<u>Original Research Article</u>

Characterization of Dominant Hydrogeochemical Processes inGroundwater in Onitsha Area, Southeastern Nigeria.

ABSTRACT

The characterization of the dominant hydrogeochemical processes in groundwater in Onitsha area, southeastern Nigeria was carried out to assess the chemistry of the water and identify the dominant hydrogeochemical processes and mechanisms responsible for the evolution of the chemical composition of the water sources. A total of fifteen (15) groundwater samples were collected from different locations in the study areain August 2022 and these samples were subjected to chemical analysis using standard methods.The results indicated that the water quality parameters were within the World Health Organizationacceptable limits for drinking quality though turbidity in some of the samples exceeded the guideline values.The hydrochemical facies were determined using various plots. The Piper diagramsindicated that Ca^{2+} - Mg^{2+} - Cl^{-} – $SO_4^{2-}$was the dominant facieswith Ca^{2+} and Cl^{-} as the dominant ions. Also, the Durov diagram classified the water aswater related to recharge water in limestone and sandstone aquifers and water associated with important ion exchange reactions. However, the Gibbs plots mainly plotted in the rock dominance zone indicating that the major processes controlling water chemistry in the study area was water-rock interaction and dissolution of rock minerals.Furthermore, the ionic ratio plotswere employed to determine the mechanisms and reactions prevalent in the study area that influenced the water chemistry.**T**he Na/Cl plot indicated that the excess of Cl^{-} over Na^{+} is balanced by Ca^{2+} and Mg^{2+} while the depletion of Na^{+} with respect to Cl^{-}indicated ion exchange reaction which could be attributed to silicate weathering.The relative abundance of anionic facies shows that Cl + SO_4 were more abundant than $HCO_3$and the plot of Ca + Mg ions against HCO_3 ions depict samples with excess Ca + Mg. However, Ca +Mg/HCO_3 ratio was less than one (<1) and indicated fresh recharge water.

Keywords: Hydrogeochemistry, Hydrochemical facies, Geochemical processes, Water chemistry and Rock-dominance

1.0. Introduction

Groundwater has immensely become an important water supply in urban and rural areas in both developed and developing nations for domestic, industrial and agricultural purposes (Ramkumar et al., 2010; Olayinka et al., 1999). Groundwater is replenished from precipitation and surface run-off. The dominant role of groundwater is clear and its uses and protections are, therefore, of paramount importance to human life and economic activity. In any hydrogeological setting, surface water and groundwater are the main sources of water supply. These sources of water are prone to contamination and pollution by geogenic and anthropogenic activities (Kurwadkar et al., 2020, Okolo et al 2017).

The chemistry of groundwater is afunction of the mineralogical structure in the aquifer, the composition of the recharge water, the residence time, the length of the flow path and the chemical processes in the environment (Baghdadi *et. al.,* 2019; Siddique *et. al.,* 2020). Geochemical processes taking place inside the groundwater system include dissolution, percolation, precipitation, and cation exchange (Ezzeldin, 2023). These phenomena happen together with the groundwater flow direction and depend on the residence time and recharging capacity that controls the chemical composition of the groundwater system. Groundwater chemistry is affected by many issues, including the quality of infiltrated water, the geological nature of the aquifer rocks, the decay of organic matters, partial pressure of soil carbon dioxide and various anthropogenic factors.The interaction of these factors results in various water types (Apello and Postman, 2005). The groundwater chemistry depends on different hydrogeochemical processes that the groundwater undergoes over space and time.Thus, hydrogeochemical composition ofgroundwater can be indicative of the origin and history ofits spatial flow.It has been shown that the geochemicalprocesses are responsible for the seasonal and spatialvariations in groundwater chemistry (Olea-Olea *et al.,* 2022).Evaluation of the groundwater chemistry anddelineation of various hydrogeochemical processes thatare involved in the evolution of groundwater qualityusing various conventional graphical methods andinterpreting different indices were carried out by Elango *et al*.,(2003). Theyreported that hydrogeochemical processescontrol the chemical composition of groundwater and concluded that the character of groundwater in differentaquifers over space and time is an effective tool insolving different geochemical problems. The dissolution of minerals and other anthropogenic activities have been identified as important processes controlling the hydrogeochemistry of Polar River basin (Rajmohan and Elango, 2006). Additionally, the studies of the major ions have been used to identify the hydrochemical facies of water. Also, evaluation of groundwater chemistry and hydrogeochemical consideration has been carryout by various researches by developing geochemical modelling and adopting graphical method for the interpretation of water quality parameters (Mondal *et al.,* 2010, Wanda *et al.,* 2011, Okolo *et al.,* 2020). Thus,knowledge of hydrogeochemical processes that controlgroundwater chemical evolution could lead to improvedunderstanding of hydrogeochemical characteristics of anaquifer. This could contribute to sustainabledevelopment of water resources and effectivemanagement of groundwater as a resource.

