## **Original Research Article**

# Hydrochemical Characterization of Groundwater Quality in the Nkalagu District of Southeastern Nigeria, Using Statistical Tools

## Abstract

A comprehensive groundwater quality assessment in the Nkalagu District of southeastern Nigeria was carried to determine the main factors controlling the chemistry of the 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 is in the order  $Cl^{>}HCO_3^{-}>SO_4^{-}>NO_3^{-}$  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 results were further subjected to water quality index (WQI) and multivariate analysis. The results also show that the groundwater of the district is mainly controlled by carbonate and silicate mineral weathering. Three main flow regimes were identified with Q-mode cluster analysis. Based on the WQI analysis results, the groundwater quality in the district was classified as generally 'poor' to 'excellent' for drinking purpose. Generally, the quality of groundwater for drinking purpose deteriorates as one move from west towards the east of the district, whereas water in the north and south indicate the best quality in the district. The groundwater of the district also show excellent quality for irrigation purpose based on the United States Salinity Laboratory and Wilcox diagrams. Implementation of stringent rules and guidelines are recommended to enhance health and preserve groundwater sources in the district for future generations.

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

#### Introduction

Groundwater generally plays a vital role in meeting the water supply needs for various human activities. The quality of groundwater is very essential for evaluating its use for domestic, irrigation and industrial purposes (Bhuiyan et al. 2016). 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 gcroundwater quality and usage in various parts of the area. These factors could be in form of geogenic processes or anthropogenic activities and are known to influence the quality of a water supply sources. Anthropogenic activities have been identified in the literature as major sources of groundwater degradation (Anku et al. 2009; Eneke 2011; Selvakumar et al. 2017; Sunkari et al. 2019). Therefore, it is necessary to holistically assess the parameters that affect the quality of groundwater as well as identify the sources of these contaminants as a means of sustainable management of the resource in accordance with Balkhair and Ashraf 2016 and Rather et al. 2017. Integration of geostatistical and conventional hydrochemical plots had provided powerful tools for determining the main factors controlling the hydrochemistry of groundwater and assessing groundwater quality for drinking and irrigation

purposes in Nigeria and other parts of the world (Onwuka et al. 2013, Omonona et al. 2014, Ravikumar et al. 2015, Islam et al. 2018).

Shihab and AbdulBaqi (2010) used principal component analysis (PCA) and cluster analysis (CA) to characterize groundwater quality in Makhmor Plain, 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 of northcentral 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 characterize groundwater quality for drinking and irrigation purposes. The main factors controlling the hydrochemistry of groundwater in the Nkalagu district of southeastern Nigeria were also evaluated. The findings of the study provide more insights into the impact of geogenic and anthropogenic factors in groundwater quality and its management.

## **Study Area**

## Location, Topography, and Climate

Nkalagu lies within the boundaries of latitudes 6°10′ and 6°40′N and longitudes 7°35′ and 7°50′E in the southeastern geopolitical zone of Nigeria on the scale of 1:100,000 (**Fig. 1**). It shares boundaries with Enugu Municipal to the north and east, it has a total land area of about 550 km<sup>2</sup>. Majority of the inhabitants ( $\geq$  90%) in the district are peasant farmers. Small-scale mining, artisanal stone crushing, agro-processing, charcoal burning, firewood harvesting, and irrigation farming constitute the other sources of income of the inhabitants of the district.

The topography of the district is generally flat with relatively undulating lowlands, with gentle slopes ranging between 3 % and 7 %. Elevations range between 60 m and 105 m. According to Ezeh and Anike (2009) several rivers and tributaries are drained in the district during the rainy season, however, during the dry season, most of the tributaries dry up leaving only portions of the Iyioke and Uzuru Rivers flowing through the eastern and southern boundaries. 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.

The district is characterized by semiarid conditions with a rainy season that runs from May to October. The rest of the months of the year are characteristically dry, with barely any rains. Recent annual rainfall records (2009 – 2018) from the Climatological department (FARM Unit, EBSU, 2017), suggest yearly rainfall that ranges between 503 and 997 mm, with an annual average of 837mm.



