

The Hydrochemical Characteristics and Evolution of Groundwater in Semiarid Yola Area, Northeast, Nigeria

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Abstract: The aim of the study is to characterize groundwater in semiarid Yola area of northeastern Nigeria employing chemical indicators. The dissolution of halite, gypsum, dolomite and calcite determines Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} and HCO_3^- chemistry while other processes such as evaporation and ion exchange also influence the water composition. Surface water and groundwater chemistry data enabled geographical zones and chemical types to be differentiated. Groundwater in the study area is slightly acidic to neutral in nature. Chemistry of groundwater suggests that alkaline earths (Ca+Mg) significantly exceed the alkalis (Na+K) and weak acids ($\text{HCO}_3^- + \text{CO}_3$) exceed the strong acids ($\text{Cl}^- + \text{SO}_4$), suggesting the dominance of CO_3 weathering followed by silicate weathering. Hydrogeochemical studies disclosed that $\text{Na}^+ - \text{HCO}_3^-$ and $\text{Na}^+ - \text{Cl}^-$ are the dominant ion types for the shallow groundwater (<25 m), $\text{Mg}^{2+} - \text{Cl}^-$, $\text{Mg}^{2+} - \text{HCO}_3^-$ and $\text{Na}^+ - \text{Cl}^-$ for the deep groundwater (>25 m) and $\text{Na}^+ - \text{Cl}^-$ for the surface water bodies. A high positive correlation ($r^2 = 0.87$) between Na^+ and Cl^- suggests that the salinity of groundwater is due to intermixing of two or more groundwater bodies with different hydrochemical compositions. Chemical fertilizers and anthropogenic activities are contributing to sulphate, nitrate and chloride concentrations measured in some surface water and groundwater samples in the study area as evidenced by the relatively high sulphate, nitrate and chloride concentrations. Most of the groundwater samples are suitable for domestic purposes.

Key words: Chemical indicators, dissolution, hydrogeochemical studies, Nigeria, Yola area

INTRODUCTION

Groundwater is one of the most important resources for human life. The water quality depends upon the geological environment, natural movement, recovery and utilization. The chemical quality of the groundwater percolating through the soil zones of anthropogenically polluted layers, are significantly reduced. Hence understanding the groundwater quality changes, solute transport and identifying recharge areas in the groundwater zone has become important in protecting human health. This is because groundwater contains a wide variety of dissolved inorganic species in various concentrations, as a result of chemical and biochemical interactions between groundwater and geological materials through which it flows; and to a lesser extent because of contributions from the atmosphere, surface water bodies and anthropogenic activities.

Previous records on the hydrogeology and groundwater conditions in Yola area (Jackson, 1995; Obiefuna *et al.*, 1999) discussed the hydrogeology and

geotechnical properties of the study area but lacked in depth 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, b; Mclean *et al.*, 2000; Pannatier *et al.*, 2000; Garlindo *et al.*, 2001; Walraevens *et al.*, 2003; Jezersky, 2007; Zhu *et al.*, 2008). They employed ionic ratios to draw conclusions on the hydrogeochemical characteristics and groundwater evolution of the aquifer systems of their various areas of study. They pointed out that increased understanding of the chemical processes affecting groundwater chemistry in a basin would give an insight into the hydrogeology of the basin. This study intends to examine the variations of groundwater chemistry of the study area as well as interpret the processes that control the groundwater chemistry.

The study area: The study area falls within latitudes $9^{\circ}11' \text{N}$ and $9^{\circ}24' \text{N}$ and longitudes $12^{\circ}20' \text{E}$ and $12^{\circ}34' \text{E}$ and lies about 50 km south of the Hawal Massifs. It is

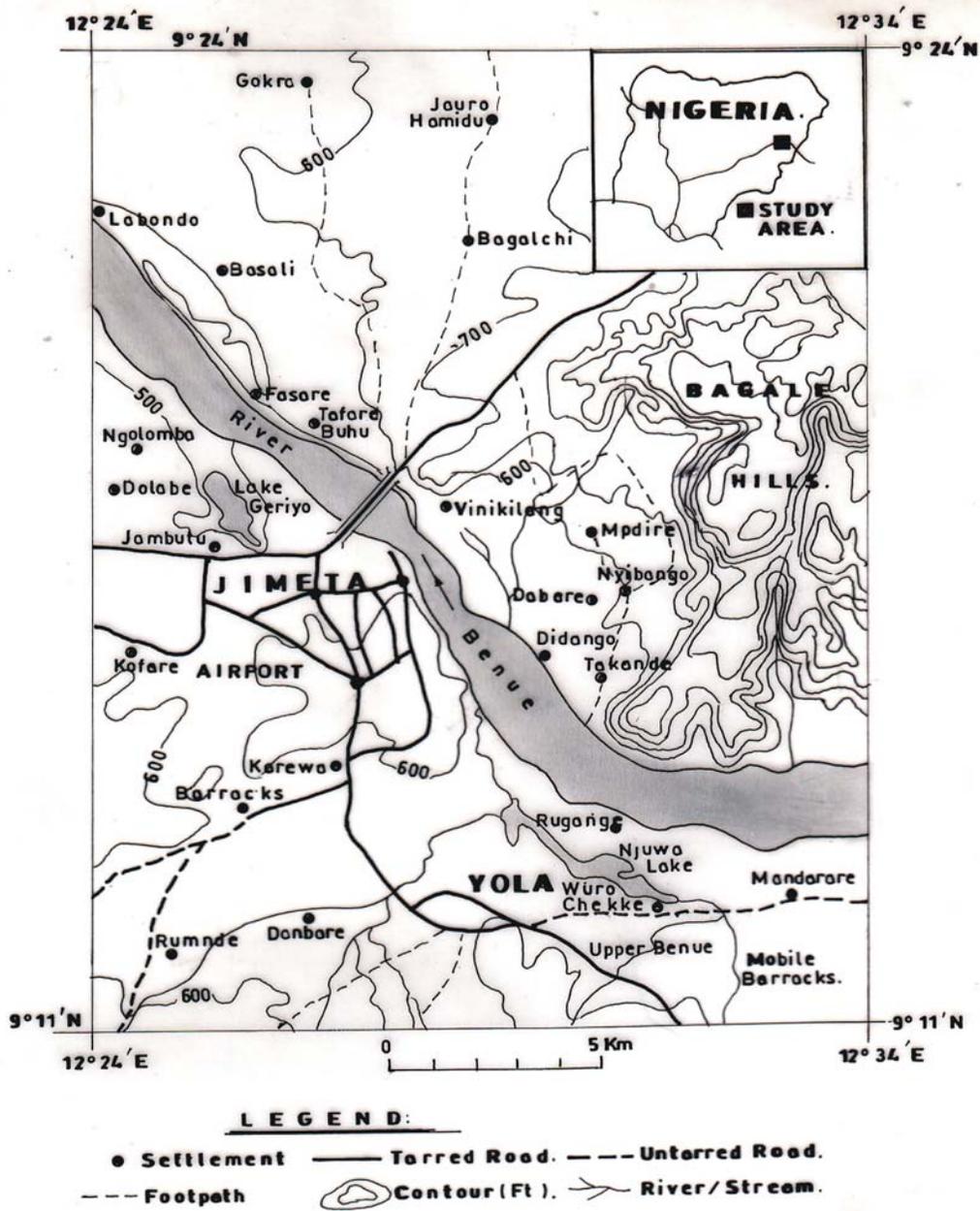


Fig. 1: Location map of the study area

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 431 km² of the land surface (Fig. 1).

