Hydrogeochemical evolution and groundwater quality assessment using chemical systematics, statistical techniques, and pollution index of groundwater (PIG): a case study

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Hydrogeochemical evolution and groundwater quality assessment using chemical systematics, statistical techniques, and pollution index of groundwater (PIG): a case study

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ABSTRACT

Herein, we investigate the hydrogeochemical processes influencing the chemistry and suitability of groundwater for drinking in Mubi south area, north-eastern Nigeria based on physicochemical results of water samples collected from 30 boreholes in the area. The cations and anions distribution in the samples are in the order $Mg^{2+} > K^+ > Na^+$ and $HCO_3^- > NO_3^- > Cl^- > SO_4^{2-} > CO_3^{2-}$ respectively. The low turbidity (0.02–4.86 NTU) and neutral–mildly alkaline nature ($pH = 6.65–8.70$) of the groundwater indicate high clarity, low level of cloudiness, high CO_2 abundance and dissolve ions in form of HCO_3^- . Hydrogeochemical (e.g., Piper, Durov, bi-variant and scatter plots) and statistical (PCA and HCA) evidences highlight the biogeochemical hydrolysis (i.e. silicate weathering) of silicate minerals (such as K-feldspars, pyroxenes, amphiboles) as the major process controlling the groundwater chemistry. The dominance of Ca^{2+} – Mg^{2+} – HCO_3^- water type, coupled with the strong positive correlation between EC and K^+ ($r = 0.75$), and the strong positive loading of Ca^+ (0.74) are robust evidences for the silicate weathering process. However, the elevated Cl^- concentrations (15–206 mg/l), and the insignificant variation of Na^+/Cl^- ratio with increasing EC as well as the high positive loadings of EC and TDS imply other secondary processes (e.g., evaporate salts and anthropogenic pollution) were also involved in the hydrogeochemical evolution. The pollution index of groundwater (PIG = 0.27–0.737) fall below the insignificant pollution state of less than 1, diagnostic of good water quality for drinking purpose and sustainability of public health.

Key words: Hydrogeochemistry; Pollution index of groundwater, Multivariate statistical analysis; Drinking water.

1. Introduction

Groundwater is invariably the main source of fresh water essential to life globally (Foster and Chilton, 2003). Sufficient groundwater quantity with good quality is necessary for the increasing household and agricultural needs. Typically, groundwater is clear and colorless with constant temperature. Groundwater is preferentially used for many purposes due to the presence of dissolved minerals and some peculiar characteristics as compared with the surface water (e.g., Rajankar et al., 2009; Kulinkina et al., 2017). Most communities especially in the rural areas often use groundwater without proper treatment which makes it hazardous to public health in cases of elevated content of undesirable elements, most of which exist primarily due to the hydrogeochemical processes. Chemical reactions during this process can greatly affect the potency of some elements since precipitated elements are less hazardous than mobile elements. Therefore, the degree to which these mobile elements affect groundwater quality depends mainly on the chemical species, characteristics, and concentration of the elements (e.g., Mapoma et al., 2017). The variable compositions of these elements in groundwater are largely controlled by natural and anthropogenic activities. The influence of the latter process either pollute the groundwater or change the hydrological cycle (e.g., Helena et al., 2000).

A plethora of researchers (e.g., Chilton and Foster, 1995; Chimphamba et al., 2009; Pietersen 2009; Walraevens et al., 2018; Oyedele et al., 2019) consented that most groundwater quality in basement aquifers are within the satisfactory pollution state, owing to the low level of mineralizations and low solubility of the aquifer-forming materials. However, the heterogeneity of basement aquifers as a result of the complex and spatial variations of the hydrochemical parameters even within a short distance is highly problematic (e.g., Foster and Chilton, 1995; Tarits et al., 2006; Stober and Bucher, 2015). For example, some studies revealed poor water quality associated with elevated sulphate content during anhydrite dissolution or sulphide minerals in basement aquifers (e.g., Akiwumi, 1997; Reuschel et al., 2012). Additionally, elevated trace element contents in reduced and acidic environment such as mine site is highly detrimental to groundwater in basement aquifers (e.g., Kortatsi et al., 2008; Doulmas et al., 2018). Similarly, high salinity due to evaporate salts leaching and upward injection of saline waters in faulted areas can also influence groundwater quality (e.g., Williams et al., 2013; Mapoma et al., 2014; Walraevens et al., 2015).

The study area lies wholly within the Hawal Massif, which, together with the Adamawa Massif and Oban Massif constitute the Eastern Nigerian Basement Complex that extend into the Cameroon Republic (Fig. 1). The area is underlain by migmatite-gneiss complex, which are discordantly intruded by the Pan-

African Older granites and their extrusive volcanic equivalents, most of which are overlain by alluvial deposits. These rocks are frequently exploited for groundwater through borehole drilling and hand-dug wells. However, artisanal mining of monazite in the east-central part of the area, coupled with intensive agricultural practices involving uncontrolled fertilizer and manure applications could exacerbate the mobility of trace elements (Romic and Romic, 2003; Monged et al., 2020). These activities may also exert enormous pressure on water quality and availability (Foster et al., 2013; Chen et al., 2017; du Plessis, 2019). This brings to fore the need to critically examine the chemistry and quality of groundwater in the area for the sustainability of public health.

Understanding the hydrogeochemistry of groundwater is a crucial step for long-term borehole water quality assessment. In this contribution, we present physicochemical constituents of groundwater within the basement aquifers in Mubi South area, north-eastern Nigeria. We evaluated the important hydrogeochemical processes controlling groundwater chemistry in 30 selected boreholes from a combined hydrochemical concepts (e.g., Piper, Durov, bi-variant and scatter plots), and multivariate statistical analysis points of view. Importantly, groundwater suitability for drinking was evaluated based on pollution index of groundwater (PIG).

