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ORIGINAL ARTICLE

Hydrochemical characterization of shallow and deep groundwater in Basement Complex areas of southern Kebbi State, Sokoto Basin, Nigeria

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Abstract

Groundwater under Basement Complex areas of southern Kebbi has been characterized in order to determine its suitability for drinking and irrigation use. Water samples were drawn from shallow groundwater (hand-dug shallow wells < 5 m) and deep groundwater (boreholes > 40 m). Physical parameters (i.e., temperature, TDS, pH, and EC), were determined in situ, using handheld meters. Discrete water samples were obtained for determination of chemical parameters. Results from several-sample ANOVA (Kruskal–Wallis test) suggested that heterogeneity in water table appeared to exert significant influence on groundwater chemistry which is characterized by a significant difference in pH, EC TH, Na^{+}, Zn^{2+}, Mg^{2+}, PO_4^{3-}, Cl^{-}, HCO_3^{-}, SO_4^{2-}, and NO_3^{-} concentrations. Also, ions including Fe^{3+}, Zn^{2+}, Mg^{2+}, Na^{+}, PO_4^{3-}, and SO_4^{2-} are above World Health Organization (2011) and National Standard for Drinking Water Quality (2007) reference guidelines. Most of the groundwater sources are moderately hard. Groundwater classification based on chloride, EC, and TDS revealed water of excellent quality for all types of uses. However, groundwater classification based on nitrate pollution revealed water of poor quality. Rock mineral is the major mechanism controlling water chemistry, as revealed by the Gibbs model. Most of the water sources have positive Scholler index, indicative of overall base exchange reactions in the underlying aquifers. Such condition was well explained by Piper trilinear diagram, which revealed two types of faces: Ca–Mg–HCO_3 and Ca–Mg–SO_4–Cl. The HCA categorized wells into three groups according to their hydrogeochemical physiognomies. Despite the significant difference in ions concentration and chemical indices, groundwater composition is more influenced by rock weathering than anthropogenic inputs. Groundwater evaluation for irrigation use indicates a significant difference in SAR level which is related to poor permeability index in shallow groundwater. Higher values of Kelly's index and magnesium adsorption ratio threatened groundwater suitability for irrigation use in the study area.

Keywords Sodium adsorption ratio · Sodium hazard · Magnesium hazard · Scholler index · Kelly's index · Molar ratio

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Introduction

Groundwater is one of the most important environmental reserves exploited for industrial, agricultural, and domestic uses (Wagh et al. 2016). The composition of groundwater tends to be good in most natural aquifers, and as a result, groundwater is increasingly been exploited as it meets the basic requirements for most uses. Groundwater quality is primarily influenced by the aquifer rock mineral and recharge pathways (Kohlhepp et al. 2017; Liu et al. 2017; Gu et al. 2017; Kumar et al. 2019). As water passes through its recharge pathways from recharge to discharge points, several other types of hydrogeochemical processes alter its physical and chemical properties and in some aquifers, water may be unsuitable for drinking and agriculture (Abd El-Aziz 2017; Dehnavi et al. 2011; Farid et al. 2017). At least, one-third of the global population rely on groundwater for drinking (Panaskar et al. 2016). While groundwater is increasingly exploited in response to population pressure (Bertrand et al. 2016; Shang et al. 2016; Parisi et al. 2018; Cavalcante Júnior et al. 2019), increased urbanization (Minnig et al. 2018; Tam and Nga 2018; Hughes 2019), industrialization (Zheng et al. 2019) and irrigation farming (Panaskar et al. 2016; Fabbri et al. 2016; Pulido-Bosch et al. 2018), only about 22% of the Earth's 37 km^3 (freshwater) is found in aquifers as groundwater (Panaskar et al. 2016). Remarkably, about 97% of this quantity is accessible for human use (Panaskar et al. 2016). Overexploitation of groundwater in key sedimentary aquifers is a global phenomenon (Joshi et al. 2018). The rate of annual global groundwater withdrawal, even though may vary with climate and geography, is about 1500 km^3, which is above the normal rates of annual global groundwater recharge or replenishment (Joshi et al. 2018).

Growing demand for water driven by economic growth (Hertel and Liu 2016; Kummu et al. 2016; Shahzad et al. 2017; Flörke et al. 2018), urbanization (Kulabako et al. 2007; Sperling and Sarni 2019), generation of electricity (Powell et al. 2019), irrigation (Erban and Gorelick 2016; Wu et al. 2016), and domestic uses has inflamed global groundwater withdrawal (Shahid et al. 2015; Wada et al. 2016; Veldkamp et al. 2017; Agarwal and Garg 2015; Thomas et al. 2019), causing water table declines in aquifers (Joshi et al. 2018). Shallow groundwater is often the most affected by small-scale irrigation farming (Li et al. 2018), particularly in developing countries. In alluvial basins (e.g., Sokoto Basin), groundwater pollution is primarily derived from reinfiltering groundwater from irrigation fields (Selck et al. 2018) and municipal and industrial sewage (Wali et al. 2018a, b). Geophysical investigations showed alluvial aquifers (e.g., Sokoto Basin) are often in hydraulic conductivity with surface water (Emujakporue et al. 2018; Kudamnya and Andongma 2017; Nwankwo 2015; Nwankwo and Shehu 2015; Onuigbo et al. 2017), with shallow aquifers serving as conduits through which pollutants from surface water are transported to deep groundwater reservoirs.