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 431 km² 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

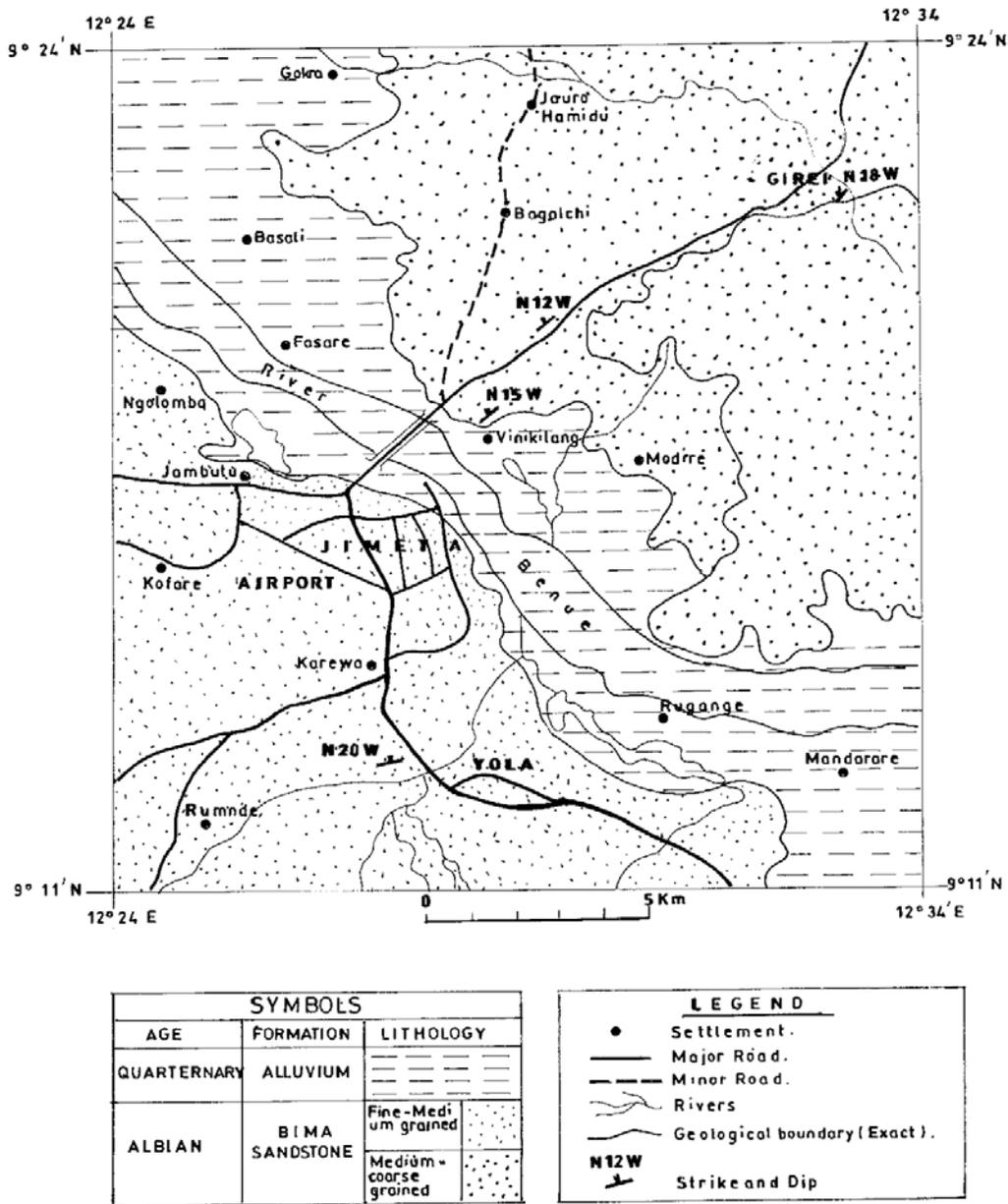


Fig. 2: Geological Map of the study area

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. Temperature goes low during the harmattan sub-season and may be as low as 19 to 22.9°C but may be as high as

39.7°C. The rainy season follows the advancing Atlantic Maritime Air which is accompanied by high humidity ranging from 62.5 to 79% in the rainy season (Obiefuna, 2011 in Preparation). The mean annual rainfall is about 827.7 mm (32.6 inches) while the mean annual evapotranspiration is about 2384.6 mm (97.8 inches).

The soil consists mainly of calcic luvisols to the north and the eutric regosols to the south. The luvisols are

derived from sandstone formation and have typical clay-ended horizons with high base saturation of more than 50%. They have high ferric properties with iron oxide concentration and are red to deep brown in colour in the B horizons. They are lateritic calcic hydromorphic and lime enriched. These soils are moderately acidic and shallow to moderately deep and well drained. They have gravelly to loamy sand surface horizons with pH ranging from 5.1 to 6.1 and moderate to high organic matter.

The regosols are generally loose, extensively drained and intensively leached. Apart from the humus-rich surface layer, the regosols indicate little evidence of pedogenesis except for the oxidation and consequent reddish to brownish colouration of the sands. The soils normally have a clay enriched B horizon suggesting some degree of elevation. They are poorly leached and contain montmorillonitic clays with high water and nutrient holding capacities. They are coarse textured with low to moderate organic matter. They are generally dark grey to grayish brown in colour with pH value of about 6.4 and are suitable for cultivation of maize, sorghum and millet and are found around Bajabure.

The study area falls within the northern Guinea savannah vegetation belt. Hence within this belt is an interspersed of thickets, free savannah open grass savannah and fringing forests in the river valleys. However, large scale deforestation resulting from indiscriminate extraction of wood for fuel and expansion of agricultural land areas has left areas within this vegetation type with few indigenous woody plant species. Most areas especially those close to settlements are covered with exotic species such as the neem and eucalyptus trees.

The topographic relief is up to 90 m in 1 km which is relatively high. It is characterized by high relief with cirques at upper elevations and deep valleys at lower elevations. People of the study area are pioneer users of surface water, shallow and deep wells for drinking and irrigation purposes. Some of the arable lands are usually irrigated by both surface water and groundwater to grow crops such as mainly High Yielding Varieties (HYV) rice, maize, guinea corn and various types of vegetables during both the dry and rainy seasons in the area.

Geological and hydrogeological setting: 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 100 to 300 m and has its maximum thickness at the Lamurde anticline where it exceeds 3000 m. The differing degrees 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 Sandstone, the Middle Albian Bima Sandstone and the late Albian/Cenomanian Upper Bima Sandstone (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 (Fig. 2). The depth to the bedrock varies from 30 m to more than 45 m. 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 m 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.

The grain-size ranges from 0.43 to 2.2 mm indicating a fine to coarse grained sandstone that is poorly to moderately sorted. The mineralogical composition of the Bima Sandstone consists 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.

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. The sandstone 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 leading 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. The Bima Sandstone has abundant soft-sediment deformation structures that include cusps, droplets, convolute bedding, deformed cross-bedding and sand volcanoes (Abubakar *et al.*, 2006). The structures in most outcrops are sandwiched between undeformed cross-bedded strata that have no major textural differences with the sediments hosting them. The cusps are both simple internal cusps and interpenetrative cusps and are formed by post-depositional fluidization triggered by seismic shocks, where the interpenetrative cusps serve as conduits through which sands rose to the surface to form volcanoes. The droplets are the discrete type associated mostly with complex deformed cross-beddings while the convolute bedding forms concentric antiforms and synforms without any evidence of faulting and gradually die out vertically upward (Abubakar *et al.*, 2006). The deformed cross-bedding is represented by both simple and complex recumbent folds of flow and seismically induced origins respectively. The source of the seismic shocks may be episodic syndepositional Mesozoic Volcanism of Jurassic to Albian times within the Upper Benue Trough (Abubakar *et al.*, 2006) Overlying the Bima Sandstone in the study area is the river course alluvium which is composed of sands, silts, shales and clays and is confined mainly along the course of the River Benue and its tributaries. Field studies have shown that there is hydraulic connection between the river course alluvium and the underlying Bima Sandstone Formation.

