



## Groundwater chemistry of the Oban Massif, South-Eastern Nigeria

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### ABSTRACT

Hydrogeochemical study of the fractured/weathered basement of the Oban Massif, southeastern Nigeria has been carried out. Results indicated that concentrations of major cations and anions exhibited the following order of abundance: Ca>Na>Mg>K and HCO<sub>3</sub>>SO<sub>4</sub>>Cl, respectively, with minor variations across sampling seasons. Ca-Na-Cl-SO<sub>4</sub> and Ca-Mg-HCO<sub>3</sub> water types have been identified as major facies, resultant from congruent influences of weathering (mainly silicates), ion exchange processes, and water mixing.

**Keywords:** groundwater; cation; anion; weathering; ion exchange; Oban massif; Nigeria.

## Química das águas subterrâneas do Maciço Oban, Sudeste da Nigéria

### RESUMO

Estudo hidrogeoquímico do embasamento fraturado / intemperizado do Maciço Oban, sudeste da Nigéria foi realizado. Os resultados indicaram que as concentrações de cátions e ânions apresentaram a seguinte ordem de ocorrência: Ca> Na> Mg> K e HCO<sub>3</sub>> SO<sub>4</sub>> Cl, respectivamente, com pequenas variações entre as estações de amostragem. Os tipos de água Ca-Na-Cl-SO<sub>4</sub> e Ca-Mg-HCO<sub>3</sub> têm sido identificados como os principais fácies, resultantes de influências congruentes de desgaste (principalmente silicatos), processos de permuta iônica e água de mistura.

**Palavras-chave:** água subterrânea; catiônica; ânion; intemperismo; troca iônica; Oban maciço; Nigéria.

### 1. INTRODUCTION

The ability to estimate the rate and extent of water-rock interaction and chemical transport depends on the quantitative understanding of the physical and chemical properties of the rocks and fluids participating in reactive transport properties in natural systems (Oelkers, 1996).

Composition of sub-surface waters in basement areas is a function of many variables, which include; composition of recharge water, petrologic and mineralogic composition of sub-surface rocks and hydrogeologic properties of the rocks, which influence water-rock reactions and groundwater flow velocities. According to Caritat et al. (2004), generally chemical quality of groundwater from basement bedrock is often very different from waters from superficial deposits. Bedrock groundwater is often more mature more basic, more

reducing, and more sodium rich and contains more of most minor/trace elements than groundwater from shallow aquifers.

Variations in physical and chemical composition of basement groundwater may also be due to mixing with shallow groundwater from the overburden. Present increases of population with higher demands for water resources are typical in most developing Sub-Saharan countries. This has led to water scarcity and increasing water stress in most of these regions. Nigeria belongs to this equatorial region with most of its harnessed water resources being of surface and sub-surface origin.

The Oban Massif lies in the southeastern part of Nigeria and it is considered the most important groundwater reservoir in Cross River state (Nigeria), providing water to the various cottage industries and communities in the area. The rock types are mostly gneisses, granodiorites, and schist. Groundwater extraction is mainly through shallow wells and hand pump fitted boreholes and in some cases surface water.

Natural geochemical processes play an important role in groundwater quality. The aim of this work is to characterize the chemical processes occurring in the water-bearing horizon.

Previous studies in the area have been on the geology, petrology, and geochemical aspects of the massif. This study therefore forms the first ever study on the hydrochemical evolution of groundwater in the area.

## **2. DESCRIPTION OF STUDY AREA**

The Oban Massif lies between Longitudes 8<sup>00</sup>E and 8<sup>55</sup>E and Latitudes 5<sup>00</sup>N and 5<sup>45</sup>N covering an area of about 8,740 square kilometers (Edet et al., 1998), Figure 1. The crystalline basement complex lies at an average height of about 150m, rising gradually from the south northwards and falls away towards the Cross River to the North (Ayi, 1987). Fractures and joints control drainage within the massif. The massif is well drained with a network of rivers and associated streams, actively engaged in erosion of channels (juvenile stage). The area is characterized by a tropical climate with two distinct seasons viz wet and dry. The wet season spans from May to October, while the dry season lasts from November to April. The average monthly temperature in the area ranges from 29 - 34<sup>0</sup> C. Mean annual rainfall of about 2,300mm have been reported for the area, with annual mean daily relative humidity and evaporation of 86 % and 3.85 mm/day respectively (CRBDA, 2008).

The Oban Massif is described as being underlain by highly deformed Precambrian crystalline basement rocks, mainly migmatites, granites, gneisses, and schists (Ekwueme and Ekwere, 1989; Ekwere and Ekwueme, 1991). These rocks exhibit varying degrees of weathering across the massif. They are intruded by pegmatites, granodiorites, diorites, tonalites, monzonites, charnokites and dolerites (Ekwueme, 1990).