There are immeasurable number of studies comparing groundwater quality between shallow and deep aquifers around the world: Basharat (2012), assessed the groundwater quality by demarcating the zones where brackish water exists in the form of depths and zones; Brancelj et al. (2016), showed variations in physical and chemical composition between shallow boreholes in distinct aquifers situated a few kilometers away from each other; Das and Mukherjee's (2019), depth-dependent groundwater response to coastal hydrodynamics, showed variability in salinity between 1 and 4 ppt at > 100 mbgl depths, indicating a mixing between chemically discrete groundwater aquifers; Hubalek et al. (2016) showed that deepest aquifers had the least taxon richness and unexpectedly held *Cyanobacteria*; Pandith et al. (2017) revealed differences in fluoride absorption in shallow (basalt − 10 to 167 m) and deeper (granite less than 167 m) aquifers; Rajmohan et al. (2017) also discovered variability of water quality of deep and shallow wells; Holbrook et al.'s (2019) analysis of the relationship between physical and chemical showed that weathering occurs from a 65-m-deep well over earth's critical zone; and Long et al. (2019) outlined a cavernous rotation and regularity of groundwater movement between aquifers. Evaluations of this kind are imperative since they help to describe the connections between groundwater tables, and this affects both the quality of shallow and groundwater aquifers (Hubalek et al. 2016; Park et al. 2018; Holbrook et al. 2019).

However, groundwater has been studied using different techniques: geothermal techniques (Nwankwo 2015; Nwankwo and Shehu 2015; Olatunji and Musa 2013; Toyin et al. 2016), isotope techniques (Adelana et al. 2003; Geyh and Wirth 1980; Fillion et al. 2014, 2018; Selck et al. 2018; Kattan 2018; Alemayehu et al. 2019; Besser et al. 2019), multivariate statistics (Mondal et al. 2010; Azhar et al. 2015; Yidana et al. 2018), univariate statistics (Marghade et al. 2010; Selvakumar et al. 2017; Wali et al. 2018a, b), modeling (Ebrahim et al. 2019; Locatelli et al. 2019), and chemical indices (Marghade et al. 2010; Panaskar et al. 2016; Wagh et al. 2016). Results obtained from these studies showed groundwater quality is influenced by both the natural geogenic processes and anthropogenic activities. In some environments, the groundwater quality is largely dependent on the water table depths (Dhar et al. 2008; Han et al. 2013; Deng et al. 2014).

Nigeria is the fastest growing country in sub-Saharan Africa (SSA) in terms of the human population (Akombi et al. 2019; Young 2019). Improved water supply which is