Obiefuna (2011 in Preparation) have defined the main hydrogeologic characteristics of Yola Area based on data from pumping test, statistical grain-size test, hydrological 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 unconfined to confined aquifer systems exist in areas underlain by the recent Quaternary river coarse alluvial stratigraphic unit which laterally changes to upper unconfined aquifer system in areas underlain by the Cretaceous sandstone. This is subsequently underlain by the lower semi-confined to confined aquifer systems.

Thus 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 0-80 m whereas the latter occurs within the depth range of 80-250 m. The shallow aquifer occurs 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 (Obiefuna and Orazulike 2010a).

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; and are thus recharged by percolation of rainfall and direct infiltration of the River Benue.

The hydraulic conductivity, K , obtained from both the pumping test and the statistical grain size methods for the upper unconfined alluvial aquifer revealed values ranging from 0.051 to 56.98 m/day with a mean value of 2.54 m/day. The hydraulic conductivity obtained for the lower semi-confined to confined aquifer employing the pumping test and the statistical grain-size methods indicate values ranging from 0.22 m/day to 10.48 m/day with a mean value of 3.81 m/day. The transmissivity values for the upper unconfined alluvial aquifer ranges from 1.52 to 349.86 m²/day with a mean value of 37.99 m²/day whereas those obtained from granulometric methods vary from 9.97×10^{-3} to 1.53 m²/s (Obiefuna 2011 in Preparation).

The transmissivity values for the lower semi-confined to confined aquifer varies from 9.18m²/day to 349.93 m²/day with a mean value of about 103.51 m²/day. The variation in transmissivity values in the two aquifer systems are due to 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} 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 occurs to the west whereas to the southwest the recharge area is northeastwards towards the Benue River. The groundwater in the two aquifer systems 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 (Obiefuna and Orazulike, 2010b).

METHODOLOGY

Ninety-six water samples from different water sources such as precipitation, surface water and groundwater were collected in the study area during extensive geological and hydrogeological field work. A Global Positioning System (GPS), Garment 12, was used for location and elevation readings. This was confirmed from topographic sheets made available from the Ministry of Lands and Survey, Adamawa State of Nigeria. In-situ measurements include pH, Electrical Conductivity (EC), temperature, and identification and recognition of the water bearing layers.

The geological and hydrogeological field work was carried out on 5th February 2009 and subsequently followed by sampling and chemical analyses of groundwater samples between 12th February and 26th February 2009. The chemical analyses of groundwater samples was done in the chemical laboratory of the Adamawa State Water Board Yola Nigeria.

Groundwater samples were collected in polyethylene bottles after pumping the (sampled) wells for about 30 minutes. This was done to remove groundwater stored in the well itself and to obtain representative samples from the aquifer. Samples were filtered through a 0.45 µm filter paper and subsequently analyzed in the Laboratory of the Adamawa State water Board Yola for Na⁺, K⁺, Ca²⁺ Mg²⁺, HCO₃⁻, Cl⁻, SO₄²⁻, F⁻, and TDS. Standard methods were used for the determination of the chemical characteristics of the water samples (APHA/AWWA/WPCF).

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

Ions were converted from milligram per litre to milliequivalent per litre and anions balanced against cations as a control check of the reliability of the analyses.

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

Parameter	Rainfall (n = 5)				Surface water (n = 11)				Shallow groundwater (n = 81)				Deep ground water (11)			
	Mean	Min.	Max.	SD	Mean	Min.	Max.	SD	Mean	Min.	Max.	SD	Mean	Min.	Max.	SD
Temp (°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
pH	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
<i>E. coli</i> (Per 100 mL)	0	0	0	0	13.80	8	21	3.54	5.60	0	7	2.12	2	0	4	1.21

Table 2: Classification of the water samples of the study area on the basis of their major ion percentages

S.No.	Water source	Major cation types	Major anion types	Hydrogeochemical
1	Rain water	Ca ²⁺ (1) No dominant (4)	Cl ⁻ (1) HCO ₃ + CO ₃ (4)	SO 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)
3	Shallow Groundwater	No dominant (1) 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)
4	Deep ground-water	No dominant (3) Mg ²⁺ (6) Na ⁺ + K ⁺ (2)	Cl ⁻ (5) HCO ₃ + CO ₃ (6)	SO ₄ ²⁻ + Cl ⁻ (4) Ca ²⁺ + Mg ²⁺ (7)

The results of the chemical analyses of the different water sources are summarized in Table 1.

RESULTS AND DISCUSSION

Hydrochemical characteristics of surface water and groundwater: 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 Fig. 3, 4 and 5. 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 sample.

The present study takes into consideration the geologic and hydrogeologic features and anthropogenic activities because of the role of groundwater as a geologic agent (Todd, 1995). Thus the spatial distribution of the major ions, the main chemical characteristics of the groundwater as well as the mineralogical composition and grain-size of the sediments in contact with the water was used to define the three hydrogeochemical zones. The waters are of various hydrogeochemical types, and the following features of the groundwater chemistry are of particular interest.

In the rainwater the chemical composition is of the calcium-bicarbonate type, whereas the predominant hydrogeochemical facies is the $Ca^{2+}+Mg^{2+}$ type indicating fresh water.

In the surface water zone the water is of the $Na^{+}+K^{+}-Cl^{-}$ type whereas the predominant hydrogeochemical facies are the $SO_4^{2-}+Cl^{-}$ type (Table 2). 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.

In the shallow groundwater zone the chemical composition of the groundwater is a combination of $Na^{2+}-K^{+}-HCO_3^{-} +CO_3^{2-}$ and $Na^{+}-K^{+}-Cl^{-}$ types whereas $Ca^{2+}+Mg^{2+}$ and $SO_4^{2-}+Cl^{-}$ are the predominant hydrogeochemical facies (Table 2). This is as a result of a longer time of contact with the finer sediments, a moderate interaction with the atmosphere and mixing with deeper more saline groundwater probably of marine origin.

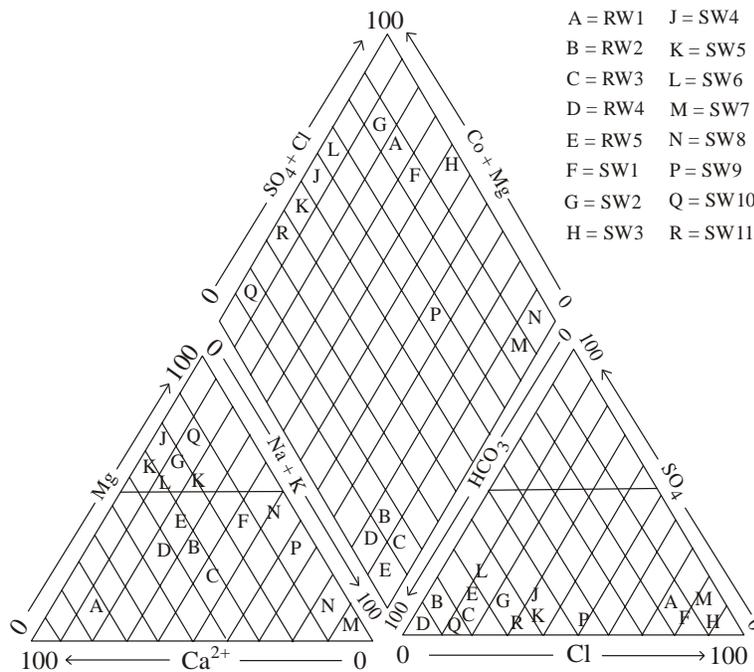


Fig. 3: Piper Trilinear diagrams for surface water and rain water in the study area

