Hydrogeochemical Investigation of Groundwater Quality in Zing and its environs, part of Jalingo Sheet 236NE, North-Eastern Nigeria

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Abstract

Hydrogeochemical investigation in Zing and its Environs, North-Eastern Nigeria, aimed at determining groundwater quality characteristics has been carried out. Geological mapping was accompanied by sampling of 19 rocks out of which 12 representative samples of the rock were analysed for elemental and mineralogical composition using X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) methods. Similarly, 28 groundwater samples were collected and analysed for their physicochemical parameters using standard water analysis methods. The study suggests that the area is underlain by granites, granodiorites, gneisses, and pegmatites comprising of heavy and light elements and minerals species such as quartz, albites, microcline, and biotite as major minerals. All measured chemical ions in the groundwater samples except Cl^-, F^-, Fe^{+2}, $Zn^{+2,}$ Cr^{+3} and Pb^{+2} are within national and international permissible limits. Ca^{+2} and HCO_3^- are the dominant ions. The hydrogeochemical facies infer four classifications with 71.4% characterized as Ca^{2+}- Mg^{2+}- HCO_3^-, 14.3% as Na^+- K^+- HCO_3^- while others are of Na^+- K^+- Cl^- SO_4^{2-} and Ca^{2+}-Mg^{2+}- Cl^--SO_4^{2-}facies. The hydrogeochemical processes and reactions within the aquifer materials influencing groundwater chemistry and concentration of chemical ions in the study area were identified as rock-water interaction and a combination of evaporation and precipitation, reverse ion exchange, ion exchange and simple dissolution or mixing.

Keywords:

INTRODUCTION

Groundwater is one of the major sources of water supply for various uses globally because it is comparatively fresh and widely distributed unlike the surface water. However, the presence of certain chemical ions at a higher concentration has made groundwater unsuitable for utilization in some places (Brindha and Elango, 2011). Hydrogeochemical processes are responsible for the seasonal, temporal, and spatial variations of groundwater chemistry and subsequently their quality (Waziri *et al*., 2019).

The chemical composition of groundwater therefore is adjudged safe for utilization when it is within the permissible limit prescribed by the international and national water quality regulating agencies otherwise it becomes unsuitable for use and of great concern to humans' lives. Consequently, in response to the high demand for groundwater and the increased risk of contamination induced by natural or human factor, a better understanding of groundwater quality and its availability is needed for efficient management of the resource (Montcoudiol, 2015).

The aim of the research is to determine the groundwater quality characteristics of Zing and its Environs, North-Eastern, Nigeria.

The study area is Zing and its Environs, Jalingo Sheet 236NE, Taraba State, Northeastern, Nigeria. The area lies between Latitudes 08^0 44′.00” to 09^0 05′.00” and Longitudes 11^0 40′.0” to 11^0 52′.00”E with a total land area of about 707km^2 and with a population of 170,600 (Nigerian Population Commission, 2006). The area is underlain by crystalline basement complex dominated by low rising hills and rock outcrops of the Adamawa massif of Northeastern. The area consists of both igneous and metamorphic rock units. Groundwater development in the area is met with difficulties due to lack of primary porosity in the bedrock. However, the secondary porosities such as fractures (joints and faults) and weathered zones are the sources of groundwater occurrence and movement (Chiton and Foster, 1995, Foster et al 2008, Srinivasa, 2000, Wright and Burgess, 1992). Hence, these features constitute the different aquifer systems and influences the storage, transmission, and distribution of groundwater in the area.

METHODOLOGY

The research methodology includes reconnaissance and desk study, field work, laboratory analysis, data processing and interpretation of results. A total of nineteen (19) locations of rock exposure were sampled and represented on a topographic map. The elevation of rock exposures and attitudes of geological structures were also determined with the aid of a Global Positioning System (GPS) device and a compass-clinometer. Local sources of pollution such as latrines, burial grounds, cattle pens, and market areas including waste dump sites were also observed. The images of geological features were also captured in the field with a portable digital camera. Consequently, the results obtained from this exercise was finally utilized to update the existing geological map of the study area.

The inventory of boreholes which are mainly hand pumps where groundwater samples were collected were recorded accurately on a field data sheet. The respective sample locations such as latitudes and longitudes, altitude/elevation was also recorded with a handheld Global Positioning System (GPS). A total number of twenty-eight (28) water samples from boreholes were sampled. At each sampling location, two (2) water samples each were collected in a 250ml capacity high density polyethene plastic bottles. The samples earmarked for Cations analyses is acidified with concentrated Tri-oxo-nitrate V Acid also known as Nitric Acid (HNO_3) to homogenize, preserve and prevent absorption/adsorption of cations on the walls of the plastic bottles while the other sample scheduled for Anion’s determination is collected as non-acidified in a separate container.

Physical parameters of water samples such as pH, Temperature ($O^{C)}$, Total Dissolve Solids (TDS) and Electrical Conductivity (EC) were measured *in-situ* in the field using **HANNA**198191- multi-parameter equipment for pH and Temperature determination while **HANNA**198192 for determination of Electrical Conductivity and Total Dissolved Solids.

The chemical constituents in water samples such as Sodium (Na), Potassium (K), Calcium (Ca), Magnesium (Mg) Chloride (Cl), Carbonate (CO_3), Bicarbonate (HCO_3), Sulphate ($SO_{4,)}$, Nitrate (NO_3), Fluoride (F) Manganese (Mn), Zinc (Zn), Chromium (Cr), Lead (Pb), Cupper (Cu), Cadmium (Cd) and Cupper (Cu) were analysed at the stated laboratory. The Ethaline Diamine Tetra Acetic (EDTA) titrimetric method was used to analyse calcium, magnesium and total hardness concentrations, sodium and potassium was determined by Flame Photometer while carbonates and bicarbonates ions were determined by potentiometric method using HACH DR-890 Photometer. The CHROMA Colorimetric (252) method was utilized for determination of Sulphate, Nitrates and Nitrites were both determined by Nitraver-5 (HACH DR-900) equipment while Fluoride was analysed with Palin test Photometer and SPADNS Reagent. Heavy and Trace elements such as Lead, Copper, Zinc and Manganese were analysed by Trace O Metalyzer through Anodic stripping while Chromium and Iron by HACH DR-900 Photometer (Carbazide Method) and Phenanthroline Method (HACH DR-900 Photometer) respectively.

