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REVIEW ARTICLE

HYDROGEOCHEMICAL ASSESSMENT OF CHEMICAL COMPOSITION OF GROUNDWATER; A CASE STUDY OF THE APTIAN-ALBIAN AQUIFER WITHIN SEDIMENTARY BASIN (NIGERIA)

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ABSTRACT

The research was carried out to evaluate major source influencing chemical quality of groundwater within suburban area of Abakaliki. A total of twenty one (21) groundwater samples were collected and analyzed. Parameter analyzed were; EC, pH, TDS, Cl^-, Na^+, Mg^{2+}, NO_3^-, SO_4^{2-}, Ca^{2+}, HCO_3^-, K^+, CO_3^{2-} these parameter were analyzed using American Public Health Association standard method. Gibbs, Mg^{2+}/Ca^{2+}, End-member, Diamond field of Piper and Parson plots were used to indentify major source influencing groundwater chemistry within the study. Finding, from Gibbs plot and Mg^{2+}/Ca^{2+} against Mg^{2+}/Na^+ revealed that rock dominance is the major process that control groundwater chemistry, while End-member plot showed that silicate and carbonate weathering are the two weathering process that influence groundwater chemistry within the study area. Diamond field of Piper by Lawrence and Bal-Subramanian modified, revealed that groundwater falls within High Ca + Mg & SO_4 + Cl. Parson plot revealed that 65 % of groundwater falls within Ca - Mg – Cl water type, while 35 % falls within Ca - Mg - SO_4. Relationship between TDS vs TH plots showed that groundwater samples fall within soft - fresh water category. The results of the geochemical survey reveal major ionic components trend in other of Mg>Ca>Na>HCO3>SO4>Cl, result reveal that there is no particular trend of ions movement in groundwater.

KEYWORDS

Water-rock interaction, Plot, Weathering, Influence and Nigeria.

1. INTRODUCTION

The continuous and severe increase of water demands, due to the rapid population growth, have led to over-exploitation of groundwater and have severely depleted its chemical quality. Emphasis on groundwater potential within the study area is placed on fractured shale. Groundwater within the study area exist in fractured shale and limestone aquifers [1,2]. Recent, hydrogeochemical studies revealed presence of high calcium concentration in groundwater(s) as the source of water hardness [3-9]. A researcher assessed the effect of anthropogenic activities on water quality within Ekaeru Iyimagu area of Ebonyi state, from their findings it was observed that mining activities and improper disposal of refuges waste has resulted in decline in water quality of the area for domestic use. A group of researchers pointed out that different geologic formations has directly or indirectly influenced the origin and chemical constituents of groundwater in south-south and southeastern part of Nigeria [10,11]. Various authors have also stated that mining activities has influence on groundwater quality [12-14]. A researcher stated that unsustainable groundwater development, overexploitation, and improper management of mining waste, wastewater from mining areas causes adverse impact on quality of groundwater [15,16]. Decline in groundwater is directly or indirectly influenced by the leaching of geogenic contaminants through mining activities as a result of rock-water interaction, during the process of percolation water moves through a hydrological cycle it transfers both inorganic and organic components from soil to water thereby decreasing its chemical quality [17]. Based on a study, the hydrochemical evaluation of groundwater systems is usually based on the availability of a large amount of information concerning its chemistry [18,19]. Its chemistry depends on a number of factors, such as general geology, degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources other than water rock interaction. Such factors and their interactions result in a complex groundwater quality [20]. Several researchers further pointed out that the interaction of all factors has leads to various water facies [21,22]. Previous studies carried out on water quality within Ebonyi state revealed that the major factor that influences groundwater quality are anthropogenic activities such as mining activities and water-rock interaction. Although various studies has been carried out on hydrogeochemical assessment of water resources in Ebonyi state for domestic and irrigation use [23]. Studies have not been carried out within the study area to evaluate that influence chemical quality of groundwater within the study area. Hence the need for this research, the objectives of this paper are, first of all is to, determine factors that influence chemical quality of ground within the area of study and to know the dominant factor that influences its chemistry.

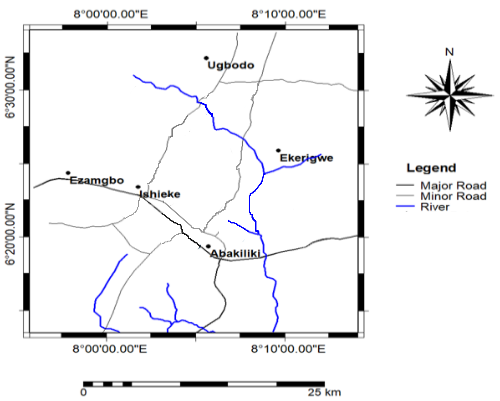


Figure 1: Location map of the study area.

