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Evaluation of Shallow Groundwater in Cretaceous and Tertiary Aquifers of Northern Kebbi State, Nigeria

Wali SU[1], Umar KJ[2], Gada MA[3] and Usman AA[1]*

[1]Department of Geography, Federal University Birnin Kebbi, P.M.B 1157, Kebbi State, Nigeria

[2]Department of Pure and Applied Chemistry, Federal University Birnin Kebbi, P.M.B 1157, Kebbi State, Nigeria

[3]Department of Geography, Usmanu Danfodiyo University Sokoto, P.M.B 2346, Sokoto State, Nigeria

Abstract

The chemical composition of groundwater affects its suitability for domestic, agricultural and industrial uses. About 80% of diseases in the world and one-third of deaths in developing countries are associated with drinking of water of mediocre quality. Evaluation of groundwater in Cretaceous and Tertiary Aquifers of Northern Kebbi State (NKS) was carried out to determine its suitability for drinking and irrigation uses. Water samples were collected at random from hand-dug shallow wells.

Results revealed that, TDS, EC, Mg^{2+}, K^{+}, Cl^{-}, PO_4^{3-}, NO_3^{-} and SO_4^{2-} concentrations do not follow the World Health Organization (WHO) and National Standard for Drinking Water Quality (NSDWQ) reference guidelines. Water samples having high TDS levels also have high Na^{+}, Cl^{-} and SO_4^{2-} levels. The order of cations and anions in the study area is thus: Na > K > Ca > Mg > Zn > Fe > Cu; and Cl > SO_4 > HCO_3 > NO_3 > PO_4 > CO_3. The hydro geochemical faeces showed groundwater in NKS fall in the class of Ca-Mg-Na-K and Mixed HCO_3-SO_4 water types. Rock weathering is the dominant mechanism controlling groundwater chemistry in NKS. Permeability indices fall in good to excellent class in most sampled points; however, Residual Sodium Carbonate levels are greater than 2.5 in most of sampling points, suggesting water which is unsuitable for irrigation use. Currents findings agree with most findings in literature. However, a comprehensive study evaluating groundwater from both shallow and deep aquifers of NKS over wider spatial and temporal scales is recommended because NKS is one of the most intensively irrigated fields in Nigeria.

Keywords: Sodium Adsorption Ratio; Sodium Percent; Scholler Index; Molar Ratio; Permeability Index; Residual Sodium Carbonate

Introduction

There is increasing concern on groundwater contamination in many parts of the world, due to geogenic and anthropogenic activities. Groundwater is highly variable owing to spatial variabilities in hydrogeological conditions resulting from differentiated geological, climatological and topographic settings [1]. The natural composition of groundwater is influenced by both the aquifer properties and anthropogenic activities. For example, undue applications of fertilizer, pesticide and improper disposal of municipal/industrial wastes can lead to permanent contamination of groundwater aquifers [2]. Groundwater in its natural form contains a variety of dissolved inorganic chemical elements in different concentrations, derived from chemical and biochemical interactions between water and the rock materials. Inorganic contaminants including salinity, chloride, fluoride, nitrate, iron and arsenic are important in evaluating the suitability of groundwater for drinking and irrigation uses. Elevated levels of magnesium and sodium in groundwater, for instance, may render it unsuitability for irrigation [3].

Basically, two groups of geologic formations have been identified in the Sokoto Basin, depending on characteristically different hydraulics of groundwater, viz: Porous Formations (Cretaceous and Tertiary Sediments) and Fissured Formations (Pre-Cambrian Basement Complex). Underlying the sedimentary rocks of the Sokoto Basin and rising to the land surface in the uplands to the south and east of the basin, are crystalline rocks of pre-Cretaceous age [4]. Groundwater in Sokoto Basin is found both confined as artesian water or unconfined just beneath the water table in most of the permeable members of the Cretaceous and Tertiary Sedimentary sequence [5]. However, there is considerable depletion of shallow aquifers in the study area, reflecting the contribution of old meteoric water that recharged the Cretaceous Aquifers in pluvial times, i.e. between 5000 and

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***Correspondence:**
Saadu Umar Wali, Department of Geography, Federal University Birnin Kebbi, P.M.B 1157, Kebbi State, Nigeria.
E-mail: *saadu.wali@fubk.edu.ng*

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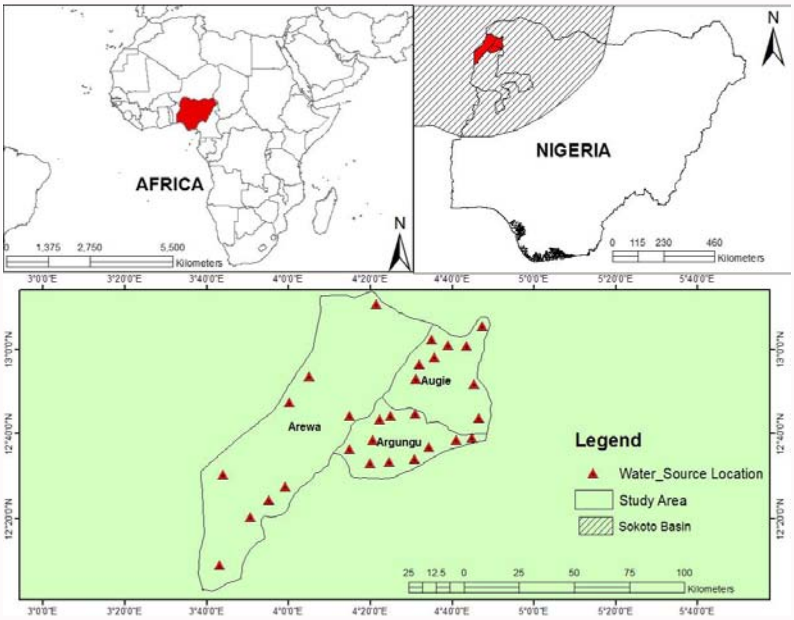

Figure 1: The Study Area (A) Map of Africa showing Nigeria, (B) Map of Nigeria showing Kebbi Sate and (C) Map of Northern Kebbi State.

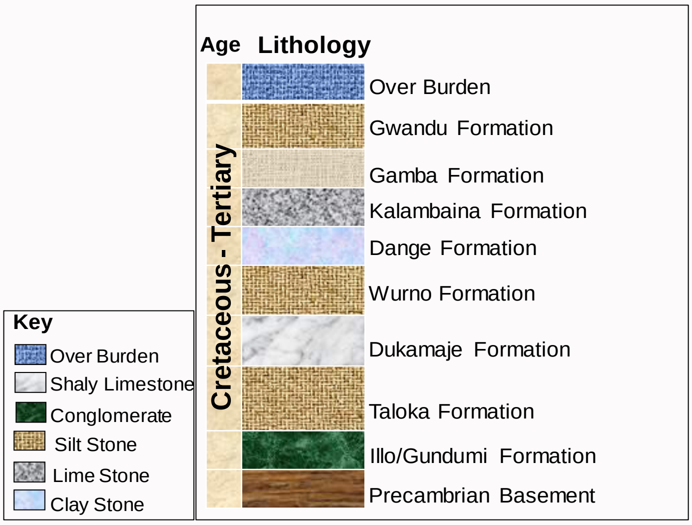

Figure 2: Generalized chronostratigraphic column for Sokoto Basin. After Adelana et al. [6].