2. Geologic setting

2.1 Local geology

Geologically, Mubi south area in northern Adamawa State, north-eastern Nigeria is composed of undifferentiated migmatitic-gneisses, Pan-African Older Granites, granite-gneisses, amphibolites, basalts, rhyolites and alluvial deposits. The Pan-African granites occur as highly rugged hills in the central, north-eastern and eastern part of the area, but are low-lying in the northwest (Fig. 2). They are characterized by alternating bands of closely spaced medium to coarse-grained leucocratic and melanocratic mineral assemblages of platy biotite markedly discernable from the light-colored quartz and dominant feldspars. Undifferentiated migmatitic-gneisses occur as steeply dipping hills in the southeastern and northern parts of the area (Fig. 2). These rocks are coarse-grained with leucocratic quartzo-feldspartic crystals well interlocked within the dark-colored biotites.

The granite-gneisses are characterized by conspicuous dark bands of minerals embedded in a medium-grained mass of light-colored quartz and feldspars and are intrusive into the migmatitic-gneisses (Fig. 2). The

amphibolites are of restricted occurrences well exposed in a blasted quarry. The rock mass is characterized by essentials of dark colored minerals and tiny specks of quartzofeldspathic crystals. Rhyolites and basalts are light- and dark colored respectively well exposed within the southwestern extremity of the study area, some of which outcropped as small rounded hills. These volcanic rocks probably represent volcanic remnants from the adjacent Cameroon Volcanic line (CVL). The granitic rocks in the NE, NW and SW are overlain by alluvium and eluvium constituting mainly of sands, silts, gravels, clays and reddish laterites which serves as targets for some boreholes and shallow hand-dug wells in the area.

2.2 Hydrology and hydrogeology

The occurrence of water resources, its extraction, uses and chemical quality and quantity define the scope of hydrogeology and entails both the surface water and groundwater potentials of the area. The Mubi area is characterized by high mean annual rainfall (1050 mm), with an early mean onset date of rain (10th May), late mean cessation dates of rain (16th to 20th October), and long duration of mean rainy season (about 160 to 170 days, [Fig. 3](#)). Unfortunately, there are no facilities that can store the excess overflow of the abundant surface water. Nonetheless, its underflow is exploited through the construction of boreholes and hand-dug wells into the alluvium and weathered/fractured basement to cater for the increasing household, agricultural and livestock needs of the people.

Hydrogeologically, fresh crystalline basement rocks in the area, akin to any other basement complexes hardly any groundwater potential and flow. Groundwater in the area occur within a wide range of secondary porosities and permeabilities which were developed as a result extensive fracturing, jointing, shearing and deep weathering ([Jones, 1985](#); [Boutt et al., 2010](#)). These structures and weathering profile are evidenced by the litho-logs from boreholes in the area and the results of integrated (electromagnetic and resistivity) geophysical investigation which was conducted prior to groundwater sampling. These network of fractures and weathered regoliths supply moderate groundwater to boreholes in the area. Variations in groundwater yield at different location within these zones is mainly controlled by the nature of bedrock, fracture and weathering intensity and density ([Banks et al., 2009](#); [Guihéneuf et al., 2014](#)).

The crystalline basement aquifers are recharged through infiltration from the upper levels of the saturated weathered regolith ([Holland, 2011](#)), consisting of collapsed zone (laterites, illuviated clay and stone lines) and saprolite zone (weathered and disaggregated domain) ([Figs. 5a–b](#); [Wright, 1992](#)). Field studies have shown that variable thickness of the weathered regoliths, coupled with the variations in groundwater potential

at different zones in the area are controlled by the contrasting distribution pattern of the rock types, their mineralogical assemblages and differential degree of weathering. The saprock region (weathered bedrock) is characterized by sharp or transitional boundary against coarse-grained massif rocks or fine-grained rocks (Figs. 5a–b). Fracture permeability within the saprock zone often increases due to weathering (unlike in the fresh bedrock) unless it is filled with illuviated clay materials (Wright, 1992; Anand and Paine, 2002). The water table in the study area probably occurs at shallow levels (less than 10–15 m) due in part to the moderate-high annual rainfall (>600 mm per annum; e.g., Wright, 1992) (Fig. 3a).

3. Materials and Methods

3.1 Groundwater sampling and analysis

Thirty community boreholes in Mubi South area were targeted during the peak of dry season (late March, 2017). Preliminary analyses of the selected groundwater points included field in-situ measurements of the physical parameters. The pH and temperature were measured using Pen pH/Temperature Meter (Model CT6021). The electrical conductivity (EC) was determined using Pen conductivity meter (model CT306) while the total dissolved solids (TDS) was measured using pen TDS meter (Model 21000). Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) were measured using titrimetric method (HACH digital titrator 16900). Coordinates of sample locations was recorded using GPS (Global positioning system and adequately marked on the hydrogeologic map of the area.

Groundwater samples for laboratory studies were filtered through a 0.45 μm filter into an already pre-washed and pre-labeled 1 liter polythene bottle and triple rinsed prior to sampling from boreholes after 30 seconds of pumping, provided no one was fetching the water. If the borehole was rarely used, it was pumped for about 2 minutes prior to collection. During groundwater sampling, quality assurance and control was achieved following the procedures in the Water Quality Sampling Manual (APHA, 2012). Accuracy of sample labelling and the use of standard solutions which ensured the precision and accuracy as well as reproducibility of the results was based on Taiwo et al. (2015). The sampled groundwater was controlled using 3 ml analytical-grade nitric acid (HNO_3) until a standard pH of 2 was achieved. The acidification was done in order to stabilize the water and further prevent precipitation of metals. All the samples were preserved in a refrigerator at a temperature below 4°C in order to stop the metabolism and activities of organisms before the analysis at the laboratory.