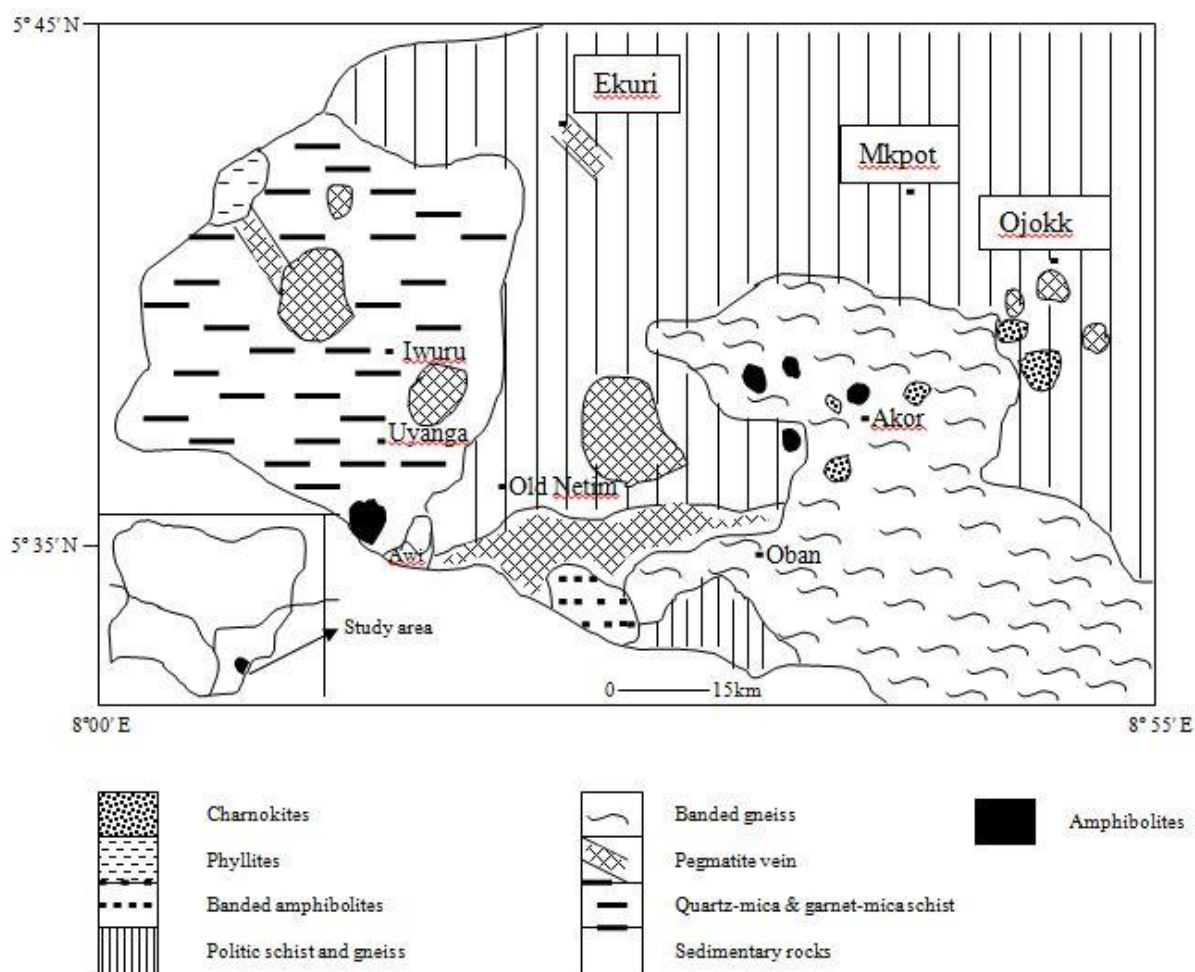
## **3. MATERIALS AND METHODS**

Seventy-four water samples, covering both dry and wet seasons were collected. The dry season samples were collected in the month of February and those for the wet in the July of 2009. The sample locations straddled the various geologic units within the study area. The water samples were obtained from motorized and hand pump fitted boreholes, open wells, and stream channels.

Three samples were collected from each location in 75cl polyethylene bottles. The sample bottles were soaked in 10% HNO<sub>3</sub> for 24 hours and rinsed several times with de-ionized water prior to use. At the sampling locations, the bottles were thoroughly rinsed with aliquots of the sampled waters, prior to collection.

One sample from each location was preserved by acidifying to pH ca.2 with 0.5ml of concentrated HNO<sub>3</sub> acid before analysis for trace metals. All samples were packaged (airtight), labeled and stored in coolers for onward transportation to the laboratory for analysis.

Measurements of temperature, conductivity, TDS, pH, Eh were carried out in the field using standard field equipment (PHT-027 multi-parameter). Prior to measurement of pH, the electrode was calibrated using pH 6.88 and 4.01 buffer solutions at a similar temperature to the water samples. The same meter and an ionodes ORP electrode were used to measure Eh. Calcium, magnesium, sodium, and potassium contents were determined with reference to the APHA (1995) method. Major and trace element contents were determined by atomic absorption spectrophotometer (AAS), model UNICAM 939. The anion contents of samples were determined by colorimetric method using UNICAM UV2 spectrophotometer. All instrumental analyses were carried out in the laboratories of the Aluminum Smelting Company of Nigeria (ALSCON), Ikot Abasi, Nigeria.



**Figure 1.** Geologic map of the study area (Oban massif): insert map of Nigeria (modified from Ekwueme, 2003).

## 4. RESULTS AND DISCUSSION

Compositions of ground and surface waters in the wet and dry seasons within the Oban massif are given in Tables 1 and 2. Statistical summary shows the water is slightly acidic-alkaline (5.08 - 8.65), fresh with total dissolved solids (TDS) < 1000 mg/l.

The cations were in the order  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$  and the anions generally showed  $\text{HCO}_3^{2-} > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ .

### 4.1. Seasonal variation of ions

The analytical results show the slightly acidic nature of water in the dry season as pH ranged from 5.08 - 6.86. The waters tended to be slightly acidic to alkaline in the wet season with pH range of 5.88 – 8.65. The pH values of the dry season fall within the 4.5-7.0 range. This range represents a weak acidic activity, usually that of carbonic acid and smaller amounts of organic acid such as fulvic acid (Langmuir, 1997). Lower pH values of (5.08, 5.40 and 5.12) were recorded at locations with high human population density and can be attributed to low buffer capacity of the regolith in such settings (Edet et al, 2005; Edet and Ekpo, 2008). The pH values however increased markedly in the wet season reflecting the effects of dissolved salts. Sources of such salts may be from weathering of silicates, carbonates, evaporites and sulphide minerals, atmospheric contribution (cyclic salts) as well as anthropogenic inputs (Berner and Berner, 1996).

The electrical conductivity (EC) which expresses ionic strength of solution, varied between 20.9  $\mu\text{s}/\text{cm}$  to 622  $\mu\text{s}/\text{cm}$  in the dry season and 60 - 800  $\mu\text{s}/\text{cm}$  in the wet season. Statistical analysis of results reveals a minimum average electrical conductivity value of 199  $\mu\text{s}/\text{m}$  in the dry season and a high of 243  $\mu\text{s}/\text{cm}$  in the wet season. Somewhat high values within the dry season are reflective of increase in ionic strength and could be related to evaporation effects witnessed during this low water level period and aided by an elevated temperature regime in the area.