15000-year BP [6]. A comprehensive study of groundwater quality in the Sokoto Basin was first carried out by du Preez and Barber [7]. Later, Anderson and Ogilbee [5]; Uma [8]; Alagbe [1]; and Wali et al., [9] trailed with assessments of groundwater quality in some parts of the basin. It is hard with TDS concentration ranging from 130 - 2,340 mg/l, sodium and nitrate are the major anions and vary widely, in some locations, above WHO reference guidelines [1]. The shallow aquifers of Sokoto Basin are formed by a combination of permeable regolith overlying impermeable clays. The saturated thickness of shallow aquifers in the study area is highly variable and ranges from 6 to over 10 meters under favourable environments [5].

Groundwater table in NKS is shallow, which make it easily available for irrigation use through open-wells and shallow tube wells. The shallow water table support irrigated agriculture in most parts of northern and central Kebbi State. However, the relatively shallow groundwater table and semi-arid climatic conditions make the soils in NKS disposed to salinity development. Evaluation of water levels and lithologic logs over 200 shallow hand-pumps, boreholes and dug wells in the Sokoto Basin by Uma [8], suggest that the aquifer is in hydraulic continuity with the deeper aquifers, especially the limestone aquifer and the aquifers of the Gwandu Formation in the west of the area (Kebbi State). The regolith aquifer sustains the numerous dug wells, which form the principal water source of the rural communities [10]. The Gwandu aquifer which is the most promising in the study area, usually receive its recharge in the east where it outcrops, making it prone to contamination. To highlight this problem, we looked at the shallow aquifers of NKS. Northern Kebbi State, is underlain by sedimentary formations (Figure 2). The Gwandu Formation which is the most promising aquifer in Sokoto basin, lies uncomfortably on the Kalambaina Formation. The sediments are continental in origin and consist of interbedded, partially consolidated sands and clays. The clay beds are mostly thick, massive, white, red grey black and brown (Figure 2). The sands ranges from fine to coarse in texture [11].

The Gwandu Formation is more important owing to the

Table 1: Principal aquifers in Sokoto Basin, Nigeria.

Age	Formation	
Eocene	Gwandu Formation	Sokoto Group
Paleocene	Kalambaina Formation	
	Dande Formation	
Maastrichtian	Wurno Formation	Rima Group
	Dukamaje Formation	
	Taloka Formation	
	Illo Formation	
Pre-Maastrichtian	Gundumi Formation	
Pre-Cambrian	Basement Complex	

After Offodile [11].

basal sands, highly saturated with water and confined by both the underlying 16 meters grey plastic clay of Kalambaina Formation and the overlying 10 meters of clays of the Gwandu Formation [11]. The Formation contains two aquiferous zones: the lower-most basal confined sandy zones and the upper most unconfined sandy sections. Groundwater recharge in these zones is derived from in filtering rainfall and run-off in the out crop in the eastern Sokoto Basin. While the shallow aquifers are exposed to direct recharge in the area, we have poor understanding of the impacts of land use on groundwater composition in this groundwater rich section of Sokoto Basin. Evaluation of groundwater over space and time proved to be a valuable tool in resolving diverse hydrogeochemical problems [12]. Because understanding the aquifer geochemistry is important, for maintaining water quality and for effective utilization of, and development of this finite resource [12]. Therefore, this study was carried out to evaluate groundwater suitability for drinking and

Table 2: Summary of field and laboratory methods.

Parameters	Methods	Description	Reference
Physical Temperature (°C)	Field	Temp/Salinity-meter (DKMsG01)	[22]
Conductivity (EC)	Field	Conductivity/TDS meter (DIST)	[9]
pH	Field	pH Meter (pHep)	[23]
Water table		Conductivity/TDS meter	[24]
TDS	"	Temp/Salinity-meter	[23]
Cations			
Potassium (mg/l)	Laboratory	AAS	[18]
Sodium (mg/l)	"	"	"
Calcium (mg/l)	"	"	"
Copper (mg/l)	"	AAS	"
Iron (mg/l)	"	"	"
Zinc (mg/l)	"	"	
Magnesium (mg/l)	"	"	"
Anions			
Phosphate (mg/l)	"	AC	[18]
Chloride (mg/l)	"	Titration	"
Bicarbonate (mg/l)	"	"	"
Nitrate (mg/l)	"	AC	"
Sulphate (mg/l)	"	IC	"
Carbonate (mg/l)	"	Titration	[19]

Note: AAS: Atomic Absorption Spectrometry; AC: Automated Colorimetry; IC: Ion Chromatography.

irrigation in shallow aquifers of Northern Kebbi State.

The Study Area

Location and climate

Northern Kebbi State, is in western Sokoto Basin, which constitutes the Nigerian sector of the Iullemmeden Sedimentary Basin centred in Niger Republic. Northern Kebbi State is situated between Latitudes 12° 20" and 13° 00" N and Longitudes 3° 40" E. The actual size of the study area covers about 6639.08Sqkm (Figure 1). It has a semi-arid climate with an average annual rainfall of about 600mm [9]. Rainfall distribution in the study area is highly variable and increases from north to south. Evapotranspiration rate is very high, and potential evapotranspiration can exceed 2500mm per annum [6]. It is important to plan the future water supply system of its fast-growing population, considering the low annual rainfall and recurrent drought in most part of the basin. Surface runoff is high and unpredictable; therefore, groundwater remains the only source of water supply particularly in the remote communities [10].

Hydrogeology and water resources

The sedimentary section of the basin is predominantly composed of gentle undulating plain with an average elevation varying from less than 250 to over 300 metres above sea level [4]. The plains are occasionally interrupted by steep-sided, flat-topped hills. Low escarpments occasionally occur and are closely related to geology [4]. Generally, the Cretaceous and Tertiary Formations in the Sokoto Basin strike in a north-easterly direction and dip about 20 feet per mile to the northwest [5]. These sediments underlie most of the area and were deposited in a broad shallow basin. These formations further thicken down dip, but southwards the outcrops become thinner and the Rima and Sokoto Groups pinch out completely. These materials are mostly clay-shales and poorly consolidated sandstones with limited beds of limestone and lignite streaks. The succession has an average thickness of about 1000 meters [1]. The age relationship of the formations is illustrated in Figure 2. Underlying the Fadama (floodplain) areas of the River Sokoto and its larger tributaries are thin unconsolidated deposits of alluvial sand, silt, and gravel of Quaternary age. The Geologic materials are capped by fine to medium sandy regolith produced by mixing of wind-blown materials and mechanically disintegrated bedrock [13]. The principal aquifers of the Sokoto Basin can be illustrated according to the Geography of the study area. These are: Gundumi Formation (Lower Cretaceous); Illo Group (Cretaceous); Rima Group (Upper Cretaceous); Sokoto Group (Palaeocene); and Gwandu Formation (Eocene-Miocene) (Table 1).

Table 3: Summary of chemical indices and analytical methods.

