Hydrochemical Characterization of Groundwater Quality in Nkalagu District, Southeastern Nigeria

Abstract

Hydrochemical characterization of groundwater quality inNkalagu District, southeastern Nigeria was carried to determine the main factors controlling the chemistry of groundwater and its suitability for drinking and irrigation purposes. Sixty (60) groundwater samples collected from boreholes and hand-dug wells in different parts of the area were analyzed for a range of physiochemical parameters and heavy metal constituents.The results show that concentration of the major ions were in the order $Cl^{-}>HCO_3^{-}>SO_4^{2-}>NO_3^{-}$ and $Na>Ca^{2+}>Mg^{2+}>K^{+}$. The groundwater samples are slightly acidic with pH of 5.28 to 8.04; moderately hard with TH of 112.88 to 467.78 mg/l. The district is mainly controlled by carbonate and silicate mineral weathering based on the available result. Three main flow regimes were identified with Q-mode cluster analysis. Based on the WQIanalysis results, the groundwater quality in the district was classified, generally as 'poor' to 'excellent' for drinking purpose. Groundwater quality for drinking purposewere noted to deteriorates as one movefrom westtowards the east of the district, while the north and southpart pf the study area indicated the best quality in the district. Groundwater quality for irrigation purpose showedexcellent quality based on the United States Salinity Laboratory and Wilcox diagrams. For future use of groundwater resource in the district we recommend implementation rules and guidelines in the area to enhance health and preserve groundwater sources in the district.

Keywords: Physiochemical parameters, Water quality index, Groundwater quality, Drinking water quality

Introduction

Groundwater generally plays a vital role in meeting the water supplyneeds for various human activities.Nkalagu district is one of such places where the inhabitant relies on groundwater through boreholes and hand-dug wells for their potable water and other domestic and agricultural related water needs.

Despite the importance of groundwater as a source of water supply in this Nkalagu district, not much has been done to understand the natural phenomena that control its chemical composition and various factors that are capable of affecting groundwater quality and usage in various parts of the area. Anku et al. 2009; Eneke 2011; Selvakumar et al. 2017; Sunkari et al. 2019 identified anthropogenic activities and geogenic processes as major sources of groundwater degradation.Shihaband AbdulBaqi(2010)impliedprincipal component analysis (PCA) and cluster analysis (CA) to characterize groundwater quality inMakhmorPlain, North Iraq. Their work revealed that groundwater from deep wells exhibit lesser variation in $Ca^{2+}$and HCO_3^-ions, while groundwater from shallow wells exhibit lesser variation in K^+ and NO_3^-ions. They concluded that geogenic factors are impacting the groundwater quality more than anthropogenic activities especially when sourced from greater depth.

Okogbue et al. (2012) used PCA to characterize the groundwater from Egbe–Mopa Basement Complex area ofnorthcentral Nigeria. They observed that three main factors (weathering/leaching of host rock minerals and anthropogenic sources, iron and other heavy metals concentrations in groundwater, and presence of bacteria in groundwater) affected the groundwater quality characteristics of the area. With the help of principal component score, they were able to identify the principal controlling processes of each and all the sampled wells.

This present study adopts standard laboratory, statistical tools and hydrochemical classification methods to assess the hydrochemistry of groundwater in the Nkalagu district of southeastern

Nigeria. The findings of the study provide more insights into the impact of geogenic and anthropogenic activities in the area.

Study Area

The study area, Nkalagudistrict is located in SE part of Nigeria, within the boundaries of latitudes 6˚10´ and 6˚40´N and longitudes 7˚35´ and 7˚50´E on the scale of 1:100,000 (**Fig. 1**).Study area elevationis between 60 m and 105 m.The river flows toward eastern and southernparts of the study area. The Iyioke and Uzuru Rivers meander in and out of the district until it flows down towards the southwestern part of the district and discharge into the Ebonyi River.Two main climatic seasons exist in the study area, namely the dry and the rainy seasons. Rainy season (wet season) commonly begins in April and ends in October, while the dry season often begins in November and ends in March. Annual rainfall ranges from 503 mm to 997 mm (FARM Unit, EBSU, 2017). The most important economic activity in the study area is mining, artisanal stone crushing and agriculture.

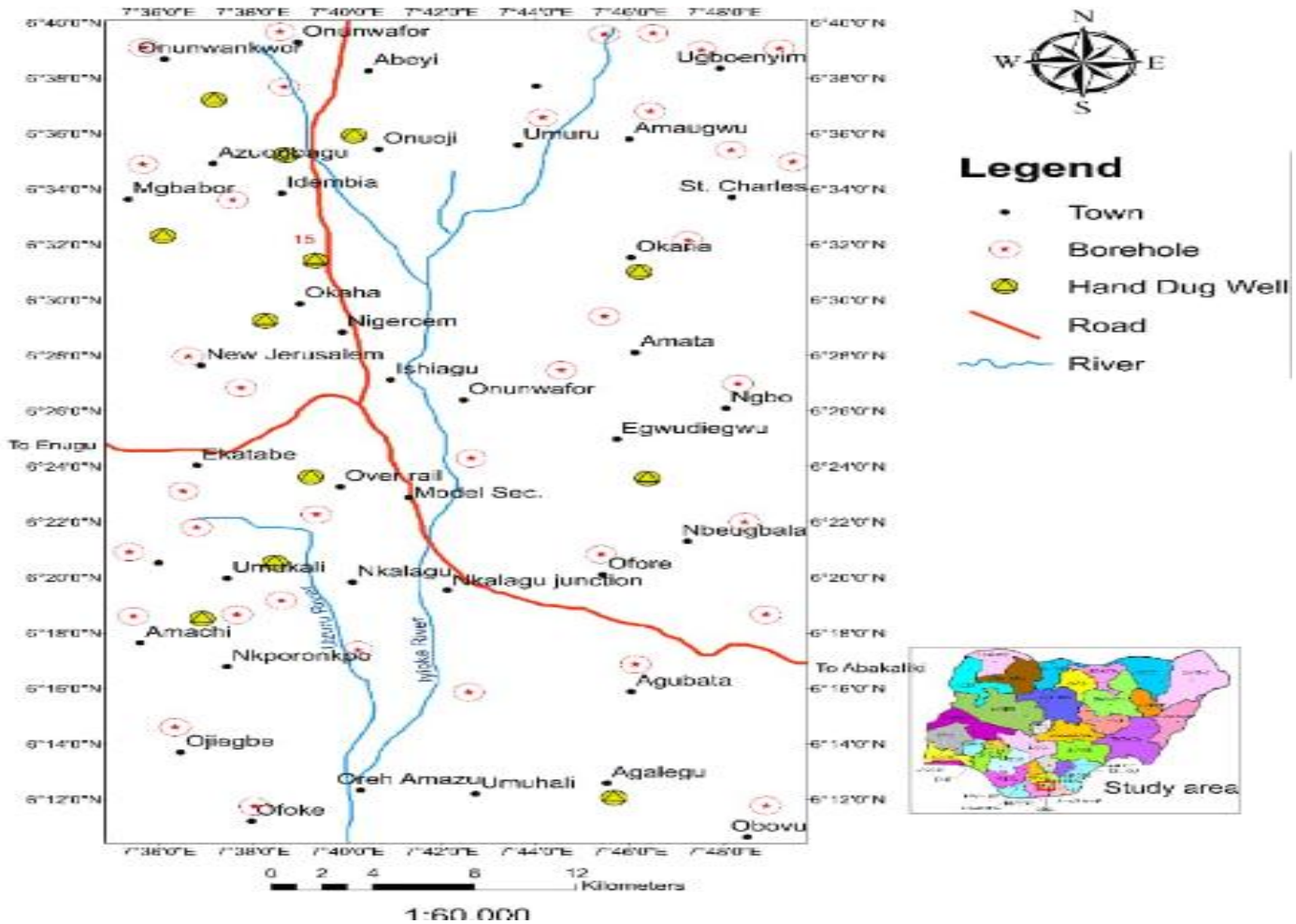

Fig. 1 Location and Accessibility map of the study area

GeologyandHydrogeology

The study area is sedimentary rock terrain and is geologically composed of rocks belonging to Eze-Aku Formation, Agwu shale and Asu-River Group (**Fig. 2**). This Formation consists of black shales, limestones, and siltstones (Reyment 1965). An alternating sequence of thick limestone or sandstone units occurs with calcareous shales in places within the Eze Aku Formation (Phillips et al. 2009). The limestone beds in the district have NE – SW strike, dip averagely 6˚ - 8˚ to the NW and grade laterally into shale (**Fig. 2**). A total of 25 limestone beds have been identified and serially numbered in the area by Amajor (1992).

