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GEOCHEMICAL STUDIES OF GROUNDWATER SYSTEMS OF SEMIARID YOLA AREA, NORTHEAST, NIGERIA

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ABSTRACT

Geochemical studies of Yola area of Northeast Nigeria were studied during a dry season period (November 2008). This was to determine the process controlling the water chemistry and to assess the quality of water. The results show that, based on ionic ratios, precipitation and water-rock interaction (silicate weathering) are the main controlling factors contributing to solute concentration in these areas. The main water types in the area include Mg^{2+}-HCO_3^- and Na^+-Cl^- are the dominant ion types for the shallow groundwater, Mg^{2+}-Cl^-, Mg^{2+}-HCO_3^- and Na^+-HCO_3^- for the deep groundwater and Na^+-Cl^- for the surface water bodies.

Equilibrium specification calculations revealed that the water samples are largely undersaturated with respect to calcite and dolomite in the water samples.

Groundwater samples from the shallow groundwater indicate pH values (6.10 to 7.08) and Eh values (mean 0.72 volt) whereas those of the deep groundwater revealed pH range (6.60 to 7.80) and Eh values (mean 0.75 volt). They are slightly acidic to neutral, largely soft, clean waters with fairly low to moderate concentration of dissolved solids that fall within the international acceptable limits for drinking, domestic and irrigation purposes.

However some samples indicate iron and nitrate values that are above the recommended limits and should be treated before use. Employing Electrical Conductivity (EC), Total Dissolved Solids (TDS), Sodium Adsorption Ratio (SAR), Magnesium Adsorption Ratio (MAR), Permeability Index (PI), Kellys Ratio (KR), and Residual Sodium Bicarbonate (RSBC) as criteria, the waters appear suitable for irrigation purposes.

KEYWORDS; Geochemical studies, Weathering, Equilibrium calculations, Yola area, Nigeri

INTRODUCTION

The development of groundwater resources for water supply is a widespread practice in Nigeria, favored by the existence of basins with thick Quaternary deposits that form aquifers with good quality water. The aquifer systems of the study area are particularly productive (Obiefuna and Orazulike 2010). Further intensive use for irrigation makes groundwater in the area a critical resource for human activities. Despite its importance, little is known about the natural phenomena that govern the chemical composition of the groundwater or the anthropogenic factors that presently affect them.

Previous records on the hydrogeology and groundwater conditions in Yola area (Jackson 1995 and Obiefuna et al (1999) lacked indepth hydrogeochemical information.

However few number of similar relevant studies in other parts of the world exist (Stuyfzand 1986; Walraevens 1990; Stuyfzand 1993; Garcia et al 1998a; Garcia et al 1998b; MClean at al 2000; Pannatier et al 2000; Garlindo et al 2001; Walraeven et al 2003; Jerzersky 2007).

The main objective of this paper is to carryout a geochemical study of groundwater systems of the study area as well as identifies the relevant water-sediment interactions.

The Study Area

The study area fall within longitudes $12^0 20'$E and $12^0 34'$E and latitudes $9^0 11'$N and $9^0 24'$N and lies about 50km south of the Hawal Massifs. It is bounded to the east by the Republic of Cameroun and to the west by Ngurore town. The northern boundary is demarcated by Gokra town and the southern boundary by the Mandarare town and occupies approximately 431km^2 of the land surface (Figure1).

The main access routes are tarred roads such as Yola-Maiduguri road to the north and Yola-Fufore road to the south as well as Yola-Numan road to the west. These road networks enhanced accessibility by linking the urban and rural areas as well as agricultural and upland areas. Thus the study area encompasses an arable land mass of about 431km^2 of which 16.2% are urban 14.5% are upland 10.1% are agricultural and 59.2% are rural. The study area which falls within the semi-arid climatic zone of Nigeria in Sub-Saharan Africa is characterized by two distinct seasons; a hot dry season lasting from November to April and a cool rainy season lasting from April to October. The Saharan air causes the dry season which is accompanied by low relative humidity (31% to 35.4%) and intense aridity that makes the atmosphere very dusty. Available data for temperature for the study area show that the maximum temperature for the dry months ranged from 19^{o}C to 39.7^{o}C compared to the wet months with temperature in the range of 26.7^{o}C to 42.6 ^{o}C (Obiefuna and Orazulike 2010). The rainy season follows the advancing Atlantic Maritime Air which is companied by high humidity ranging from 62.5% to 79% in the rainy season (Obiefuna and Orazulike 2010). The mean annual rainfall is about 827.7 mm (33 inches) while the mean annual evapotranspiration is about 2384.6 mm (98 inches).

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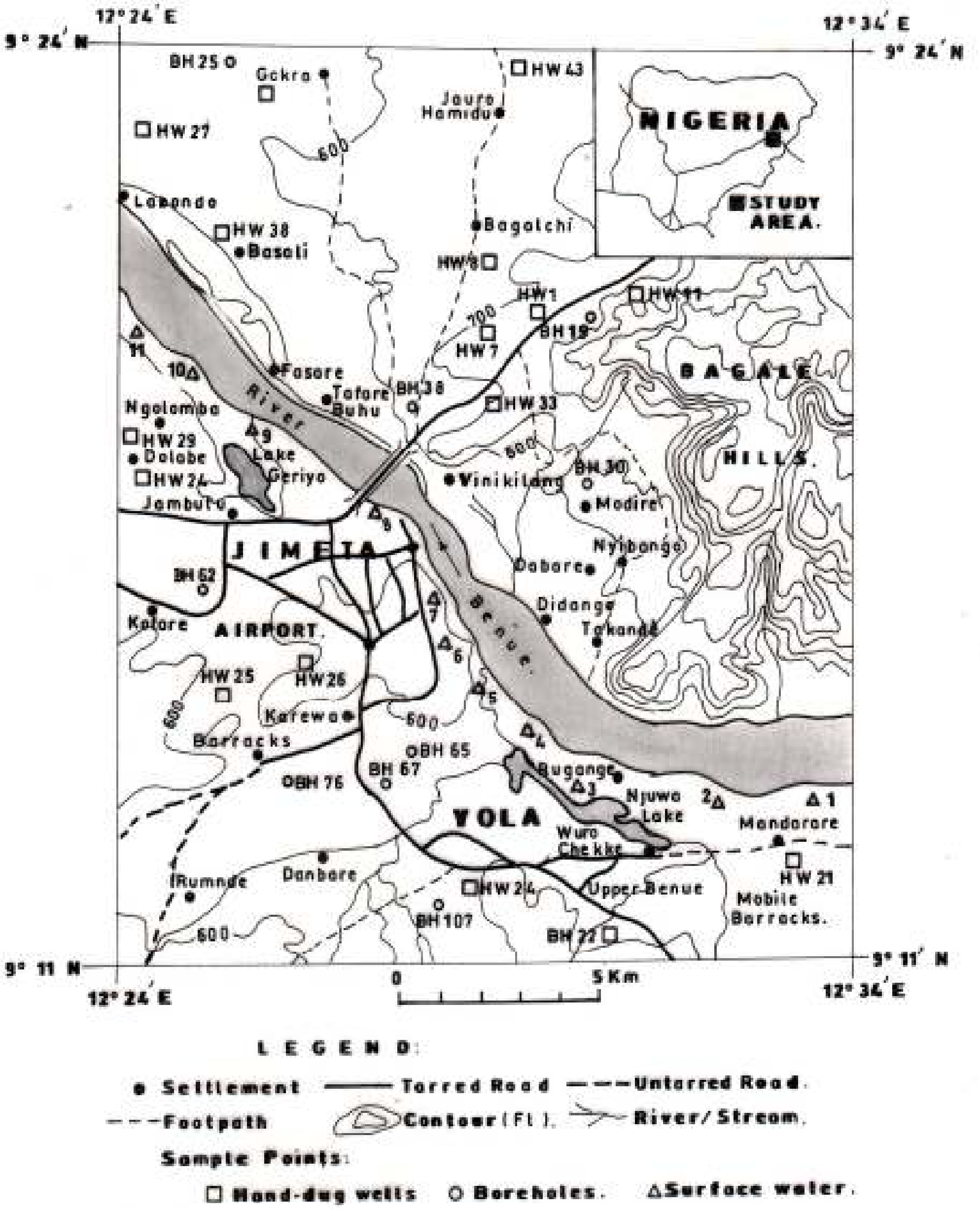

Fig. 1: Map of the study area showing some well locations and sampling points.

Geology and Hydrogeology

The Bima Sandstone marks the base of the sedimentary succession in the Upper Benue Trough and it overlies uncomfortably on the undulating Precambrian Basement Complex. It varies in thickness from 100m to 300m and has its maximum thickness at the Lamurde anticline where it exceeds 3000m. The differing degree of sediment accumulation in the basin and the irregular relief of the crystalline basement on which the sediments accumulated are probably responsible for the variation in thickness. The Bima Sandstone rocks in the Upper Benue Basin have been sub-divided from base to top into three sandstone members. These include the Lower Aptian/Albian Lower Bima (B1), the Middle Albian Bima Sandstone (B2) and the late Albian/Cenomanian Upper Bima Sandstone (B3) (Carter et al 1963).

The study area is underlain by the upper member of the Bima Sandstone (B3) which is a cretaceous sedimentary unit of the Yola Arm of the Upper Benue Trough. The Upper Bima Sandstone (B3) was marked by the deposition, during the cenomanian? Of fluvio-deltaic sandstones and arkoses, which commenced in the south and extended progressively northwards? Several episodes of transgressions and regressions (often linked with sedimentary disturbances) are registered in the Bima Sandstone. The surface geologic units of the study area are the fine-medium grained sandstone to the north and south and the coarse grained sandstone to the northeast (Figure 2). The depth to the bedrock varies from 30 meters to more than 45 meters. Stratigraphically, the Bima Sandstone consist of alternating layers of poorly to moderately consolidated fine to coarse grained sandstones, clay-shales, siltstone and mudstone with an average thickness of more than 250 meters as seen from their outcrops in the field. This geologic formation which reaches several hundred meters in thickness is of significant hydrogeologic interest. From field observations, exposures of Bima Sandstone in the study area is light brown to reddish brown in colour, feldspathic and fine to coarse grained in texture. It is highly crystalline and cemented in places especially north of Jimeta and Yola around Girei area (Obiefuna and Orazulike 2010).