Chemical analyses was performed at the chemistry laboratory of the Adamawa State Water Board Headquarters, Yola using the spectrophotometer (Model HACH DR 2000) at specified (error range) wavelength (APHA, 2012). Chemical parameters analyzed include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{2+}), potassium (K^{+}), sulphate (SO_4^{2-}), chloride (Cl^{-}), nitrate (NO_3^{2-}), fluoride (F^{-}), iron (Fe^{2+}), manganese (Mn^{2-}), copper (Cu^{2+}), total hardness (TH, CaCO_3), zinc (Zn^{2+}), phosphate (PO_4^{2-}), hydrogen Sulfide (H_2S), cyanide (CN), Arsenic (As), cadmium (Cd^{2+}), Lead (Pb^{2+}) and chromium (Cr^{6+}). However, six of the parameters (H_2S , CN, Cr, Cd, As, and Pb) has been excluded from the list because they were below detection limit. Quality assurance and control during water analysis was achieved following the Standard Methods for the Examination of Water and Wastewater (APHA, 2012), and the use of laboratory blanks and calibration standards. The accuracy in the measurements of ions was confirmed through the estimation of ionic balance errors, the results of which of fall within the acceptable range of $\pm 5\%$.

3.2 Hydrochemical Evolution

3.2.1 Hydro-geochemical facies and processes

The grouping of hydrochemical facies on Piper diagram is based on the important ions that contributed in the chemistry of groundwater (Piper, 1944). The diagram was plotted using AQqa computer software (v. 1.5) and graphically demonstrates the chemical equilibrium between the prominent cations (e.g., Ca^{2+} , Mg^{2+} , Na^{+} and K^{+}) and major anions (e.g., Cl^{-} , SO_4^{2-} , CO_3^{2-} and HCO_3^{-}). The Piper diagram constitutes two triangles of the prominent cations and anions, and a quadrilateral (diamond shape) at the middle showing the ions distribution and their associated water types.

A similar diagram known as Durov diagram (Durov, 1948) was also plotted using AQqa software (v. 1.5). This diagram shows the main anions and cations as percentages (in meq/l) in two ternary graphs where these ions are plotted. A middle square graph bounded to both triangles illustrates the processes influencing groundwater chemistry. For each sample, the sum total of ions in both triangles is 100%. Verification of the Kaiser-Meyer-Olkin (KMO) sample adequacy measure and Bartlett's Sphericity Test was done using SPSS v.16. The result is adequate if KMO value is greater than 0.5 (Kaiser, 1974; Field, 2000). Bartlett's Sphericity Test with significant value less than 0.05 implies that the factor analysis data is normal and acceptable (Field, 2000; Pallant, 2013). The KMO adequacy value (0.689; Table 1) of the data exceeds the standard value of 0.5, indicating adequacy and acceptability of the results. Similarly, Bartlett's Sphericity Test yielded a

significant value of 0.000 ([Table 1](#)), which is less than the recommended value of 0.05, indicating that the data is normal and acceptable for factor analysis.

3.2.2 Ion-exchange process in the aquifers

The ion-exchange processes occurring between the groundwater and host aquifer during residence time is represented by the chloro-alkaline indices I and II:

$$\text{Chloro - alkaline index CA-I} = \frac{\text{Cl} - \text{Na} + \text{K}}{\text{Cl}} \quad (1)$$

$$\text{Chloro-alkaline index CA-II} = \frac{\text{Cl} - \text{Na} + \text{K}}{\text{SO}_4 + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3} \quad (2)$$

During the cation exchange in groundwater, the reaction between Ca^{2+} and Mg^{2+} ions with clay minerals releases Na^{2+} ions. The Na^{2+} and K^+ are replaced by Mg^{2+} and Ca^{2+} ions. As such, positive values are indicative of base-exchange while negative values represent chloro-alkaline disequilibrium. During this process, the dissolved solids likely originated from the host aquifers (cf. [Schoeller, 1967](#)).

In order to determine the functional source(s) and compositions of dissolved chemicals in the groundwater, the Gibbs ratio, (i.e., the ratio of $\text{Na}^+/\text{Na}^+ + \text{Ca}^{2+}$ and $\text{Cl}^-/\text{Cl}^- + \text{HCO}_3^-$), which is closely associated with total dissolved solids was employed (cf. [Gibbs, 1970](#)). The diagram illustrates the influence of various hydrogeochemical processes (e.g., precipitation, evaporation and rock-water interaction) on groundwater chemistry. Gibbs ratio is computed from the relation:

$$\text{Gibbs ratio I (for anion):} \quad \frac{\text{Cl}}{\text{Cl} + \text{HCO}_3} \quad (3)$$

$$\text{Gibbs ratio II (for cations):} \quad \frac{\text{Na} + \text{K}}{\text{Na} + \text{K} + \text{Ca}} \quad (4)$$

Notably, the processes associated with rock-water interaction include chemical weathering, dissolution or precipitation of secondary carbonates, and cation–anion exchange involving groundwater and clay minerals ([Gibbs, 1970](#)).

3.3 Multivariate statistical analysis

Multivariate statistical analysis is primarily employed for data reduction to examine the possible source(s) of elements as well as the different chemical factors controlling them (cf. [MacGregor and Kourti, 1995](#)). The IBM® SPSS® computer software (v. 16) was utilized for the multivariate analysis of the hydrochemical data set. Rotated component matrix was generated and principal component analysis and

Kaiser Normalization varimax were selected as extraction and rotated methods respectively. During hierarchical cluster analysis, dendrogram was extracted using ward's method with a combine rescaled distance cluster. For the factor analysis (FA) of the data set, Pearson's correlation using two-tailed significance was used.

3.4 Groundwater quality for drinking

3.4.1 Pollution index of groundwater (PIG)

Pollution index of groundwater (PIG) is an important numerical scale developed by Subba Rao (2012). It quantifies the degree of contamination and has been successfully employed in the evaluation of the variations in groundwater quality for drinking purpose (e.g., Elumalai et al., 2017; Subba Rao et al., 2018; Chaturvedi et al., 2019; Subba Rao and Chaudhary, 2019; Adimalla et al., 2020; Egbueri, 2020). In assessing the groundwater quality for drinking based using the PIG technique, five steps were taken.

