundwater of the Zamfara aquifers are majorly of evolved type with mixing of ionic concentrations. Alkalis are more in abundant that alkaline earth, while Cl and HCO_3 dominate SO_4 and NO_3. The water samples in the study area are basically 'Alkali waters' with 'Earth Alkaline' components that are predominantly HCO_3^- and Cl^-. The relative abundance of the three (3) dominant water types are as thus: **Na-HCO_3-Cl** > Ca-Mg-HCO_3-Cl > Na-Ca-Cl. Simple mineral dissolution or mixing processes is mainly responsible for the variation in the hydrochemistry of the water samples in the study area.

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