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Characterization and Classification of the Saline Groundwaters within Parts of the Central Benue Trough, Nigeria

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Abstract: *The aim of this study is to characterize and classify the saline groundwaters within parts of the Central Benue Trough, Nigeria employing chemical indicators. Saline groundwater samples were collected and analyzed for a wide range of major and trace elements through Inductively Coupled Plasma Mass-Spectrometry using direct current plasma Optical Emission Spectrometry (ICP-OES). Piper/Trilinear diagram was used in classifying the groundwaters. Rock-water interaction, leaching of bed rock, carbonates weathering, oxidation of Fe-bearing sulfide minerals and silicate weathering were interpreted as major processes controlling the saline groundwater geochemistry.*

Keywords: *Central Benue Trough, Carbonate-Pyrite-Oxidation, ion-exchange reaction.*

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I. Introduction

The study area is defined by longitudes $8^{O}\ 30^{/}$E and $9^{O}\ 30^{/}$E and latitudes 8^{O} N and $8^{O}\ 30^{/}$N on a total area of about $600m^2$.

The dissolution of halite, gypsum, dolomite and calcite minerals determines Na+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} and HCO_3 chemistry in groundwaters, while others such as evaporation and ion exchange influences its composition. The contents of dissolved solids in groundwater vary highly from one location to another on earth, both in terms of specific constituents (e.g. halite, anhydrite, carbonates, gypsum, fluoride-salts, and sulphate-salts) and regarding the concentration level. The latter, often called salinity level is a convenient macro-parameter for a first general characterization of water quality. It is usually expressed as Total Dissolved Solids (TDS) – i.e. milligrams dissolved solids per litre of water, but the use of proxies such as the Chloride Content (mg/l) or the Electrical Conductivity (EC, in µS/cm) is widespread as well.

In practice, water often is classified into a number of discrete salinity classes. Number and names of classes, parameters to which class limits are linked (Total Dissolved Solids, chloride content, EC) and numerical values of class limits vary among published classifications. The occurrence of saline groundwaters (brines) has been known for a long time in parts of the Benue Trough of Nigeria. Prominent occurrences have long supported local salt production at Uburu-Okposi, Enyigba-Abakaliki and in the Ogoja-Okpoma area,in the Lower Benue Trough; Awe, Azara, Ribi, Akiri and in the Kanje area in the Middle Benue Trough [19], [20].

II. Geology of the Study Area

The Benue Trough of Nigeria is a linear NE-SW trending rift system whose development is closely associated with the separation of Africa from South America and the opening of the South Atlantic Ocean during the Cretaceous period, with its origin and evolution being fairly well documented [1], [2], [3], [5], [7], [8].

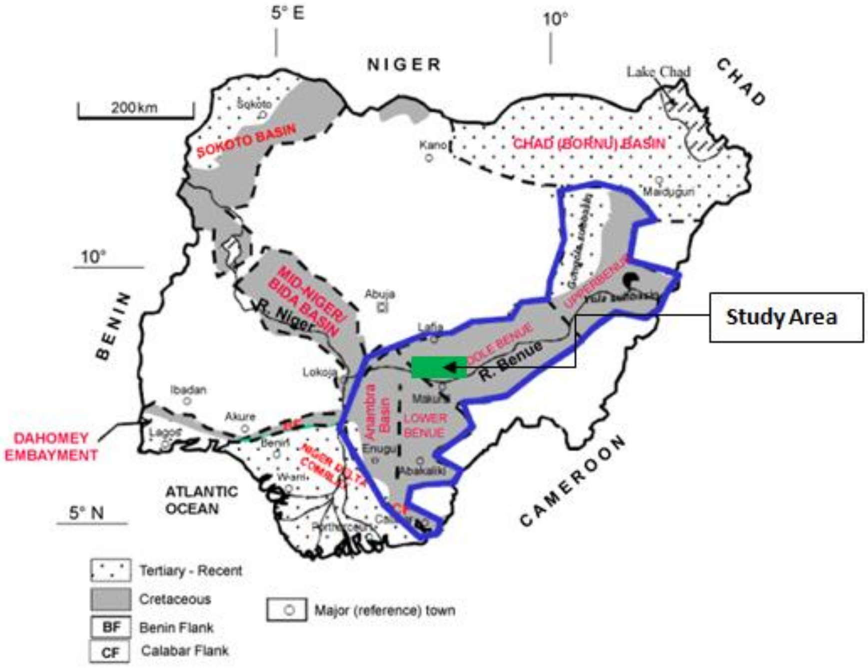


Fig.1: Geological and geographic settings of the Benue-Trough, Nigeria, [1]