Piper (1944), proposed an effective graphic procedure to segregate relevant analytical data to understand the sources of the dissolved constituents in water. This procedure was born under the statement that most natural waters contain cations and anions in chemical equilibrium.According to the location of the sample, the hydrochemical facies can be identified(Nwankwoala and Udom, 2011). The facies are the diagnostic chemical aspect of water solutions occurring in the hydrologic systems. The Durov plot is a composite plot based on the percentage of major ion miliequivalent and two (optional) additional water quality parameters (Durov, 1948). The Durov plot also allows for the direct comparison of two other groundwater parameters, typically pH and the total dissolved solids (TDS) or electrical conductivity.
This study focuses on investigating the major hydrogeochemical aspects of groundwater chemistry and processes responsible for groundwater chemical composition in Onitsha area.

Location and Accessibility of the study area

The study area is located between latitudes 6°10′0″N and 6°7′0″N, and longitudes 6°46′30″E and 6°48′30″E. The area includes the following communities; Fegge, Odoakpu, Woliwo, Awada, Obosi, and Okpoko all in Onitsha area. The area is easily accessible throughmajor, minor and track roads (Figure.1). It is located on the eastern bank of the Niger River, in Anambra State, Nigeria. It is a metropolitan city with great prospects for economic and commerce activities. Two major climatic seasons namely the rainy and the dry season control the study area. The rainy season is from April to November, while the dry season is from December to March. The rainy season is characterized by high rainfall amount and good groundwater recharged because of good porosity and permeability of the geology formations. However, the study area is underlain by alluvium deposit at the bank of the river Niger, the Ameki Formation comprising mainly Nanka Formation and Nsugbe Formation in the northern parts of the study area and the Ogwashi-Asaba Formation in the southern parts of the study area. The Nanka Formation is mainly sand and minor calcareous clay or mud with heterolith (Nwajide, 2013, Ekwenye*et al.*, 2014). The Nsugbe Formation is predominantly sands with some conglomerate bands (Nwajide, 2013). Also, the Ogwashi-Asaba Formation comprises alternating coarse sands, silts, and clays with thin to thick lignite seams (Kogbe, 1976, Nwajide, 2013).

