
Hydrogeochemical Processes of Groundwater from Basement Complex Rocks in Keffi, Central Nigeria

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ABSTRACT: *Hydrochemical study of groundwater was done in a typical Basement Complex terrain to identify geochemical evolution of the resource and possible quality issues. In addition to water samples, overburden and fresh rock samples were analyzed for major ion concentration. Relative abundance of these ions in groundwater was compared to their concentrations in the weathered and fresh rock. Conventional graphical plots (Gibbs, Piper, and ionic ratio plots) of ionic concentrations in the groundwater were used to characterize water Facies and identify major processes responsible for the ionic assemblage. The study area is underlain by two main rock types, schist and gneiss. Relative abundance of major cations in groundwater is in the order: $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ while relative abundance of major anions is in the order: $Cl^- > HCO_3^- > CO_3^{2-} > SO_4^{2-}$. In comparison, a depletion in the concentration of calcium, magnesium and sodium was observed in the weathered zone while being enriched in the fresh rock. This indicates the possibility of the ions being leached by infiltrating/percolating groundwater. Physical parameters indicate that pH of groundwater ranges from 5.6 to 13.1; TDS is also high ranging from 146.10mg/l and 9146.00mg/l. The main water type identified is mixed Ca-Mg-Cl type; others are Na-Cl, mixed Ca-Na-HCO₃, and Ca-HCO₃ types. Results of the analysis indicate that the main sources of ions into the groundwater are from water rock interaction i.e. dissolution and leaching from silicate minerals in the study area. Ground water is a mixture of the multiple processes involved in its evolution but especially that mineralogy of the aquifers plays an important role in determining the water chemistry. Most sampling points were hand dug wells and boreholes for domestic use; the high TDS and alkalinity of the water therefore presents some quality concerns.*

KEYWORDS: groundwater, hydrogeochemical, basement complex, Keffi

Introduction

Groundwater remains a very important resource especially since it requires little or no treatment before consumption and it is relatively available and more or less easily accessed. The largest available source of freshwater lies under ground i.e.: groundwater (Ariyo *et al.*, 2005); it amounts to about 98% of the world's freshwater (Bouwer, 2002). Three important factors that affect the quality of groundwater are: nature of surface run-off; weathered products soil/rock-water interaction during recharge and groundwater flow; and prolonged storage in the aquifer leading to dissolution of rock minerals and mineralogical composition of the underlying rocks (Edet, 2009). This implies that the geology of an area plays an important role in the chemistry of groundwater. The study area is Keffi, Central Nigeria and is underlain

by the Basement Complex rocks that consist of gneisses and schist, intruded by veins, which are pegmatite, quartz or quartzo-feldspathic veins and occur as discordant low lying dykes.

Hydrogeochemical processes operating in the subsurface have been studied using major ion chemistry; for example by developing a series of relationships between the major and minor ions, Sanchez-Martos *et al.*, (1999) assessed hydrogeochemical processes in arid regions of Europe. In another study relating to salinization processes in Namibia, Shanyengana *et al.*, (2004) used major ion chemistry. To assess groundwater quality degradation, Baghvand *et al.*, (2010) used major ion concentration. Hydrogeochemical characteristics of groundwater are excellent tools for identifying such hydrochemical processes as water rock interaction – mainly silicate weathering and dissolution and remobilization of ions, ion exchange processes. In addition to identifying these processes, they can be further linked to other processes such as anthropogenic activities (e.g.: Rajmohan and Elango, 2006). It has been suggested by Jianhua *et al.*, (2009) from analysis of major ion concentration in groundwater that SO₄/Cl ratio is a good indicator for identification of gypsum-halite dissolution.

Groundwater quality and its chemistry along the African coast are enhanced by the presence of Na⁺, Ca²⁺, Mg²⁺ and HCO₃⁻, due to silicate and carbonate weathering while NO₃⁻ is enhanced from indiscriminate waste disposal from human activities (Edet, 2008; Olufemi *et al.*, 2010; Nduka and Orisakwe, 2011). Variation in levels of water constituents (major anions, cations and trace elements) may be attributed to the differential derivation from source rocks, discharge of untreated effluents from industries, agricultural and domestic waste (Edet, 2009).

Hydrogeochemical processes drive water-rock interaction which in turn determines the chemical characteristics of groundwater. The need therefore to study hydrogeochemical processes of groundwater arises as this has consequences on groundwater quality. The composition of elements which are contained in both surface and groundwater is largely controlled by the interaction of water with the geology in which they occur. Dynamics of TDS (Total dissolved solid), temperature and pH of groundwater determine the nature of such interactions. This has environmental consequences as it affect the quality of groundwater used for domestic, agricultural and even industrial purposes. The aim of the present study is to establish hydrogeochemical processes of groundwater in the study area; in so doing establish consequences of such processes especially environmental impacts.

The Study Area

Location and Accessibility

The study area forms part of Keffi Sheet 208NE (Federal Surveys Nigeria, 2016) and lies within: latitudes 8°49'N and 8°53'N, and longitudes: 7°50'00"E to 7°58'00"E. It covers Old barracks, Angwan Jarmai, Angwan Lambu, GRA, Keffi town up to Angwan Sokotowa. The area is accessible through Keffi – Abuja express road; Keffi town has a network of minor roads, while footpaths and dry stream channels provide accessibility in remote areas. The study area falls within a tropical climate which is characterized by two seasons, namely; the rainy season and dry season. Annual rainfall and temperature vary between 1300 mm – 1500 mm and 28 °C – 36 °C, respectively.

The Study Area falls within the Guinea savannah vegetation belt of Nigeria which is characterized by thick vegetation, tall grasses and trees but which has been greatly altered by human activities such as tree felling, land tilting, building structures and forest. Geomorphologically, the terrain is undulating; Gneisses constitute the highlands while schistose rocks occupy the lowlands. The highest elevation within the area is the Maloni Hill standing over 400m above sea level, This hill is part of a NE-SW trending range of hills which flanks Keffi main town. Three main rivers drain the study area in a roughly north-south direction; these are: River Uke; River Anto and River Kodo.

