

## **MAJOR ION CHEMISTRY AND HYDROCHEMICAL PROCESSES OF NGENEAGU SPRING WATER AT AKPUGOEZE, OJI RIVER, ENUGU, SOUTHEASTERN NIGERIA**

**T.C. Dikeogu, O.C. Okeke, L.O. Ogbekhiulu & P.C. Ogbenna**

Department of Geology,  
Federal University of Technology,  
P.M.B. 1526, Owerri,  
Imo State, Nigeria.

### **ABSTRACT**

Physicochemical characteristics of Ngeneagu spring water at Akpugoeze, Oji River, were investigated using hydrochemical facies and ionic ratios determined using hydrochemical analysis of water samples collected at different reaches from the stream. However, the stream was recognized as an outcrop of the groundwater system underneath and hence, attempts were made to relate the hydrochemical characteristics and processes to the ground-water system. Emphasis were placed on  $p^H$  and major ion concentrations such as Ca, Mg, Na, K, Cl,  $HCO_3$  and  $NO_3$ . Results of the analysis show that the concentrations of these anions and cations exhibit minimal spatial and temporal variations. Abundance of these ions are in the following order:  $Mg > Ca > K > Na = HCO_3 > Cl > NO_3 > PO_4$ . The dominant facies of the water are Mg, Ca,  $HCO_3$ , and Cl. Ion exchange as well as carbonate and silicate weathering are the processes controlling groundwater chemistry in the area. Minimal marine influence and low-salt inland waters were inferred on the basis of ionic ratios [ $Mg/Ca$  and  $Cl/HCO_3$ ] and cation exchange values. Two principal water types; Calcium-Magnesium-Bicarbonate and Calcium-Magnesium-Chloride were delineated.

**Keywords:** Groundwater, Spring, Hydrochemistry, Cations, Anions, Ionic ratios, Facies.

## INTRODUCTION

Water quality depends on a number of factors which include geology, degree of chemical weathering of prevailing lithology, quality of recharge water as well as water-rock interactions. Dikeogu (2005) noted that the quality of water is affected by the chemical reaction between water and its geologic environment. Through percolation and groundwater-surface water interactions, agricultural, domestic and industrial wastes commonly find their way into the groundwater system, altering the groundwater chemistry as well as the chemistry of spring water emanating from the groundwater domain. Thus, the quality and chemistry of spring water are highly dependent on the geochemical characteristics of the underlying groundwater system.

The inhabitants of Akpugoeze in Oji River, Enugu, Southeastern Nigeria, depend on surface and groundwater systems for various purposes. However, most of the inhabitants who could not afford groundwater exploitation resort to the use of spring water to meet their daily water needs. The Ngeneagu spring water at Akpugoeze, which comes out from an impermeable source rock serves as a major source of water for the inhabitants and as such, the provenance of the spring water is shaded with roofing sheets and barricaded to prevent impurities from getting into the flow channels. In view of the fact that springs are susceptible to contamination by the aforementioned factors and recognizing the importance of the spring water to the inhabitants, there is need to assess the physicochemical constituents of the spring water. Assessment of physicochemical characteristics of water resources as a basis for ascertaining their suitability or otherwise for various purposes as well as extent of contamination provides excellent options for the management and utilization of water resources considering that the chemical character of springs represent to a large extent, the actual ion chemistry and chemical processes that take place in the aquifer system beneath. Thus, this work evaluates the physicochemical characteristics of the Ngeneagu spring water as a basis for ascertaining its suitability or otherwise for various purposes in line with the water needs of the inhabitants. While recognizing the spring as an outcrop of the groundwater, attempt is made to relate the hydrochemical characteristics and processes of the spring water to the groundwater system underneath. The findings would be very relevant in ensuring proper and sustainable management of water resources in the area.

### **The Study Area**

The study area (Ngeneagu spring water) is located within the Anambra Basin, Southeastern, Nigeria, and lies at latitude  $7^{\circ}12'52.2''N$  and longitude  $6^{\circ}08'02.5''E$  with an elevation of 242 feet above sea level. It is located in Oji River Local Government Area of Enugu State, eight (8) kilometres away from Ufuma which is a major town in the region. Other towns close to the study area include Inyi and Orasiana. Figures 1 and 2 show respectively, the topographic map of the study area and Ngeneagu spring.