The grain-sizes range from 0.43mm to 2.2mm indicating a fine to coarse grained sandstone that is poorly to moderately sorted. The mineralogical composition of the Bima Sandstone consist essentially of 50-60% quartz, 26-28% plagioclase feldspar, 4% microcline feldspar 8% clay matrix, 8% iron oxide and 3% calcite and are thus classified as arkosic sandstone (Obiefuna and Orazulike 2010).

In thin section, the quartz is sub-angular to sub-rounded and rimed by reddish brown colouration indicating iron-oxide. The feldspars are largely plagioclase and microcline parts of which have been altered to clay matrix. It is thus both texturally and mineralogically immature and hence competent. The predominance of quartz grains could be due to diagenetic effect of compaction and pressure solution at greater depths. Hence the quartz grains responded by shifting into more dense packing arrangements during the middle to later stages of diagenesis lending to reduction in porosity of the sandstone. The sandstone is thus highly indurated and has reduced porosity probably due to increased siliceous cementation especially adjacent to lineaments. Field studies have shown that there is hydraulic connection between the river course alluvium and the underlying Bima Sandstone Formation.

Obiefuna and Orazulike (2010) have defined the main hydrogeologic characteristics of Yola Area based on data from pumping test, statistical grain-size test, hydrolithological analysis of borehole logs and field work. The study area is limited by the Bagale hills in the east and northeast and the River Benue valley to the south and southwest respectively. The Bagale hills are situated almost parallel to the country border with the Republic of Cameroun and acts as the boundary to the groundwater flow.

The accurate definition of the limits and types of aquifers in the study area is not simple because of the heterogeneity of the sedimentary sequence and the different criteria used in the lithological descriptions in the well records.

However, based on available borehole lithologic logs two aquifer systems have been identified namely the upper alluvial aquifer system and the lower semi-confined to confined aquifer system

The recent quaternary sediments constitute the shallow upper alluvial aquifer whereas the Older Cretaceous sediments constitute the lower semi-confined to confined aquifer system. The former occur within the depth range of 0-80m whereas the later occur within the depth range of 80-250m. The shallow aquifer occur in the recent alluvial sediments consisting of gravels, sands, silts and clays whereas the deep aquifers occur in the underlying fine to coarse grained Bima Sandstone Formation (Figures 3 and 4).

Groundwater within the alluvial aquifer occur largely under water table conditions at outcrops and in places it is confined by interstitial clays especially in areas close to the banks of the River Benue. The aquifers are recharged by percolation of rainfall and direct infiltration of the River Benue.

A summary of the hydraulic conductivity, k, values obtained from both the pumping test and the statistical grain size methods for the upper unconfined alluvial aquifer indicate values ranging from 0.051m/day to 56.98m/day with a mean value of 2.54m/day. The hydraulic conductivity values obtained for the lower semi-confined to confined aquifer employing the pumping test and the statistical grain-size methods indicate values ranging from 0.22m/day to 10.48m/day with a mean value of 3.81m/day. . The transmissivity values for the upper unconfined alluvial aquifer ranges from 1.52m^2/day to 349.86m^2/day with a mean value of 37.99m^2/day whereas those obtained from granulometric methods vary from 9.97 x 10^{-3} m^2/s to 1.53m^2/s (Obiefuna and Orazulike 2010).

The transmissivity values for the lower semi-confined to confined aquifer varies from 9.18m^2/day to 349.93m^2/day with a mean value of about 103.51m^2/day. The variation in transmissivity values in the two aquifer systems are because of variations in the thickness of the aquifer rather than in hydraulic conductivity. The k,values obtained for these aquifer systems fall within the range of 10^{-2}m/day to 10^{2}m/day which indicate an aquifer system of moderate to good performance (Todd, 1995).

The flow directions in the two aquifer systems are assumed to be in the same direction due to similar depth to static water levels. To the northeast a localized recharge area of the aquifer occurred to the west whereas to the southwest it is northeastwards towards the Benue River. It discharges naturally at points or areas where the aquifer with its underlying relatively impermeable alluvial units such as clay-shales and mudstone intercepts the ground surface in river or stream valleys (Figure 5)

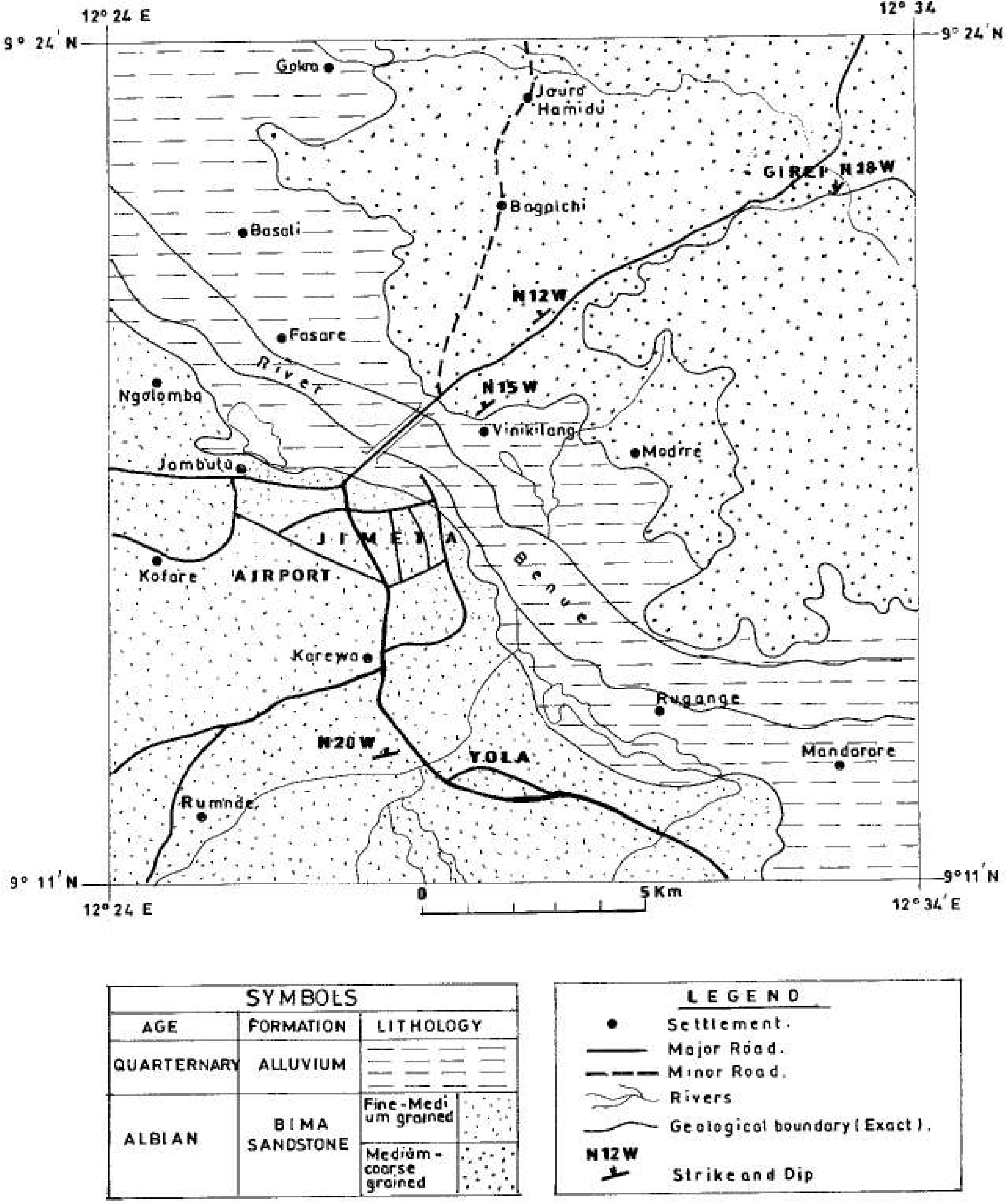

Fig. 2: Geological map of the study area.