The Trough is seen to consist of a series of rift basins which form a part of the Central West African Rift System. Basement fragmentation, block faulting, subsidence and rifting accompanied the opening of the South Atlantic Ocean which led to the deposition and accumulation of sediments ranging between 4000m to 6000m along the 800km axis over a width of 120km, stretching from the northern parts of the Niger Delta Basin in the south west to the fringes of the Chad Basin on the north east. Localized geological factors controlled the basin's development and are reflected in the lithostratigraphy and ages of the facies' associations [1], [5], [7], [8], [14], [19], [20], Fig.1.

The Trough consist of a long stretch of sedimentary basin running from about the northern tip of the Niger Delta Basin and terminates under the Chad Basin and sandwiched by the Basement Complex areas in the north and south of river Benue. It is filled by sediments that are Middle-Late Albian in age (Fig. 2). The oldest sediments belong to the Asu River Group and consist of shales and siltstones of marine origin, representing the first Middle Albian transgression into the Benue Trough, found at the crest of the Keana anticline to the east of Keana town (Fig. 3). It is overlain by the transitional beds of the Awe Formation, which consist of flaggy, whitish, and medium to coarse-grained sandstones which are interbedded with carbonaceous shales or clays from which brine springs issue continuously (Fig. 4). The Awe formation marks the beginning of the regressive phase of the Albian sea and is overlain by continental fluviatile sands of the Keana Formation, which is of late Cenomian to Early Turonian. The Eze-aku, Agwu and Lafia Formations are also found within the study area, which are of Turonian to Early Maestriachian. The Eze-aku Formation consists essentially of calcareous shales, micaceeous fine to medium grained friable sandstones and occasional beds of limestones. The Agwu Formation, which is Coniacianin age, consists mainly of black shales, sandstones and some coal seams. The Lafia Formation is the youngest formation in the Benue Trough, Maestrichian in age, consists of coarse grained ferruginous sandstones, red loose sand, flaggy mudstones and clays [1], [3], [8], [14], [19], [20].

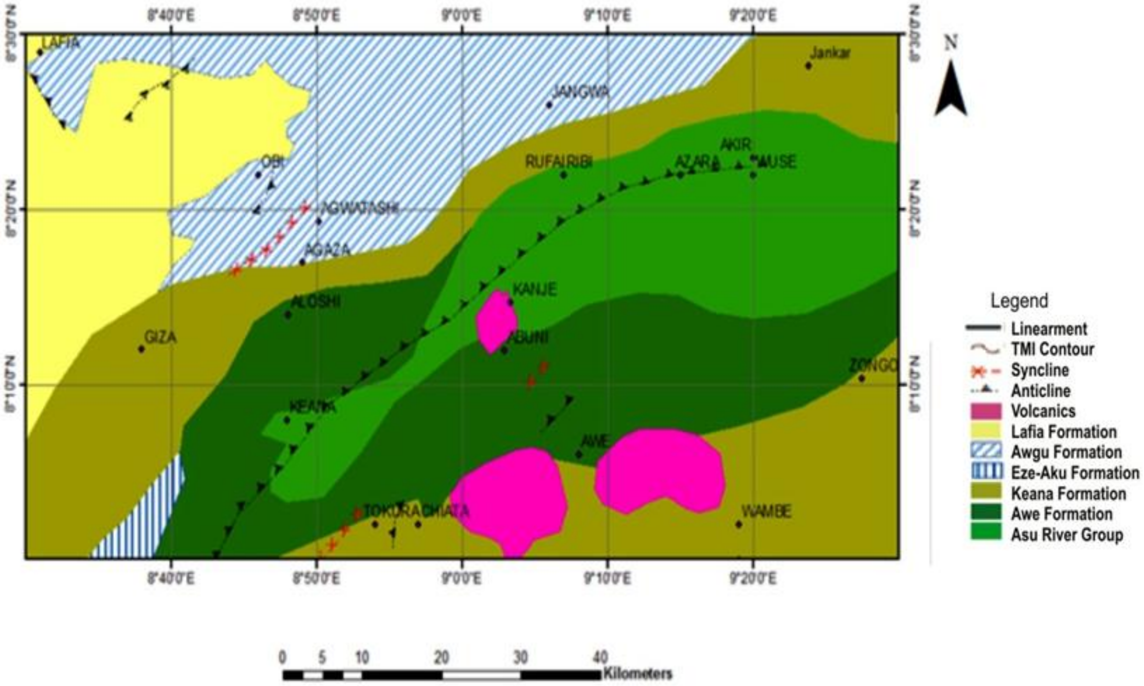


Fig. 2: Geological Map of the Study Area, [12].