Firstly, a relative weight (Rw) was allotted for each of the analyzed physical and chemical parameters of the groundwater on a numerical scale of 1 to 5, taking into consideration their relative significance in groundwater quality evaluation and effects on human health. Accordingly, Relative weight (Rw) of 5 was assigned to most important parameters such as pH, TDS, NO_3^{2-} , SO_4^{2-} , and F^- , while HCO_3^- , which is the next important parameter was assigned a relative weight (Rw) of 3. Calcium (Ca^{2+}) and Mg^{2+} were allotted a relative weight (Rw) of 2. Potassium (K^+), being the least significant parameter was assigned a minimum weight of 1.

Secondly, the weight parameter (Wp) for each of the groundwater quality variables was calculated to evaluate their relative significance on the overall water quality. The weight parameter (Wp) is the ratio of relative weight (Rw) of each water quality parameter divided by the summation of all the relative weights (Rw) (Equation 5):

$$Wp = \frac{Rw}{\sum Rw} \quad (5)$$

The third step involved status of concentration (Sc) estimation for each groundwater sample in relation to the quality standards of each variable. To calculate Sc of sample, the concentration (C) of each parameter was divided by their respective permissible quality standards (Ds). Of note, the permissible standards of the World Health Organization (WHO, 2017) and Canadian drinking water quality (GCDWQ, 2007) was adopted in the PIG evaluation. The latter was used specifically for HCO_3^{2-} .

$$Sc = \frac{c}{Ds} \quad (6)$$

The fourth step involved calculation of the overall water quality (Ow) of each variable. This was achieved by multiplying the weight parameter (Wp) with its corresponding status of concentration (Sc) (Equation 7).

$$Ow = Wp \times Sc \quad (7)$$

In the final step, the pollution index of groundwater (PIG) was quantified by adding all the overall water quality (Ow) values of each variable in every groundwater sample (ΣOw):

$$PIG = \Sigma Ow \quad (8)$$

The pollution index of groundwater (PIG) reflects the relative contributions of all the physical and chemical parameters of each water sample, thus, indicates the different conditions of physicochemical contamination on the host aquifer (e.g., [Subba Rao, 2012](#); [Subba Rao et al., 2018](#); [Subba Rao and Chaudhary, 2019](#)). Pollution index of groundwater (PIG) < 1 is interpreted as insignificant pollution, 1 to 1.5 is considered as low pollution, 1.5 to 2 is regarded as moderate pollution, 2.0 to 2.5 is interpreted as high pollution, and > 2.5 is interpreted as very high pollution ([Subba Rao, 2012](#)).

4. Results and Discussion

4.1 Hydrogeochemical profile

[Table 2](#) shows the physical/organoleptic field measurements of groundwater samples, whereas the results of hydrochemical analyses are presented in [Table 3](#). The overall summary of physicochemical parameters and their respective permissible standards are shown in [Table 4](#). Notably, standards for bicarbonate (HCO_3^-) and zinc (Zn) are based on Guidelines for Canadian drinking water quality ([GCDWQ, 2007](#)) and Nigerian Standard for Drinking Water Quality ([NSDWQ, 2015](#)) respectively. Temperature and pH range from 23.62 to 29.00°C (average, 27.1°C.) and 6.65 to 8.70 (average = 7.73) respectively whereas EC and TDS range from 27 to 570 $\mu S/cm$ (average = 198.4 $\mu S/cm$) and 87 to 382 mg/l (average = 150.23 mg/l) respectively ([Table 4](#)). All the measured parameters are within the WHO allowable limits. The temperature is reflective of the average temperature of air at the time of groundwater sampling. The pH values indicate a neutral to mildly alkaline affinity for the studied groundwater. Because temperature and pH are highly influential during dissolution of minerals in groundwater, the estimated pH average value of 7.57 is

diagnostic of free CO₂ abundance in the studied groundwater and the dissolve ions are entirely in the form of HCO₃⁻ (Freeze and Cherry, 1979). The low TDS values indicate low mineralized groundwater with a limited history of migration and water-rock interactions (Talabi and Tijani, 2013). The turbidity values vary from 0.02 to 4.86 NTU with an average of 1.52 NTU and falls within the 5 NTU guideline (WHO, 2017), implying a high level of clarity and low level of cloudiness and murkiness.

Calcium (Ca²⁺) is the dominant cations and display the highest concentration (27.63 to 71.00 mg/l, average = 41.84 mg/l) in the studied groundwater, followed by Mg²⁺ with concentrations ranging from 18.67 to 66.12 mg/l (average = 42.40 mg/l). The higher concentration of Ca²⁺ relative to Mg²⁺ probably indicate the release of excess Ca²⁺ from weathering of Ca-bearing silicate minerals such as K-feldspars, pyroxenes and amphiboles. The alkali metals display relatively low concentrations (Na⁺ = 0.49 to 6.85 mg/l, average = 1.87 mg/l; K⁺ = 6 to 12 mg/l, average = 8.55), much lower than their permissible standards of 200 mg/l and 30 mg/l, respectively (Table 4). The dominant anion in the groundwater is bicarbonate (HCO₃⁻), with concentrations ranging from 189 to 367 mg/l (average = 238 mg/l), followed by Cl⁻ (15 to 206 mg/l, average = 33.56 mg/l), NO₃²⁻ (12.83 to 99.7 mg/l, average = 35.93 mg/l), SO₄²⁻ (10.52 to 43.07 mg/l, average = 22.15 mg/l), CO₃²⁻ (0 to 5.1 mg/l, average = 1.13 mg/l), and F⁻ (0 to 0.29 mg/l, average = 0.064 mg/l) (Table 2). All the anion concentrations are within the WHO (2017) permissible guidelines (See Table 4).

The studied groundwater samples display Total Hardness (TH) concentration between 51.67 to 146.12 mg/l with an average of 75.91 mg/l (Table 3). Based on the Canadian drinking water quality hardness (Health Canada, 2012), water with TH (in form of CaCO₃) < 60 mg/l is regarded as soft, while 60 to 120 mg/l is interpreted as medium hard. Total Hardness (TH) between 120 to 180 mg/l is interpreted as hard, and >180 mg/l is interpreted as very hard. Based on this guidelines, the studied groundwater (average TH = 75.91 mg/l) can be interpreted as soft to medium hard. Moreover, 17% of the water samples display TH < 50 while 83% range from 60 to 120 mg/l, all of which are within the WHO permissible standard of 500 mg/l (Table 4). The medium hardness portrayed by majority of the groundwater could be due to weathering of Ca²⁺ rich minerals in the crystalline bedrocks.

