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Hydrogeochemical Approach of Groundwater Evaluation of the Effects of Mining in the Enyigba Mining District, Southeast Nigeria

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Abstract

Hydrochemical approach has been used to study and to appraise the features that control the groundwater characteristics and chemical attributes in the Enyigba mining district. Atomic Absorption Spectrophotometric method was used to analyse twenty groundwater samples collected from the area. Results were further subjected to geochemical parameters including Ion Exchange, Soltan's, Diamond, Parson, Flickin, Gibbs, and Chadba's plots. The result showed acidic to basic waters (pH ranges from 3.34 to 7.0). The concentration of heavy metals is Cd>Hg> Pb>Co>Mn. Soft to moderate water has been deduced with Ca+Mg and SO_4+Cl, Ca-Mg-Cl, Na^+ + HCO_3^- water types in the area. Geochemical studies indicate rock-water interaction and ion exchange due to the dissolution of silicate sand carbonate weathering as the major factor that influences groundwater evolution in the area. Deduction from Soltan's classification revealed a deep meteoric water type for the groundwater within the area. Potential health effects have been opined due to the carcinogenicity and toxicity of heavy metals.

Keywords: *Groundwater, Influence, Mine waste, Hydrochemistry, and Enyigba.*

INTRODUCTION

Mining activities have been ongoing in the Enyigba area for over ninety years (Obiora et al., 2018). The area is renowned for its large deposit suites of galena and associated minerals (Nnabo et al., 2011; Obiora et al., 2018; Obarezi and Nwosu, 2013; Obasi and Akudinobi, 2019a; Obasi et al., 2015; Obasi, 2020; Ezeh et al., 2007). Many researchers have opined that the mining of these mineral deposits has aggravated population growth and economic activities basically around the mining communities (Obasi and Akudinobi, 2019a). This has also facilitated the deterioration of the basic ecological value of soil and water quality in the area (Eyankware et al., 2016, 2021; Obasi and Akudinobi, 2019a, 2020; Obiora et al., 2016). Further, the area has witnessed an increased population with a subsequent rise in the water need of the people (Eyankware et al., 2016, 2021; Eyankware et al., 2016, 2021; Obasi, 2020). This is mostly due to the open-cast method used in the mining process. Discharges and mine wastewater are usually discharged into arable farmlands and water channels without recourse to environmental damages. The fouling of soil and water in the area through heavy metal discharge has been studied (Obasi et al., 2018; Obasi, 2020, Obasi and Akudinobi, 2019a; Obiora et al., 2016). Effluents and mine wastes from over the world have been shown to contain Potentially Harmful Elements (PHEs) and Metallic Trace Elements (MTEs) that are harmful to humans and animals when they occur in excess above their thresholds (Owor et al., 2007; Hakkou et al., 2008a; Moreno-Jimenez et al., 2009; Khan et al., 2008, 2010; Obasi and Akudinobi, 2019a,2019b, 2020;Oti and Nwabue, 2013; El-Amari et al., 2014; Obiora et al., 2016; Moye et al., 2017; Martinez-Martinez et al., 2013; Musah et al., 2013). The use of groundwater for any purpose depends on the major ionic species and heavy metals concentration. Obasi and Akudinobi (2019a) have linked different kinds of health diseases and medical conditions to the consumption of water of poor quality. This is due to bioaccumulation in the food chain. The distribution and dispersion of ionic components of groundwater in the geochemical cycle of aquifers is due to rock weathering (Eyankware et al., 2018a). This has led to the interaction between pore-fluid content and the mineral composition of the rocks. This is certain as groundwater movement play an important role in the chemistry diversity and quality variation of groundwater. Anthropogenic activities also contribute to groundwater deterioration (Kelepertsis et al., 2006; Skeppstrom and Olofsson, 2007; Arumugam and Elangovan, 2009; Eyankware et al., 2018b; Omo-Irubor et al., 2018). Hence, there exists a need to appraise the factors that influence the processes of groundwater chemistry around the mineralized zones of Enyigba. Many authors have worked in the area, especially (Oti and Nwabue, 2013; Obiora et al.,2015, 2016,2018; Obasi and Akudinobi, 2019a, 2020; Obarezi and Nwosu, 2013). However, currently, no work has been done in the area on the assessment of factors that play major roles in groundwater quality around the mining area. The work, therefore, is aimed at applying hydrogeochemical approach to estimate the different processes that affect groundwater chemical qualities and evolution in the area. The potential sources for the heavy metals' occurrence have been evaluated. Water types and hydrochemical attributes have been established.

Geology, Climate, and Physiography

Enyigba mining region is within Ebonyi State, Nigeria, and the region is located about 14km away from the state capital (Abakaliki). It is bounded by longitudes 6º03'E to 6º 21'E and latitudes 8º03'N to 8º21'N. Regionally, Obiora et al (2015) have described the area as an integral part of the Lower Benue Trough. Locally, the area is dominated by the Abakaliki shales which is a deposit of Albian transgression (Asu River Group). The transcurrent movement and several tectonic events resulted in the creation of structures and compressional folding which was also accompanied by hydrothermal activities that initiated sulphide ore mineralization, hence the shale serving as the host rock for the mineral deposits (Nwajide, 2013; Ogundipe, 2017; Obaje, 2009; Ani et al., 2023). The Formation consists of majorly dark grey to black fissile, laminated, and calcareous shales. They are hard, indurated, and fractured with interbeds of limestone, siltstone, and mudstones. The shale trend is dominantly in the NE-SW direction concordant with the regional architecture of the Benue Trough, and they have low dip direction (about 5°) and steep dips (about 42°) all in the NW-SE.

The perennial Ebonyi River drains the entire area (Egbueri et al., 2022). It has a characteristic N-S flowing pattern. Major tributaries of the Ebonyi River in the area include Iyinu, Ikpete, AkparaIzzi, Nwoniyi Offia, and Akpara Ezza. They form the major sources of water for drinking, agriculture, and other purposes (Kawo and Karuppannan, 2018). The rivers conform to a dendritic pattern, although there is a hint of the trellis pattern suggested by a tendency for the drainage lines to be approximately straight. The flow direction of the drainage systems is eastward where they join the Cross River. The climate of the study area is part of the South-East Nigeria tropical rainforest zone, with a characteristic rainfall range of 1750-2000m/ annum (Obasi and Akudinobi, 2020). The bilateral season (Rainy and dry season) is prevalent in the area. The wet season usually lasted from March to October, being domineering during July through August and attenuating towards September (Edet and Okereke, 2022: Akpa et al., 2022). The wet season in the area results from the tropical maritime airmass (southeast trade wind), blowing across the Atlantic Ocean. The dry season is occasioned by the northeast trade wind from Sahara Dessert and the season usually spans from November to February. Temperatures range in the area is 16^0c to 28^0c and 20^0c to 38^0c, for rainy and dry seasons respectively (Iloeje, 1981).

MATERIALS AND METHODS

Twenty (20) samples of groundwater were collected from different locations across the area, using plastic bottles. Prior to the sampling, sample bottles and beakers were thoroughly washed and drenched for three days in acidified distilled water (1.0mL of HNO_3). Thereafter they were cleaned using dilute HNO_3 followed by carefully washing with the sampled water (at least three times) at the point of sample collection. Before sampling, the boreholes (Hand pump wells) were pumped for 5 to 10 minutes whereas, in the case of hand-dug wells, any visible debris/waste was cleared before collecting samples. The resulting sample was filtered using disposable filters of 0.45µm diameter to enable the removal of any impending particles prior to storage in already-prepared bottles. Freshly prepared HNO_3 (concentration of 1.0 mL) was used for sample acidification with new syringes. This was done to avoid sorption. Ice-packed containers were used for sample storage to ensure a relatively stable transportation temperature.

The Cation concentrations were determined through laboratory analysis using Fast Sequential (FS) (Varian 240 AA) Atomic Absorption Spectrophotometer, while titrimetric methods were used for anions. Physical parameters including electrical conductivity pH were measured at points of sample collection (in-situ) using a pH meter (Hanna model H1991300) and electrical conductivity meter (DDS 307 model) respectively. Generally, sampling steps and data analysis was done relative to Standard methods for water and wastewater of APHA (1999).