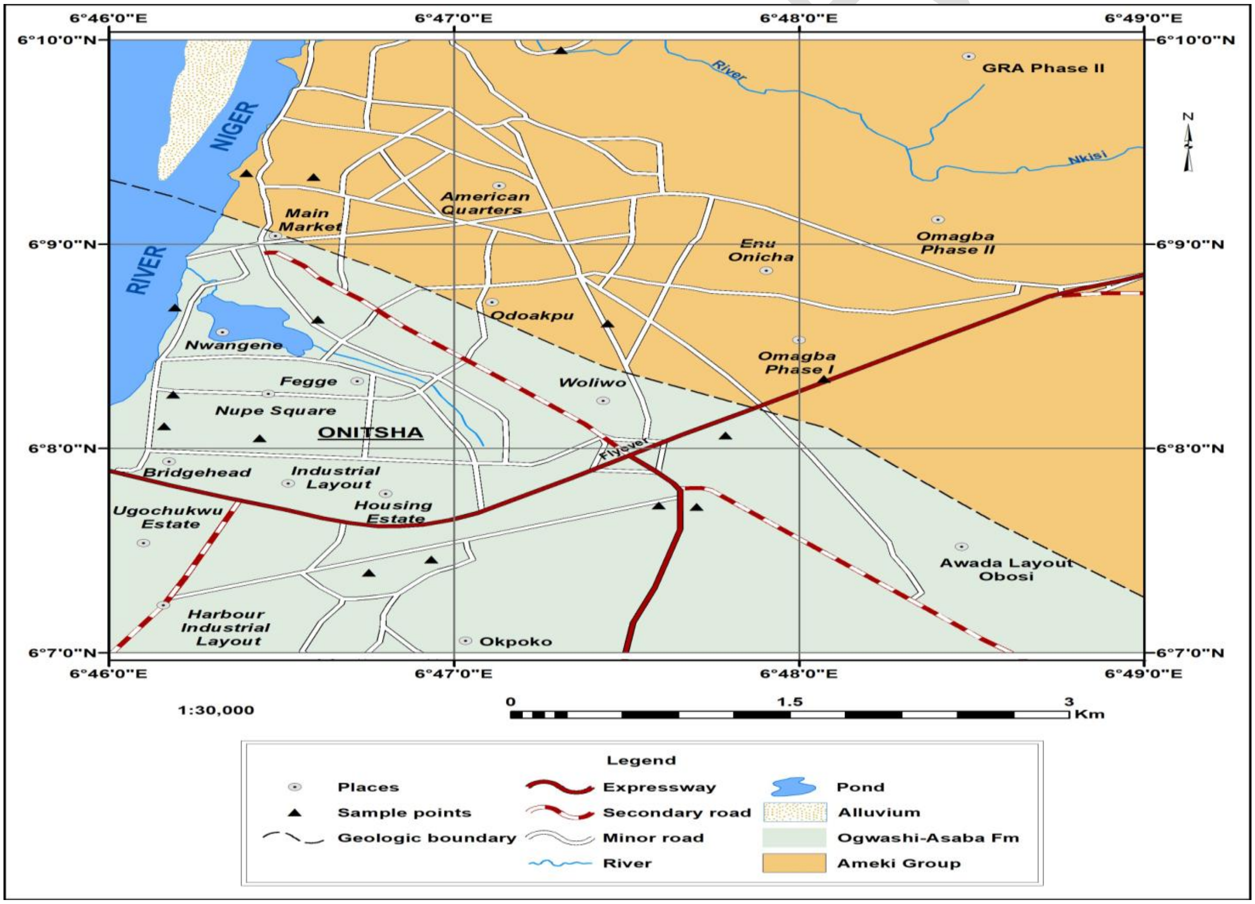


Fig. 1: Geologic and water sample location map of the study area

2.0. Materials and Methods

A total of fifteen (15) water samples were collectedfrom groundwater sources in the study area. The samples were collected in duplicates with a one-liter bottle at every sampling point. One batch of the samples was filtered, acidified and labelled Awhile the second batch of the samples wasneither filterednor acidified and were labelled B. The samples labelled A were used for cation analysisand the samples labelled B were used for anion analysis.The bottles were previously washed and were later rinsed three times using the sample water before collecting the actual samples. In order to collect groundwater samples, the taps were opened and allowed to run for about fiveminutes to ensure that the water standing in the plumbing column were removed before collecting the sample.This is to ensure that representative samples were collected. After collection, the sample bottles were corked immediately to prevent any chemical deterioration.The samples bottles were stored in a box with ice cubes and transported to the laboratory for analysis.

The collected samples were analyzed for various physicochemical parameters using standard methods (APHA, 1998). Distilled water was used in the preparation of solutions and rinsing of all equipment before use. In-situ measurements of electrical conductivity and pH, were carried out using EC meter (Model DDS-307) and pH meter (Hanna model HI991300) respectively. Argentometric method was used to determine chloride, nitrate was determined using (PD303) UV spectrophotometerand volumetric titration against ethylenediamine tetra-acetic acids (EDTA) was used for magnesium and calcium ions. Heavy metal analysis was conducted using Varian (AA240) Atomic Absorption Spectrophometer

The results of the chemical analysis were compared with the WHO (2010) permissible limit for drinking water quality. Also graphical methods such as Piper (1944), Durov (1948), Gibbs (1970) and other ionic plots were employed in the data interpretation and assessment of the hydrogeochemical processes and mechanisms responsible for groundwater chemistry in the study area.

3.0. Results and Discussion

The result of the chemical analysis is presented in Table 1.The physicochemical parameters are within the WHO guideline limit for drinking water quality except turbidity which exceeded the guideline values in some samples (2, 3, 4, 6, 9, and 15). The values for turbidity imply that water sources should be filtered before use as drinking water. Turbidity may also indicate microbial presence in water sources. Farrell*et al.,* (2018)noted the attachment of microorganisms to turbidity causing particles.

Table: 1 The result of the physiochemical parameters in the water samples

Samples	pH	**Ec us/cm**	**Turb NTU**	**NO_3 mg/l**	**CO_3 mg/l**	**SO_4 mg/l**	**Cl mg/l**	**Mg ppm**	**Na ppm**	**Ca ppm**
1	7.24	44.10	2.50	5.175	22	41.234	20	0.260	1.776	3.433
2	7.18	46.60	6.50	3.257	8	52.469	40	0.118	0.771	3.866
3	7.41	33.80	17.90	11.053	30	65.418	113	0.055	0.339	5.755