Fig. 1 Location and Accessibility map of the study area

## **Geology and Hydrogeology**

A large portion of the district (about 85%) is underlain by limestone. Over 174 million tonnes of limestone exist in the area, within the Turonian, Eze Aku Formation (Fatoye and Gideon 2013). The Eze-Aku Formation is unconformably underlain by the Albian Asu River Group in the area. 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  $6^{\circ}$  -  $8^{\circ}$  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**

#### Sampling

A total of 60 groundwater samples comprising 45 boreholes and 15 hand-dug wells were collected with depth ranging between depths of 10 and 55 m in the month of March, 2019, when water resources in the district are 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 areas. American Public Health Association (APHA 2012) standard protocols for water sampling and storage for various purposes were

adopted throughout the study. During sampling, boreholes were first purged for about five to ten minutes to rid them of stagnant waters before sampling was done. Physical parameters such as pH, Electrical Conductivity (EC), Total Dissolved Solids (TDSs), and temperature were measured immediately in each location at the point of collection using field probes, due to their transient characteristics. The groundwater samples were filtered through a 0.45  $\mu$ m cellulose acetate membrane and collected in 250 ml sterilized low density polyethylene bottles in two sets: 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, 2005) standard.

## Laboratory Testing

Groundwater samples were analyzed for physicochemical parameters such as pH, electrical conductivity (EC), calcium ( $Ca^{2+}$ ), magnesium ( $Mg^{2+}$ ), sodium ( $Na^{+}$ ), potassium ( $K^{+}$ ), sulphate ( $SO_4^{2^{-}}$ ), chloride ( $Cl^{-}$ ), bicarbonate ( $HCO_3^{-}$ ), nitrate ( $NO_3^{-}$ ) and Total Dissolved Solid (TDS) and heavy metals in the Chemical Research Laboratory, Abakaliki, Nigeria. Physical parameter such as pH was measured using pH model metre, while EC and TDS were measured using Wissenschaftlich Technische Werkstatten Conductivity (WTWC) metre.

Bicarbonate (HCO<sub>3</sub><sup>-</sup>), calcium (Ca<sup>2+</sup>), and total hardness (TH) were determined by titrimetric methods. Atomic absorption spectroscopy (AAS) was used to determine the cations and heavy metals. Anions such as Cl<sup>-</sup>,  $SO_4^{2-}$  and  $NO_3^{-}$  were analyzed using the HACH DR/2010 spectrophotometer.

## **Charge Balance Error (CBE)**

CBE was evaluated to check the accuracy of the dataset analyzed (Eq. 1). A charge balance error value of  $<\pm5\%$  and below is generally acceptable and show that the analysis of the parameters are a good balance of the cations and anions (Singh and Hassin, 2002).

$$CBR = \frac{Sum of cations - Sum of anions}{Sum of cations + Sum of anions} \times 100$$

Where cations include Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> and anions include Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> are expressed in meq/l and inserted with charge sign.

#### **Statistical Tools**

Descriptive statistics, cluster analysis (CA), principal component analysis (PCA) and Pearson correlation were employed in characterizing the groundwater quality of the district. Datasets that were not normally distributed were standardized to their *z*-score values before they were statistically analyzed (Eq. 2):

$$z = \frac{\chi - \mu}{s}$$

Where z is the score, x is sample value,  $\mu$  is mean and s is the standard deviation.

Q-mode hierarchical cluster analyses (HCAs) were performed using the transformed dataset. The squared Euclidean distance and Ward's agglomeration method was employed in this study following guidelines provided in Aljumily (2016) and Yidana (et al. 2010), although several similarity/dissimilarity and agglomerative techniques are available in HCAs. 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 datasets.

## Water quality index (WQI) and Facies determination

The water quality index (WQI) determination procedure described in previous works by (Benvenuti et al. 2015; Fathi et al. 2018; Kumar et al. 2014; Ravikumar et al. 2015; Samlafo and Ofoe 2018) was adopted in this study. Parameters such as  $NO_3^-$  and TDS which are considered to be of critical health importance and significant impact of the quality of groundwater were assigned the maximum value of 5 while other parameters (pH, EC, TDS, TH, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, Fe<sup>2+</sup>, Cd<sup>2+</sup>, As<sup>3+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup>) were assigned values of 1 to 4 (Table 1), as recommended by Larry et al. (2020). This method also involves the computation of relative weights (Wi) (Eq. 3) and quality rating scale (qi) (Eq. 4) and determination of the subindex (SI) (Eq. 5) and water quality index (WQI) (Eq. 6). The computed WQIs were then classified according to Sahu and Sikdar (2008).