Soltan Classification

Constructed on meteoric genesis ($r2$) and base-exchange ($r1$) indices, Solten (1999) has classified groundwater into two sources (equations 1a and 1b).

$$r1 = (Na^{+} - Cl^{-})/SO_4^{2-} \quad (1a)$$

$$r2 = [(Na^{+} + K^{+}) - Cl^{-}/SO_4^{2-}] \quad (1b)$$

Chadha Classification

$$HCO_3^{-} - (Cl^{-} + SO4^{2+} + NO3 -)meq/L \quad (2a)$$

$$Ca^{2+} + Mg^{2+}/(Na^{+} + K^{+})\ meq/L \quad (2b)$$

Gibbs Plots

A schematic approach to understanding and interpreting chemical constituents of water relative to aquifer lithologies was proposed by Gibbs (1970).

For Cations:

$$Na^{+}/(Na^{+} + Ca^{2+})\ meq/L \quad (3a)$$

For Anions:

$$Cl^{-}/(Cl^{-} + HCO_3^{-})\ \text{meq/L} \quad (3b)$$

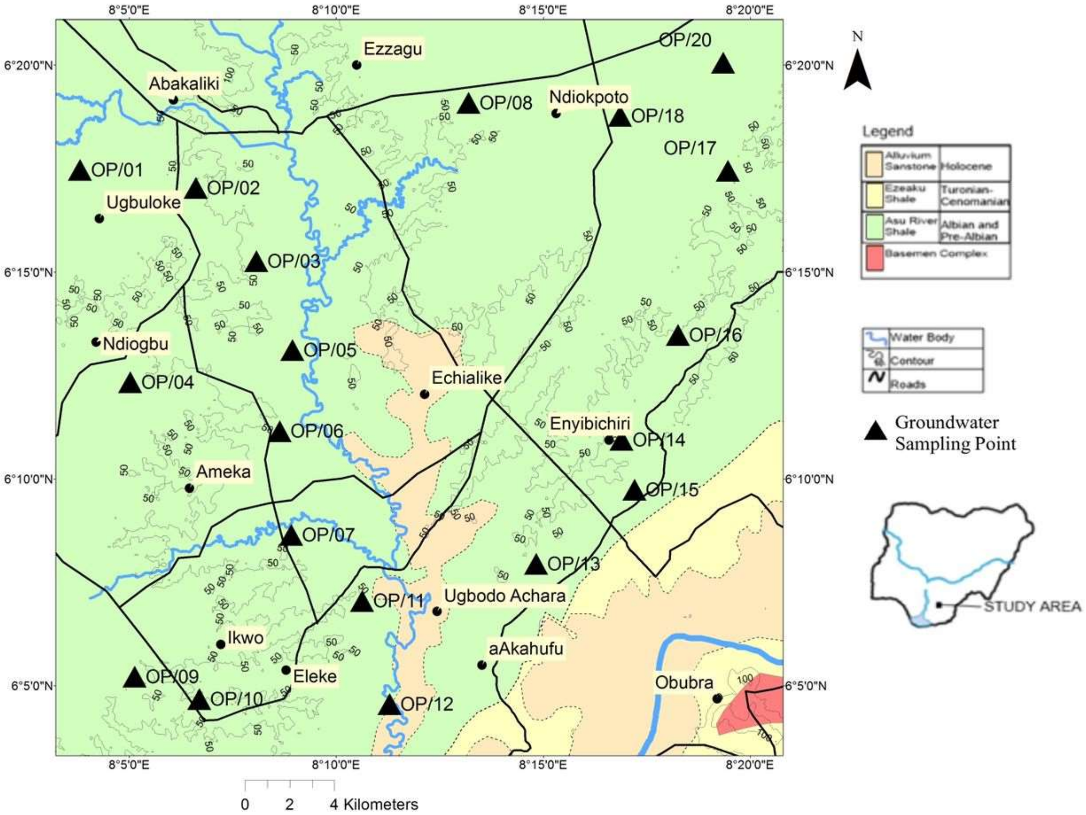

Figure 1: Geological Map and sample location.

RESULTS AND DISCUSSION

Table 1 is the results of analysis conducted on the samples against the sample locations. minimum, maximum, and average values were also calculated and presented.

Table 1: Results of analysis

Sample code	**Ec**	**pH**	**TDS**	**Na^+**	**Cl^-**	**Mg^{2+}**	**K^+**	**HCO_3^-**	**SO_4^{2-}**	**NO_3^-**	**CO_3^-**	**Ca^{2+}**	**Cd**	**Fe**	**Ag**	**Mn**	**Co**	**Hg**	**Pb**	**Zn**
	(µS/cm)		(mg/L)																	
OP/01	152.0	5.8	71.6	4.0	2250.0	0.0	4.3	117.2	6.6	64.0	126.0	12.8	0.0	0.0	0.3	2.9	0.0	2.3	0.0	1.4
OP/02	327.0	4.0	53.0	4.4	37.0	1.0	5.9	113.5	18.9	81.0	172.0	33.0	0.6	0.1	0.2	9.1	0.0	1.9	0.0	0.1
OP/03	345.0	6.3	43.0	8.0	36.0	10.6	1.1	9.8	35.4	4.3	5.0	45.0	0.0	0.0	0.5	4.8	0.0	0.7	0.0	0.0
OP/04	79.0	6.1	67.2	8.8	55.0	0.0	1.3	11.7	13.6	6.1	134.0	37.2	0.0	0.0	0.9	12.1	0.0	0.0	0.0	2.1
OP/05	376.0	4.9	1.3	9.1	53.0	0.0	1.8	180.6	16.5	5.9	70.0	24.4	0.3	0.0	0.0	1.3	0.0	0.2	0.0	0.0
OP/06	257.0	3.3	0.8	5.5	52.0	10.4	2.4	72.0	19.3	5.5	62.0	8.6	0.4	0.0	0.0	0.0	0.0	0.1	0.2	0.0
OP/07	103.0	5.3	4.0	6.1	37.0	8.3	8.4	8.4	4.5	5.1	114.0	9.8	0.2	0.0	0.0	2.5	0.2	0.2	0.0	0.0
OP/08	98.5	6.4	28.4	11.1	39.0	5.1	13.3	10.5	6.1	5.6	72.0	19.6	0.7	0.0	0.0	0.0	0.0	0.4	0.0	0.0
OP/09	88.3	6.0	34.2	6.1	2360.0	4.0	12.4	231.3	4.6	5.0	168.0	26.8	0.6	0.0	0.0	0.0	0.0	0.2	0.0	0.0
OP/10	79.8	5.8	21.6	9.2	47.0	9.2	3.3	156.2	5.5	6.2	241.0	26.3	0.8	0.0	0.0	0.0	0.0	0.4	0.0	0.1
OP/11	850.0	4.9	50.0	4.3	55.0	3.6	6.7	69.6	10.1	70.0	301.0	20.6	0.3	0.0	0.0	0.0	0.1	0.4	0.8	0.1
OP/12	78.2	7.1	17.4	6.9	54.0	1.0	9.8	155.6	2.1	62.0	292.0	32.7	0.5	0.0	0.0	0.0	0.0	0.2	0.4	0.1
OP/13	648.0	7.1	4.2	5.0	92.0	0.1	9.2	150.7	4.3	11.4	210.0	26.6	0.8	0.0	0.0	0.0	0.1	0.4	0.3	0.2
OP/14	543.0	7.0	4.0	7.7	97.0	0.7	73.9	147.1	9.3	72.0	248.0	191.0	0.1	0.0	0.0	0.0	0.0	0.4	0.7	0.0
OP/15	418.0	7.0	3.8	4.6	40.0	0.6	4.4	61.6	30.1	4.2	141.0	43.9	0.1	0.0	0.0	0.0	0.0	0.4	0.7	0.0
OP/16	420.0	7.1	3.0	7.9	4.5	0.0	12.2	141.0	5.3	5.6	121.0	15.6	0.2	0.0	0.0	0.0	0.1	0.3	0.0	0.0
OP/17	521.0	7.0	3.4	11.9	4.7	0.0	3.3	89.1	8.1	4.3	276.0	9.0	0.4	0.0	0.0	0.0	0.1	0.4	0.0	0.0
OP/18	587.0	6.7	16.0	8.7	3.7	10.9	6.7	67.1	10.3	5.9	142.0	191.0	0.5	0.0	0.0	0.9	0.0	0.3	0.0	0.1
OP/19	357.0	7.0	4.0	8.6	32.0	0.0	9.8	93.4	13.6	5.4	82.0	52.0	0.4	0.0	0.0	0.7	0.0	0.5	0.0	0.0
OP/20	325.0	7.0	12.4	9.4	38.0	4.8	9.2	64.7	6.2	3.8	74.0	45.2	0.9	0.0	0.0	1.2	0.0	0.4	0.2	0.2
Min	**78.2**	**3.3**	**0.8**	**4.0**	**3.7**	**0.0**	**1.1**	**8.4**	**2.1**	**3.8**	**5.0**	**8.6**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Max	**850.0**	**7.1**	**71.6**	**11.9**	**2360.0**	**10.9**	**73.9**	**231.3**	**35.4**	**81.0**	**301.0**	**191.0**	**0.9**	**0.1**	**0.9**	**12.1**	**0.2**	**2.3**	**0.8**	**2.1**
Average	**344.6**	**6.0**	**6.0**	**7.4**	**352.3**	**3.7**	**12.5**	**99.6**	**12.2**	**23.6**	**152.6**	**48.7**	**0.4**	**0.0**	**0.1**	**1.8**	**0.0**	**0.5**	**0.1**	**0.2**

DISCUSSION

Hydrochemical Evaluation.