Parameter	Formula for calculation	Source
Kelly index (Ki)	Na/(Ca + Mg)	Kelly, [25]
Magnesium hazard (MH)	Mgx100/(Ca + Mg)	Szablocs and Darab, [24]
Molar ratio (MR)	Na/Cl	Meybeck, [21]
Permeability index (Pi)	$Na^{+}\sqrt{HCO_3}$/(Ca+Mg+Na) x100	Doneen, [27]
Residual sodium carbonate (RSC)	(HCO_3+CO_3)–(Ca+Mg)	Eaton, [28]
Scholler index (Si)	Cl(Na + K)/Cl	Shoeller, [29]
Sodium adsorption ratio (SAR)	Na+/$\sqrt{Ca+Mg/2}$	Ayers and Wescot, [30]
Sodium percent (SP)	Na^{+}x100/(Ca+Mg+Na+K)	Ragunath, [31]
Total Hardness (CaCO3)	2.5(Ca)+4.1(Mg)	Sawyer and McCarty, [32]
Versluys index (Vi)	Na/(Na+Ca+Mg)	Versluys, [33]

Table 4: Summary of Physical and Chemical Constituents of Groundwater in Northern Kebbi State (Values in bold did not follow WHO, 2006 and NSDWQ, [15] reference guidelines).

Parameter	Groundwater Composition				Reference Guidelines	
Physical	**Mean**	**Min**	**Max**	**SE**	**WHO [14]**	**NSDWQ [15]**
Temp. °C	31.7	27.9	36	5.8	Ambient	Ambient
EC (uS/cm)	**1319**	40	**4190.1**	240.8	1000	1000
pH	**5.2**	2	8.3	0.9	8.5	8.5
TDS (mg/l)	**1043.3**	100	**3200**	190.5	500	500
TH (mg/l)	97.1	24.1	**227**	17.7	200	150
Cations						
K^+ (mg/l)	56.3	34.6	156	10.3	-	-
Na^+ (mg/l)	**324.6**	1.5	**621**	**59.3**	12	12
Ca^{2+} (mg/l)	21.6	3.3	56.7	3.9	500	500
Cu^{2+} (mg/l)	0.7	0.1	1.7	0.1	1	1
Fe^{3+}(mg/l)	1.9	0.1	6.2	0.3	2	1
Zn^{2+} (mg/l)	5.8	2.1	8.5	1.1	3	3
Mg^{2+} (mg/l)	**10.5**	2	**21.4**	1.9	-	50^*
Anions						
PO_4^{3-} (mg/l)	**20.2**	**10**	**54**	**3.7**	0.2	0.2
NO_3^- (mg/l)	**79.2**	45.1	**101.3**	14.5	50	50
SO_4^{2-} (mg/l)	**117.2**	54.2	163.8	21.4	200	100
Cl^- (mg/l)	**250.6**	10.6	**959**	45.7	200	200
HCO_3^- (mg/l)	80	10.7	244	14.6	250	250
CO_3^{2-} (mg/l)	0.004	0.001	0.013	0.001	-	-

Note: *WHO [34].

These aquifers remain the sole source of drinking water in most parts of the basin. Gwandu Formation is the most prolific aquifer with an annual recharge exceeding 6.6x10^7 m^3 [6]. The artesian aquifer of Gwandu Formation gave free flowing boreholes in about 20% of area of occurrence (14,767sqkm), comprising mainly the Fadama areas and the low land areas extending from Balle (Sokoto State) to Bachaka (Kebbi State). Also, artesian conditions occur in the narrow lowland stretching some 30km southwest of Yeldu (northern Kebbi State). This is the largest proving artesian area in the Sokoto Basin. Also relevant is the generally high heads obtained on the boreholes. The boreholes drilled in NKS gave positive heads of 7.6m at Argungu, 3m at Birnin kebbi and 4m at Yeldu [11]. There is no doubt that due to uncontrolled and continuous development of the aquifer, these pressures must have dropped considerably.

Materials and Methods

Field sampling and Laboratory analysis

Table 2, summarized both the field and Laboratory methods employed in this study. Groundwater samples were drawn from 30 shallow wells in the study area. Physical parameters including Temperature, pH, EC and TDS were determined *in situ* using water quality probes (Table 1). Water quality Probes were first calibrated by deionised water and then by water from sampled wells. Separate water samples were collected in a 1 litre polyethylene bottles for Laboratory analysis. Water samples were stored in insulated containers <5°C. Bottles were rinsed twice; first by using deionised water and later with water from sampled wells before water samples are collected. All water samples were analysed in triplicates and results were found reproduceable within ±5 error limit. The suitability of groundwater for drinking was evaluated by comparing results with World Health Organization [14] and Nigerian Standard for Drinking Water Quality [15] reference guidelines (Table 4).

Suitability for irrigation use

Groundwater suitability for irrigation was evaluated using chemical indices (Table 3). The suitability of groundwater for irrigation use was evaluated using total concentration of soluble salts (SAR) which is express in terms of specific conductance [16]. Sodium percent was however, calculated following Kumar et al. [3]. Because soil often reacts with sodium to decrease soil permeability, which results in to high sodium concentration and causes cation exchange between Mg^{2+} and Ca^{2+} in soil under wet condition. Water and air circulations are reduced consequent to this process. When sodium level is low, its indicates ion exchange reaction between Ca^{2+} and Na^+ perhaps, caused by dwelling time and sluggish groundwater movements in aquifers. Kelly's Index and Magnesium Hazard were also calculated. Kelly's indices greater than 1, designates water of excellent quality for irrigation use. However, indices less than 1, designate water which is unsuitable for irrigation, because of alkali hazards. In calculating Kelley's index, Ca^{2+} and Mg^{2+} are measured against Na^+. Elevated levels of Mg^{2+} in groundwater disturb the soil quality by changing it to alkali which subsequently decreases crop yield [3]. Values of Magnesium Hazard (MH) less than 50 in groundwater are considered appropriate for irrigation use. Often in aquifers, Ca^{2+} and Mg^{2+} are found in a state of equilibrium. Elevated Mg^{2+} in groundwater at levels greater than Ca^{2+} fast-tracks the degree of Mg^{2+} saturation and destroys soil structure, thereby reducing its output [17].

Statistical analysis

Groundwater data were standardised and summarised using rudimentary descriptive statistics: - mean, range and standard error. Pearson's correlation (r) was used to test the relationship between physical and chemical constituents of groundwater. All the statistics was conducted using a significant level of α=0.5.

Results and Discussion

Groundwater suitability for drinking

Table 4, presents a summary of physical and chemical constituents of groundwater in northern Kebbi State (NKS). Temperature (mean ± standard error) was 31.7±5.8°C and ranged from 27.9°C to 36.0°C in the study area. Temperature is an important physical constituent of groundwater, because a variation of temperature of 10°C in aquifer may lead to doubling of chemical reactions [18]. At levels greater than 30°C temperature affects palatable water taste [18]. In most aquifers, temperature is closely associated with electrical conductivity. The latter increases by 2% with raised temperature level of 1°C [18]. There was strong positive correlation (r=0.69) between EC and temperature (Table 5). Electrical conductivity (mean ± standard error) was 1319.0±240.8 (µS/cm) and ranged from 40 to 4190.0 (µS/cm). EC level in the study area did not follow WHO and NSDWQ reference guidelines (Table 2). Often EC in groundwater is associated with Total Dissolved Solids.

pH level in shallow aquifers of NKS was 5.2 ± 0.9 and ranged from 2.0 to 8.5. Although, pH has a lesser amount of effect on consumers, it is essential to understanding groundwater chemistry. Consequently, evaluation of pH level in drinking water is required at all steps of water analysis. Because failure to lessen corrosion, can lead to contamination of drinking water [18]. Moderate pH level is

Table 5: Correlation Matrix of Physical and Chemical Constituents of Groundwater (Values in bold indicate significant correlation between parameters).

