RESEARCH ARTICLE   OPEN ACCESS

Ionic Abundance and Distribution in Groundwater Systems within Parts of the Central Benue Trough of Nigeria

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ABSTRACT
A hydrochemical evaluation of ionic abundance in groundwater systems within parts of the Central Benue Trough, Nigeria was carried out. This study aimed at identifying the hydro-geochemical processes that control the groundwater chemistry, ionic abundance and distribution in the study area. The analytical results show the abundance of the cations as $Na^+ > Mg^{2+} > K^+ > Ca^{2+}$, with Na^+ constituting more than 75% in most cases while for the anions the order is $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^{3-}$ with Cl^- forming at least 80% in all cases. In determining groundwater types and visualizing trends of groundwater chemistry, plots were made on the Piper-trilinear diagram which revealed Magnesium-Bicarbonate, Calcium-Chloride, Sodium-Chloride, Sodium-Bicarbonate and Mixed water types within the study area. Sodium Bicarbonate type of groundwater was most prominent. The high concentration of Na^+, Ca^{2+} and HCO_3^- in the groundwater could be due to the dissolution of plagioclase feldspars, ferromagnesian minerals, carbonate weathering and ion exchange reactions within the sedimentary units.

I. INTRODUCTION

The chemistry of groundwater not only depends on the processes in the vadose zone but also on the reactions operating along the saturated flow system (Freeze & Cherry, 1979). Most of the same processes affecting ion concentrations in the unsaturated zone are also operative in the saturated zone including the dissolution and precipitation of various minerals and cation exchange. Groundwater chemistry is largely a function of the mineral composition of the aquifer through which it flows (Nwankwoala & Udom, 2011). The order in which groundwater encounters strata of different mineralogical composition influences its final chemistry (Freeze & Cherry, 1979).

The study area falls within the Benue Trough of Nigeria, consisting of a series of rift basins which form a part of the Central West African Rift System (Cratchley & Jones, 1965; Burke et al., 1970; Grant, 1971; Nwachukwu, 1972; Wright, 1981; Genik, 1992, 1993; Akande et al., 2011; Nwajide, 2013; Brownfield, 2016). It had been shown that the structure is a set of pull-apart sub-basins or grabens generated by sinistral displacements along a pre-existing zone of northeast-southwest trending transcurrent faults (Benkhelil, 1986, 1989; Genik, 1992, 1993; Akande et al., 2011; Nwajide, 2013; Brownfield, 2016). Its orientation must have been pre-determined by northeast-southwest trending shear

zones of the late Pan-African age reactivated during the break-up of the Gondwana (Benkhelil, 1986, 1989; Nwajide, 2013).

The Benue Trough is filled essentially by marine Cretaceous rocks, starting from the Albian and ranging to the Maastritchian (Peters, 1978; Offodile, 1984; Ofoebgu, 1990; Nwajide, 2013). The depositional processes and the associated tectonics caused the emplacement of a number of important lithofacies of sedimentary and igneous origin (Offodile, 1984; Ofoebgu, 1990; Nwajide, 2013).

The hydro-geochemical processes and hydro-geochemistry of the groundwater vary spatially and temporally, depending on the geology and chemical characteristics of the aquifer (Nwankwoala & Udom, 2011). In the study area, there is no comprehensive evaluation of hydro-geochemical attributes. Thus, knowledge on geochemical processes that control groundwater chemical evolution was used in the understanding of the hydro-geochemical characteristics.

II. METHODS

A total of nineteen (19) water samples were collected for analysis. The positions of sites were determined using the Global Positioning System (GPS). Physical parameters such as temperature, pH, conductivity and total dissolved solid (TDS) were measured in the field using

TDS/conductivity meter (HACK KIT, Optima 2000 DV Perkielner model). Major cations and trace elements were analysed with Inductively Coupled Plasma Mass-Spectrometry using direct current plasma Optical Emission Spectrometry (ICP-OES) at the Geology Laboratory of the University of Jos-Nigeria. The major anions (HCO_3, Cl, Br, F, SO_4, and NO_3) were analyzed with Ion Chromatography at Activation Laboratories, Ontario, Canada. Hydrogeochemical characterization and classification of the groundwaters were evaluated by means of physico-chemical analysis and plots on the piper-trilinear diagram.