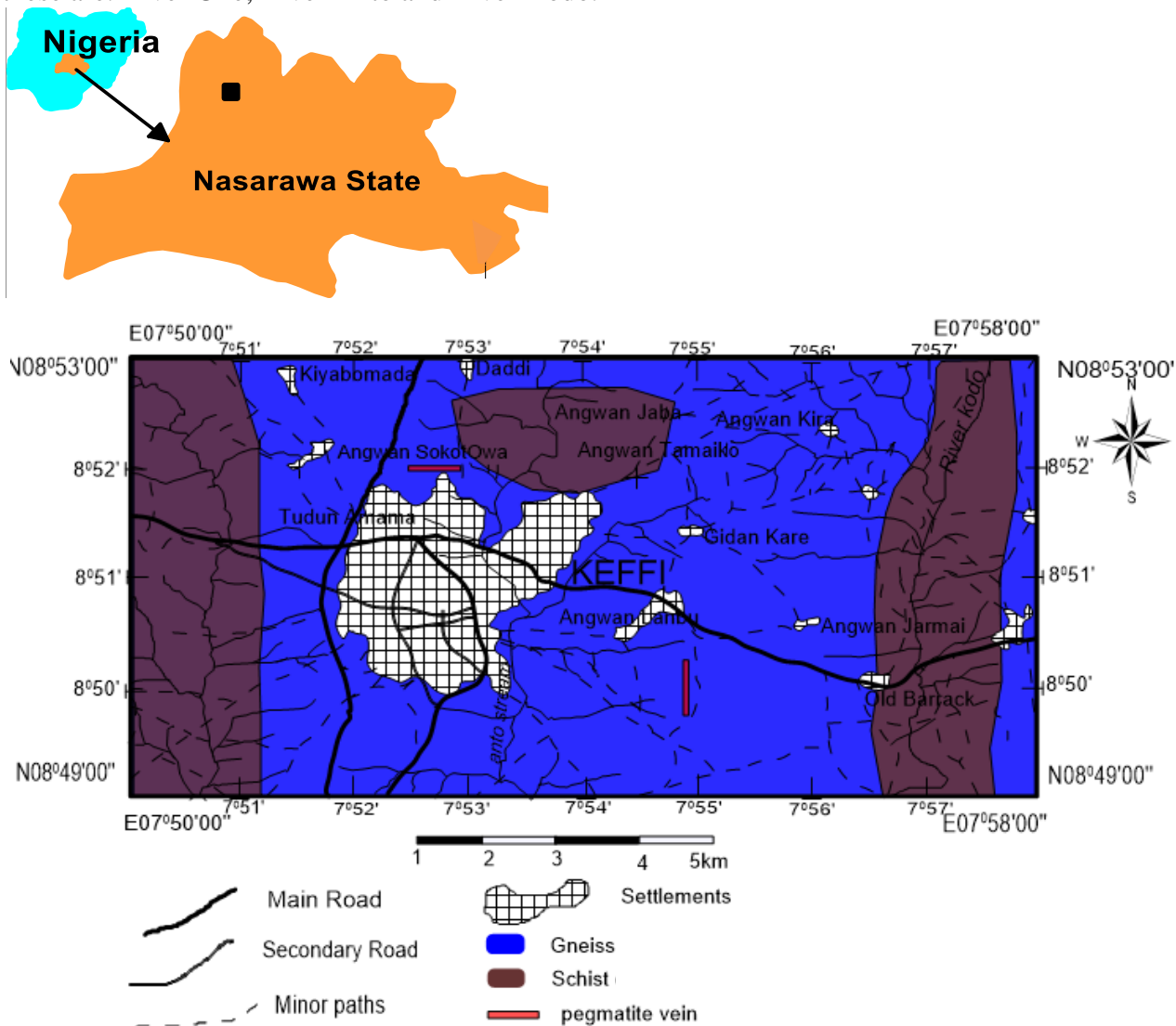


Figure 1. Location and Accessibility map of the study area showing major geologic units.

Geologic setting

The Study Area is underlain by rocks that form part of the North-Central Basement Complex rocks of Nigeria, (Wuyep and Tanko, 2012). These Basement Complex rocks were emplaced during the Pan

African Orogeny before the Jurassic Younger Granites intruded through peripheral ring structures (Aga *et al.*, 2012). Three main lithological units can be identified i.e.: Schist, Gneiss, and Pegmatite. Gneiss outcrops appear as hills (Abzat Quarry, Maloney Hill and Tudun Amama) and cover the central portion of the study area. Schist exposures are low lying; occupying less than 50% of the study area, precisely the eastern and western boundaries of the area and also a portion was mapped in the north central part of the study area. The Pegmatites intrude both rock units throughout the study area as veins of varied thicknesses. Structures include: joints, fractures, faults and quartzofeldspathic veins. The dominant structural trend is NE-SW and NNE-SW. photomicrographs of the rocks show that the following minerals are dominant: Quartz, Feldspars, Micas (Biotite, Muscovite) (figure 2).