The water in the massif exhibited low mean values of total dissolved solids (TDS) concentration of 121 ppm in the dry season and 265 ppm in the wet season. The data shows that electrical conductivity and TDS concentration values were lower in the dry season with an increase in the wet season.

An assessment of data shows a general decrease in cation concentration from the dry to wet seasons. Calcium ( $\text{Ca}^{2+}$ ) was the most dominant accounting for about 78 % and 61 % of total cation in the dry and wet seasons respectively. Concentration of  $\text{Ca}^{2+}$  recorded ranges of 7.27 mg/l – 135.2 mg/l in the dry season and 6.04 – 97.14 mg/l in the wet season. This dominance of  $\text{Ca}^{2+}$  may reflect the process of chemical weathering of silicates and the common occurrence of calcium carbonate (Langmuir, 1997). Water-rock reactions of mineral phases such as plagioclase, calcite, aragonite, anhydrite and dolomite from basement and the sedimentary terrain lying in close proximity to the study area can be adjudged from this.

Sodium ( $\text{Na}^+$ ) was next in dominance with concentration ranges of 1.2 - 9.0 mg/l and 1.8 – 7.0 mg/l in the dry and wet seasons respectively. The lower mean value for  $\text{Na}^+$ , 3.98 mg/l was recorded in the dry season and the higher of 4.35 mg/l in the wet season.

The other cations, magnesium ( $\text{Mg}^{2+}$ ) and potassium ( $\text{K}^+$ ) ranged between 0.4 - 5.4 mg/l and 0.5 - 5.9 mg/l respectively in the dry season. In the wet season, ranges were 0.3 - 3.7 mg/l for Mg and 0.2 - 32.18 mg/l for K. Potassium exhibited the lowest concentration levels relative to other cations. This is common in natural waters due to its tendency to be fixed by clay minerals and precipitate in the formation of secondary minerals (Matthess, 1982). However,  $\text{K}^+$  recorded the highest concentration mean of 13.97 mg/l next to calcium (23.09 mg/l) in the wet season. Potassium shows a reverse trend marked by an increase from the dry to wet season. This increase could be attributed to agricultural practice by the use of fertilizers

for farming by the local populace. Increased surface run-off in the wet season washes these fertilizers, which  $K^+$  is a major component and subsequently percolates into the sub-surface water reservoirs. However, the decrease in concentration levels of cations in the wet season reflects the impacts of dilution by surface run-off percolating into the sub-surface reservoirs.

**Table 1.** Descriptive statistics of parameters as measured in the dry season.

Source	Statistics	Temp (°C)	pH	EC (µs/cm)	TDS (ppm)	Ca	Mg	Na	K	SO <sub>4</sub>	NO <sub>3</sub>	HCO <sub>3</sub>	Cl
Ground water	Min	26.0	5.1	24.8	15.9	7.3	0.5	1.2	0.5	0.6	0.0	18.3	0.9
	Max	28.0	6.9	622.0	398.7	135.2	5.3	4.6	5.9	117.9	45.9	122.3	93.0
	Mean	27.1	6.0	300.7	180.2	39.5	3.7	3.9	3.2	40.9	15.6	45.6	23.5
	SD	0.8	0.5	255.6	169.7	43.1	1.7	0.9	1.7	32.8	15.8	29.1	28.7
Surface water	Min	26.0	5.1	34.6	22.2	12.3	0.4	2.0	0.8	1.1	0.0	12.3	2.5
	Max	32.0	6.3	250.0	209.0	122.1	5.4	9.0	3.5	564.1	47.5	97.6	57.0
	Mean	27.8	5.7	96.4	61.8	34.8	3.0	4.1	2.0	80.8	12.2	49.3	15.3
	SD	1.8	0.4	92.3	59.2	30.7	2.1	1.8	1.0	158.8	15.2	35.2	16.2
<b>WHO (2001)</b>			<b>6.5-8.5</b>	<b>1400</b>	<b>1000</b>	<b>100</b>	<b>50</b>	<b>200</b>	<b>12</b>	<b>400</b>	<b>50</b>		<b>250</b>

**Table 2.** Descriptive statistics of parameters as measured in the wet season.

Source	Statistics	Temp (°C)	pH	EC (µs/cm)	TDS (ppm)	Ca	Mg	Na	K	SO <sub>4</sub>	NO <sub>3</sub>	HCO <sub>3</sub>	Cl
Ground water	Min	27.0	5.9	80.0	60.0	6.0	0.3	2.5	1.0	13.6	0.2	12.1	22.1
	Max	30.0	7.7	580.0	890.0	97.1	3.4	7.0	32.2	471.7	11.7	67.0	308.7
	Mean	28.0	6.8	285.9	333.8	23.1	1.7	4.7	14.0	97.2	2.7	55.0	97.2
	SD	0.9	0.5	176.3	262.6	24.4	1.0	1.5	13.8	107.7	3.4	88.9	79.2
Surface water	Min	26.0	6.3	60	40.0	7.5	0.3	1.8	0.2	25.0	0.1	24.2	50.6
	Max	30.4	8.7	430	570.0	60.1	3.7	5.7	4.7	839.6	10.0	213.5	596.6
	Mean	28.1	7.2	200	196.2	19.5	1.5	3.9	1.8	148.6	2.6	84.9	164.5
	SD	1.1	0.7	124	149.6	16.3	1.1	1.5	1.5	224.9	3.1	59.5	146.2
<b>WHO (2001)</b>			<b>6.5-8.5</b>	<b>1400</b>	<b>1000</b>	<b>100</b>	<b>50</b>	<b>200</b>	<b>12</b>	<b>400</b>	<b>50</b>		<b>250</b>

Anion concentration levels generally increased from the dry to the wet seasons. Chloride exhibited a marked increase along this seasonal trend. Sulphate and bicarbonate were the dominant anions within the dry season with mean concentration values of 61 mg/l and 48 mg/l respectively. In the wet season, chloride was most dominant with an average concentration value of 130.5 mg/l. Sulphate had a mean value of 123 mg/l and bicarbonate, 70 mg/l. Nitrate was least with mean values of 14 mg/l and 2.7 mg/l in the dry and wet seasons respectively.