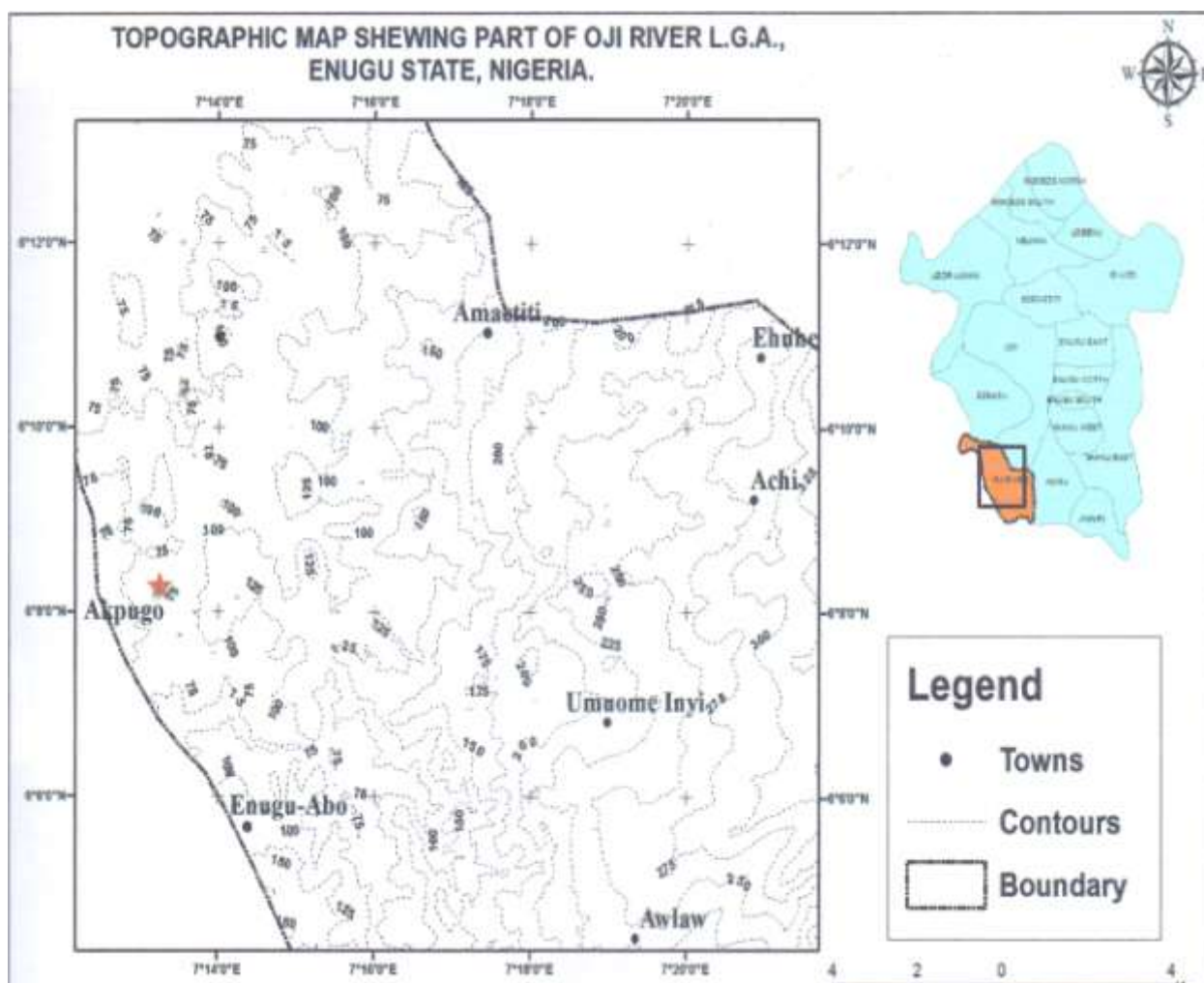


Figure 1: The Topographic map of the study area



**Figure 2: Ngeneagu spring**

The area falls within the tropical rainforest belt of Nigeria with temperature range of 30°C to 32°C. The total annual rainfall ranges from 1600mm to over 2000mm. The rainy season occurs between April and October with short dry season in August whereas the dry season occurs between November and March. The area is characterized by two air masses: the Tropical Maritime Air Mass which originates from the southern high pressure belts and the Tropical continental Air Mass emanating from the Arabia – Eurasia high pressure belt.