Parameter	Temp.	EC	pH	TDS	K^+	Na^+	Ca^{2+}	Cu^{2+}	Fe^{3+}	Zn^{2+}	Mg^{2+}	PO_4^{3-}	NO_3^-	SO_4^{2-}	Cl^-	$HC0_3^-$	CO_3^{2-}
Temp.	1																
EC	**0.69**	1															
pH	0.17	0.27	1														
TDS	**0.66**	**0.73**	-0.26	1													
K^+	0.05	-0.14	-0.14	-0.01	1												
Na^+	0.33	**0.5**	-0.35	**0.62**	0.22	1											
Ca^{2+}	**0.58**	**0.64**	-0.27	**0.8**	0.04	**0.59**	1										
Cu^{2+}	0.12	0.03	-0.26	0.21	0.04	0.13	0.12	1									
Fe^{3+}	**0.58**	0.43	-0.02	**0.67**	0.21	0.41	**0.52**	-0.13	1								
Zn^{2+}	0.38	**0.53**	0.01	**0.54**	0.14	**0.51**	0.4	0.29	0.38	1							
Mg^{2+}	**0.54**	**0.58**	-0.41	**0.87**	-0.02	**0.5**	**0.69**	0.21	**0.55**	0.43	1						
PO_4^{3-}	0.21	0.27	-0.05	0.36	-0.23	0.12	0.09	-0.03	0.14	0	0.32	1					
NO_3^-	-0.19	-0.11	0.06	-0.22	-0.07	-0.26	-0.19	0.12	-0.44	-0.16	-0.19	-0.36	1				
SO_4^{2-}	0	-0.01	-0.46	0.22	-0.01	0.14	0.33	0.19	0.01	-0.14	0.37	0.17	-0.11	1			
Cl^-	0.36	0.28	-0.5	**0.58**	0.3	**0.63**	**0.54**	0	0.43	0.33	**0.53**	-0.05	-0.2	0.27	1		
$HC0_3^-$	-0.44	-0.37	-0.52	0.07	0.04	0.13	-0.13	0.09	-0.11	-0.13	0.11	0.19	0.12	0.34	0.2	1	
CO_3^{2-}	-0.3	-0.32	-0.62	0.04	-0.02	0.31	0.04	0.32	-0.3	-0.03	0.04	0.16	0.18	0.36	0.24	**0.62**	1

Note: All concentrations are in mg/l, except pH and EC is in µS/cm at 25°C.

Table 6: Groundwater Classification Based on TDS and Hardness.

(a). TDS (mg/l)	No. of Samples	% of Samples	Classification	(b). Hardness ($CaCO_3$) mg/l	No. of Samples	% of Samples	Classification
>500	13	43.3	Essential for drinking	0 - 75	14	46.7	Soft
500-1000	3	10	Required for drinking	75 – 150	7	23.3	Moderate Hard
1000-3000	13	43.3	Suitable for drinking	150 - 300	9	30	Hard
>3000	1	3.3	Unsuitable for drinking and irrigation	>300	0	0	Very Hard
Total	**30**	**100**		**Total**	**30**	**100**	

After (a) David and De West (David, S.N. and De West, R.J.M. Hydrogeology. Wiley, New York. 1966; 4463) and (b) Ragunath [31].

therefore, essential depending on the composition of groundwater and aquifer properties, since it controls the character of several water chemical elements. TDS were 1043.3 ± 190 and ranged from 100.0 to 3200.0 mg/l. Mean TDS concentration in NKS did not follow WHO and NSDWQ reference guidelines. Groundwater classification based on TDS by David and De West (David, S.N. and De West, R.J.M. Hydrogeology. Wiley, New York. 1966; 4463) showed about 43% of groundwater in NKS have TDS concentration less than 500mg/l. This is most required for drinking (Table 6).

Cation chemistry

The summary of cationic composition in NKS is presented in Table 4. Potassium (mean ± standard error) was 56.3±5.8 and ranged from 34.6 to 156.0 mg/l. K^+ is not limited in drinking water, however, extreme ingestion may cause health risk. While it is an essential element of many non-natural fertilizers, K^+ is regulated in lakes when evaluation of nutrients effect is being carried out [18]. Often Na^+ concentration in most natural waters is found in low concentrations far below maximum permissible limits [18]. Sodium is the outstanding cation in NKS (324.6±59.3 mg/l). Na^+ concentration in NKS exceeded WHO and NSDWQ reference guidelines (Table 4). Although, it is a nutritional necessity, it is important to monitor Na^+ in drinking water because of the joint effects it exercises with SO_4^{2-}. High intake is associated with hypertension [18]. Similarly, Mg^+ concentrations in NKS exceeded WHO and NSDWQ reference guidelines Mg^+. Like Na^+, Mg^+ is an essential dietary requirement (0.3–0.5 g/day) [18]. Excessive consumption in drinking water is not associated with any serious health risk. Some incidental health effects may be caused when considered in combination with sulphate. Mg^+ is a vital water quality parameter since it is the second major constituent of hardness ($CaCO_3$). Therefore, groundwater in NKS may be hard in some locations. Calcium concentration follows WHO and NSDWQ reference guidelines. High Ca^{2+} concentration in groundwater is beneficial, but elevated level is often associated with hardness. Some groundwater sources in NKS are hard (Table 6). Depending on pH and alkalinity, hardness above 200mg/litre can result in scale deposition, particularly on heating. Soft waters with a hardness of less than 100mg/litre have a low buffering capacity and may be more corrosive to water pipes. Many ecological and analytical epidemiological studies have shown a statistically significant inverse relationship between hardness of drinking-water and cardiovascular disease. There are some indications that very soft waters may have an adverse effect on mineral balance, but detailed studies are needed for further evaluation [14].