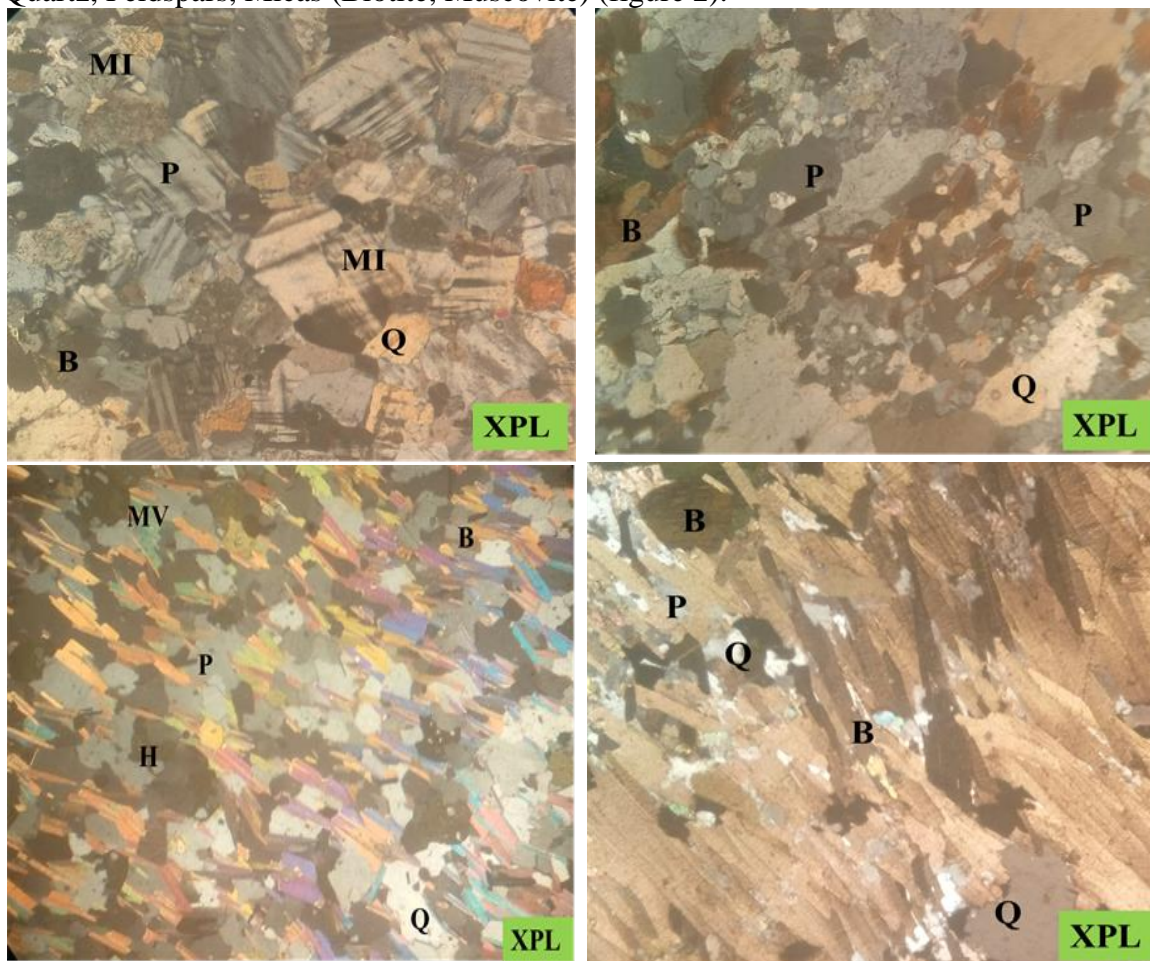


Figure 2. Photomicrographs of Gneiss (Top left and right) and Schist (bottom left and right). Groundwater is found within the weathered overburden and fractured basement rocks of the study area. Hard rock terrains usually hold water in fissures, fractures, joints and weathered portions. Overburden (weathered) aquiferous zones are tapped by hand dug wells while deeper fractured aquifers are accessed by boreholes. The weathered rock forms shallow aquifers up to 40m in some parts of the study area; while the fractured rock forms deep aquifers. Groundwater movement determined from a contour plot of hydraulic heads measured in wells is shown in figure 3. Hydraulic head is highest in the northeastern part

of the study area reaching 325m above mean sea level. Two main flow directions are evident; north east-south west and northwest to south east. These flow directions appear to converge at a point within the study area.

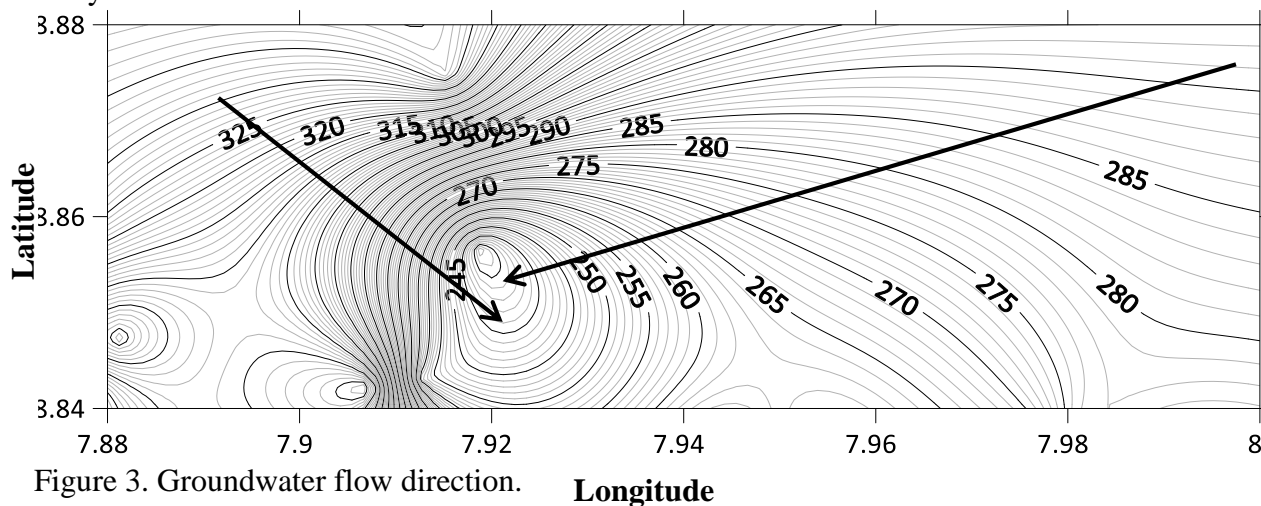


Figure 3. Groundwater flow direction.