III. RESULTS AND DISCUSSION
Table 1: Results of Physico-Chemical Parameters

S/No	Samples Location	pH	eH	Tempt.	TDS (ppm)	Elev. (M)	Ca mg/l	Fe mg/l	Mg mg/l	K mg/l	Na mg/l	P mg/l	S mg/l	Se mg/l	Cl mg/l	F mg/l	Br mg/l	SO₄ mg/l	H₂CO₃ mg/l	¹⁸O per mil	D per Mil
1	ZC's House, Keana	5.48	0.56	30.8	376	138	26.45	<DL	62.36	0.014	41.82	0.073	33.7	0.114	10	0.07	0.06	6.14	255		
2	Akyana Gbogbo, Keana	5.64	0.77	29.9	489	134	63.82	<DL	11.22	28.74	231.2	0.248		<DL	81.6	0.1	0.06	3.33	426	-4.8	-23.5
3	Fed. Govt. Girl's Coll. Keana	10.8	0.32	33.6	172	153	1.045	0.392	0.247	1.126	34.23	0.052	19.25	<DL	5.23	0.32	0.03	16.7	149		
4	Alosi Water Works	10.5	0.41	29.3	237	197	0.987	0.672	0.126	4.089	38.85	0.048	9.259	0.001	1.85	0.17	0.03	33.5	206		
5	Obi Town	6.7	-	29.4	183	174	4.705	0.2	0.39	<DL	5.623	1.711	49.24	0.015	34.4	0.07	0.03	17.9	84		
6	Ribi Town	6.39	0.12	32.1	870	156	331.3	21.9	77.33	168	6463	0.142	2.232	1.048	589	0.14	0.46	58.3	214		
7	Azara Town	5.96	0.72	31.5	410	118	548	<DL	121	306	7622	<DL	<DL	44.8	22.1	0.11	4.53	22.3	341		
8	Akiri Hot Brine Spring	4.76	6.76	46.7	598	115	200	97610	8738	3749	11700	2875	6392	<DL	3300	0.98	1.8	1.81	371		
9	Akiri Town	4.66	0.2	34.6	120	120	883	<DL	20.2	82.9	2381	<DL	<DL	8.3	11.2	0.11	2.4	8.67	83		
10	Wuse Town	4.91	0.38	32.3	222	120	68.16	0.029	28.56	4.087	103.1	<DL	<DL	0.763	8.58	0.16	0.03	6.1	188		
11	Ribi Health Center	5.52	9.01	35.6	489	163	122.3	0.664	24.44	4.836	4342	0.109	326.3	<DL	4550	0.81	6.13	14.3	238	-6.13	-35.5
12	Adudu Town	5.7	0.61	31.7	356	188	90.74	0.001	0.02	<DL	0.166	<DL	<DL	<DL	8.5	1.41	0.06	17.3	267		
13	Kanje town	6.3	0.91	30.2	536	178	69.61	1.317	29.49	103.4	2357	0.119	10.19	0.497	68.8	0.08	0.1	4.73	404		
14	Abuni town	5.85	0.79	31.8	531	163	36.62	0.794	32.06	4.412	78.45	0.008	12.97	<DL	161	0.4	0.1	0.94	256		
15	New Awe Town	7.03	0.37	31	334	144	10.32	0.01	4.48	8.9	22.83	<DL	<DL	<DL	13.7	0.18	0.06	34.6	207		
16	Old Awe Town	6.85	-	41.3	951	104	134	<DL	40.25	53.99	38360	0.85	35.49	<DL	5430	1.62	3.57	13.6	431	-5.98	-34.4
17	Agwatashi, Obi	6.26	0.5	29.6	590	190	221.6	0.742	10.59	<DL	26.83	0.322	124.1	0.015	70.6	0.2	0.18	33.6	110		
18	ERCC P College, Obi	6.23	0.32	29.8	360	203	2.994	0.055	0.404	<DL	6.931	<DL	39.51	0.015	3.56	0.01	0.03	3.02	9		
19	Agaza Town	9.18	0.66	30	365	156	69.61	1.317	29.49	103.4	2357	0.119	10.19	0.824	9.77	0.27	0.06	27.5	264		