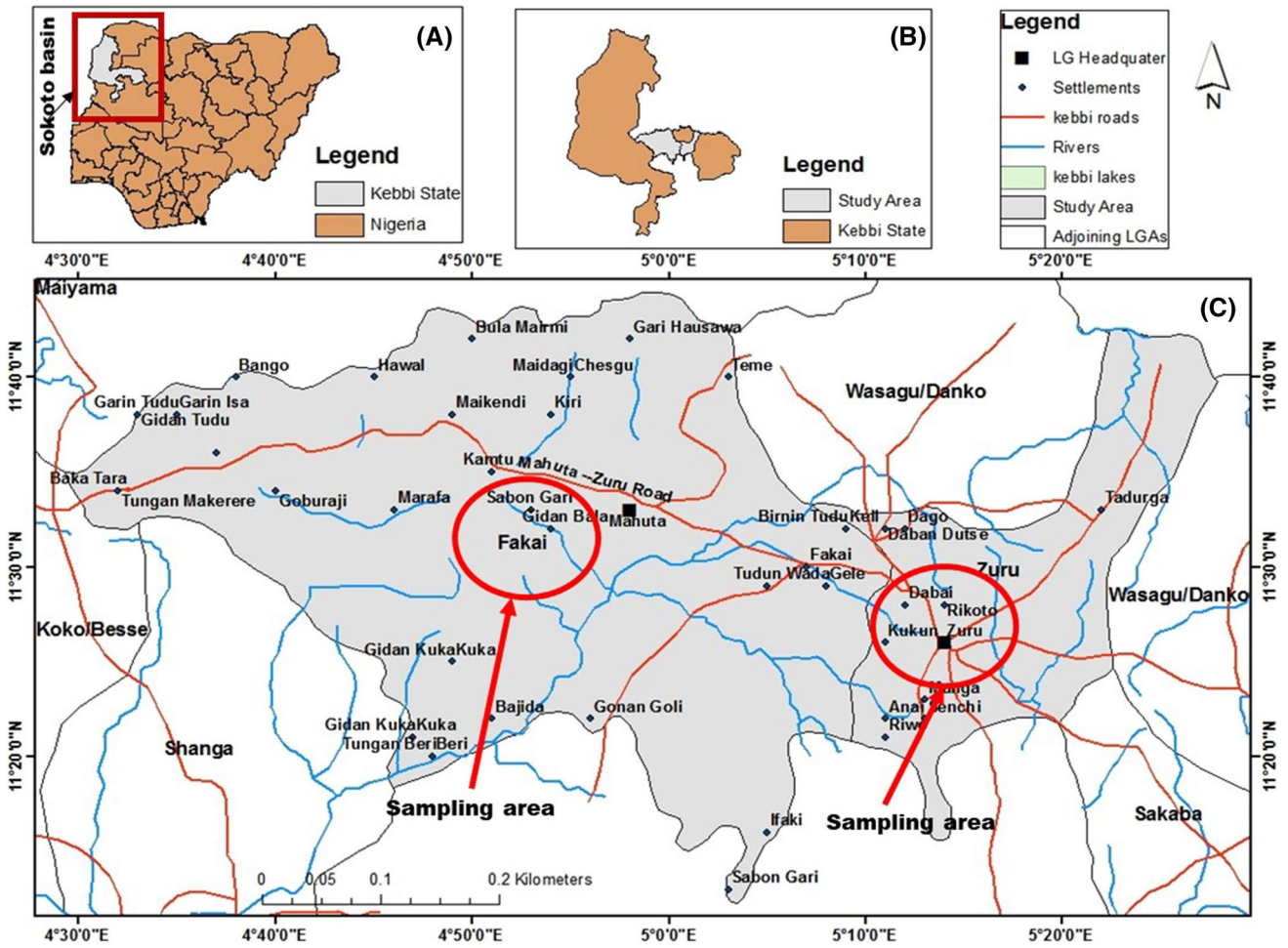


Fig. 1 Map of the study area **a** Sokoto Basin; **b** Kebbi State; and **c** Study area

one of the essentials for a healthy living has been constrained by uncontrolled anthropogenic activities (Vijay et al. 2011; Qin et al. 2013; Chen et al. 2016; Chitsazan et al. 2019) and by lesser extent natural conditions (Izah et al. 2016; Makinde et al. 2017; Zadawa and Omran 2018). Characterization of groundwater in Nigeria, is further constrained by lack of data, especially from Basement Complex areas of northern Nigeria (Akinluyi et al. 2018; Olubusola et al. 2018; Oyedele and Olayinka 2019; Tajudeen et al. 2019), owing to difficulties associated with groundwater exploration and accessibility (Betzler et al. 2017; Muhammad and Saad 2018; Oyeyemi and Aizebeokhai 2018; Ahmed and Mansor 2018).

The Basement Complex areas of southeastern Sokoto Basin are in southern Kebbi State (Fig. 1) and are underlain by Pre-Cambrian Basement Formation (Akujieze et al. 2002; Joseph and Bamidele 2018; Oseji and Egbai 2019). Groundwater in the study area is generally available in small quantity derived from fractures and tabular partings and from the regolith, just below the earth surface (Anderson and Ogilbee 1973; Edet 1990; Paul and Bayode 2012; Odukoya 2015). The fissures are usually most open above a depth of 91 m but even so, yields to boreholes are relatively low and cause high drawdown (Anderson and Ogilbee 1973; Offodile 2002). While boreholes are widely used in the study area as sources for improved water supply, shallow groundwater remained the most reliable source of drinking water especially in rural areas (Mohammed et al. 2007; Adelana et al. 2003; Aleke and Nwachukwu 2018; Olorunfemi and Oni 2019). However, the geological settings in addition to changes in land use combined with rock mineral influence groundwater composition (Dehnavi et al. 2011; Khatri and Tyagi 2014; Redwan and Abdel Moneim 2016; Venkatramanan et al. 2017; Jebreen et al. 2018; Mukate et al. 2019). Effluents from municipal, industrial, and crop fields are transported to groundwater by surface flows via infiltration (recharge) zones. These impurities are first collected

into shallow aquifers (Kong et al. 2018; Narr et al. 2019), before their eventual downward movement to deep groundwater reservoirs, where they may stay for decades or even centuries.

To highlight this problem, we look at the Basement Complex areas of southeastern Sokoto Basin. The study area is underlain by intrusive granite of igneous origin and deformed metamorphic rocks, chiefly gneiss, schist, hyalite, and quartzite (Toyin et al. 2016; Toyin and Adekeye 2019; Omolabi and Fagbohun 2019). Groundwater in this type of aquifer (often one-aquifer system), tend to be highly mineralized. Further, the topography of the study area presents another obstacle to groundwater development (Kogbe 1986). Therefore, groundwater is cheaply found along with low-lying areas and is largely hauled out using handlines from shallow wells particularly in rural areas (Anderson and Ogilbee 1973; Offodile 2002). Groundwater quality studies in Sokoto Basin (du Preez and Berber 1965; Anderson and Ogilbee 1973; Adelana et al. 2003; Amadi et al. 2015; Ekpoh and Ekpenyong 2011; Ette et al. 2017; Toyin et al. 2016; Wali et al. 2016, Wali et al. 2018a, b) revealed water of excellent quality and of Holocene age (100–10,000 years BP). These studies were carried out in Cretaceous and Cenozoic Sediment sections of north-western and central Sokoto Basin. Groundwater quality in the Basement Complex section of southeastern Sokoto Basin remained poorly reported in the literature (Anderson and Ogilbee 1973; Offodile 2002; Nwankwoala 2015), even though hydrochemical evaluation of groundwater over space and time proved to be an important technique for solving different hydrogeochemical problems (Edmunds 2009; Li et al. 2018; Yin et al. 2019). Understanding the aquifer hydrochemistry is important for effective utilization of, and development of this finite resource (Kashiwagi et al. 2006). Thus, the objective of this study is to assess the variability of groundwater quality between shallow and deep aquifers and evaluate its suitability for drinking and irrigation uses.

The study area

Location and climate

The Basement Complex areas of southeastern Sokoto Basin are in southern Kebbi State. The study area is situated between Latitudes 11°20″ and 11°40″N and Longitudes 4°30″E and 5°30″E (Fig. 1) and covers about 2411.69 km^2. This area overlays Fakai and Zuru local government areas (LGAs). From the conglomeration point along Koko-Mahuta road, just about 40 km before Mahuta, surface elevation increases steadily passing through Fakai and reaching over 400 m above sea level in Dabai. The rock outcrops formed a triangle of basement rock outcrop, which extends from Fakai to Zuru and Yauri.