Longitude

METHODOLOGY

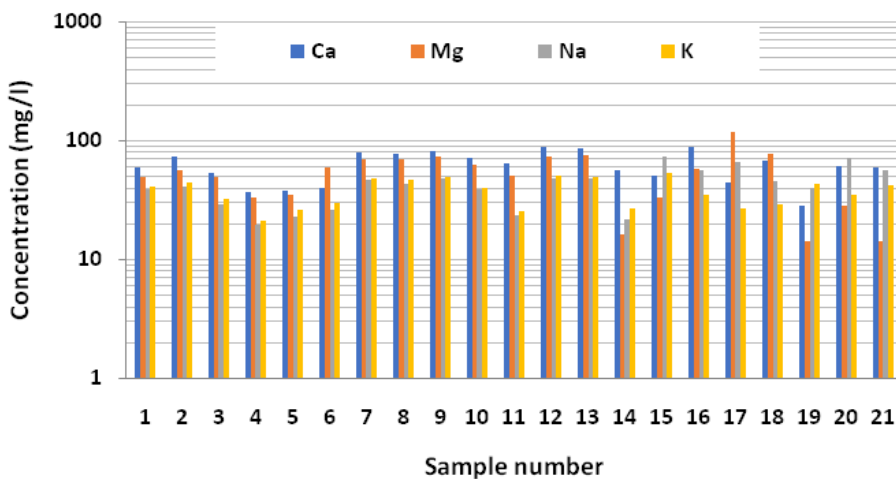
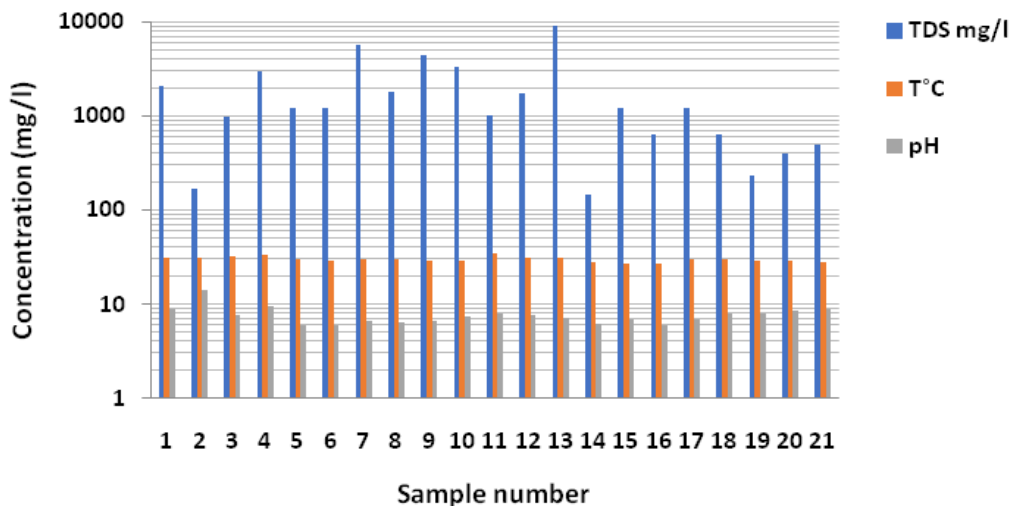
A total of 21 groundwater samples were collected from different parts of the Study Area from boreholes, springs and hand dug wells. For boreholes, water samples were collected in most cases directly from tap heads while bails were used to collect water samples from hand dug wells. For each sample collection point, EC, TDS, pH and Temperature were recorded *in-situ*. Water was pumped out for a fair amount of time prior to the collection. Water samples were collected in polyethylene bottles (250ml capacity); bottles were sealed and brought to the laboratory for analysis, and stored properly before analysis. In each case, two samples were collected; one was acidified with nitric acid to keep metals in solution. Major ions such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , CO_3^- , HCO_3^- , Cl^- and SO_4^{2-} were analyzed in the laboratory; the anions were analyzed by titration, except for sulphate which was analyzed using a spectrophotometer. Sodium and potassium were analyzed using a flame photometer. Calcium and magnesium were determined by titration with EDTA.

RESULTS AND DISCUSSION

Hydrogeochemistry – physical parameters and major ion chemistry

Physical parameters measured in the study area are presented as graphs in figure 4. The pH of groundwater in the study area ranges from 5.9 to 13.1; a median value of 7.4 and standard deviation of 1.8; i.e.: predominantly alkaline in nature i.e.: exceed permissible limits (6.5-8.5, WHO, 2011). Temperature ranges between 27.4°C and 35.5°C with a median value of 30.1°C and standard deviation of 2.01. Total dissolved solids TDS vary from 174 mg/L to 9156 mg/L; TDS for all locations except two exceed the permissible limit (500mg/L, WHO, 2011). Total dissolved solids in water comprise all inorganic salts that include carbonates, bicarbonates, chlorides, fluoride, sulphates, nitrates, calcium, magnesium sodium and

potassium (Sawyer, 1994). Groundwater samples predominantly (76, 66% of groundwater samples) contain these salts in amounts that contribute in making the TDS high (US Geological Survey, 2000). High concentration of TDS can also be in response to anthropogenic sources such as percolation of domestic sewage into groundwater, leaching of salts from soil and also from septic tanks and agricultural activities (Krishna Kumar *et al.*, 2017). In addition to these reasons, the high TDS observed may be due to sampling at the peak of dry season. Concentration of the major elements in groundwater is plotted in figure 4. Relative abundance of major cations is in the order: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ while relative abundance of major anions is in the order: $\text{Cl}^- > \text{HCO}_3^- > \text{CO}_3^{2-} > \text{SO}_4^{2-}$. The elements display some degree of variation in their concentrations. Ca^{2+} ranged from 28.1 to 88mg/L, Mg^{2+} ranged from 16.1 to 118.1mg/l, K^+ ranges from 21.21 to 53.6 mg/l and Na^+ ranges from 19.6 to 73.2 mg/l; the concentrations of these elements are within permissible limits set by WHO (2011). The sources of these elements groundwater can therefore be attributed to dissolution of weathered silicate minerals from the rock units of the study area.