4	7.23	33.70	16.70	12.334	10	65.349	185	0.059	0.490	4.875
5	6.97	54.10	3.80	6.236	12	54.719	47	0.027	0.424	4.899
6	7.01	54.20	7.20	9.551	22	62.469	46	0.102	0.372	6.754
7	7.35	54.30	4.80	5.241	16	70.699	39	0.019	0.291	7.543
8	6.98	44.70	3.40	7.834	12	56.173	68	0.105	0.230	6.383
9	6.77	45.0	5.90	4.830	16	44.115	15	0.053	0.267	4.787
10	7.22	45.10	4.40	6.055	16	75.761	25	0.096	0.259	5.876
11	6.98	55.5	3.10	12.916	10	45.349	35	0.035	0.261	6.784
12	7.55	79.55	2.30	7.346	16	48.230	11	0.039	0.293	6.784
13	6.92	68.92	2.90	4.473	8	64.938	95	0.084	0.290	6.083
14	6.93	68.93	3.20	3.311	10	43.704	17	0.027	0.255	5.744
15	7.20	79.20	5.60	5.451	18	63.704	132	0.022	0.157	6.559

3.1. The determination of the Hydrochemical Facies and the Dominant Chemical Processes

The classification of water samples using Piper diagram is shown in Figure 2 and the interpretation was carried out according to the interpretation proposed by Back and Hanshaw (1965) (Figure 3).On the basis of this diagram, it was observed from the division of the triangle on the left (cation ion domain) that $Ca^{2+}$is the dominant cation. The order of cation distribution in water sources is $Ca^{2+}> Mg^{2+}> Na^+$. However, from the triangle on the right hand (anion domain),it was observed that 33% of the samples were located in the chloride dominant zone, 20% in SO_4^{2-} dominant zone and 47% in the no dominant ion zone. Hence, the order of distribution is no dominant ion > $Cl^-> SO_4^{2-}> CO_3^{2-}$thus making Cl^- the most dominant ion.This order of distribution was also observed by Nwankwoala and Udom (2011) in Port Harcourt area of River State Nigeria. The hydrochemical facies observed were Ca^{2+} - Mg^{2+}- Cl^- – $SO_4^{2-}$and Ca^{2+} - Mg^{2+} - HCO_3^-facies. The water type has $(Ca^{2+} + Mg^{2+})$ >$(Na^- + K^{-)}$, and $((SO_4^{2-} {}_{+} Cl^-)$ > $(CO_3^{2-} + HCO_3^-)$. This means that the alkaline earth metals exceed the alkali metals and the strong acids exceed the weak acids. Also, Ravikumar and Somashekar (2017) reported the same trend with alkaline earth metals dominating over alkalis and strong acidic anions dominating over weak acidic anions in Varahi River basin in India. The water type indicates water that has been affected by mixing. Some points plotted in the 10% area of the diamond shape indicating Cl^- – SO_4^{2-} and Ca^{2+} – Mg^{2+} dominance. The water type is associated with permanent hardness and saline water (Back and Hanshaw, 1965).

The Durov diagram (Figure 4)was interpreted using the interpretation proposed by Lloyd and Heatcoat (1985). From the diagram it was observed that 20% of the samples is a water type dominated by HCO_3^- and Ca^{2+} ions.However, 80% of samples were observed to be dominated by Ca^{2+} and HCO_3^- ions. These partitioning indicate recharge water in limestone, sandstone, or many other aquifers. Also an important $Na^+ + K^+$ cation exchange was suspected to have taken place.Replacement of Na^+ by Ca^{2+} or Mg^{2+} ions was also reported by Mussa and Mjemah (2023) in Tanzania.

3.2. Mechanisms of Chemical Reactions

The Gibbs diagram and other ionic plots were used to ascertain the common hydrogeochemical processes prevalent in the water sources. The processes are responsible for the presence of the major ions in the water. The Gibbs (1970) plots were plotted with ionic concentration in mg/L (figure 5).The Gibbs plot was plotted using Na/Na+Ca against total dissolved cations, and $Cl/Cl+HCO_3$ against total dissolved cations. The plot was divided into three zones representing evaporation dominance, rock dominance and precipitation dominance zones. The plotted points fall in the region of rock dominance zoneimplying that the major process controlling water chemistry in the study area was mainly precipitation induced chemical rock weathering with dissolution of rock forming minerals to a minor extent by evaporation.Additionally, other ionic ratios were also employed to determine the processes and reactions prevalent in the study area that influence the water chemistry. It was observed that chemicalweathering of rock-forming minerals is the maincausative factor in the evolution of chemical compositionof groundwater in the study area. It was also reported by Rao *et al.*, (2020) that the hydrogeochemistry of confined groundwater in South India is dominantly governed by natural water-rock interaction including evaporation dissolution, silicate weathering and ion exchange.