Wi = 
$$\frac{wi}{\sum wi}$$
 3  
qi = [(V<sub>n</sub> - V<sub>id</sub>) / (S<sub>n</sub> - V<sub>id</sub>)] x 100 4

Where,  $V_n$  = Estimated value of n<sup>th</sup> water quality parameter at a given sample location.

 $V_{id}$  = Ideal value for n<sup>th</sup> parameter in pure water.

(According to Sahu and Sikdar (2008) Vid for pH = 7 and 0 for all other parameters)

4

 $S_n$  = Standard permissible value of n<sup>th</sup> water quality parameter. ( $S_n$  = 8.5)

$$SI = Wi x qi$$
 5

$$WQI = \sum_{n=1}^{n} SI$$
 6

Classification plots such as Piper (1944) was used in conjunction with the geostatistical techniques to characterize and classify groundwater quality in the district for drinking purpose.

## Groundwater quality for irrigation purpose

Groundwater quality for irrigation purpose in this study was assessed using Wilcox (1955), United States Salinity Laboratory (1954) and sodium-based techniques, which compare the concentration of Na<sup>+</sup> to other ions. Relatively high levels of Na<sup>+</sup> as compared to other cations such as  $Mg^{2+}$  and  $Ca^{2+}$  tend to reduce soil permeability which results in poor soil structure for drainage (Ta'any et al. 2013; Yidana et al. 2011) since, through ion exchange, Na<sup>+</sup> tends to get absorbed to surfaces of clay materials and displace  $Ca^{2+}$  and  $Mg^{2+}$  in solution. The sodium adsorption ratio (SAR) is one of the methods used for irrigation water quality assessment. This index measures the relative content of sodium to the sum of calcium and magnesium in water used for irrigation (Eq. 7) whereas EC is used as a yardstick to measure the salinity of the water.

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}}$$

All concentrations of ions are in meq/l

Similarly, the Wilcox (1955) diagram was also used to assess the quality of groundwater for irrigation purposes, by plotting the percent of sodium in the water versus salinity.

The percent of sodium is calculated as a fraction of the concentration of the total major cations in the water (Eq. 8). The Wilcox diagram and the United State Salinity Laboratory (USSL) diagram

were used to categorize irrigation water into various suitability ranges based on sodium and salinity hazards.

$$Na\% = \frac{Na+K}{Ca+Mg+Na+K} \times 100$$

All concentrations of ions are in meq/l

Table 1 S	tandards, weights, and relative	weights used for WQI	computation	
S/No	Chemical Parameters	Weight <i>w</i> <sub>i</sub>	Relative weight <i>W<sub>i</sub></i>	limits values
1	pH	4	0.0678	6.6 - 8.5
2	EC	4	0.0678	1400
3	TDS	5	0.0847	500
4	TH	2	0.0339	200
5	HCO <sub>3</sub>	3	0.0508	120
6	Cl	3	0.0508	250
7	$SO_4$	4	0.0678	250
8	NO <sub>3</sub>	5	0.0847	50
9	Ca	2	0.0339	75
10	Mg	2	0.0339	30
11	Na	3	0.0508	200
12	К	1	0.0169	12
13	Zn	1	0.0169	3
14	Fe	4	0.0678	0.3
15	Mn	4	0.0678	0.5
16	Pb	4	0.0678	0.01
17	As	4	0.0678	0.01
18	Cd	4	0.0678	0.003
		$\sum w_i = 59$	$\sum W_i = 1$	

## 4. Results and Discussion

## Physiochemical and Hydrochemical Data

Table 2 is the summarized result for physiochemical parameters and heavy metal concentration with percentage measures above WHO water limits.

pH in the district ranges from 5.28 - 8.04 with an average of 6.86 pH units and a standard deviation of 0.59 (Table 2). This reveals that the groundwater system in the study area is acidic to slightly alkaline in nature. pH is known to influence the dissolution of minerals in a groundwater system as well as affect the quality of water for various purposes (Larry et al. 2020).