Despite the high amount of rainfall in the area, groundwater resources are relatively scarce. This is because of the hard limestone, which predominantly underlay the study area and is massive

and impermeable and rarely aquiferous. One major aquifer type has been observed in the area by Egboka et al. (1993), that is the fractured zone aquifer of the shales. They opined that this aquifer type has high value of transmissivity and hydraulic conductivity, hence, preferred for groundwater supply. They estimated borehole depth of about 35 m to 45 m to obtain water of good quality in the area.

Groundwater flow through secondary porosity as a result of alteration, cementation and intensive structural deformation in the area and dominated by fracture flow. In a typical fractured hydrogeological system, the occurrence of open water-bearing fractures is greatest at shallow depths (Egboka et al. 1993). Typically, the hydraulic conductivity declines with depth as fractures aperture becomes tighter and less prominent. Therefore, the groundwater flow paths are likely to be shallow, predominantly in the upper layer of the aquifer with enhanced weathering and open fractures (Aghamelu et al. 2013). However, the limestone in the area may have permeable zones at greater depths, relating to earlier periods of alteration.

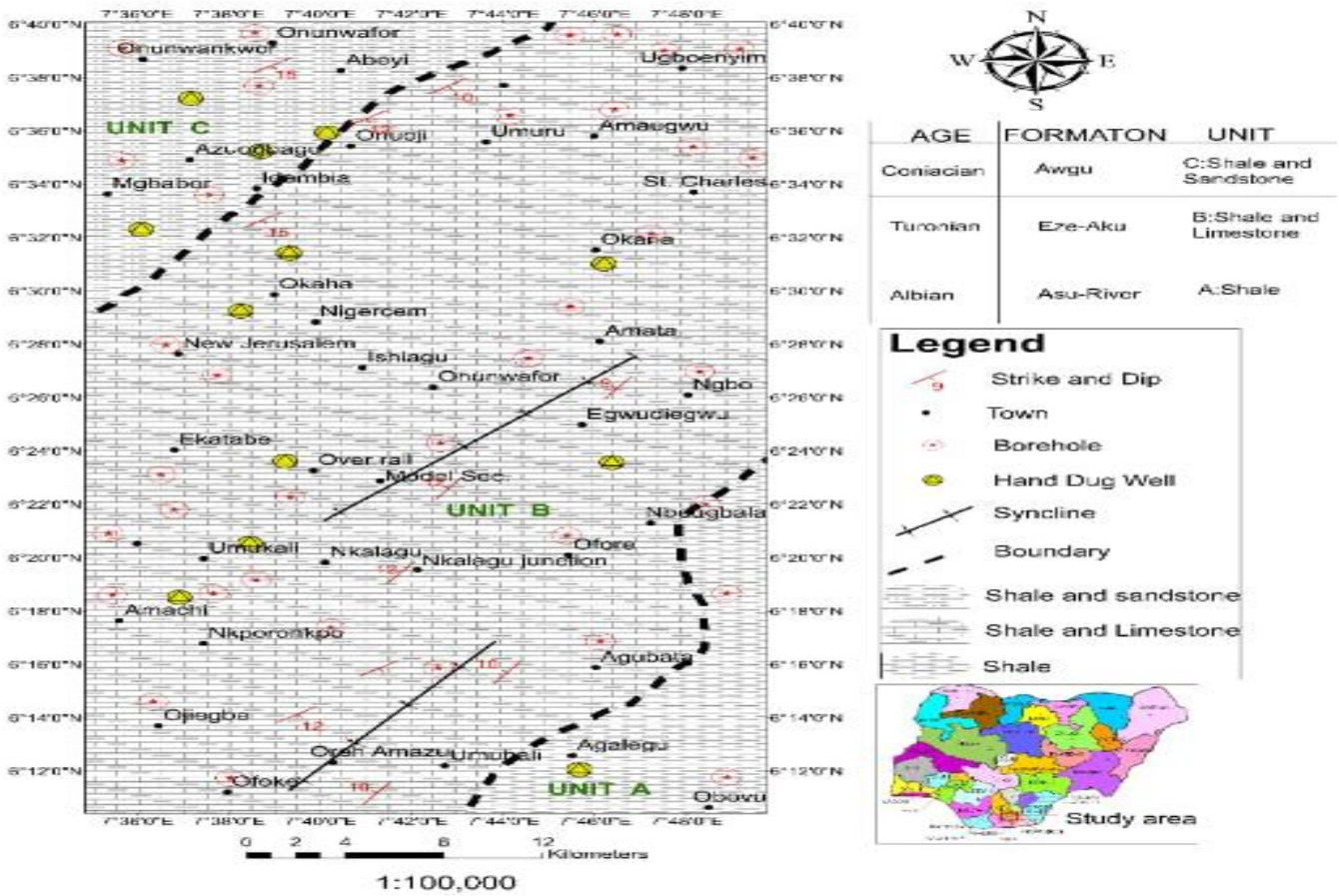

Fig. 2 Geological map of Nkalagu District, Southeastern Nigeria

Materials and Methods

A total of 60 groundwater samples (comprising 45 boreholes and 15 hand-dug wells) were collected in March, 2019, when water resource in the district is expected to be of low quantity and quality for physiochemical parameters and heavy metals constituent investigation. The groundwater samples are herein encoded BH1 – BH45 for boreholes and HDW1 – HDW15 for hand-dug well as shown in **Fig. 1**.Samples were spatially collected so as to cover the residential, agricultural and industrial areasusing the standard guidelines (APHA, 2012).The samples were collected after pumping the wells for 5-10 minutes and by subsequent filtering through 0.45 lm membranes. Two sets of groundwater samples were collected in 250 ml sterilized low density

polyethylene bottles. One set for cation and heavy metal tests and the other set for anion tests. Samples for cation and heavy metal tests were stabilized with 2 to 3 drops of dilute HCl at the point of collection. This was necessary prior to transport to the laboratory in order to suppress hydrolysis, sorption and other processes that could influence concentration, all aimed at enhancing the accuracy of the result. Preservation and transportation of water samples were performed according to (APHA, 2012) standard.

The analyzed parameters include hydrogen ion concentration (pH), electrical conductivity (EC), Total Dissolved Solid (TDS), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), sulphate (SO_4^{2-}), chloride (Cl^{-}), bicarbonate (HCO_3^{-}), nitrate (NO_3^{-}) and heavy metals were done in the Chemical Research Laboratory, Abakaliki, Nigeria.

The pH was measured using pH model metre, while EC and TDS were measured using WissenschaftlichTechnischeWerkstatten Conductivity (WTWC) metre. HCO_3^{-}, calcium Ca^{2+}, and total hardness (TH) were determined by titrimetric methods. Na^{+} and K^{+} measured by flame photometry. Cl^{-}, $SO_4^{2-}$and NO_3^{-} were analyzed using the HACH DR/2010 spectrophotometer.Heavy metals were determined by Atomic absorption spectroscopy (AAS). The ionic charge balance error was within 5%.

Descriptive statistics, principal component analysis (PCA),cluster analysis (CA)and Pearson correlation were adopted in this study to characterize groundwater quality of the district. The number of principle components chosen was based on the Ayuba et al. (2013) with eigenvalues $\geq$ 1.0 and factor loading $\geq \pm$ 3.5 were considered significant. Software tools used for the data analyses were the Stagraphics Centurion XVI, Surfer 12, and Microsoft Excel was used for graphical display and contouring of the hydrochemical datasets.

Water quality index (WQI) and facies in the study area was determinedby procedure described in previous works by (Benvenuti et al. 2015; Fathi et al. 2018; Kumar et al. 2014; Ravikumar et al. 2015; Samlafoand Ofoe 2018; Piper 1944)**.**Groundwater quality for irrigation purpose in this study was assessed usingWilcox (1955), United States Salinity Laboratory (1954), sodium adsorption ratio (SAR)and percent of sodium (Na %).

Results and Discussion

The chemical compositions of the groundwater samples were statistically analyzed, and the results are given in Table 1.

The pH ranges from5.28-8.04 with an average of 6.86 (Table 1). This reveals that the groundwater in the study area is acidic to slightly alkaline in nature. According to Larry et al. (2020), pH influences the dissolution of minerals in a groundwater well as affect the quality of water for various purposes.

