Effect of Seasonal Variation on Physicochemical Properties of Shallow Groundwater in a Typical Basement Complex Terrain of Nigeria

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Abstract

Analyses of Sixty-nine (69) groundwater samples have been carried out. This was aimed at evaluating major ions and their origin; establishing hydro-chemical facies and determining the suitability of groundwater in a typical basement complex terrain for drinking and irrigation purposes. Hydrochemical analyses revealed ionic dominance in the order of $Ca^{2+}>Mg^{2+}$ *during the wet season and* $Ca^{2+}>Mg^{2+}>Na^{+}+K^{+}$ *in the dry season. The pattern of dominance of the major anions is* $HCO_3^{-}>Cl^{-}>SO_4^{2-}$ *for both seasons which is an indication of change in seasonal effect. Physical evaluation revealed that pH, turbidity and colour are higher in order of degree of pollution at the wet season than dry season while other parameters are higher during dry season. The hydrochemical facies of groundwater during dry season were found to be* $CaHCO_3$*, (Ca+Mg)Cl, CaCl and NaCl while only* $CaHCO_3$ *and (Ca+Mg)Cl are present during wet season. The source of the ions in the waters were examined and classified accordingly as rock weathering dominance. Correlation exists among major cations and Total Dissolved Solid with average positive correlation coefficients of 0.71 and 0.49 for wet and dry seasons respectively, which is a clear indication of the contribution of these ionic components to the overall mineralization. Results however showed that the water resources are suitable for drinking and irrigation as at the time of study when compared with Standards.*

Keywords: Groundwater, Irrigation, Season, Hydrochemical facie, Standards

1.0 Introduction

Water is the essence of life and safe drinking water is a basic human right essential to all [1]. It is essential for the well-being of mankind and for sustainable development. Though, necessary for human survival, many are denied access to sufficient potable drinking water supply and sufficient water to maintain basic hygiene. Consumption of water in Ekiti metropolis has increased over the year probably, due to increase in population as a result of migration, procreation, industrialization and agricultural practices. Water is capable of dissolving minerals present in the rock below the surface and also some polluting effluents are capable of percolation into the subsurface, thereby, contaminating the potable groundwater [2, 3]. With increasing human population, industrialization, urbanization and the consequent increase in demand for water for both domestic and industrial uses, the attendant increase in the implication of polluted water on man and the environment have been severally studied [4, 5]. Therefore, there is a need for thorough assessment of the quality of water available for human consumption as well as agricultural and industrial purposes. In addition, effect of seasonal variation on water quality and sources of pollutants are other elements of groundwater that should be constantly evaluated

The study area is Oye Local Government Area (LGA) in Ekiti state, Nigeria, bounded by Ilejemeje Local Government to the North, Irepodun/Ifelodun LGA to the South, Ikole LGA to the East and Ido/Osi LGA to the west (Figure 1). It comprises several towns out of which samples were taken from; Oye, Imojo, Itaji, Oloje, Ilemosho, Ilafon, Isan and Eda-Oniyo. The area lies within latitudes $7^{0}53$"N and $7^{0}54$"N and Longitudes $5^{0}18$"E and $5^{0}22$"E [6]. The climate of the study area is tropical and the natural vegetation consists of rain forests. The drainage is generally dendritic with hummocky and undulating topography. Annual rainfall is about 1300 mm and its distribution is bimodal within hydrologic year. The first peak occurs in June to July, while the second peak occurs in September to October rainy season. The two wet seasons are normally separated by a drought (August-break), while the dry season is defined by little or no rainfall between November and April [7].

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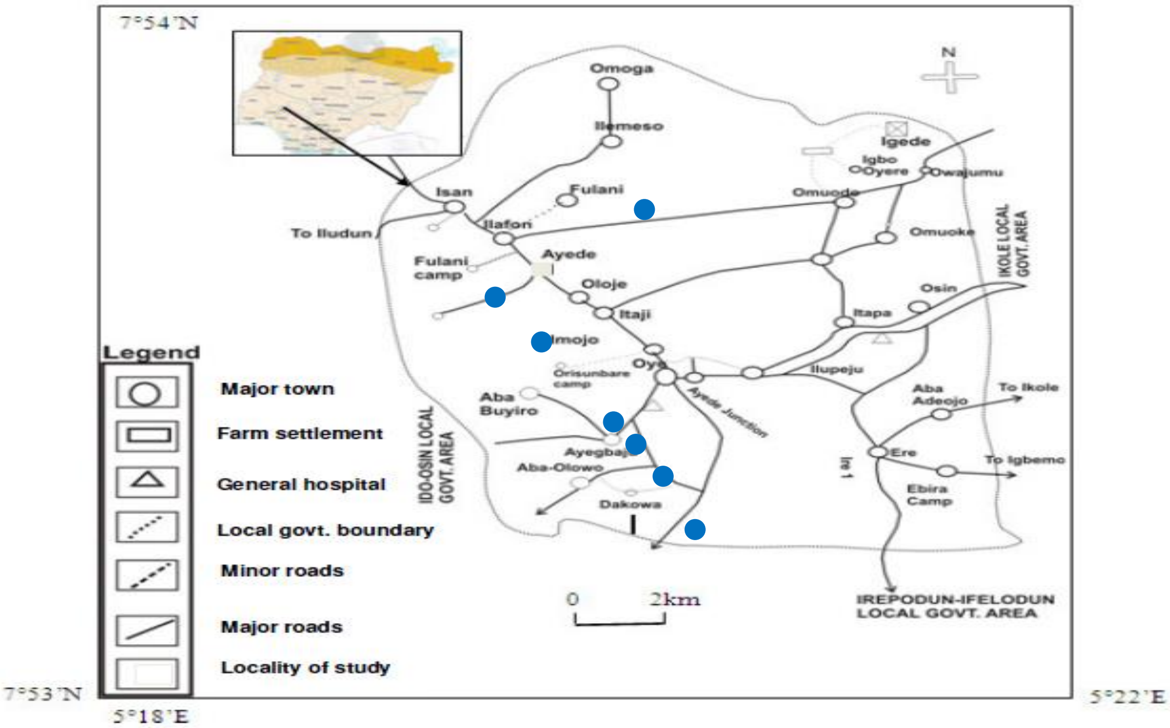