#### 4.2. Spatial variations of ions

Spatial variations for measured parameters across the massif are presented in Table 3. The differences are reflective of degree of regolith development and lithologic characteristics. The western sector of the massif is composed mainly of granodiorites, granites, granitic gneisses and schists and characterized by thick overburden of 29-47m as revealed from drilled sections. The eastern sector on the other hand is mainly of migmatites, amphibolites and schists with thinner overburden of 6-12m. The lineament density, higher for western and



lower for eastern sectors, as reported by Edet et al., (1994), supports the trend in overburden variability.

Electrical conductivity values across the massif exhibited a lower mean value of 191.42  $\mu\text{s/cm}$  for the eastern sector and 216.21  $\mu\text{s/cm}$  for the western sector. A lower mean TDS value of 226.9 ppm was recorded for the eastern sector of the massif while a mean value of 296.70 ppm was recorded for the western sector. This shows an increase of TDS and EC from the east to the west of the massif. This is probably due to the depth of the weathered profile as revealed by litho-logs from both sectors and an expected increase of TDS along flow path of groundwater as groundwater flows from the east to west.

The mean value of pH for the western sector was 6.23 and 6.84 was deduced for the eastern flank. Relatively lower pH mean value for the western sector may be attributed to sub surface run-off, inputs of organic waste and other anthropogenic inputs due to higher human population density on this flank while higher values for the eastern flank may be due to decrease in dissolved solute (Ekwere, 2010).

The concentration of mobile cations were higher on the western sector of the massif as these are products of mineral dissolution as water flows through the more porous sub-surface media from the eastern to the western sector. Anions  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  however, showed higher mean values on the eastern arm of the massif. This could be attributed to accumulation and concentration of soluble salts in the aquifers as a function of topographic alternation within this axis of the Oban massif (Ekwere, 2010). However, mean values of nitrates were higher on the western sector. This is related to high concentrations of communities and attendant increase in human activity.

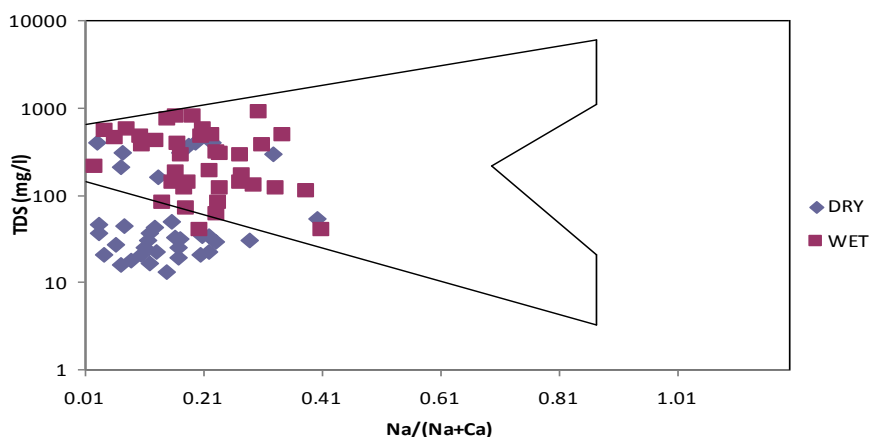
**Table 3.** Mean variations of parameters across western and eastern sectors of the massif.

Parameter	Western Sector	Eastern Sector
Temp. ( $^{\circ}\text{C}$ )	27.7	27.9
pH	6.2	6.8
Conductivity ( $\mu\text{s/cm}$ )	216.2	191.4
TDS (ppm)	296.7	226.9
SWL (m)	2.8	3.1
Yield ( $\text{m}^3\text{hr}^{-1}$ )	6.1	6.2
Ca	31.7	15.6
Mg	2.7	1.5
Na	4.3	3.6
K	6.9	1.4
$\text{SO}_4$	71.6	159.9
$\text{NO}_3$	9.1	4.7
$\text{HCO}_3$	59.4	92.4
Cl	67.1	106.6
$\text{PO}_4$	1.3	0.2
$\text{SiO}_2$	2.0	6.9
Lithology	Gneiss, quartzite, schist, granodiorite, pegmatite, gneissic-granite.	Migmatites, schists, amphibolites, quartzite, syenites.

#### 4.3. Hydrochemical processes controlling water characteristics

Dissolved species and their relations with each other can reveal the origin of solutes and the processes that generated the observed composition of water. Cross plots and ionic ratios have been used as tools for interpretation of groundwater composition in the study area.

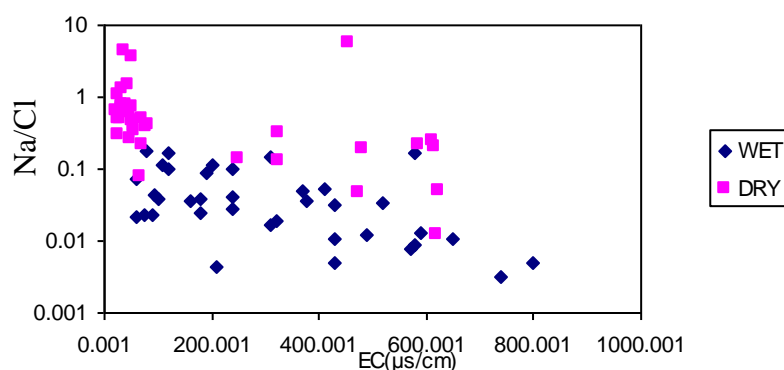
Gibbs (1970) proposed a simple explanation for the general chemistry of both surface and sub-surface waters. He showed that: (1) rainfall (rain dominated), (2) rock-weathering reactions (rock-dominated) and (3) evaporation-crystallization or a combination of these influences, determine the chemistries of surface and ground waters. The plot of TDS against weight ratio of Na/ Na+Ca (Figure 2), indicates the mechanisms that determined the major ion composition of sampled waters. Rock dominance appears to be the major controlling factor of the chemistry of sampled waters from the wet season. The plot reveals about 86% of the sampled waters to be within the rock dominance field. Majority of the waters from the dry season (72%), plot within the rainfall/precipitation dominance field. This can be explained by effects of evaporation, giving less time for water-rock reactions and dissolution. The waters are of relatively less resident times and their chemistry is of the recharge source (rainfall). The remaining 28% of the waters plot within the rock dominance field, reflecting some form of structural control leading to higher resident times and effective mineral dissolution processes.