Copper (mean ± standard error) was 0.7 ± 0.1mg/l and ranged from 0.1 to 1.7 mg/l. Unfriendly palates can occur at concentrations above 1mg/l. In drinking water high Cu^{2+} consumption is not detrimental to humans as therapeutic doses of ~20mg/l are occasionally permitted [18]. All the analysed water samples have Cu^{2+} levels following WHO and NSDWQ reference guidelines. Iron concentration was 1.9±0.3 mg/l and ranged from 0.1 to 6.2 mg/l. High Fe^{3+} concentrations

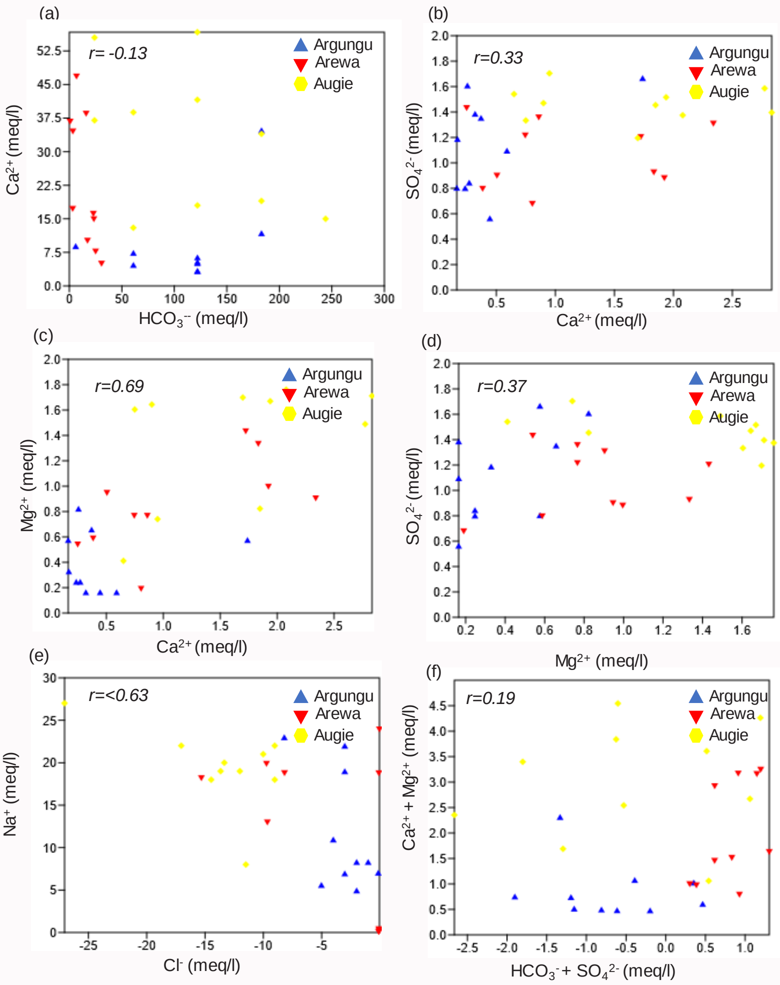

Figure 3: Correlations between cations and anions.

in water can be harmful to aquatic animals. Elevated Fe^{3+} levels in groundwater is not associated with any health hazard, in natural waters Fe^{3+} concentrations range from 0.5 to 50 mg/l [18]. Fe^{3+} level in NKS are within WHO reference guidelines. Zinc concentration was 5.8±1.1 mg/l and ranged from 2.1 to 8.5 mg/l. High consumption of Zn^{2+} is associated with emetic effect and higher concentration can be toxic to aquatic animals. At levels ranging from 3 to 5 mg/l, water might look opalescent and can form an oily film when boiled [18]. Natural waters scarcely contain Zn^{2+} concentrations >1mg/l. There were higher Zn^{2+} concentrations above WHO and NSDWQ reference guidelines.

Anion chemistry

Phosphate and nitrate are the major anions in shallow aquifers of NKS. NO_3^- (mean ± standard error) was 79.2±14.5 mg/l and ranged from 45 to 101.3 mg/l. Phosphate was 20.2±3.7 and ranged from 10.0 to 54.0 mg/l. High PO_4^{3-} concentration in NKS can be attributed to anthropogenic activities, since PO_4^{3-} is mainly derived from organic wastes. However, leaching and run-off are the major contributors to PO_4^{2-} in both surface and groundwater. Elevated PO_4^{3-} and NO_3^-, aid plant and algal growths, consequently, causing variation of diurnal dissolved oxygen, blooms and littoral slimes [18]. Elevated NO_3^- ion in NKS is attributed to anthropogenic activities (Manure slurries and chemical fertilizer), since NO_3^- is derived mainly from oxidation of ammonia and agricultural fertilizer. High NO_3^- in drinking water is dangerous to infants- blue baby syndrome. The presence of nitrate in NKS lead to suspicion of past manure effluence or excessive application of manure slurries over farmlands. NO_3^- and PO_4^{3-} concentrations exceed WHO and NSDWQ reference guidelines. Table 7, presents groundwater classification base on NO_3^- pollution. All the analysed water samples fall in severe class, suggesting past anthropogenic inputs in shallow aquifers of NKS.

Table 7: Groundwater classification based on nitrate pollution.

Nitrate (mg/l)	No. of samples	% of samples	Classification
<5	0	0	Acceptable
5-30	0	0	Moderate
>30	30	0	Severe
Total	30	100	

After Bhat et al. [35].

Chloride and sulphate concentration in NKS did not follow WHO and NSDWQ reference guidelines (Table 4). The variability of SO_4^{2-} in NKS may be connected to the geology. High SO_4^{2-} levels in groundwater is associated with emetic effects especially when considered in conjunction with Mg^+ and/or Na^+. At high concentrations above 250mg/l, SO_4^{2-} is reduced to sulphide causing toxic odours [18]. Like SO_4^{2-}, Cl^- is derived mostly from soil and rocks mineral in groundwater aquifers. High consumption does not pose any health risk to humans. At concentrations above 250mg/l

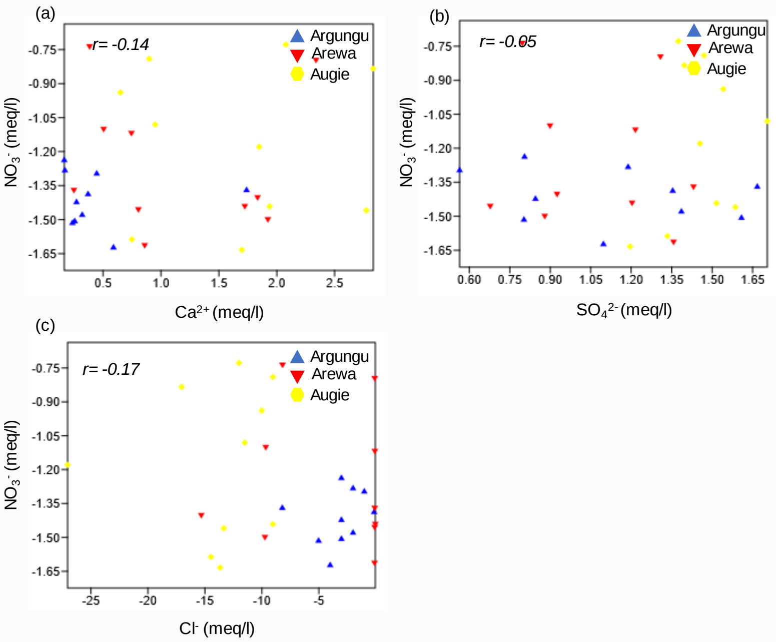

Figure 4: Relationship between (a) Ca^{2+} and NO_3^-, (b) NO_3^- and SO_4^{2-} and (c) NO_3^- and Cl^-.

in groundwater salty taste will occur. However, raised Cl^- level of ~5mg/l at one location may lead to the suspicion of groundwater pollution from sewage release, especially if ammonia levels are also elevated [18]. Cl^- values in NKS do not follow WHO and NSDWQ reference guidelines (Table 4). Bicarbonate (mean ± standard error) was 80.0±14.6 mg/l and ranged from 10.7 to 244.0 mg/l. $HC0_3^-$ concentrations in NKS is within WHO and NSDWQ reference guidelines (Table 4). Carbonate concentration was 0.004±0.001 and ranged <0.01 to 0.013 mg/l. If CO_3^{2-} and $HC0_3^-$ are joint with Ca^{2+} and Mg^{2+} carbonate hardness is formed. Further, when soil concentrates in drying solution it advances as $CaCO_3$ or $MgCO_3$. The concentrations of Ca^{2+} and Mg^{2+} drops relative to Na^+ and the SAR index increases, causing alkalizing effect and raised pH levels [19]. Therefore, when groundwater analysis designates high pH concentrations, it may be a sign of a high content of carbonate and bicarbonate ions [18].