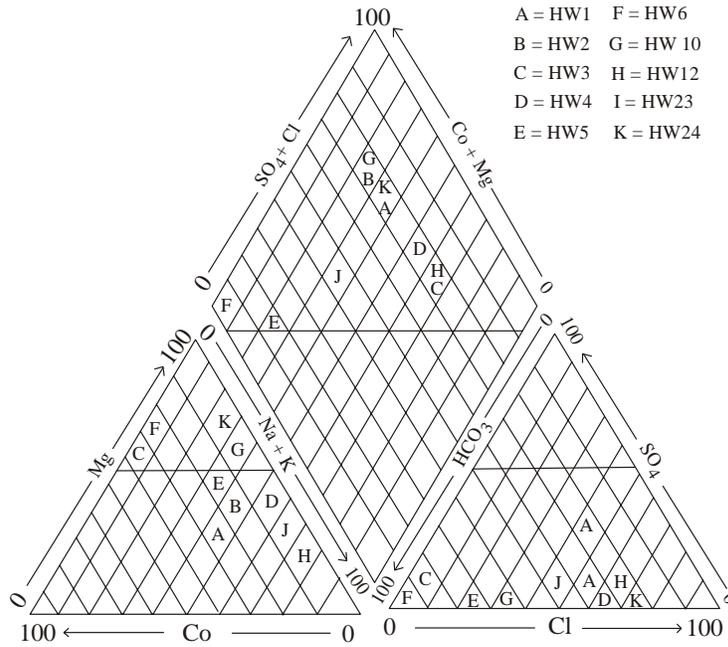


Fig. 4: Piper Trilinear diagrams for shallow groundwater samples in the study area

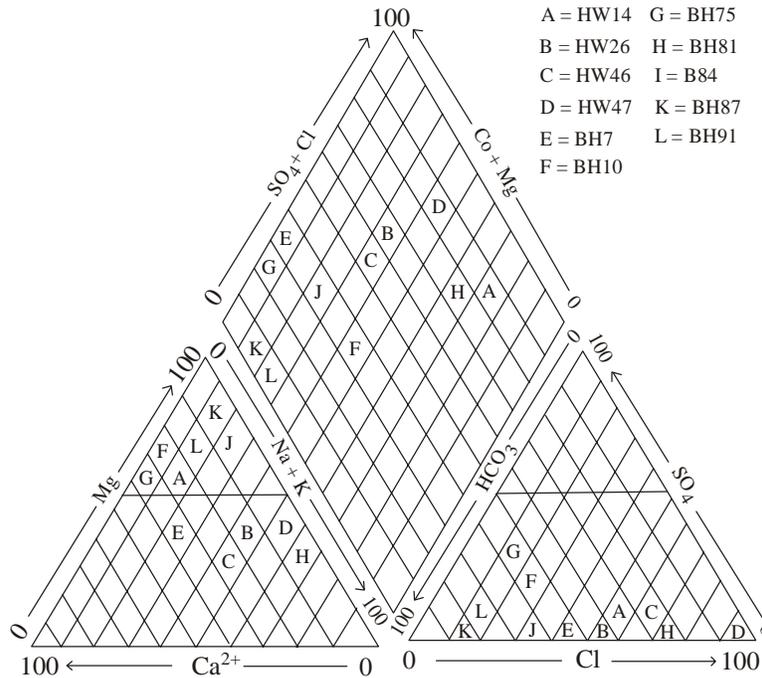


Fig. 5: Piper Trilinear diagrams for deep groundwater samples in the study area

However based on thin section studies of the underlying Bima sedimentary rock montmorillonite, kaolinite, calcite, gypsum and halite appear to

predominate. A source of these evaporates could be traced to the Precambrian igneous rocks around the northern margins as well as Paleozoic and Tertiary volcanic rocks

Table 3: Relevant elemental composition of Bima sandstone deposit in the study

S.No.	Location	Sample no.	SiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	Fe ₂ O ₃	SiO ₃	P ₂ O ₅	Mn ₂ O	TiO ₂	LOI
1	Bajabure	A	92.68	4.65	0.010	0.29	0.040	0.64	0.58	0.030	0.010	0.040	0.230	1.75
2	Jambutu	B	92.42	5.65	0.010	0.01	0.060	1.22	0.37	0.030	0.010	0.040	0.360	1.16
3	Jimeta	C	88.78	7.25	0.010	0.20	0.010	0.01	1.20	0.020	0.010	0.040	0.330	2.87
4	Sangirei	D	91.41	6.02	0.010	0.01	0.006	0.01	1.12	0.012	0.010	0.038	0.170	2.31
5	Lainde	E	90.75	6.29	0.010	0.01	0.070	1.45	0.50	0.014	0.010	0.059	0.470	1.38
6	Jimeta	F	94.93	4.97	0.000	0.01	0.029	0.01	0.59	0.017	0.010	0.072	0.240	1.59
7	Karewa	G	90.12	5.92	0.023	0.19	0.049	0.56	0.95	0.022	0.010	0.058	0.451	1.69
8	Yola	H	92.45	4.49	0.004	0.01	0.018	0.01	0.56	0.055	0.010	0.044	0.185	1.65
9	Kofare	J	84.76	6.50	0.040	0.67	0.050	1.17	1.54	0.080	0.010	0.115	0.549	2.21
10	FCE	K	92.08	4.45	0.016	0.01	0.075	1.76	0.47	0.046	0.010	0.048	0.187	1.36
11	Girei	L	92.84	5.01	0.010	0.01	0.005	0.01	0.43	0.027	0.006	0.040	0.349	1.81
12	Damilu	M	92.67	4.30	0.010	0.01	0.012	0.01	0.95	0.051	0.010	0.043	0.209	1.41
13	Vinikilang	N	91.99	5.91	0.005	0.01	0.016	1.31	0.63	0.049	0.010	0.040	0.124	1.76
14	Sabonger	P	89.11	7.19	0.015	0.058	0.001	0.01	0.81	0.058	0.129	0.061	0.070	2.09
15	Tofare Buhu	Q	93.66	3.75	0.001	0.057	0.049	0.83	0.18	0.059	0.225	0.045	0.213	1.17
16	ABTI	R	80.61	5.90	0.010	0.01	0.060	1.49	6.04	0.015	0.010	0.450	0.250	2.57

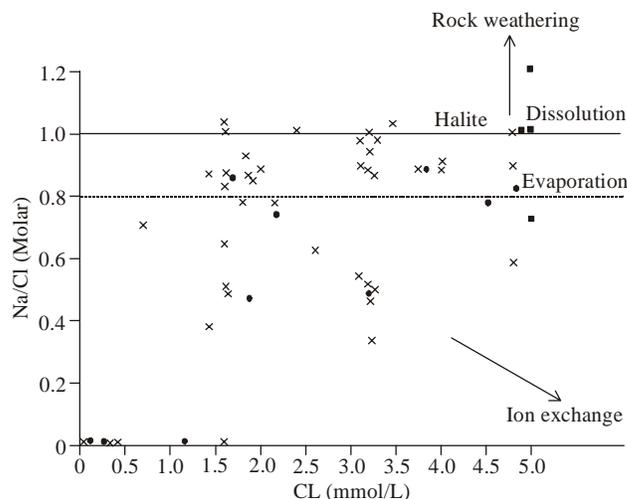


Fig. 6: Relation between Na/Cl ratio and Cl in water samples of the study area

The ions in groundwater are mainly derived from the atmospheric input and the acid weathering of minerals of the skeleton of the aquifer such as aluminosilicates including albite, anorthite and microcline. As dissolution of aluminosilicate minerals is a slow process, the low to moderate TDS of the groundwater (mean TDS of 58.80 mg/L for shallow groundwater and 67.67 mg/L for deep groundwater) may be interpreted as the consequence of short to moderate residence time of solutions within the aquifers. The TDS of the groundwater thus increased with depth. The low to moderate mineralization of the groundwater and the heterogeneity of the major ion composition (Na⁺-Mg²⁺-HCO₃⁻-Cl⁻ type water) revealed the occurrence groundwater mixing. However the TDS of the upstream wells (mean TDS of 61.02 mg/L) changed slightly from those of the downstream wells (mean TDS of 59.08 mg/L) indicating homogeneity in chemical