Rock samples were analysed using the Thermo Fisher Scientific Energy Dispersive X-ray Fluorescence (EDXRF) Analyser and the X-Ray Diffraction Empyrean diffractometer for determination of elemental and mineralogical composition of rock samples respectively.

RESULTS AND DISCUSSIONS

Geology

The geology of the area has been studied and based on field observations, the major rock units in order of increasing abundance are the porphyritic granites, granodiorites, coarse-grained granite, fine-grained granite, granite-gneiss, and pegmatites.

Geochemistry and Mineralogical Composition of Rocks in the Study Area

The elemental composition of major elements of the rocks in the study area (Figures 1 and 2) revealed that Silica (Si) and Aluminium (Al^{3+}) are the most enriched elements in the rocks compared to other elements as contained in the XRF analyses. The concentration of Silica ranges from **30.18% to 39.18%** with a mean value of **35.14%** while aluminium ranged from **7.14% to 12.09** with an average 8.19%. Other chemical elements with mean values in order of decreasing abundance are Potassium (K^+) 3.44%; Iron (Fe^{+2}) 1.72%; Sodium (Na^+)1.67%; Calcium (Ca^{2+})0.78%; Magnesium (Mg^{2+})0.72%. The least elemental concentrations in the rocks are the Titanium (Ti) 0.23%; Phosphorous(P)0.19%; Manganese (Mn^{2+}) and Chromium (Cr^{3+})0.00%.

The trace elements in the rock samples measured in ppm showed significant concentration of Strontium (Sr) and Barium(B) compared to other elements. The Sr concentration in the rocks ranged from 1.27ppm to 6,760ppm with a mean value of 3,343.4ppm while B is between -400ppm to 4,300ppm with a mean value of 1,035.4ppm. others are Lead (Pb^{2+}) with a mean value of 239ppm; Chloride (Cl^-)205.17ppm; Rubidium (Rb)188.21ppm; Zinc ($Zn^{2+)}$171ppm; Cupper ($Cu^{2+)}$53.1ppm; Thorium (Th)31.03ppm, Vanadium (V)25.57ppm; and Gallium (Ga)24.61ppm, Nickel (Ni) with 5.83ppm while the least is Arsenic with 0.00ppm in order of decreasing abundance.

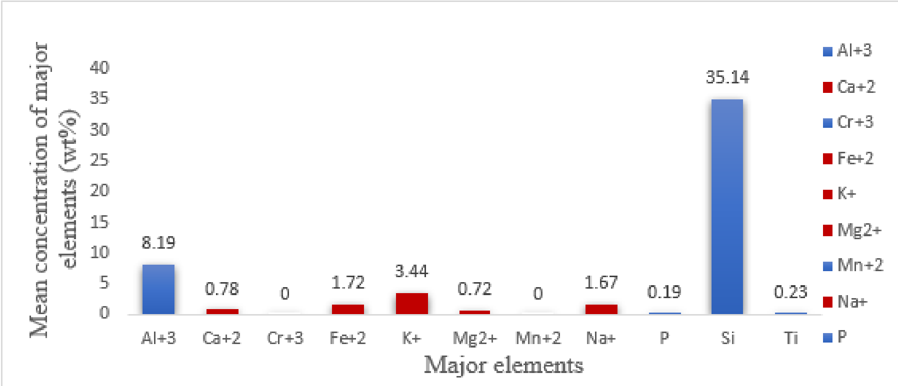

Figure 1: Mean concentrations of major elements of the study Area

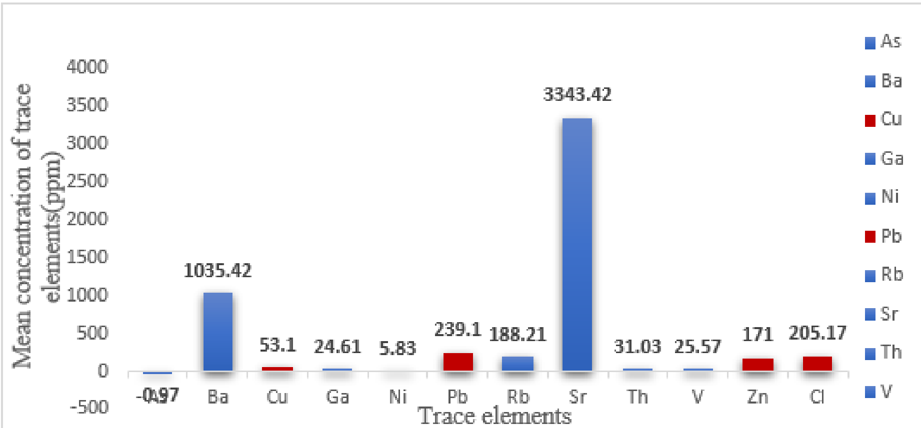

Figure 2: Mean concentrations of trace elements of the study Area

Petrogenesis and Bulk Chemical Composition of Rocks in the study Area

The rock samples subjected to XRF analyses were plotted in Total Alkaline Silica (TAS) diagram and they signify that they are felsic rocks. The plot of the oxides of Silica (SiO_2) versus that of Sodium (NaO) and Potassium(K_2O) indicates that they are of granite and granodiorite types as documented by Haruna *et al*., 2010 and confirmed by the geology of the present study respectively. This also indicates that the origin of the rocks is because of partial melting of the upper crust as reported by Cox *et al*., 1969. The bulk chemical composition of all the rock samples confirmed percentage weight (wt%) of SiO_2, Al_2O_3, K_2O and MgO suggesting enrichment of felsic and alkaline minerals. The SiO_2 ranges from 64.54% to 75.81% with a mean value of 70.75%; Al_2O_2 ranges between 12.56% and 18.83% with a mean value of 14.88%, K_2O between 2.62% and 5.89% and a mean of 4.40%; Na_2O between 2.04% and 4.45% and a mean of 3.5%. others are MgO content between 0.47% and 3.40% and a mean of 1.19%. The low concentration of Fe_2O_3, MnO, CaO, MgO and P_2O_5 reflects the felsic nature of the rock and indication that its granitic in origin.