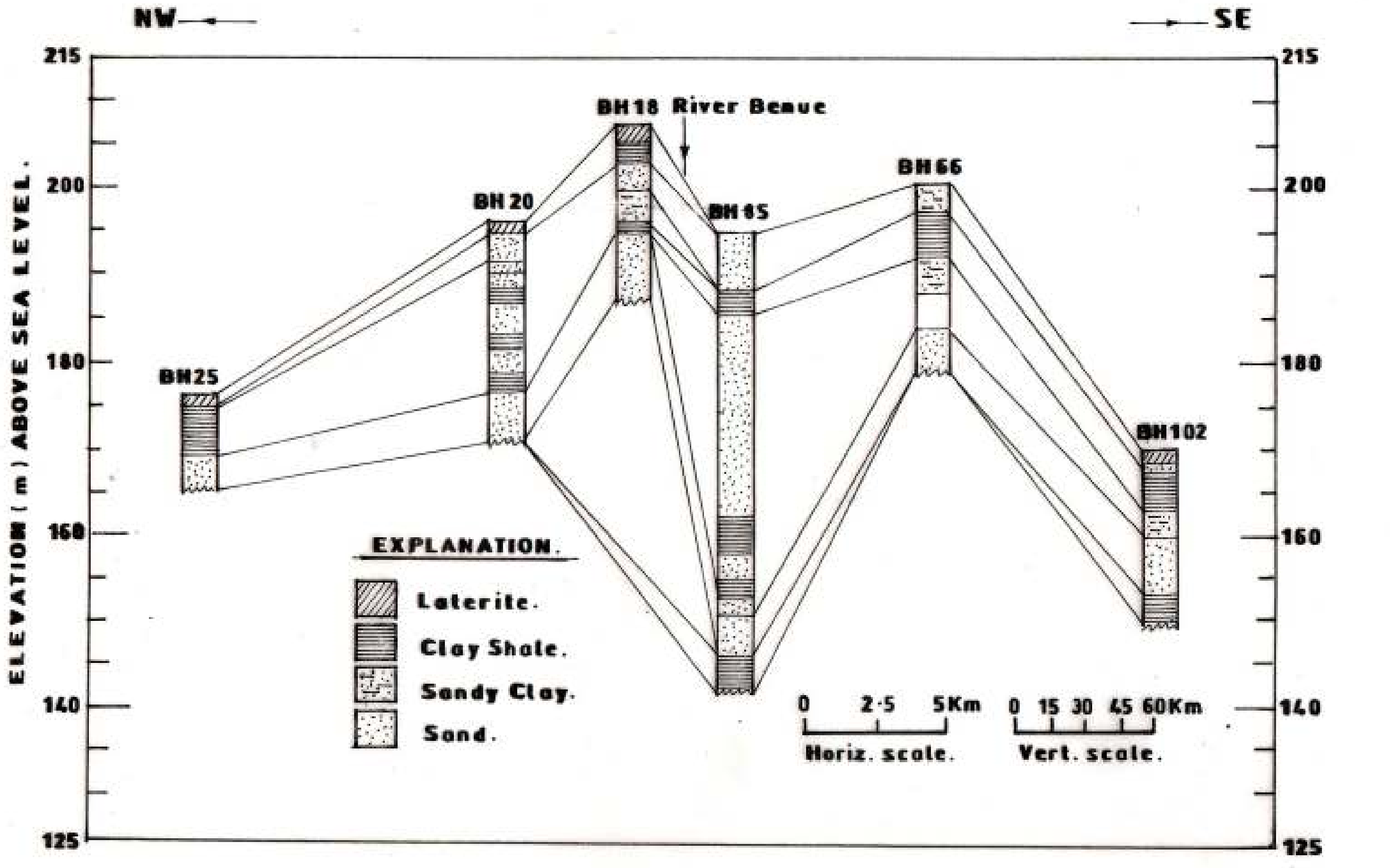

Fig. 3: Correlation of some boreholes log showing the nature of the aquifer in the study area.

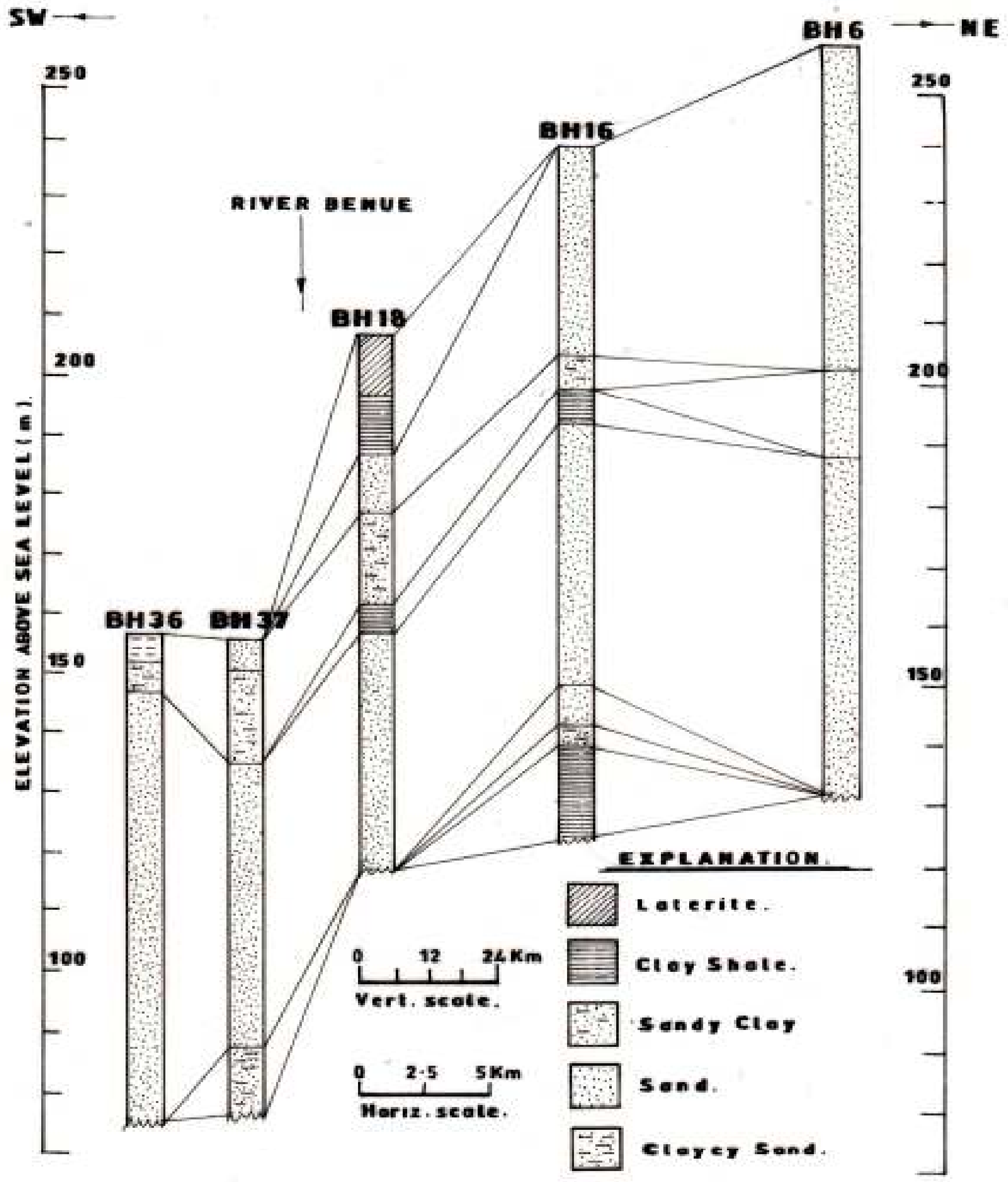

Fig. 4: Correlation of some boreholes log showing the nature of the aquifer system in the study area.

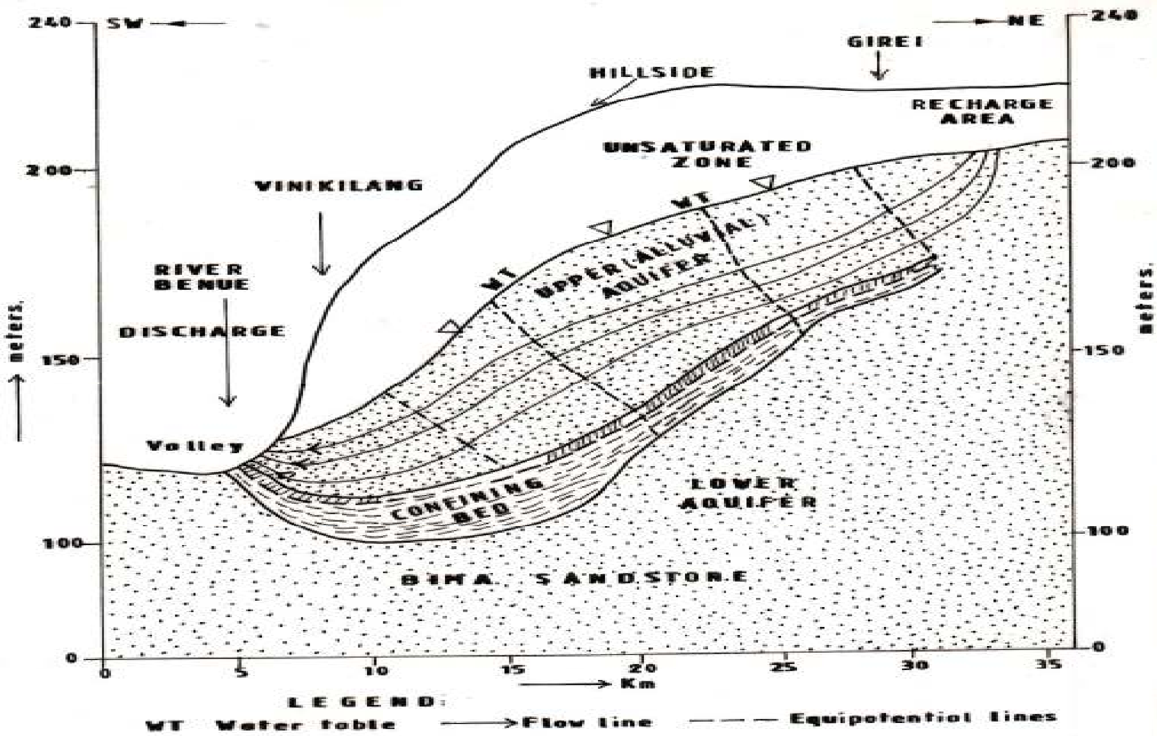

Fig. 5: Idealized flownet for the acquifer systems of the study area.

MATERIALS AND METHODS

A total of ninety-six (96) water samples were collected from fifty-seven (57) locations between the months of November and December 2007.

Of this number, sixty (60) locations (consisting of 92 groundwater, 11 surface water and 5 rainwater samples) were sampled. These samples were designated as SW1 to SW11 for surface water, RW1 to RW5 for rainwater and HW1 to HW48 and BH17 to BH139 for groundwater samples) respectively (Figure 1) A global positioning system (GPS), Garment 12, was used for well location and elevation readings. This was supported by topographic sheets made available from the Ministry of Lands and Survey, Adamawa State of Nigeria.