The climate of the study area is hot, semiarid tropical (AW) in Koppen's classification. It is dominated by two opposing wind systems: Tropical Maritime and Tropical Continental air masses (Gada 2014). These give the study area two contrasting seasons—wet and dry. The dry season results from continental air mass blowing from the Sahara Desert. The dry season lasts from October to April, whereas wet season lasts from May to October. From March onward, the temperature rises to over 35 °C (Fig. 2a). Temperature is generally high and showed marked seasonal variation. Mean maximum temperature is highest in April. Mean minimum temperature is the lowest in December < 20 °C. Monthly rainfall ranges from < 50 mm to over 250 mm. Most of the precipitation falls in July, August, and September (Fig. 2b).

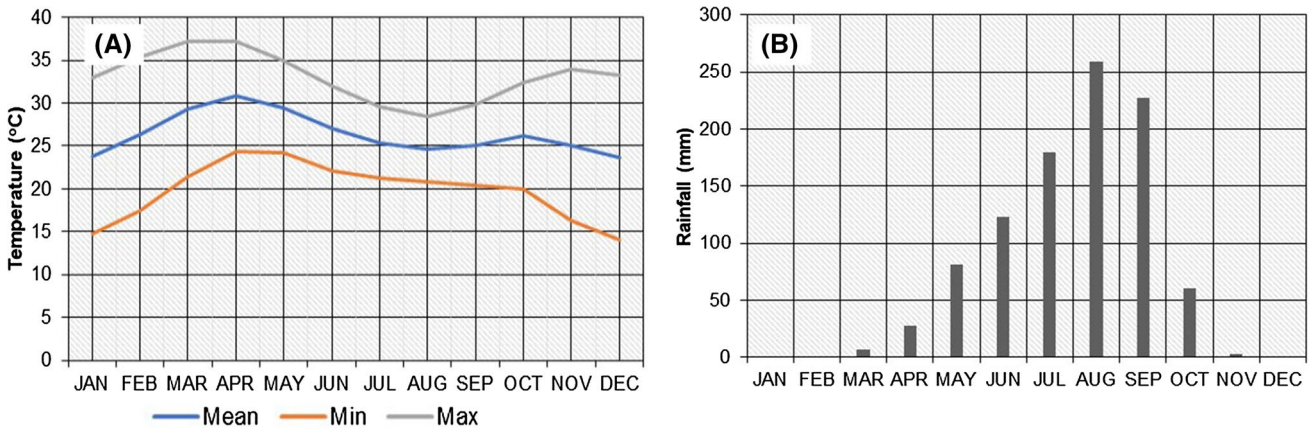


Fig. 2 A chart showing the variability of **a** temperature; and **b** rainfall in the study area. *Source of Data*: Climate-Data Org. Retrieved from https://en.climate-data.org/africa/nigeria/kebbi/zuru-380580/on 10/06/2019