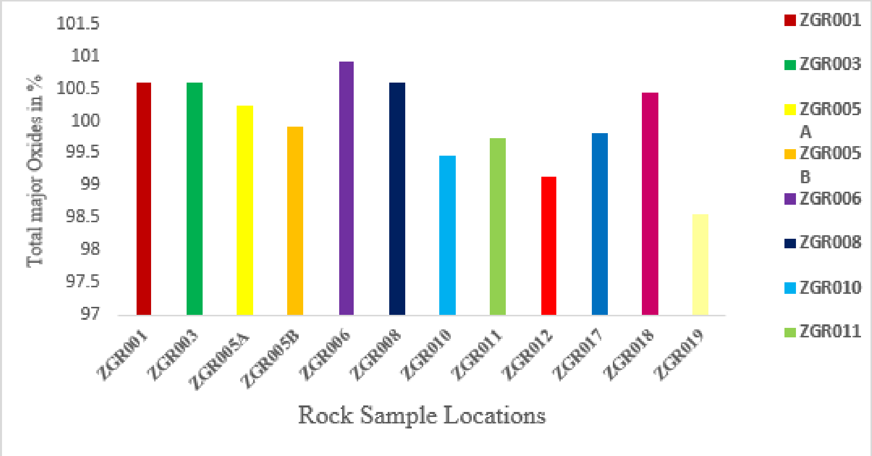

Figure: 3a: Bar Chart of XRF mean concentrations of major oxides of the study Area

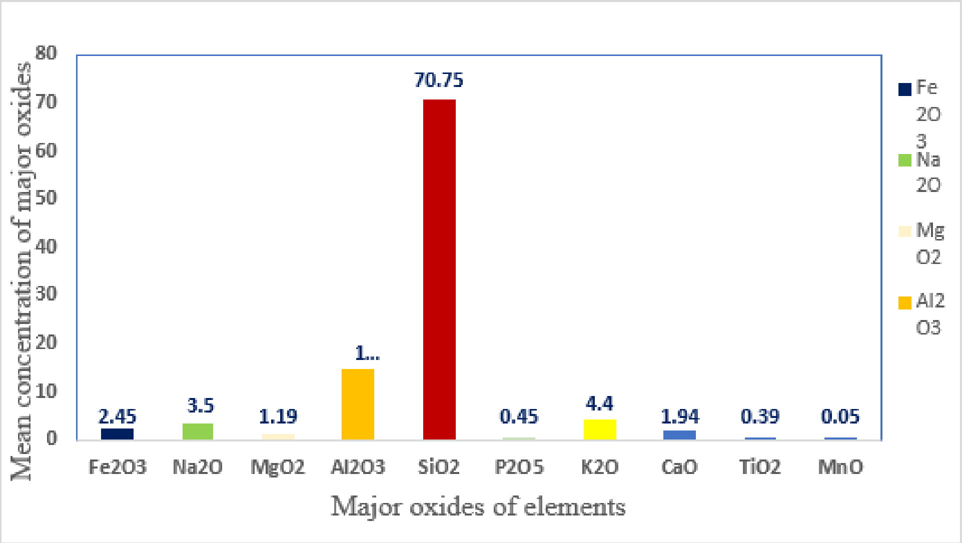

Figure: 3b: Bar Chart of XRF mean concentrations of major oxides of the study Area

Mineralogical Composition of Rocks in the study Area

The overall mineralogy of the rocks indicates that Quartz, Albite, Microcline and Biotite are the major mineral composition. Quartz occurred in all the 12 rock samples representing 100%, albite in 10 samples indicating 83% occurrence, microcline in 9 samples representing 75% occurrence in the rocks analysed and biotite showing 50% in 6 of the rock samples. Other minerals such as Kaolinite indicated 16.7% occurred in 2 samples while Sanidine, Annites, Actinolite, magnetite and Phlogopite represents 8.3% in 1 sample each. The elemental and mineralogical composition of the rocks therefore suggests that they are integral part of the rock at formation and emplacement stage.

1.1.Physiochemical Analyses of Water Samples

The physiochemical results of geochemical and mineralogical analyses of water and rock samples collected respectively within the framework of this research work were interpreted using relevant data processing software, tables, and graphical representations.

The result of the physical parameters of groundwater water samples of the study area are summarized in Table 1.

Table 1: Summarised results of measured physical parameters of water samples

Locality	**EC (μS/cm**	**TDS (ppm)**	**pH**	**Temp(ºC)**
Min Value	97.1	63.1	6.62	28.2
Max Value	1138	740	7.5	31.3
Mean	562.11	365.43	7.14	29.49
Stand. Deviation.	231.34	150.36	0.26	0.79
WHO, 2017	1000	600-1000	6.5-8.5	Ambient?
NSDWQ, 2015	1000	500	6.5-8.5	Ambient

Physical Characteristics

The wide range of EC and TDS values observed particularly in two groundwater samples of the study area particularly in some locations could be due to mineralization because of rock-water interaction as well as residence time of groundwater within the aquifer matrix

The plot of Electrical Conductivity (EC) μS/cm Versus Total Dissolved Solids (TDS) mg/l of groundwater samples (Figure 4) gives a high correlation coefficient of 1.00 thus confirming the linear relationship of the parameters and the efficacy of field measurements.