Groundwater interaction with rock mineral

Relationships between dissolved elements in groundwater show the origin of solutes and the process that formed the detected groundwater properties. It is expected that a considerable percentage of HCO_3^- in groundwater is derived from dissolution of carbonate through the action of percolating waters with enhanced CO_2 after interaction with the atmosphere [19]. CO_2 is unconstrained in to solution by suspension of carbonate, forming Ca-HCO_3^- water type. Therefore, evaluation of the slops of HCO_3^- by means of Na^+, Ca^+ and Mg^{2+} gives vigorous evidence connecting to the process of stoichiometry [19]. Ca^{2+} and HCO_3^- were negatively correlated (Figure 3a), demonstrating that calcite rocks were not source of Ca^{2+} in NKS. Therefore, Ca^{2+} and SO_4^{2-} ions in NKS might have been derived from gypsum. Weak positive correlation between Ca^{2+} and SO_4^{2-} (Figure 3b) showed groundwater samples are nearer to 1:1 line, suggesting that, Ca^{2+} was derived from dissolution of gypsum. There was significant correlation between Ca^{2+} and Mg^{2+} (Figure 3c), indicating that the two ions are derived from the same source. There was weak positive correlation between SO_4^{2-} and Mg^{2+} (Figure 3d). SO_4^{2-} and Mg^{2+} might have been derived from the weathering of magnesium sulphate minerals [19]. When Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^- +SO_4^{2-} are derived from simple dissolution of gypsum, dolomite and calcite, a charge balance exists between cations and anions. There is no deficiency of (Ca^{2+} + Mg^{2+}) relative to (HCO_3^- + SO_4^{2-}) and (HCO_3^- 274 + SO_4^{2-}) relative to (Ca^{2+} + Mg^{2+}) in shallow aquifers of NKS. Therefore, no need for balance by major ions since there was no excess positive charge of Ca^{2+} and Mg^{2+}. Indicating that, gypsum, dolomite and calcite were not derived from Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}.

However, Na^+ - Cl^- relationship has recurrently been used as a trick for defining salinity in groundwater especially in semi-arid regions like Sokoto Basin. There was significant correlation between Na^+ and Cl^- (Figure 3e), suggesting that Na^+ was derived from halite. Uniform concentrations of Na^+ and Cl^- in groundwater are attained through dissolution of halite. The observed good correlation between Na^+ and Cl^- suggest that Na^+ in NKS was not consequent of dissolution of halite. This technique was first used by Meybeck [20], to evaluate the process of silicate weathering reactions. Na^+/Cl^- molar ratio showed about 93.3% of groundwater samples in NKS have molar ratio >1, which suggest that Na^+ in NKS was resultant of silicate weathering. Na^+/Cl^- molar ratio >1 in groundwater aquifer indicates Mg^{2+} + Ca^{2+} deficiency which is equivalent to Ca^{2+} - Na^+ cation exchange process. Therefore, groundwater in NKS may be soft in most locations. In aquifers with clay minerals, Ca^{2+} + Mg^{2+} is exchanged with Na^+, resulting in decreased Ca^{2+} + Mg^{2+} and raised Na^+ levels. This may probably explain the softened water in shallow aquifers of NKS.

Groundwater contamination

Geochemical properties of an aquifer are controlled by the underlying rock properties and anthropogenic activities. Variations in TDS in groundwater are an indicator of pollution from land use. Na^+, SO_4^{2-}, NO_3^- and Cl^- ions in groundwater are derived from anthropogenic sources municipal wastes, fertilizer application and organic wastes [19]. Correlations between these ions and TDS are a strong indicator of pollution from anthropogenic activities. Figure 4, presents correlations between Ca^{2+} and NO_3^- and Cl^- and

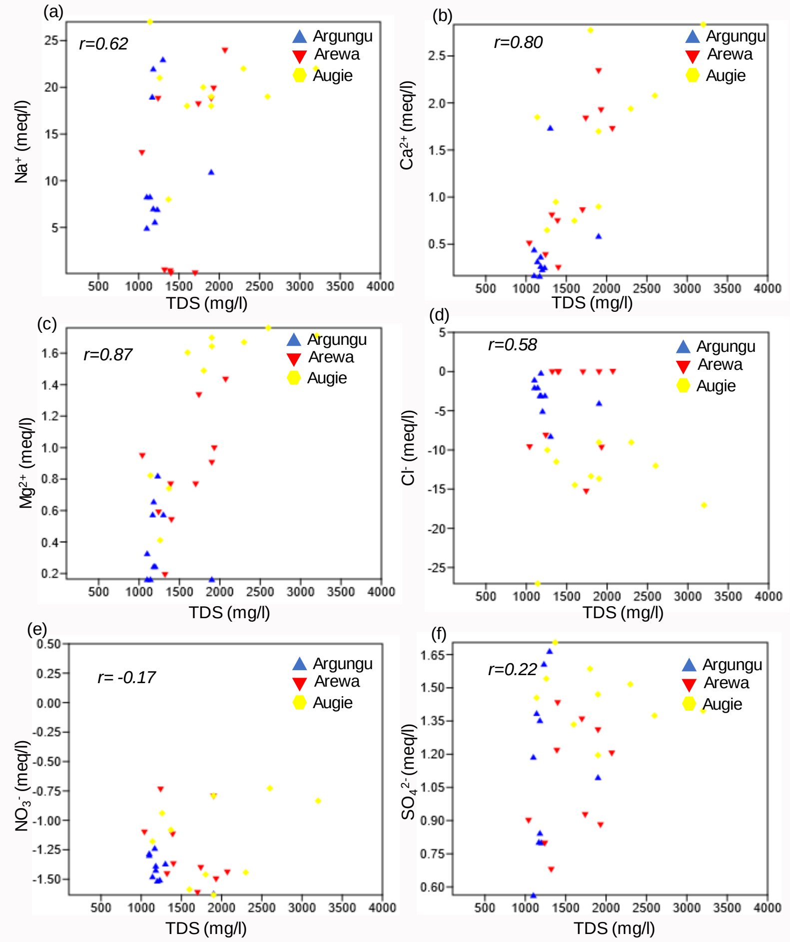

Figure 5: Relatioship between cations/anions and TDS.