The samples were collected in polyethylene bottles after pumping the sampled wells for about 30 minutes and kept cool until analyses. This was done to remove groundwater stored in the well itself and to obtain representative samples. Various physical parameters were measured in the field using standard equipments. These include Temperature and conductivity (DR2010), dissolved oxygen (Hach 2400 electronic meter) and pH/Eh (DR2010 pH meter) measurements were made in the field. Samples for bacteriological analyses were collected in 250 ml brown bottles and incubated for 5 days and multiple tube techniques was used for coliform enumeration.

The samples were filtered through a thin polycarbonate membrane with 0.45µm pore size and subsequently analyzed in the Laboratory of the Adamawa State Water Board Yola for Na^+, K^+, Ca^{2+} Mg^{2+}, HCO_3^- Cl^-, SO_4^{2-}, F^{-1}, and TDS. The chemical analyses were based on the standard methods presented in APHA/AWWA/WPCF (1998).

Total hardness was determined by EDTA titrimetric method. Na^+ and K^+ were measured using flame photometry. Sulphate by Spectrophotometric Turbidimetry and phosphate, nitrate and silica by Calorimetry with a uv-visible Spectrophotometer (Hach/2400).

All the samples were assessed for charge balance and were all within the acceptable range of ± 5

The chemical analyses results of the different water sources are summarized in Tables 1 to 3.

RESULTS AND DISCUSSION

Details and a summary of the physicochemical parameters for the different water sources for the rainwater, groundwater and surface samples are given in Table 1

Table 1: Summary of physicochemical parameters in water samples for the study area

	Rainfall (n=5)				Surface water (n=11)				Shallow groundwater (n=81)				Deep ground water (11)			
Parameter	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD
Temp (^{0}C)	27.62	26.70	29	1.03	29.56	26	34	3.02	30	30	31	0. 06	30.20	30	32	0.60
$_P$H	6.40	4.30	7.70	1.34	7.57	7.20	8.00	0.23	7.09	6.10	7.08	0.39	7.22	6.60	7.80	0.41
EC (ds/m)	0.03	0.02	0.05	0.11	0.22	0.07	0.45	0.11	0.09	0.05	0.21	0.03	0.09	0.04	0.18	0.04
DO	6.07	4.81	7.20	0.87	3.22	1.10	7.40	1.75	0.90	0.01	2.80	0.70	0.96	0.05	2.10	0.83
EH (volts)	0.83	0.76	0.96	0.13	0.76	0.73	0.83	0.07	0.72	0.46	0.82	0.10	0.75	0.60	0.85	0.10
TDS	18.19	13.40	30.60	7.04	155	41	298	72.60	60	33	137	18.83	63	27	121	26
TH	4.59	2.26	6.90	1.74	61	21	112	24.54	54	0.18	190	36.41	59	10	105	28
Ca	3.61	1.95	5.80	1.59	26	8	37	9.25	12.19	0.48	25	6.19	11.30	0.50	38	11.68
Mg	1.78	1.10	2.50	0.50	35	12	84	19.09	21	0.50	51	9	31	8	55	13.46
K	2.56	0.00	4.21	1.56	5	1.20	9	2.40	4	0	37	6.89	4.32	0	12	4.16
Na	1.23	0.00	1.98	0.80	73	2.23	211	89.04	34	0	157	33.74	34	0	91	34.30
HCO_3	17.93	16.20	19.20	1.17	137	49	273	63.27	93.4	19.90	251	41.26	103	50	207	44.41
NO_3	1.44	0.00	2 .23	0.83	35	9	59	17.97	4.36	0	23	4.63	6	0.66	31	8.63
SO_4	2.83	1.60	4.50	1.21	18	2	29	7.52	11	0	61	12.28	14.80	0	65	19.66
Cl	0.65	0.50	0.80	0.11	146	28	455	138.28	68	0	239	56	76	0	172	61.82
Fe	0.21	0.00	0.39	0.17	0.30	0	0.73	0.26	0.35	0	1.80	0.41	0.09	0	0.32	0.10
Mn	0.00	0.00	0.01	0.00	0.00	0	0 .02	0.00	0.00	0	0.00	0.00	0.00	0	0.00	0.00
E coli (Per 100ml)	0	0	0	0	13.80	8	21	3.54	5.60	0	7	2.12	2	0	4	1.21

Surface water/Precipitation Chemistry

The surface water temperature in the study area ranged from 26 to 34 ^{o}C. The electrical conductivity (EC) varies between 0.07 and 0.45 ds/m. The mean total dissolved solids (TDS) are 155 mg/l (Surface water) and 18 mg/l (precipitation).

The EC and TDS are low in comparison to the WHO (2006) standard of 1.4 ds/m for EC and 1000 mg/l for TDS indicating that the waters are fresh.

The mean pH for the surface water bodies and precipitation are 7.57 and 6.40 with ranges of 7.20 and 8.00 (Surface water) and 4.30 and 7.70 (precipitation). Considering the entire sample set, about 13 out of 16 samples had pH>7. In addition, all the surface water and precipitation samples have pH values that fall within the limits of the World Health Organization (WHO 2006), of 6.5-8.5. Most of the samples are thus neutral in nature which is attributed to the fact that the surface waters are neutralized as they flow through calcareous rocks in the process.

The dissolved oxygen (DO) varied from 1.10 to 7.40 for the surface water and from 4.81 to 7.20 for the precipitation. The surface water samples show moderately high (Standard deviation SD= 24.54) variation in terms of hardness with values ranging from 21 to 112 mg/l as CaCO3 for the surface water and low (SD=1.74) for the precipitation with values ranging from 1.95 to 5.80 mg/l as $CaCO_3$. However, all of the samples can be described as moderately hard to hard with hardness values of more than 61 mg/l (Freeze and Cherry 1979).

The mean concentration of cations in the surface water samples are Na (73 mg/l), Ca (26 mg/l), K (5 mg/l), Mg (35 mg/l) and Na (1.23 mg/l), Ca (3.61mg/l), K (2.56 mg/l), Mg (1.78 mg/l) for the precipitation respectively. The mean values of chloride concentration are 146 mg/l and 0.65 mg/l for the surface water and precipitation respectively. The maximum and minimum values of bicarbonate in the surface waters are 273 and 41 mg/l and 19.20 and 16.20 mg/l for the precipitation.

The amount of sulphate varies from 2 to 29 mg/l for the surface water and 1.60 to 4.50 mg/l for the precipitation. The concentrations of the sulphate are below the WHO (2006) limits of 250 mg/l.

In the surface water samples, the nitrate concentrations varied from 9 to 59 mg/l and 0 to 2.23 mg/l for the precipitation. The concentrations are lower than that are normally expected for unpolluted water, 0.124-9.92 mg/l (Custodio and Llamas 1983) and 11.3 mg/l (WHO2006) maximum recommended value for drinking purposes.

Shallow groundwater chemistry

Shallow groundwater temperatures ranged from 30 to 31 ^{o}C. The values of EC vary from 0.05 to 0.21 ds/m whereas the total dissolved solids vary from 33 to 137 mg/l. The EC and TDS are relatively low in comparison to the WHO (2006) standard of 1.4 ds/m for EC and 1000 mg/l for TDS indicating that the waters are also fresh.

The pH values vary from 6.10 to 7.08 indicating slightly acidic to neutral water which could be attributed to rainfall and the absence of buffering materials within the aquifers. The hardness values (as $CaCO_3$) ranged from 0.18 to 190 mg/l. Data from Table 1 shows that out of all the 81 samples considered for the study area only 25 samples can be described as hard with hardness values of > 60 mg/l.

The data on chemical composition (Table 1) show that the mean concentrations of the cations in groundwater are Na (34 mg/l), Ca (12.19 mg/l), K (4 mg/l) and Mg (21 mg/l). The values of chloride concentrations vary from 0 to 239 mg/l whereas the value of sulphate concentration varied from 0 to 61 mg/l. The relatively low concentration of both chloride and sulphate could be attributed to natural maximum concentrations derived from anthroponenic reactions.

Nitrate values ranged from 0 to 23 mg/l with mean of 4.36 mg/l (as N) for the groundwater samples. Thus all the samples have lower concentrations reflecting little pollution (eg Custodio and Llamas 1983) and less than 11.3 mg/l (WHO 2006) maximum recommended value for drinking purposes.

Deep groundwater chemistry

Deep groundwater temperatures ranged from 30 to 32 ^{o}C. The mean value of EC varies from 0.05 to 0.21 ds/m whereas the mean total dissolved solid varies from 27 to 121 mg/l. The EC and TDS are relatively low in comparison to the WHO (2006) standard of 1.4 ds/m for EC and 1000 mg/l for TDS indicating that the waters are also fresh.

The pH values vary from 6.60 to 7.80 indicating slightly acidic to neutral water which could be attributed to rainfall and the absence of buffering materials within the aquifers. The hardness values (as CaCO3) ranged from 10 to 105 mg/l. Data from Table 1 shows that out of all the 11 samples considered for the study area only 6 samples can be described as hard with hardness values of > 60 mg/l.

The data on chemical composition (Table 1) shows that the mean concentrations of the cations in groundwater are Na (34 mg/l), Ca (11.30 mg/l), K (4.32 mg/l) and Mg (31 mg/l). The values of chloride concentrations vary from 0 to 172 mg/l whereas the value of sulphate concentration varied from 0 to 65 mg/l. The relatively low concentration of both chloride and sulphate could be attributed to natural maximum concentrations derived from anthropogenic reactions.

Nitrate values ranged from 0.66 to 31 mg/l with mean of 6 mg/l (as N) for the groundwater samples. Thus all the samples have lower concentrations reflecting little pollution (eg Custodio and Llamas 1983) and less than 11.3 mg/l (WHO 2006) maximum recommended value for drinking purposes.