Fig. 3: Crest of the Awe minor anticlinorium, Old Awe town with pockets of brine lakes and salt crystals on the sandstone series of the Keana Formation. Extreme left corner is the fold direction of the anticline.

Fig. 4: Steeply dipping sandstones of the Keana Formation, Old Awe town

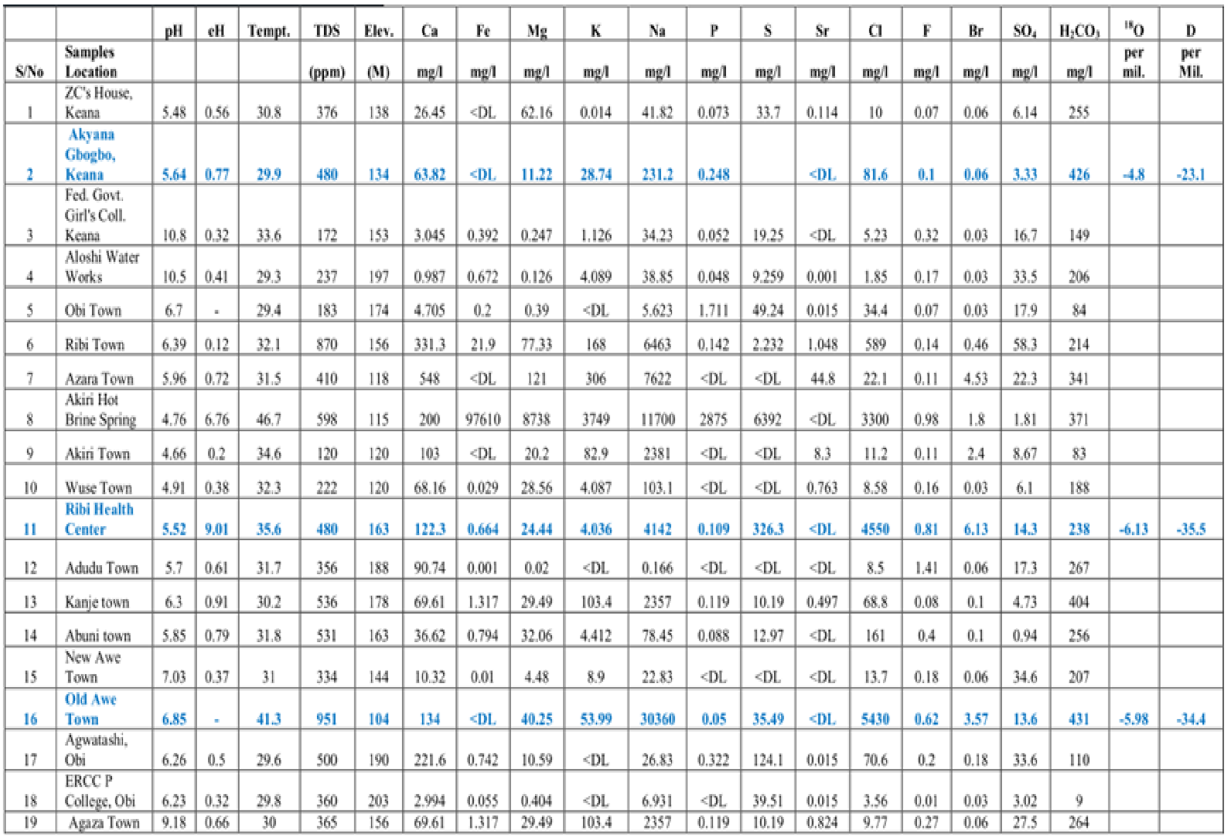
Sedimentation and stratigraphic settings are characterized by transgressive and regressive cycles, starting in the pre-Albian or mid-Albian times with the Asu-River Group, which lies directly over the Precambrian Basement and is followed by subsequent Cretaceous sediments up to the Maastrichtian. These sedimentary fills range from predominantly shale to various degrees of interlayering of moderate to well-indurated shale, mudstone, sandstone and even limestone and have been affected by two main (major) tectonic episodes during the pre-Turonian and Santonian periods. In terms of the hydrogeological setting, the saline groundwaters and brines in the Central Benue Trough are primarily confined to the predominantly shaly marine and paralic sequence of the Asu-River Group, Awe Formation (Albian-Cenomanian) and the Eze-Aku as well as the Awgu Formation (Turonian-Coniacian [1], [3], [8], [14].