Figure 1: Map of Oye Local Government Area, Ekiti State, Nigeria, showing the studied area (Inset: Map of Nigeria showing Ekiti State)

2.0 Materials and methods

2.1 Collection of samples

A total number of sixty-nine (69) water samples; thirty seven (37) samples during the wet season and thirty-two (32) samples during the dry season were collected mainly from shallow domestic hand-dug wells (not deeper than 8m) for physiochemical analysis. All water samples were collected in 2 L preconditioned polyethylene bottles. They were conditioned by rinsing initially with 10% nitric acid and followed by several rinsing with distilled water to ensure that the sample bottles were free from any impurities. At each sampling location, samples were collected into polyethylene bottles in duplicate for cation and anion analyses.

2.2 Physicochemical Analysis

Samples for cations analysis were acidified with concentrated nitric acid. Prior to this, some physical parameters such as pH, temperature and electrical conductivity were measured *in situ* using Multi-parameter Testr^{Tm} 35 series Meter as well as static water level recording. The samples were then preserved in a refrigerator prior to the laboratory analyses. Anions were analysed at ACTLABS Laboratory, Canada using the Inductively Coupling Plasma Oxygen Emission Spectrometer (ICPOES) analytical method while the cations were analysed at the Lower Niger River Basin Development Authority, Ilorin, Nigeria. Hydrochemical facies and suitability for drinking purpose was evaluated using Piper's trilinear diagrams while suitability of the water for irrigation was determined using Wilcox's Diagram, Sodium Percent, Residual Sodium Carbonate (RSC), Magnesium Hazard (MH) and Kelley's Ratio (KR). MH values was computed with the equation; $MH = Mg/(Ca+Mg) \times 100$. In addition, the source of ion in water was examined and classified using the Gibb's diagram.

2.3 Statistical Analysis

Statistical analyses of measured parameters were carried out using Pearson correlation factor to establish interdependency of parameters.

3.0 Results

Table 1 shows the results of Kelley's Ratio (KR), Residual Sodium Carbonate (RSC), Magnesium Hazard (MH) and Sodium Percent (SP) during each season for the evaluation of water samples suitability for irrigation purpose while Table 2 shows the summarized of evaluated physicochemical parameters of water samples during the wet and dry seasons for the purpose of drinking. The pH of groundwater varied from 7.01 – 7.97 with a mean of 7.43 and 6.46 – 7.85 with a mean of 7.19 for wet and dry seasons respectively. The pH values revealed that the groundwater in the study area is slightly acidic to slightly alkaline; it influences the dissolution and precipitation of minerals in groundwater.

The electrical conductivity (EC) ranges from 20 – 880µS/cm with a mean of 199 µS/cm and 90 - 1190µS/cm with a mean of 664 µS/cm for wet and dry season respectively while the TDS was generally less than 1000 mg/L, ranging from 13-590 mg/L with an average value of 132.05 mg/L and 60 - 902 mg/L with an average value of 476 mg/L for wet and dry season respectively. The total hardness (TH) varied from 12 - 260 mg/L with an average value of 80.43 mg/L and 112-575 mg/L with an average value of 240 mg/L for wet and dry seasons respectively.

Calcium is the dominant cation with its values ranging from 1.60 - 72.80 mg/L with an average value of 21.45 mg/L and 19.80 - 200 mg/L with an average value of 54.35 for wet and dry season respectively while magnesium ranges from 1.14-22.88 mg/L with an average value of 7.67 mg/L and 2.40 - 67.21 with an average value of 22.94 for wet and dry season respectively. With respect to the alkalis metals, the concentrations of sodium ranged from 0.05 - 22.10 mg/L (mean 3.64 mg/L) and 1.89 - 44.90 mg/L (mean 18.78 mg/L) for wet and dry seasons respectively while that of potassium varied from 0.05 - 23.60 mg/L (mean 3.68 mg/L) and 0.40 - 76.95 mg/L (mean 25.68 mg/L).

Bicarbonate is the dominant anion with concentration of 19.52 - 204.96 mg/L (mean 77.55 mg/L) and 28.56 - 224.50 mg/L (mean 98.36 mg/L) for wet and dry season respectively. This is followed by chloride ranging from 1.00 - 67.74 mg/L (mean 13.51 mg/L) and 0.98 - 185.49 (mean 76.54 mg/L) for wet and dry season respectively. Sulphate has concentrations in the range of 1.00 - 20.00 mg/L (mean 4.38 mg/L) and 1.00 - 57.00 mg/L (mean 20.59 mg/L) for wet and dry seasons respectively.