Table 2: Major Anions Analysis Results

Samples Location	Cl mg/l	F mg/l	Br mg/l	SO₄ mg/l	HCO₃ mg/l	NO₂ mg/l	NO₃ mg/l	PO₄ mg/l	CO₃²⁻ mg/l	Sum Anions mg/l	HCO₃/Sum Anions	Cl/Sum Anions
ZC's House, Keana	10	0.07	0.06	6.14	255	0.02	0.02	0.04	nd	271	0.94	0.037
Akyana Gbogbo, Keana	81.6	0.1	0.06	3.33	426	0.02	0.02	0.04	nd	511.08	0.834	0.16
Fed. Govt. Girls Coll. Keana	5.23	0.32	0.03	16.7	149	0.01	0.01	0.02	nd	171.32	0.87	0.031
Alosi Water Works	1.85	0.17	0.03	33.5	206	0.01	0.01	0.2	nd	241.59	0.853	0.008
Obi Town	34.4	0.7	0.03	17.9	84	0.01	4.8	0.02	nd	141.23	0.595	0.244
Ribi Town	589	0.14	0.46	58.3	214	0.01	38.3	0.2	nd	900.41	0.238	0.654
Azara Town	22.1	0.11	4.53	22.3	341	0.04	1.13	0.04	nd	391.25	0.872	0.056
Akiri Town	11.2	0.11	2.4	8.67	83	0.01	0.01	0.02	nd	105.42	0787	0.106
Wuse Town	8.58	0.16	0.03	6.1	188	0.01	5.34	0.02	nd	208.24	0.903	0.041
Ribi Health Centre	4550	0.81	6.13	14.3	238	0.5	0.5	nd	nd	4810.24	0.049	0.946
Adudu Town	8.5	1.41	0.06	17.3	267	0.02	1.15	0.04	nd	295.48	0.904	0.029
Kanje Town	68.8	0.08	0.1	4.73	404	0.04	0.04	0.08	19	496.87	0.813	0.138
Abuni Town	161	0.4	0.1	0.94	256	0.04	0.04	0.08	nd	418.6	0.612	0.385
New Awe Town	13.7	0.16	0.06	34.6	207	0.02	1.47	0.04	nd	257.07	0.805	0.053
Old Awe Town	5430	0.62	3.57	13.6	431	0.5	0.5	nd	nd	5879.83	0.073	0.923
Agwatashi, Obi	70.6	0.2	0.18	33.6	110	5.03	26.3	0.04	nd	245.95	0.45	0.287
ERCC P College, Obi	3.56	0.01	0.03	3.02	9	0.01	1.12	0.02	nd	16.77	0.537	0.212
Agaza Town	9.77	0.27	0.06	27.5	264	0.02	0.81	0.04	nd	302.47	0.873	0.032