III. Methodology

A total of nineteen (19) saline groundwater samples were collected for analysis. Their positions 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 PerkinElmer 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 of the saline groundwater was evaluated by means of physico-chemical analysis. Trilinear diagram of Piper was employed in the hydrogeochemical classification. Geochemical processes were studied and interpreted using.

IV. Results

Table 1: Physico-Chemical Parameters and Results



		pH	eH	Tempt.	TDS	Elev.	Ca	Fe	Mg	K	Na	P	S	Sr	Cl	F	Br	SO_4	H_2CO_3	^{18}O	D
S/No	**Samples Location**				**(ppm)**	**(M)**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**per mil.**	**per Mil.**
1	ZC's House, Keana	5.48	0.56	30.8	376	138	26.45	<DL	62.16	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**	**480**	**134**	**63.82**	**<DL**	**11.22**	**28.74**	**231.2**	**0.248**		**<DL**	**81.6**	**0.1**	**0.06**	**3.33**	**426**	**-4.8**	**-23.1**
3	Fed. Govt. Girl's Coll. Keana	10.8	0.32	33.6	172	153	3.045	0.392	0.247	1.126	34.23	0.052	19.25	<DL	5.23	0.32	0.03	16.7	149		
4	Aloshi 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	103	<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**	**480**	**163**	**122.3**	**0.664**	**24.44**	**4.036**	**4142**	**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	0.088	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**	**30360**	**0.05**	**35.49**	**<DL**	**5430**	**0.62**	**3.57**	**13.6**	**431**	**-5.98**	**-34.4**
17	Agwatashi, Obi	6.26	0.5	29.6	500	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		

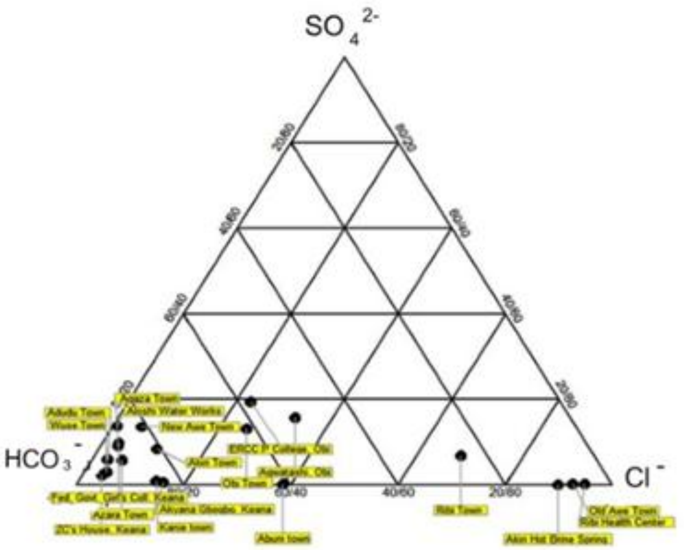


Fig. 5: Ternary diagram displaying relative percentage of major cations within the study area