Table 1: Irrigation Suitability Parameters for wet and dry seasons

Sample no	Kelley's ratio		RSC		Magnesium Hazard		Sodium percent	
	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season
1	0.480	0.174	-1.273	-9.056	37.34	55.27	36.15	14.36
2	0.109	0.149	-0.717	-6.760	42.69	31.23	10.97	17.14
3	0.002	0.073	0.548	-1.983	41.68	50.32	0.25	18.38
4	0.033	0.244	1.077	-3.720	38.83	40.66	4.90	35.22
5	0.127	0.167	0.756	-4.170	48.71	34.27	10.84	21.09
6	0.009	NS	0.209	NS	54.39	NS	0.98	NS
7	0.013	NS	0.048	NS	70.55	NS	1.26	NS
8	0.284	0.079	-0.622	-5.519	34.64	63.21	23.64	7.75
9	0.043	0.034	-2.436	-3.470	44.27	73.81	4.59	4.47
10	0.002	0.078	0.723	-4.695	35.14	79.86	0.25	17.42
11	0.065	0.189	-0.028	-3.433	51.05	4.73	7.77	27.31
12	0.043	0.165	0.163	-6.322	35.14	33.80	5.08	21.34
13	0.036	0.175	0.018	-8.127	34.64	53.85	6.77	16.41
14	0.070	NS	-0.126	NS	47.18	NS	9.46	NS
15	0.047	0.119	-0.846	-8.235	12.50	48.36	6.43	17.21
16	0.191	0.139	-0.011	-8.666	30.84	51.05	19.09	12.64
17	0.103	0.150	-0.970	-11.186	33.73	15.16	11.33	20.84
18	0.473	NS	-2.008	NS	40.82	NS	35.66	NS
19	0.129	0.057	-0.686	-3.143	20.33	52.56	14.11	12.44
20	0.211	0.027	-0.382	-3.766	54.39	80.66	19.16	13.83
21	0.004	0.572	-0.095	-1.331	12.93	22.31	0.47	40.08
22	0.252	0.480	-2.021	-1.104	44.76	27.85	19.61	35.41
23	0.005	0.189	0.065	-0.193	16.52	27.57	0.60	17.60
24	0.003	0.356	-0.252	-1.216	54.36	17.49	0.33	29.65
25	0.437	NS	-1.304	NS	38.34	NS	34.42	NS
26	0.003	0.987	0.083	0.874	49.83	15.04	0.36	55.65
27	0.045	0.383	-0.630	0.436	35.84	11.59	5.02	29.73
28	0.033	0.129	-0.393	0.021	47.83	14.93	3.61	11.79
29	0.122	0.074	-0.428	-0.886	34.27	18.03	13.67	6.24
30	0.003	1.083	0.051	0.545	58.23	36.62	0.30	55.95
31	0.002	1.016	-0.235	0.447	37.25	15.23	0.27	56.97
32	0.091	1.028	0.003	1.329	37.34	51.27	9.73	52.56
33	0.065	0.708	-3.067	-0.312	34.38	34.00	7.52	42.94
34	0.035	0.869	-0.412	1.784	17.80	43.06	4.62	49.87
35	0.075	0.411	-1.082	-0.815	42.33	29.36	8.18	31.54
36	0.006	0.294	-0.031	-1.630	37.36	36.85	0.67	23.08
37	0.010	0.415	0.021	-2.211	31.77	7.82	1.14	33.89

NS= Not Sampled

Table 2: Summary of Physicochemical Parameters of water samples for both seasons

Parameters	Wet season			Dry season		
	Mean	Standard deviation	Variance	Mean	Standard deviation	Variance
pH	7.43	0.22	0.05	7.19	0.34	0.12
EC (µs/cm)	198.92	170.21	28971.02	663.56	340.55	115971.29
TDS (mg/l)	132.05	114.12	13024.22	475.53	228.75	52328.06
Turbidity (FTU)	21.63	27.87	776.80	1.09	3.57	12.73
Chloride (mg/l)	13.51	14.67	215.22	76.54	53.10	2819.63
Bicarbonate (mg/l)	77.55	48.53	2354.69	98.36	54.78	3001.12
Sulphate (mg/l)	4.38	3.97	15.74	20.59	16.08	258.70
Calcium (mg/l)	21.45	15.70	246.63	54.35	40.21	1617.04
Magnesium (mg/l)	7.67	5.39	29.08	22.94	21.38	457.02
Sodium (mg/l)	3.64	5.95	35.38	18.78	11.78	138.88
Potassium (mg/l)	3.68	5.89	34.75	25.68	18.04	325.55

4.0 Discussion

4.1 Physicochemical Properties

Comparing the results for both wet and dry season, the latter showed high values with the exception of turbidity, pH and colour which were high during wet season (Table 1). Average pH of 7.43 during wet season is indicative of the presence of free CO_2 and that the dissolved anions exist almost entirely in HCO_3 ion form [8].The lower values of these parameters suggest that the runoff water contributes to dilution in the rainy season while impurities from runoff into the various open wells or faulty constructed wells contributes to the elevated level of turbidity. Values of EC and TDS obtained are in the range of values obtained from Ayede in Ekiti State [6]. The low TDS are indications of low mineralized water with limited migratory history and water rock interactions.