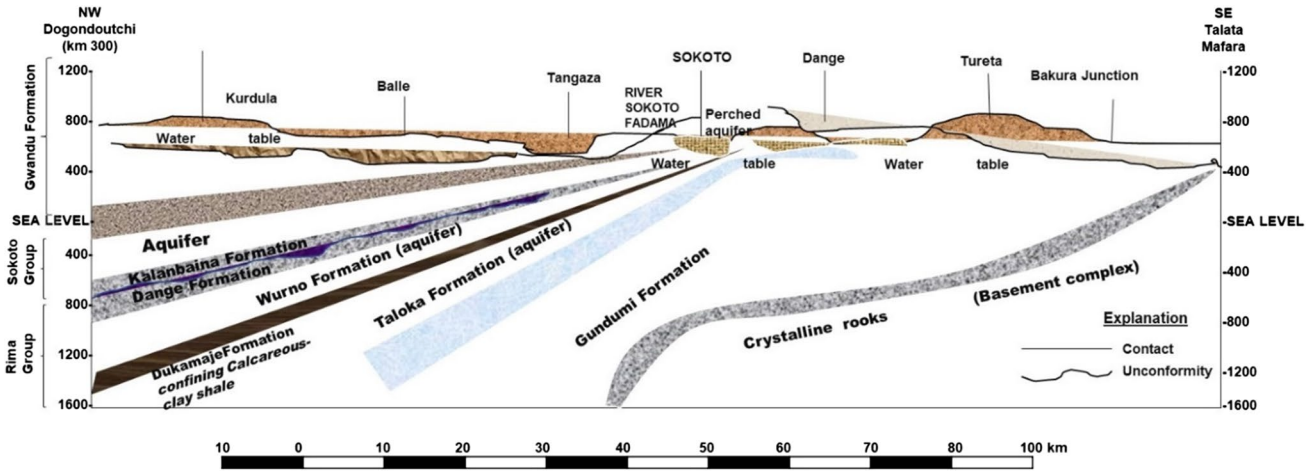


Fig. 3 The geological cross section of Sokoto Basin

Geological setting

Figure 3 shows the geological cross section of Sokoto Basin. In terms of geology, the Sokoto Basin is extensively studied (Emujakporue et al. 2018; Ette et al. 2017; Kogbe 1981; Moody and Sutcliffe 1991; Nwankwo 2015; Nwankwo and Shehu 2015; Onuigbo et al. 2017). The sediments of Sokoto Basin were accrued during three main stages of deposition, i.e., the first and last phases were the continental Mesozoic and Tertiary, with a second phase which is the marine Maastrichtian to Paleocene. Superimposing the Pre-Cambrian Basement unconformably are the grits and clays of the Illo and Gundumi Formations, forming part of the "Continental Intercalaire" of West Africa (Emujakporue et al. 2018; Kamba et al. 2018; Kogbe 1981; Moody and Sutcliffe 1991). These formations are superimposed unconformably by the Rima Group (Maastrichtian), consisting of mudstones and friable sandstones (Taloka and Wurno Formations), separated by the fossiliferous, shelly Dukamaje Formation (Emujakporue et al. 2018; Kamba et al. 2018; Kogbe 1981; Moody and Sutcliffe 1991). The Dange and Gamba Formations (mainly shales) of Paleocene are separated by the Kalambaina Formation (Calcareous). The Gwandu Formation (Continental Terminal) which covers these formations is of Tertiary age. These sediments dip gently and thicken gradually toward the northwest, with a maximum thickness of over 1200 m near the border with the Niger Republic (Emujakporue et al. 2018; Kamba et al. 2018; Kogbe 1981; Moody and Sutcliffe 1991).

Hydrogeological setting

Lying below the sedimentary rocks of the Sokoto Basin and rising to the land surface in the highlands to the south and east of the basin are crystalline rocks of pre-Cretaceous age. These comprise of plutonic granite of igneous derivation and warped metamorphic rocks, mainly gneiss, schist, phyllite, and quartzite (Kogbe 1986). Groundwater in the high ground zones of crystalline rocks is usually obtainable in small amounts from fissures or other flat separations and from the regolith (worn rock) just underneath the ground surface (Anderson and Ogilbee 1973). The fissures are typically found above a depth of 91.44 m but, even so, yields to boreholes are rather low and cause high drawdowns (Anderson and Ogilbee 1973). The formation is Pre-Cambrian in age and is made up of schists, granite gneisses, phyllites, and quartzite. Of hydrogeological importance is the slight, north–south elongate belt of metasediments intersecting the basement rocks. The formation is splintered in places and occasionally deeply battered below ground surface. Likewise, the western peripheries of the basement rocks are marked by penetrating fracture systems (Anderson and Ogilbee 1973).

Hydrogeological studies of the pre-Cretaceous Basement Complex Formations of Nigeria (Akinluyi et al. 2018; Anderson and Ogilbee 1973; Olorunfemi and Oni 2019), revealed an average borehole yield of 14.67 gallons per sec (gps) from a mean depths of 37.49 m. Though, few boreholes in the unweathered rock, typically granite or gneiss produced more than a meager amount of water; in many wells, no water was found (Anderson and Ogilbee 1973). In contrast, wells tapping weathered granite and gneiss, where fully saturated, are found to yield the highest quantity of water (51.67 gps); the average yield for boreholes tapping battered rock was estimated to be around 23.33 gps per borehole (Anderson and Ogilbee 1973). Also, drawdowns during pumping were very high (62.48 m) from some wells. The normal depth of wells tapping the weathered materials is estimated to be 38 m

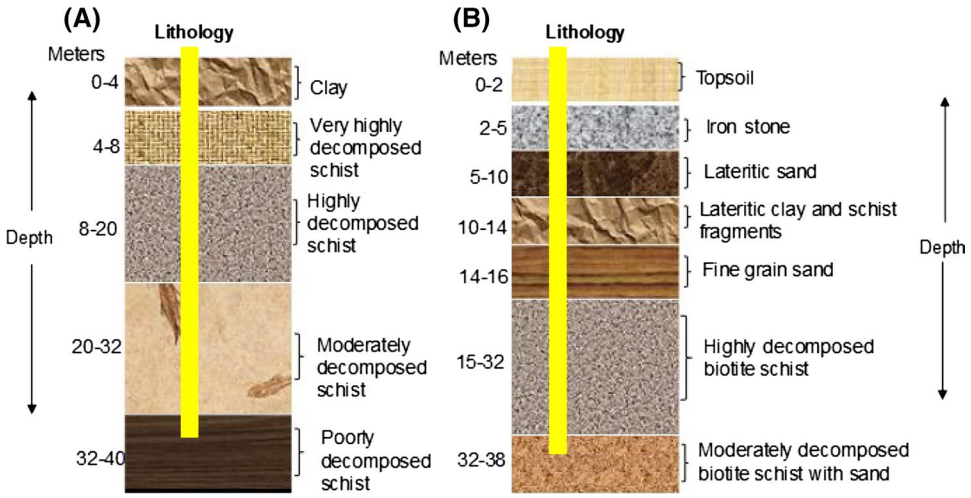


Fig. 4 Lithologic section of boreholes in the study area **a** Zuru and **b** Fakai

and the normal depth to water stand at about 6 m (Anderson and Ogilbee 1973). Generally, groundwater condition in the basement section of Sokoto Basin is typical of the Nigerian Basement Complex described by (Akinluyi et al. 2018; Olorunfemi and Oni 2019).