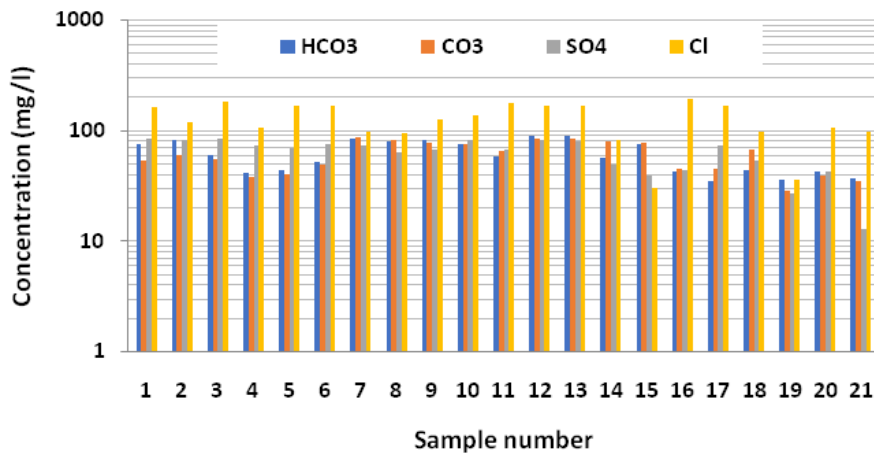


Figure 4. (a) Temperature, pH and TDS; (b) and (c) are plots of major cation and anion concentration respectively for groundwater samples in the study area.

Cl⁻ was found to range from 16.3 to 195.7mg/l, CO₃²⁻ ranges from 28.5 to 88 mg/l, HCO₃⁻ ranges from 35 to 86.16 mg/l and SO₄²⁻ range from 12.9 to 86.01 mg/l, these concentrations are all within the desirable limits set by WHO (2011). Fe values ranged between 0.01 and 0.74 mg/l and were found to be within limits set by WHO. Due to the lack of carbonate rocks in the study area, the possible sources of bicarbonate include weathering from silicate minerals in addition to cations such as Ca²⁺, Mg²⁺ and HCO₃⁻ along with presence of organic matter in the groundwater which is oxidized to produce carbon dioxide, which in turn promotes dissolution of minerals.

Groundwater type – hydrogeochemical facies

Hydrogeochemical facies of groundwater is derived by plotting the concentration of major cations and anions on a trilinear diagram i.e.: Piper diagram (Piper, 1935). The plot for the study area is shown in figure 5. Four water types can be identified although most samples fall in the field of one particular water type i.e.: Mixed Ca-Mg-Cl type; others are Na-Cl, Mixed Ca-Na-HCO₃, and Ca-HCO₃ types.

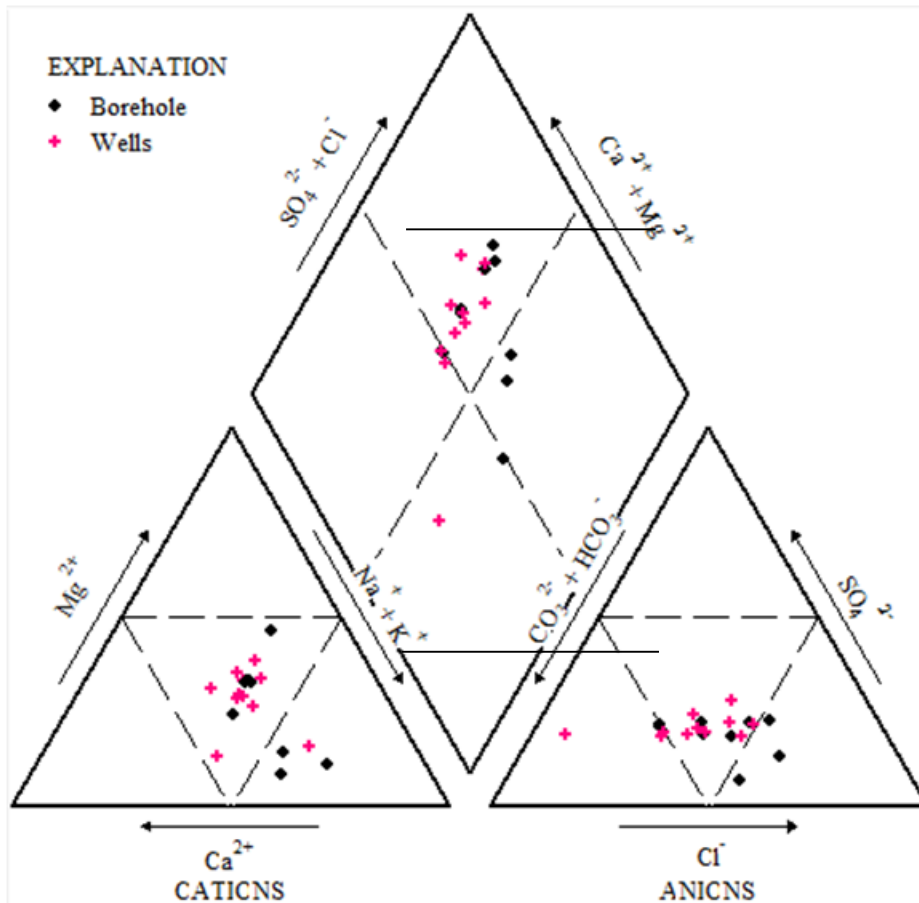


Figure 5. Piper diagram showing hydrogeochemical facies or water types in the study area.