Table 3: Elemental Ratios

S/No	Sample Location	Na/Cl	Br/Cl	Ca/Cl	Mg/Cl	Cl/Br	Na/K	Ca/Na	Br/Na	Mg/Ca	Na/Br
1	ZC's House, Kana	4.18	0.006	2.65	6.22	166	2887	0.63	0.002	2.35	697
2	Akpan Ghojty, Kana	2.83	0.0007	0.78	0.14	1360	5.05	0.28	0.0005	0.18	3835
3	Fed. Govt. Grl's Col. Kana	6.35	0.006	0.58	0.06	174	30.4	0.09	0.0009	0.08	1241
4	Aloshi Water Works	21	0.016	0.53	0.07	61.67	9.5	0.03	0.0008	0.13	1295
5	Obi Town	0.16	0.0009	0.137	0.011	1146	-	0.84	0.005	0.08	187.4
6	Eih Town	10.97	0.0008	0.56	0.13	1280	30.47	0.05	0.0001	0.23	14050
7	Agan Town	344.9	0.005	24.8	5.40	4.88	24.91	0.07	0.0006	0.22	1603
8	Ahri Hot Brine Spring	3.55	0.0006	60.67	2.65	1833	3.12	17.11	0.0002	0.04	6500
9	Ahri Town	202.6	0.005	9.2	1.8	4.59	20.72	0.04	0.001	0.2	976
10	Kisei Town	12	0.0004	7.94	3.33	286	-	0.66	0.0005	0.42	3456.7
11	Eih Health Center	0.91	0.002	0.03	0.01	742	1026	0.03	0.002	0.2	673
12	Adishi Town	0.02	0.007	10.68	0.002	142	-	546.6	0.342	0.0002	2.7
13	Kanje town	34.3	0.002	1.01	0.43	688	22.8	0.03	0.00004	0.42	22570
14	Abani town	0.5	0.0006	0.23	6.2	1610	17.78	0.47	0.0013	1.89	784.5
15	New Arre Town	1.67	0.005	0.73	0.33	228	2.57	0.45	0.003	0.43	300.5
16	Old Arre Town	5.5	0.0007	0.02	0.01	1521	652	0.004	0.0001	0.5	8584.2
17	Agwatashi, Obi	0.38	0.005	3.34	0.15	392	-	8.3	0.006	0.05	149
18	EROC P College, Obi	1.95	0.008	0.84	0.11	120	-	0.43	0.004	0.14	231
19	Agan Town	241.3	0.006	7.13	3.02	161	0.07	0.03	0.00003	0.42	39285
	Seawater Evaporation Ratio. *	0.85	0.002	0.04	0.21	292	47	0.04	0.002	5.53	163
	* After Collins, 1975 in Tijani, 2004.										

Fig. 3: Na/Cl versus Cl/Br Ratios

Fig. 4:   Na/Cl Ratio plot
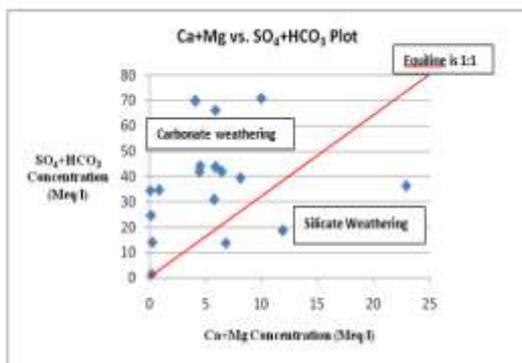
Fig. 1: Scatter diagram of $(Ca + Mg)$ vs $(SO_4 + HCO_3)$
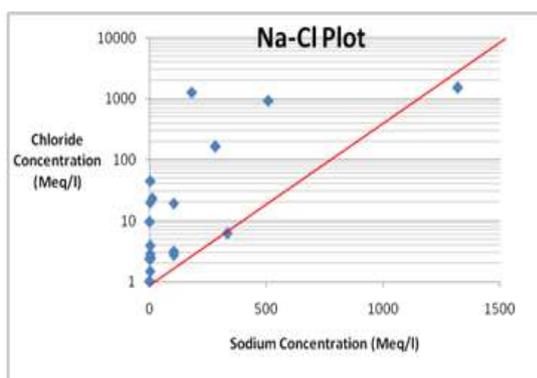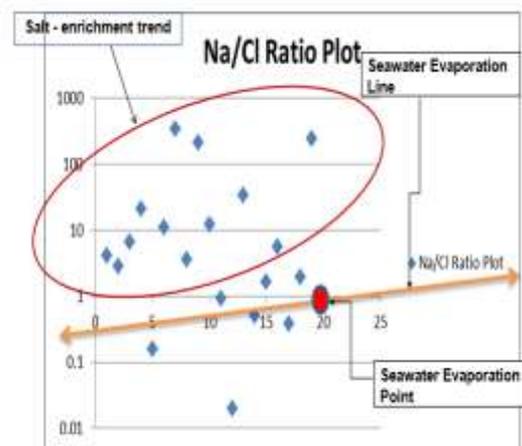
Fig 2 : Scatter diagram for sodium-chloride plot
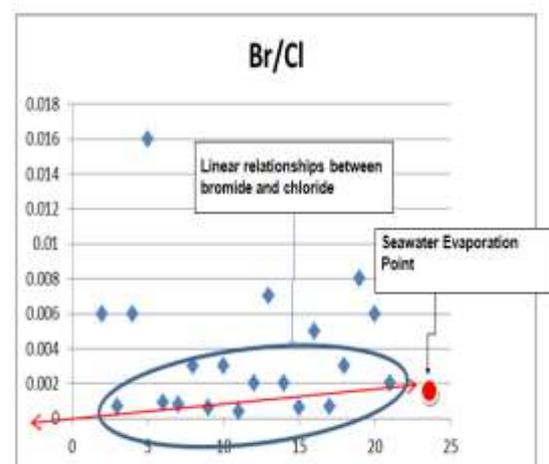
Fig. 5:   Br/Cl Ratio plot