Many wells were developed in the crystalline rocks particularly in the eastern parts of the basin (Gusau-Mafara axis). The borehole yield was found to be higher in the metasediments with splintered quartzites (Anderson and Ogilbee 1973). Yet borehole in most parts of the Basement Complex section of the basin is low. This kind of poor yields is also characteristic of Basement Complex Formation of Nigeria. Such low yield zone results from aquifers of weathered or fractured materials, with limited areal scope, such that during pumping or well development the spreading cone of depression hits the highly indurated frontier rocks in a short time (Akinluyi et al. 2018; Anderson and Ogilbee 1973; Olorunfemi and Oni 2019). The water level, or the drawdown, drops sharply and steadily decrease the yield per individual boreholes. Numerous boreholes and hand-dug wells have been drilled in the area and are still been drilled or dug in the Basement Complex zones of the basin for both the rural and urban water supply. High yields can be attained in some areas in the Basement Complex, contingent on the tectonics in those areas. Despite the poor yields, boreholes and hand-dug wells in Basement Complex zones are sufficient to sustain hand pumps, in rural water supply programs (Akinluyi et al. 2018; Anderson and Ogilbee 1973; Olorunfemi and Oni 2019). Figure 4 illustrates a typical lithologic section of the study area.

Groundwater quality

Geological work in Sokoto Basin dates to 1800 s. Reporting of fossil fuel localities was the main objective. A Comprehensive study of groundwater was carried out by du Preez and Berber (1965). Groundwater recharge (Adelana et al. 2002) is highly variable across the basin. Groundwater quality (Anderson and Ogilbee 1979; Uma 1993; Alagbe 2006; Graham et al. 2006; Wali et al. 2016; Wali and Bakari 2016; Wali et al. 2018a, b) is highly variable with TDS concentration ranging from 130 to 2340 mg/l. Sodium and nitrate concentrations exceed WHO reference guidelines in some locations. The hydrogeochemical faces (Alagbe 2006; Wali et al. 2018a, b) are predominantly of two types: calcium–magnesium–bicarbonate and calcium–magnesium–sulfate–chloride in nature. These faces perhaps are derived from dissolution of calcium and magnesium carbonates.

Materials and methods

Groundwater sampling and laboratory analysis

Forty groundwater samples were collected, 20 each from deep and shallow aquifers. Groundwater samples were collected mainly from shallow wells and boreholes which are currently in use. Samples were drawn from water sources constructed by Kebbi State Government. Because these sources are expected to meet all the necessary requirements for water supply, physical parameters—temperature, pH, EC, and TDS—were determined in situ using water quality probes (Table 1). Probes were first calibrated by deionized water and then by water from shallow wells and boreholes. Discrete water samples were collected in 1-l polyethylene bottles for determination of cations (K^+, Na^+, Ca^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+} and Mg^{2+}) and anions (Cl^-, HCO_3^-, CO_3^{2-}, PO_4^{3-}, NO_3^-, and SO_4^{2-}).

Table 1 Summary of field and laboratory methods

Parameters	Methods	Description	Source
Physical			
Temperature	Field	Temp/salinity meter (DKMsG01)	Makoto et al. (2003)
Conductivity	Field	Conductivity/TDS meter	Wali and Bakari (2016) and Wali et al. (2018a, b)
pH	Field	pH meter (pHep)	Mondal et al. (2010) and Wali et al. (2018a, b)
TDS	Field	Temp/salinity meter	Mondal et al. (2010) and Wali et al. (2018a, b)
Cations			
Potassium (mg/l)	Laboratory	AAS	EPA (2001) and Wali et al. (2018a, b)
Sodium (mg/l)	Laboratory	AAS	EPA (2001) and Wali et al. (2018a, b)
Calcium (mg/l)	Laboratory	AAS	EPA (2001) and Wali et al. (2018a, b)
Copper (mg/l)	Laboratory	AAS	EPA (2001) and Wali et al. (2018a, b)
Iron (mg/l)	Laboratory	AAS	EPA (2001) and Wali et al. (2018a, b)
Zinc (mg/l)	Laboratory	AAS	EPA (2001) and Wali et al. (2018a, b)
Magnesium (mg/l)	Laboratory	AAS	EPA (2001) and Wali et al. (2018a, b)
Anions			
Phosphate (mg/l)	Laboratory	AC	EPA (2001) and Wali et al. (2018a, b)
Chloride (mg/l)	Laboratory	Titration	EPA (2001) and Wali et al. (2018a, b)
Bicarbonate (mg/l)	Laboratory	Titration	EPA (2001) and Wali et al. (2018a, b)
Nitrate (mg/l)	Laboratory	AC	EPA (2001) and Wali et al. (2018a, b)
Chloride (mg/l)	Laboratory	AC	EPA (2001) and Wali et al. (2018a, b)
Sulfate	Laboratory	IC	EPA (2001) and Wali et al. (2018a, b)

AAS atomic absorption spectrometry, *AC* automated colorimetry, *IC* ion chromatography

Samples were stored in insulated containers less than 5 °C. Prior to the collection of water samples, polyethylene bottles were washed twice; initially by using deionized water and then with the water from sampled boreholes and hand-dug shallow wells. Water samples were analyzed within 24 h, and as a result, no acid treatment for samples was made. All analyses were carried out in triplicates, and results were found reproducible within ±5 error limit. Table 1 summarizes field and laboratory methodologies employed in this study.

Ions, including potassium, sodium, calcium, copper, iron, magnesium, and zinc, were analyzed using atomic absorption spectrometry. It is a method in which free gaseous atoms engross electromagnetic radiation at a specific wavelength to produce a calculable signal. The absorption of those free absorbing atoms in the optical path is proportional to the absorption signal (Fernández-Cirelli et al. 2009). Consequently, for AAS measurements, the analyte was first converted into gaseous atoms, typically by applying heat to a cell (i.e., atomizer). The nature of atomizer outlines the two main AAS-based analytical techniques: flame atomic absorption spectrometry (FAAS) that consistently offers analytical signals and electrothermal atomic absorption spectrometry (ETAAS) sending analytical signals in an intermittent mode (2–4/sample). In both approaches, liquid (or dissolved) samples are presented into the analyzer, as an aerosol as in the case of FAAS which is used in this study or as a fully marked low microliter volume in ETAAS (Fernández-Cirelli et al. 2009).