Hydrogeochemical Facies and Classification of the waters

For illustrating chemical differences between the different water sources and geochemical changes along the groundwater flow paths, samples from different water sources are plotted in a Piper Trilinear diagram (Piper 1944) in Figures 6, 7 and 8.

The Piper diagrams (1944) in Figures show the relative concentrations of the different ions from the individual samples based on average values for each location.

The different water sources include the shallow groundwater tapped mainly by hand-dug wells and shallow boreholes, the deep groundwater tapped mainly by deep wells, the surface water bodies as well as rainwater samples.

Five types of hydrogeochemical facies based on the classification given by Deutsch (1997) were identified for both the shallow groundwater and the deep groundwater samples in the study area. These include Na^{2+}-K^{+}-HCO_3^{-} $+CO_3^{2-}$, Na^{+}-K^{+}-Cl- ,$Ca^{2+}+Mg^{2+}$,$SO_4^{2-}+Cl^{-}$, and Mg^{2+}-$HCO_3^{-}+CO_3^{2-}$ types (Table 2). The water samples are thus characterized mainly by HCO3, SO_4 and Cl indicating active groundwater mixing and flushing as well as significant water rock interaction.

The $Ca^{2+}+Mg^{2+}$-HCO_3 major ion type based on the classification given by Deutsch (1997) was identified for precipitation whereas Mg^{2+}-HCO_3 and Mg^{2+}-Cl^{-} types are identified for the surface water bodies.

For the shallow groundwater the dominant ions are Mg^{2+} and $Na^{+}+K^{+}$ for cations and Cl^{-} and HCO_3^{-} for anions. The deep groundwater also indicate Mg^{2+} and $Na^{+}+K^{+}$ as the major cations and HCO_3^{-} and Cl^{-} as the major anions.

The water samples from precipitation characterized mainly by HCO_3 indicate fresh water (with TDS less than 200 mg/l) whereas surface water characterized by HCO_3 and Cl^{-} indicate significant water rock interaction.

The results also indicate that both the shallow and deep groundwater are more mineralized in comparison with those of the precipitation and surface water samples suggesting longer residence time in the subsoil before being discharged to the surface.

Classification of the water samples based on the proposed scheme by Chadha (1999) using a bivariate plot of $(CO_3^{2-} + HCO_3^{-})-(Cl^{-} + SO_4^{2-})$ versus $(Ca^{2+} + Mg^{2+})-(Na^{+} + K^{+})$ presented in Figure 9 show that for all the 103 water samples, 8% are classified as Alkali metals (Na + K) > Alkaline metal (Ca + Mg) and weak acidic anions (HCO_3) > Strong acidic anions (Cl + SO_4). This group represents contribution from water-rock interactions. Thirty two (32 %) percent are classified under the Alkali metals (Na + K) > Alkaline metal (Ca + Mg) and Strong acidic anions (Cl + SO_4) > weak acidic anions (HCO_3). This class represents mostly contributions from rainfall. Forty one (41 %) percent belong to the Alkali metals (Na + K) < Alkaline metal (Ca + Mg) and weak acidic anions (HCO_3) > Strong acidic anions (Cl + SO_4) whereas the remaining 20 % belong to the Alkali metals (Na + K) < Alkaline metals (Ca + Mg) and Strong acidic anions (Cl + SO_4) > weak acidic anions (HCO_3). This represents a transition between rainfall and silicate weathering.

This composition is controlled by the interaction of the water with the relatively highly permeable fine to coarse grained alluvial sediments underlying the surface water bodies in the area. The minerals which have been indentified during microscopic study of the underlying Feldspathic Bima Sandstone Formation include quartz, K-feldspar, biotite illite and gypsum. In this zone water infiltrates rather rapidly and there is a restricted interaction time with the atmosphere.

These results thus indicate that both the deep and the shallow ground waters are less chemically evolved than the surface water which probably has had a longer residence time in the subsoil before being discharged to the surface. The near homogenous composition between the deep and shallow ground waters appear to indicate mixing, significant water-sediment interaction as well water that has evolved from shallower to deeper levels in the order of $Ca^{2+}>Mg^{2+}>Na^{+}+K^{+}>HCO_3^{2-}+CO_3^{2-}>Cl^{-}$.

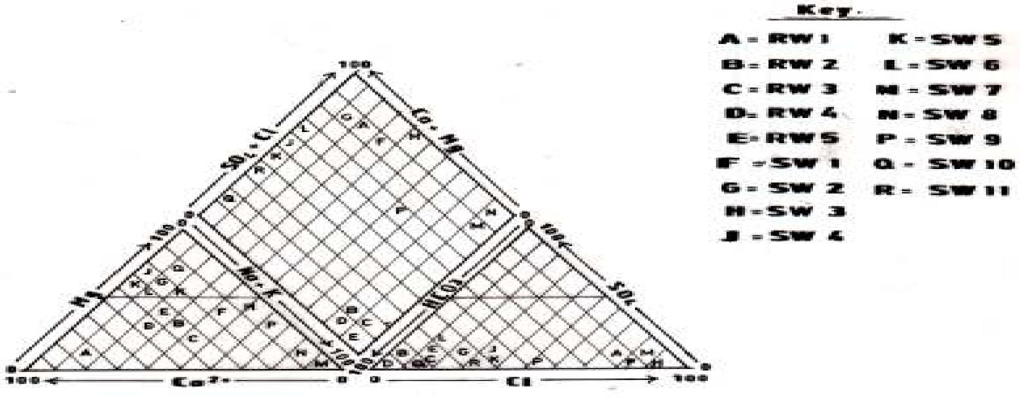

Fig. 6: Piper diagram for rainfall and surface water samples.

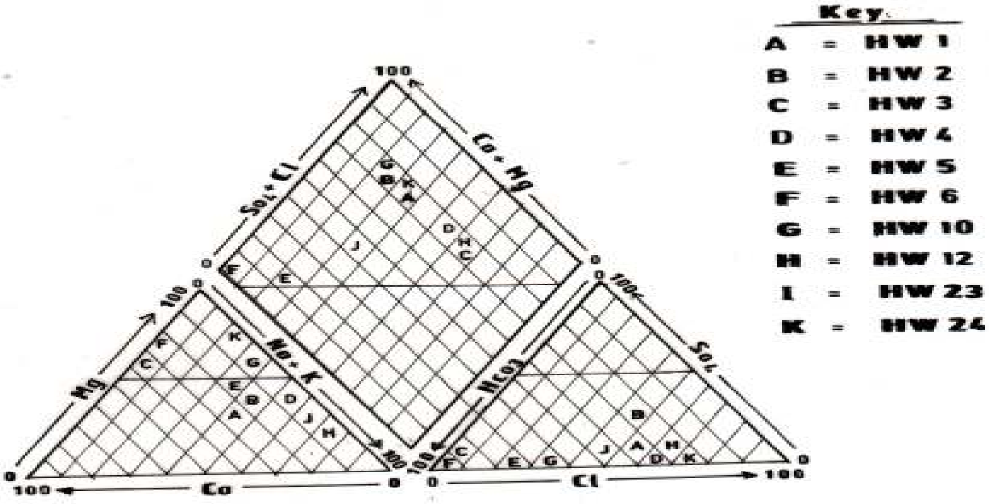

Fig. 7: Piper diagram for shallow groundwater samples.

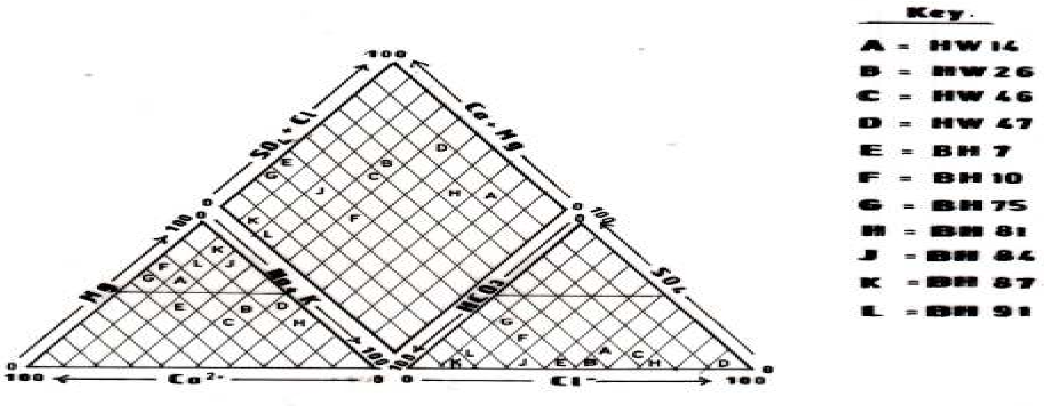

Fig. 8: Piper diagram for deep groundwater samples.

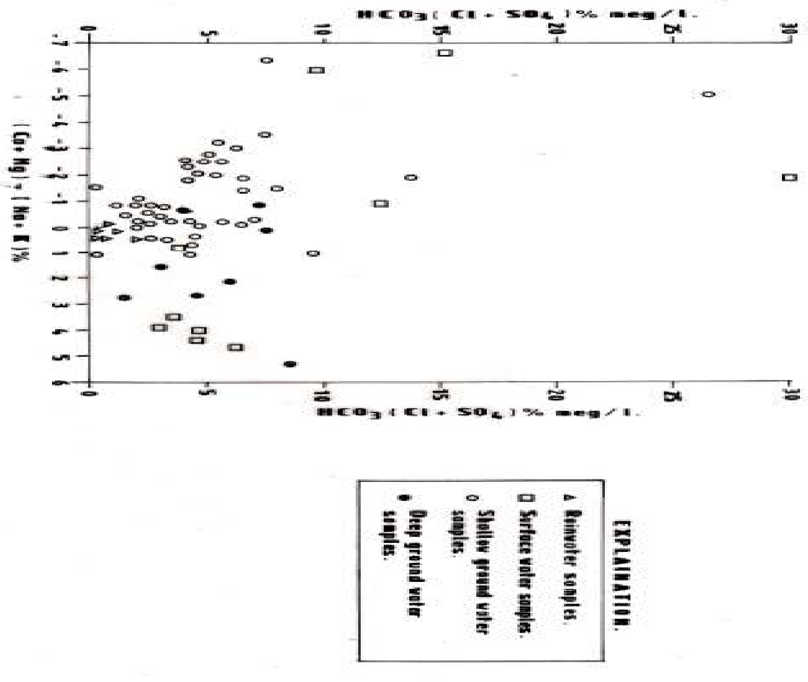

Fig. 9: Hydrogeochemical classifications based on the bivariate plot of $(CO_3 + HCO_3) - (Cl + SO_4)$ versus $(Ca + Mg) - (Na + K)$ of different water types.