According to Solten (1999), the hydrogeochemical evolution of groundwater is controlled by physiochemical processes such as evaporation, ion exchange, weathering, oxidation–reduction, precipitation, and dissolution.

Physical parameter

pH: pH indicates the intensity of the acidity or alkalinity of a solution. This is very important as it strongly determines the chemical activity that goes on in any physio-chemical environment (Obasi and Akudinobi, 2019a). Several factors control the pH of water, this includes soil composition and bedrock geology, and inorganic constituents in the water bodies. Heavy metals' bioavailability is usually influenced by pH mostly in soil though this variability is affected by the precipitation of insoluble organic complexes, hydroxides, and carbonates (Roy et al., 2015; Khaled and Muhammad, 2016; Akpa et al., 2023a).Values of pH in the area range from 3.34 to 7.09 (Table 2). This indicates acidic to basic waters for the area.According to Jong et al (2017), low pH is attributed to rainwater. This is due to the percolation of rainwater through the soil. This process results in a buildup of CO_2accentuated during microbial oxidation in the unsaturated zone with rich organic matter content forming carbonic acid (Akpa et al., 2023a). Dissolution of CO_2 enhances the integral concentrations of inorganic carbon in the aquifer and attenuates pH in line with the carbonic acid dissociation formed in the process (Henderson, 1995).

Electrical Conductivity: The Ec of water samples ranges from 78.2 - 850μScm^{-1}. The groundwater shows very high conductivity values. This can be linked to the relatively high content of charged ions resulting from the oxidational progressions occurring in the mix (Obasi, 2017). Generally, the conductivity values of the samples were below WHO's (2011) permissible limit (1000μS cm^{1}).

TDS: The TDS of the samples analysed ranges from 0.80 – 71.58 mg/L. The foremost version of the WHO stipulation on drinking water quality (WHO, 1984) has a permissible value of1000mg/L for TDS relative to consideration of taste. Objectionable taste is likely to be detected when the TDS > 1200mgL by the consumers (WHO, 2011). High dissolved metallic content could influence the TDS quotient and induce taste and odour, this usually aggravates water quality degradation especially when stored (Egbueri and Mgbenu, 2020; Akpa et al., 2023b). Groundwater TDS and pH variations are usually a result of geogenic processes than anthropogenic factors (Ukah et al., 2019; Akpa et al., 2023b), however, metallic content diversity is more of anthropogenic influences (Obasi et al., 2023; Egbueri, 2019). Water that has an extremely low TDS value could also be intolerable for consumption following its flat, insipid taste (Obasi, 2017).

Hydrochemical Parameters

Figures 2 to 7 have been used to show the hydrochemical process that affects groundwater geochemistry. The plot of $Ca^{2+}/(HCO_3^{-} + SO_4^{2-})$ versus Na^{+}/Cl^{-} indicates that samples OP/01, 02, 03, 05, 06, 08, 09, 11, 12, 13, 15 and 20 fall under the natural state. This result shows that the dissolution of carbonate and silicate rock is the key factor that affects the composition of groundwater in the area. Samples OP/04, 10, and 19 coincide with the reverse cation exchange envelope whereas OP/07, 14, 16, 17, and 18 are outside the various categories of factors that affect groundwater in the mining district. The hydrochemical characteristics of groundwater can be studied using an End-member diagram (Table 2).

Gaillardet et al. (1999) stated that end-point indices could be applied to groundwater studies to analyse the sources of rock-weathering components in the water. This analysis indicates that the source 99.9% of groundwater chemistry within the study area is from the dissolution of carbonate and silicate minerals (Fig. 3). Silicate weathering has affects other processes, especially the dissolution of carbonate rocks (Raju et al., 2010).

Table 3: Chemical compositions of the silicate and carbonate end members (Gaillardet et al 1999)

Chemical Composition	**Silicate End Members**	**Carbonate End Members**
$Ca^{2+}/Na+$	0.35 ± 0.15	50
Mg^{2+}/Na^+	0.24 ± 0.12	10
HCO_3^-/Na^+	2 ± 1	120

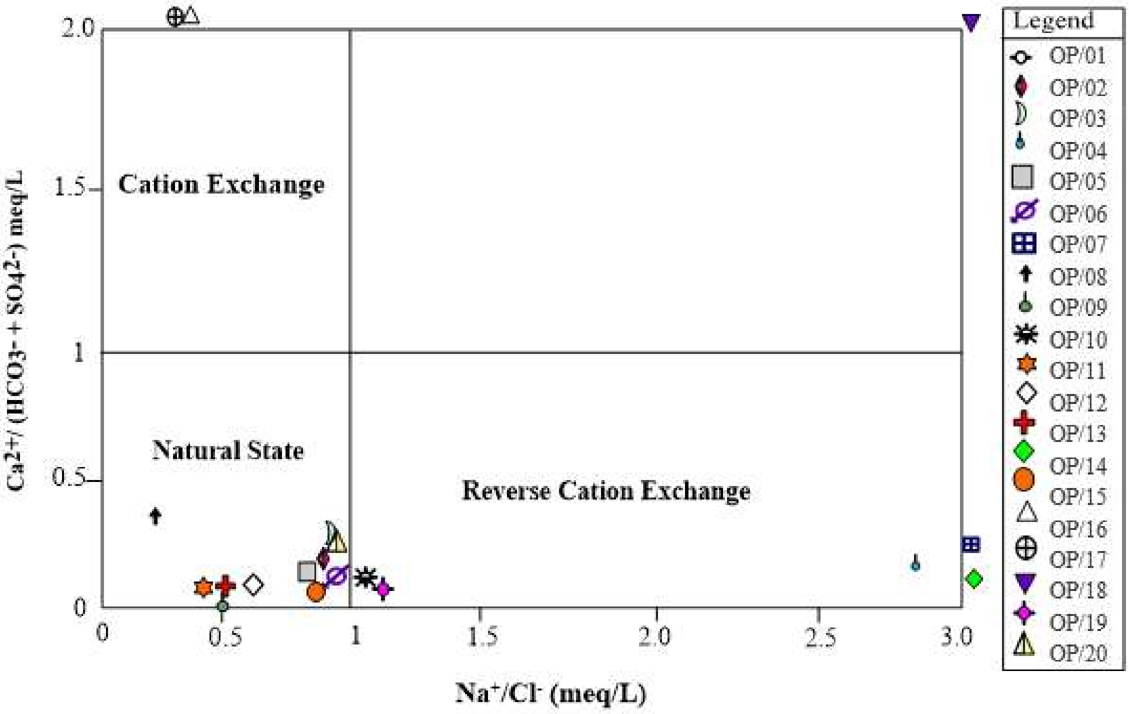

Figure 2: The plot of $Ca^{2+}/ (HCO_3^- + SO_4^{2-})$ versus Na^+/Cl^-

Analysis of Mg^{2+} / Na^+ against Mg^{2+} /Ca^{2+} on the end diagram (Fig 4) portrays that evaporation effects, weathering of rocks, and chemical leaching constitute the major factors that control the chemical evolution of groundwater sources across the area. Li (2018) noted that rock–water interaction is an acute phase of mineral dissolution.