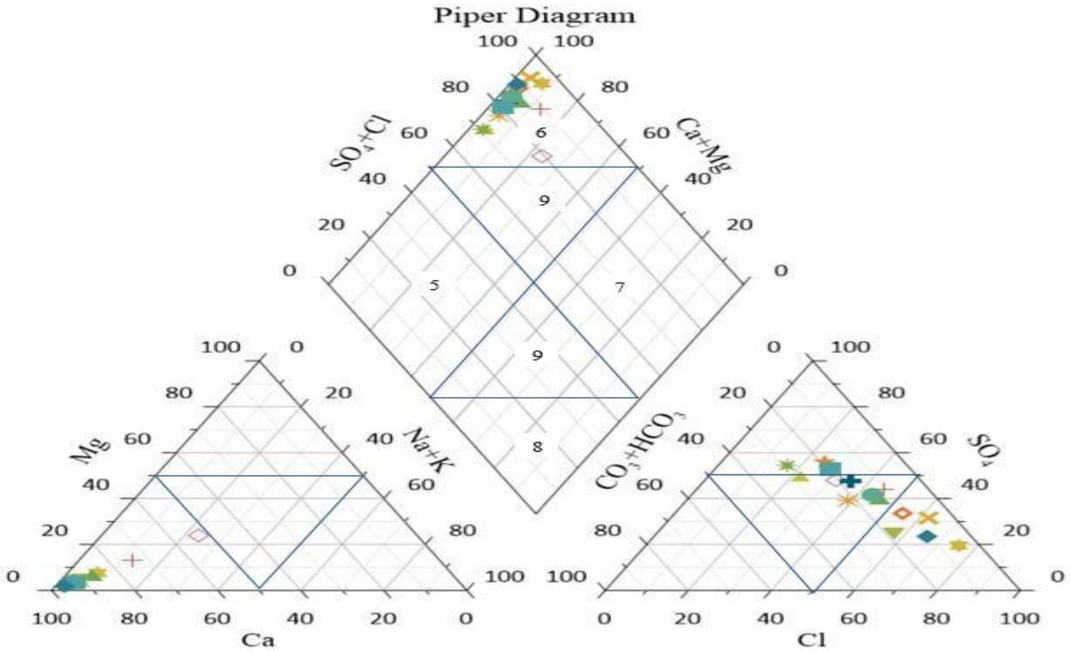


Figure 2: Piper diagram showing the distribution of the different components of the water samples

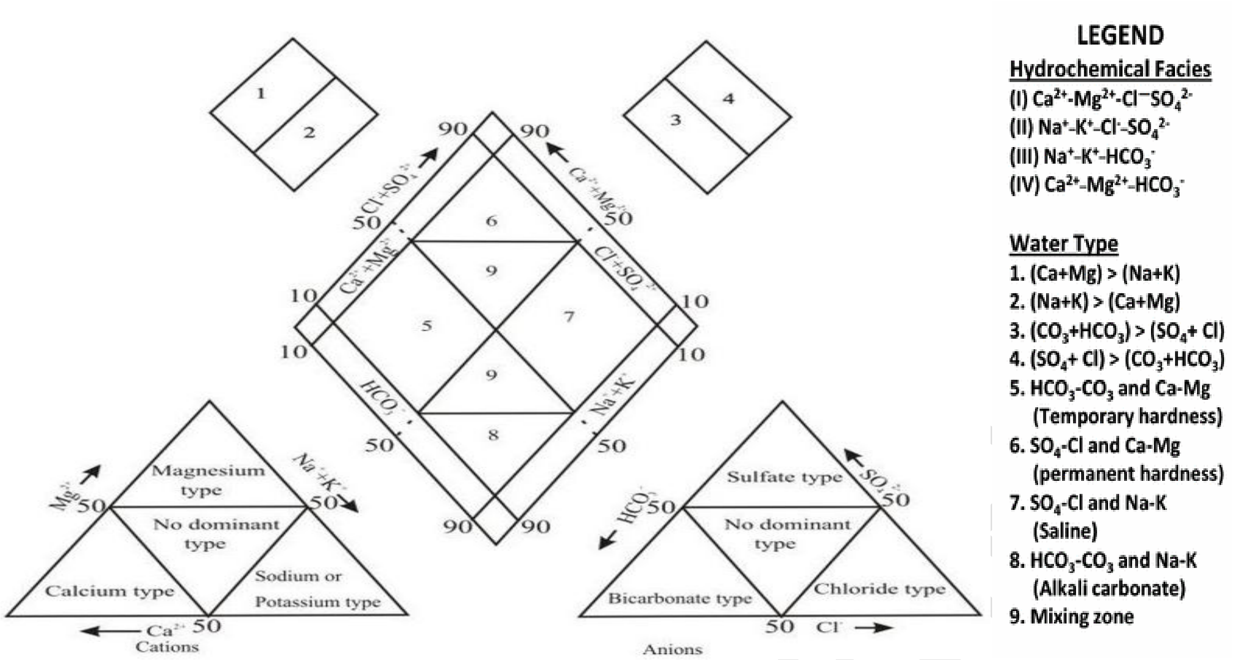


Figure3: Diagram showing Hydrochemical Facies (Back and Hanshaw, 1965)