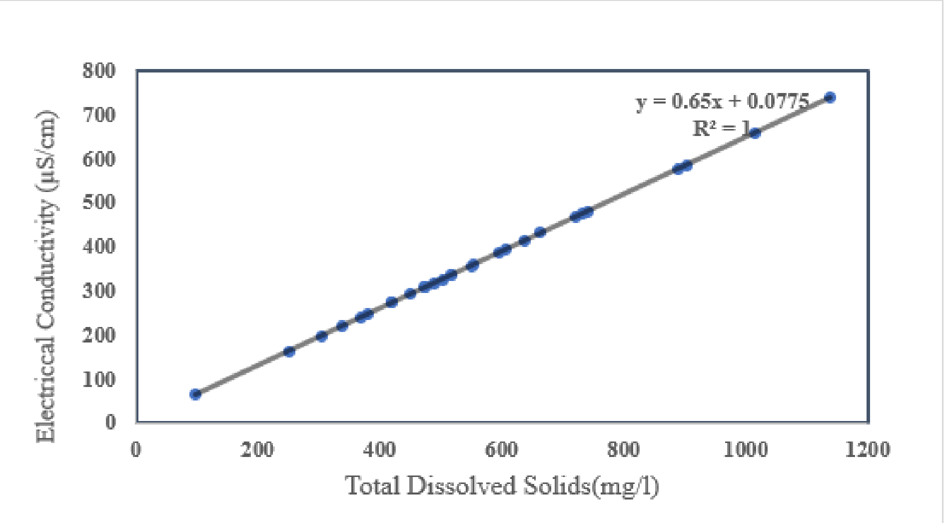

Figure 4: Electrical conductivity (EC) Versus Total Dissolved Solids of groundwater of the study area.

The total hardness of groundwater samples of the study area ranged between 66.0mg/l and 2250mg/l with a mean value of 303.43mg/l. Statistically, the values of 11(39.3%) samples out of 28 shows that it is higher than the prescribed guideline of 150mg/l by WHO, 2017 and NSDWQ, 2015 while the remaining 17(60.7%) fall within the prescribed limits (Table 2). According to Hems,1970 classification of water hardness, the groundwater samples can be classified into moderate to very hard water considering the as represented in Table 2. The hardness of water is usually indicated by precipitation of soap scum and the need for excess use of soap to achieve cleaning. Depending on the interaction of other factors, such as pH and alkalinity, water with a hardness above approximately 200 mg/l may cause scale deposition in the treatment works, distribution system and pipework and tanks within buildings.

Table 2: Classification of Groundwater based on hardness (Hem, 1970)

Total Hardness(mg/l)	**Water Class**	**No of Samples**	**% of Samples**
0-60	Soft	0	0
61-120	Moderately Hard	12	42.9
121-180	Hard	9	32.1
>180	Very Hard	7	25

Hardness is beneficial in drinking water despite the problem it creates for the piping systems and laundry (Oteze,1991). Hardness is medicinal and people that live in hard water areas suffer less from cardiovascular diseases than those who live in soft water areas

(Schroeter, 1966). The water hardness map of the studied groundwater shown in figure concentration map according to groundwater hardness of Hems, 1970 classification is displayed in figure 4.3

Chemical Characteristics

Chemical characteristics of the water showed that Fluoride, lead, chromium, and iron are the elements found to have concentrations higher than both national and international standards.

Fluoride

Fluoride concentration in groundwater samples ranged between 0.47mg/l and 5.84mg/l with a mean value of 2.52mg/l. A total of 21 samples out of 28 representing 75% of the total samples analysed has fluoride concentration above 1.5mg/l while 7 samples representing 25% contains fluoride concentration less than 1.5mg/l. These values imply that the fluoride concentration in groundwater in most locations exceeds the permissible limit of 1.5mg/l by WHO, 2017; NSDWQ, 2015. Because there is absence of industries in the area that could have discharged fluoride rich effluent into the soil or surface water, the high fluoride concentration in groundwater of the area may be attributed to weathering and dissolution of rocks as well as irrigation processes which also accelerates weathering of rocks.

Fluoride concentration between 1.5-4.0mg/l leads to dental fluorosis, skeletal and crippling fluorosis (Msonda *et al*., 2007 and Ndolo, 2002) while other studies revealed that the effects of fluoride could also lead to mental retardation in children (Andy and Silas., 2020). Other conditions and health challenges associated with excess fluoride intake include, abdominal pain, excessive saliva, nausea and vomiting, seizures, and muscle spasm (Chae et al, 2007; Aminu and Amadi, 2014).

The result of XRD analyses of rock samples in Tables 4.1d and 4.1e revealed the presence of biotite and Actinolites, a fluoride rich mineral could have been responsible for their high concentration in groundwater system of the area. Fluoride concentration and risk maps (Figures 4.5 and 4.6 and **Plates** XXVI to XXXII are evidence of fluorosis in the study area.

Table 3: Statistical summary of Heavy and Trace Elements of Water Samples Compared with WHO, 2017 and NSDWQ, 2015 Guidelines

Locality	**Pb**	**Cu**	**Cd**	**Cr**	**Zn**	**Mn**	**Fe**
Min	0.00	0.00	0.00	0.00	0.011	0.002	0.16
Max	0.068	0.081	0.012	0.34	0.472	0.127	0.84
Mean	0.011	0.013	0.001	0.047	0.071	0.023	0.431
Standard Deviation	0.014	0.022	0.002	0.069	0.102	0.033	0.182
WHO, 2017	0.01	2.0	0.003	0.05	0.1	0.1	0.3
NSDWQ, 2015	0.01	1.0	0.003	0.05	3.0	0.2	0.3

Lead (Pb)

Lead concentration in the groundwater samples ranged between 0.00mg/l and 0.068mg/l with a mean value of 0.011mg/l. A total of 8 (28.6%) samples have lead concentration greater than 0.01mg/l which is the prescribed permissible limit for drinking water by WHO, 2017 and NSDWQ, 2015(Table 3). The remaining 20 (71.4%) samples are withing the prescribed limits by the stated national and international organization. Lead is relatively a minor element in the earth crust and widely distributed in low concentration in rock and soils. High concentration of lead result from atmospheric input originating from its use in leaded gasoline or from smelting operations. Industrial and mine, or smaller operation may contain relatively large amount of lead.

The concentration of lead in drinking water are generally low but much higher concentration has been measured where lead services connections of fittings are present (WHO, 2017). The primary source of lead is from service connections and plumbing in buildings. Lead concentration can also be varied according to the period which water has being in contact with lead containing materials. Lead is toxic to aquatic organisms and the degree of toxicity varies greatly and depends on water quality characteristics as well as species being considered. Lead exposures is associated with a wide range of effects including various neurodevelopmental effects, mortality mainly due to cardiovascular diseases, impaired renal function, hypertension, impaired fertility, and adverse pregnancy outcomes (WHO, 2017). The sources of lead therefore could be from the rocks and soil or atmospheric input due to the absence of industries in the area.