The area is also characterized by grassland with some plant species of lowland rainforest such as bamboo, and oil palm tree. Short and tall grasses are also found along the stream channels.

### Geology and Hydrogeology of the Study Area

The area is characterized by gently sloping topography that is vulnerable to erosion. The spring water flows down into the Oji River. The area is underlain by the paleocene Imo Shale Formation which lies within the Anambra Basin in the lower Benue tectonic unit. According to Kogbe (1975), the formation is an aquiclude consisting of thick clayey shale with occasional admixture of clay ironstones and thin sandstone bands. The thin bands of sandstone may serve as productive aquiferous layers when saturated and exploited. Maduabuchi (2010) noted that the formation is essentially an aquiclude that consists predominantly of thick bluish to grayish shales and produces artesian water from underlying Nsukka Formation and Ajali Sandstone when wells are sank over it. Within the southwestern parts of Anambra Basin, the formation could be extremely thick, in some places up to 400 – 1000 metres. Figure 3 shows Geologic and Mineral Resources Map of the area.

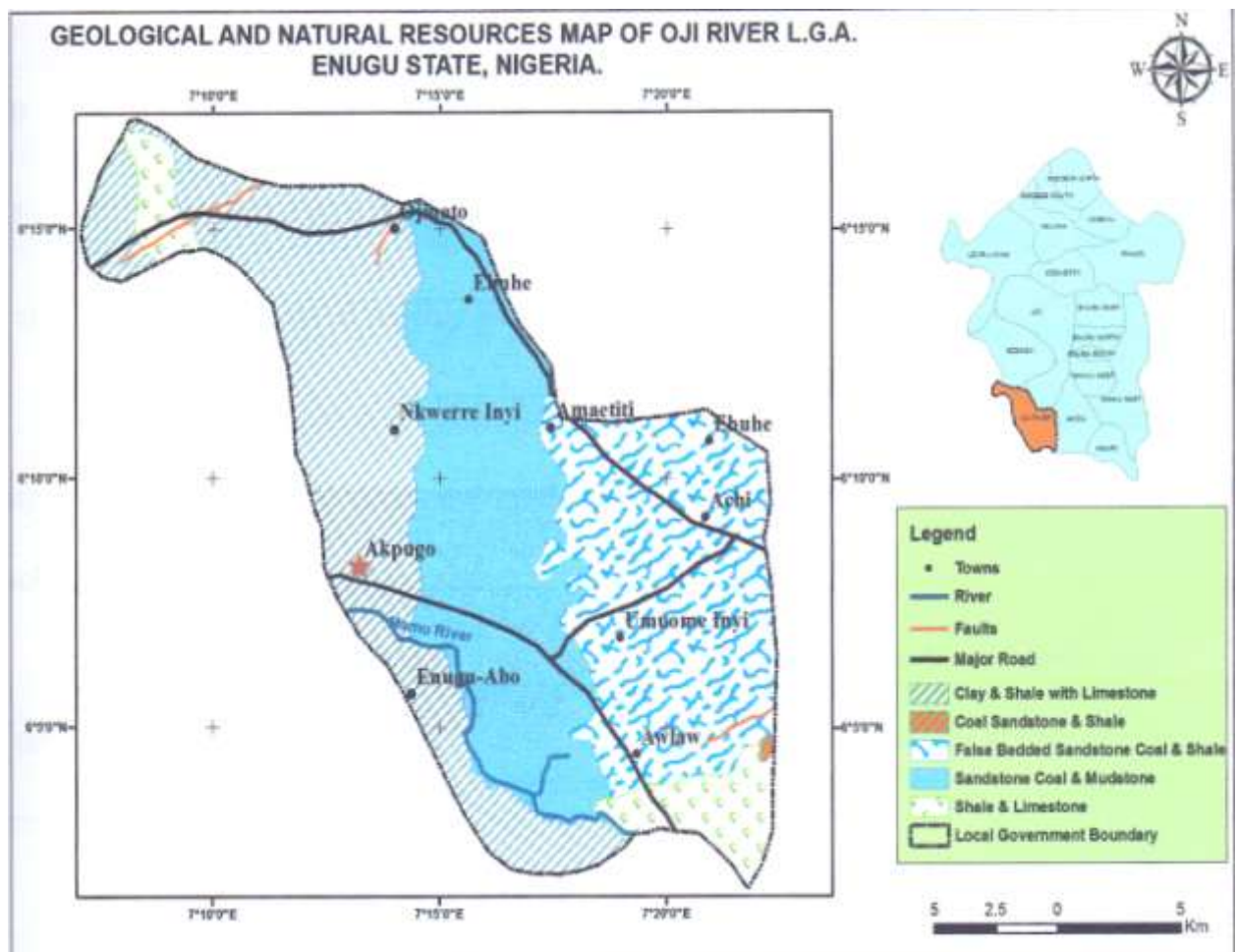


Figure 3: Geological and Mineral Resources Map of Oji River