EC ranges from 430 to 3996  $\mu$ S/cm, with an average value of 1707.53  $\mu$ S/cm and standard deviation of 934.69 (Table 2). This wide range in EC values revealed the high diversity in the geochemical processes that shape the chemistry of the groundwater of the area. TDS ranges from 202 to 1879 mg/l, with an average of 838.42 mg/l and standard deviation of 440.63. Generally, about 43.3 % and 28.3 % of EC and TDS values respectively fall within the WHO (2017) recommended standard of 2500  $\mu$ S/cm and 1000 mg/l, respectively, for drinking water purpose. The values of total hardness (TH) ranged from 112.88 to 467.78 mg/l, with an average of 258.42 mg/l and standard deviation of 74.94. Based on the TH, groundwater of the area ranged from moderately hard water to very hard water.

Parameters	WHO (2017)	Minimum	Maximum value	Mean	Standard	% above limit
	limit	value		value	deviation	
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 <sub>4</sub> <sup>2-</sup> (mg/l)	250	31.56	225.57	111.53	56.40	13.3
NO <sub>3</sub> <sup>-</sup> (mg/l)	50	10.50	42.31	24.00	9.27	33.3
HCO <sub>3</sub> <sup>-</sup> (mg/l)	120	36.47	254.10	144.93	53.61	65.0
Cl <sup>-</sup> (mg/l)	250	57.12	314.00	156.00	47.41	28.3
Ca <sup>2+</sup> (mg/l)	75	20.80	117.56	65.84	21.98	41.7
Mg <sup>2+</sup> (mg/l)	30	12.73	42.34	22.85	6.26	43.3
Na <sup>+</sup> (mg/l)	200	16.46	154.00	84.83	32.29	11.7
K <sup>+</sup> (mg/l)	10	3.29	20.54	10.32	3.67	61.7
Pb <sup>2+</sup> (mg/l)	0.01	<0.01	0.09	0.03	0.03	65.0
Zn <sup>2+</sup> (mg/l)	3	<3.00	2.68	0.60	0.66	Nil
Mn <sup>2+</sup> (mg/l)	0.5	<0.5	1.22	0.23	0.29	28.3
As <sup>3+</sup> (mg/l)	0.01	< 0.01	0.07	0.02	0.06	20.0
Cd <sup>2+</sup> (mg/l)	0.003	< 0.003	0.010	0.010	0.013	30.0
Fe <sup>2+</sup> (mg/l)	0.3	0.01	5.52	1.19	1.75	66.7

Table 2 Summarized result with percentage measures above limits in groundwater samples analyzed (n = 60)

The calculated charge balance error (CBE) between the sum of cations and sum of anions was 1.91 %, and is within the acceptable limits of  $< \pm 5$  %. This thus confirms the reliability of the analytical results (Singh and Hassin, 2002). The abundance of the major ions in the groundwater samples in decreasing order is CI<sup>></sup>HCO<sub>3</sub><sup>-</sup>>SO<sub>4</sub><sup>2</sup>>NO<sub>3</sub><sup>-</sup> and Na>Ca<sup>2+</sup>>Mg<sup>2+</sup>>K<sup>+</sup>. CI<sup>-</sup>is the most dominant ion with the average CI<sup>-</sup>concentration accounts for about 25.15 % of the total major ions, while K<sup>+</sup> accounts for only 1.67 % of the total major ions expressed in the equivalent units. 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 processes control the parameters in the district.

## Main Controls on Groundwater Chemistry

Pearson's correlation coefficients ( $r^2$ ) of various analyzed parameters were calculated as a basis for making certain inferences and drawing relationships among parameters and, to a large extent, predicting values of other parameters. Variables with  $r^2$  values that are significantly related at 0.01 and 0.05 levels are written with asterisks. Mishra et al. (2003) reported that ionic pairs that are statistically related at 0.01 and 0.05 levels are thought to be released from the same sources or through same geochemical processes. Table 3 provides a quick way to identify trends within the groundwater quality parameters. The dataset shows that the EC exhibits a significant positive correlation with TDS, TH, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The  $r^2$  value 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<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> with relative positive  $r^2$  values 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  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $CI^-$  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. Similarly, the dataset also shows that the total hardness (TH) exhibits a significant positive correlation with  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $HCO_3^-$  and CI. This inferred that Calcium and magnesium appear to be the main contributors to TH.