Chromium (Cr^{+3})

The groundwater samples of the study area ranged between 0.00mg/l and 0.34mg/l with a mean value of 0.47mg/l which is within the permissible limit of 0.05mg/l by WHO, 2017 and NSDWQ, 2015 (see table 4.4). The above values obtained from chromium samples particularly in eight locations representing 28.6% of the total samples were above the permissible limits of 0.05mg/l prescribed by the WHO, 2017 and NSDWQ, Hence, could portend serious health challenge such as cancer to humans when consumed (WHO, 2017 and NSDWQ, 2015).

Chromium concentration in natural water is usually in very low and elevated chromium concentration can result from mining and industrial purposes. The ultra-mafic igneous rocks are higher in chromium composition than other rock types, chromite ($FeCr_2O_4$) may be concentrated in lateritic residue overlying ultramafic rocks. Chromium is also found naturally in most rocks, plants, soil, and volcanic dust as well as sea animals.

Iron (Fe^{+2})

Iron II concentration of water samples varied from 0.16mg/l to 0.84mg/l with a mean value of 0.43mg/l. A total of 17 water samples representing 60.7% of the total sample have Iron II, concentration greater than 0.3mg/l prescribed as permissible limit for consumption by WHO, 2017 and NSDWQ, 2015 while the remaining 11 samples representing 39.3% are within the limits. Iron is an abundant element in the earth crust but exists generally in minor concentrations in natural waters). Iron is an essential element in human nutrition which are taken as supplements for pregnant and lactation women or prescribed on specific clinical requirement. Iron also promotes the growth of "iron bacteria", which derive their energy from the oxidation of ferrous iron to ferric iron and in the process deposit a slimy coating on the piping. At levels above 0.3 mg/l, iron stains laundry and plumbing fixtures. No health-based guideline for Iron has been proposed by either WHO or NSDWQ.

Igneous rock minerals whose iron content is relatively high include the biotite, magnetite, amphiboles, pyroxenes and particularly the nesosilicates olivine (Olasumbo and Olufemi, 2020*)*. Iron may also be present in drinking water because of the use of iron coagulants or the corrosion of steel and iron pipes during water distribution. The form of solubility of iron in natural waters are strongly dependent on pH and oxidation-reduction of the water. (Olasumbo and Olufemi, 2020). The source of Iron II, in groundwater of the study area could either be from the underlying rock bearing minerals or because of corrosion of steel and iron pipes considering the make of the water source which are majorly hand pumps. The Iron concentration map displayed in Figure 4.8 give an overview of iron distribution in the study area. The possible source of iron in the area could be the reaction of water with iron steel pipes of the hand pumps in the affected wells.

Hydrochemical Assessment

The initial chemical composition of groundwater usually begins as soon as water percolates/infiltrates into the subsurface of the earth. To assess the relative concentration of chemical constituents, hydrochemical facies, hydrogeochemical processes and sources of measured chemical parameters in groundwater of the study area, the Schoeller, Stiff, Piper, Durov and Gibbs diagrams were employed.

Schoeller Plot

The Scholler diagram represents a semi - logarithmic diagram of the concentration of groundwater samples of the study area, it is employed to illustrate the relative concentration of both cations and anions expressed in milliequivalent per litre. It is also used for visual comparison of ionic concentration in water. It is beneficial because it allows multiple comparisons of water analyses and finding the degree of saturation in water. The Schoeller diagram of the study area as revealed in figure 4.9a indicates that the dominant ions in groundwater samples in order of abundance is $\mathbf{Ca^{+2} > K > Na^{+} > Mg^{+2}}$ or $\mathbf{Mg^{+2} < Na^{+} < K^{+} < Ca^{+2}}$ for major cations while $\mathbf{HCO_3 > Cl > CO_3 > SO_4 > NO_3 > NO_2}$ or $\mathbf{NO_2 < NO_3 < SO_4 < CO_3 < Cl < HCO_3}$ for major anions with possible $CaMgHCO_3$ water type as the most dominant water type in the area.