Hydrogeochemical processes

Generally, the common hydrogeochemical processes in operation in any groundwater system are precipitation, evaporation and water-rock interaction. A generalized classification can be obtained by plotting ion concentration (meq/L) on a Gibbs diagram (Gibbs, 1970); from the diagram, the relative influence of the major processes can be discerned. The Gibbs diagram has three distinct fields which are precipitation dominance, evaporation dominance and rock– water interaction dominance areas. For this study area, the ratios plot predominantly in the field of water-rock interaction dominance with a few samples plotting in the evaporation dominance region (figure 6). This implies that weathering of the silicate rocks in the study area significantly impact on the water chemistry since Central Nigeria represents a non arid area. However, the samples were collected in the peak of dry season during which evaporation may be relatively significant.

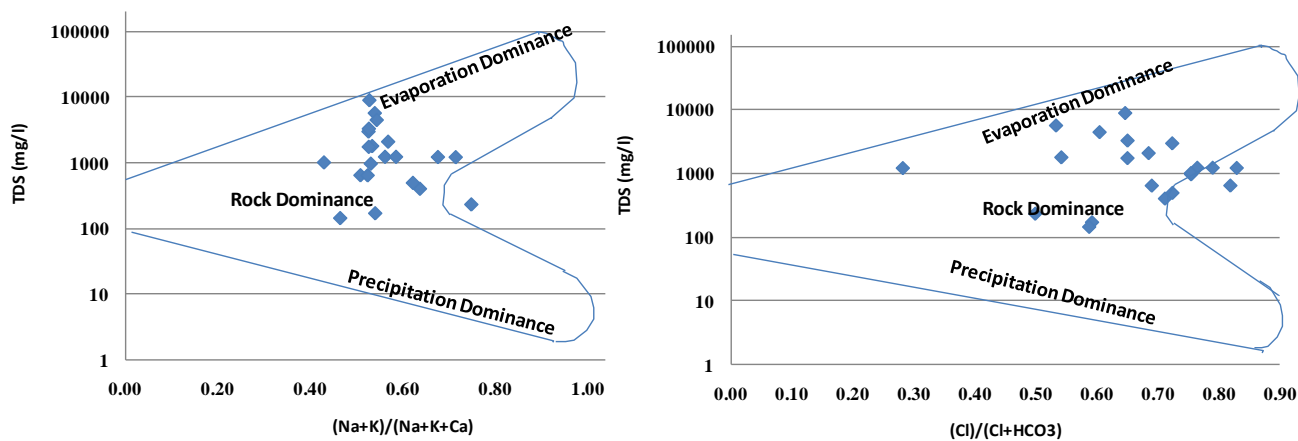
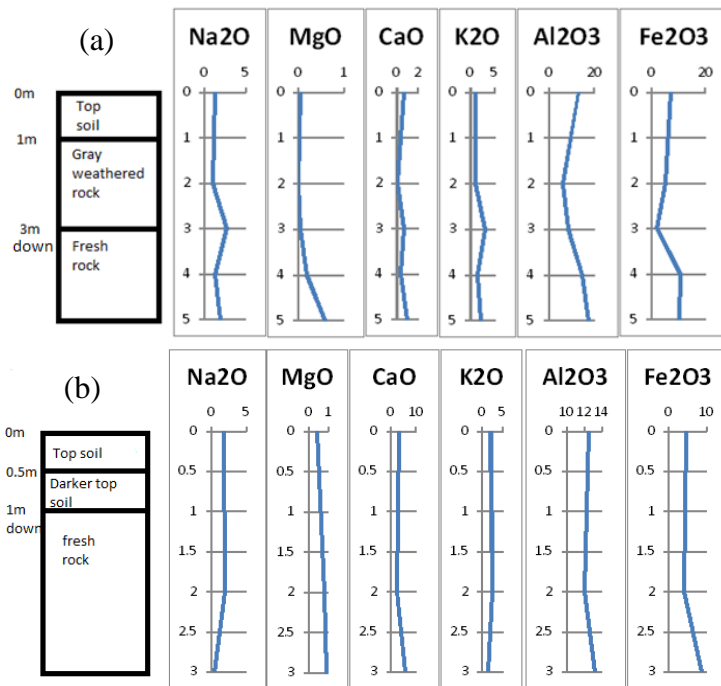


Figure 6. Gibbs diagram showing dominant geochemical processes of groundwater in the study area. Silicate weathering is one of the key geochemical processes controlling the major ions chemistry of the groundwater, especially in hard rock aquifers (Mackenzie and Garrels, 1965; Rajmohan and Elango, 2004; Kumar *et al.*, 2006). Interactions between groundwater and aquifer mineral framework significantly impact on groundwater chemistry. In the study area, two major rock types were identified *viz*: gneiss and schist meaning silicate minerals are the major sources of mineralization in the area. Petrographic analysis showed that the rocks contained predominantly plagioclase and orthoclase feldspars in addition to micas (muscovite and biotite), these will readily weather making ions available for dissolution by percolating groundwater.