	pН	EC	TDS	TH	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	$SO_4$	NO <sub>3</sub>	Pb	Zn	Fe	Mn	As	Cd
pН	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											
К	0.273*	0.304	0.525**	0.331	0.487**	0.317	0.607**	1.000										
HCO <sub>3</sub>	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 <sub>3</sub>	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

Table 3 Pearson's correlation matrix between water quality parameters

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

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

#### **Hierarchical Cluster Analysis and Hydrochemical Facies**

The groundwater samples from across the district (selected 60 samples) were subjected to Qmode hierarchical cluster analysis (HCA) in order to unveil the spatial relationships in the groundwater parameters, the flow regimes in the district and the flow paths as it moves from recharge to discharge zones. Three main spatial groundwater relations were identified based on a dendrogram generated using Ward's method (see **Fig. 3**), with a phenon line drawn at a linkage distance of about 800 in Q-mode cluster analysis. 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 (see **Fig. 2**) characterized by the shales and limestones. The first group (CA- 1) also presents a weakly mineralized groundwater, characterized by relatively lower levels of major ion concentration.

The CA-1 illustrated a conducive environment for rock mineral weathering, specifically, the majority is silicate minerals and the minority is carbonate minerals that characterized the geology of the district, which releases ions such as  $Na^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  in solution.

Cluster 3 (CA-3) and Cluster 2 (CA-2) show relatively moderate to high mineralization respectively, suggesting a longer residence time and a higher 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 Orah Amazu areas considered to have relatively medium to low elevations in the district and are therefore characterized accordingly as discharge zones (Freeze and Cherry 1979).



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

The hydrochemistry of the district is characterized further by constructing Piper's (1944) diagram. From the Piper's diagram (see **Fig. 4**), it is apparent that most of the groundwater samples (72%) are dominated by Ca-Mg-Cl-SO<sub>4</sub> (field II), implying the dominance of alkali metals over alkaline earth metals (Na<sup>+</sup> + K<sup>+</sup> > Ca<sup>2+</sup> + Mg<sup>2+</sup>). The remaining 18% of the water samples fall within field III which represents Na-K-Cl-SO<sub>4</sub> water type, also signifying the dominance of alkali over alkaline earth. None of the water samples fell within fields I and IV in the groundwater system, which signifies Mg-Ca-HCO<sub>3</sub> and Na + KHCO<sub>3</sub>, respectively. Cluster 3 samples appears to be more enriched in Mg and Ca than Clusters 1 and 2 samples, hence, the main contributors to the Ca-Mg-Cl-SO<sub>4</sub> water type identified in the groundwater system of the district. Samples from CA-1 and CA-2, on the other hand, drift more closely to a Na<sup>+</sup>+K<sup>+</sup>

enrichment, with CA-2 being even more so, and therefore, the main contributor to the Na-K-Cl- $SO_4$  hydrochemical facies observed in the Piper's diagram (**Fig. 4**).



Fig. 4 Piper's diagram showing major hydrochemical facies

## Sources and factors controlling Groundwater Chemistry in the Study Area

Table 4 summarizes the results of the three main principal component loadings for the hydrochemistry of the district that explained 65.15% of the total dataset. The extracted factor

loadings (Table 4) 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<sup>-</sup>,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Na^+$ . According to Larry et al. (2020), such a high component loading of  $HCO_3^-$ , Cl<sup>-</sup>,  $Mg^{2+}$ ,  $Ca^{2+}$  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-Pb mining activities from the district, while component 3 (PC3) accounts for the lowest variance of about 7% and has high negative loadings with  $SO_4^{2-}$  and  $NO_3^-$ . The high negative loading of  $SO_4^{2-}$  and  $NO_3^-$  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.  $CI/(CI^- + HCO_3^-)$  scatter diagrams. The Gibbs diagrams (see **Figs. 5a and b**) indicate that rock-water interaction is the dominant source of the chemical constituents of the water sources in the district compared to other sources such as precipitation and evaporation. This indicates that the chemistry of the groundwater samples is influenced by geology. However, the distribution of samples show a slightly influences of evaporation. This is an indication that the weathering of the host rocks and evaporation are the primary factors that control the hydrochemistry of the water in the district. This is primarily due to the inadequate precipitation in the area, which has increased the intensity of evaporation.