Monochromators, based on Czerny-Turner, Ebert, and Littrow designs are the most conventional wavelength selectors used in AAS. More recently, echelle optics is being fused to commercial AAS devices. The introduction of an echelle configuration in association with a powerful continuous lamp creates significant capabilities, for instance, analysis of the spectral background near the line and concurrent multi-elemental scrutiny (Fernández-Cirelli et al. 2009). The said ions were analyzed using Atomic Absorption Spectrophotometer (Model: Rs 12.5 Lakh/Piece). Nitrate and phosphate were analyzed using automated colorimetry (BluVisionTM discrete analyzer). In addition, sulfate concentration was analyzed using iron chromatography (Agilent 6890 Plus GC with FPD and 7683 Autosampler). Lastly, chloride, carbonate, and bicarbonate were determined by titration (Table 1). Table 2 presents the results of physicochemical composition of shallow and deep groundwater in the study area. Groundwater suitability for drinking was evaluated by comparing the results with World Health Organization

Table 2 Physicochemical parameters of groundwater samples from deep and shallow groundwater sources

Location	Water source	*T* (°C)	pH	TDS	EC	K^+	Na^+	Ca^{2+}	Cu^{2+}	Fe^{3+}	Zn^{2+}	Mg^{2+}	PO_4^{3-}	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-
Fakai	DGW1	34.0	8.1	111.0	226.0	33.4	2.9	13.6	0.1	1.3	0.4	21.1	0.6	2.8	20.3	84.1	21.1
Deep groundwater	DGW2	33.0	8.0	114.0	227.0	39.9	6.7	56.4	0.3	0.2	0.3	17.4	0.5	3.5	2.7	67.3	37.2
	DGW3	33.0	7.3	382.0	763.0	39.9	0.1	53.9	0.4	0.6	1.0	26.8	0.1	2.6	2.9	91.2	24.5
	DGW4	31.0	7.3	394.0	796.0	39.5	0.1	2.7	0.3	0.3	0.9	26.3	0.4	2.1	2.8	87.5	38.1
	DGW5	33.0	7.8	65.0	138.0	38.4	0.9	10.1	0.4	1.1	0.5	9.3	0.6	2.8	12.0	133.2	45.7
	DGW6	32.0	7.7	68.0	136.0	40.3	6.7	14.6	0.6	1.6	0.4	8.2	0.4	2.5	33.3	130.1	41.2
	DGW7	34.0	8.2	111.0	225.0	38.8	2.8	3.2	0.4	0.4	0.5	18.6	0.6	1.4	10.4	154.6	12.5
	DGW8	33.0	8.2	116.0	232.0	38.8	2.8	3.6	0.4	0.2	0.6	14.2	0.1	3.1	19.5	205.8	40.1
	DGW9	34.0	8.0	94.0	189.0	37.2	0.9	14.3	0.2	0.5	0.4	19.8	0.3	1.5	17.0	214.7	17.6
	DGW10	33.0	8.4	96.0	192.0	40.7	9.8	7.0	0.5	0.0	0.5	18.6	0.2	2.4	16.7	188.4	37.9
Shallow groundwater	SGW1	30.4	7.6	140.0	110.0	39.0	414.0	13.0	0.3	1.1	6.3	5.0	17.0	71.0	183.0	281.3	52.1
	SGW2	30.8	7.5	320.0	260.0	39.0	437.0	32.0	0.6	1.6	4.2	5.0	11.0	320.0	183.0	213.1	49.8
	SGW3	28.0	7.7	270.0	240.0	78.0	598.0	51.0	0.3	0.5	6.3	14.0	22.0	888.0	61.0	197.2	38.2
	SGW4	31.0	7.6	110.0	80.0	39.0	439.0	19.0	0.4	2.1	3.2	8.0	20.0	213.0	183.0	125.6	60.0
	SGW5	30.4	7.7	120.0	80.0	39.0	483.0	20.0	1.1	2.7	2.0	3.0	23.0	72.0	183.0	208.4	47.9
	SGW6	30.7	7.8	220.0	160.0	39.0	552.0	30.0	1.6	2.0	4.1	30.0	22.0	249.0	244.0	218.7	26.1
	SGW7	28.0	8.1	140.0	100.0	78.0	460.0	20.0	0.3	1.1	4.4	20.0	22.0	178.0	183.0	321.8	18.7
	SGW8	21.4	8.0	90.0	70.0	39.0	552.0	12.0	0.8	0.9	6.3	5.0	23.0	249.0	122.0	206.1	68.0
	SGW9	28.0	7.3	90.0	70.0	39.0	460.0	20.0	0.2	2.0	6.1	1.0	21.0	107.0	122.0	71.7	49.3
	SGW10	24.2	7.1	50.0	30.0	39.0	552.0	7.0	1.3	2.1	6.3	3.0	18.0	107.0	122.0	89.3	55.4
Zuru	DGW1	34.0	7.4	105.0	212.0	36.4	6.7	11.5	0.2	3.1	0.5	17.0	0.3	2.6	5.4	136.2	36.9
Deep groundwater	DGW2	32.0	7.4	108.0	215.0	38.4	0.9	14.2	0.2	2.1	0.5	17.4	0.5	2.6	1.3	135.1	38.5
	DGW3	32.0	7.5	146.0	293.0	38.8	6.7	5.4	0.6	0.6	0.7	16.2	0.6	2.3	31.2	183.4	39.4
	DGW4	31.0	7.5	147.0	295.0	39.1	2.9	129.3	0.2	0.8	0.6	19.4	0.6	2.1	8.1	56.5	36.3
	DGW5	31.0	8.2	327.0	660.0	35.0	3.9	17.3	0.4	0.1	0.3	26.3	0.2	2.9	31.7	62.7	46.8
	DGW6	32.0	8.0	330.0	659.0	32.3	0.0	14.7	0.4	2.5	0.5	22.4	0.4	2.9	16.4	98.4	41.5
	DGW7	31.0	8.0	326.0	653.0	39.9	9.8	4.4	0.3	0.4	0.7	26.3	0.1	3.3	0.3	45.1	40.7
	DGW8	30.0	8.1	327.0	655.0	36.1	2.9	43.7	0.4	0.7	0.5	23.7	0.6	0.6	12.7	64.3	39.6
	DGW9	31.0	8.1	125.0	251.0	38.8	3.6	2.9	0.3	0.2	0.2	16.2	0.3	3.5	19.8	245.9	42.5
	DGW10	33.0	8.1	124.0	249.0	33.4	7.7	14.2	0.2	1.4	0.4	23.7	0.3	2.1	16.0	237.9	41.8
Shallow groundwater	SGW1	26.8	7.6	50.0	40.0	39.0	437.0	15.0	0.3	0.8	6.3	18.0	18.0	107.0	183.0	223.8	53.7
	SGW2	25.3	7.3	200.0	10.0	39.0	460.0	5.0	0.2	1.7	5.2	14.0	18.0	107.0	122.0	327.1	44.4
	SGW3	27.6	7.0	50.0	20.0	39.0	552.0	7.0	1.0	2.7	8.4	2.0	13.0	72.0	122.0	98.4	24.5
	SGW4	23.4	7.4	160.0	60.0	39.0	483.0	15.0	0.1	1.5	6.3	6.0	14.0	71.0	183.0	87.9	47.1
	SGW5	22.3	7.5	210.0	200.0	39.0	2.0	40.0	0.1	0.6	5.7	3.0	19.0	4.0	549.0	256.1	12.6
	SGW6	26.0	7.2	80.0	60.0	39.0	414.0	8.0	1.0	2.4	4.3	4.0	20.0	107.0	183.0	310.4	36.7
	SGW7	24.3	7.8	240.0	170.1	39.0	437.0	42.0	1.0	2.3	5.9	7.0	14.0	497.0	122.0	316.8	45.8