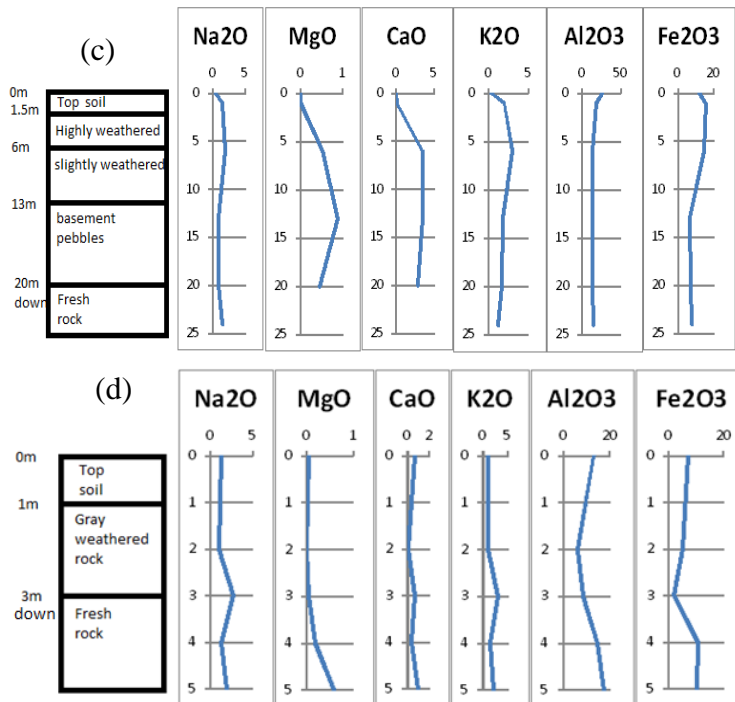


Figure 7. Major oxide concentrations along weathering profiles over gneiss in the study area ((a) and (b)); borehole samples collected at the Faculty of Law Nasarawa State University Keffi (c) along a weathering profile over schist (d).

The ultimate weathering product of silicate minerals are clays. Three weathering profiles over these rocks and one borehole log were identified and studied. Samples of soils, weathered rock and fresh rock were analyzed for major oxide concentration. The objective of the geochemical analysis was to identify major oxide concentration in the weathered zone relative to that in the fresh rock and possibly relate that to the water species.

Major oxide concentrations of the weathered zone (figure 7) show that there is depletion in the concentration of calcium, magnesium and sodium in the weathered zone while being enriched in the fresh rock. This indicates the possibility of the ions being leached by infiltrating/percolating groundwater. From the major ion chemistry of the groundwater, calcium, magnesium and sodium (and potassium) are the dominant for the cations while chloride and sulfate are present in significant amounts in addition to carbonate and bicarbonate. The ions may have leached and mixed with the groundwater. HCO₃ may be derived from the dissolution of silicate minerals (Orthoclase, Plagioclase, Hornblende, and Biotite likely present in the host rocks of the study area) by carbonic acid (Tesoriero *et al.*, 2004). A general reaction for the weathering of silicate rocks with carbonic acid is as follows:

(Cations) silicates + H₂CO₃ = H₄SiO₄ + HCO₃ + cations + solid products (mostly clay minerals).

Bivariate plots - Evidence of silicate weathering

From section 4.3, it can be concluded that weathering and dissolution are the major processes contributing to groundwater chemistry. To further buttress this, plots of Mg^{2+}/Na^+ versus Ca^{2+}/Na^+ and HCO_3^-/Na^+ versus Ca^{2+}/Na^+ shows that the points fall within the field of silicate weathering implying therefore that the cations are majorly derived from silicate weathering (figure 8). Similar results have been reported from silicate aquifers (Brindha *et al.*, 2016, Kumar, 2014). Also, silicate weathering can be further ascertained by estimating the ratio between $Na^+ + K^+$ and total cations (Mohammed and Allia, 2015); all but 3 of the samples in the study area plot in the region above $Na^+ + K^+ = 0.5 \text{ total cations}$ (figure 9a). This according to Kuldeep Singh *et al.*, (2011) indicates the involvement of silicate weathering as a geochemical process affecting groundwater in the study area. In addition to this, a ratio: $Ca^{2+} + Mg^{2+} / HCO_3^-$ more than 3 is indicative of silicate weathering (Mohammed and Allia, 2015); samples plot in the region above this number (figure 9b).

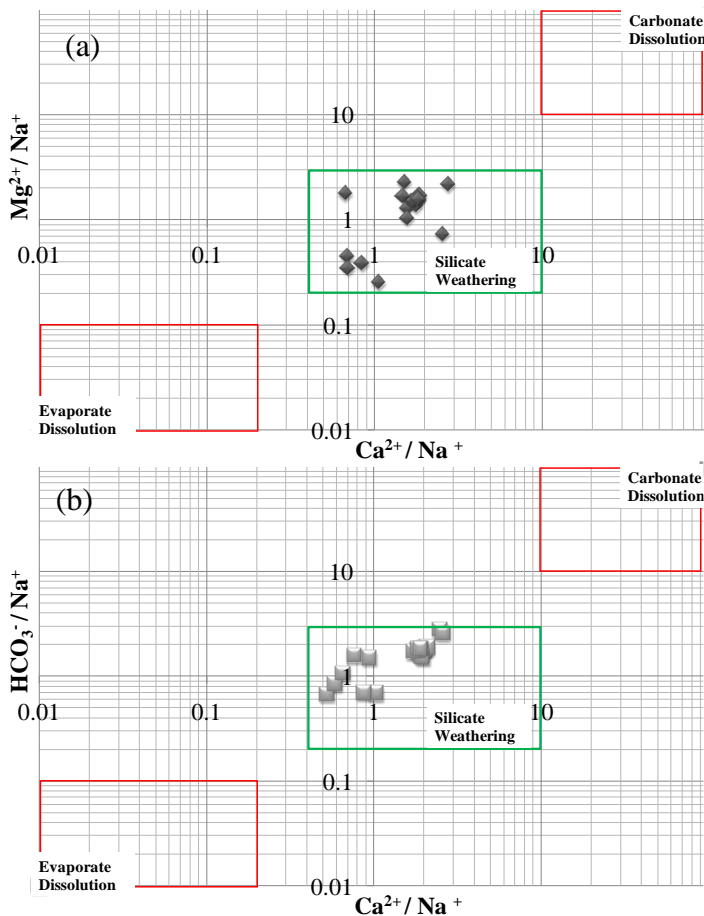


Figure 8. Bivariate plots of the ratios: (a) $Mg^{2+}/Na^+ : Ca^{2+}/Na^+$ and (b) $HCO_3^-/Na^+ : Ca^{2+}/Na^+$.