To gain further understanding of the origin of the groundwater, scatter plots of the major ions which readily dissolve or react with other ions in groundwater, were plotted. Hwang et al. (2017) noted that major cations of groundwater type are usually dominated by  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Na^+$ ,

which are thought to be associated with the weathering and dissolution of minerals such as silicate, carbonate, and sulphate minerals and many more as showed in Equations 9 to 13.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
 (carbonic acid) (9)

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$
 (calcite dissolution) (10)

 $CaMg(CO_3)_2$  (dolomite) +  $2H_2CO_3 \rightleftharpoons Ca^{2+} + Mg^{2+} + 4HCO_3^{-}$ (dolomite dissolution) (11)

$$H_2O + CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 3H_2O$$
 gypsum dissolution (12)

$$2NaAl_2Si_3O_8$$
 (albite) +  $2H_2CO_3$  +  $9H_2O \rightleftharpoons Al^2Si^2O_5$  (OH)<sub>4</sub> (Kaolinite) +  $2Na^+$  +  $4H_4SiO_4$ 

$$+ 2HCO_3^{-1}$$
 (Silicate weathering) (13)

A plot of  $Ca^{2+}+Mg^{2+}$  versus  $SO_4^{2-}+HCO_3^-$  gives more insight into the weathering 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 (Eqs. 9 to 11). 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 4	Component	weights
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Parameters	PC 1	PC 2	PC 3
рН	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 <sub>4</sub> <sup>2-</sup>	0.207910	-0.041048	-0.490273
NO <sub>3</sub> <sup>-</sup>	0.282798	-0.063584	-0.353077
HCO <sub>3</sub>	0.379242	-0.037021	-0.099263
Cl	0.361011	0.067762	-0.259734
$\mathrm{Mg}^{2+}$	0.353983	0.015141	-0.073637
Ca <sup>2+</sup>	0.381274	-0.015665	-0.003940
$Na^+$	0.395961	0.023254	-0.085630
$\mathbf{K}^{+}$	0.207026	-0.089523	-0.057792
$Pb^{2+}$	-0.118277	0.419304	0.0607845
Zn <sup>2+</sup>	-0.017256	0.381236	-0.030230
Fe <sup>2+</sup>	0.062777	0.489032	-0.125026
Mn <sup>3+</sup>	-0.117607	-0.225404	-0.197939
As <sup>2+</sup>	0.050280	-0.048609	0.276296
$\mathrm{Cd}^{2+}$	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<sub>3</sub>) showing the main sources of variation in groundwater chemistry in the district

The origin of calcium and magnesium could also be understood by the plot of  $Ca^{2+}+Mg^{2+}$  versus  $HCO_3^-$  (**Fig. 6b**). 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 Drinking Purposes**

Chemical parameters with critical health implications were examined to ascertain the groundwater suitability for drinking purpose in the district. pH distribution in the district ranges from 5.28 to 8.04. The pH values showed that about 15 % are below WHO (2017) recommended limits for drinking water purpose and occur in and around Ngbo, Ugboenyim, Nkalaha and New Jerusalem in the northeastern portions of the district, underlain mainly by limestone. This can be attributed to the discharge of mine waters from active mines into adjoining streams and river channels in these areas. Abour 85 % of the pH values are within WHO (2017) recommended limits for drinking water purpose and occur in Amachi, Mkporomkpo, Amazu mission, Ojiegbe and Over-rail in the southwestern part of the district.

TH values showed that 83.3 % are above WHO (2017) recommended limits for portable and domestic water usage. Generally, groundwater in the district is a very hard water type with only

about 16.7 % being soft water. Although WHO (2017) reports an inverse relationship between TH and cardiovascular diseases in areas with hard water, TH above 200 mg/l is likely to cause scales deposition in water treatment systems, storage systems and pipes, and excessive soap consumption, since it does not lather easily, and subsequent scum formation (WHO, 2017).