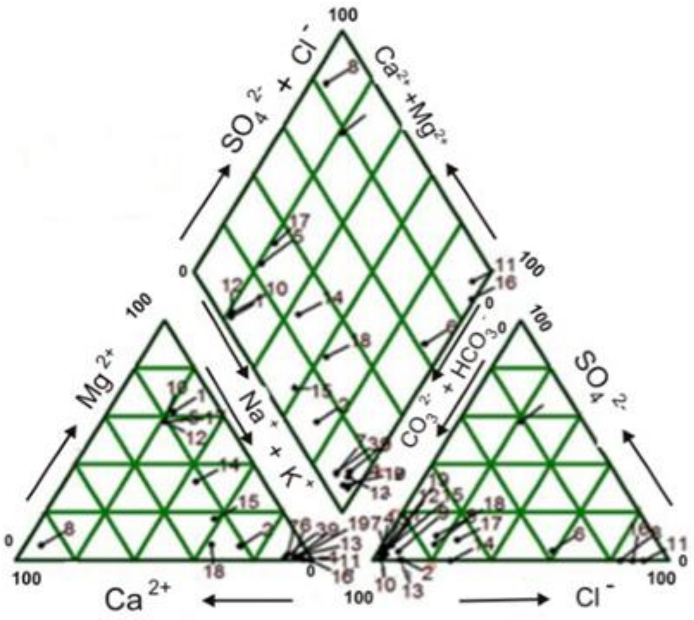


Fig. 6: Saline groundwater samples location plots on piper diagram

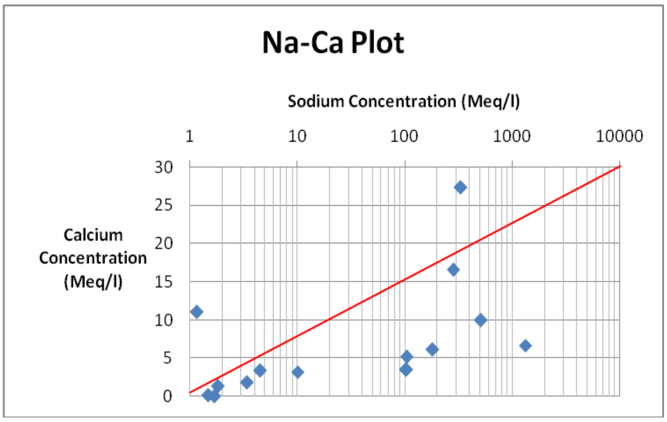


Fig. 7: Sodium-Calcium plot

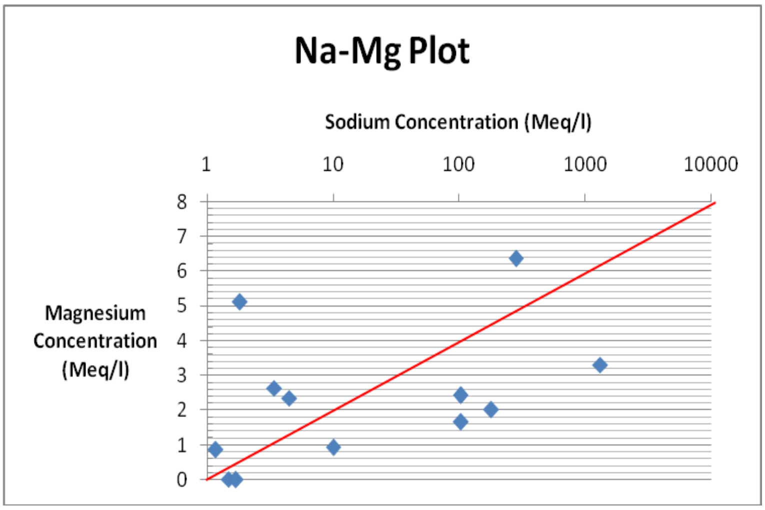


Fig. 8: Sodium-Magnessium plot

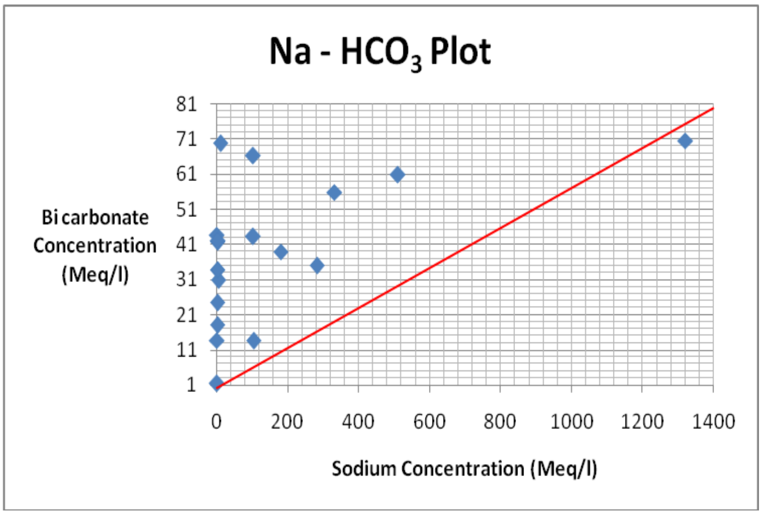