composition along the flow direction (Table 4a, b). The downstream runoff indicates a mean TDS of 96 mg/L and Na⁺-Cl⁻ type water corroborating the hypothesis of hydraulic connectivity between the groundwater and the surface water (River Benue) of the study area. Most of the groundwater from both aquifers are undersaturated with respect to calcite (SI = -5.11 to 0.51) and with respect to other evaporite minerals (Table 5) Consequently carbonate dissolution and other secondary processes such as mixing and the pollution modify the groundwater mineralization in the study area.

Much higher Na/Cl ratios of up to 1.2 have been recorded in the more saline surface waters of the study area. Therefore the relative contribution of feldspar weathering to the solute load of the groundwater is minor. This is also consistent with the low saturation indices of aqueous silica (SI = -5.11 to 0.51; Table 5).

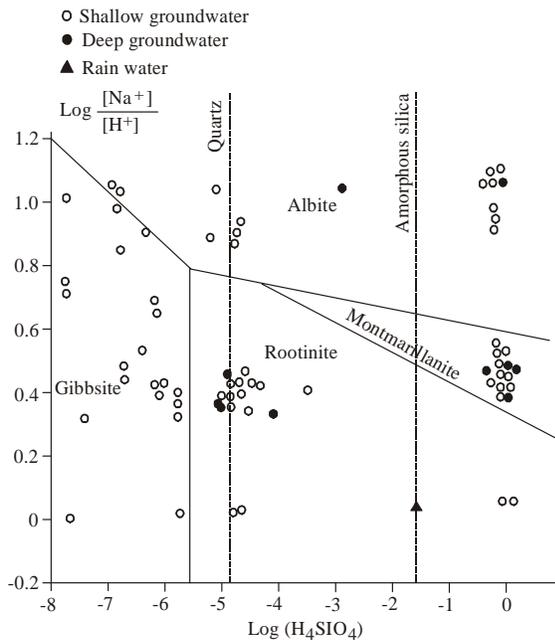


Fig. 7: Logarithmic function of Na/H and H₄SiO₄ values in the water samples in a stability diagram for K-aluminosilicate

Trends of K/Cl vs Cl shown in Fig. 8 are similar to those of Na/Cl vs Cl, suggesting that weathering of muscovite and K-feldspar, both of which are present in the aquifer sediments, contributes to the relatively high K contributions in the lowest salinity groundwater.

Mg/Cl ratio with increasing salinity due to ion exchange between Mg and Na. The low salinity with high Mg/Cl ratios reflects the input of Mg from silica

weathering (Fig. 9). High Ca/Cl ratios in the freshest groundwater reflect weathering of calcium silicate minerals eg plagioclase feldspar (Fig. 10). Many of these samples are close to saturation with respect to calcite, dolomite and gypsum (Table 5), indicating that precipitation of these minerals may limit calcium and sulphur concentrations in the groundwater.

Pannatier *et al.* (2000) proposed a calculated relation (SO₄F) as the relative deviation of the sulphate/chloride ratio in groundwater and sea water as follows:

$$SO_4F = \frac{(SO_4/Cl)_{GW} - (SO_4/Cl)_{SW}}{(SO_4/Cl)_{SW}} \quad (2)$$

when the SO₄F ratio is larger than -0.2, a large sulphate content is assumed and sulphate reduction is still going on or is not yet started whereas in samples with an SO₄F ratio smaller than -0.2, sulphate is reduced. Pannatier *et al.* (2000) proposed a value of -0.2 instead of 0 to take into account small analytical errors.

For the surface waters the SO₄F ratio are -0.7 and -0.66 (Lakes Njuwa and Geriyo); whereas its values at River Benue at Jimeta and Yola water Treatment Plant are -0.35 and -0.95, respectively.

The SO₄F ratio in shallow groundwater ranges from -1 to 699 (mean 35.07) and -1 to 10.33 (mean 1) for deep groundwater. The SO₄F ratio for surface water samples are generally smaller than -0.2 indicating that sulphate is reduced whereas those of groundwater samples which are generally larger than -0.2 suggests on-going sulphate reduction. Thus reduction of Fe-oxides and hydroxides brings Fe²⁺ into the solution, while the reduction of sulphate removes iron from the solution as a result of the formation of iron sulphides. Methane was not analyzed but Stumm and Morgan (1981) indicate that

Table 4a: Comparison of the chemical analyses for both shallow groundwater and surface water samples, upstream and downstream of the study area, values are mean concentrations in mg/L, unless indicated otherwise

Parameters	Upstream shallow groundwater	Downstream shallow groundwater	Downstream runoff	Rainwater
TDS	61.02	59.08	96.00	13.40
Electrical conductivity (ds/m)	0.09	0.09	0.14	0.02
pH	7.10	7.06	7.20	4.30
T(°C)	30.00	30.01	32.50	29.0
Sodium	26.83	41.78	182.25	0.00
Potassium	3.29	4.44	3.53	0.00
Calcium	11.56	12.56	18.10	5.80
Magnesium	21.65	19.96	37.81	1.10
Sulphate	9.93	11.76	14.03	1.80
Chloride	55.76	79.79	298.58	0.00
Nitrate	4.81	3.90	22.48	0.00
Bicarbonate	95.77	91.47	134.08	19.20
Alkalinity	110.12	105.04	150.75	19.31
Iron	0.31	0.39	0.26	0.00
Phosphate	2.15	1.23	9.40	0.22
Dissolved Oxygen	0.74	0.99	1.53	5.66

Table 4b: Comparison of the chemical analyses for both deep groundwater and surface water samples, upstream and downstream of the study area, values are mean concentrations in mg/l, unless indicated otherwise

Parameters	Upstream deep groundwater	Downstream deep groundwater	Downstream runoff	Rainwater
TDS	57.25	77.33	96.00	13.40
Electrical conductivity (ds/m)	0.086	0.12	0.14	0.02
pH	7.08	7.60	7.20	4.30
T(°C)	30.25	30.00	32.50	29.00
Sodium	33.84	33.32	182.25	0.00
Potassium	3.13	7.50	3.53	0.00
Calcium	12.83	7.20	18.10	5.80
Magnesium	33.13	24.83	37.81	1.10
Sulphate	18.86	4.01	14.03	1.80
Chloride	75.76	75.10	298.58	0.00
Nitrate	6.58	3.62	22.48	0.00
Bicarbonate	103.94	101.17	134.08	19.20
Alkalinity	117.44	111.67	150.75	19.31
Iron	0.12	0.026	0.26	0.00
Phosphate	2.09	0.0367	9.40	0.22
Dissolved Oxygen	0.92	1.067	1.53	5.66

Table 5: Result of saturation indices and equilibrium calculations for different water sources