EC ranges from 430μS/cmto 3996 μS/cm with an average of 1707.53 μS/cm.This wide range in EC values revealed the high diversity in the geochemical processes in the study that influencegroundwater chemistry in the area. TDS ranges from 202mg/l to 1879 mg/l with an average of 838.42 mg/l.According to WHO (2017) guideline; the permissible limit of EC is 2500 μS/cm and TDS is 1000 mg/l for drinking water purpose. Lower values ($\leq$2500 μS/cm and 1000 mg/l) were noticed in 43.3 % and 28.3 %of EC and TDS values respectively.

TH ranges from 112.88 mg/l to 467.78 mg/l with an average of 258.42 mg/l.Based on the TH, groundwater of the area ranged from moderately hard water to very hard water.

Table 1Comparison of groundwater quality with standards (n = 60)

Parameters	WHO (2017) limit	Minimum value	Maximum value	Mean value	Standard deviation	% above limit
pH	6.5 - 8.5	5.28	8.04	6.86	0.59	Nil
EC (µS/cm)	1400	430.00	3996.00	1707.53	934.69	56.7
TDS (mg/l)	500	202.00	1879.00	838.42	440.63	71.7
TH (mg/l)	200	112.88	467.78	258.42	74.94	83.3
SO_4^{2-} (mg/l)	250	31.56	225.57	111.53	56.40	13.3
NO_3^- (mg/l)	50	10.50	42.31	24.00	9.27	33.3
HCO_3^- (mg/l)	120	36.47	254.10	144.93	53.61	65.0
Cl^- (mg/l)	250	57.12	314.00	156.00	47.41	28.3
Ca^{2+}(mg/l)	75	20.80	117.56	65.84	21.98	41.7
Mg^{2+}(mg/l)	30	12.73	42.34	22.85	6.26	43.3
Na^+(mg/l)	200	16.46	154.00	84.83	32.29	11.7
K^+(mg/l)	10	3.29	20.54	10.32	3.67	61.7
Pb^{2+} (mg/l)	0.01	<0.01	0.09	0.03	0.03	65.0
Zn^{2+} (mg/l)	3	<3.00	2.68	0.60	0.66	Nil
Mn^{2+} (mg/l)	0.5	<0.5	1.22	0.23	0.29	28.3

As^{3+} (mg/l)	0.01	<0.01	0.07	0.02	0.06	20.0
Cd^{2+} (mg/l)	0.003	<0.003	0.010	0.010	0.013	30.0
Fe^{2+} (mg/l)	0.3	0.01	5.52	1.19	1.75	66.7

The calculated ionic charge balance error (CBE) was 1.91 %, and is within the acceptable limits of < ± 5 %. This thus confirms the reliability of the analytical results (Singh and Hassin, 2002).

The concentration of major ions were in the order of $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$ and $Na > Ca^{2+} > Mg^{2+} > K^+$ with Cl^-most dominant ion (25.15 %) of the total major ions whileK^+least ion (1.67 %) of the total major ions. The degree of accumulation of heavy metals was in order Fe > Zn >Mn>Pb> As > Cd. This implies that Fe has the highest water pollution index while Cd has the least water pollution index.From the results obtained, it suggested that diverse geochemical processes control groundwater chemistry in the district.

Main Controls on Groundwater Chemistry

Variables with correlation coefficients (r^2) values that are significantly related at 0.01 and 0.05 levels are written with asterisks. Mishra et al. (2003) noted that ionic pairs that are ignificantlyrelated at 0.01 and 0.05 levels are thought to be released from the same sources or through same geochemical processes. Pearson's correlation analysis shows that the EC exhibits a significant positive correlation with TDS, TH, Ca^{2+}, Mg^{2+}, Na^+, Cl^- and SO_4^{2-} (Table 2). The r^2value between EC and TDS is 0.983, implying that TDS is very significantly and positively correlated with EC. Also, the EC value of the groundwater samples has high positive correlation with TH, Ca^{2+}, Mg^{2+}, Na^+, Cl^- and SO_4^{2-} with relative positive r^2values of 0.828, 0.804, 0.830,

0.889, 0.824 and 0.858 respectively. This positive correlation between EC and some of the major ions buttresses the fact that an increase in these ions concentrations would obviously increase the EC value of the water. The strong correlation of the major elements Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-} and SO_4^{2-} with EC is an indication of the contribution of these elements to the salinity or hardness of the water due to concentration of ions from evaporation of recharge water and water interaction with the geological formations.

Table 2Correlation matrix of physicochemical parameters in the study area

	pH	EC	TDS	TH	Ca	Mg	Na	K	HCO_3	Cl	SO_4	NO_3	Pb	Zn	Fe	Mn	As	Cd
pH	1.000																	
EC	0.162	1.000																
TDS	0.145	0.983**	1.000															
TH	0.259*	0.828**	0.826**	1.000														
Ca	0.231	0.804**	0.833**	0.984**	1.000													
Mg	0.127	0.830**	0.784**	0.788**	0.719**	1.000												
Na	0.092	0.889**	0.696**	0.543**	0.584**	0.620**	1.000											
K	0.273*	0.304	0.525**	0.331	0.487**	0.317	0.607**	1.000										
HCO_3	0.191	0.268	0.587**	0.552**	0.596**	0.573**	0.646**	0.677**	1.000									
Cl	0.221	0.824**	0.831**	0.524**	0.851**	0.603**	0.835**	0.810**	0.668**	1.000								
SO_4	0.207	0.858**	0.722**	0.218	0.771**	0.748**	0.833**	0.859**	0.613**	0.936**	1.000							
NO_3	0.146	0.171	0.782**	0.300	0.254	0.301	0.297	0.260	0.649**	0.901**	0.871**	1.000						
Pb	-0.228	-0.341	-0.328*	-0.205	-0.191	-0.322*	-0.414**	-0.197	-0.317*	-0.258*	-0.259*	-0.246	1.000					
Zn	0.144	-0.202	-0.217	-0.028	-0.204	-0.081	0.202	0.060	-0.049	-0.022	0.061	-0.005	-0.169	1.000				
Fe	0.197	0.146	0.137	0.169	0.076	0.195	-0.020	0.291*	0.173	0.158	0.173	0.059	-0.200	0.111	1.000			
Mn	-0.297*	-0.279	-0.299*	-0.302	-0.257*	-0.208	-0.154	-0.319*	-0.369**	-0.281*	-0.255*	-0.327*	0.072	0.075	-0.215	1.000		
As	0.176	0.080	0.083	0.150	0.238	0.018	0.180	0.024	0.085	0.157	0.157	0.126	-0.071	-0.190	-0.172	-0.080	1.000	
Cd	-0.290*	0.207	0.220	0.114	0.219	0.413**	0.330*	0.462**	0.431**	0.378**	0.377**	-0.378*	0.015	-0.107	-0.119	0.041	-0.006	1.000

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

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

Cluster Analysis and Hydrochemical Facies

The groundwater samples across the district were subjected to Q-mode hierarchicalcluster analysis (HCA) in order to know the spatial relationships in the groundwater parameters, the flow regimes and the flow paths.Three spatial groundwater relations were identified based on adendrogramgenerated using Ward`s method (**Fig.3**), with aphenon line drawn at a linkage distance of about 800 m.Cluster 1 (CA-1) suggests a fresh water type in the groundwater flow regime with a relatively low average pH of 6.58. The low pH is traceable to the reaction of CO_2 with precipitation which resulted in carbonic acid. CA-1 is consists mainly of samples from Amazu mission, Mkporomkpo, Ojiegbe, Over-rail and Amachi areas which are geographically within the same locality (**Fig. 2**) characterized by the shales and limestones. CA- 1 also presents a weakly mineralized groundwater, characterized by relatively lower levels of major ion concentration.

Cluster 3 (CA-3) and Cluster 2 (CA-2) show relatively moderate to high mineralization respectively, indicating a long residence time and a high groundwater-rock interaction as the water travels from recharge areas to discharge zones (Yidana et al. 2011; Freeze and Cherry 1979). CA-2 and CA-3 consist of samples mainly located around Agubata,Umuhali, Azuogbagu, Ofoke, Otere and OrahAmazu areas considered to have relatively medium to low elevations in the district.