2. MATERIAL AND METHOD

2.1 Study Area

The study area is located in the sub-urban area of Abakaliki, Ebonyi state, southeastern Nigeria. It lies between latitudes 6°15′ and 6°35′N and longitudes 7°40′ and 8°15′E. The area is quite accessible through a network of major roads and footpaths as shown in Fig. 1.

2.2 Vegetation and climate

The study area belongs to the rainforest region of Nigeria as described by Igbozuruike (1975). The vegetation is characterized by orchard bush of short trees with varying densities of dominant elephant grasses. Two major seasons are experienced in the area—the wet and dry season. The wet season starts from March and ends in October, while the dry season begins in November and ends in February. These two seasons are dependent on the two prevailing winds blowing across the country at different times of the year—the dry harmattan Wind, the North East Trade Wind from the Sahara Desert that prevails in the dry season, and the marine wind, the SW Trade Wind, from the Atlantic Ocean which introduces the rainy season. Temperature in the dry season and rainy season ranges from 20 to 38 °C and 16 to 28 °C, respectively. The average monthly rainfall ranges from 3.1 mm in January and 270 mm in July. The average annual rainfall varies from 1750 to 2250 mm. The climate of the area, no doubt, favours the dispersion of the resultant pollutants from the mining activities. A researcher stated that high amount of rainfall results in surface run-of that moves the pollutants and also assists percolation. The drainage pattern of the area is dendritic.

2.3 Geology and Hydrogeology of the Study Area

The Benue Trough is a linear NE–SW trending trough that is divided into three parts, namely the Upper, Middle and Lower parts [25]. Sedimentation in the Abakaliki Basin of the Lower Benue Trough started with deposition from the Asu River Group of Upper Albian age which overlies the Precambrian Basement Complex rocks disconformably as shown in Table 1. The Asu River Group consists of Abakaliki Shale with volcano clastics, sandstone and sandy limestone lenses [26]. The Asu River Group is overlain by the Eze-Aku Formation of Turonian age. This formation consists of flaggy, grey or black shales with sandstones and subordinate limestone [27]. An alternating sequence of thick limestone or sandstone units occurs with calcareous shales in places where the Eze-Aku Formation is found [28]. The hydrogeology of the study area is typified by poor aquifer conditions. This is a result of the dominant shale units (Aquiclude) which are neither porous nor permeable and do not transmit water to wells found in the area. A researcher further pointed out that groundwater on a regional scale is impossible to find. However, conditions for the presence of groundwater may occur at weathered/fractured zones or at points of sandstone intercalations. The structure and hydrogeology of the fractured aquifer in the study area are typical of a multilayer complex system. Obviously, due to drilling distribution on aquifer. The depth of groundwater within the aquifers ranges from 30 to 80 m, while static water level within the study area ranges from 3.5 to 98 m respectively for Asu River Group. As water bearing formation within the study area exists in fractured shale and limestone. The major sources of water are stream, hand-dug well, manual borehole and motorized borehole

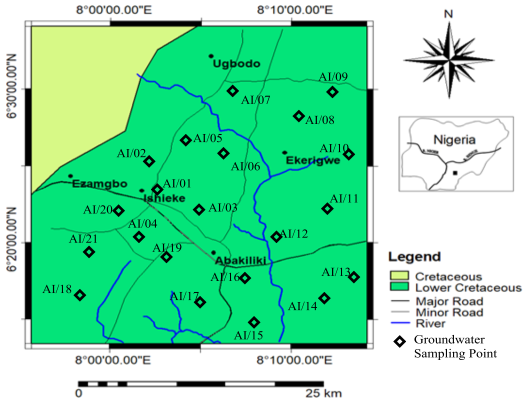


Figure 2: Geology Map of the Study area Showing Groundwater Sampling points

Table 1: Lithostratigraphic framework of the Southern Benue Trough showing the position Aptian and Albian Age, Lower Cretaceous

AGE		STRATIGRAPHIC UNIT		BASIN CYCLE
Tertiary	Oligocene - Pliocene	Benin Formation		Niger Delta Basin
	Eocene	Ameki / Agbada Formation		
	Paleocene	Imo/Akata Formation		
Upper Cretaceous	Danian	Nsukka Formation		Anambra Basin
	Maastrichtian	Ajali Sandstone Mamu Formation		
	Campanian	Nkporo Group	Afikpo SS/Nkporo Sh/ Owelli SS /Enugu Sh.	
	Santonian	Unconformity (due to erosion and non-deposition)		Tectonic uplift and folding
	Coniacian	Awgu Group		Southern Benue Trough
	Turonian	Eze- Aku Group	Amasiri Sandstone Eze- Aku Shale	
	Cenomanian	Odukpani Fm		
Lower Cretaceous	Albian	Asu River Group	Abakaliki Formation	
	Aptian		Mamfe Formation	
PRECAMBRIAN BASEMENT COMPLEX				