The contents of cations and anions in the studied groundwater are within the range of Ca²⁺ > Mg²⁺ > K⁺ > Na⁺ and HCO₃⁻ > NO₃⁻ > Cl⁻ > SO₄²⁻ > CO₃²⁻ respectively. The negligible concentration of CO₃²⁻ in most of the water samples invariably portray the HCO₃⁻ as predominant weak acid. The dominance of HCO₃⁻ in the water samples reflect extensive chemical weathering of silicate minerals rich in alkaline earths, in part,

due to the high residence time of groundwater in the aquifers (e.g., Hem, 1989). The HCO_3^- was probably formed within the soil zone during its passage to the groundwater region following the disintegration of organic matter, which liberates CO_2 that further reacts with groundwater in the soil (e.g., Talabi and Tijani, 2013). This reaction consequently produced weak carbonic acid (H_2CO_3) which triggered the decomposition of minerals in the rock. This reaction facilitated the dissolution and subsequent liberation of cations and anions into the groundwater, which accounts for the wide range of hydrochemical characteristics (e.g., Talabi and Tijani, 2013; Carmi et al., 2019).

4.2 Chemical characteristics

4.2.1 Piper diagram

Fig. 6a shows Piper trilinear diagram of the studied groundwater samples while their corresponding classification and interpretation is presented in Table 5. The samples plot within the field (IV), corresponding to $\text{Ca}^{2+} - \text{Mg}^{2+} - \text{HCO}_3^-$ hydrochemical facies. This water type implies an exceedance of alkaline earth elements ($\text{Ca}^{2+} + \text{Mg}^{2+}$) over alkalis ($\text{Na}^{+} + \text{K}^{+}$) and dominance of weak acid ($\text{CO}_3^{2-} + \text{HCO}_3^-$) over strong acid ($\text{SO}_4^{2-} + \text{Cl}^- + \text{F}^-$). The water type is consistent with field (A) (Fig. 6a), which is interpreted as normal earth alkaline associated with carbonates (See Table 5) (Langguth, 1966). The water depicts a fresh-brackish water of almost ancient and non-contemporary recharge, which ascends from deep-seated aquifers along major faults. This water type is probably attributed to rainfall recharge processes, with low EC content. The Ca^{2+} ion in the groundwater most likely originated through dissolution of precipitates (e.g., CaCO_3 and $\text{Ca-Mg}(\text{CO}_3)_2$) during recharge. This implies that the studied groundwater consists of mixtures of various alkaline metals with a temporary hardness (Singh and Kumar, 2015). The samples are trending towards the bicarbonate and sulphate/chloride field (B) with three samples plotting within the boundary of fields (A) and (B) (Fig. 6a). This behaviour depicts a mild mixing of fresh and saline water, or probably fresh water that underwent evaporation (Panagopoulos et al., 2005) and affect only 10% of the total groundwater in the area. Indeed, none of the groundwater samples plot within the zones (II) and (III), thus, preclude the presence of $\text{Na}^{+} - \text{K}^{+} - \text{Cl}^- - \text{SO}_4^{2-}$ and $\text{Na}^{+} - \text{K}^{+} - \text{HCO}_3^-$ water facies.

4.2.2 Durov diagram

The Durov diagram (Fig. 6b) and its corresponding water classification (Table 6) has been used to shed light on the important hydrochemical processes. The cationic triangle to the left shows clustering of water samples within the Mg^{2+} water type field, while few samples straddle the intermediate and Ca^{2+} water type

fields (Fig. 6b). Similarly, majority of the water samples are concentrated in the HCO_3^- water type domain in the anionic triangle, with two samples plotting within the intermediate Cl^- water type zone. The clustering within the cationic ($\text{Ca}^{2+} - \text{Mg}^{2+}$) and anionic (HCO_3^-) triangles is consistent with the water type ($\text{Ca}^{2+} - \text{Mg}^{2+} - \text{HCO}_3^-$) extrapolated from the Piper trilinear diagram (Fig. 6a). In the Durov diagram, majority of the samples plot in the ionic exchange field while some are unevenly distributed within the fields (1), (2) and mixing or dissolution field (5) (Fig. 6b). This behaviour further confirm the possible low-level mixing between the fresh and saline water end-members observed in the Piper diagram. Notably, the extensive anionic and cationic exchange are most likely the major chemical processes that led to the mixing or dissolution during groundwater flow and recharge (cf. Kumar et al., 2006).

4.2.3 Bi-variant plots

Table 7 shows the summary of computed ion-exchange process in the studied basement aquifer and the associated Gibbs ratio. The chloro-alkaline index (CA-I and CA-II) yielded positive values (0.0383 to 0.75 and 0.00248 to 0.08346). This implies that Na^+ and K^+ ions exchange is basically from the water with Mg^{2+} and Ca^{2+} ions of the rock, consistent with a direct base-exchange reaction associated with soft water (Kumar et al., 2013). Gibbs (1970) introduced the diagram of cation ($\text{Na}^+/\text{Na}^+ + \text{Ca}^{2+}$) versus TDS and anion ($\text{Cl}^-/\text{Cl}^- + \text{HCO}_3^-$) versus TDS to demonstrate the natural processes controlling groundwater chemistry. These processes include dominance of rainfall, rock weathering (rock-water interaction), evaporation and precipitation. The groundwater samples plot in the field of rock dominance (Fig. 7a–b), indicating that weathering of minerals and base-exchange reaction are the major processes controlling the groundwater chemistry. However, the groundwater samples form a horizontal straight line in the plot of EC versus Na^+/Cl^- (Fig. 7c), precluding a significant variation in Na^+/Cl^- ratio with increasing EC. This pattern indicates that the ionic concentration of the studied groundwater is also controlled by evaporation/evapotranspiration (Jankowski and Acworth, 1997).