NO_3^-. Negative correlations between Ca^{2+} and NO_3^- and Cl^- and NO_3^- suggest that these ions have different source. Figure 5, presents correlations between cations/anions and TDS. TDS correlates significantly with Ca^{2+}, $Na^{+,}$ Mg^{2+} and Cl^- (Figure 5a-5d). Good correlation between TDS and Na^+ suggest silicate weathering in the study area. However, significant correlation between TDS and Ca^{2+} and Mg^{2+} is an indication of anthropogenic contributions from municipal and industrial sewage. Positive correlations between TDS and Cl^-, TDS and SO_4^{2-} (Figure 5e and 5f) further indicate pollution from anthropogenic sources [19]. TDS correlates positively with $(NO_3^- + Cl^-)/HCO_3^-$. The molar ratio backs the anthropogenic input to groundwater contamination (Table 5, Figure 6b). NO_3^- is the major pollutant in the study area and perhaps derived from Fadama areas where effluents are collected from all parts of Sokoto Basin. Parts of groundwater recharge to the underlying aquifers occur in the Fadama areas, where effluents are leached down during recharge.

Mechanism controlling groundwater chemistry

Groundwater chemistry in NKS was further evaluated using Gibbs plot. TDS was measured against (Na+K)/Na+K+Ca and $(Cl)/(Cl+HCO_3)$ ratio for cations and anions [20]. Rock weathering appeared to be the dominant mechanism controlling groundwater chemistry in shallow aquifers of northern Kebbi State (Figure 7).

Groundwater classification

Figure 8, presents groundwater classification using Piper trilinear diagram. The classification showed that, groundwater in NKS fall in the class of Ca-Mg-Na-k, and Mixed HCO_3-SO_4 water types. Current finding concurs with Alagbe [1]. Groundwater in Sokoto basin is mainly of two facies; Ca–Mg–HCO_3 and Ca-Mg-SO_4–Cl in nature. These facies perhaps, are derived from dissolution of Ca^{2+} and Mg^{2+} carbonates.

Ion exchange in aquifers

The process of ion exchange in groundwater aquifer takes place when recharge water interacts with rock formation via it flow paths. This process is evaluated using Scholler index. Values of Scholler index tend to be positive when Ca^{2+} and Mg^{2+} exchange with Na^+ and K^+ resulting in to chloro-alkaline balance. Negative Scholler index indicate chloro-alkaline disequilibrium. All the analysed water samples have positive Scholler index, indicating overall base exchange reactions (chloro-alkaline balance) in NKS (Table 8). In aquifers where alkaline rocks mineral is exchanged with Na^+ ions (HCO_3 > Ca + Mg) designates base exchange soft water. Hardened water is formed when Na^+ ions are exchanged with alkaline rocks (Ca + Mg > HCO_3) [19]. In addition, Versluys index are positive in all the analysed water samples in the study area (Table 8).

Aptness for irrigation use

The suitability of groundwater for irrigation use in NKS was evaluated using chemical indices (Table 8). Groundwater classification using SAR shows that 43.3% of groundwater in NKS have SAR values <20 while 56.7% have values >20. SAR values >20 indicate water which is unsuitable for irrigation use, because of

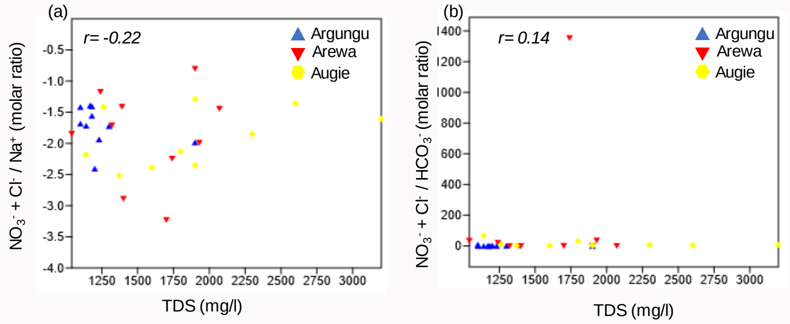

Figure 6: Variation of TDS vs. (A) (NO_3^- + Cl^-) / Na^+ and (B) (NO_3^- + Cl^-) / HCO_3^- molar ratio.

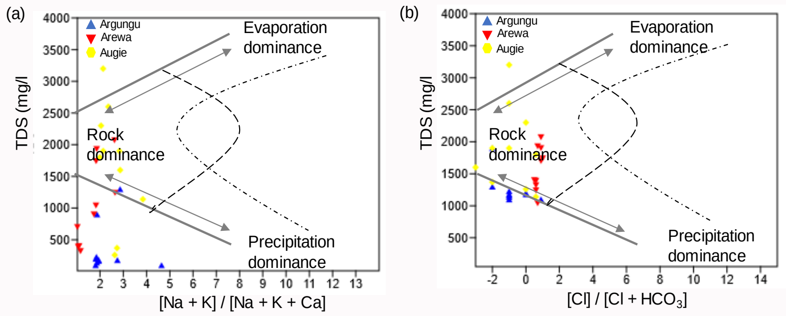

Figure 7: Mechanism controlling groundwater chemistry.

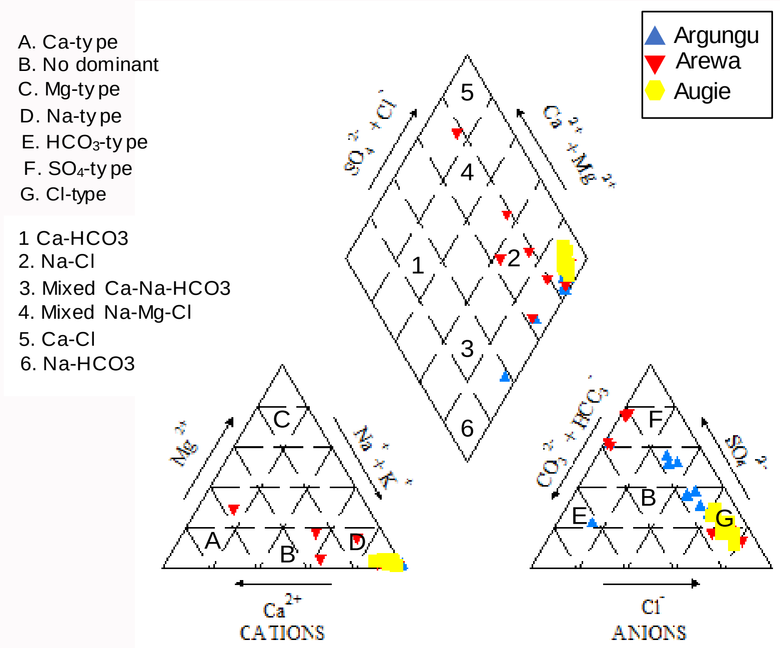

Figure 8: Groundwater classification using Piper trilinear diagram [37].

sodium hazard. Base on U.S salinity diagram (Figure 9), about 50% of groundwater samples in the study area fall in low sodium-low salinity class, 23% fall in low sodium-medium salinity class, 20% fall in low sodium-medium salinity class and 7% fall in low sodium-high salinity class. The suitability of groundwater for irrigation use was further evaluated using Wilcox plot (Figure 10). Based on Wilcox plot, 43.3% of groundwater is good to excellent for irrigation use, 20% is excellent to doubtful, 3.3% is permissible to doubtful, 16.7% is doubtful to unsuitable and 16.7% is unsuitable for irrigation use. Further evaluation using Residual Sodium Carbonate shows about 33.3% of groundwater in NKS have RSC values <2.5 and 66.7% have values >2.5. According to U.S Department of Agriculture, irrigation water having RSC values >2.5 is unsuitable for irrigation [16]. Groundwater classification based on permeability index (Table 9) shows about 86.7% of groundwater fall in good to excellent class, this is especially required for irrigation use.