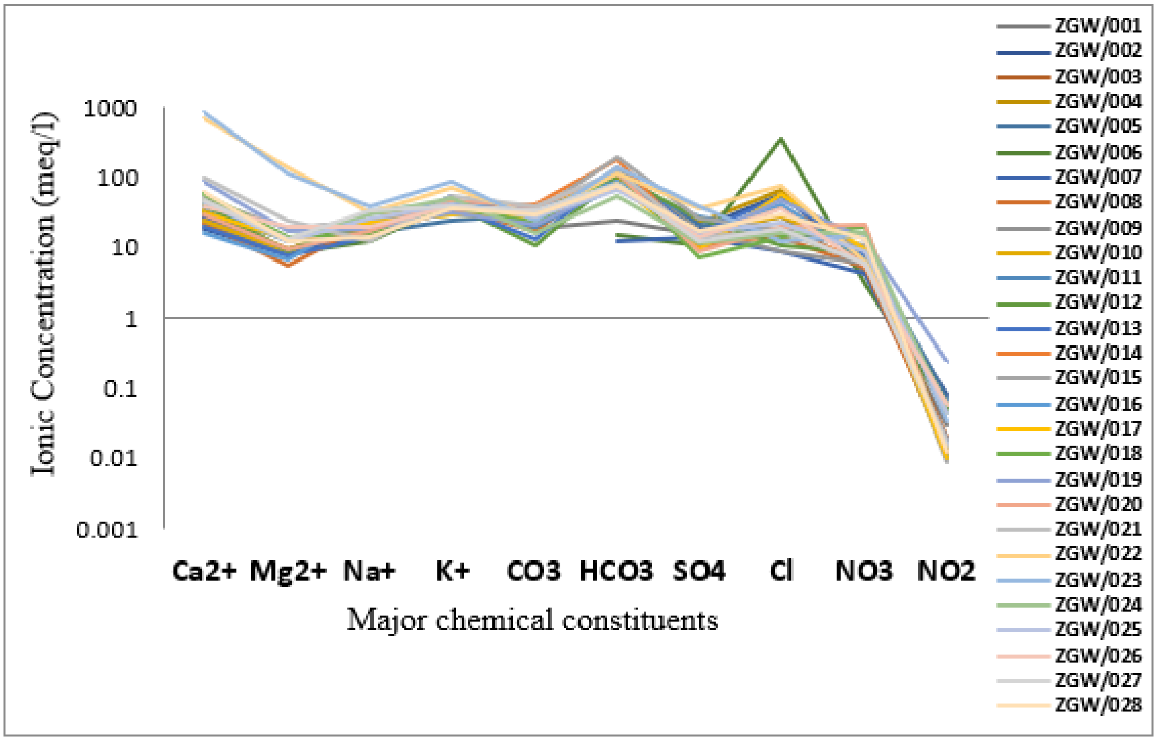

Figure 5: Scholler Plot of water samples in the study area

Stiff Plot

The stiff plot of groundwater samples of the area as presented in Figure 4.9b showed that the dominant anion in 27 (96%) out of the 28 groundwater water samples is HCO_3 + CO_3 with Cl^- as the dominant anion in only 1 (4%) sample. The dominant cation is Ca^{2+} in 20 (71.4%) of the samples while Na^+ is dominant in the remaining 8 (28.6) samples. The ionic abundance for the cations is $Ca^{2+}>Na^++K^+>Mg^{2+}$ in 15 samples and $Na^++K^+>$ $Ca^{2+}>Mg$ in the remaining 13 samples while the ionic abundance for the anions is HCO_3->Cl^->SO_4^{2-} in 23 samples and HCO_3-> SO_4^{2-} >Cl^- in 5 samples.

The stiff pattern in figure 6 showed similarity in almost all the samples except in four samples where the pattern appears to be distinctive. The variation in chemical constituents connotes groundwater evolution as its flows along its path over a period.

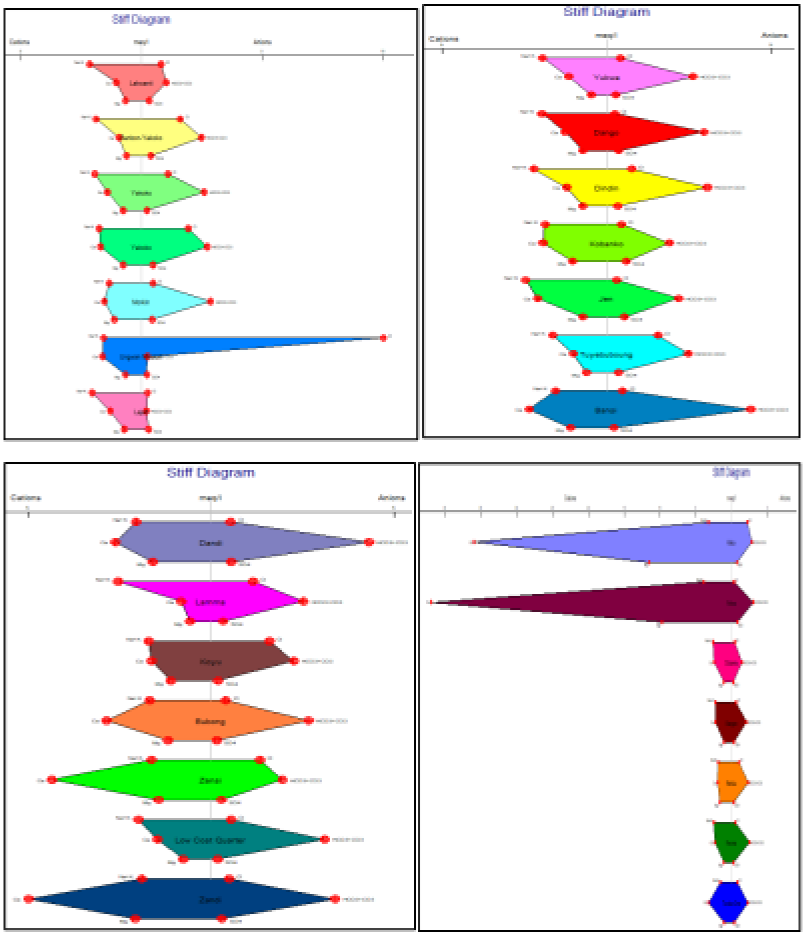

Figure 6: Stiff Plot of water sample of the study area

Piper Plot

The piper diagram of the study area, figure 7 indicates groundwater in the studied area is composed of four (4) water types and four (4) hydrochemical facies respectively.

The groundwater types and hydrochemical facies showed 21 (75%) samples out of the 28 correspond to the earth alkaline water with prevailing HCO_3, 4 (14.3%) samples conforming to alkaline water with prevailing HCO_3 while three (3) samples with 1 (3.6%) sample each corresponds to normal earth alkaline water with prevailing HCO_3 and SO_4 or Cl, earth alkaline water with prevailing SO_4 and Cl water respectively. Hydrochemical facies indicates four types with 20 (71.4%) samples corresponding to the Ca^{2+}-Mg^{2+}-HCO_3^- as the dominant facie, 4 (14.3%) samples corresponding to Na^+-K^+-HCO_3^- while 2 samples each fall corresponding to Na^+-K^+-$Cl^-SO_4^{2-}$ and Ca^{2+}-Mg^{2+}-Cl^--SO_4^{2-} respectively. The variations in the hydrochemical facies suggest possible groundwater evolution which could have been influenced by rock water interactions and residence time of groundwater.