3. METHOD

Twenty one (21) water samples were randomly collected from boreholes see (Fig. 2). Sampling was carried out during the dry season when there was a decrease in the water level and the concentration of cations and anions were more stable. Though the study area consists of two geology formation, groundwater sampling was carried within the Asu River Group. Precautionary measures were taken by washing the bottles with clean water, and cleaning reagents and thoroughly rinsing with distilled, de-ionized water prior to collection of water samples from the site. The samples were analyzed for eleven parameters, namely pH, electrical conductivity, total dissolved solids, magnesium, calcium, chloride, nitrate, sulphate, potassium, sodium and bicarbonate following APHA, 2012 standard (Table 2).

Table 2: Methods used to analyze physicochemical parameters

S/No	Parameters	Analytical Method
1	pH	pH meter Hach sensION + PH1 portable pH meter and Hach sensION + 5050 T Portable Combination pH Electrode
2	Electrical Conductivity (EC)	HACH Conductivity
3	Total dissolved solids (TDS)	TDS meters (model HQ14D53000000, USA).
4	Magnesium (Mg^{2+})	EDTA titrimetric method
5	Calcium (Ca^{2+})	Titrimetric method
6	Chloride (Cl^-)	Titrimetric method
7	Nitrate (NO_3^-)	Ion-selective electrode (Orion 4 star)
8	Sulphate (SO_4^{2-})	Turbidimetric method using a UV-Vis spectrometer
9	Potassium (K^+)	Jenway clinical flame photometer (PFP7 model)
10	Sodium (Na^+)	Jenway clinical flame photometer (PFP7 model)
11	Bicarbonate (HCO_3^-)	Titrimetric method

Table 3: Results of Physicochemical Parameters

Sample No	EC µS/cm	pH	TDS mg/L	Cl^- meq/L	Na^+ meq/L	Mg^{2+} meq/L	NO^{3-} meq/L	SO_4^{2-} meq/L	Ca^{2+} meq/L	HCO_3^- meq/L	K^+ meq/L	CO_3^{2-} meq/L
AI/01	263	7.4	392	0.38	0.17	0.09	0.65	0.49	0.19	1.02	0.29	1.03
AI/02	1042	6.9	559	0.11	1.05	0.14	0.19	0.01	0.39	2.49	0.06	1.58
AI/03	291	7.1	68	0.59	0.64	1.40	1.00	0.37	0.01	1.39	0.01	1.65
AI/04	404	7.8	103	0.31	0.03	0.03	0.25	1.39	0.29	0.50	0.13	1.27
AI/05	938	7.0	494	0.10	0.11	0.00	0.85	0.57	0.18	1.44	0.87	1.09
AI/06	848	6.8	135	0.25	0.06	0.17	0.06	0.03	0.03	0.92	0.06	1.51
AI/07	72	7.2	99	0.83	0.19	0.16	0.32	0.19	0.06	0.84	0.96	1.99
AI/08	125	6.8	569	0.17	0.04	0.22	0.05	0.72	0.28	1.03	0.18	1.87
AI/09	203	7.5	602	0.95	0.15	0.17	0.83	0.08	0.19	0.94	0.56	1.03
AI/10	127	7.7	394	1.43	0.00	1.40	0.05	0.35	0.02	0.99	0.64	1.59
AI/11	1022	7.1	416	0.09	0.09	0.04	0.20	0.01	0.38	1.03	0.88	1.83
AI/12	293	7.3	69	0.78	0.83	0.25	0.49	0.02	1.22	0.58	0.16	1.04
AI/13	144	6.8	91	0.86	0.27	0.08	0.55	0.06	0.38	1.49	0.71	1.36
AI/14	593	7.4	242	0.49	0.16	0.10	0.19	0.03	0.47	2.01	0.48	1.59
AI/15	602	7.1	495	0.70	0.39	0.04	0.22	0.01	0.91	1.49	0.91	1.89
AI/16	1032	6.7	502	0.14	0.17	0.07	0.30	0.17	0.49	1.92	0.10	1.08
AI/17	494	7.5	169	0.05	0.16	0.61	0.96	1.20	0.52	2.30	0.49	1.22
AI/18	830	7.9	304	0.04	0.13	0.21	1.42	0.02	0.48	1.90	0.22	1.96
AI/19	294	6.9	193	0.17	0.26	0.30	0.59	0.04	0.50	0.83	0.74	1.50
AI/20	103	7.1	85	0.18	0.01	0.17	0.11	0.19	0.80	2.11	0.28	1.99
A/21	207	6.3	92	0.03	0.02	0.29	0.43	0.01	0.33	1.03	0.05	1.74
Min	72	6.3	68	0.03	0.00	0.00	0.05	0.01	0.01	0.50	0.01	1.03
Max	1042	7.9	602	1.43	1.05	1.40	1.43	1.39	1.22	2.49	0.96	1.99
Mean	480.04	7.15	293.17	0.43	0.26	0.31	0.31	0.32	0.40	1.35	0.42	1.51