Parameter	Rainfall (n = 5)				Surface water (n = 11)				Shallow groundwater (n = 81)				Deep ground water (11)			
	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD
Log SI 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
Log SI 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
Log SI 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
Log SI Quartz	-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
Log SI 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
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
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
MH ₂ CO ₃ mol/kg																
H ₂ O 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
DIC mmol/kg	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
H ₂ O x 10 ⁻³																

DIC = Dissolved Inorganic Carbon; SI = Saturation Index; P_{CO₂} = Partial Pressure of CO₂

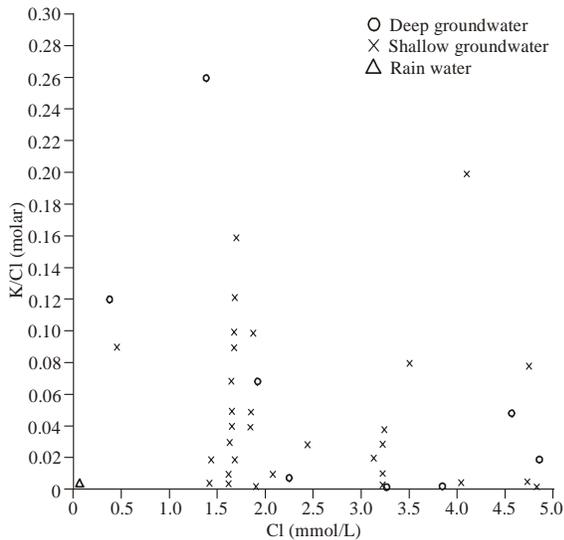


Fig. 8: Relation between K/Cl ratio and Cl in water samples of the study area

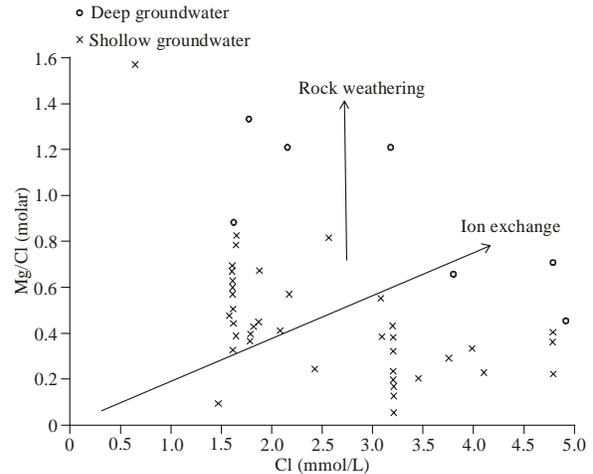


Fig. 9: Relation between Mg/Cl ratio and Cl in the water samples of the study area

methanogenesis occurs at about the same redox potential as sulphate reduction; so it is very likely to take place in the deeper parts of Bima sediments.

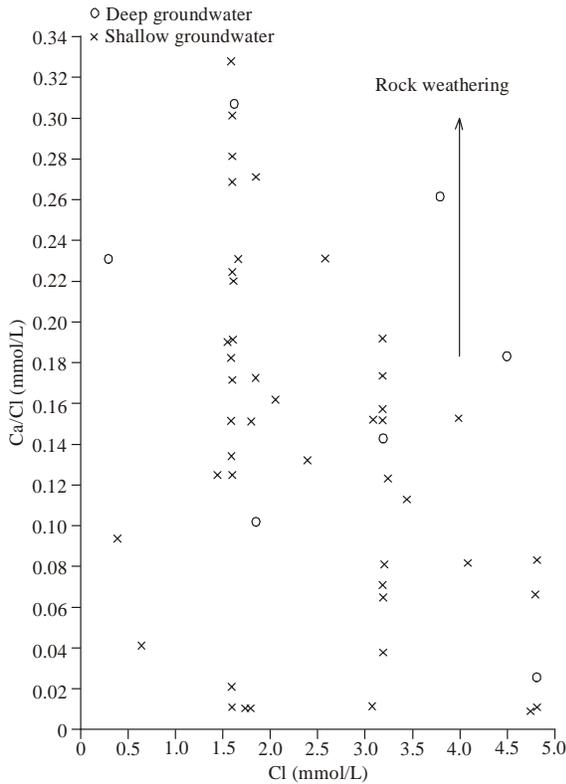


Fig. 10: Relation between Ca/Cl and Cl in the water samples of the study area

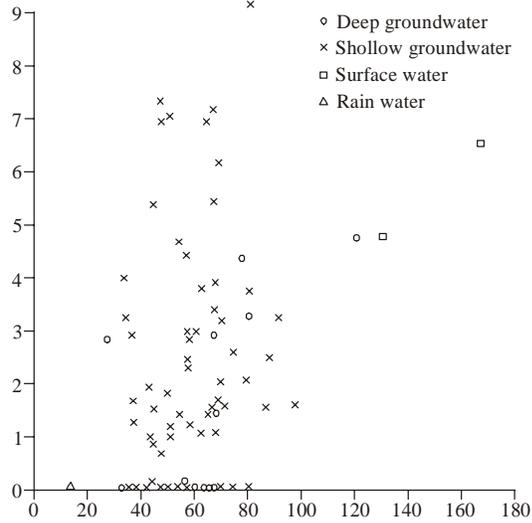


Fig. 11: Relation between Na/Ca and TDS in the water samples of the study area

The mean value of SO_4/Cl ratio for shallow groundwater is 5.41 whereas those of deep groundwater

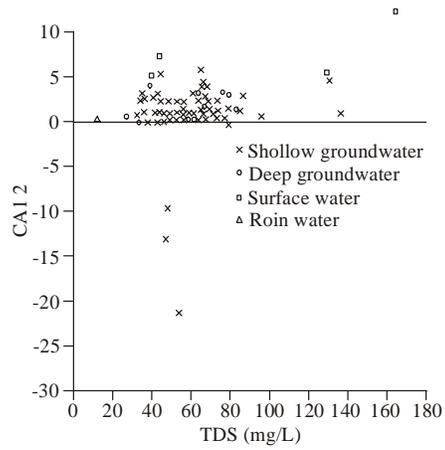


Fig. 12: Relation between choloalkaline index (CAI, I) and TDS in the water sample of the study area

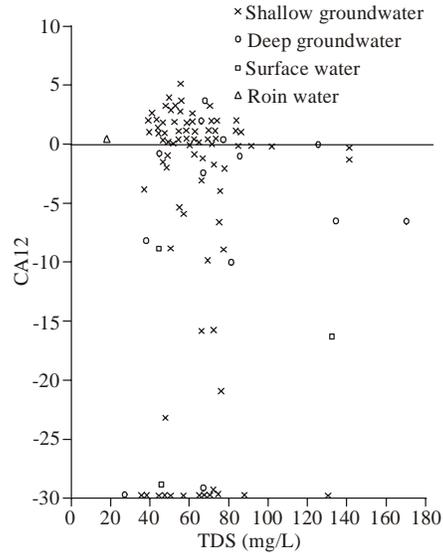


Fig. 13: Choloalkaline index (CAI, 2) and TDS in the water sample of the study area

and surface water are 0.30 and 0.05, respectively. The mean SO_4/Cl value of 0.5 and above suggests an additional sulphate input from fertilizer application, leaching of contaminated fill or oxidation of sulphide in shallow groundwater.