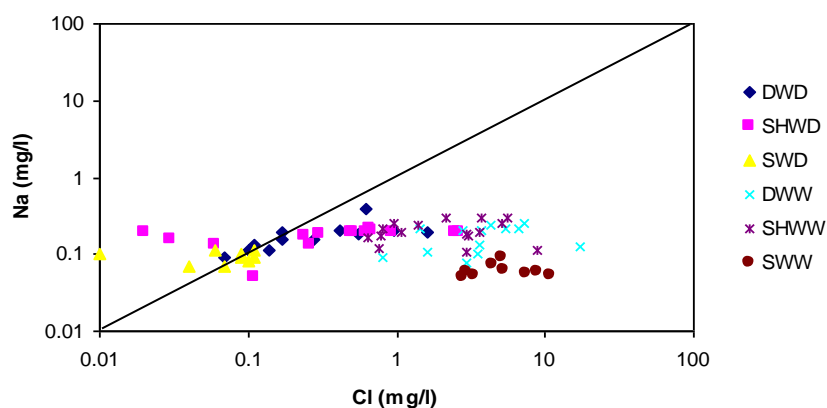
**Figure 2.** Plot of TDS versus weight ratio of Na/(Na+Ca) for sampled waters across seasons.

Plots of Na versus Cl have been used to identify the mechanism for acquiring salinity and saline intrusions in aquifers (Zhu et al., 2008; Singh et al., 2005). Generally, evaporation causes an increase in the concentrations of chemical species in water. If the evaporation process is dominant, and no mineral species are precipitated, the  $\text{Na}^+/\text{Cl}^-$  ratio is unchanged (Jankowski and Acworth, 1997). Thus, a plot of  $\text{Na}^+/\text{Cl}^-$  versus EC would give a horizontal line, which would indicate concentration by evaporation and transpiration (Figure 3a). If simple dissolution of halite is responsible for sodium, then  $\text{Na}^+/\text{Cl}^-$  molar ratio would be approximately one. Mean ratios of Na/Cl in the dry season was 1.261 and 0.076 for the wet season, Ekwere (2010). Plot of Na versus Cl (Figure 3b) shows an excess of Cl to Na, particularly for samples from shallow and deep aquifers as well as surface waters from the wet season. Most samples of the shallow and deep aquifers also plot below the equiline. Few shallow aquifer and surface water samples from the dry season plot above the equiline reflecting excess of Na to Cl. The excess of sodium for point plots suggests background levels of Na that originate from weathering of Na-silicate minerals (e.g. sodium plagioclase) from the crystalline basement. Chloride excess over  $\text{Na}^+$  suggests other sources contributing  $\text{Cl}^-$  to groundwater. A possible source of the excess Cl in the waters could be saline water from sedimentary rocks adjacent to the crystalline basement. Such saline waters are believed to be

probably of primitive marine origin (Michard et al., 1996). Ca-Cl water type has been reported from the area, (Ekwere, 2010) and this water type is a result of reverse cation exchange due to the removal of Na out of solution for bound Ca.



**Figure 3a.** Plot of Na/Cl versus electrical conductivity (EC) for sampled the waters.



**Figure 3b.** Plot of Na versus Cl for sampled waters.

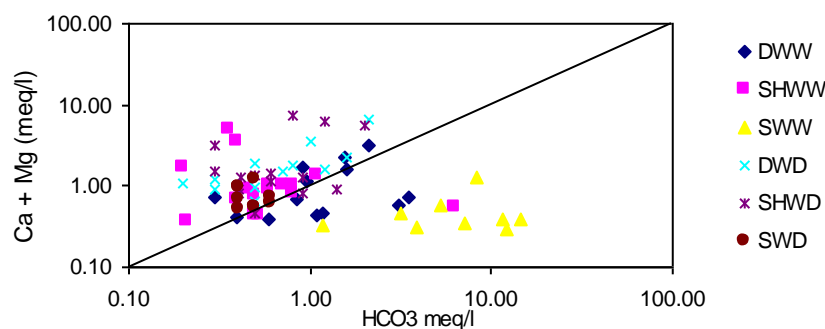
**Note:** DWD- deep well dry season; SHWD-shallow well dry season; SWD-surface water dry season; DWW- deep well wet season; SHWW- shallow well wet season; SWW- surface water wet season.

Ca-Cl type waters could also be a result of the process of mixing between younger, fresher water with more saline older water (Adams et al., 2001). Increased water in aquifers, resultant from recharge levels in the wet season, leads to higher groundwater flow. This supports interaction of water from the adjacent sedimentary terrain with the basement through porous sub-surface media. Another possible source is cation ion exchange processes. Zhu et al. (2008) have shown that low Na/Cl ratio of groundwater probably results from ion exchange of Na for Ca and Mg in clay. This is evident in the ratios of these pairs of ionic species from the sampled waters (Ekwere, 2010).

A plot of Ca + Mg versus HCO<sub>3</sub> (Figure 4) shows that about 81% of sampled waters plot above the 1:1 equiline, for groundwater from both sampling seasons. This indicates an excess of Ca + Mg to HCO<sub>3</sub>. The remaining fraction, plot around the equiline showing a good correlation between these two factors. This indicates congruent dissolution of silicates (feldspars) and calcite. Surface water samples from the wet season plot below the equiline reflecting excess bicarbonate relative to Ca + Mg. The excess of Ca + Mg over bicarbonate in the waters indicates some extra source of these ions, and a demand that part of these excess



positive charges has to be balanced by other anions like  $\text{SO}_4^{2-}$  and/or  $\text{Cl}^-$ . Besides carbonate weathering, silicate weathering (chiefly plagioclase and feldspar), evaporite dissolution can be possible sources of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in water (Ettazarini, 2005; Singh et al., 2005).