A diamond field diagram was applied to classify the groundwater based on major chemical processes prevalent in the groundwater aquifers. The result indicates that the groundwater lies within the hydrogeochemical facies of high Ca + Mg and SO_4 + Cl (Fig. 5). The primary sources of hardness have been indicated as Ca and Mg. A Ca –Mg – Cl water type was also indicated in the area using Parson's plot (Fig 6). A variation from soft, fresh, and moderately hard groundwater types has been indicated using TDS and total hardness (TH) hydrochemical classification (Fig. 7). Increase in TDS could lead to increased Ec.

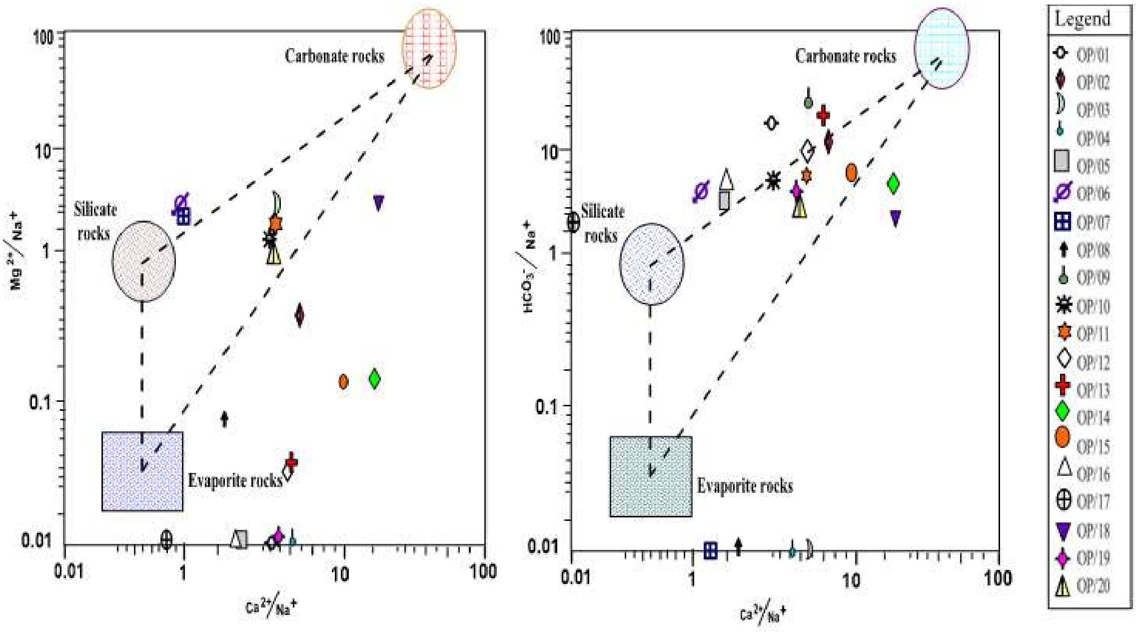

Figure 3: End-member plot for groundwater samples of the study area

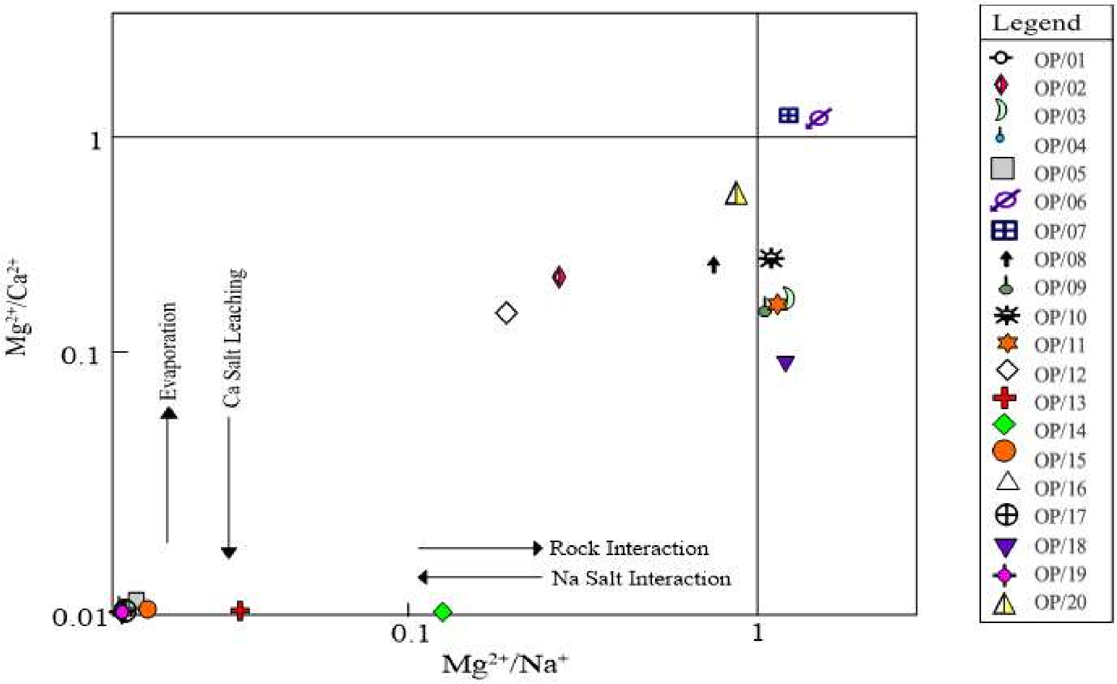

Figure 4: Plot of Mg/Ca versus Mg/Na of the study area.

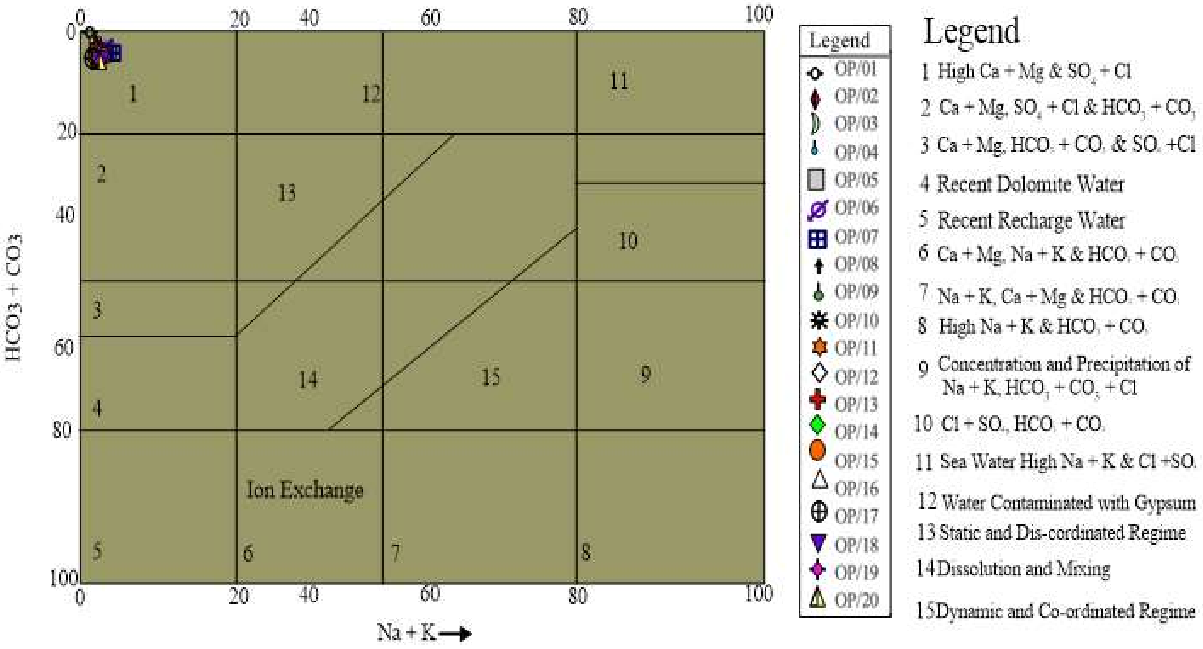

Figure 5: Diamond field Plot (of Piper by Lawrence and Bal-Subramanian, 1994).