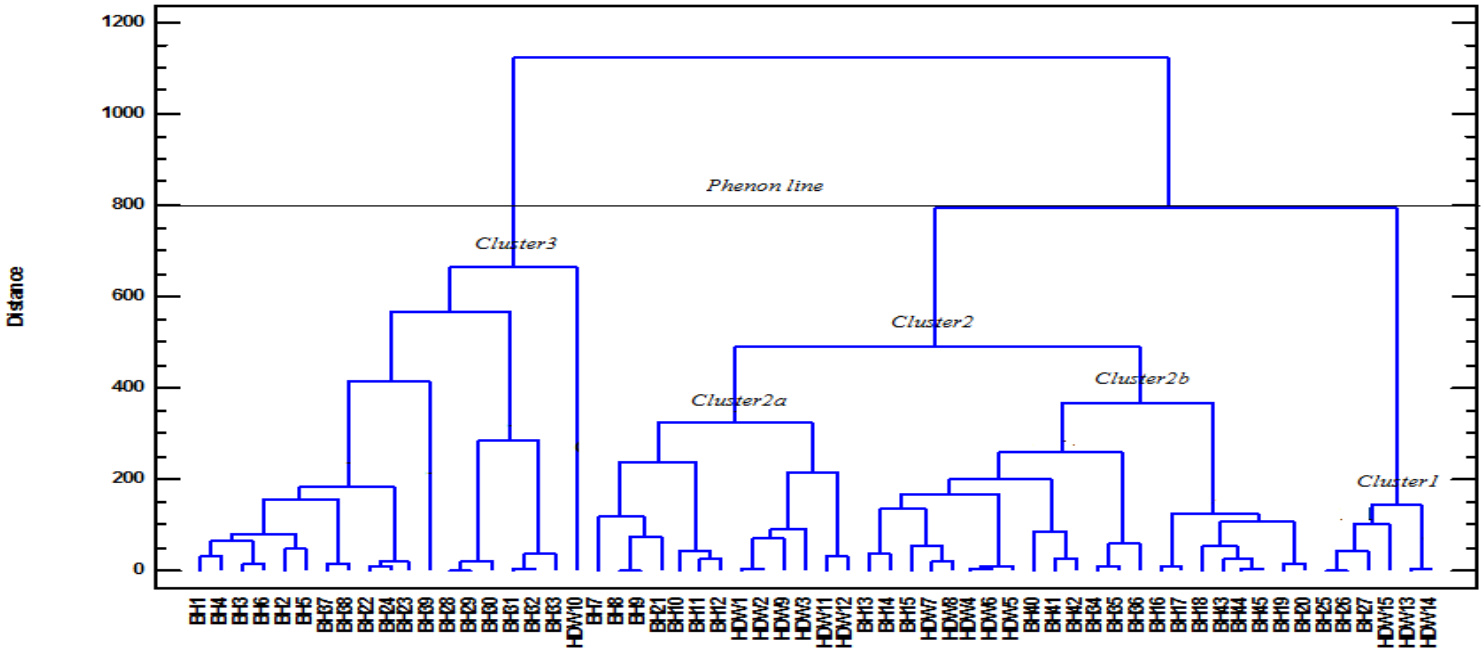

Fig.3 Dendrogram for groundwater spatial associations from Q-mode cluster analysis

Piper diagram(1944)was used to infer hydrochemical facies. Two hydrochemical facies were delineated from the Piper'sdiagram (**Fig.4**); Ca-Mg-Cl-SO_4 (field II) and Na-K-Cl-SO_4 (field III). Field II occupy 72 % of the groundwater samples in piper plot and this imply the dominance ofalkali metals over alkaline earth metals ($Na^+ + K^+ > Ca^{2+} + Mg^{2+}$). The remaining 18% of the groundwater samples fall within field III.None of the water samples fell within fields I and IV in the groundwater system, which signifies Mg-Ca-$HCO_3$and Na + $KHCO_3$, respectively.

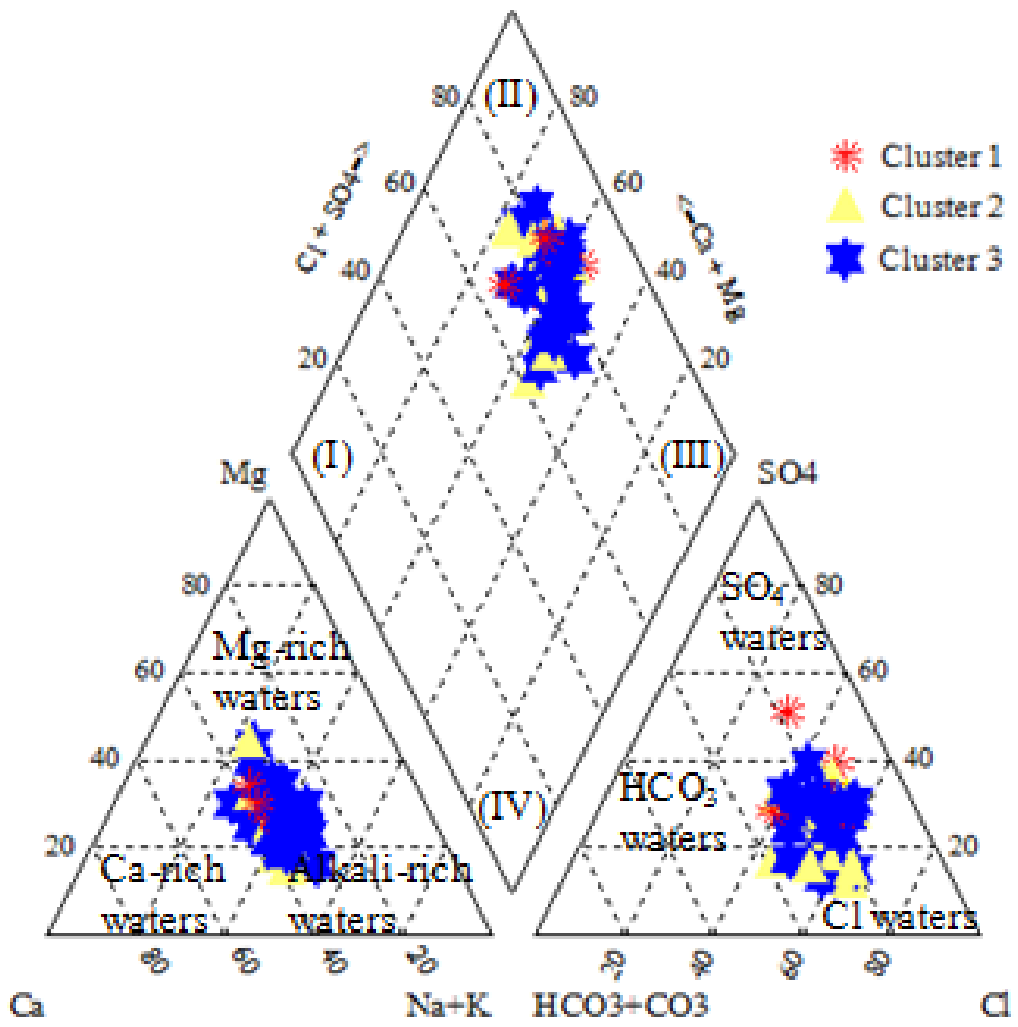

Fig.4 Piper's diagram showing major hydrochemical facies

Sources and factors controlling Groundwater Chemistry in the Study Area

Three principal components were identified in the district from principal component analysis(Table 3) that explained 65.15% of the total dataset. Extracted principal components show that Component 1 (PC1) accounts for the highest variance of about 47% and has high factor loadings with EC, TDS, TH, HCO_3^-, Cl^-, Mg^{2+}, Ca^{2+} and Na^+. According to Larry et al. (2020),such a high component loading of HCO_3^-, Cl^-, Mg^{2+}, Ca^{2+} and Na^+indicates a combined

set of factors influencing the groundwater chemistry such as chemical weathering processes and precipitation. Component 2 (PC2), on the other hand, represents about 9% of the total variation in the hydrochemistry and loads significantly with Zn^{2+}, Fe^{2+} and Pb^{2+} which suggests the influence of Zn-Pbmining activitiesfrom the district,while component 3 (PC3) accounts for the lowest variance of about 7% and has high negative loadings with SO_4^{2-} andNO_3^-. The high negative loading of SO_4^{2-} andNO_3^- with PC3 suggests the influence of domestic wastewater and agrochemicals from farming activities.

Gibbs (1970) reported that the presence of rock-water interaction in water could be identified using TDS vs. Na^+/ (Na^+ + Ca^{2+}) and TDS vs. Cl^-/ (Cl^- +HCO_3^-) scatter diagrams. The Gibbs diagrams (**Figs. 5a and b**) indicate that rock-water interaction is the dominant source of the chemical constituents of the water sources in the district. This implies that groundwater the chemistry is influenced by geology of the area. However, the distribution of samples show a slightly influences of evaporation.

To identify the sources of the groundwater, scatter plots of various major ions which readily dissolve or react with other ions in groundwater were plotted and explained below.