Furthermore, concentrations of cations was in the order of Ca^{2+}>Mg^{2+}>Na^++K^+ while that of anions was HCO_3^->Cl^- >SO_4^{2-} for both seasons. The higher concentrations of Ca^{2+} in the groundwater of the study area may be due to the dissolution of plagioclase feldspars. HCO_3^- might have been generated in the soil zone en route to the groundwater zone as a result of decomposition of organic matter, which releases carbon dioxide that reacts with water in the soil zone. The reaction generates weak carbonic acid (H_2CO_3) that aids the breakdown of minerals in the rocks resulting in dissolution and the release of the ions into the groundwater which was responsible for its hydrochemical characteristics. All evaluated parameters compared favorably well to WHO and NIS standards (Table 3)

4.2 Wilcox Diagram

The Wilcox diagram is used to determine the suitability of water samples for irrigation [12]. It is a plot of percentage sodium against the electrical conductance. Water used for irrigation always contains measurable quantities of dissolved substances as salts. The Wilcox plot for both wet and dry season shows that all the water samples are within the recommended value since all samples fall within the very good to good and good to permissible region of the plot (Figures 2a and 2b).

4.3 Sodium percent

The sodium percent also influence the suitability of water for irrigation. Maximum sodium of 60% is recommended for irrigation water. Therefore, all samples are good for irrigation since they are all less than 60% as shown in Table 1.

4.4 Residual Sodium Carbonate (RSC)

The quantity of bicarbonate and carbonate in excess of alkaline earths (Ca+Mg) also influence the suitability of water for irrigation purposes. When the sum of carbonates and bicarbonates is in excess of calcium and magnesium, there may be possibility of complete precipitation of Ca and Mg [15]. As a result, water in the soil becomes more concentrated and the relative proportion of sodium in the water is increased in the form of sodium carbonate. To quantify the effects of carbonate and bicarbonates, residual sodium carbonate (RSC) has been computed as;

$$RSC = (CO_3 + HCO_3) – (Ca + Mg)$$

A high value of RSC in water leads to an increase in the adsorption of sodium on soil. Irrigation water having RSC values greater than 5meq/l are considered harmful to the growth of plants, while water with RSC values above 2.5meq/l are not suitable for irrigation purpose. In the analysed water samples for both wet and dry season, all are less than 2.5meq/l as shown in Table 1, therefore, it indicates that all samples are good for irrigation.

4.5 Magnesium Hazard (MH)

The quantity of magnesium also influences the suitability of water for irrigation. Magnesium hazard values greater than 50 are considered harmful and unsuitable for irrigation use. In the analysed water samples, almost all are suitable for irrigation with MH less than 50 except for some samples that are slightly above 50 as shown in Table 1.

Table 3: Comparison of range of parameters with WHO (2011) and SIN 544

Parameters	Wet season	Dry season	WHO (2011) Acceptability Threshold/ Optimum value	NIS 544 (2007)
PH	7.01-7.97	6.46-7.85	6.5-8.5	6.5-8.5
E/C (µs/cm)	20-880	90-1190	1000	1000
Colour (TCU)	0-80	0-15	15	15
Turbidity (FTU)	0-137	0-20	<5	5
TDS (mg/L)	13-590	60-902	1000	500
Magnesium (mg/L)	1.14-22.88	2.40-67.21	150	200
Calcium (mg/L)	1.60-72.80	19.80-200	200	250
Iron (mg/L)	-	-	NE	0.3
Potassium (mg/L)	0.05-23.60	0.40-76.95	NE	
Sodium (mg/L)	0.05-22.10	1.89-44.90	200	200
Sulfate (mg/L)	1.00-20.00	1.00-57.00	≤ 250	100
Nitrate (mg/L)	0.16-7.65		50	50
Chloride (mg/L)	1.00-67.74	0.98-185.49	200-300	250
Carbonate (mg/L)	-	-	120	
Hardness (as $CaCO_3$)	12-260	112-575	200	150
Bicarbonate (mg/L)	19.52-204.96	28.56-224.50	NE	
Phosphate (mg/L)	-	-	50	

WHO = World Health Organization; NIS = Nigerian Industrial Standard; NE= Not Established