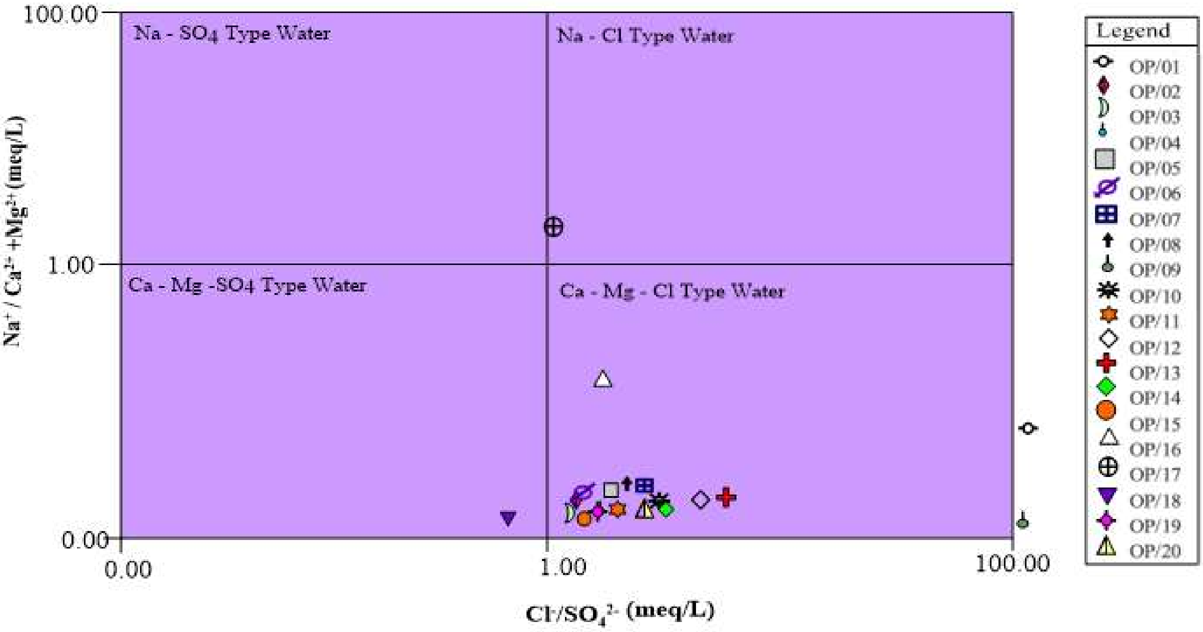

Figure 6: Parson’s Plot of the study area.

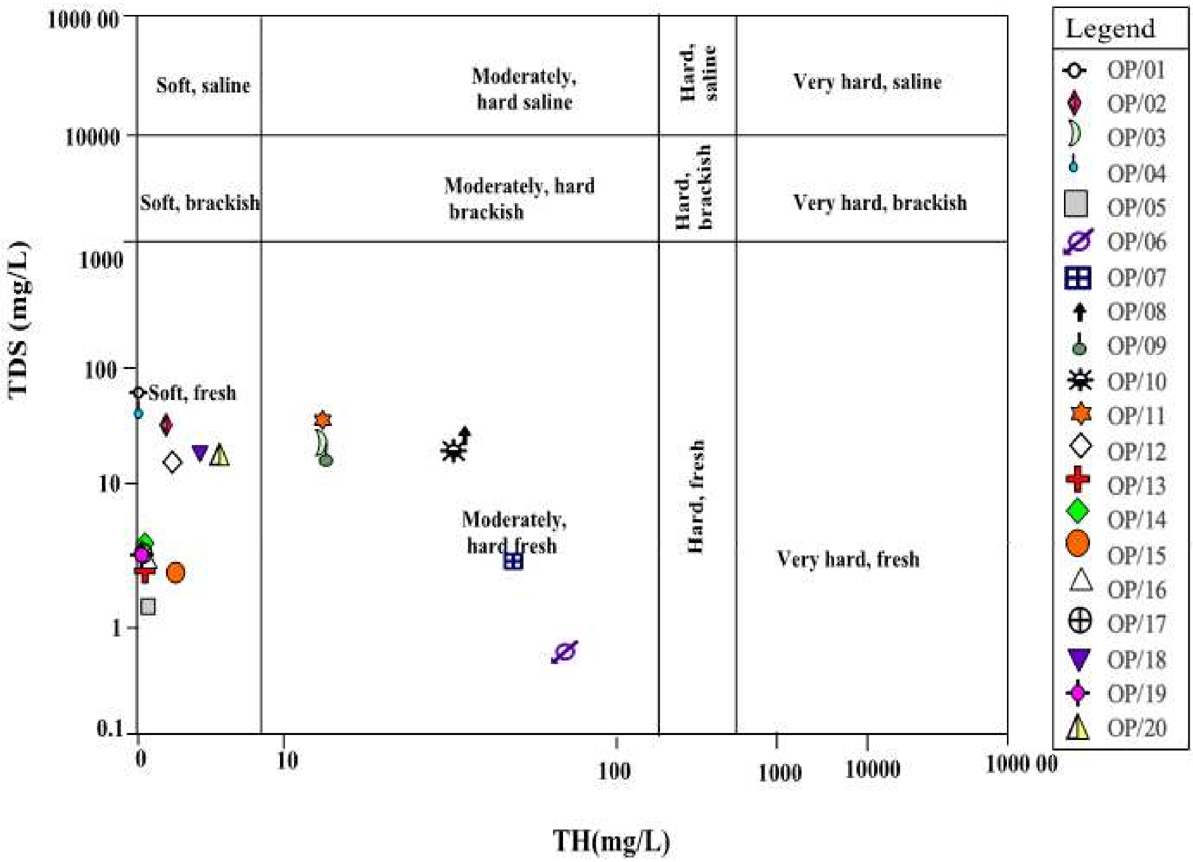

Figure 7: Classification of Groundwater based on TH and TDS

Geochemical classification of groundwater

Chadha Plot: The groundwater of the study area on Chadha plots (Fig 8) shows that they fall within group 8 ($Na^+ + HCO_3$). This group indicates the excessiveness of Alkali metals beyond the counterpart alkaline earth metals, this also corresponds with the dominance of weak acidic anions surpassing strong acidic anions.

Gibbs Plot: Gibbs Plot uses the distribution of TDS, cations (Na^+, Ca^{2+}), and anions (Cl^-, HCO_3^-) to designate groundwater types (Equation 3a and 3b; Fig. 9). This is a very important tool, and it underscores the role of rock-water interaction, precipitation, and evaporation on groundwater geochemistry characterization (Kawo and Karuppannan, 2018). According to Gibbs (1970), the variation in the ratio of $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ results from TDS which is also significant in assessing the sources of dissolved ions. This is possible following the research of Eyankware et al. (2018a) and Jong et al. (2017), suggesting that the physical and chemical attributes of groundwater can be deduced from the characteristics of cations and anions, which is influenced by the soil–water interaction as groundwater evolves in the aquifer system. No dominance was indicated in the area.

Soltan classification

The Soltan (1999) groundwater characterization indices anchors on base-exchange indices (*r*1) and meteoric genesis indices (*r*2) computed using equations 1a and 1b. When $r1<1$ and $r2<1$, the groundwater sources designate $Na^+ – SO_4^{2-}$ and deep meteoric type, respectively, whereas when $r1>1$ and $r2>1$ it suggests groundwater sources from $Na^+ – HCO3^-$ and shallow meteoric type. Following the above characterizations, the groundwater sources in the area are basically $Na^+ – SO_4^{2-}$ type (Table 4), this might have resulted from the geogenic events (marine deposits, saline water intrusion, and hydrothermal activities) that occurred in the area.

Ion Exchange

Bivariate plots of Na/Cl ratio against EC, Mg against Ca +Mg, Na against Ca, Cl against Na, and Ca + Mg against $HCO_3 + SO_4$ (Fig. 10 a- e) were also applied to determine the main factor that controls the chemical characteristics of groundwater in the area. The analysis indicates the weathering of Na-feldspar and/or other Na-silicate minerals and Ca-carbonate or Ca-silicate dissolution as a major component of the groundwater evolution of the area. This is because of significant cation exchange instigated by rich silicate rocks within the groundwater-bearing zones, solutes from weathering processes, and precipitation of dissolved species into the aquifer through infiltration. This also implies a recharge zone for the area.