## MATERIALS AND METHODS

Water samples were collected from two different parts of the spring at intervals of ten (10) minutes. The first sample was collected at latitude  $07^{\circ}12'52.2''\text{N}$  and longitude  $06^{\circ}08'02.5''\text{E}$ , at an elevation of 239 feet whereas the second sample was collected at latitude  $07^{\circ}12'52.3''\text{N}$  and longitude  $06^{\circ}08'02.4''\text{E}$ , at an elevation of 245 feet.

The samples were collected with plastic containers that were prior to sampling, sterilized and rinsed with the spring water, so as to ensure that the chemical characters represent the actual chemistry of the spring, and corked immediately to avoid percolation oxidation. The samples were labeled and taken to the laboratory in ice box within six (6) hours to prevent chemical character variation from field values. However,  $\text{p}^{\text{H}}$ , Temperature, and Electrical conductivity were measured in-situ due to the instability associated with these parameters. The laboratory methods used are of international standards and include those of American Public Health Association and American Standards for Testing and Materials.

Cations and anions were analysed using Atomic Absorption Spectrophotometer, and Calorimetric methods with UV-visible spectrophotometer respectively. Figure 4 shows the collection of water samples from the location of study.



**Figure 4: Collection of water samples**

## DATA ANALYSIS AND DISCUSSION

### Hydrochemical Analysis

Analyses were done with more emphasis on total ionic constituents. The chemical composition of the spring water is presented in Table 1.