4. DISCUSSION

4.1 pH

pH is a term used universally to express the intensity of the acid or alkaline condition of a solution. From the Table 3, the measured pH is found to be slightly acidic to basic and ranges from 6.3 to 7.9 with mean value of 7.15 as shown in Table 3. Various factors are responsible for change in pH value. It is important to highlight the mechanism of processes taking place in this area, When water is in equilibrium with both CO_2 from the atmosphere and carbonate containing rock, the resultant solution will be a buffer with a pH of 8.3, this is close to the pKa of the weak acid bicarbonate ion HCO_3^- (pKa = 8.4). This will resist further changes in pH to any added acid or base. This is a natural mechanism for balancing the considerable dissolution of lime from the underlying formation and precipitation of lime from the water body [29]. Omo-irabor, further stated that groundwater pH varies depending on the composition of the sediments that surround the travel pathway of the recharge water infiltrating to the groundwater and also due to prolong stay in particular rock that serves as aquifer which host the water, the longer the stay, the larger the rock water interaction.

4.2 Total Dissolved Solid (TDS)

The water samples were classified with regard to total dissolved solids (TDS). The results of geochemical analysis (Table 3) indicated that Total dissolved solids (TDS) ranged from 68 mg/L to 602 mg/L with mean value as 293.73 mg/L. Table 4 shows that sampling points within the study area falls within freshwater category. The sources of material in TDS can come from nature, i.e. geological condition and seawater, and from human activities, i.e. domestic and industrial waste and also agriculture [30-32].

Table 4: Classification of water samples

Quality Parameter	Range	Classification	Water Type (Groundwater)	Reference
TDS (mg/L)	<1000	Fresh Water	AI/01 to 21	Freeze and Cherry (1979)
	1000 – 10000	Brackish Water		
	10000- 10000	Saline Water		
	1000000	Brine		

4.3 Electrical Conductivity (EC)

EC is one of the important water quality parameters that shows the ability of electrical current in the water. Electrical conductivity in water is due to ionization of dissolved inorganic solids minerals, salts, metals, cations or anions that dissolved in water. EC values of the water samples ranged from 72 to 1042 µS/cm with mean value of 480.04 µS/cm as shown in Table 3.

4.4 Major Factors Influencing the Groundwater Chemistry

4.4.1 Work Rock Interaction

Gibbs plots are useful for determining the major mechanisms controlling water chemistry and are widely used in studies of the relationships between water chemical composition and climate or geological characteristics. It is represented as plots of TDS versus $Na^+/(Na^+ + Ca^{2+})$ and TDS versus $Cl^-/(Cl^- + HCO_3^-)$, and the controlling hydrochemical mechanisms can be divided into three zones: evaporation, precipitation, and water rock interaction [33]. Most groundwater samples were plotted in the middle of the diagram except for samples AI/03 and 07 that is been influenced by precipitation. (Fig. 3), indicating that rock weathering is the primary factor controlling the groundwater chemistry. In addition to the Gibbs diagram, the ratio of Mg^{2+}/Na^+ and Mg^{2+}/Ca^{2+} can also be used to determine whether evaporation and rock interaction are likely to be influencing groundwater quality [34]. A Gibbs diagram and Mg^{2+} / Na^+ versus Mg^{2+} /Ca^{2+} diagrams were applied to the data obtained in this study and the results' area is shown in Fig. 3a, b, respectively. These diagrams suggest that rock weathering is the main mechanism controlling the chemical constituents of groundwater in the study area. An important process of water rock interaction is mineral dissolution and the assessment of ionic meq/L ratios can indicate which minerals are likely to have the largest influence on groundwater quality.