Mechanism controlling water chemistry

The ionic composition may be caused by many factors during chemical interaction. Thus it is necessary to use the ionic ratios and plots to discriminate between them. The contribution of atmospheric sources to the dissolved salts has been discussed by many authors (Garrels and Mackenzie, 1971; Berner and Berner 1996; Edet and Ekpo, 2008). Chloride is the most useful parameter for evaluating atmospheric input to water as it shows very little fractionation (Appelo and Postma 1993).

Sodium and chloride inputs are likely to be mainly from rainfall and thus reflect the ration observed in seawater as indicated by the Na/Cl ratio of 0.20 to 0.66. The ratios greater than 1 are typically interpreted as released Na from silicate weathering reactions whereas ratio close to 1 is related to halite dissolution. The analysed water samples have Na/Cl ratios that are less than 1 indicating halite dissolution. Cation exchange may account for a reduction in the Na concentration, and halite dissolution may account for high concentration of Na and Cl (Figure 10) (Edet and Ekpo 2008). The low concentration of potassium in natural water is a consequence of the tendency to be fixed by clay minerals and participate in the formation of secondary minerals (Matheis 1982)

Figure 11 shows the plot of Ca + Mg vs HCO_3 for the different water sources. The water samples have an average (Ca + Mg)/HCO_3 of 0.39 indicating contributions from silicate weathering. The HCO_3 thus occur in excess of Ca + Mg, the magnitude of which is balanced by Na and K derived from silicate weathering. In the study area, HCO_3, Ca^{2+}, Mg^{2+}, Na+ may be derived from weathering of chiefly Ca-Mg silicates, mainly plagioclase and feldspar possibly from the nearby basement rocks to the north, east and south of the study area.

About 25% of the concentrations of iron in the water samples are higher than the maximum acceptable concentration of 0.3 mg/l (Table 1). The present investigation indicates that pH is negatively correlated with Fe which is attributed to the fact that low pH value result in higher solubility and mobility of the element in water (Edet and Ekpo 2008; Obiefuna and Orazulike 2010). The waters in the study area are also supersaturated with respect to Geothite (FeOOH), Hematite (Fe_2O_3), and Siderite (Table 3).

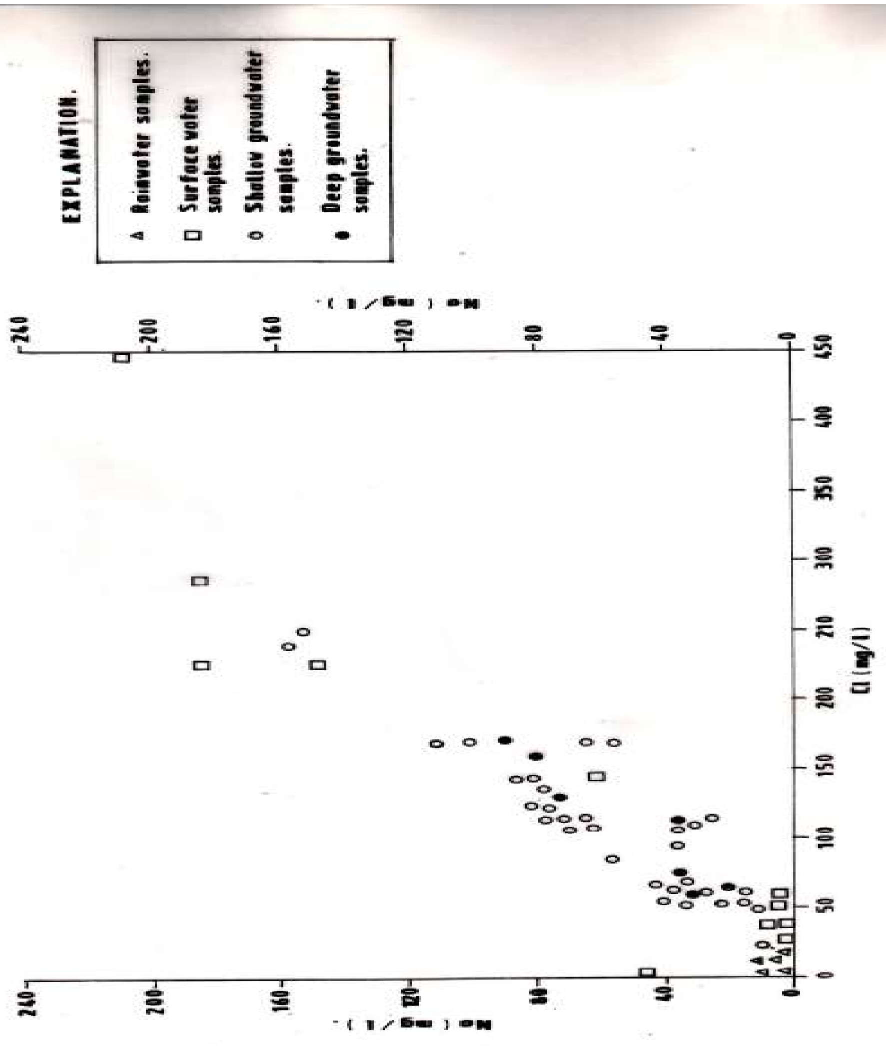

Fig.10: Plot for Na versus Cl for the different samples.

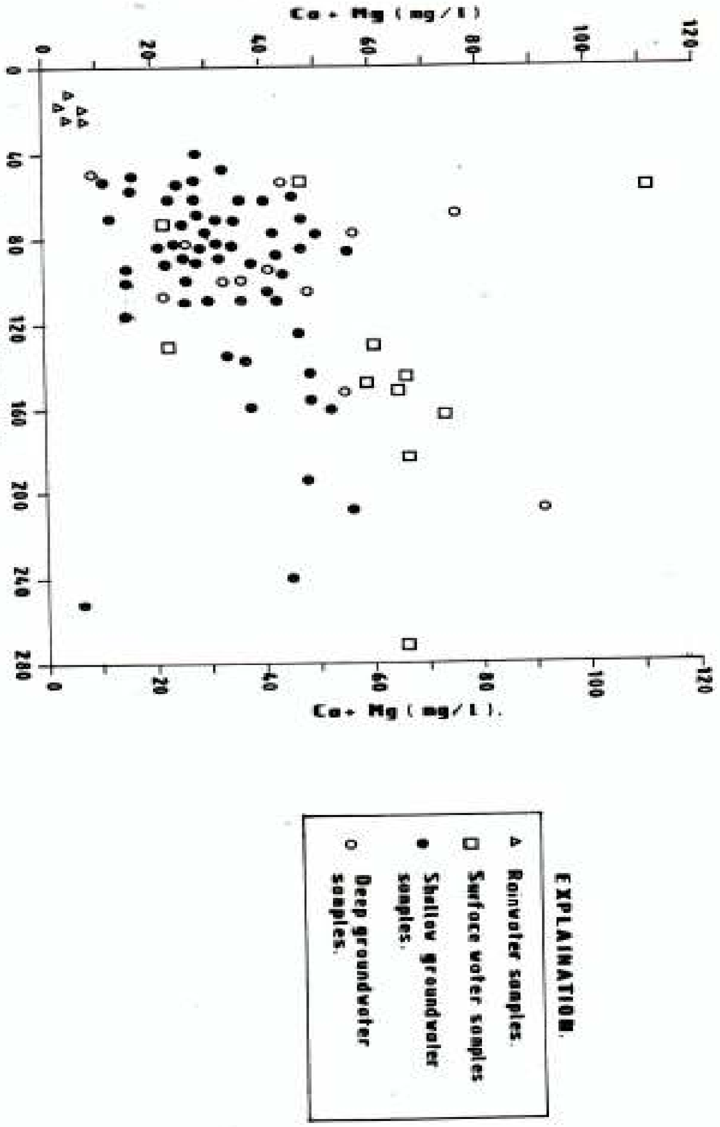

Fig. 11: Plot for Ca+Mg versus HCO_3 for the different samples.