The plot of Ca^{2+}+Mg^{2+} versus SO_4^{2-}+$HCO_3^-$is used to determine the ion exchange processes that led to the release of these ions in solution (**Fig. 6a**). According to Larry et al, (2020), samples below the equiline might have resulted from the weathering of silicate minerals, whereas samples above the equiline could be from carbonate mineral weathering of gypsum, calcite, or dolomite (**Fig. 6a**). In such cases, carbonic acid from atmospheric reactions with water dissolves carbonate minerals which release Ca^{2+} and Mg^{2+} in solution. The high concentration of Ca^{2+}+Mg^{2+} relative to SO_4^{2-}+$HCO_3^-$is also attributable to reverse ion exchange, since the ratio is not exactly a 1 : 2.5 (Rajmohan and Elango, 2004).

Table 3 Component weights

Parameters	PC 1	PC 2	PC 3
pH	0.086682	0.065064	0.180228
Temp	-0.040645	0.116852	0.067441
EC	**0.388555**	-0.033428	0.190862
TDS	**0.390346**	-0.045979	0.203078
TH	**0.375793**	-0.009034	-0.021948
SO_4^{2-}	0.207910	-0.041048	**-0.490273**
NO_3^-	0.282798	-0.063584	**-0.353077**
HCO_3^-	**0.379242**	-0.037021	-0.099263
Cl^-	**0.361011**	0.067762	-0.259734
Mg^{2+}	**0.353983**	0.015141	-0.073637
Ca^{2+}	**0.381274**	-0.015665	-0.003940
Na^+	**0.395961**	0.023254	-0.085630
K^+	0.207026	-0.089523	-0.057792
Pb^{2+}	-0.118277	**0.419304**	0.0607845
Zn^{2+}	-0.017256	**0.381236**	-0.030230
Fe^{2+}	0.062777	**0.489032**	-0.125026
Mn^{3+}	-0.117607	-0.225404	-0.197939
As^{2+}	0.050280	-0.048609	0.276296
Cd^{2+}	0.135304	-0.271298-	-0.101844
Eigenvalue	9.11941	1.83648	1.42342
% variation	47.997	9.666	7.492
Cumulative % variation	47.997	57.663	65.155

Significant loading factors are in bold

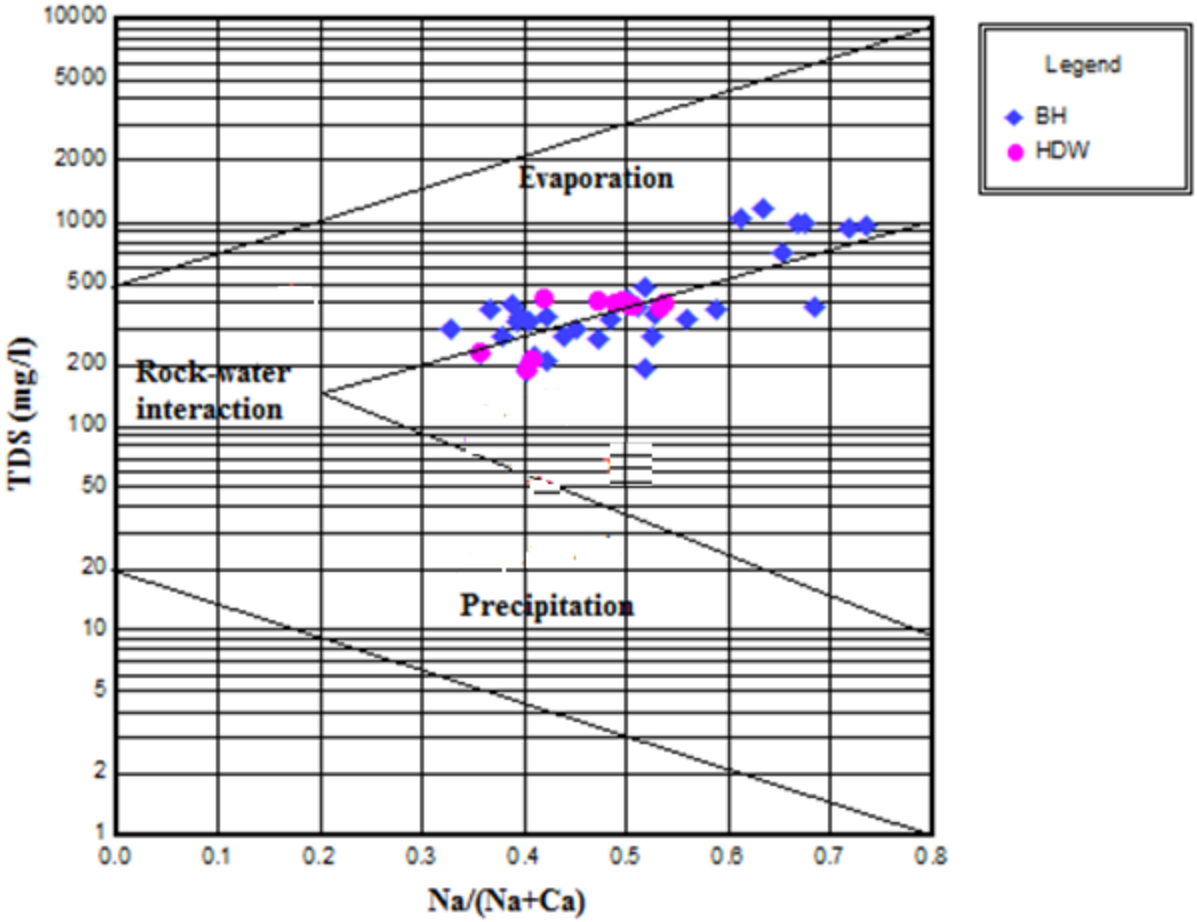

Fig.5a Gibbs diagram TDS vs. Na/(Na+Ca) showing the main sources of variation in groundwater chemistry in the district

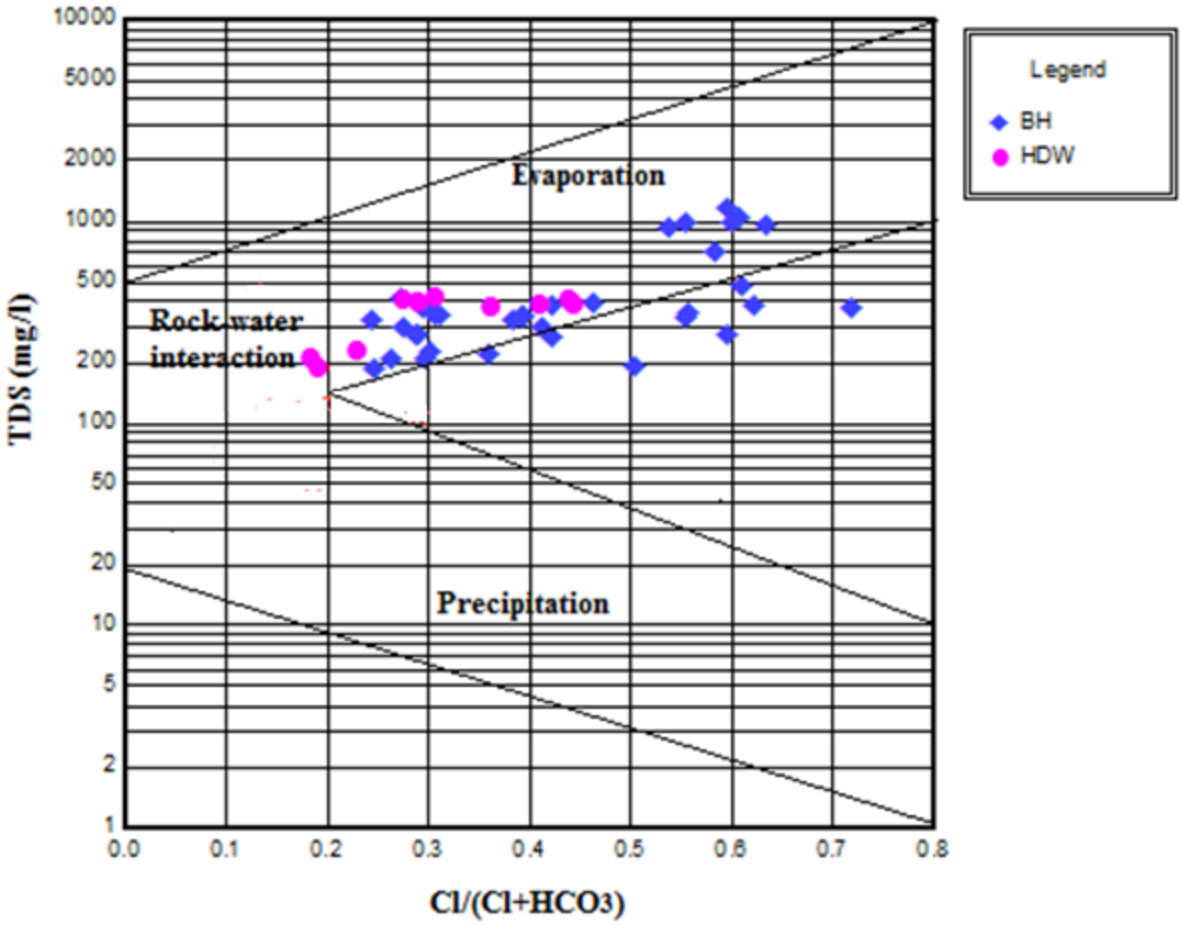

Fig. 5b Gibbs diagram TDS vs. Cl/(Cl+HCO_3) showing the main sources of variation in groundwater chemistry in the district