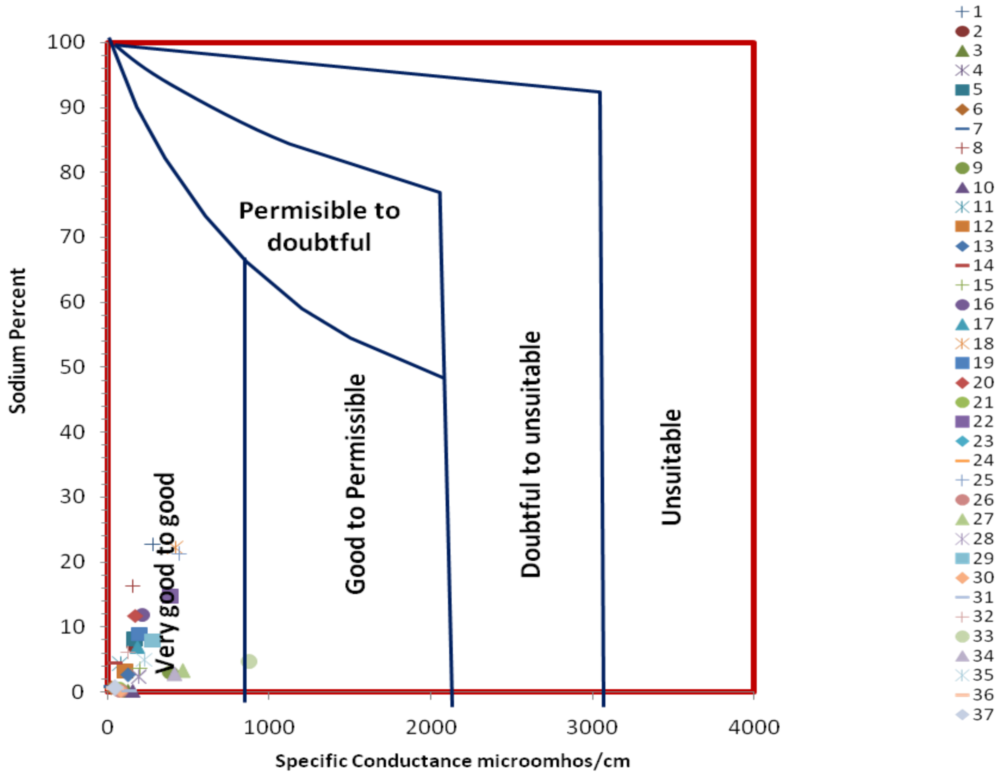

Figure 2a: Wilcox plot for wet season water samples in the study area

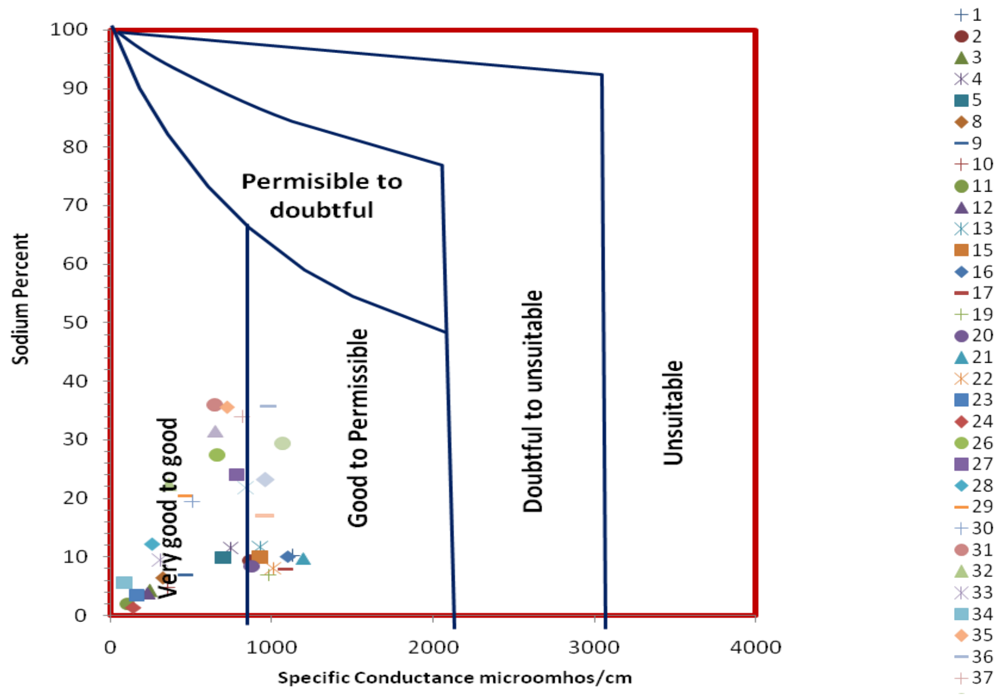

Figure 2b: Wilcox plot for dry season water samples in the study area

4.6 Kelley's Ratio

Kelley's ratio is used to find whether groundwater is suitable for irrigation or not. Sodium measured against calcium and magnesium was considered by Kelley [16]. Groundwater having Kelley's ratio greater than one (1) is generally considered as unfit for irrigation. In all the water samples analyzed only three samples during dry season are slightly above one (1). That is, 1.083, 1.016 and 1.028 for samples 30, 31, and 32 respectively (Table 1). It could therefore be said that all water samples are fit for irrigation.

4.7 Correlation Analysis

Correlation exists among major cations and TDS with average positive correlation coefficient greater than 0.71 and 0.49 for wet and dry seasons respectively as shown in Table 4 and 5, which is a clear indication of the contribution of these ionic components to the overall mineralization (TDS). It can be seen inthe wet season that the highest correlation has been found between Ca and TDS (0.93), the correlation coefficient for other constituents such as Cl (0.88), Mg (0.85), SO_4 (0.71), HCO_3 (0.54), Na (0.54) and K (0.52) with TDS reduce progressively, this indicates proportionately lesser contribution of these constituents to the overall mineralization. Similarly for dry season, it was found that the highest correlation is between Cl and TDS (0.92) while the correlation coefficient for other constituents such as Na (0.78), K (0.48), Ca (0.46), SO_4 (0.41), Mg (0.21) and HCO_3 (0.14) with TDS reduce progressively, this also indicates proportionately lesser contribution of these constituents to the overall mineralization. Also, positive correlations among elements indicate a common source of ionic contribution.