Molar Na^+/Ca^{2+} ratios vary between 0 and 9.20 and increase along the groundwater flow direction (Fig. 11). The existence of abundant Na^+ may promote cation exchange. This is confirmed by two indices of Base Exchange (IBE), namely the chloro alkaline indices (CAI 1 and CAI 2; Schoeller, 1965), where

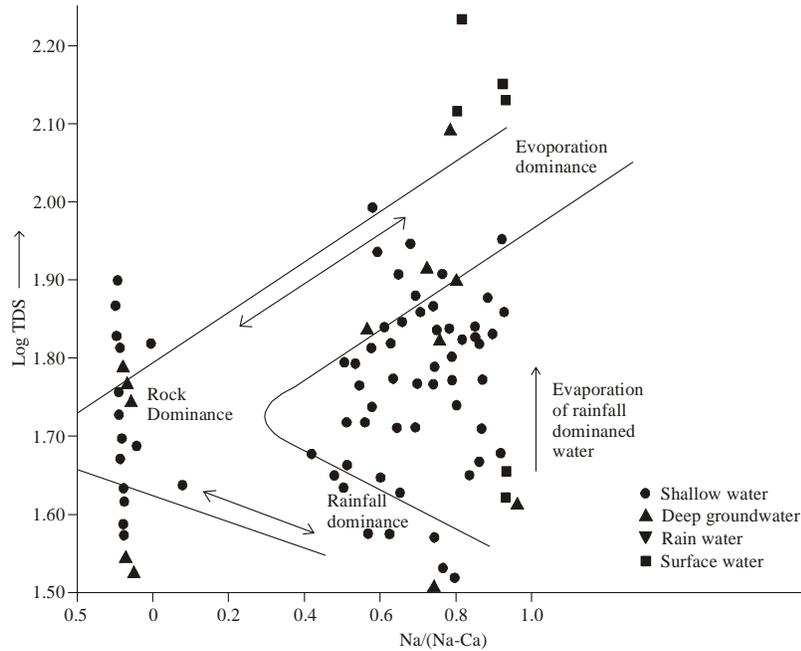


Fig. 14: A Gibbs plot indicating the mechanism that determines the major ion composition of different water sources of the study area

$$CAI1 = Cl - (Na+K) / Cl \quad (3)$$

$$CAI2 = Cl - (Na+K) / SO_4 + HCO_3 + CO_3 + NO_3 \quad (4)$$

when there is an exchange between Na^+ and K^+ in groundwater with Mg^{2+} or Ca^{2+} in the aquifer material, both of the indices are positive, indicating ion exchange of Na^+ in groundwater with Ca^{2+} or Mg^{2+} in the alluvium or weathered materials. In general, these indices show positive values; whereas the low-salt waters give negative CAI 1 values (Fig. 12 and 13). The increase in groundwater salinity was accompanied by a slow rise in reverse ionic exchange, which indicates a cationic exchange that increases the hardness of these waters. The contribution of K^+ to the groundwater in these samples is modest. The low levels of potassium in natural waters are a consequence of its tendency to be fixed by clay minerals and to participate in the formation of secondary minerals.

A plot of log TDS against $Na^+ / (Na^+ + Ca^{2+})$ ratio (Fig. 14) indicate that majority of the water samples plotted in the centre of the boomerang diagram implying that the rock types and their weathered products have significantly contributed to the modification of the water chemistry. As illustrated in the Gibbs plot in Fig. 14 (Gibbs, 1970, 1971), other dominant processes determining the water composition are evaporation and precipitation. Evaporation of surface water and moisture in the unsaturated zone has been found as the most

influential process in the development of the chemical composition of shallow groundwater (Richter and Kreitler, 1993). Evaporation concentrates the remaining water and leads to precipitation and deposition of evaporite that are eventually leached into the saturated zone. This source of groundwater evaporites is amplified in semi-arid lands such as the study site, due to the high evaporation rate and low rainfall which encourage the above mentioned processes and also reduce the dilution effects on the groundwater. This is clearly reflected in the Gibbs (1971) plot, which indicates a trend towards evaporation (and precipitation of the least soluble minerals) as well as rock dominated weathering.

However some points which plotted outside the centre of the diagram signify a period of short rock-water contact characteristic of groundwater in tropical African and South American countries (Ogunbajo, 2003).

Mineral equilibrium calculations for groundwater 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).

In the present study, to determine the chemical equilibrium between minerals and water, SI of calcite,

dolomite, and gypsum were calculated based on the following equation (Lloyd and Heathcote, 1985):

$$SI = \log (IAP/K_s T) \quad (5)$$

where;

IAP = Ion activity product

$K_s(T)$ = Equilibrium constant of the reaction considered at the temperature T

The calculated values of SI for calcite, dolomite and gypsum range from -2.80 to 0.28, -4.00 to 0.54 and -7.23 to -2.11 with averages -1.25, -1.79 and -3.28, respectively (Table 5). These indicate that majority of the water samples are undersaturated with respect to calcite, dolomite and gypsum respectively.

CONCLUSION

Groundwater in the study area is slightly acidic to neutral in nature whereas the chemistry of the groundwater suggests that alkaline earths (Ca + Mg) significantly exceed the alkalis (Na + K) and weak acids exceed the strong acids (Cl + SO₄), suggesting the dominance of carbonate weathering followed by silicate weathering.

About ninety-six water samples were analyzed chemically for physicochemical parameters. The study revealed that most of the water samples are undersaturated with respect to dolomite and calcite minerals.

In the rainwater the chemical composition is of the calcium-bicarbonate type whereas the predominant hydrogeochemical facies is the Ca²⁺ + Mg²⁺ type indicating fresh water.

In the surface water zone the water is of the Na⁺+K⁺-Cl⁻ type whereas the predominant hydrogeochemical facies are the SO₄²⁻ + Cl⁻ type. 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.

In the shallow groundwater zone the chemical composition of the groundwater is a combination of Na⁺-K⁺-HCO₃⁻ + CO₃²⁻ and Na⁺-K⁺-Cl⁻ types whereas Ca²⁺+Mg²⁺ and SO₄²⁻+Cl⁻ are the predominant hydrogeochemical facies. This is as a result of a longer

time of contact with the finer sediments, a moderate interaction with the atmosphere and mixing with deeper more saline groundwater probably of marine origin.

However based on thin section studies of the underlying Bima Sedimentary rock montmorillonite, kaolinite, calcite, gypsum and halite appears to predominate. A source of these evaporites could be traced to the Precambrian igneous rocks around the northern margins as well as Paleozoic and tertiary volcanic rocks in the southeast and northwest (Ngurore Basalts) of the study area.

In the deep groundwater zone the chemical composition of the groundwater is a combination of Mg²⁺-Cl⁻, Mg²⁺-HCO₃⁻+CO₃²⁻ and Na⁺+K⁺-Cl⁻ whereas the predominant hydro geochemical facies are the SO₄²⁻+Cl⁻ and Ca²⁺+Mg²⁺, respectively.

These results indicate that both the deep and the shallow groundwaters 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 Ca²⁺>Mg²⁺>Na⁺+K⁺>HCO₃²⁻+CO₃²⁻>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. However, some wells with high nitrate and iron content should be treated before use.

The scientific results have important implications for groundwater management in the Bima Sandstone aquifer of the Upper Benue Basin, probably one of the most water-stressed of the Basins in Northeast Nigeria and in a region destined for development under the current Millennium Development Goals (MDG) of Nigeria.