The plot of Ca^{2+}+Mg^{2+} versus HCO_3^- (**Fig. 6b**) was used to determined theorigin of calcium and magnesium. Sami (1992) indicated that a molar ratio value of $Ca2^{+}$+Mg^{2+}/HCO_3^- close to 0.5 suggests carbonate/silicate mineral weathering as the main source of Mg^{2+} and Ca^{2+} in groundwater, influenced mainly by carbonic acid. Some samples, however, fall below this 0.5 ratio which can be attributed to the depletion of HCO_3^- (Zaidi et al. 2015).The chemical processes in the study was further understood by plotting Ca^{2+} against Ca^{2+} + SO_4^{2-}(**Fig. 7a**) and Mg^{2+} against Ca^{2+} + Mg^{2+}(**Fig.7b**).

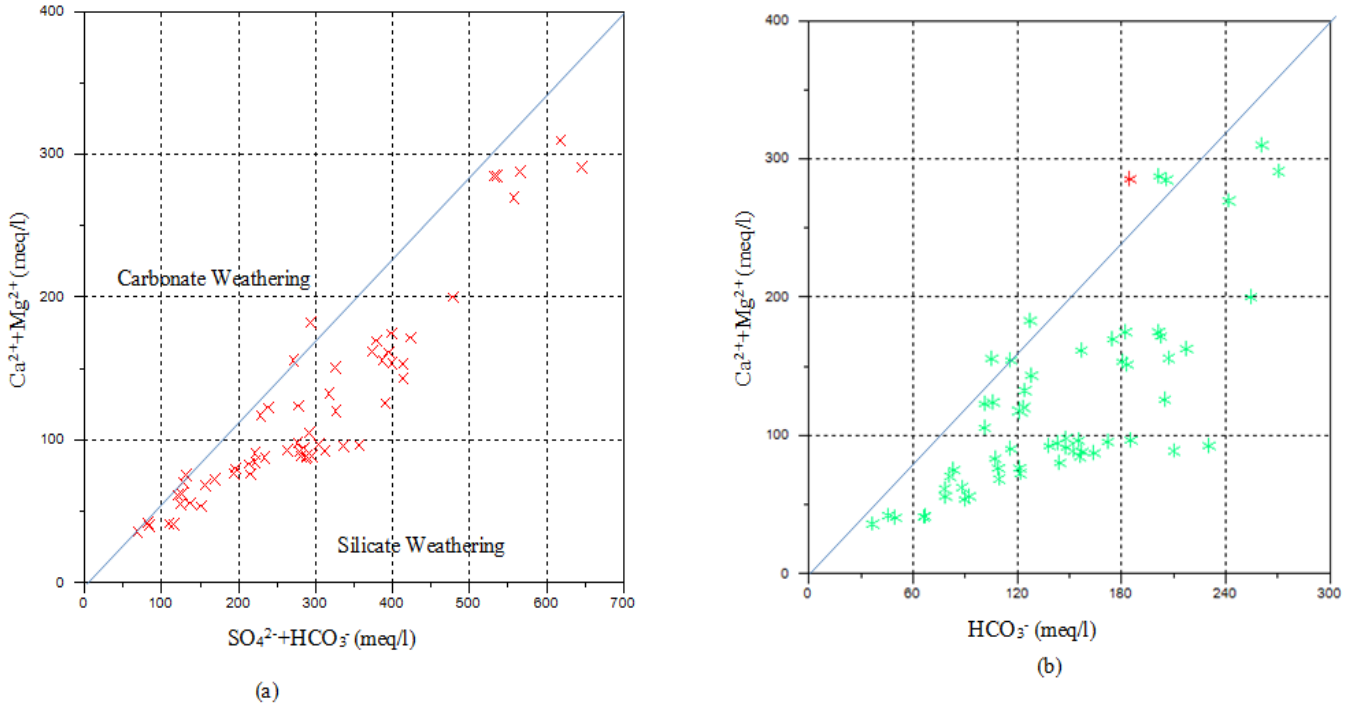

Fig.6 Plots of(a) Ca^{2+}+Mg^{2+} versus SO_4^{2-}+$HCO_3^-$and (b) Ca^{2+}+Mg^{2+} versus HCO_3^-showing the main sources of ions in groundwater chemistry

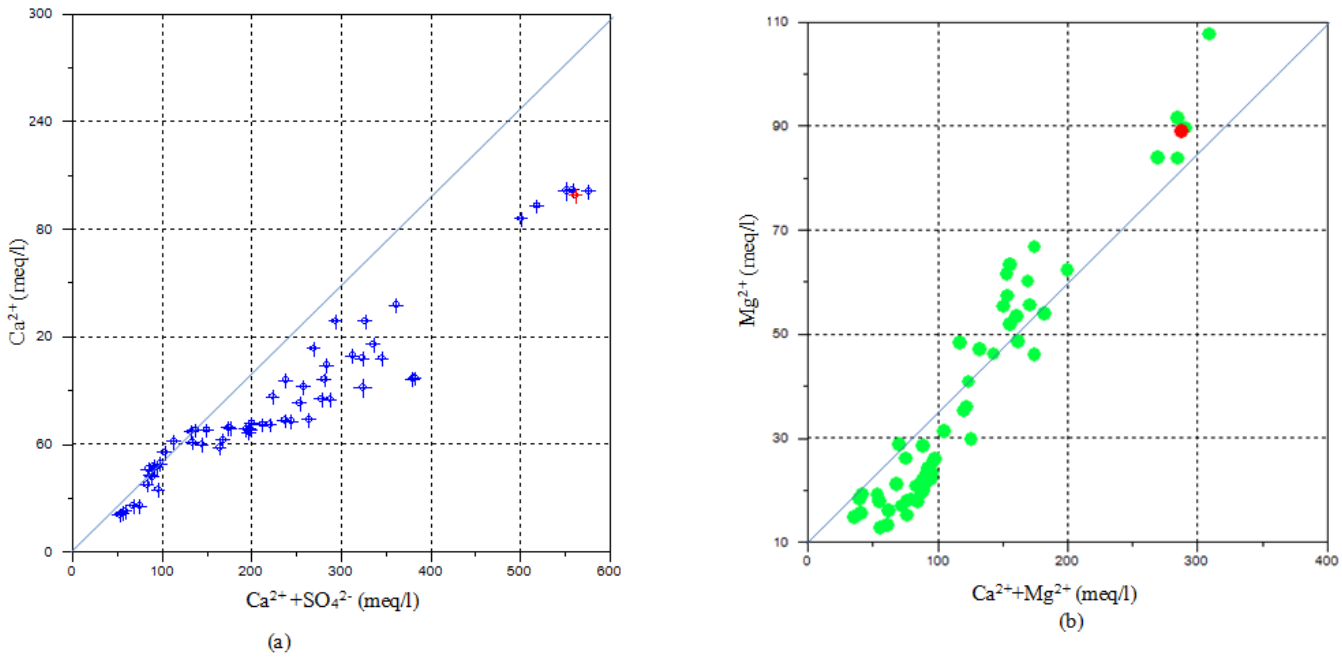

Fig. 7 Plot suggesting (a) gypsum weathering and (b) dolomite weathering

Groundwater Quality Assessment for DrinkingPurposes

The pH distribution in the district ranges from 5.28 to 8.04.ThepH values showed that about 15 % are below WHO (2017) recommended limitsfor drinking water purpose and These samples were noticed in the northern part of the study area (Ngbo, Ugboenyim, Nkalaha and New Jerusalem) that is underlain mainly bylimestone.This pH influence may be linked to the discharge of mine waters from active mines into adjoining streams and river channels in these areas. About85 % of the pH valuesare within WHO (2017) recommended limitsfor drinking water purpose and occur in Amachi, Mkporomkpo, Amazu mission, Ojiegbe and Over-rail inthe southwestern part of thedistrict.