4.2.4 Scatter diagrams

The $\text{Na}^+ - \text{Cl}^-$ relationship is often used to identify the major processes responsible for the marked increase in the salinity of groundwater in arid/semi-arid regions. According to Meybeck (1987), if sodium is sourced from halite dissolution, the ratio of $\text{Na}^+ - \text{Cl}^-$ will be approximately 1. However, the sample points in Fig. 8a deviated from the 1:1 relation line, indicating that halite dissolution is unlikely the major source of

Na⁺ in the studied groundwater. This lives open the possibility that the mild/low salinity may be due to silicate weathering and ion exchange reaction. Moreover, the trend of Cl⁻ versus K⁺/Cl⁻ (Fig. 8b) displays K⁺/Cl⁻ ratio > 0.2, diagnostic of dissolution and weathering of silicate minerals (such as K-feldspar and plagioclase) in the crystalline basement rocks (e.g., Chang and Wang, 2010) as buttressed by the reaction:

A hydrogeochemical system with ratio of (HCO₃⁻+SO₄²⁻) versus (Ca²⁺+Mg²⁺) close to the relation line (1:1) implies chemical reaction mainly associated with dissolution of dolomite, calcite and gypsum (e.g., Su, 2009). The binary plot of (HCO₃⁻+SO₄²⁻) versus (Ca²⁺+Mg²⁺) shows a larger percentage of the samples fall above the 1:1 line (Fig. 8c). This further indicates that dissolution/weathering of silicate and sulphate minerals and cation exchange is the main chemical reaction in the system (e.g., Fisher and Mulican, 1997), rather than calcite, dolomite and gypsum dissolution. Further, the water samples display slight positive correlation in the alkalinity versus Mg²⁺ diagram (Fig. 8d), with low correlation coefficient (R = 0.35) between the variables. Most of the sample points plot below the 1:1 equiline, implying that the excess alkalinity in the groundwater must have been balanced by alkalis (e.g., Rao 2008; Ganyaglo, 2012). Evaporation in arid regions often elevate Cl⁻ contents in groundwater, and reflects the level of mineralization (e.g., Yang et al., 2016). The plot of TDS versus Cl⁻ display an increase in Cl⁻ with increasing TDS (Fig. 8e), indicating the relative role of evaporation process in the studied groundwater.

Another important organoleptic parameter reflecting the extent of salinity or mineralization is the electrical conductivity (EC). High concentration of EC implies groundwater with a long residence time (e.g., Walraevens et al., 2018). Therefore, concentration of EC in the studied groundwater (127 to 337 µs/cm) is reflective of the extent of aluminosilicate weathering and the roles of other secondary processes (e.g., evaporative concentration, evaporate salts dissolution and anthropogenic pollution). A fairly positive correlation is demonstrated between EC and other important ions such as Ca²⁺ (r = 0.65), Na⁺ (r = 0.71), K⁺ (r = 0.75), Cl⁻ (r = 0.62) and NO₃⁻ (r = 0.60) (Table 8). These positive correlations imply an increase of these elements with increasing EC, thus, a proper replicate of TDS (e.g., APHA-AWWAWEF, 2012). These elements are products of rock-water interactions, particularly the weathering of silicate minerals. The strong correlation between EC and K⁺ (r = 0.75) implies that the weathering of K-feldspar and micas (which resulted

in the liberation of K⁺) has also been influential in the mild salinity of the studied groundwater (cf. Petrides et al., 2006).

The Cl⁻-Ca²⁺ ratio (in meq/l) is an important parameter controlling the hydrodynamics of groundwater (Li et al., 2011). In a low mineralized setting, Ca²⁺ is usually the dominant cation. Progressive increase in TDS can lead to an increase in Mg²⁺, and further increase in TDS can make Na⁺ to become the dominant cation in the hydrochemical system. High TDS in groundwater can hinder the migration of Cl⁻, leading to a marked increase in Cl⁻ with increasing TDS (Fig. 8e). Consequently, the Cl⁻/Ca²⁺ ratios progressively increase with increasing TDS (Fig. 8f), reflective of an extensive hydrodynamic worsening (Li et al., 2011). Based on the plot of TDS versus Cl⁻/Ca²⁺ (Fig. 8f), there is a marked hydrodynamic heterogeneity in the studied groundwater which is believed to be controlled by extensive weathering of the parent rock (Dewandel et al., 2006, 2012; Tziritis et al., 2017). During this process, the minerals in the rock experienced biogeochemical hydrolysis weathering (i.e., reaction between hydrogen ion and silicate minerals such as feldspars) which consequently transform them into clay-rich materials (Nahon, 1991). The abundance of feldspars in the rock, coupled with the widespread alluvial deposits consisting of clay, sand, silt, river bed sand and gravel (See Figs. 2 & 4) invariably attest to aforementioned process in the study area.

According to Li et al. (2013), the ratio of Na⁺ and Cl⁻ (in mmol/l) is supposed to be 1 if these ions are derived mainly from halite dissolution. However, almost all the groundwater samples plot strictly below the 1:1 relation line (Fig. 9a), indicating higher Cl⁻ relative to Na⁺ and precluding halite dissolution as the major source of these ions. Thus, it is probable that other reactions (e.g., water-rock interaction and anthropogenic activities) may have influenced their concentrations. Notably, Na⁺ deficiency in the hydrogeochemical system is buttressed by cation exchange (equations 10 and 11). This process probably enhanced the absorption of Na⁺ into the aquifer which consequently decreases the Na⁺ ion in the groundwater thereby making most of the samples to plot below the 1:1 relation line (Fig. 9a).