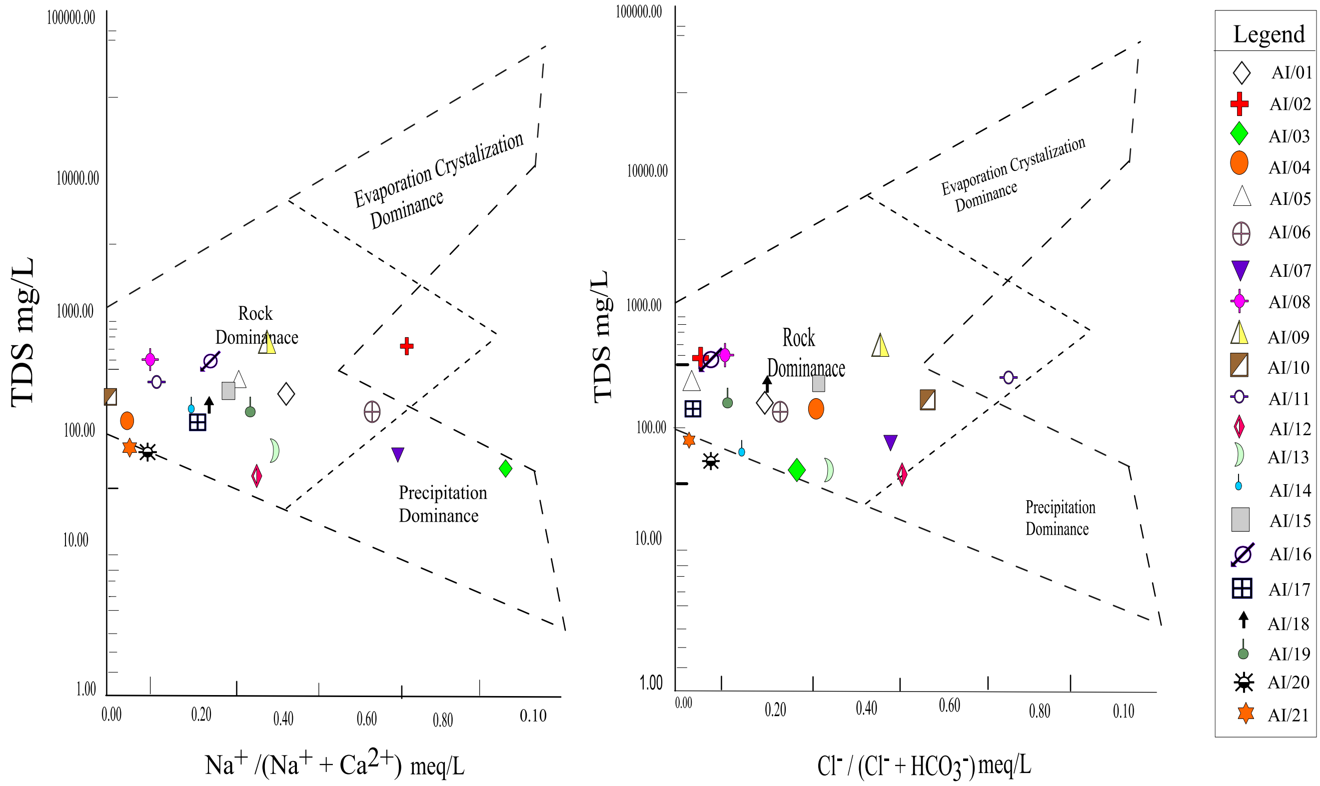


Figure 3: (a) Gibbs diagram for groundwater samples of the study area

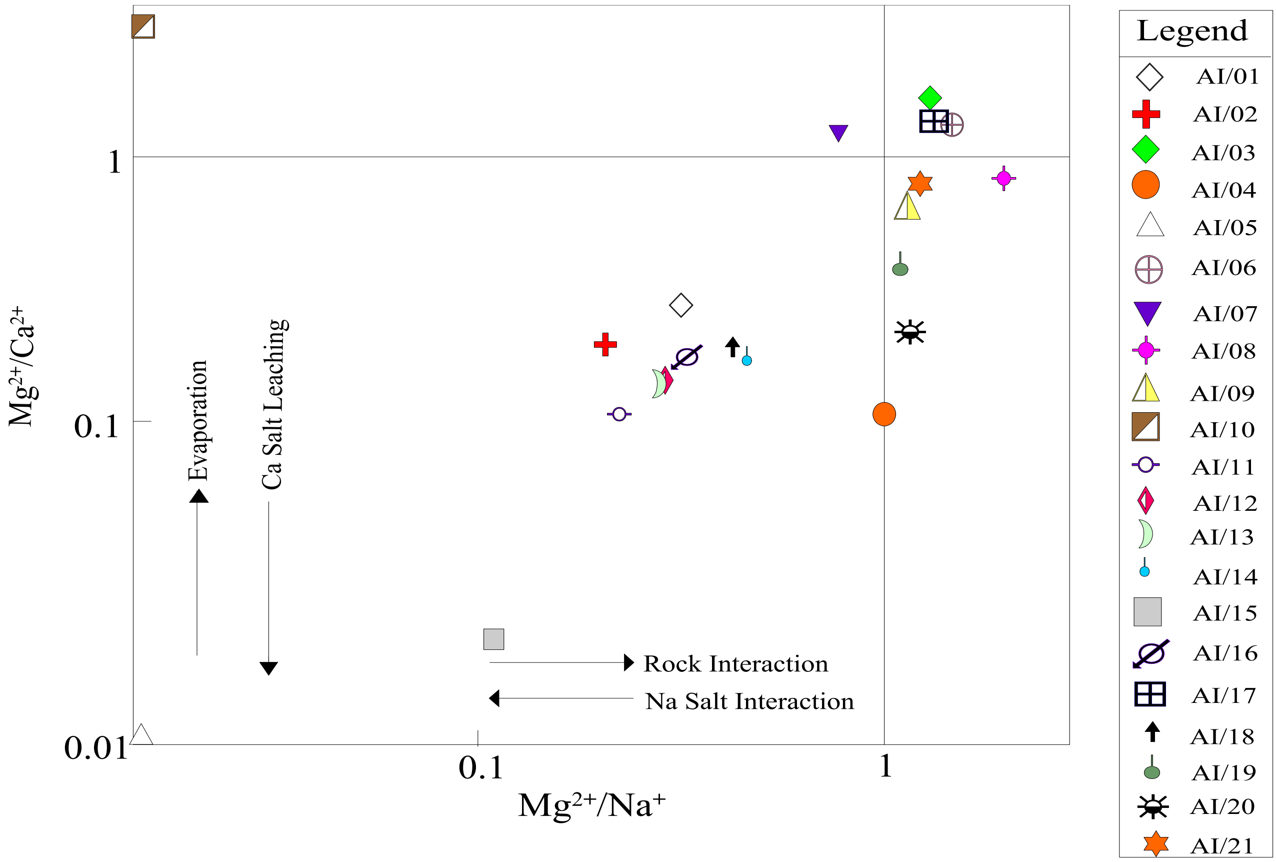


Figure 3: (b) Plot of Mg/Ca versus Mg/Na of the study area

A researcher stated that End-member diagram can be used to analyze and determine the types of rock-weathering sources related to the hydrochemical characteristics of groundwater in the study area [35,36]. Same researcher further identified the following chemical composition of $Ca^{2+}/Na^{+} = 0.35 \pm 0.15$, $Mg^{2+}/Na^{+} = 0.24 \pm 0.12$ and $HCO3^{-}/Na^{+} = 2 \pm 1$ for the silicate end member, and $Ca^{2+}/Na^{+} = 50$, $Mg^{2+}/Na^{+} = 10$ and $HCO3^{-}/Na^{+} = 120$ for the carbonate end member. Fig. 4, shows that the 99.9 % groundwater chemical composition originates from the weathering of carbonate and silicate. Silicate dissolution has influence on carbonate weathering as shown in Fig. 4.