Fig. 9 Sodium-Bicarbonate plot

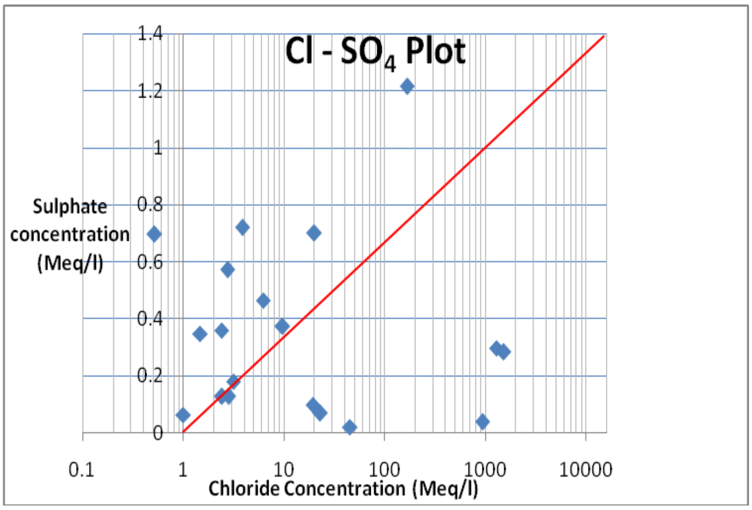


Fig. 10: Chloride-Sulphate plot

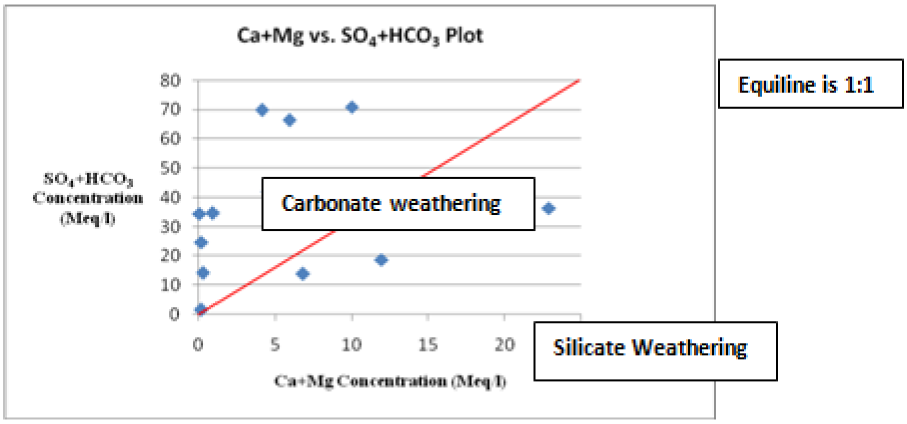


Fig. 11: Scatter diagram of (Ca + Mg) vs (SO_4 + HCO_3)

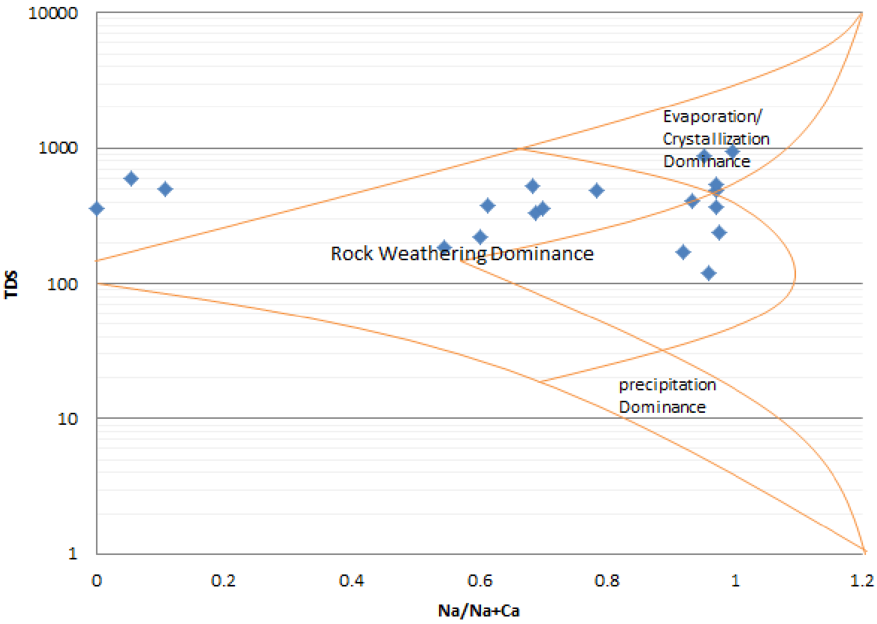


Fig. 12: Reaction Dominance Diagram [6].