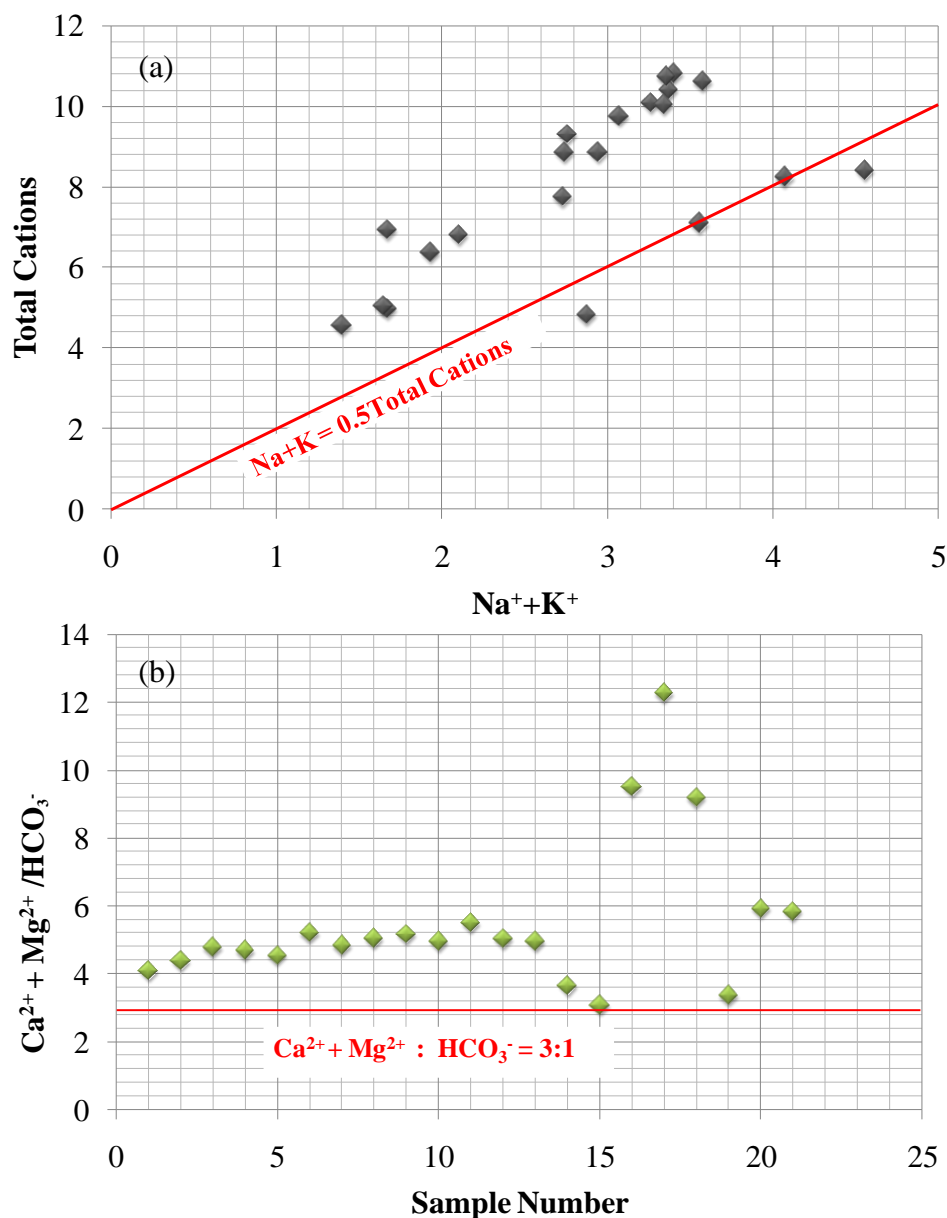


Figure 9. (a) Plot of $\text{Na}^+ + \text{K}^+$ and total cations; (b) plot of the ratio: $\text{Ca}^{2+} + \text{Mg}^{2+} / \text{HCO}_3^-$ against sample numbers.

CONCLUSIONS

The preceding analyses attempted to identify hydrogeochemical processes of groundwater from a basement complex terrain using major ion concentrations. Major rock types in the area are Gneiss and Schist intruded by pegmatite veins; thin section photomicrographs of these rocks showed predominantly plagioclase and orthoclase feldspars in addition to micas (muscovite and biotite), these will readily

weather making ions available for dissolution by percolating groundwater. Aquifers in the area are therefore the weathered overburden and fractured basement complex rocks. Physical parameters of groundwater indicated that temperature and pH and TDS values were within permissible limits of WHO (2011) although some samples had slightly high TDS and alkaline pH. Water type in the area is predominantly Ca-Mg-Cl type; while ionic plots indicate that the main process controlling groundwater chemistry was that of water rock interaction. Meaning the chemical constituents was derived from weathering of silicate minerals and subsequent leaching by infiltrating/percolating groundwater. This was further buttressed by geochemical profiles along weathered and fresh rock in the study area; these showed depletion in the concentration of calcium, magnesium and sodium in the weathered zone while being enriched in the fresh rock. This indicates the possibility of the ions being leached by infiltrating/percolating groundwater. From the major ion chemistry of the groundwater, calcium, magnesium and sodium (and potassium) are the dominant for the cations while chloride and sulfate are present in significant amounts in addition to carbonate and bicarbonate. It is believed that the ions may have leached and mixed with the groundwater. The concentrations of carbonates may be from the CO₂ present in the soil zone that combines with rainwater to form carbonates HCO₃ which may be derived from the dissolution of silicate. Bivariate plots that indicate relationship between ions were also used to further assess the contribution of water rock interaction in the groundwater chemistry. From the foregoing; the levels of major physicochemical properties of the water have not exceeded the permissible limits set by WHO (2011) and is thus suitable for use.

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