TH values showed that 83.3 % are aboveWHO (2017)recommended limits for drinking water.TH in the area is generally> 200 mg/l except few groundwater samples (16.7 %) that had values <

200 mg/l. The high values in these locations can be attributed to the influence of bedrock geology and anthropogenic activities in these areas.

The water quality index (WQI) was used to determined part of the study area that is best for groundwater quality. From WQI (Table 4) suggested that 40 % of thegroundwater sampled in the district is of acceptable quality and 57%fell within poor category whereas the remaining 3%, which is just two samples, fell within the very poor category. The very poor water is a sample from New Jerusalem and Umuru, with high levels of Pb and NO_3^-.Groundwater around the north and south part (**Fig. 8**)of the district were noticed to be of the best quality for drinking purpose.

Table 4 Rating of water in the study area on the basis of WQI

WQI value*	Rating of water quality*	Grading*	Number of samples
< 50	Excellent water	A	2
50 – 100	Good water	B	22
101 – 200	Poor water	C	34
201 – 300	Very poor water	D	2
> 300	Unsuitable for drinking	E	-
	Total		60

*After Sahu and Sikdar (2008)

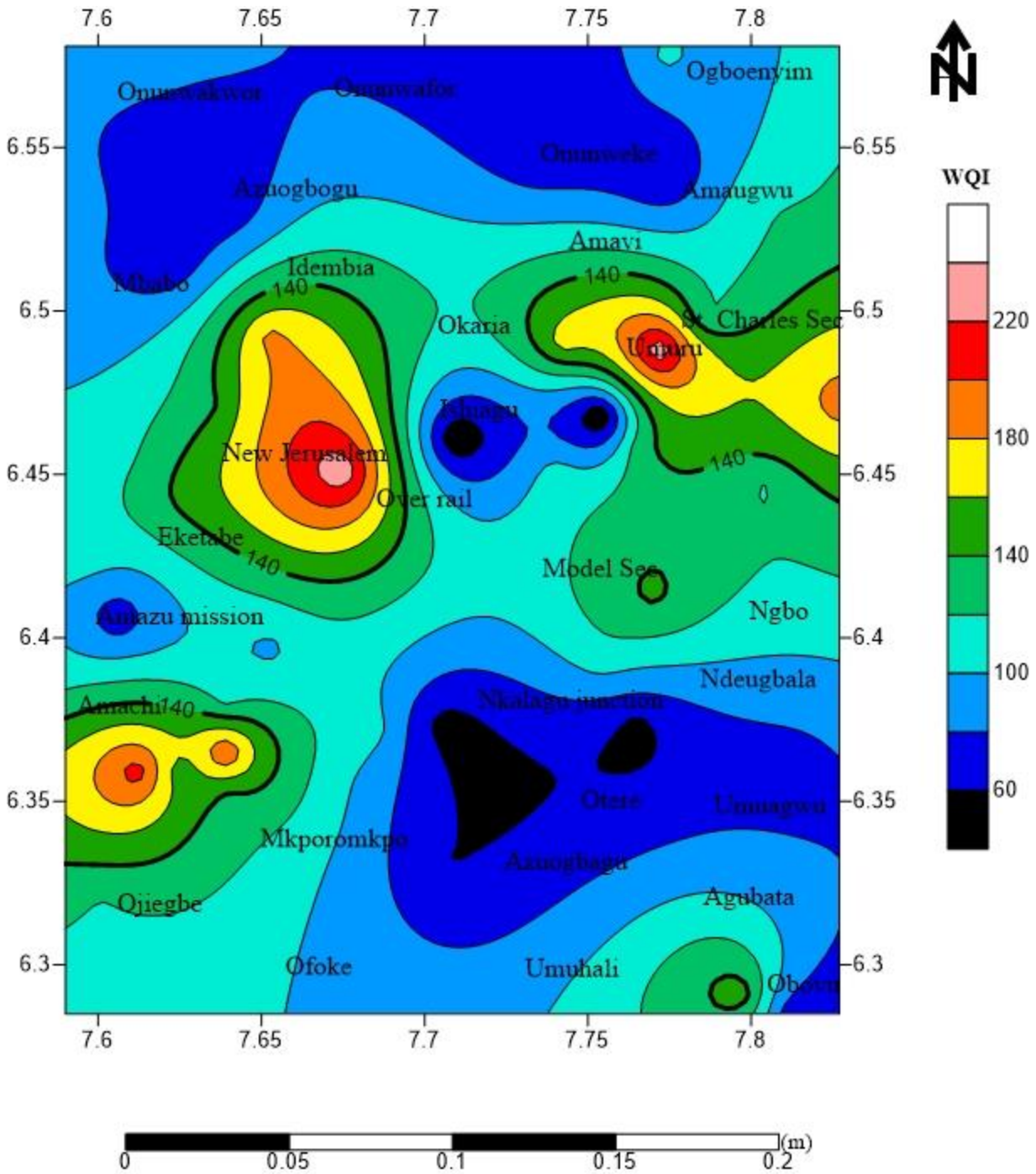

Fig.8 Spatial distribution map of WQI in the study area

IrrigationQuality Assessment

Irrigation water quality indices (USSL, 1954;Wilcox, 1955; SAR, Na %)were used to determinethe suitability of the groundwater of the area for irrigation purpose.

SAR values in the study area ranged from 3.38 to 25.20meq/l, this imply that not all groundwater samples are suitable for irrigation purpose. Classification of groundwater samples based on SAR (Table 5) shows that majority of the samples is suitable for irrigation purpose except 15 % samples that is within doubtful category.

Based on the USSL diagram classification 67 % of the groundwater samples in the district fell in (S1-C1), whereas 22 % (S1-C2) category and 11 % fell in (S3-C3)category (**Fig.9**). Therefore, 67 % of the groundwater samples that fell in (C1-C1) are of excellent quality for irrigation purpose and this can be used for irrigation without any hazard to the soil or crops in the district.The 11 % of the samples in the S3-C3 category in USSL diagram can also be used for irrigation, however, in a well-drained soil due to the high salinity hazard associated with this water type.

Table 5 Classification of irrigation water based on SAR values

*Range	*Classification	Number of samples	% of samples
< 10	Excellent	11	18
10 – 18	Good	40	67
18 – 26	Doubtful	9	15
> 26	Unsuitable	Nil	Nil
	Total	60	100

*Adapted from Richards (1954)