The chemical composition of the analyzed groundwater samples within the study area are thus: Eh ranges from 0.12-9.01us/cm, Principal Component constituents (PCC) shows an order of abundance for the cations as $Na^+ > Mg^{2+} > K^+ > Ca^{2+}$, with Na^+ constituting more than 75% in most cases while for the anions the order is $Cl > HCO_3 > SO_4 > NO_3$ with Cl^- forming at least 80% in all cases, Calcium constituents vary between 0.987mg/l-90.74mg/l, Sodium concentration vary from 0.166mg/l-30360mg/l, Chloride concentration ranges from 1.85mg/l-5430mg/l, Sulphate concentration ranges from 0.94mg/l-58.3mg/l, Bromide concentration ranges from 0.03mg/l-6.13mg/l. From the Ternary and Piper diagrams (Figs.3,4.), the water samples within the study area are seen to display relative high percentage of major cations of Mg and Na with prominent anions as Cl and HCO_3. The pH values range from 4.66-10.8 in Akiri town through to Federal Government Girls' College, Keana, respectively, indicating slight to high alkalinity. Temperature range within the study area span from 29.3^O C to 41.3^O C in Aloshi and Old Awe town spring, respectively. The Total Dissolved Solutes (TDS), range between 120ppm -951ppm in Akiri and Old Awe town spring, respectively.

Ionic Abundance in Groundwater

Generally, the chemical composition of groundwater is primarily dependent on the geology as well as the geochemical processes taking place within the groundwater system. Major and minor ions in groundwater from the study area were plotted on Piper (1944) diagram in order to identify hydrochemical facies in the study area.

Major ions constitute the most significant part of the total dissolved solids present in the groundwater and the concentration of these ions in groundwater depends on geology and hydrochemical processes that place in the aquifer system (Nwankwoalo & Udom, 2011). Major ions in the groundwater present a definite spatial trend (Figs. 1 & 2). The distributions of the ionic components and relationships of the groundwater in the study area are shown in Figs.3 -5.

Distribution of Ionic Ratios

Ionic ratios of groundwaters have been often used to evaluate seawater intrusion in coastal areas (Sachez-Martos et al., 2002). Table 3 shows some selected ionic ratios and hydrochemical processes of the groundwater in the area. Results revealed that the values of the ratios gradually increase and approach the seawater value as TDS increases, which indicated increase in influence of seawater intrusion (Figs. 2 – 7). As previously noted, TDS is a perfect surrogate for Cl. Consequently, the ratio (HCO3/Cl) can be a good indicator for salinization due to seawater encroachment. Ratios of Na/Ca, indicating cation exchange reaction (Edet and Okereke, 2001), showed some mixed behaviour but it mostly increased with increase of TDS. The ratios of Na/Cl showed insignificant correlation with TDS level but they are very similar (not distinctive) to the seawater value. They decreased as TDS increased, which was derived from Cl enrichment in groundwaters due to saline water intrusion.