The water quality index (WQI) approach adopted in this study suggests that 40 % of the groundwater sampled in the district is of acceptable quality (Table 5). About 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  $NO_3^-$ . This is most likely a localized problem which might have resulted from the leaching of dissolved metals or agrochemicals into these wells, since these particular wells are hand-dug wells and shallow in depth. Groundwater around the north and south sections of the district (**Fig. 8**) proves to be of the best quality for drinking purpose.

WQI value*	Rating of water quality*	Grading*	Number of samples
< 50	Excellent water	А	2
50 - 100	Good water	В	22
101 - 200	Poor water	С	34
201 - 300	Very poor water	D	2
> 300	Unsuitable for drinking	Е	
	Total		60
*After Sahu and Sik	dar (2008)		

Table 5 Rating of water in the study area on the basis of WQI





#### **Groundwater Quality Assessment for Irrigation Purposes**

The groundwater was assessed to examine its suitability for irrigated agriculture which could augment the predominantly rain-fed agriculture. The USSL (1954) diagram, which plots SAR against EC on a semilogarithmic scale and the Wilcox diagram, has been used in this study to assess irrigation groundwater quality. 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 6) shows that majority of the samples is suitable for irrigation purpose except 15 % samples that is within doubtful category.

The USSL diagram classified irrigation water in the ranges of low to very high sodicity on the SAR axis and low to very high salinity hazard on the EC axis. Based on this categorization, 85% of the groundwater samples in the district fell in the low sodicity category (S1), whereas 18% and 67% fell in low and medium salinity (C1-C2) category, respectively, with nine samples falling in the S3-C3 category (**Fig. 9**). Hence, about 85% of the groundwater samples show excellent quality for irrigation purpose and this can be used for irrigation without any hazard to the soil or crops. Depending on the initial soil conditions, however, such that soils with excess sodium and salinity must be treated prior to irrigation with any water type. The nine 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, to prevent restricted flow and subsequent accumulation of salts in the root zone of crops which leads to salinity and permeability problems (Yidana et al. 2008; Ta'any et al. 2013).



Table 6 Classification of irrigation water based on SAR values

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

The Wilcox (1955) diagram, on the other hand, presents the categories of water types in the district for irrigation purposes, on the basis of combination of sodium percent and salinity hazard. Considering the irrigation water quality rating based on Na %, Table 7 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). From Wilcox diagram, 76% of the groundwater samples in the district were plotted within the 'excellent to good' class, while 12% fell within the 'good to permissible' class and 12% within 'permissible to doubtful' class (**Fig. 10**).

Generally, groundwater samples in the district is of excellent quality and may be used for irrigation without posing any threat to the soil or crops except in few areas where treatment is required before use for both drinking and irrigation purpose.

*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

Table 7 Classification of irrigation water based on Na %

\*Adapted from Richards (1954)



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

## Conclusion

The results of this study had provided insight into the main factors that controls the groundwater chemistry in Nkalagu district and its suitability for drinking and irrigation purposes. Water quality indices (WQIs) calculated in this study to assess the suitability of groundwater for drinking purpose suggested that groundwater in the district is of acceptable quality for such purpose, as this classification method placed 96% of the samples within poor to excellent water category. Generally, the quality of the groundwater for drinking purpose deteriorates as one

move towards the east of the district, whereas waters in the extreme north and south present the best quality.

Multivariate statistical analysis and conventional graphical methods applied to groundwater samples suggested silicate and carbonate mineral weathering as the main control of groundwater chemistry in the district. High nitrate and lead levels in the district have been attributed to agrochemicals and wastewater from farms and homes. Furthermore, Q-mode cluster analysis identified three zones of groundwater flow regimes, in which the water evolves from a Na + K–Mg–HCO<sub>3</sub> dominant fresh water type in Cluster 3, identified as intermediary flow zones, to Mg–Na +K–HCO<sub>3</sub> fresh water type in Cluster 2, designated as discharge zones with corresponding increased mineralization of the groundwater. USSL and Wilcox diagrams presented excellent quality for irrigation purpose in this study.

This study showed the significant of multivariate analysis techniques and water quality index to assess and interpret a dataset for effective evaluation of groundwater. To preserve water resource in the district against pollution, the implementation of stringent rules and guidelines are needed to enhance health and preserve water resources for future generations.

#### **UNDER PEER REVIEW**

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