Table 4: Correlation Matrix for Wet Season

	pH	EC	TDS	Turb	Cl	HCO_3	SO_4	Ca	Mg	Na	K
Ph	1										
EC	-0.49	1									
TDS	-0.46	0.87	1								
Turb	-0.03	-0.20	-0.16	1							
Cl	-0.45	0.91	0.88	-0.23	1						
HCO_3	-0.33	0.55	0.54	0.09	0.23	1					
SO_4	-0.44	0.72	0.71	-0.01	0.61	0.48	1				
Ca	-0.51	0.93	0.93	-0.14	0.77	0.67	0.68	1			
Mg	-0.47	0.84	0.85	-0.17	0.80	0.55	0.58	0.78	1		
Na	-0.26	0.54	0.53	-0.05	0.68	0.08	0.24	0.44	0.51	1	
K	-0.28	0.54	0.52	-0.04	0.68	0.09	0.27	0.44	0.47	0.98	1

Table 5: Correlation Matrix for Dry Season

	pH	EC	TDS	Turb	Cl	HCO_3	SO_4	Ca	Mg	Na	K
pH	1										
EC	0.25	1									
TDS	0.22	0.78	1								
Turb	0.19	-0.29	-0.30	1							
Cl	0.20	0.90	0.92	-0.27	1						
HCO_3	-0.06	0.23	0.14	-0.04	0.09	1					
SO_4	-0.17	0.58	0.41	-0.26	0.42	0.71	1				
Ca	0.16	0.62	0.46	-0.06	0.54	-0.15	0.25	1			
Mg	0.17	0.10	0.21	0.05	0.02	-0.14	-0.04	0.39	1		
Na	0.14	0.80	0.78	-0.24	0.77	0.53	0.63	0.33	-0.10	1	
K	0.28	0.51	0.48	-0.05	0.43	0.27	0.45	0.585	0.21	0.53	1

4.8 Piper's Diagram

The evolution of hydrochemical parameters of groundwater can be understood by plotting the concentration of major cations and anions in the Piper's diagrams [9]. Figures 2a and 2b shows the distribution of water samples for wet and dry season respectively. The dominant water types during wet season are of two types; $CaHCO_3$ represent 89% of total water samples while (Ca+Mg)Cl represents 11% of total water samples. $CaHCO_3$ is typical of groundwater chemistry in the basement complex area of Nigeria [5] and [6]. During dry season, there are four water types dominating; $CaHCO_3$ represents 34% of total water samples, (Ca+Mg)Cl represents 34%, CaCl represents 22% and NaCl represents 10% of total groundwater samples. Generally, all the water samples are good for drinking purpose due to their position in the Piper's plot [9].

4.9 Gibbs' Diagram

The source of the dissolved ions in groundwaters can be understood by Gibbs diagram [10]. It is a plot of $(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$ versus log TDS and $Cl^- /(Cl^- + HCO_3^-)$ versus log TDS. Figure 3(a) and (b) shows that all the samples fall in the rock weathering dominance area. The Gibbs' diagrams suggest that chemical weathering of the rock forming minerals is the main process which contributes the ions concentration in the water.