**Table 1: The chemical composition of the spring water**

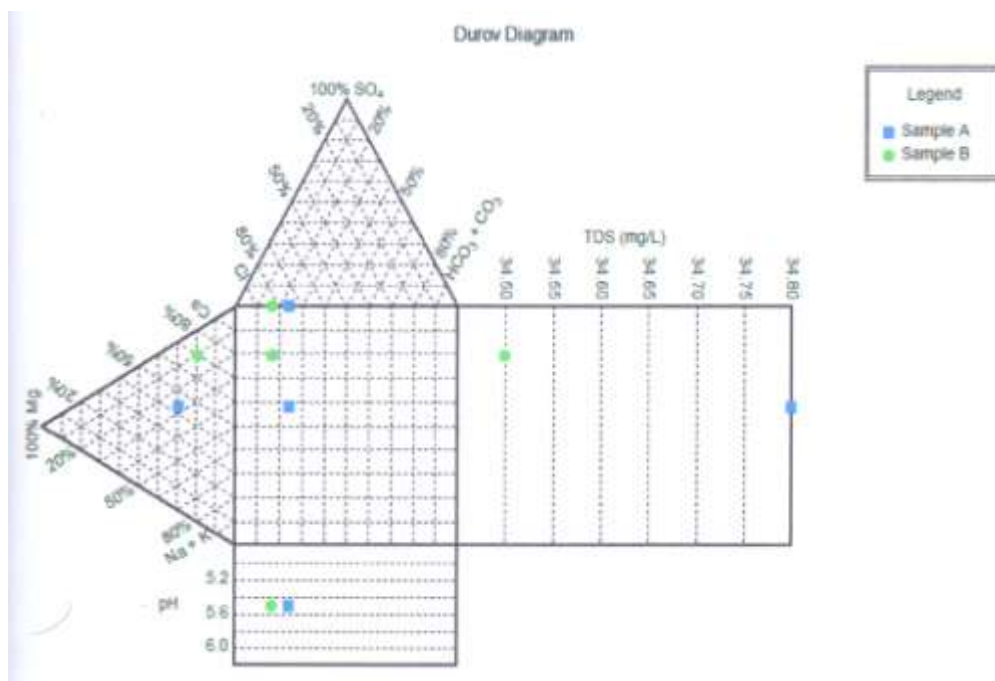
PARAMETER	SAMPLE A	SAMPLE B	AVERAGE	WHO (2006)
<b>PHYSICAL</b>				
Appearance	Clear	Clear	--	Clear
Temperature (°C)	23.3	23.5	23.4	25
Colour (colour units)	-	-	-	50
Turbidity (FTU)	18.0	18.0	18.0	25
<b>CHEMICAL</b>				
Conductivity (ohm/cm)	58.0	57.5	57.75	500
p <sup>H</sup>	5.5	5.5	5.5	6.5 - 8.5
Total iron (mg/l)	0.013	0.0125	0.0128	0.3
Alkalinity (mg/l)	32.0	30.0	31.0	400
Bicarbonate (mg/l)	51.84	48.60	50.22	500
Nitrate (mg/l)	9.4	6.2	7.8	10
Phosphate (mg/l)	0.84	0.70	0.77	0.5
Chloride (mg/l)	10.79	16.47	13.63	200
Total hardness (mg/l)	10.0	10.6	10.3	500
Magnesium (mg/l)	0.96	1.82	1.39	250
Calcium (mg/l)	2.4	1.2	1.8	200
Potassium (mg/l)	3.0	3.5	3.25	200
Sodium (mg/l)	3.2	3.7	3.47	3.47
Total dissolved solid (mg/l)	34.8	34.5	34.65	500

The hydrogen ion concentration (p<sup>H</sup>) of the spring water is 5.5, and this value indicates that the spring water and the underlying groundwater is slightly acidic. The value is also below the lower permissible limit recommended for potable water by the World Health Organization (WHO, 2006). It may be reasonably presumed that the low pH of the water is likely caused by the soil. Organic matter decomposition leads to a decline in p<sup>H</sup>, not only in the soil but also in the groundwater system. Low p<sup>H</sup> induced by the presence of organic

matter exhibits gradual decline from the vadose zone to the groundwater system. This is derived in part from the fact that the level of organic contamination in the soil zone would vary ideally with depth of the soil strata, decreasing from the top.

Gas flaring releases carbon dioxide which reacts with the atmospheric precipitation to form carbonic acid, which percolates into the groundwater system, reduce the  $p^H$  of the water thereby increasing acidity (Dikeogu, Onyewudiala, Ezeabasili and Swift, 2014). Though no incidence of gas flaring has been noted within the study area, atmospheric carbon dioxide including those generated from agricultural practices such as bush burning may be sufficient to react with atmospheric precipitation to form carbonic acid, which lowers the  $p^H$  of the groundwater and springs, thereby increasing acidity.

Figure 5 shows Durov diagram for the spring water samples. The spring water, as evident from the diagram can generally be classified as soft water because it is not highly mineralized and as fresh water on the basis of hardness and TDS.



**Figure 5: Durov diagram for the spring water samples**

Nitrate values are also low with respect to WHO (2006) limits for potable water. The low nitrate ( $NO_3$ ) concentrations may be attributed to redox processes that consumes nitrogen.



## Major Ion Chemistry and Chemical Processes

Lakshmanan, Kannan and Kumar (2003) observed that the concentrations of ions in groundwater depend on the hydrogeochemical processes that take place in the aquifer system. Recognizing that springs are outcrops of groundwater system, and considering that the chemical processes of groundwater are initiated when groundwater moves towards equilibrium in major ion concentrations (Dikeogu et al, 2014), determination of the concentration of these ions is relevant in identifying chemical processes.