The Na⁺/Cl⁻ ratio < 1:1 is associated with animal excrement and domestic sewage which infiltrate into the shallow weathered aquifer and increases the Cl⁻ content in the groundwater (cf. Li et al., 2014). The plot of Cl⁻ versus Cl⁻/HCO₃⁻ demonstrates a strong positive correlation (r = 0.96), with almost all the samples

displaying $\text{Cl}^-/\text{HCO}_3^-$ ratios < 0.5 (Fig. 9b), implying that the studied groundwater is fresh and unaffected by domestic and animal sewage.

4.2.5 Multivariate statistical techniques

Analysis of the principal components of the studied groundwater has been carried out to identify the significant factors (with eigenvalue >1) controlling the groundwater chemistry. The analysis revealed three factors characterized by cumulative percentage variance of 76.70% and progressively decreasing eigenvalues and percentage variances from factor 1 to factor 3 (Table 9). The three factors yielded a cumulative percentage variance of 76.70%. Factor 1, with eigen value of 5.50 accounts for 45.80% of the total variance characterized by strong positive loading (<0.75) with respect to Ca^{2+} , Na^{+} , Cl^- , NO_3^- , EC and TDS. Calcium (Ca^{2+}) display high loading of 0.74 which may be ascribed to its liberation as by-product of weathering/dissolution of silicate minerals (e.g., amphiboles, feldspars, and pyroxenes), while high loadings of Na^{+} and Cl^- (0.884 and 0.774) is likely attributable to natural (mild) salinity, a process that is also corroborated by the high positive correlation between Na^{+} and Cl^- ($r = 0.703$, See Table 8). The high loading of Na^{+} may also be related to weathering of feldspar or cation exchange, while that of Cl^- may be associated with anthropogenic activities (Singh et al., 2005; Huang et al., 2013). Similarly, the strong positive loading portrayed by NO_3^- (0.901) and TDS (0.718) may be due to anthropogenic activities such as runoff from animal waste (manure) and fertilizer lawns as well as failure of on-site septic systems (Wang et al., 2020). High loading of EC (0.715) is probably attributable to rapid evaporation, which increases the natural salinity of the water as seen from the strong positive loading of Na^{+} . Therefore, factor 1 can be interpreted as rock-water interaction during silicate weathering, natural salinity and anthropogenic activities.

Factor 2 shows lower eigenvalue (2.50) and %variance (20.79) as compared with factor 1 (5.50 and 45.80). This factor yielded high loadings with respect to Mg^{2+} , Cl^- , TH and pH (Table 9). Strong positive loading displayed by Mg^{2+} (0.874) likely reflects weathering of mafic minerals (e.g., biotite), while that of pH (0.777) may be attributable to the precipitation-dissolution of Ca^{2+} and Mg^{2+} , a process that probably enhanced the mild salinity of the groundwater. Further, strong positive loading with respect to TH (0.886) is largely controlled by the availability of the major ions (Ca^{2+} and Mg^{2+}), as corroborated by the strong positive correlation of TH with Mg ($r=0.801$) (Table 8). Thus, this factor can be interpreted as natural hardness and rock-water interaction (weathering).

Factor 3, with eigen value and %variance of 1.22 and 10.14%, respectively is the least significant contributor of groundwater chemistry. This factor is characterized by a high fluoride loading of 0.851, attributable to fluoride-containing pesticides and fluorinated pharmaceuticals, hence, can also be interpreted as anthropogenic activities. The strong positive correlation of TDS and EC with the main cations and anions (See Table 8), coupled with the high loadings of TDS, EC and K^+ (Table 9) reflect their significant contribution to the overall mineralization in studied groundwater. This shows that the ions in the basement aquifers originated from geogenic source during weathering and dissolution or precipitation (Saxena and Ahmed, 2003; Sahu et al., 2021).

Dendrogram of hydrogeochemical data generated from the hierarchical cluster analysis (HCA) indicates two clusters (Fig. 10). Cluster 1 is further divided into two separate sub-clusters. The sub-cluster 1 comprised of EC, TDS, K^+ with Ca^{2+} loosely bound to it. This cluster can be interpreted as anthropogenic activities probably controlled by K^+ as well as rock-water interaction (silicate weathering) and natural salinity associated with dissolution of Ca^{2+} , which can cause a mild hardness in the groundwater. This agrees well with factor 1 in the principal component analysis. The second sub-cluster indicate similarities between Na^+ , NO_3^- , and Cl^- with loosely attached F^- . As the cluster comprised of Na^+ and Cl^- , it can be described as natural salinity, in line with factor 1 in PCA. By virtue of NO_3^- and F^- , it can also be interpreted as anthropogenic activities, which is consistent with factor 1 and 3 in the PCA. Cluster 2 consist of Mg^{2+} , TH, pH with HCO_3^- loosely bound to it. This cluster can be interpreted as temporary hardness and precipitation, which can cause residual bicarbonate hazard (e.g., Kumar et al., 2016). This cluster is consistent with factor 2 in the PCA.

4.3 Groundwater quality assessment

The pollution index of groundwater (PIG) examines the relative contributions of the major physicochemical parameters from each water sample. Subba Rao (2012) proposed that water quality parameter with an overall water quality (Ow) greater than 0.1 (i.e., 10% of the PIG value of 1.0) has the greatest influence on the pollution state of the groundwater. In the present study, the pH of 70% of the groundwater samples (i.e. 21 out of the 30 samples) yielded Ow values greater than 0.1 (0.11 to 0.16, average = 0.12) while NO_3^{2-} of 23.3% of the water samples also yielded Ow values greater than 0.1 (0.11 to 0.24, average = 0.17) (Table 10). These elevated values indicate that pH and NO_3^{2-} have the highest impact on the groundwater quality, even though all the groundwater samples yielded pollution index of groundwater (Σ PIG) less than 1 (0.27 to 0.737) (Table 10), indicating an insignificant pollution based on the standard rating of

Subba Rao (2012). The elevated Ow of pH in most of the samples may be as a result of the precipitation-dissolution of Ca^{2+} and Mg^{2+} which invoked natural salinity of the water. The high Ow of NO_3^{2-} in some of the groundwater samples may be attributable to the use fertilizer (e.g., NPK) and animal manure on farm lands, the pollution effect of which is insignificant given the low PIG (<0.1) of the all the studied groundwater samples.