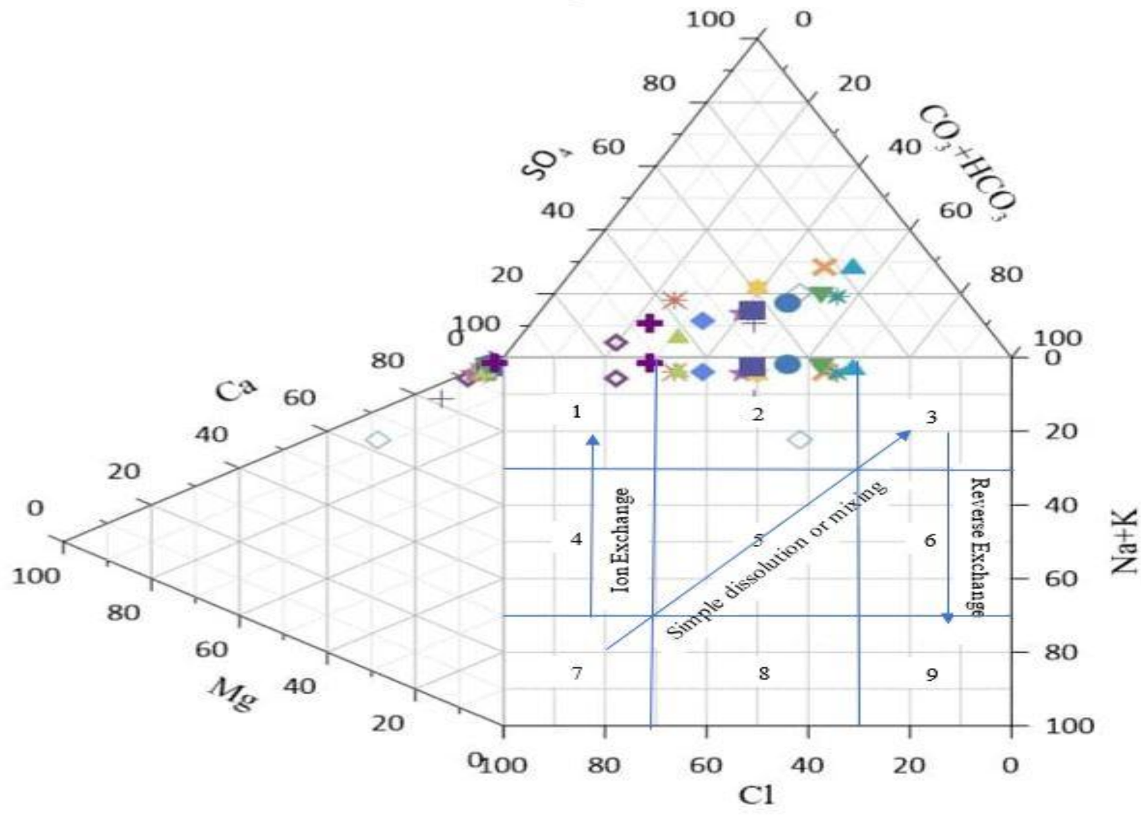


Figure 4: Classification of water samples using Durov diagram.