Whereas bicarbonate ( $\text{HCO}_3$ ) is the dominant anion, on the basis of the relative concentrations of the cations, it is reasonable to say that magnesium dominates. The abundance of these ions are in the following order:



Concentration of dissolved salts could be influenced by atmospheric sources, and Chloride is the most reliable parameter for evaluating atmospheric input to water as it shows very little fractionation (Appelo and Postma, 1993). Sodium (Na) values for the two (2) samples, a and b, are 1.5 mg/l and 1.6 mg/l respectively whereas correspondingly the values for Chloride are 10.79mg/l and 16.47mg/l. These values fall below WHO (2006) standards (see table 1). Sodium and Chloride concentrations are likely to come from rainfall, as well as groundwater-surface water interactions. Thus, in both cases, the values will represent to a large extent, the ratios observed in sea water. However, decline in Sodium concentration and high Chloride content may be attributed to cation exchange and halite dissolution.

## Ionic Relationships and Cation Exchange

The ionic relationships;  $\text{Mg}/\text{Ca}$ ,  $\text{Cl}/\text{HCO}_3$  and the Cation Exchange Value ( $\text{CEV} = [\text{Cl} - (\text{Na} + \text{K})]/\text{Cl}$ ) were determined in order to assess the salinity level and understand the origin of the spring and underlying groundwater. Table 2 shows the values for the ionic relationships and cation exchange.

**Table 2: Ionic ratios and cation exchange values**

Sample	Mg/Ca	Cl/HCO <sub>3</sub>	CEV
A	0.4	0.21	0.42
B	1.51	0.34	0.56

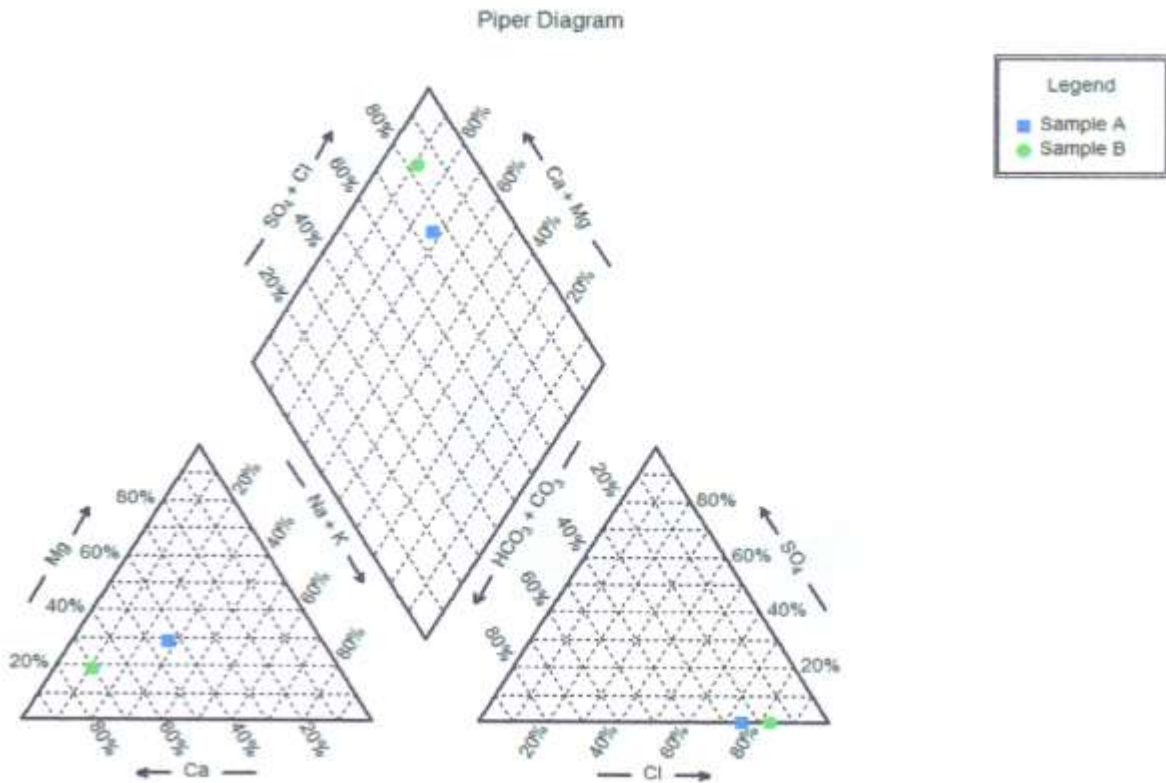
The CEV values for seawater ranges from +1.2 to +1.3 (see Custodia, 1983). In- land waters give values of close to zero, either positive or negative. The CEV values for the spring water are generally less than 1.0 (see table 2), and these values indicate inland origin.