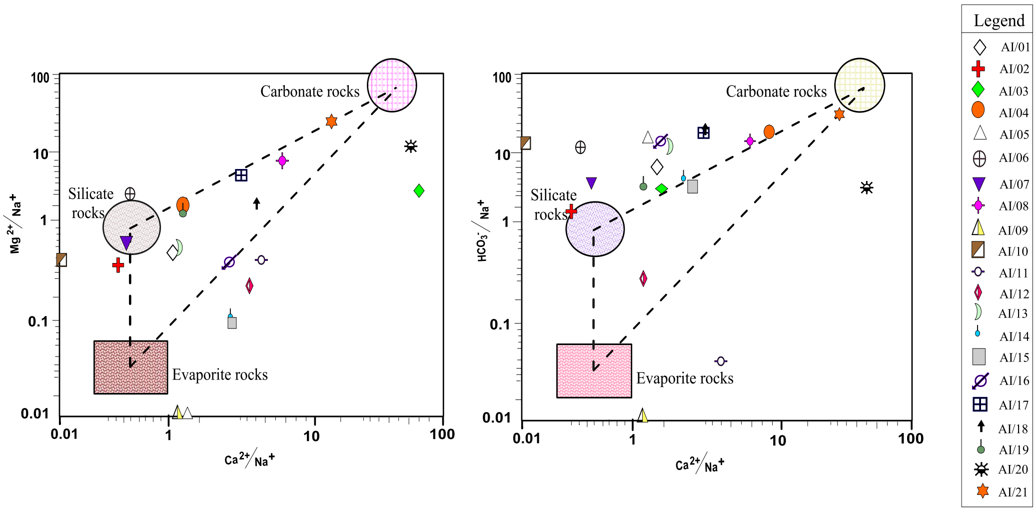


Figure 4: End-member plot for groundwater samples of the study area

The water classification of hydrogeochemical facies of Piper diagram was reconstructed by a group of researchers in the new reconstructed diamond field (Fig. 5) [37]. It classified water in the various zones on the basis of various reactions occurring in the groundwater aquifer system. The reconstructed diamond field shows that groundwater sample falls within High Ca + Mg + SO₄ + Cl hydrogeochemical facies as sown in Fig. 5. This implies that, Ca and Mg, are the primary courses of hardness in water. Any water with high Ca + Mg is said to be hard.

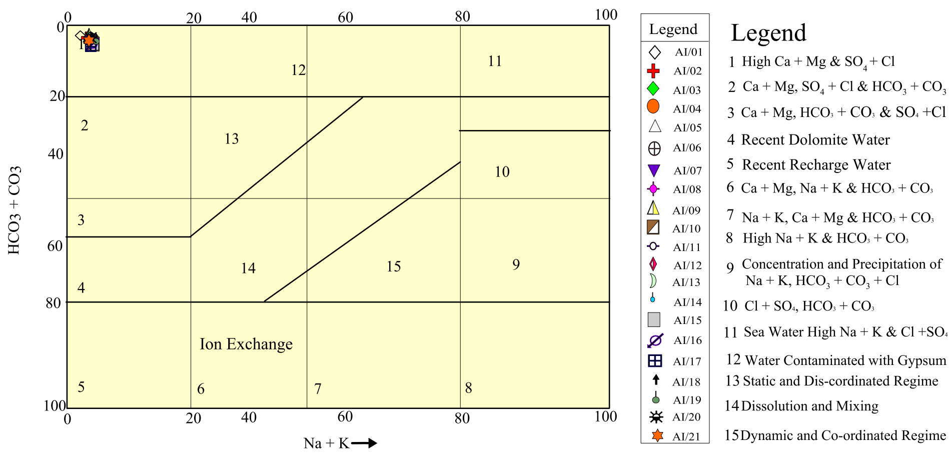


Figure 5: Classification of Hydrogeochemical Facies (Reconstructed Diamond field of Piper by Lawrence and Bal-Subramanian, 1994) of the study area

From Fig. 6. It was observed that groundwater falls within three water type; Na - S04, Ca - Mg – S04 and Ca –Mg – Cl water type. That implies that groundwater is of different origin.

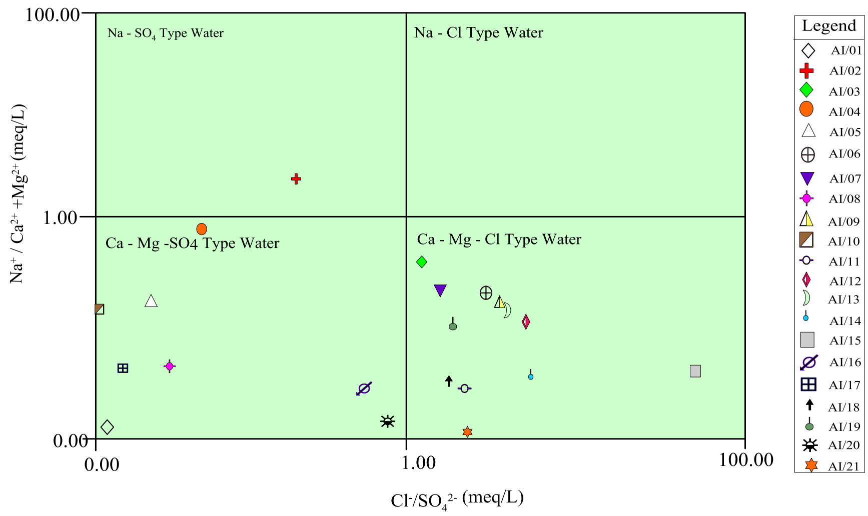


Figure 6: Parson's Plot Modified of the study area showing ground water origin.