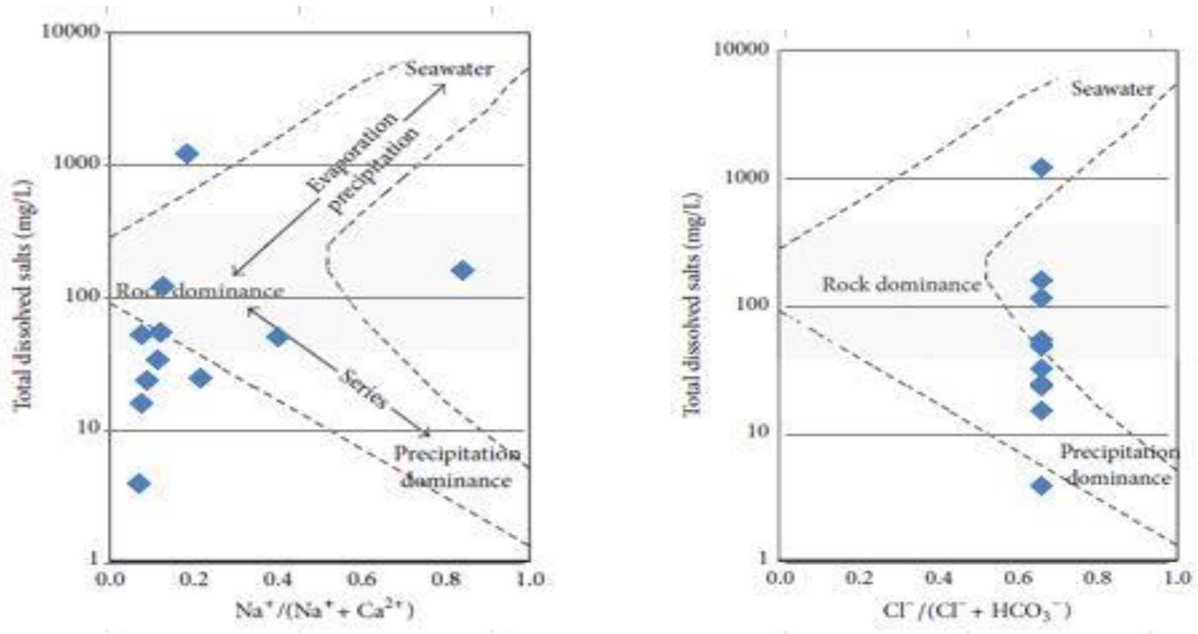
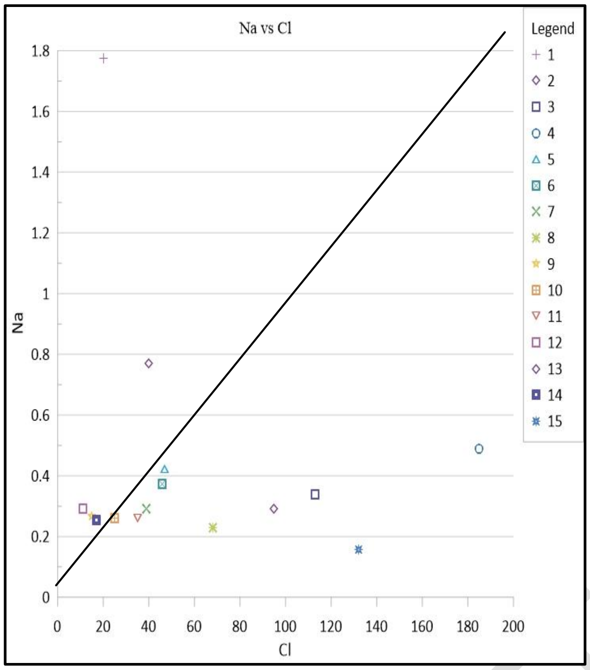


Figure 5: The Gibbs Plots for rainy season showing the dominant hydrochemical processes

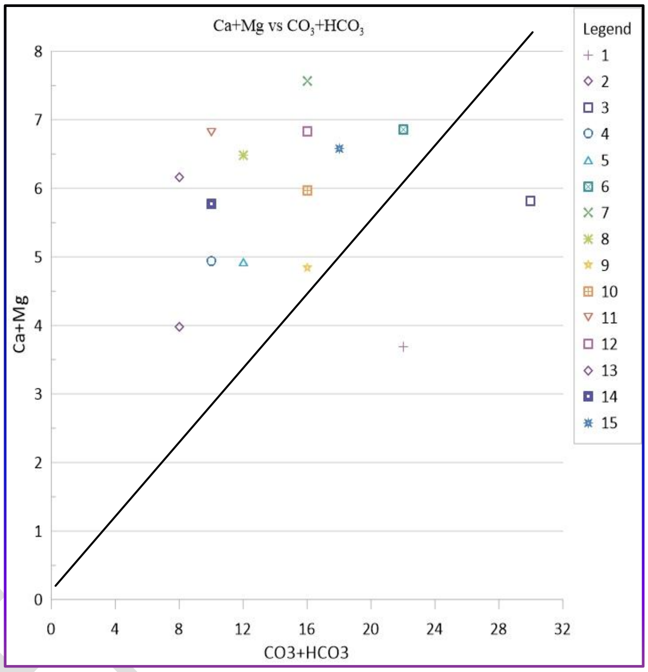
The Na versus Cl plot was equally used in determining that evaporation was not the dominant process in the study area. Evaporation process does not affect the Na/Cl ratio. The plot of Na versus Cl for the water sources show variations and these variations indicate that silicate weathering has a major influence on the water chemistry.