The Na/Cl ratios of the saline groundwater probably result from ion exchange of Na for Ca and Mg in clays, which is common in saline groundwater. In addition, the simultaneous enrichment in both ions indicates dissolution of chloride salts or concentration by evaporation process This is responsible for the relatively high Na+ and Cl- in the saline groundwater and in coastal aquifers. The dissolution of halite in groundwater releases equal concentration of Na and Cl in the solution due to dissolution of salt horizons (Uma, 1998; Ekwere and Ukpong, 1994; Tijani et al., 1996; Tijani, 2008) and coastal groundwater affected by sea water intrusion (Amadi et al., 1989; Edet and Okereke, 2001; Nwankwoala & Udom, 2008). Almost all the samples have Na/Cl molar ratio > 1, which indicates that ion exchange is the major process.

Groundwater Classification

The classification of the groundwater was done by plotting the concentrations of the major cations and anions on the Pipper-trilinear diagram (Francisco et al., 2002; Leybourne & Cameron, 2007; Sappa et al., 2014) in Figs. 6 and 7. Major ion concentrations in Meq/l for each groundwater samples are reported as percentages of the total anion and cation content (Chow, 1975; Rittenhouse, 1967).

The concentration of 8 major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, CO_3^{2-}, HCO^-_3 and SO_4^{2-}) are represented on the Piper trilinear diagram by grouping the (K^+ with Na^+) and the (CO_3^{2-} with HCO^-_3), thus reducing the number of parameters for plotting to 6. On the piper diagram, the relative concentration of the cations and anions are plotted in the lower triangles, and the resulting two points are extended into the central field to represent the total ion concentration. The degree of mixing between waters can also be shown on the piper diagram (Figs.6 and 7). The Piper diagram was developed (Piper, 1944) and used to classify the hydrochemical facies of the water samples according to their dominant ions. From these plots it is clear that some samples in the cation triangle show a tendency towards the alkaline earth compositin with others closer to the $Na^+ + K^+$ vertex, with the later indicating relationship to

volcanic activities in the the study area and highlighting enrichment in K derived from the alkaline-potassic rocks (Sappa et al., 2014).

The trilinear plots suggest that among the anions, Cl^- and HCO_3^- are having dominance with cations Na^+ and Mg^{2+} dominating. The higher concentrations of Na+ + K+ and HCO4- in the groundwater may be due to the dissolution of plagioclase feldspars in the rocks resulting in the release of these elements (Francisco et al., 2002; Leybourne & Cameron, 2007; Sappa et al., 2014).
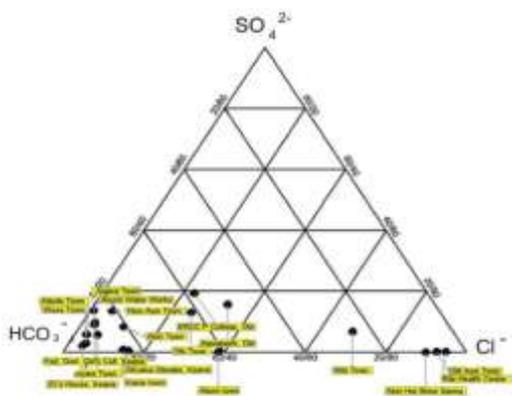
Fig. 6 : Groundwater sample location plots on ternary diagram displaying relative percentage of major cations within the study area
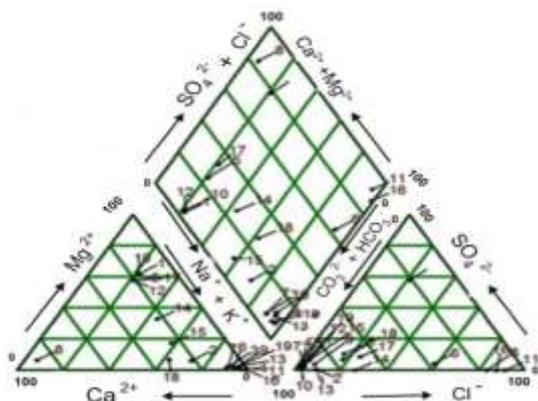
Fig 7.: Groundwater Sample Location Plots on Piper-Trilinear displaying characterization within the study area

From the plots on the Piper-trilinear diagram, the groundwaters within the study area are classified into five groups;
 i. Magnesium-bicarbonate
 ii. Calcium-chloride
 iii. Sodium-chloride
 iv. Sodium-bicarbonate and

v. Mixed types.