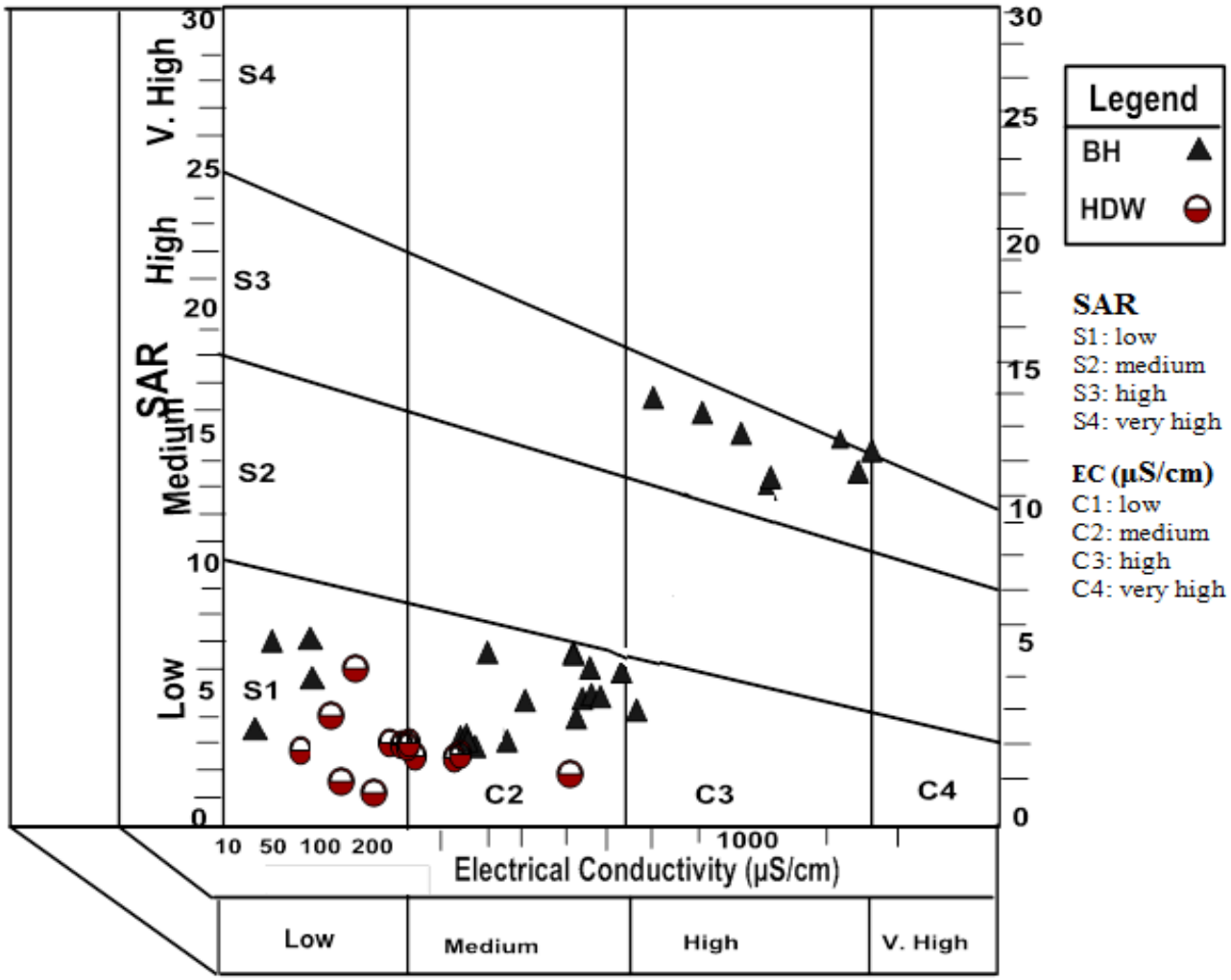

Fig.9 Groundwater quality classification in the district for irrigation (USSL 1954)

Considering the irrigation water quality rating based on Na %, Table 6 reveals that 96 % of groundwater samples fall within 'good to permissible' class, while 4 % of the samples fall within 'doubtful' class. Dissolution of minerals from lithological compositions and addition of chemical fertilizers are likely the major causes of high Na % in the district and can produces undesirable effects such as soil dispersion (Ajala et al. 2018).Using Wilcox (1955) diagram, 76% of the groundwater samples were noticed to be within the 'excellent to good' class, 12% of the

groundwater samples are within the ‘good to permissible’ class and 12% within ‘permissible to doubtful’ class (**Fig. 10**).

Table 6 Classification of irrigation water based on Na %

*Range	*Classification	Number of samples	% of samples
< 20	Excellent	Nil	Nil
20 – 40	Good	20	33
40 – 60	Permissible	38	63
60 – 80	Doubtful	2	4
	Unsuitable	60	100

*Adapted from Richards (1954)

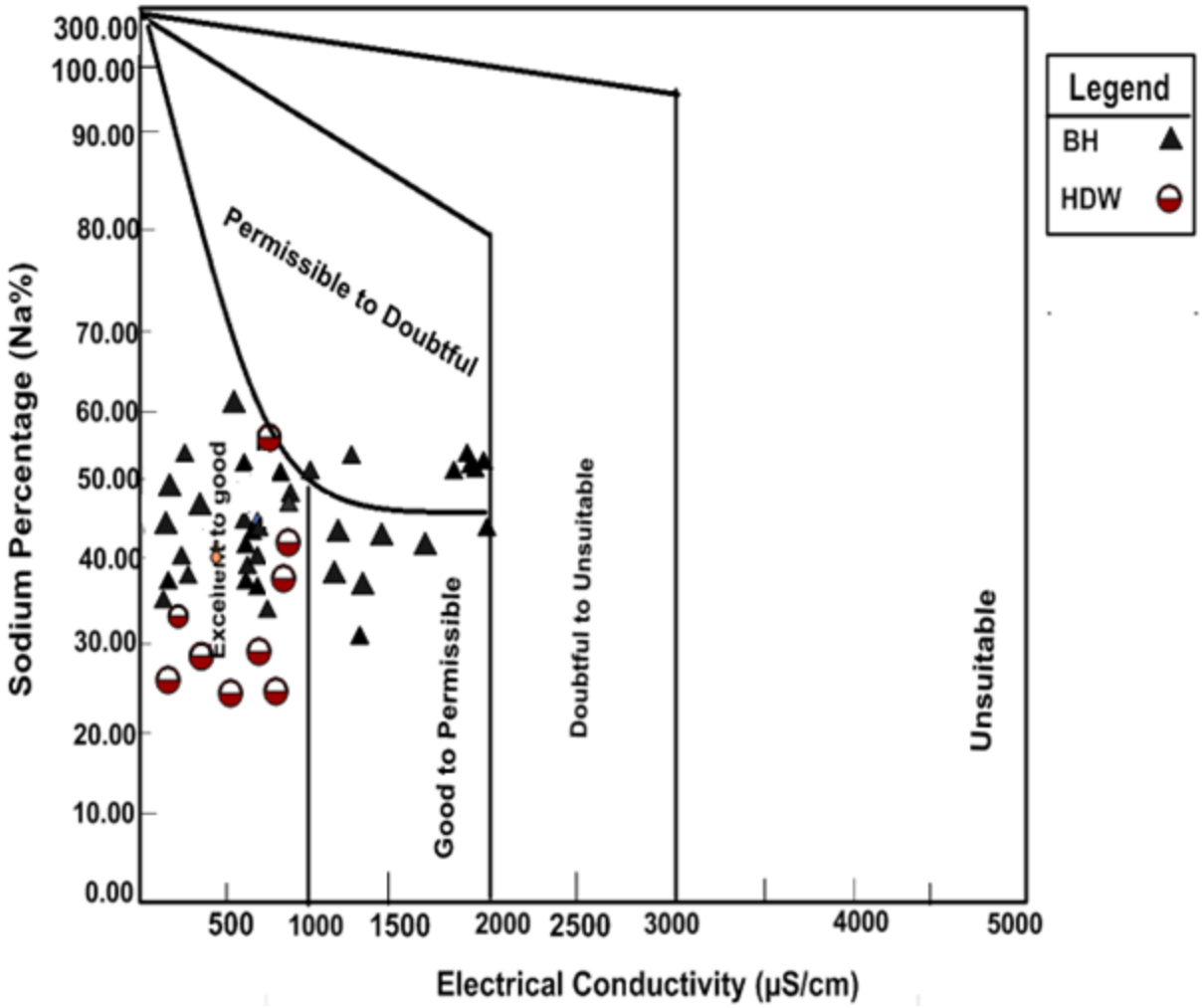

Fig. 10 Groundwater quality assessment using Wilcox (1955) diagram

Conclusion

Hydrochemical composition of groundwater quality inNkalagu District was used to assess the main factors controlling the groundwater chemistry and its suitability for drinking and irrigation purposes.The concentration of the major ions were in the order $Cl^{-}>HCO_3^{-}>SO_4^{2-}>NO_3^{-}$ and $Na>Ca^{2+}>Mg^{2+}>K^{+}$.The drinking water quality assessment shows that 15 % samples have pH values belowWHO (2017) recommended limits for drinking water purpose.This implies that

thegroundwater is slightly acidic in nature. 83.3 % of TH are above WHO (2017) recommended limits for drinking water except few samples (16.7 %) that is within the maximum permissible limit. WQI suggested that 40 % of the groundwater sampled in the district is of acceptable quality and 57% fell within poor category. Groundwater system in the north and south part of the district were noticed to be of the best quality for drinking purpose. Assessment of groundwater quality for irrigation purpose based on SAR shows that majority of the samples is suitable for irrigation purpose except 15 % samples that is within doubtful category.Generally, groundwater samples in the district are of excellent quality for both drinking and irrigation purposes except in few areas where treatment is required before use.

Q-mode cluster analysis identified three spatial groundwater flow regimesbased on adendrogramdiagram Ward`s method. Two hydrochemical facies were delineated from the Piper's diagram; (Ca-Mg-Cl-SO_4 (field II) and Na-K-Cl-SO_4 (field III) in the area that show the dominance of alkali metals over alkaline earth metals. Three principal components were identified in the district from principal component analysisthat explained 65.15% of the total dataset. The Gibbs diagram indicates that rock-water interaction is the dominant source of the chemical constituents of the water sources in the district. To preserve water resource for future use in the district, we recommend implementation rules and guidelines in the area to enhance health and preserve groundwater sources in the district.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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