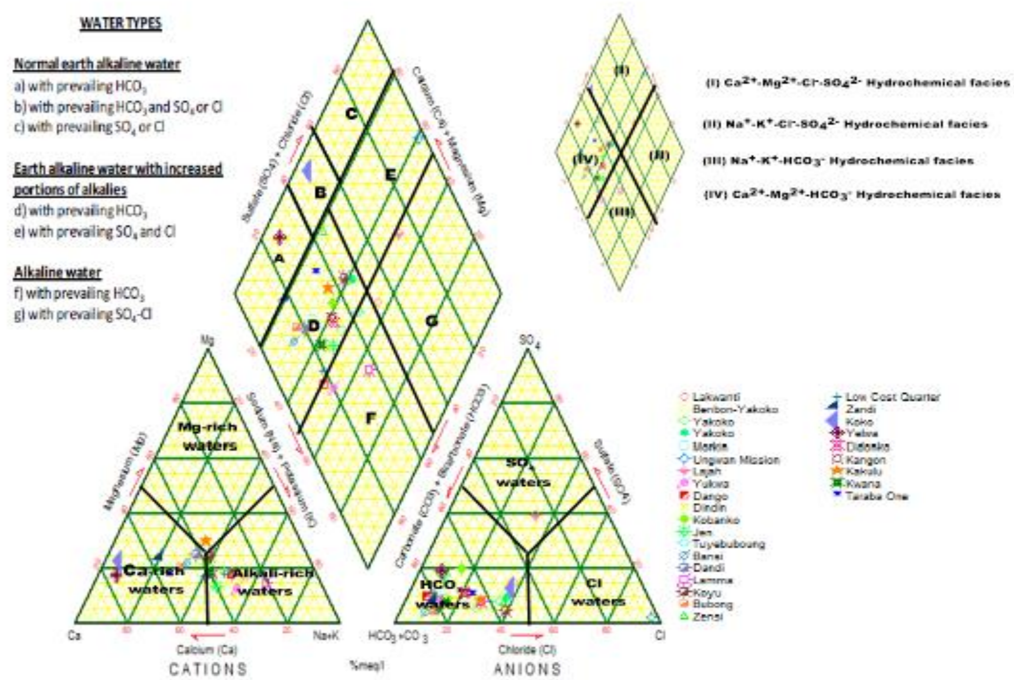

Figure 7: Piper Diagram of the study area

Assessment of Hydrogeochemical Processes

The Gibbs, Durov Diagrams and Source Rock Deduction and Reasoning have been employed to establish the geochemical processes influencing water chemistry including the origin and sources of measured parameters in groundwater samples of the study area.

The Gibbs diagram proposed by Gibbs, 1970, represents the ratios of sodium and potassium ions to sodium, potassium and calcium ions $(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$ for cations and chloride to chloride and bicarbonate ions $Cl^- / Cl^- + HCO_3^-$) for Anions as a function of Total Dissolved Solid (TDS) is widely used to determine the sources of chemical constituents such as rock water interaction, precipitation and evaporation dominance in groundwater. Therefore, the Gibbs plot of water sample of the area in figure 8 show three distinct parameters such as rock water interaction dominance, precipitation dominance, and evaporation dominance as the principal parameters controlling groundwater chemistry of the area.

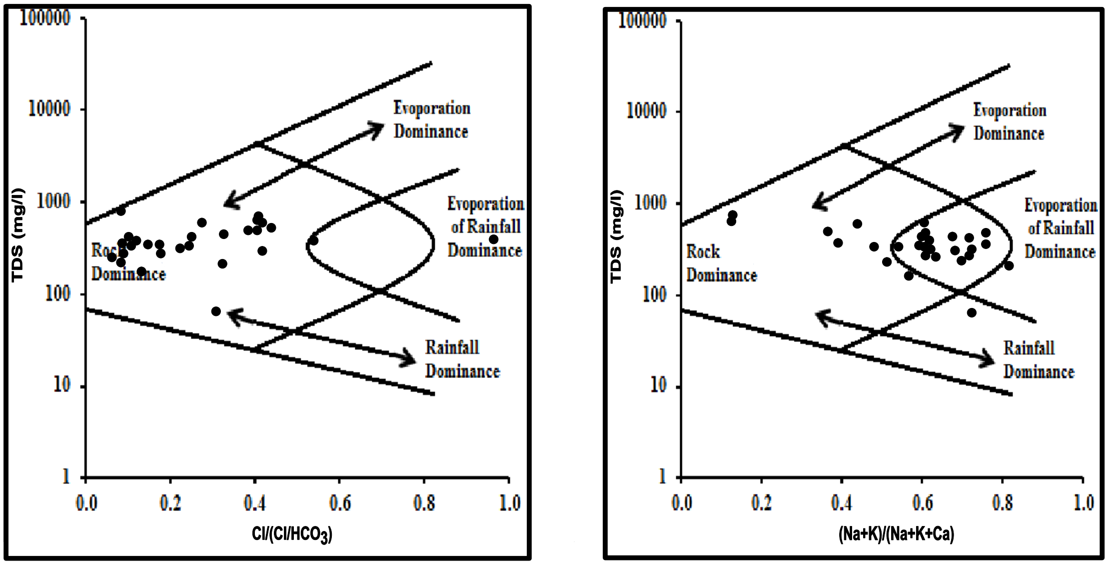

Figure 8: Gibb's diagram of the study area

Statistical analysis of the Gibb's diagram infers that the geological processes responsible for the chemistry of 26 (92.8%) of the water samples is dominantly Rock-Water interaction (using the anions plot) with only 2 (7.2%) samples depicting a combination of evaporation and precipitation. Consequently, using the cations, it indicated 10 (35.7%) water samples is linked to rock-water interaction, 17 (60.7%) samples indicated a combination of evaporation and precipitation while only one (3.6%) sample indicated precipitation dominance as the geological processes responsible for the chemistry of water. The weathering of the rocks or rather rock water interactions are the main reasons for the poor water quality of some groundwater samples facilitated by evaporation thereby increasing the concentration of ions in groundwater.

The Durov Diagram of groundwater in the study area, figure 9 indicated that the reverse ion exchange reactions as shown in field 6, accounts for 17(60.7%) samples which is the most dominant. The effect is generally observed when sea water intrusion (Lloyd and Heathcote, 1985) or oil field brine contamination occurs. Reverse ion exchange reactions in groundwater of the area indicates the release of Ca^{2+} and occasionally Mg^{2+} ion and decrease of Na^{+} and K^{+} ion concentration in the groundwater.