The Mg/Ca values for both samples a and b, are 0.4 and 1.5 (see table 2). According to Sarma and Krishnaiah (1979), waters under marine influence would have values of about 5. Though processes such as cation exchange may reduce the values of Mg/Ca ratio to 4, there is relatively a large difference between 4 and the maximum value of 1.51 obtained for this spring. Thus, the underlying groundwater and its outcrop, the spring water, are of inland origin.

The Cl/HCO<sub>3</sub> values for both samples a and b, are 0.21 and 0.34. Values of this hydrogeochemical index given for inland waters are between 0.1 and 5, and for seawater between 20 and 50 (Custodia, 1987). On the basis of hydrogeochemical facies and indices (Mg/Ca, Cl/HCO<sub>3</sub> and CEV) analysed, the Ngeneagu spring water and the underlying groundwater are of inland origin.

### **Chemical Character and Water Types**

Back (1966) noted that the diagnostic chemical character of water solutions in hydrologic systems has been determined with the application of the concept of hydrochemical facies. According to Nwankwoala and Udom (2011), application of hydrochemical facies enables convenient subdivision of water compositions by identifiable categories and reflects the effects of hydrochemical processes occurring between rock minerals and the water environment. Within this context, and in order to understand better, the hydrochemical processes operating in the spring and groundwater systems in the area, the piper diagram (figure 6) was used to show the relative concentrations of the main cations and anions. On this basis, two (2) principal hydrochemical water types were delineated; Calcium – Magnesium – Bicarbonate (Ca – Mg – HCO<sub>3</sub>) and Calcium – Magnesium Chloride (Ca – Mg – Cl).



**Figure 6: The piper diagram**

**Table 3: Major Ion concentration (meq/l) with % present in the spring water**

Parameters	Mean Concentration(Mg/L)	Equivalent Mass(Mg/L)	Milliequivalent Mass (Meq/L)	% Equivalent Mass
Ca <sup>2+</sup>	1.80	20	0.09	31.36
MgI <sup>+</sup>	1.39	12.2	0.114	39.72
K+	3.25	39.1	0.083	28.92
HCO <sub>3</sub> <sup>-</sup>	50.22	61.0	0.823	61.74
Cl <sup>-</sup>	13.63	35.5	0.384	28.81
NO <sub>3</sub> <sup>-</sup>	7.8	62.0	0.126	9.45

The former and latter indicate respectively, secondary alkalinity (carbonate hardness) and secondary salinity (non-carbonate hardness). As noted by Karanth (1994), Calcium – Magnesium – Bicarbonate water is dominated by alkaline earth and weak acids. Table 3 shows major ion concentration (meq/l) with % present in the spring water.

## CONCLUSION

The pH values indicate that the spring water and the groundwater underneath are slightly acidic. On the basis of TDS and hardness values obtained, the water is not highly mineralized. The decline in Sodium concentration and high Chloride content is attributed to cation exchange and halite dissolution.

The water exhibits secondary alkalinity and salinity as well as carbonate and non-carbonate hardness and is dominated by the following major ionic components; Mg, Ca, HCO<sub>3</sub> and Cl.

The hydrochemical indices indicate that the water is of inland origin, with cation exchange value (CEV) generally less than 1.0 indicating low-salt inland water.

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