TABLE 2 CLASSIFICATIONS OF THE WATER SAMPLES OF THE STUDY AREA ON THE BASIS OF THEIR MAJOR ION PERCENTAGES

S/N	Water Source	Major Cation Types	Major Anion Types	Hydro geochemical
1	Rain water	Ca^{2+} (1) No dominant (4)	Cl^- (1) $HCO_3 + CO_3$ (4)	$S0_4^{2-} + Cl^-$ (1) $HCO_3 + CO_3$ (4)
2	Surface water	Mg^{2+} (6) $Na^+ + K^+$ (4) No dominant (1)	Cl^- (5) $HCO_3 + CO_3$ (6)	$SO_4^{2-} + Cl^-$ (4) $Ca^{2+} + K^+$ (6) $Na^+ + K^+$ (1)
3	Shallow Groundwater	No dominant (21) Mg^{2+} (36) $Na^+ + K^+$ (23)	Cl^- (36) No dominant (10) $HCO_3 + CO_3$ (34)	$SO_4^{2-} + Cl^-$ (27) $HCO^-_3 + CO_3{}^{2-}$ (3) $Ca^{2+} + Mg^{2+}$ (45) $Na^+ + K^+$ (5)
4	Deep ground-water	No dominant (3) Mg^{2+} (6) $Na^+ + K^+$ (2)	Cl^- (5) $HCO_3 + CO_3$ (6)	$S0_4^{2-} + Cl^-$ (4) $Ca^{2+} + Mg^{2+}$ (7)

TABLE: 3: SATURATION INDICES CALCULATED WITH PHREEQC FOR AVERAGE SAMPLES OF RAINWATER, SURFACE WATER, SHALLOW GROUNDWATER AND DEEP GROUNDWATER

Phase	Formula	Ion	Shallow Groundwater		Deep Groundwater		Surfacewater	Rainwater
			Discharge Area	Recharge Area	Discharge Area	Recharge Area	Logsi	Logsi
			Logsi	Logsi	Logsi	Logsi		
Anhydrite	$CaSO_4$	Na^+	-0.084	-0.94	-1.53	-0.71	-3.02	-4.33
Aragonite	$CaSO_3$	Ca^{2+}	1.40	1.43	1.71	1.43	-0.29	-3.13
Calcite	$CaSO_3$	Mg^{2+}	1.54	1.57	1.85	1.57	-0.15	-2.99
Chalcedon	SiO_2	K^+	0.14	-0.45	1.70	-0.02	-0.40	-0.50
y	$CaMg(CO_3)_2$	Cl^-	3.48	3.61	4.46	3.75	0.22	-5.91
Dolomite	CaF2	SiO_4^{2-}	-1.63	-1.22	-3.65	-1.51	-4.01	-6.57
Fluorite	FeOO H	Alk	8.65	8.81	6.14	8.34	8.60	5.81
Geothite	$CaSO_4$. $2H_2o$	NO_3^-	-0.65	-0.74	-1.34	-0.52	-2.82	-4.12
Gypsum	NaCl	pH	-4.35	-4.69	-4.47	-4.48	-6.56	-10.62
Halite	Fe_2O_3	T^0C	19.33	19.65	14.31	18.72	18.15	13.63
Hematite	$Ca_5(PO_4)3O$	Si	7.29	8.03	3.98	7.73	5.23	-6.32
Hydroapatit	H	Fe	27.65	26.50	27.87	25.60	22.74	-
e	FeS_2	F	0.55	-0.03	2.11	0.39	0.01	-0.12
Pyrite	SiO_2	PO_4^{2-}	1.74	1.84	-1.87	1.42	-1.23	-2.00
Quartz	$FeCO_3$	H_2S	-0.69	-1.27	0.88	-0.85	-1.23	-1.37
Siderite	SIO_2		13.17	12.57	15.34	12.34	11.75	-
$Si0_2$	S		-0.36	-0.38	-0.91	-0.34	-2.55	-2.04
Sulpur	CO_2		-0.36	-0.49	-0.33	-0.39	-1.02	-0.75
CO_2 (g)	O_2							
O_2 (g)								

Equilibrium Calculations

Equilibrium calculations help us to determine the saturation state of groundwater with respect to various minerals and gases of interest. They are useful in predicting the presence of reactive minerals in the groundwater system and estimating mineral reactivity (Deutsch 1997). By using the saturation index (SI) approach, it is possible to predict the reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy (Deutsch 1997). From these calculations, we learn whether a particular mineral would tend to dissolve or precipitate in a given aqueous environment. Saturation indices are employed to evaluate the degree of equilibrium between water minerals. Changes in the state of saturation are used to discriminate between the different stages of hydro chemical evolution and to find out which are the main geochemical reactions controlling water chemistry.

In addition to providing information on saturation indices, these calculations can define masses of elements that may not have been analyzed. Hence dissolved inorganic carbon can be calculated from field pH and alkalinity. A computer programme PHREEQC (Parkhurst and Appelo 1999) was used for all the calculations. Saturation indices for four hypothetical samples (average for the whole data-base: 11 surface water, 5 rainwater, 81 shallow groundwater and 11 deep groundwater samples) are compiled in Tables 3 and 4.

From Table 5, the different water types are undersaturated with respect to calcite, dolomite, and gypsum. Thus since the values of the saturation indices for calcite are less than unity, the following reaction:

$$CaCO_3=Ca^{2+}+CO_3^{2-} \qquad (1)$$

Proceeds to the right indicating mineral dissolution. The dolomite equilibrium is given by the following equation:

$$CaMgCO_3=Ca^{2+}+Mg^{2+}+CO_3^{2+} \qquad (2)$$

Thus since the values of the saturation indices of dolomite are also less than unity, the reaction proceeds to the right which indicates the dissolution of dolomite.

The undersaturation of calcite, gypsum and dolomite suggest that their soluble Ca^{2+}, Mg^{2+}, SO_4^{2-} and CO_3^{2-} component concentrations are limited by mineral equilibrium.

The higher saturation indices of calcite may have been influenced by the P_{CO2} values. According to Freeze and Cherry (1979) mineral dissolution in groundwater is seriously affected by P_{CO2} and temperatures. The temperatures measured in the field for the groundwaters range from 30°C to 32°C whereas the computed values of P_{CO2} range from $10^{-1.15}$ to $10^{-2.95}$(Table 4). The studied groundwater exhibit high concentration of bicarbonate (mean value of 93.50 mg/l) as expected from the calculated P_{CO2}.

The accuracy of P_{CO2} calculations however depends on pH measurements. Field measurements of the pH were employed in the calculations. The dissolved inorganic carbon (DIC) was determined from field pH and alkalinity values. At recorded pH (6.1 to 7.8), DIC is mainly represented by H_2CO_3.

The values of the dissolved inorganic carbon (DIC) in (mmols/KgH_2O) range from 2.496×10^{-4} to 3.502×10^{-3}(Table 6).

The relatively high dissolved inorganic carbon (DIC) is probably due to the presence of decaying organic matter. Under such a sub-equatorial dry and semi-arid climate, the inorganic carbon geochemistry in groundwater is probably strongly controlled by production of biogenic CO_2 in the unsaturated zone. Oxidation of organic matter in the unsaturated zone may be invoked (Boukari et al, 1996). Thus organic matter which is represented by a simple carbohydrate, CH_2O can be oxidized as follows:

$1/4CH_2O+1/4H_2O=1/4CO_2(g)+H^++e^-$ (3)

The trend existing between DIC and the depth of water table seems to corroborate this hypothesis: the deeper the water table, the less the water enriched in DIC (0.0019453mmol/ kg H_2O for deeper groundwater as against 0.00266332mmol/kg H_2O for shallow groundwater). At depth, the groundwater tends to be less acidic and less mineralized in terms of inorganic carbon. The determinant parameter controlling the DIC content and the pH of groundwater seems to be the proximity to the soil and the plant root system (Oga et al, 2008). The Relatively high P_{CO2} values and the dry and semi-arid climatic conditions of the study area are expected to favour the hydrolysis of aluminosilicate minerals.

The full reactions for the redox processes involved can be displayed by combining the half-reaction for the oxidation of organic matter and the reaction are as follows:

$1/4O_2+H^++e\text{-}=1/2H_2O$ (4)

This will finally give the following equation:

$O_2(g)+CH_2O=CO_2(g)+H_2O$ (5)

Hence equation 5 represents the process of organic matter oxidation in the presence of bacteria and free oxygen. This redox process is the main source of dissolved CO_2 in the groundwaters of the study area. Accordingly the dissolved CO_2 combines with H_2O to produce carbonic acid(H_2CO_3) which explains the relatively high values of dissolved inorganic carbon(DIC) and H_2CO_3(molality of carbonic acid) obtained for the groundwater samples.

Table 4: Result of saturation indices and equilibrium calculations for different water sources

		Rainfall (n=5)	Surface water (n=11)	Shallow groundwater (n=81)	Deep ground water (n=11)
S/N	Parameter	Mean Min Max SD	Mean Min Max SD	Mean Min Max SD	Mean Min Max SD
1	Log S1 Calcite	-3.15, -4.76, -2.02, 1.02	-0.23, -1.17, 0.32, 0.52,	-1.25, -2.80, 0.06, 0.68,	-1.38, -2.33, -0.60, 0.59,
2	Log S1 Dolomite	-6.12, -9.85,-3.56, 2.34	0.05, -1.77, 1.40, 1.03	-1.79, -4.00, 0.54, 1.19,	-1.68, -3.03, -0.60, 0.83,
3	Log S1 Gypsum	-4.25, -4.62, -4.00, 0.24,	-2.93, -4.23, -2.50, 0.48,	-3.68, -6.17, -2.41, 0.89,	-4.10, -7.23, -2.11, 1.61,
4	Log S1Quartz	-0.04, -0.22, 0.17, -0.04,	-0.27, -1.94, 0.44, 0.96,	-1.78, -3.87, 0.43, 1.14,	-0.37, -0.96, 0.73, 0.68,
5	Log S1 Silica	-1.29 -1.47 -1.08 ,0.17	-1.52, -3.17,-0.82 ,-0.95,	-3.02, -5.11, -0.81, 1.14,	-1.61, -2.20, -0.51, -0.68,
6	Ionic Strength	0.74, 0.65, -0.93, 0.19,	11.17, 1.13, 7.80, 3.37,	5.85, 1.67, 43.31, 37.46,	6.17, 1.63 , 9.08, 2.91,
7	PCO_2 Bars x 10^{-3}	$10^{-2.09}$, $10^{-3.40}$, $10^{0.17}$$10^{-1.92}$	, $10^{-2.29}$, $10^{-1.94}$ $10^{-2.73}$, $10^{-0.44}$	11.78,1.12,70.80,59.02	8.02, 1.51, 28.18, 20.16,
8	$MH_2 Co_3$ mo1/kg H_2o x 10^{-3} x 10^{-3}	0.32, 0.15, 0.37, 0.05,	3.26, 1.05, 5.86, 2.60,	1.97, 0.21, 5.11, 3.14,	1.64, 0.72, 2.34, 0.70
9	DIC mmo1/kg H_2o x 10^{-3}	9.62, 0.32, 46.12, 36.5,	3.98, 1.13, 7.80, 3.82,	2.69, 0.25, 25.27, 22.58,	1.95, 0.79, 2.52, 0.57,

NB: DIC = Dissolved Inorganic Carbon, SI = Saturation Index, P_{CO2} = Partial Pressure of CO_2

Groundwater quality

Groundwater quality assessment was made using pH, dissolved oxygen, phosphate, nitrate, chloride and sulphate as contamination indicators. Most of these parameters fall below the WHO (2006) standards for drinking and domestic purposes indicating the potablity of the groundwater in the area.