The simple dissolution or mixing with 7 (25%) samples aligning along the simple dissolution or mixing line on field 5, indicates recent recharge from precipitation exhibiting simple dissolution of chemical ions in the aquifer matrix whereas the 2(7.15%) samples each positioning on the axis of ion exchange and reverse ion exchange respectively is an indication of the removal of Ca^{2+} and Mg^{2+} and replaced with Na^{+} thereby increasing Na^{+} over Cl- or reducing same respectively (Lloyd and Heathcoat (1985).

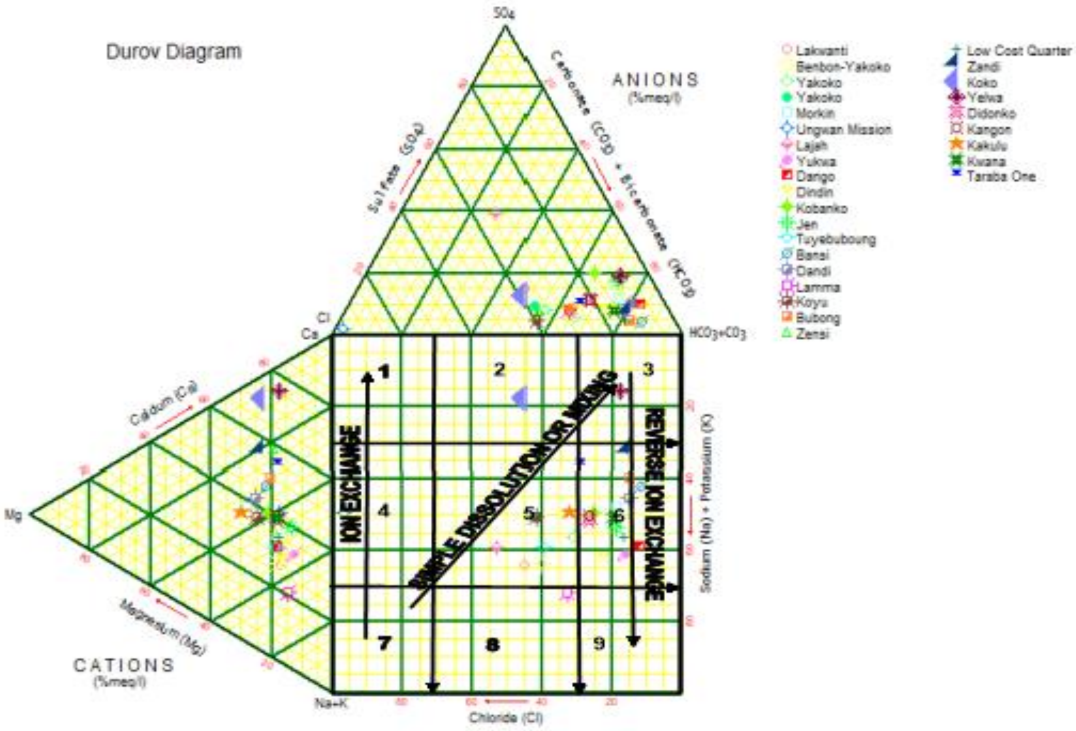

Figure 9: Durov diagram of the study area

RESEARCH FINDINGS

I. The study area is underlain by granites and granodiorites comprising of **porphyritic** granites, granodiorites, coarse-grained granite, fine-grained granite, gneiss, and pegmatites as the units in order of increasing abundance

II. The WHO (2017) and NSDWQ (2007) recommended guidelines for drinking compared with measured parameters in groundwater suggests that total hardness, Fe, Cr, Pb, Cl, Zn. and F of some wells are above the prescribed permissible limits and could be of risk to human health.

III. The moderate to very high-water hardness in the area could be associated to dissolved calcium, magnesium and bicarbonate minerals and the high levels of EC and TDS in two of the wells may be due to mineralization of groundwater by the host rock.

IV. The dormant ions in groundwater samples are the Ca^{+2} and HCO_3^{2} with $Ca^{+2}>K^{+}>Na^{+}>Mg^{+2}$ or $Mg^{+2}<Na^{+}<K^{+}<Ca^{+2}$ for major cations while $HCO_3>Cl^{-}>CO_3>SO_4>NO_3>NO_2$ or $NO_2<NO_3<SO_4<CO_3<Cl<HCO_3^{2}$ for major anions

V. The various hydrochemical facies namely, Ca^{2+}-Mg^{2+}-HCO_3^{-} , Na^{+}-K^{+}-

HCO_3^-, Na^+-K^+-$Cl^-SO_4^{2-}$ and Ca^{2+}-Mg^{2+}-Cl^--SO_4^{2-} identified suggest possible groundwater evolution attributed to rock-water interaction along its flow path over a period.

VI. The climatic conditions, neutral to alkaline water, weathering, precipitation, evaporation, dissolution, and ion exchange reactions of the aquifer materials could have aided the geochemical processes and enrichment of chemical ions in groundwater of the area

VII. The sources and origin of chemical constituents in groundwater of the study area is derived from the composition of the rock bearing minerals other associated minerals uncovered by source rock deduction and reasoning assessment.

CONCLUSION

The hydrogeochemical Investigation of groundwater in Zing and Environs aimed at determining the groundwater quality characteristics of the area have been carried out. The study revealed that all chemical ions concentration in groundwater except **F, Fe, Zn, Cl, Cr, and Pb** were within the permissible guidelines for drinking water prescribed by the World Health Organization (WHO, 2017) and the Nigerian Standard for Drinking Water Quality (NSDWQ, 2015). The quality of groundwater in the area is very poor considering the extent of fluoride (75%) and Iron (60.7%) distribution and isolated higher concentrations of chromium and lead. The health impact associated with the consumption of such water particularly with high concentration of fluoride, chromium and lead is catastrophic.

The general groundwater chemistry of the area is influenced by weathering and dissolution of rock bearing minerals facilitated by geochemical processes occurring within the aquifer materials. The leachability of the chemical ions' elements controlled by pH and dissolution of rock bearing minerals confirmed the sources to be geogenic rather than anthropogenic.

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