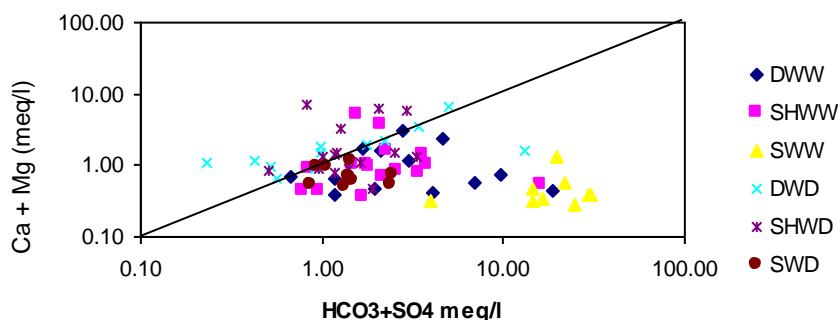


**Figure 4.** Plot of Ca +Mg versus  $\text{HCO}_3$  for sampled waters across seasons.

The excess of bicarbonate over Ca + Mg for samples from the wet season requires that part of the alkalinity should be balanced by alkalis (Na + K). This bicarbonate excess may be from hydrolysis of carbonate rocks from the Cretaceous sedimentary terrain lying adjacent to the basement complex.

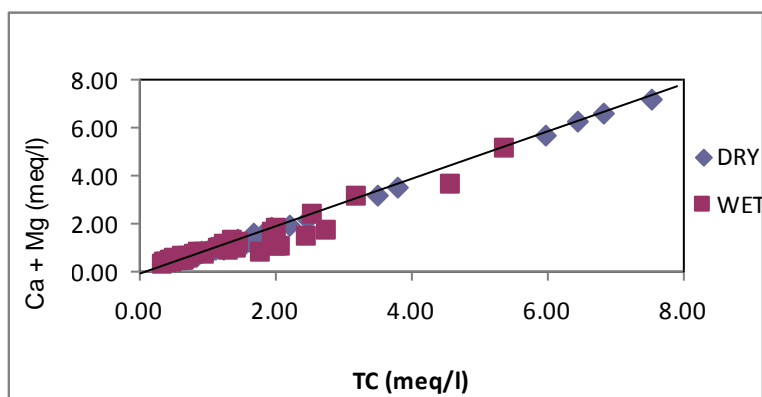
Evidence of silicate weathering and cation exchange can be adjudged by plots of Ca + Mg against  $\text{HCO}_3 + \text{SO}_4$  (Garcia et al., 2001). This reflects the amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  gained or lost relative to that provided by the dissolution of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  bearing minerals.

Figure 5 shows a plot of this ratio, with most of the points falling below the equiline, a greater percentage being the samples from the wet season. A few samples plot, evolving around the equiline, while a greater percentage of those from the dry season plot above. This demands a portion of the  $\text{HCO}_3 + \text{SO}_4$  be balanced by the alkalis Na + K. Points on and around the equiline correspond to simultaneous calcite and feldspar dissolution. If  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ , were derived from simple dissolution of calcitic minerals and feldspars, then a charge balance should exist between the cations and anions. An ion exchange process is characterized by  $\text{HCO}_3 + \text{SO}_4$  excess over Ca + Mg (86% of the wet season samples and about 17% of the dry season samples), while the reverse ion exchange is marked by Ca + Mg excess over  $\text{HCO}_3 + \text{SO}_4$ , largely for the dry season samples (Cerling et al., 1989; Fisher and Mullican, 1997; Ettazarini, 2005).

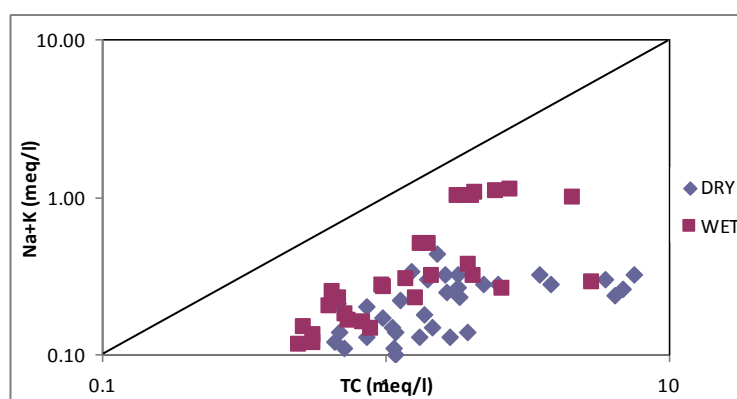


**Figure 5.** Plot of Ca +Mg versus  $\text{HCO}_3 + \text{SO}_4$  for sampled waters across seasons.

A plot of (Ca + Mg) versus TC (total cation) for samples from both seasons shows that all the points plot along and close to the equiline in a linear spread, Figure 6a. The average ratio of [Ca + Mg]/ TC were 0.86 and 0.76 for the dry and wet seasons respectively. Plot of Na + K against TC (Figure 6b) shows that, all points plot below the equiline for both seasons. The average ratios of (Na + K)/TC are 0.14 and 0.24 for the dry and wet seasons respectively. Calcium and magnesium are the dominant cations across seasons. Evaporation and  $\text{Ca}^{2+}$  precipitation alongside  $\text{Mg}^{2+}$  is responsible for the dominance of these ionic species in the dry season (Ekwere, 2010). The degree of dominance however decreases from the dry to the wet seasons. The ratio of Na + K to TC increases from the dry to the wet seasons. This indicates an increasing contribution of alkalis with increase in dissolved solids (Singh et al., 2005).



**Figure 6a.** Plot of Ca + Mg versus total cation (TC) sampled waters across seasons.



**Figure 6b.** Plot of Na + K versus total cation (TC) for sampled waters across seasons.

#### 4.4. Factor analysis

Factor analysis is a multivariate statistical technique that is widely used to aid interpretation of geochemical data and enhances subtle but significant single-element anomalies (Garret and Nichol, 1969). In other words, factor analysis has the simple objective of revealing an underlying relation that is presumed to exist within a set of multivariate observation, (Davies, 1986). By so doing, the structure of the underlying system that produced the data is well understood. Factor analyses were employed in this study to process data and determine the sources of incipient ionic species relative to physical parameters as well as factors controlling such. Results of R- mode factor analyses for both seasons of sampling are summarized in factor matrix Tables 4 and 5.