V. Interpretation and Discusion

`The chemical composition of the analyzed saline groundwater samples are thus; Eh ranges from 0.12-9.01us/cm, the Principal Component Constituents (PCC) shows an order of 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 > NO_3 with Cl^- forming at least 80% in all cases (Table 1). 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. 5 ,6.), the water samples within the study area are seen to display relative high percentage of major cations of Mg and Na and the prominent anions displayed are Cl and HCO_3. The pH values as measured within the study area 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.

Classification was achieved through the study of plots of concentrations of the major cations and anions on the Pipper Trilinear diagram [4], [6], [10], [13], [15], [18. To identify the hydrogeochemical processes controlling the chemistry within the study area, the following plots were used; (Figs 7, 8, 9, 10). These plots suggest that among the anions, Cl has a clear dominance, while cations Na^+, Mg^{2+}, HCO_3^+ dominate. In Fig. 5 & 6, the plot shows that about 36.84% of the locations have Alkaline earth (Ca+Mg) minerals exceeding Alkalies(Na+K) in the following locations: Adudu, Wuse, Keana, Abuni, Obi and Akiri, [12].

According to the Piper diagram, the distribution of hydrochemical facies of groundwater within the study area could be classified into five groups, [12];

(i) Magnesium-Bicarbonate Type (Adudu Town, Zc's House, Keana, Wuse Town, Obi Town, Abuni Town) constituting about 31.05% of the studied locations.
(ii) Calcium-Chloride Type (Akiri hot spring) accounting for about 5.26%.
(iii) Sodium-Chloride Type (Ribi Town, Old Awe Town) accounting for about 15.79%.
(iv) Sodium-Bicarbonate Type (New Awe Town, Akyana Gbogbo, Azara Town, Aloshi, Akiri Town, Agaza Town, Kanje town) accounting for about 42.11%.
(v) Mixed Type (ERCC Pastors College, Obi premises) accounting for about 5.26% of the studied locations.

The Sodium Bicarbonate type of saline groundwater therefore stood out to be the most prominent.

The High concentration of Ca^{2+}, Na^{+}, and HCO_3^{3-} in the groundwater could also be due to the dissolution of plagioclase feldspars in the rocks resulting in the release of the elements responsible for the various hydrochemical facies. These elements, (Ca, Mg, Na, K, HCO_3, SO_4, Cl) are the major ions in groundwater which could have been derived from water rock interaction [4], [5], [12], [13], [18].

The Ca^{2+}-Mg^{2+}-HCO_3^- content reflect carbonate weathering in sedimentary sequences rich in dolomite and calcite. This is further supported by the fact that alkaline earths (Ca+Mg) significantly exceed the alkalis (Na+K) and weak acids (HCO_3+CO_3) exceed the strong acids. The predominance of Mg^{2+}, $SO_4^{\ 2-}$, Na+ , Cl^- and HCO_3^- in some ground waters probably reflects the influence of evaporate minerals such as dolomite, gypsum, anhydrite, calcite and halite. The relationship between HCO_3^- and Mg2+ suggests a dolomite origin for the Mg2+ and an additional source of $CO_3^{\ 2-}$, probably of calcite dissolution. Dolomite is expected to contribute Mg^{2+} and HCO_3^- + $CO_3^{\ 2-}$ to the groundwater. The relatively high content of Na^+ and Cl^- in surface water bodies and their increasing content detected in some groundwater samples suggest mixing with saline water or halite [4], [5], [12], [13], [18].

The Chemistry of the saline groundwaters suggests that alkaline earths (Ca+Mg) significantly exceed the alkalis (Na+K) and weak acids (HCO_3+CO_3) exceed the strong acids (Cl+SO_4), suggesting the dominance of CO_3 weathering followed by silicate weathering. Hydrogeochemical studies disclosed that Na+, HCO_3^- and Na+, Cl^- are the dominant ion types within the study area [11], [12].

The resultant is the release of Ca^{2+} and Mg^{2+} from the carbonate weathering into groundwater system through recharge. The weathering of calcite minerals which is responsible for the release of the ions is expressed through the following equations [10]:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (1)$$

$$\begin{gathered} CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \\ (\text{Calcite dissolution}) \end{gathered} \qquad (2)$$

$$\begin{gathered} CaMg\ (CO_3) + 2H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \\ (\text{Magnesium calcite dissolution}) \end{gathered} \qquad (3)$$

Carbonate weathering, which was prominently found to operating within the study, 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 1-5.