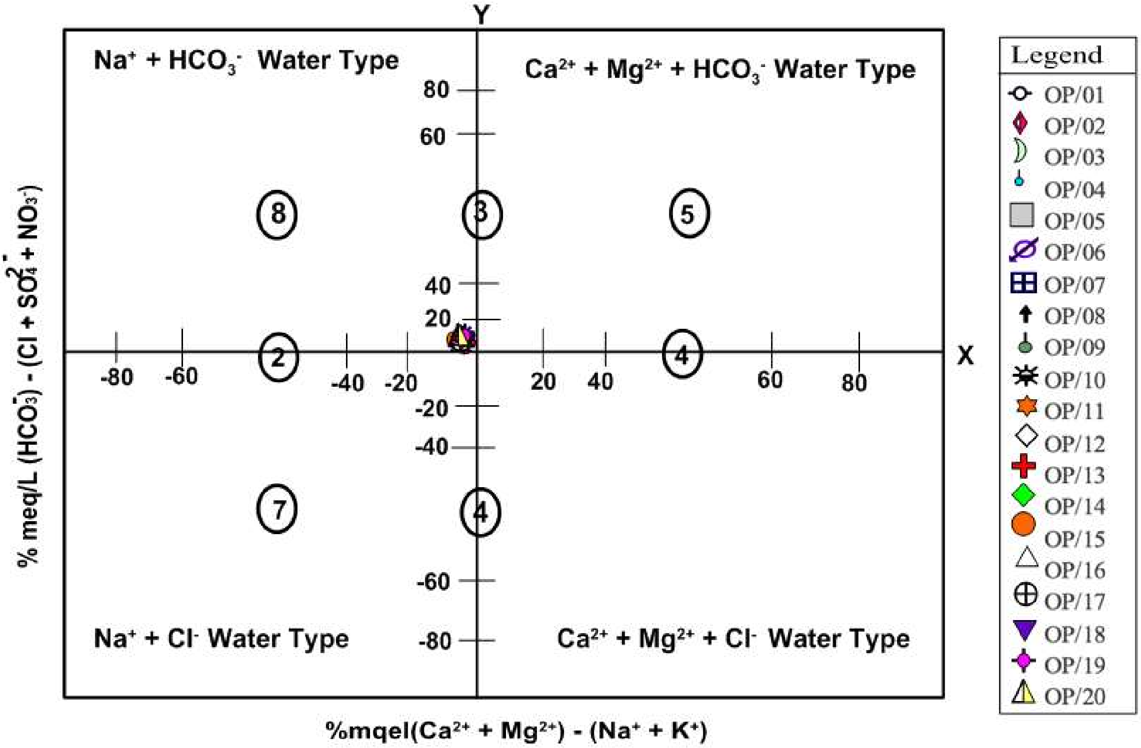

Fig. 8. Chadha’s Diagram modified after Piper for groundwater sample of the study area.

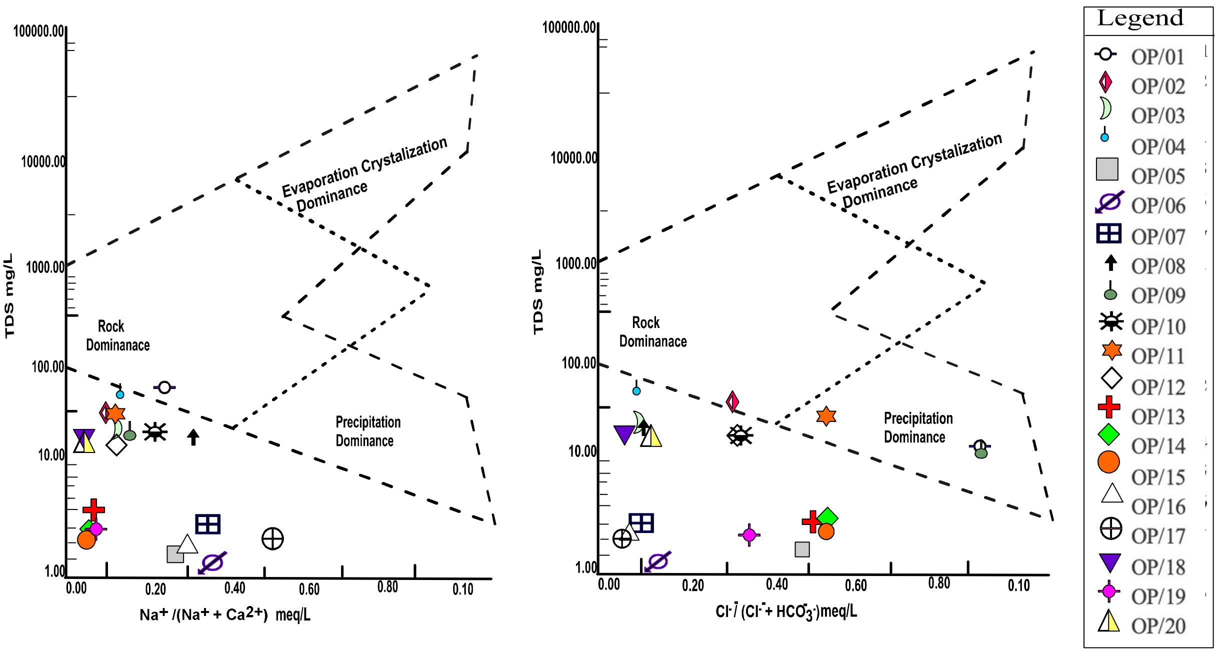

Fig. 9: Gibb's Plot of Groundwater Samples in the Area

Table 3: Results of Soltan's classification of groundwater in the Enyigba mining district

Sample Code	r1	Water Type	r2	Water Type
OP/01	-9.61	$Na^+ - SO_4^{2-}$(DM)	-964.3	$Na^+ - SO_4^{2-}$(DM)
OP/02	-0.04	$Na^+ - SO_4^{2-}$(DM)	-0.03	$Na^+ - SO_4^{2-}$(DM)
OP/03	-0.01	$Na^+ - SO_4^{2-}$(DM)	-0.01	$Na^+ - SO_4^{2-}$(DM)
OP/04	-0.08	$Na^+ - SO_4^{2-}$(DM)	-0.08	$Na^+ - SO_4^{2-}$(DM)
OP/05	-0.06	$Na^+ - SO_4^{2-}$(DM)	-0.06	$Na^+ - SO_4^{2-}$(DM)
OP/06	-0.05	$Na^+ - SO_4^{2-}$(DM)	-0.05	$Na^+ - SO_4^{2-}$(DM)
OP/07	-0.16	$Na^+ - SO_4^{2-}$(DM)	0	$Na^+ - SO_4^{2-}$(DM)
OP/08	-0.09	$Na^+ - SO_4^{2-}$(DM)	0.01	$Na^+ - SO_4^{2-}$(DM)
OP/09	-14.29	$Na^+ - SO_4^{2-}$(DM)	-14.11	$Na^+ - SO_4^{2-}$(DM)
OP/10	-0.16	$Na^+ - SO_4^{2-}$(DM)	-0.15	$Na^+ - SO_4^{2-}$(DM)
OP/11	-0.13	$Na^+ - SO_4^{2-}$(DM)	-0.11	$Na^+ - SO_4^{2-}$(DM)
OP/12	-0.59	$Na^+ - SO_4^{2-}$(DM)	-0.46	$Na^+ - SO_4^{2-}$(DM)
OP/13	0.55	$Na^+ - SO_4^{2-}$(DM)	-0.5	$Na^+ - SO_4^{2-}$(DM)
OP/14	-0.2	$Na^+ - SO_4^{2-}$(DM)	-0.05	$Na^+ - SO_4^{2-}$(DM)
OP/15	-0.03	$Na^+ - SO_4^{2-}$(DM)	-0.02	$Na^+ - SO_4^{2-}$(DM)
OP/16	0.04	$Na^+ - SO_4^{2-}$(DM)	0.05	$Na^+ - SO_4^{2-}$(DM)
OP/17	0.04	$Na^+ - SO_4^{2-}$(DM)	0.05	$Na^+ - SO_4^{2-}$(DM)
OP/18	0.02	$Na^+ - SO_4^{2-}$(DM)	0.04	$Na^+ - SO_4^{2-}$(DM)
OP/19	-0.04	$Na^+ - SO_4^{2-}$(DM)	-0.02	$Na^+ - SO_4^{2-}$(DM)
OP/20	-0.18	$Na^+ - SO_4^{2-}$(DM)	-0.15	$Na^+ - SO_4^{2-}$(DM)