However nitrate and iron contamination has been detected in some wells and should be treated before use. Possible sources of pollution are likely from fertilizer application.

In terms of agricultural purposes, parameters such as such as Electrical Conductivity (EC), Total Dissolved Solids (TDS), Sodium Adsorption Ratio (SAR), Magnesium Adsorption Ratio (MAR), Permeability Index (PI), Kelly Ratio (KR), and Residual Sodium Bicarbonate (RSBC) were assessed and compared with standard limits.

Richards (1954) classified the concentration of soluble salt in irrigation water (salinity hazard) into four classes on the basis of electrical conductivity, EC and SAR (sodium hazard). The different classes of salinity hazard include low, C1 (EC < 250μS/cm); medium, C2 (EC 250-750 μS/cm); high, C3 (EC750-2250 μS/cm); and very high, C4 (EC>2250 μS/cm). The sodium hazard classes include: low, S1 (SAR<10); medium, S2 (SAR 10-18); high, S3 (SAR 18-26); and very high, S4 (SAR > 26). According to Subramani et al., (2005) water with high EC leads to formation of saline soil a high Na leads to development of an alkaline soil. The Na or alkaline hazard in the use of water for irrigation is determined by absolute and relative concentration of cations and is expressed in terms of SAR and can be estimated by the formula: $SAR= NA/Ca[(Ca + Mg)/2]^{0.5}$.

The sodium adsorption ratio gives a clear idea about the adsorption of sodium by soil. It is the proportion of sodium to calcium and magnesium which affect the availability of the water to the crop.

The sodium adsorption ratio of both surface water and groundwater obtained in the present study are generally less than 9 and fall under the category of C2SI indicating low alkali hazards and excellent irrigation water.

Sodium percent is an important factor for studying sodium hazard. It is also used for adjudging the quality of water for agricultural purposes. High percentage sodium water for irrigation purpose may stunt the plant growth and reduces soil permeability (Joshi et al, 2009).

The Soluble Sodium Percentage (SSP) can be estimated by the formula (Todd, 1995):

$$SSP - \frac{(Na^{+}+K^{+})\times 100}{Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}}$$

Where all the ions are expressed in meq/litre

The Soluble sodium percentage (20-85%) indicates that the waters are excellent to good for irrigation purposes based on the Wilcox diagram (1995) relating sodium percentage to total concentration (Na < 80%; EC < 500 μS/cm; Total cation <7 meq/l).

The most influential water quality guideline on crop productivity is the water salinity hazard as measured by electrical conductivity (EC). The primary effect of high EC water on crop productivity is the inability of the plant to compete with ions in the soil solution for water (physiological drought). The higher the EC, the less water is available to plants; even though the soil may appear wet. Thus because plants can only transpire water ("pure water"), usuable plant water in the soil solution decreases dramatically as EC increases (Joshi et al, 2009).

The EC values of the water samples (0.04-0.25 ds/m) are generally less than 4ds/m and fall within the excellent categories for irrigation water (Eaton 1950) and below the WHO (2006) recommended limit of 1400 micro-mhos/cm (1.40 ds/m).

Magnesium content of water is considered as one of the most important qualitative criteria in determining the quality of water for irrigation. Generally, calcium and magnesium maintain a state of equilibrium in most waters. More magnesium in water will adversely affect crop yields as the soils become more saline (Joshi et al, 2009).

The Magnesium Adsorption Ratio (MAR) was calculated according to Raghunath (1987) as:

$$MAR = \frac{Mg^{2+}\times 100}{Ca^{2+}+Mg^{2+}}$$

Where all the ionic constituents are expressed in meq/litre. The values of MAR for the present work varied between 71.18 and 97.83% indicating that the samples are suitable for agricultural purposes since all the MAR values are more than 50% (Obiefuna and Orazulike 2010).

Salts of calcium, magnesium, sodium, potassium present in the irrigation water may prove to be injurious to plants. When present in excessive quantities, they reduce the osmotic activities of the plants and may prevent adequate aeration.

The soil permeability is affected by the long term use of irrigated water and the influencing constituents are the total dissolved solids, sodium bicarbonate and the soil type.

The Permeability Index (PI) was calculated according to Doneen (1964) as:

$$PI = \frac{Na^{+}+\sqrt{HCO_3^{-} \times 100}}{Ca^{2+}+Mg^{2+}+Na^{+}}$$

Where all the ions are expressed in meq/litre. The values of PI for the present investigation varied between 39.5 and 96.67% suggesting that most of the water samples fall within ClassI and ClassII and are categorized as good irrigation water (Doneen, 1964).

The concentration of bicarbonate and carbonate influences the suitability of water for irrigation purpose. The water with high RSBC has high pH. Therefore land irrigated with such water becomes infertile owing to deposition of sodium carbonate (Eaton 1950).

The Residual Sodium Bicarbonate (RSBC) was calculated according to Gupta and Gupta (1987):

$RSBC=HCO_3^{-} - Ca^{2+} + Mg^{2+}$

Where RSBC and the concentration of the constituents are expressed in meq/litre. The values of RSBC for the present work are less than 2.5 meq/l and are therefore considered safe for irrigation purposes(Raghunath 1987).

The Total Dissolved Solids (TDS) was calculated according to (Richards 1954) as:

TDS= (0.64 x EC x 106 (Micro-mhos/cm)

Where Electrical Conductivity (EC) and TDS are expresses in Micro-mhos/cm and mg/litre respectively. The values of TDS for the present investigation are generally less 200 mg/l and are classified as excellent irrigation water (Robineve et al 1958).

The Kelly Ratio was calculated according to (Kelly 1963) as:

$$KR = \frac{Na^{+}}{Ca^{2+}+Mg^{2+}}$$

Where all the ionic constituents are expressed in meq/litre. The values of KR for the present work fall below the permissible limit of 1.00 and are considered suitable for irrigation purposes.

Preliminary investigation indicate that common parameters such as hardness, Ca^{2+}, $Mg^{2+,}$ Na^{+}, Cl^{-}, HCO_3^{-}, NO_3^{-} and SO_4^{2-} are poorly correlated with electrical conductivity (EC) in groundwater(Obiefuna and Orazulike 2010).

It was also discovered that similarity in correlation matrix between both the shallow and deep groundwater was attributed to mineral dissolution as the dominant process influencing the water quality (Obiefuna and Orazulike 2010).

Finally good correlation between EC and NO_3^{-} (r= 0.80) and EC and Cl^{-} (r = 0.95) suggesting that variation in EC is controlled by both Cl^{-} and NO_3^{-} concentration (Obiefuna and Orazulike 2010).. This confirms common primary sources which are both domestic effluent/ sewage and/or fertilizer application.

CONCLUSION

The water in the area is slightly acidic to neutral. The $Ca^{2+}+Mg^{2+}$-HCO3 type of hydrogeochemical facies based on the classification given by Deutsch (1997) was identified for precipitation whereas $Na^{+}+K^{+}$-Cl^{-}, $SO_4^{2-}+Cl^{-}$ types was identified for the surface water bodies. The water samples from precipitation characterized mainly by HCO_3 indicate fresh water (with TDS less than 200 mg/l) whereas surface water characterized by SO_4 and Cl indicate significant water rock interaction.

Magnesium and Sodium are the dominant cations and bicarbonate and chloride are the dominant anions for both shallow and deep groundwater.

Five types of hydrogeochemical facies based on the classification given by Deutsch (1997) were identified for both the shallow groundwater and the deep groundwater samples in the study area. These include Na^{2+}-K^{+}-HCO_3^{-} +CO_3^{2-}, Na^{+}-K^{+}-Cl- ,$Ca^{2+}+Mg^{2+}$,$SO_4^{2-}+Cl^{-}$, and Mg^{2+}-$HCO_3^{-}+CO_3^{2-}$ types.

The water chemistry is largely controlled by rainfall and silicate weathering and minor contribution from carbonate weathering. The relatively high average (Ca + Mg)/HCO_3 of 0.385 indicate contributions from silicate weathering. In the study area, HCO_3, Mg^{2+}, Na^{+} may be derived from weathering of chiefly Na-Mg silicates, mainly plagioclase and feldspar within the underlying Bima Sandstone Formation.

The low ratio of Na/Cl (0.2 to 0.66) supports contributions from rainfall and the relatively high ratio of $(Ca^{2+}+Mg^{2+})/(HCO_3^{-}+SO_4^{2-})$ (0.023 to 49.93), $(Ca^{2+}+Mg^{2+})/HCO_3^{-}$ (0.023 to 1.026) indicate silicate weathering and contribution of HCO_3^{-} from biological activity.

The near homogenous composition between the deep and shallow ground waters appear to indicate mixing, significant water-sediment interaction as well water that has evolved from shallower to deeper levels in the order of $Ca^{2+}>Mg^{2+}>Na^{+}+K^{+}>HCO_3^{2-}+CO_3^{2-}>Cl^{-}$.

The assessment of some contamination indicators, such as pH, dissolved oxygen, phosphate, sulphate, chloride, and nitrate, indicates that the water is largely suitable for human consumption. The concentration of iron in more than 25% of the water samples is higher than the maximum acceptable concentration of 0.3 mg/l. However, some wells with high nitrate and iron content should be treated before use.

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