Conclusion

Evaluation of groundwater in shallow aquifers of NKS discovered

Table 8: Summary of chemical indices.

S/no.	Si	Vi	Ki	SAR	SP	MH	MR	Pi	RSC
Sp 01	173.5	0.8	5	30.9	49.6	6	95.5	192.3	-4.9
Sp 02	56	0.4	0.7	9.6	37.1	0.9	43	130.4	53.3
Sp 03	181.7	0.8	4.7	48.8	77.6	0.3	168.7	506.8	113.6
Sp 04	68	0.8	4.1	42.1	74.9	0.6	62.4	439	111.7
Sp 05	115	0.7	2.6	22.4	63.2	1.9	95.5	195.5	113.6
Sp 06	30	1	26.3	65.3	65.8	16.3	20.3	165.3	45.6
Sp 07	19.9	0.6	1.5	15.4	52.2	0.6	16	162.4	106.9
Sp 08	145.5	0.6	1.8	21	58	1	126	254.1	169.2
Sp 09	38.3	0.6	1.6	13.5	50.8	0.8	28.5	119.1	114.6
Sp 10	86.7	0.6	1.8	30.9	58.8	0.4	75.6	530.7	141.2
Sp 11	4.5	0.6	1.6	3.3	14.5	27.6	0.7	31.7	-0.9
Sp 12	35.5	1	127	264.2	88.3	64.2	31.6	551.4	-48.6
Sp 13	4.3	0.3	0.4	0.8	3.4	3.3	0.2	24.9	-23.4
Sp 14	70	0.6	1.5	25.2	54.4	1	60.4	433.4	10.2
Sp 15	29.1	0.5	0.9	16	43.9	0.8	25.9	299.6	-4.3
Sp 16	28.1	0.4	0.8	17.9	41.8	0.4	25.8	418.4	-52.2
Sp 17	20.4	0.7	2.2	4.4	17.2	14.4	3.8	28.7	4.5
Sp 18	40.9	0.6	1.3	24.5	54.2	0.8	37.7	458.1	-34.6
Sp 19	42.4	1	70.4	174.3	91.4	44	39.3	433.2	-51
Sp 20	6.5	0.2	0.3	0.6	3.1	39.6	0.2	20.4	19.1
Sp 21	23.2	0.5	1	21	47.1	1.4	20.4	438.3	59
Sp 22	23.2	0.6	1.3	23.1	52.8	0.6	20.7	417.4	84
Sp 23	26.7	0.5	0.8	20.5	43.5	0.5	24.3	507.1	44.5
Sp 24	24.9	0.5	0.9	19.8	43.6	0.4	21.2	438	128.4
Sp 25	25.2	0.4	0.8	18.2	41.1	0.4	21.2	414.9	209.5
Sp 26	27.9	0.5	1	21.1	46.9	0.4	25.4	461	-49.6
Sp 27	29.1	0.3	0.4	9.1	27.4	0.3	20.4	184.8	155
Sp 28	110.2	0.6	1.4	25.6	53.3	0.1	96.6	483.7	43
Sp 29	27.2	0.6	1.6	28.2	57.9	0.8	24.9	507.1	1.9
Sp 30	73.8	0.4	0.6	20	36.5	0.3	62.1	621.3	-23

Note: Index Si: Scholler Index; Vi: Versluys Index; Ki: Kelly's Index; SAR: Sodium Adsorption Ratio; MH: Magnesium Hazard; MR: Molar Ratio; Pi: Permeability Index; RSC: Residual Sodium Carbonate.

Table 9: Groundwater classification based on permeability index.

Groundwater	Range	No. of samples	% of samples	Classification
Class 3	<25	2	6.7	Unsuitable
Class 2	25-75	2	6.7	Good
Class 1	>75	26	86.7	Excellent
Total		30	100	

After Bhat et al. [35].

that, EC and TDS levels are above WHO and NSDWQ reference guidelines for drinking water quality. Among the analysed cations, magnesium and potassium are the outstanding parameters and they occur at concentrations above WHO and NSDWQ reference limits. Chloride and sulphate are outstanding anions in the study area. These ions, in addition to nitrate and phosphate occur at concentrations above WHO and NSDWQ maximum permissible limits. The order of cations and anions in shallow aquifers is thus: Na > K > Ca >Mg > Zn > Fe > Cu; and Cl > SO_4 > HCO_3 > NO_3 > PO_4 > CO_3. Evaluation of silicate weathering using Scholler index revealed positive Scholler

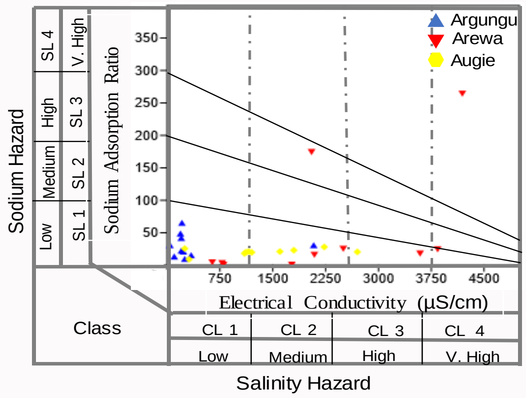

Figure 9: Irrigation water classification using U.S Salinity diagram [36].

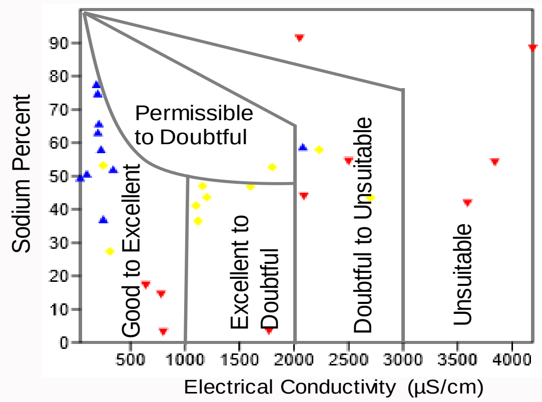

Figure 10: Wilcox plot showing irrigation water classification.

indices indicating chloro-alkaline balance. The hydrogeochemical [37] faeces indicate that groundwater in NKS fall in the class of Ca-Mg-Na-k, and Mixed HCO_3-SO_4 water types. Variations of TDS in shallow aquifers and positive correlations between TDS and cations/anions, indicate contamination from anthropogenic activities. Evaluation of groundwater suitability for irrigation using SAR and sodium percent showed most locations in NKS contain water which can be used for irrigation with little risks of sodium hazard. There is no tendency of having magnesium hazard in NKS. Permeability indices are excellent in most sampled points; however, RSC values are greater than 2.5 in most sampling points, suggesting water which is unsuitable for irrigation use. Broader studies evaluating groundwater in both shallow and deep aquifers of NKS are recommended because NKS is one of the most heavily irrigated areas in Nigeria.

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