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REFERENCES

- Abubakar, M.B., N.G. Obaye, H.P. Luterbacher, E.F.C. Dike and A.R. Ashraf, 2006. A Report on the occurrence of Albian-Cenomanian elater-bearing pollen in Nasara-1 well, Upper Benue Trough Nigeria: Biostratigraphic and Paleoclimatological Implications. *J. Afr. Earth Sci.*, 45(3): 347-354.
- Banks, D., C. Reiman, O. Royset, H. Skarphagen and O.M. Saether, 1995a. Natural concentrations of major and trace elements in some Norwegian bedrock groundwaters. *Appl. Geochem.*, 10: 1-16.
- Banks, D., C. Reimann and H. Skarphagen, 1998a. The comparative hydrogeochemistry of two Granitic aquifers: The Isles of Scilly, United Kingdom and the Hvaler Islands, Norway. *Sci. Total Environ.*, 209: 169-183.
- Banks, D., A.K. Midtgaard, G. Morland, C. Reimann, T. Strand, K. Bjorvatn and U. Sewers, 1998b. Is Pure Groundwater safe to drink? Natural contamination of groundwater in Norway. *Geol. Today*, 14(3): 104-113.
- Banks, D., B. Frengstad, A.K. Midtgaard, J.R. Krog and T. Strand, 1998c. The chemistry of Norwegian groundwaters: I. The distribution of radon, major and minor elements in 1604 crystalline bedrock groundwaters. *Sci. Total Environ.*, 209: 169-183.
- Carter, J.O., W. Barber, E.A. Tart and G.P. Jones, 1963. The geology of parts of Adamawa, Bauchi and Bornu Provinces in Northeastern Nigeria. *Geol. Surv. Nig. Bull.*, 30: 35-53.
- Deutsch, W.J., 1997. *Groundwater Geochemistry: Fundamentals and Application to Contamination*. CRC, Boca Raton, FL., USA.
- Garcia, M.C., V. Hidalgo Model, M.C. Apella and M.A. Blesa, 1998a. Chemical quality of deep groundwater in Yerba Buena and San-Miguel de Tucuman Cities (Abstract). Vol. 2, School of Environment Sciences and Technology, Buenos-Aires, pp: 498.
- Garcia, M.G., V. Hidalgo Mdol, M.C. Apella and M. Blesa, 1998b. Chemical characteristics of deep groundwater in the cities of San Miguel de Tucuman and Yerba Buena Province of Tucuman. *Proceeding 10th Latin-American Geological Congress and 6th Natural Congress of Economic Geology*, Buenos-Aires, 3: 342-347.
- Galindo, M.C., M.B. Vece, M.E. Perondi, M. Moserrate Araoz, M.G. Garcia, V. Hidalgo-Medel, M.C. Apella and M.A. Blesa, 2001. Chemical behaviour of the Sali-River Province of Tucuman, Argentina. *Environ. Geol.*, 40(7): 847-852.
- Gibbs, R., 1970. Mechanism controlling world river water chemistry. *Science*, 170: 1088-1090.
- Gibbs, R., 1971. Mechanism controlling world river water chemistry: Evaporation-crystallization process. *Science*, 172: 871-872.
- Jackson, I.M., 1995. The hydrogeology of the Upper Benue Basin in the Yola Area; NE Nigeria. Unpublished M.Sc. Thesis, University of Nigeria.
- Jezersky, Z., 2007. Hydrogeochemistry of a deep gas-storage cavern, Czech Republic. *Hydrogeol. J.*, 15(3): 599-614.
- Lloyd, J.W. and J.A. Heathcote, 1985. *Natural Inorganic Hydrochemistry in Relation to Groundwater*. Oxford University Press, New York.
- McLean, W., J. Jankowski and N. Lavitt, 2000. Groundwater Quality and Sustainability in an Alluvial Aquifer, Australia. In: Sillio, O. (Eds.), *Groundwater, Past Achievements and Future Challenges*. AA Balkema, Rotterdam, pp: 567-573.
- Obiefuna, G.I., A. Nur, A.U. Baba and N.E. Basse, 1999. Geological and geotechnical assessment of selected Gully Sites, Yola Area Northeast, Nigeria. *Environ. Hydrol. J.*, 7(6): 1-13.
- Obiefuna, G.I. and D.M. Orazulike, 2010a. Geology and hydrogeology of groundwater systems of Yola Area NE Nigeria. *J. Environ. Sci. Resour. Manage.*, 2(1).
- Obiefuna, G.I. and D.M. Orazulike, 2010b. Hydrologic characteristics of the River Benue wetland in Semiarid Yola Area, NE Nigeria. *Water Resour. J. Nigerian Assoc. Hydrogeol.*, 20(2): 54-64.
- Obiefuna, G.I. and D.M. Orazulike, 2011. Geochemical and mineralogical composition of Bima Sandstone Deposit, Yola Area NE Nigeria. *Res. J. Environ. Earth Sci.*, 3(2): 95-102.
- Obiefuna, G.I., 2011 (in Preparation). Hydrogeochemistry and groundwater quality of Yola Area Northeast, Nigeria. Unpublished Ph.D. Thesis, Abubakar Tafawa Balewa University, Bauchi, Nigeria.
- Oga, M.S., 1998. *Ressources en aux souterraines dans la region du Grand Abidjan (Cote d'Ivoire): Approches hydrochimique et isotopique*, These Doct. University Paris XI, Orsay.
- Ogunbajo, M.I., 2003. Hydrogeochemical evaluation of water resources in Mokwa Local Government Area of Niger State in relation to its geology and anthropogenic influence. *Water Resour. J. Nigerian Assoc. Hydrogeol.*, 14: 53-59.
- Piper, A.M., 1944. A graphical procedure in the geochemical interpretation of water samples. *Trans. Am. Geophys. Union*, 25: 914-923.
- Pannatier, E.G., H.P. Broers, P. Venema and G. Van Beusekom, 2000. A new Process- Based Hydrogeochemical classification of Groundwater: Application to the Netherlands National Monitoring System. INO report, NITG 00-143-B, 38, NITG, Utrecht.

- Reimann, C., H. Gem, U. Siewers, K. Bjorvatn, G. Morland, H. Skarphagen and T. Strand, 1996. Radon, fluoride and 62 elements as determined by ICP-MS in 145 Norwegian hard rock groundwater samples. *Sci. Total Environ.*, 192: 1-19.
- Richter, B.C. and W.C. Kreitler, 1993. *Geochemical techniques for identifying sources of Groundwater salinization*. CRC Press, New York, ISBN: 1-56670-000-0.
- Schoeller, H., 1965. Hydrodynamics of karst. *Actes du Colloques de Dubrovnik, IAHS/UNESCO*, Wallingford, UK and Paris, France, pp: 3-20.
- Stumm, W. and J. Morgan, 1981. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 2nd Edn., Wiley, New York.
- Stuyfzand, P.J., 1986. A new Hydrochemical classification of water Types: Principles and application to the coastal dunes aquifer system of the Netherlands. *Proceedings of the 9th Salt water Intrusion Meeting*, Delft, pp: 641-655.
- Stuyfzand, P.J., 1993. *Hydrogeochemistry and hydrology of the coastal dune area of the western Netherlands*. Unpublished Ph.D. Thesis, Free University Amsterdam, Netherlands.
- Todd, D.K., 1995. *Groundwater Hydrology*. J. Wiley and Sons, Singapore.
- Walraevens, K., 1990. Hydrogeology and Hydrogeochemistry of the Ledo-Paniselian semi confined aquifer in East and West Flanders. *Acad. Analecta*, 52(3): 11-66.
- Walraevens, K., M. Mahauden and M. Coetsiers, 2003. Natural background Concentration of trace element in aquifers of the Flemish region, as a reference for the government sanitation policy. *FZK/TNO Conference on contaminated soil (Consoil)*, Ghent, pp: 215-224.
- Yenika, M.E., K.O. Uma and G.I. Obiefuna, 2003. The impact of human activities on ground-water quality: A case study of shallow aquifers in Jimeta-Yola Metropolis, Northeast Nigeria. *Water Resour. J. NAH*, 14(2): 84-91.
- Zhu, G.F., Y.H. Su and Q. Feng, 2008. The hydrochemical characteristics and evolution of groundwater and surface water in the Heihe River Basin, northwest China. *Hydrogeol. J.*, 16(1): 167-182.