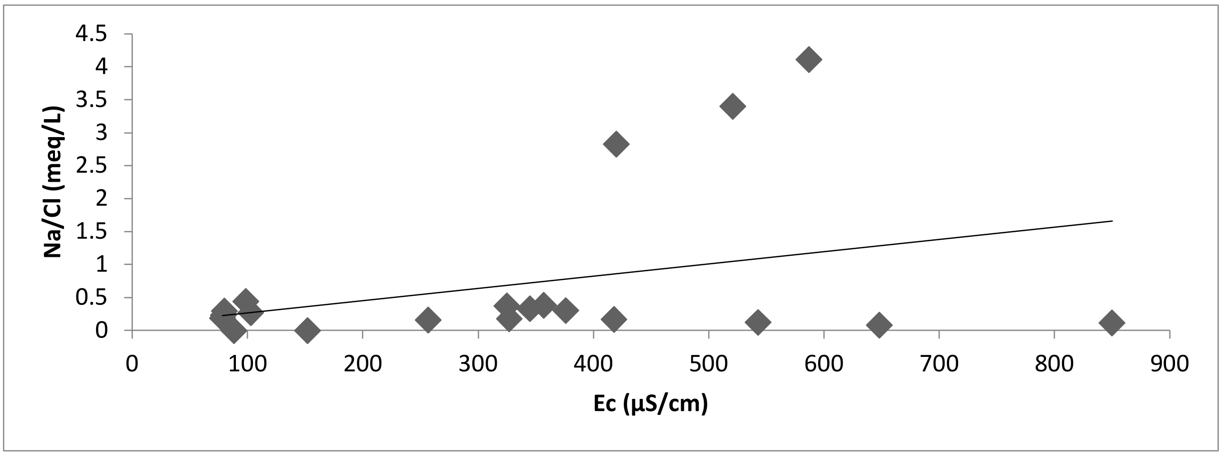

Figure 10a: Plot Na/Cl ratio versus EC.

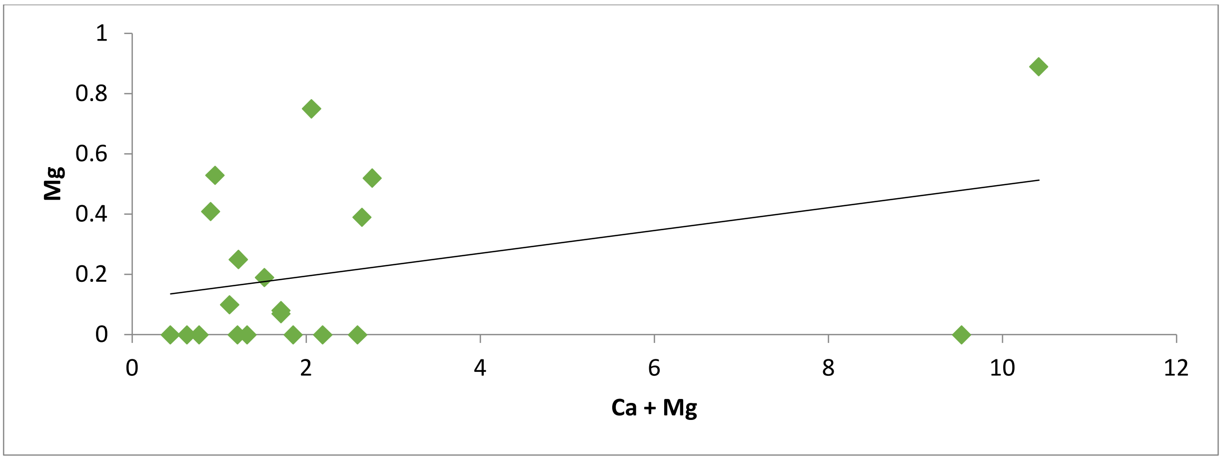

Figure 10b: Plot of Mg versus Ca +Mg

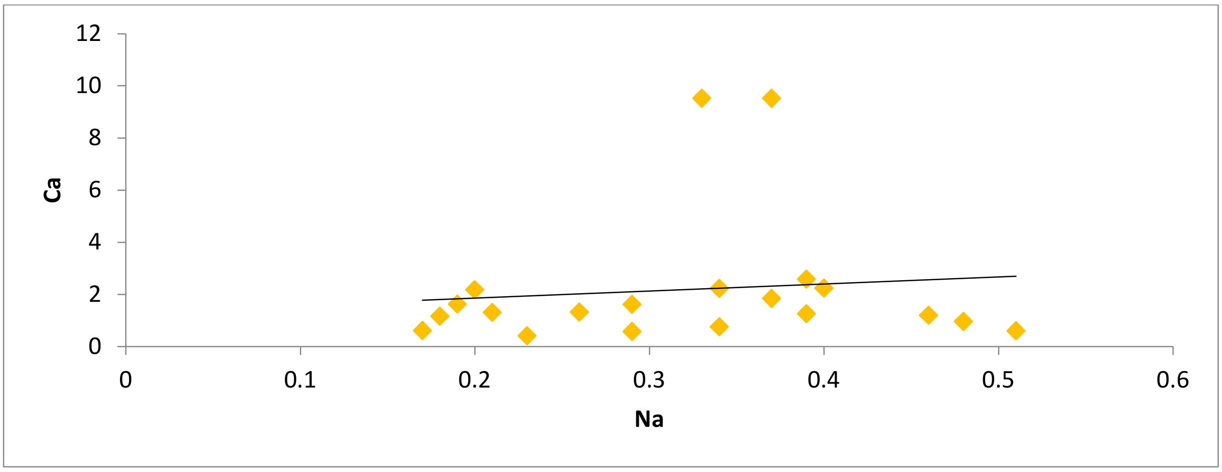

Figure 10c: Plot of Na versus Ca (meq/L).

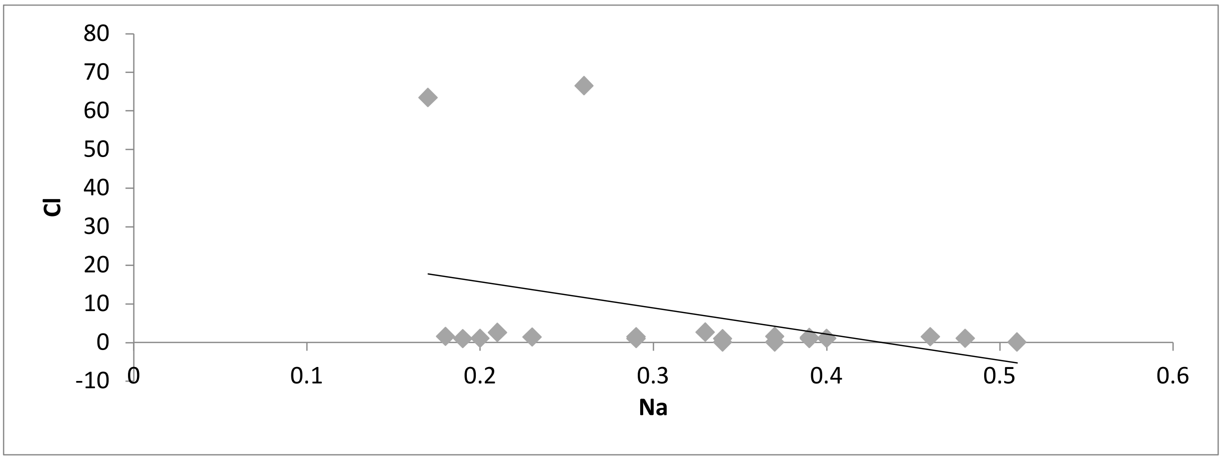

Figure 10d: Plot of Cl versus Na (meq/L).