**Table 4.** Factor loading for dry season.

Variables	FACTOR			
	1	2	3	4
Temp.	-0.004	0.020	-0.034	-0.927
EC	0.944	-0.036	0.030	-0.046
TDS	0.944	-0.036	0.030	-0.046
pH	-0.458	0.117	-0.401	0.298
Na	0.573	0.184	0.382	0.231
K	0.806	0.425	0.042	0.050
Ca	0.233	0.824	0.052	0.096
Mg	0.767	0.576	0.079	0.153
Cl	0.584	0.211	0.436	0.203
HCO <sub>3</sub> <sup>-</sup>	-0.001	0.921	0.144	-0.086
SO <sub>4</sub> <sup>2-</sup>	-0.131	0.105	0.877	-0.083
NO <sub>3</sub> <sup>-</sup>	0.332	0.147	0.734	0.227
Eigenval	4.949	1.704	1.390	1.088
% Variance	41.242	14.198	11.586	9.064
Cumul. Eigenv.	4.949	6.653	8.043	9.131
% Cumul.	41.242	55.440	67.026	76.090

On inspection, a four and three factor models were recognized for the dry and wet seasons respectively. Only variables with loadings greater than 0.50, were considered significant members of a particular factor.

In the dry season, factor one (EC, TDS, Na, K, Mg and Cl) accounted for 41.2% of total data variance and was interpreted as related to geogenic processes; infiltration of surface run-off and other sub-surface fluids, dissolution processes, mixing of waters and cation exchange processes.

The second factor (Ca, Mg, HCO<sub>3</sub>), with 14.2% data variance, was interpreted to be related to natural weathering of Ca and Mg bearing minerals and lesser extents of carbonate dissolution processes within the porous sub-surface media. The main cation exchange elements Ca<sup>2+</sup> and Mg<sup>2+</sup> relative to HCO<sub>3</sub><sup>-</sup> correlated positively indicating the influence of the geological matrix.

Factor 3 (SO<sub>4</sub> and NO<sub>3</sub>) accounted for 11.6% data variance and was interpreted to be reflective of biogenic reactions. Organic activities within the soil profile affects infiltrating water, Langmuir (1997). Impacts of land use practices could also be inferred due to the presence of the biochemical NO<sub>3</sub>, which is a principal plant nutrient (Adams et al, 2001). The fourth factor, which is temperature, shows its effects on the series of processes that control the chemistry of sampled waters.

Results from R-mode factor analysis for the wet season shows factor 1 (Na, K, Ca and Mg) accounts for 36.2% of data variation, reflecting natural weathering from water-rock interactions in geo-matrix of the basement. Factor 2, (EC, TDS, HCO<sub>3</sub>, SO<sub>4</sub>), exhibits loading that accounts for about 18.9% of data variance. This factor is believed to be related to

weathering and water-rock reactions. Inputs of mobile phases of ionic species ( $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ) from dissolution and cation exchange are evident in conductivity levels. Factor 3 (pH,  $\text{NO}_3^-$ ) accounts for 11.7% of data variance and similar to factor three of the dry season, it indicates the effects of organic activities controlled by varying pH conditions as well as effects of land use practices.

#### 4.5. Chemical types and trends of groundwater

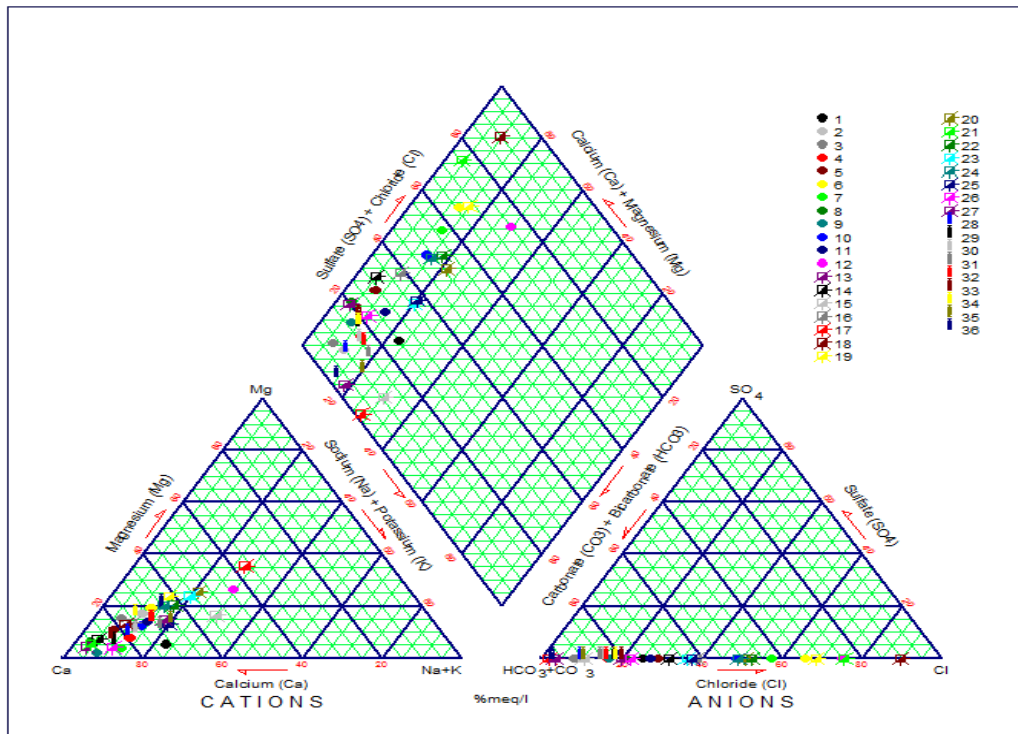
In order to ascertain the groundwater types and visualize the trends of chemistry, the Piper trilinear diagram was used (Figures 7a and 7b). These show the relative concentrations of the different ionic species for the individual sample type based on average values across the sampling seasons. Calcium is the dominant cation across both seasons. Bicarbonate is the dominant anion for the water types in the wet season, while chloride is for the dry season. The recognizable water types are; Ca – (Mg) –  $\text{HCO}_3^-$  and Ca – (Na) – Cl –  $\text{SO}_4$ .