4.5 Hydrogeochemical facies of Groundwater

A The Piper, (1944) diagram is very useful in determining relationships of different dissolved constituents and classification of water on the basis of its chemical characters [38-44]. The triangular cationic field of Piper diagram reveals that Ca + Mg + HCO3 are the dominant ionic specie. It also reveals that geochemical zone of the groundwater in the study area are magnesium bicarbonate type and that the alkaline earth exceeds the alkaline in the groundwater see Fig. 7. However, from the Scholler diagram. It shows a hydrogeochemical trend of Mg>Ca>Na>HCO3>SO4>Cl. The result also reveals that there is no particular trend of ions movement in groundwater, this implies that the groundwater is not of the same origin as shown in Fig. 8 and 9.

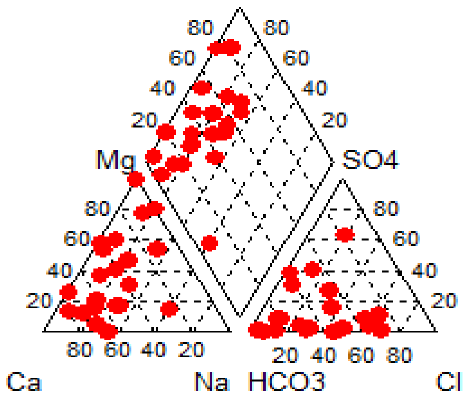


Figure 7: Piper diagram of groundwater samples of the study area.

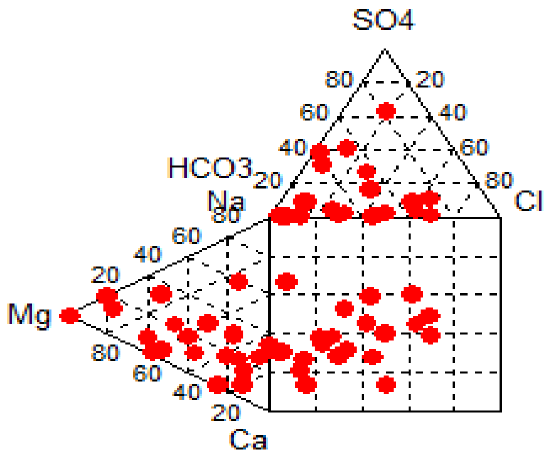
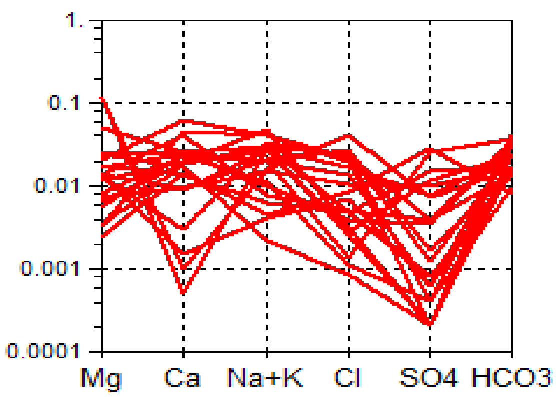


Figure 8: Durov Plot of the Study area.



Note: Concentrations are meq/L

Figure 9: Scholler Diagram of the Study Area.

5. CONCLUSION

The presented research helps to establish factors that influence chemical quality of groundwater within the study area and its environs, Ebonyi state southeastern Nigeria. From the analysis, it was observed that pH ranges from 6.3 - 7.9 hence, classified as slightly acidic to basic, TDS ranges from 68 - 602 mg/L, the value range shows that groundwater is of fresh water category, TH ranges from 2.8 - 73.5 mg/L, sampled points were classified as soft water category, EC ranges from 72 -1042 us/cm . Chemical quality of groundwater was evaluated using the following models; Gibbs plot, Mg^{2+}/Ca^{2+} against Mg^{2+}/Na^{+}, End-member plot, Diamond field of Piper modified after Lawrence and Balasubramanian, and Parson plot. Gibbs plot, Mg^{2+}/Ca^{2+} against Mg^{2+}/Na^{+} revealed that groundwater is highly influenced by rock dominance, two major that of weathering process was observed to influence groundwater, these are silicate and carbonate weathering, Diamond plots showed that groundwater is of High Ca + Mg & SO_4 + Cl type, while Parson plot revealed that 65 % of groundwater falls within Ca - Mg – Cl water type, while 35 % falls within Ca -Mg - SO_4. Diamond field Piper modified after Lawrence and Balasubramanian, and piper plots showed that groundwater(s) are of various origin. The results of the geochemical survey reveal major ionic components trend in other of Mg>Ca>Na>HCO3>SO4>Cl, result reveal that there is no particular trend of ions movement in groundwater.

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CONFLICTS OF INTEREST

The author declares no conflicts of interest regarding the publication of this paper.

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