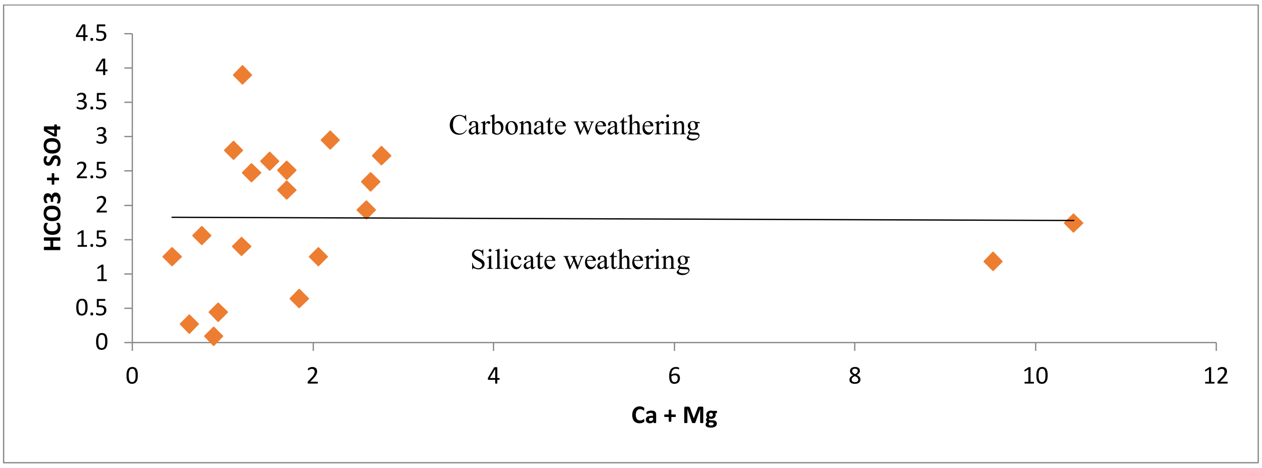

Figure 10e: Plot of Ca + Mg versus $HCO_3 + SO_4$ (meq/L)

Evaluation of Levels of Heavy Metals

Levels of Potentially Harmful Elements (PHEs) including cobalt (Co), cadmium (Cd), iron (Fe), lead (Pb), silver (Ag), zinc (Zn), manganese (Mn), and mercury (Hg) were evaluated in the area. This is necessary as some PHEs are toxic and carcinogenic. Some are more persistent in the environment and possess serious health risks (Obasi and Akudinobi, 2020; Igwe and Ukaogo, 2015). They can leach into the soil horizon and migrate into groundwater aquifers and cause severe health issues (Obasi and Akudinobi, 2019a; Sha et al., 2017).

Cadmium: High values of cadmium were observed in the analysed water samples (varying from 0.00 to 0.88mg/L). About 85% of samples indicated Cd content greater than the WHO (2011) permissible limits. This can lead to serious health problems as cadmium is among the most carcinogenic and toxic metals (Friberg et al., 1986).

Iron: Iron is highly abundant in the earth's crust (Obasi and Akudinobi, 2020). The Fe concentration ranges from 0 to 0.08mg/L. The result indicated Fe concentration below the WHO (2011) drinking water standard for all water analysed samples. This can be due to lower exposure of groundwater to oxidation processes.

Table 5a: Result of PHEs in the area.

PHEs	OP/01	OP/02	OP/03	OP/04	OP/05	OP/06	OP/07	OP/08	OP/09	OP/10	OP/11	WHO, 2011
Cd	0	0.61	0	0	0.28	0.35	0.15	0.74	0.64	0.78	0.33	0.003
Fe	0	0.08	0	0	0	0	0	0	0	0	0	0.3
Ag	0.34	0.23	0.53	0.91	0.04	0	0	0	0	0	0	0.1
Mn	2.91	9.14	4.76	12.1	1.34	0	2.49	0	0	0	0	0.4
Hg	2.3	1.9	0.7	0	0.15	0.07	0.17	0.37	0.22	0.37	0.36	0.06
Co	0.001	0.027	0	0	0.04	0.04	0.15	0.02	0.02	0	0.11	Nil
Pb	0	0	0	0	0	0.21	0	0	0	0	0.08	0.01
Zn	1.35	0.07	0	2.09	0	0	0	0	0	0.06	0.06	0.01

Table 5b: Result of PHEs in the area.

PHEs	OP/12	OP/13	OP/14	OP/15	OP/16	OP/17	OP/18	OP/19	OP/20	WHO, 2011
Pb	0.38	0.68	0.65	0.65	0	0	0	0.01	0.20	0.01
Cd	0.47	0.82	0.09	0.14	0.18	0.43	0.53	0.44	0.88	0.003
Hg	0.24	0.44	0.38	0.39	0.33	0.38	0.29	0.48	0.39	0.06
Zn	0.11	0.21	0	0	0	0.02	0.05	0.01	0.21	0.01
Ag	0	0	0	0	0	0	0	0	0	0.1
Co	0	0.10	0.02	0.02	0.11	0.06	0.04	0	0.001	Nil
Fe	0.02	0	0	0	0	0	0	0	0	0.3
Mn	0	0	0	0	0	0.02	0.93	0.66	1.22	0.4

Silver: The weathering of silver-bearing rocks is the main source of silver in the environment. A large amount of silver is also released by processes of precipitation. The result (ranges from 0.00 to 0.91 mg/L) indicates that only 20% of the water samples analysed were beyond the WHO (2011) guideline limit for drinking water. Obasi et al (2015) noted that lead, copper, and zinc occur in association with their ores.

Mercury: Mercury occurs as a native element found in rock deposits. Their occurrence in water is due to the breakdown of minerals in the rock deposits. The result (ranges from 0.00 - 2.3 mg/L) shows that about 95% of samples exceeded the WHO (2011) permissible limit for drinking water. Only sample OP/04 was below the WHO (2011) risk benchmark for drinking water. Mercury is highly toxic. Many studies have noted impairment to the kidneys, the nervous system, and the gastrointestinal tract as dangers of high mercury ingestion (Obasi and Akudinobi, 2020; Engwa et al., 2018).

Manganese: Manganese occurs in association with other PHEs in sulphide-rich rock deposits, its concentration in the study area ranged from 0.00 -12.1 mg/l. Not fewer than 55% of the samples indicated Mn^{2+} above WHO (2011) safe limit for drinking water, whereas 45%were below the set limit (Table 5a and 5b). Obasi (2020) suggested that manganese often occurs in the environment naturally through the breakdown of rocks and minerals (Obasi, 2017).

Cobalt: Its concentration ranges from 0 – 0.15 mg/l. Cobalt is mostly present in nickel-bearing deposits. Obasi (2020) also stated that Ni-Cu sulphide deposits abundant in mafic and ultramafic rocks and sedimentary rocks characterized by copper deposits are good sources of cobalt in the environment. Abakaliki tectonic framework emplaced several mafics to ultramafic intrusive rocks (Chukwu and Obiora, 2021; Ani et al., 2023), which their weathering and quarrying could have accentuated cobalt mobility in the area.

Lead: The concentration of lead ranges from 0.00 – 0.80 mg/L and indicated that 45% of samples analysed were above the WHO (2011) safe limit for drinking water. Lead is very carcinogenic and immobile; its introduction into the environment has been associated with lead ores and industrial pollution sources (Obasi and Akudinobi, 2020).

Zinc: Zinc introduction into groundwater can be aggravated through the dissolution of lead-zinc minerals, other rocks, and soil with high zinc content. The concentration of zinc ranges from 0.00 – 2.09 mg/L. 50% of samples are above the WHO (2011) permissible limit for drinking water. Though zinc is a vital nutrient for plant and animal development and growth, however, high concentrations have been associated with stomach cramps, nausea, and vomiting (Obasi and Akudinobi, 2020; Ullah et al., 2017).

CONCLUSION

The occurrence of lead-zinc and associated minerals in the Enyigba Mining district has posed a lot of geogenic and anthropogenic factors in the hydrogeochemistry of the area. Twenty groundwater samples were analysed using Atomic Absorption Spectrophotometric methods. Results were subjected to various hydrochemical plots (including Diamond field plots, Parson plots, Chadha's plots, and Gibb's plots) to determine the characterization of the groundwater and to establish the factors that control the chemical attributes of groundwater in the area. Soltan's Classification and Ficklin Diagram were applied to this study. The result indicates that silicate and carbonate weathering is the major process that affects groundwater in the area. Hydrochemical End-members study reveals that 92 % of groundwater analysed occurs in the natural state. And the plot of Mg/Ca against Mg/Na reveals that 73% of groundwater is controlled by rock-water interaction. A Ca + Mg, SO4 + Cl, Na+ + $HCO3^{-}$, and Ca-Mg- Cl water type has been described in the area. Classification of TDS against TH reveals a soft-fresh and moderate-hard category of groundwater. Ion exchange of the mineral components and rock-water interaction plays important roles in the silicate weathering process in the area.

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