The Ca - (Mg) -  $\text{HCO}_3^-$  water type is defined as the normal alkaline group of water. Amadi (1987) describes this type of water of being typical of Nigerian basement terrain with limited mixing, perhaps reflecting a primary stage of evolution of its groundwater system. Similar water type has been reported for the western basement complex of Nigeria by Elueze et al. (2004) and Tijani (1994). The chemical composition of this water type is said to be due to the dissolution of silicate minerals in the bedrock and aluminosilicates in the weathered regolith, Tijani (1994).

The Ca – Na – Cl -  $\text{SO}_4$  association is defined as a major constituent of atmospheric precipitation (Davis and De Weist, 1966). Elueze et al. (2004) reports occurrence of such water type in the western sector of the Nigerian basement complex. The chemistry of this water type is therefore influenced by precipitation.

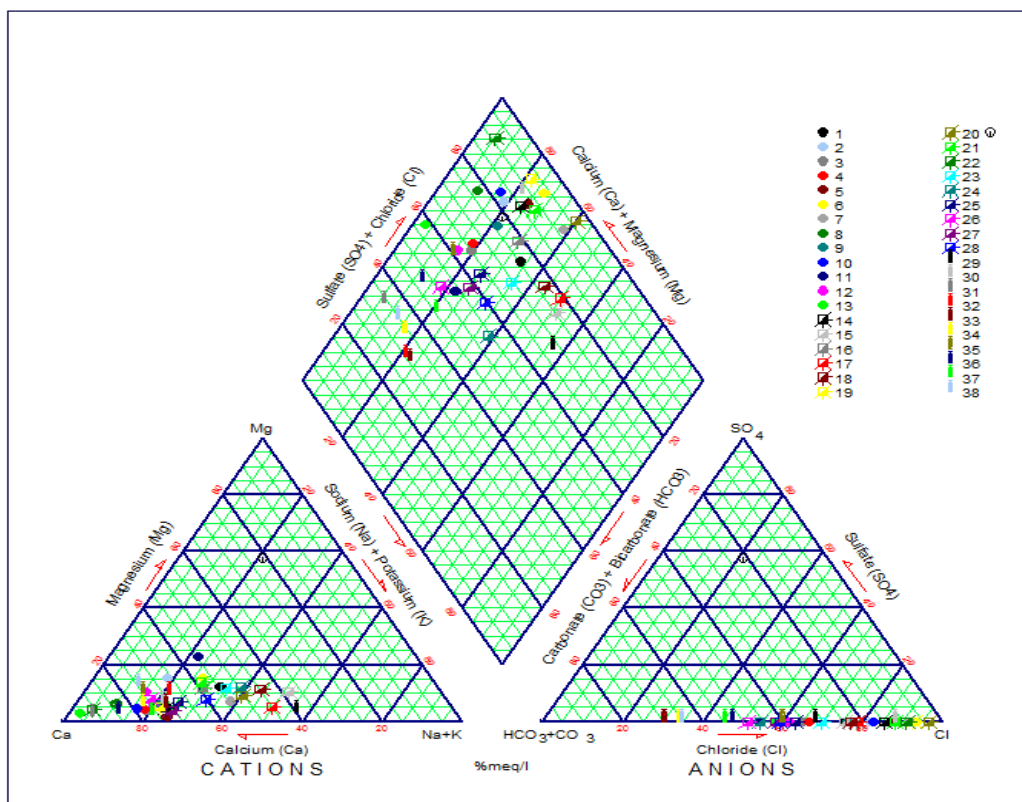
**Table 5.** Factor loading for wet season.

VARIABLE	FACTOR		
	1	2	3
Temp.	0.405	-0.385	-0.207
EC	-0.135	<b>0.945</b>	0.072
TDS	0.132	<b>0.884</b>	-0.125
pH	-0.285	-0.221	<b>0.821</b>
Na	<b>0.849</b>	-0.278	-0.117
K	<b>0.730</b>	-0.040	0.071
Ca	<b>0.631</b>	0.164	-0.009
Mg	<b>0.879</b>	-0.035	-0.028
Cl	-0.124	0.447	0.137
$\text{HCO}_3^-$	-0.500	<b>0.691</b>	0.154
$\text{SO}_4^{2-}$	-0.499	<b>0.591</b>	0.462
$\text{NO}_3^-$	0.254	0.301	<b>0.792</b>
Eigenval	4.339	2.272	1.409
% Variance	36.155	18.934	11.742
Cumul. Eigenv.	4.339	6.611	8.020
% Cumul.	36.155	55.089	66.831



1-12 boreholes; 13-27 open wells; 28-36 surface streams

**Figure 7a.** Trilinear diagram plot of water samples from the dry season.



1-13 boreholes; 14-28 open wells; 29-38 surface streams

**Figure 7b.** Trilinear diagram plot of water samples from the wet season.



## 5. CONCLUSIONS

The present hydrochemical status of the study area shows concentration levels of ionic species to be controlled by geogenic processes. Geologic and hydrogeologic features affect the chemistries as exhibited by groundwater. Order of abundance of major chemical species was  $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$  and  $\text{HCO}_3 > \text{SO}_4 > \text{Cl}$  with minor spatial variations across the sampling seasons. Deductions from ionic ratios cross plots and factor analysis support interrelations between ionic species that can be explained by geologic processes. These adjudged natural processes include weathering of mineral phases (mainly silicates), water mixing (from adjacent sedimentary terrain), and ion exchange reactions. This broad spectrum of hydrochemical dynamics is indicated by two dominant hydrochemical facies; Ca-(Na)-Cl- $\text{SO}_4$  and Ca-(Mg)- $\text{HCO}_3$  water types in the study area.

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