Despite the artisanal mining of monazite in the area, the pollution index of groundwater is within the permissible limits for drinking. This may be due to the current shallow depth of the mine pits (average of 3.2 meters) which is lower than the minimum depth of weathered regolith and collapse zone (6.3 meters) within the vicinity of the mine pits. Besides, field investigation have shown that the mine pits are sited at areas of low topographic heights with appreciable distance from the boreholes where water samples for this study were collected.

5. Conclusion

Hydrogeochemistry and quality assessment of borehole groundwater within the basement aquifers in Mubi South area, north-eastern Nigeria has been thoroughly monitored and examined. The cations–anions contents range from $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ and $\text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ respectively. Deductions from various hydrochemical systematics such as Piper, Gibbs and Durov diagrams as well as chloro-alkaline indices and statistical techniques indicate silicate weathering as the primary process controlling the hydrogeochemistry of groundwater in the area. However, other hydrochemical processes such as anthropogenic activities and evaporative concentration and anthropogenic activities (such as fertilizer application) also play a secondary role in the hydrochemical evolution of the groundwater. Estimation based on the pollution index of groundwater (PIG) indicate an insignificant pollution state of less than 1 (0.27–0.737) for the groundwater samples collected from all the 30 boreholes in the study area.

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Declarations

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors. We know no conflict of interest associated with this publication, and there has been no significant financial support for this work that could have influenced its outcome. All generated or analyzed data during this study are included in this submission as Tables. We declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere. Free version of softwares used for data analysis such as AQqa, SPSS, and CorelDraw Graphics Suit are available online.

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Figure caption

Fig. 1. Regional geological map of Nigeria (after Ferré et al., 1996 and Key et al., 2012). Distribution of rocks within the Cameroon volcanic line (after Ngako et al., 2006).

Fig. 2. Geological map of the study area.

Fig. 3. Annual rainfall pattern of the study area (after Adebayo and Tukur, 1999).

Fig. 4. Hydrogeological map of the study area and environs showing the location of boreholes (after Consulint International s.r.l and Consulint Nigeria, 1976).

Fig. 5. (a) Schematic weathered profile above crystalline basement rocks (after Wright, 1992), **(b)** Schematic basement aquifer catenary cross section (after Wright, 1992).

Fig. 6. (a) Piper Trilinear diagram classifying major hydrochemical facies. Divisions in quadrilateral and triangles (after Langguth, 1966), **(b)** Durov plot depicting hydrochemical processes. Division in the square and two triangles are after Lloyd and Heathcoat (1985) and Singh and Kumar (2015).

Fig. 7. Gibb's Diagram **(a)** cation versus TDS, **(b)** anion versus TDS showing the overriding control of rock dominance (silicate weathering) in the hydrogeochemical system of the area (after Gibbs, 1970), **(c)** Na^+/Cl^- vs. EC binary plot to interpret the evaporation/evapotranspiration (after Sahu et al., 2021).

Fig. 8. Scatter plots of cations and anions **(a)** Cl^- versus Na^+ (meq/l), **(b)** Cl^- versus K^+/Cl^- (meq/l), **(c)** $\text{SO}_4^{2-} + \text{HCO}_3^-$ (meq/l), **(d)** Alkalinity ($\text{Na}^+ + \text{K}^+$) versus Mg^{2+} (meq/l), **(e)** TDS versus Cl^- (mg/l), **(f)** TDS (mg/l) versus $\text{Cl}^-/\text{Ca}^{2+}$ (meq/l).

Fig. 9. Scatter plots of **(a)** Cl^- versus Na^+ (mmol/l) (after Li et al., 2013), **(b)** Cl^- versus $\text{Cl}^-/\text{HCO}_3^-$ (meq/l)

Fig. 10. Dendrogram of hydrogeochemical data using Ward method

Figure 1

Figure 2

Figure 2

Geological map of the study area.

Figure 3

Figure 3

Annual rainfall pattern of the study area (after Adebayo and Tukur, 1999).

Figure 4

Figure 4

Hydrogeological map of the study area and environs showing the location of boreholes (after Consulint International s.r.l and Consulint Nigeria, 1976).

Figure 5

Figure 5

(a) Schematic weathered profile above crystalline basement rocks (after Wright, 1992), (b) Schematic basement aquifer catenary cross section (after Wright, 1992).

Figure 6

Figure 6

(a) Piper Trilinear diagram classifying major hydrochemical facies. Divisions in quadrilateral and triangles (after Langguth, 1966), (b) Durov plot depicting hydrochemical processes. Division in the square and two triangles are after Lloyd and Heathcoat (1985) and Singh and Kumar (2015).

Figure 7

Figure 7

Gibb's Diagram (a) cation versus TDS, (b) anion versus TDS showing the overriding control of rock dominance (silicate weathering) in the hydrogeochemical system of the area (after Gibbs, 1970), (c) $\text{Na}^+ / \text{Cl}^-$ vs. EC binary plot to interpret the evaporation/evapotranspiration (after Sahu et al., 2021).

Figure 8

Figure 8

Scatter plots of cations and anions (a) Cl^- versus Na^+ (meq/l), (b) Cl^- versus K^+/Cl^- (meq/l), (c) $\text{SO}_4^{2-} + \text{HCO}_3^-$ (meq/l), (d) Alkalinity ($\text{Na}^+ + \text{K}^+$) versus Mg^{2+} (meq/l), (e) TDS versus Cl^- (mg/l), (f) TDS (mg/l) versus $\text{Cl}^-/\text{Ca}^{2+}$ (meq/l).

Figure 9

Figure 9

Scatter plots of (a) Cl^- versus Na^+ (mmol/l) (after Li et al., 2013), (b) Cl^- versus $\text{Cl}^-/\text{HCO}_3^-$ (meq/l)

Figure 10

Figure 10

Dendrogram of hydrogeochemical data using Ward method