Similarly, cation exchange reactions contribute to the distribution and occurrence of major ions in water. This process can be identified by use of Na and Cl^- ions. The depletion of Na ions with respect to Cl^- ions is an evidence of cation exchange reaction.Rajmohan and Elango(2004) also made similar observation in their study area. Normally in ion exchange reaction, Ca^{2+} ion is retained in the aquifer material and Na^+ ion is released into the water. Excess Na^+ ion generated by the exchange reaction is not balanced by Cl^- ion but by alkalinity and SO_4^{2-}ion. Furthermore, in the reverse ion exchange reaction Na ion is retained by the aquifer material and Ca^{2+} ion released into the water.The research of Senthilkumar and Elango (2013) made similar observations. In the present study the excess Cl^- ion over Na^+ is balanced by Ca^{2+} and Mg^{2+} ions. There is a general depletion of Na ion with respect to the Cl^- ion which indicates ion exchange reaction.The relative abundance of anionic facies shows that Cl + SO_4 were more abundant than HCO_3^-. The plot of Ca^{2+} + Mg^{2+} ions against HCO_3 ions depicts samples with excess Ca^{2+} + Mg^{2+}ions. However, Ca + Mg/HCO_3 ratio less than one (<1) indicate fresh recharge water thus, groundwater in the study area is mainly fresh recharge water.

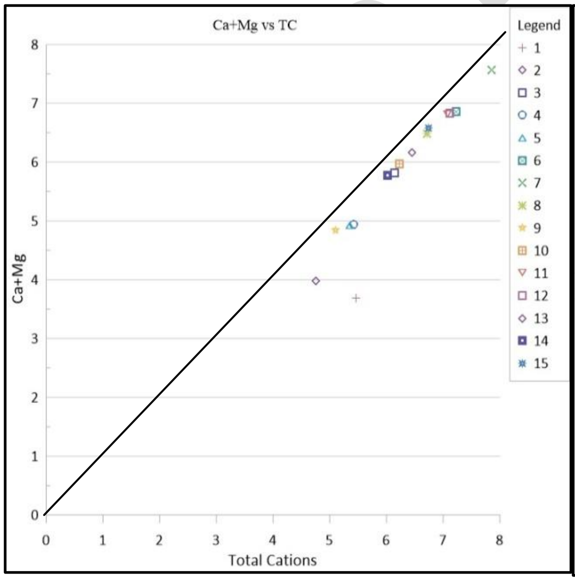
Also, the plot of Ca + Mg versus CO_3 shows that all the plotted points are above the 1:1 equiline except one point. This implies excess of Ca + Mg ions. The plot of Ca + Mg against total cations (Tc) indicates that the plotted data points fall below the 1:1 equiline (Figure 6). Additionally, the plot of Na + K versus Tc show that the plotted points fall below the 1:1 equiline. Therefore, the highest contribution of Na and K ions to dissolved cations is from silicate weathering this was also the conclusion arrived at by Mohan *et al.*,(2000), and Rajmohan and Elango *et al.*,(2004). However, Elango*et al.,* (2003) concluded that geochemical signatures of groundwater are effective tools in identifying the normal hydrogeochemical processes such as calcium carbonate dissolution, ion-exchange processes and silicate weathering. Some of these processes have been identified by the present study.



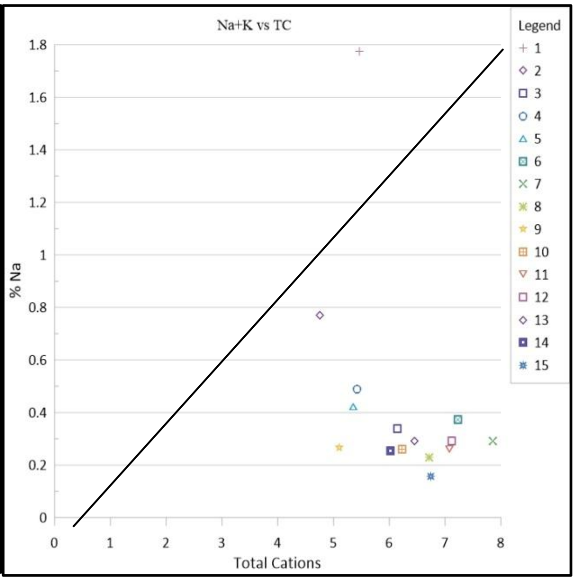
(a)



(b)



(c)



(d)

Figure 6: Relationship between (a) Na versus Cl (b) Ca+Mg versus CO_3+HCO_3, (c) Ca+Mg versus TC and (d) Na+k versus TC in wet season

4.0. Conclusion

Hydrogeochemical investigation of water was carried out in the study area and it was observed that the dominant hydrochemical facies were Ca^{2+} - Mg^{2+} - Cl^{-} – SO_4^{2-} and Ca^{2+} - Mg^{2+} - HCO_3^{-} types implying water affected by mixing and simple dissolution. Equally the water was observed to be fresh recharge water in limestone and sandstone aquifers and associated with important cation exchange reactions. The prominent mechanisms and chemical processes responsible for the chemical composition of the water is rock dominance and precipitation induced dissolution of rock minerals, and chemical weathering of rocks. Furthermore, there was general depletion of Na ion with respect to the Cl ion which supports ion exchange reaction.

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