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;

$CaCO_3\,(s) + CO_2\,(g) + 2H_2O\,(l) = Ca^{2+}\,(aq) + 2\ HCO_3^-\,(aq)$. ……(4)

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 solubility 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: $CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$ …….(5)

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.

Gibbs [12] indicated a close relationship between water composition and the hydrochemical processes involving precipitation, water interaction and evaporation. The interpretation of the plots is viewed from Figs. 11 and 12 which indicate that most points plotted in the region of rock dominance and carbonate weathering.

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. This is with particular reference to the Awe, Azara and Keana areas where sulfide minerals are mined and waste dumps, tailings, low-grade ore, overburden and run-off mill stockpiles are disposed of, without any consideration for its potential for pollution. Polluted or acid rich water released from the mines is a consequence of the oxidation of sulfide minerals mainly pyrite (FeS_2), galena (PbS), sphalerite (ZnS), pyrrhotite (FeS), marcasite (FeS_2), arseno-pyrite (FeAsS), and chalcopyrite ($CuFeS_2$).FeS_2. When these minerals are exposed to water and oxygen, they become oxidized in the presence of water to sulphuric acid and ferrous hydroxide as follows;

$2FeS_2 + 6H_20 + 7O_2 \quad \rightarrow \quad 4H_2SO4 + 2Fe\ (OH)_2$ …(6)

It is the sulphuric acid that gives the strong acidic property. 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 [11], [16].

The classification is interpreted through the scatter plots of Na vs Ca (Fig. 7) and Na vs Mg (Fig. 8), where most points plotted above the equiline of 1:1, thus indicating reduction in Na concentration in groundwater, due to ionic exchange. In the Na vs HCO_3^- scatter diagram (Fig. 9) which indicates most plots occur above the equiline of 1:1, thus indicating increased HCO_3^- compared to Na which resulted from silicate weathering. The weathering is given by the following equation [10].

$$\begin{aligned} &2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \\ &\rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4 + 2HCO_3^- \end{aligned} \qquad (7)$$

In the scatter diagram (Fig. 9), about 90% of the samples plotted above the 1:1 equiline, thus representing carbonate weathering. Carbonate weathering may be caused by atmospheric water charged with CO_2 which further results in the formation of carbonic acid. This accelerates the dissolution of carbonate rocks such as dolomite, limestone and gypsum along groundwater flow path.

The mechanisms controlling the groundwater chemistry in the study area was interpreted from the Rock-Water interaction chart of Gibbs [6]. The Calcium source in Aloshi, Abuni and Zc's House locations were from carbonates other than gypsum. Pyrite oxidation was noted to be dominant within Akiri and Wuse areas. HCO_3/Sum Anions parameter show that Ribi, Akiri and Old Awe locations are likely sourced from Seawater while Carbonate weathering might have dominated the process that influenced the geochemistry of the remaining locations within the study area. Cl/Sum Anions parameter shows that rock weathering was the prominent process that influenced the geochemistry of the study area except for Old Awe and Ribi locations. These indicate that most areas in this study are dominantly influenced by rock weathering. It could therefore, be concluded that Ion Exchange Reactions, Pyrite Oxidation, Plagioclase and Carbonate Weathering Processes could have influenced the chemistry of the groundwater within the study area, with those from around Old Awe, Akiri and Ribi locations showing prominent traces of seawater source [12], [16], [17].

VI. Concluding Remarks

Detailed assessment and evaluation of the groundwaters within parts of the Central Benue Trough, Nigeria are presented in this study. The aim of the study was to characterize and classify the saline groundwaters within parts of the Central Benue Trough, Nigeria employing chemical indicators. The study area covered Awe-Azara-Keana areas that are characterised by occurrences of prominent saline groundwater systems. Piper's trilinear diagram was used to characterized and classify the saline groundwaters as Magnesium-Bicarbonate, Calcium-Chloride, Sodium-Chloride, Sodium-Bicarbonate and Mixed Types, with Sodium-Bicarbonate type being most prevalent.

It is indicative that rock weathering, ion exchange reactions, pyrite oxidation, plagioclase and carbonate weathering processes could have influenced the chemistry of the saline groundwaters, with those from around Old Awe, Akiri and Ribi locations showing prominent traces of seawater source.

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