The Sodium-bicarbonate type of saline groundwater stood out to be the most prominent. The High concentration of Ca^{2+}, Na^+, and HCO_3^{3-} in the groundwater could be due to the dissolution of plagioclase feldspars in the rocks resulting in the release of the elements responsible for the various hydrochemical facies. Its occurrence in the aquifers within the study area may be due to the interactions between groundwater and different rocks with mineralogical compositions along the groundwater flow paths.

Carbonate weathering, which was prominently found to have operated within the study area, is usually caused by atmospheric water charged with CO_2 which further results in the formation of carbonic acid. The resultant is the release of Ca^{2+} and Mg^{2+} from the carbonate weathering into groundwater system through recharge. The weathering of carbonate minerals which is responsible for the release of the ions is expressed through equations 2, 3, 4.

Since the dissolution of carbonates and other related minerals are determined by the acidity of the environment, and having pH of 4.6 to 10.8 in the study area, it means that the acidity is generally low to slightly basic.

The reaction mechanism for carbonate within sediment, accounting for high Ca^{2+} concentration could be thus; (Freeze and Cherry, 1979).

$CaCO_3$ (s) + CO_2 (g) + $2H_2O$ (l) = Ca^{2+} (aq) + 2 HCO_3^- (aq). ……(1)
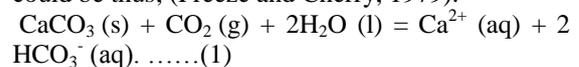
At low acid concentration, $CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$, showing that H^+ takes CO_3 away from Ca^{2+} to form the weak acid HCO_3^-.

Also the solubilty of $CaCO_3$, to an extent is determined in large part by the pH of the environment. When these carbonates dissolve in carbonic acid, eg Limestone, it equally accounts for the high Ca^{2+} concentration within the study area, thus: $CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$ …….(2)

This reaction also accounts for high bicarbonate within the study area, (110 mg/l-431 mg/l). The resultant is the release of Ca^{2+} and Mg^{2+} from the carbonate weathering into groundwater system through recharge. This ultimately accelerates the dissolution of carbonate rocks such as dolomite, limestone and gypsum along groundwater flow path.

The study area is also characterized by widespread sulphide, sulphate and coal mineralizations with mainly mineral ores like Galena (PbS), Sphalerite (ZnS), Chalcopyrite ($CuFeS_2$).FeS_2 and Baryte among others and supporting artisanal mining activities in many locations. . Polluted or acid rich waters released from the mines is a consequence of the oxidation of

sulfide minerals mainly pyrite (FeS_2), but also galena (PbS), sphalerite (ZnS), pyrrhotite (FeS), marcasite (FeS_2), arseno-pyrite ($FeAsS$), and chalcopyrite ($CuFeS_2$).FeS_2. When these minerals (like FeS_2) are exposed to water and oxygen, they become oxidized in the presence of water to sulphuric acid and ferrous hydroxide as follows;

$$2FeS_2 + 6H_2O + 7O_2 \rightarrow 4H_2SO4 + 2Fe(OH)_2 \ldots(3)$$

It is the sulphuric acid that gives the strong acidic property (Sallau, 2016). This sulphuric acid further attacks other sulphide minerals and thus breaks them down to release trace elements/metals such as Pb, As, Cd, Cu, Zn, Cr, Co, Ni, others. The stronger the acid solution, the more the metals become soluble and this continues to lower the pH.

IV. CONCLUSION

Observed characteristics and geochemical processes prevalent within the study area responsible for the high concentration of Ca^{2+}, Na^+, and HCO_3^{3-} in the groundwater which are due to the dissolution of plagioclase feldspars and ferromagnesian minerals, carbonate weathering and ion exchange reactions within the sedimentary units.

Carbonate weathering, which is usually caused by atmospheric water charged with CO_2 further results in the formation of carbonic acid. This reaction also accounts for high bicarbonate within the study area. The resultant is the release of Ca^{2+} and Mg^{2+} from the carbonate weathering into groundwater system through recharge. This ultimately accelerates the dissolution of carbonate rocks such as dolomite, limestone and gypsum along groundwater flow path.

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