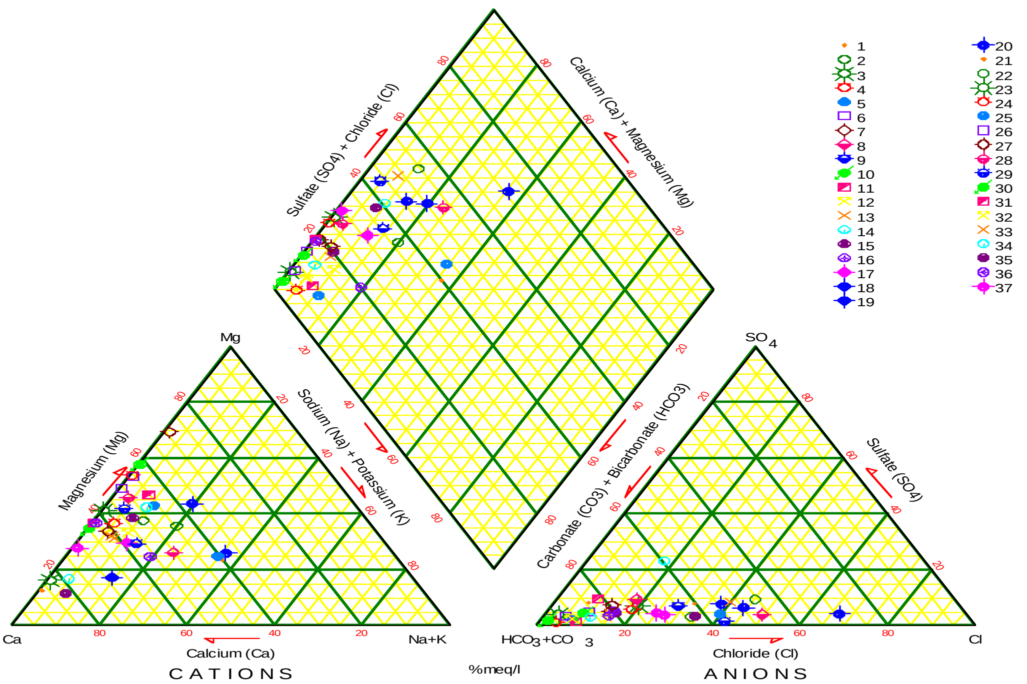

Figure 3a: Piper's plot for wet season in the study area

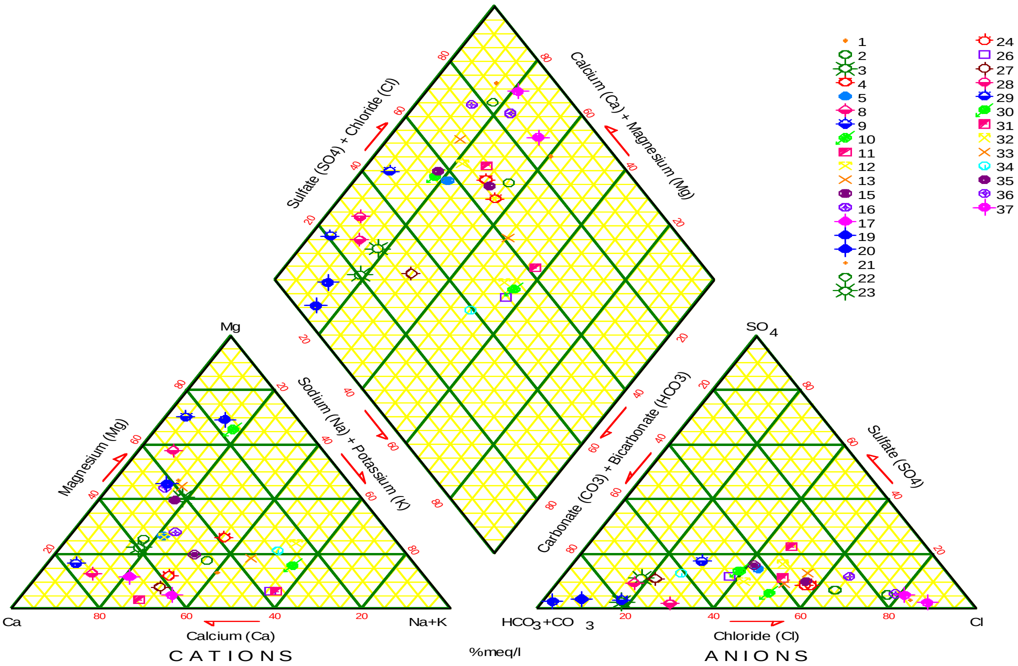

Figure 3b: Piper's plot for dry season in the study area

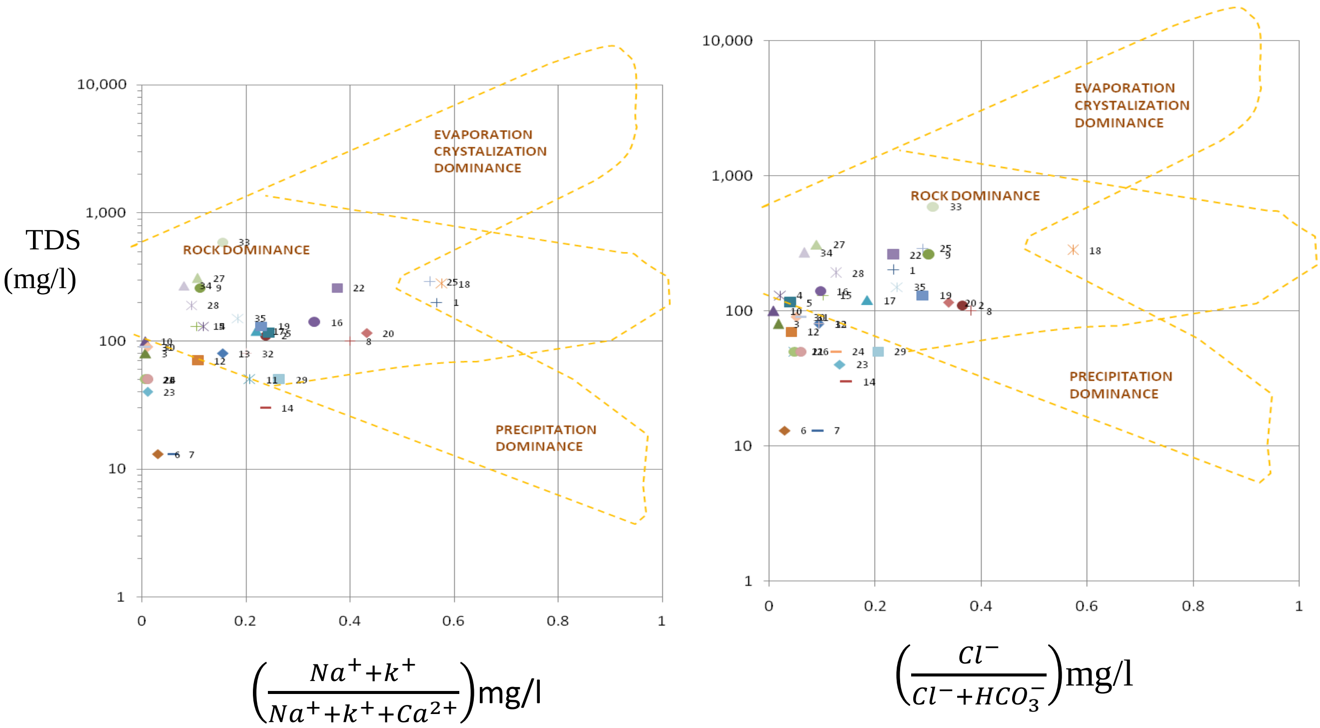

Figure 4a: Gibbs' Plot for wet season water samples in the study area

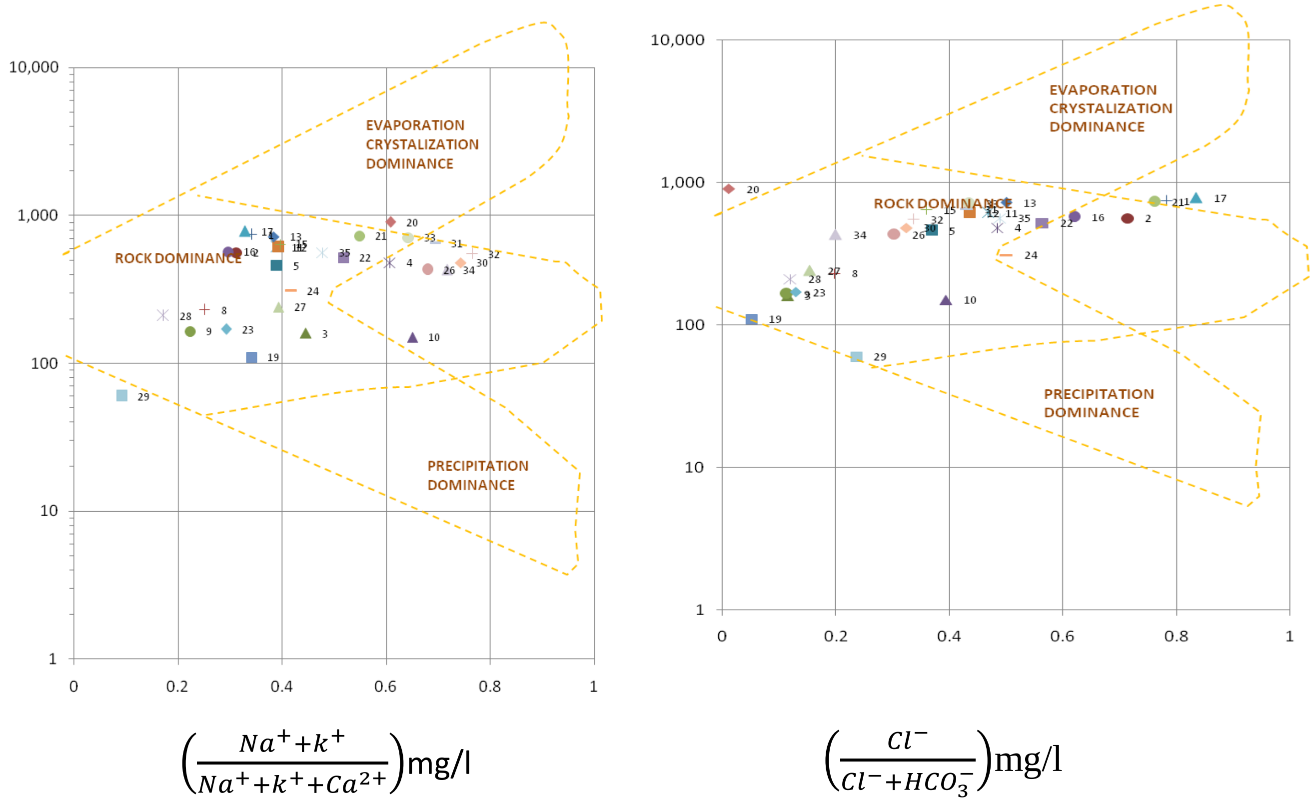

Figure 4b: Gibbs' Plot for Dry season water samples in the study area

5.0 Conclusion

Evaluation of seasonal hydrochemical data from the study area have provided information on the quality of groundwater, sources of pollution and their suitability for consumption and irrigation purposes. Physical and chemical parameters of all sampled water fell within SON [12] and WHO [14] guideline values for drinking water and reveal that the groundwater is suitable for drinking. In addition, evaluation of hydrochemical results showed that groundwater in the study area was fresh, low mineralized with little water-rock interplays. Quality evaluation for agricultural uses revealed that the calculated irrigation indices using Kelley's ratio, Magnesium Absorption Ratio and Wilcox Plot indicated that the groundwater was suitable for irrigation.

Dominantly, source of dissolved chemical substances in groundwater system of the study area was geogenic resulting from the interaction between water and rock as supported by the Gibb's diagram during both seasons. The principal hydrochemical facies in the study area were $CaHCO_3$, (Ca+Mg)Cl, CaCl and NaCl in the dry season while $CaHCO_3$ and (Ca+Mg)Cl were the dominant type in the wet season. Comparing results for both wet and dry seasons, it was observed that the concentrations of hydrochemical parameters during dry season are higher than in wet season except for turbidity, pH and colour which are the only physical parameters higher during wet season. The reduced concentrations suggest influence of surface runoff that aids dilution in the rainy season.

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