Table 2 (continued)

Location	Water source	*T* (°C)	pH	TDS	EC	K^+	Na^+	Ca^{2+}	Cu^{2+}	Fe^{3+}	Zn^{2+}	Mg^{2+}	PO_4^{3-}	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-
	SGW8	25.1	7.0	150.0	70.0	39.0	345.0	28.0	0.4	1.7	3.2	3.0	22.0	71.0	244.0	67.5	50.5
	SGW9	26.1	6.9	40.0	20.0	390.0	437.0	8.0	0.5	1.7	5.3	4.0	14.0	107.0	122.0	246.8	21.8
	SGW10	26.9	6.8	110.0	60.0	39.0	483.0	1.2	0.2	0.7	6.2	4.0	16.0	178.0	122.0	258.2	52.3

All concentrations in mg/l, except temperature: (°C); and EC (µS/cm)

DGW deep groundwater obtained from boreholes, *SGW* shallow groundwater obtained from dug wells

Table 3 Summary of chemical indices and analytical methods

Parameter	Formula for calculation	Source
Molar ratio (MR)	Na/Cl	Meybeck (1987)
Scholler index (Si)	Cl (Na + K)/Cl	Scholler (1965)
Total hardness ($CaCO_3$)	2.5 (Ca) + 4.1 (Mg)	Todd and Mays (2005)
Versluys index (Vi)	Na/(Na + Ca + Mg)	Versluys (1916)

(World Health Organization 2011) and Nigerian Standard for Drinking Water Quality (National Standard for Drinking Water Quality 2007) reference guidelines for drinking water quality (Table 2).

Calculation of chemical indices

Chemical indices, including Ki, Mg, MR, PI, RSC, Si, SAR, Na% and Vi (Table 3), were also calculated to evaluate ion exchange, silicate weathering reactions. Also contained in the table is a formula for calculating total hardness.

Statistical analysis

Groundwater data were standardized and summarized using basic descriptive statistics: mean, minimum, maximum, and standard error (Table 4). Pearson's correlation (r) was used to test the relationship between physical and chemical elements of groundwater following Margahde et al. (2011). Prior to this, a nonparametric test (Kruskal–Wallis) was used to test whether there is a significant difference in groundwater composition between shallow and deep groundwater sources, using several samples ANOVA (Table 4). This method allows for comparing several independent random samples and can be used as a nonparametric substitute to the one-way ANOVA (Cruz et al. 2019; Montcoudiol et al. 2019; Morris et al. 2019). The Kruskal–Wallis test statistic for k samples, each of size n_i is defined viz:

$$T = \frac{1}{s^2}\left[\sum_{i=1}^{k}\frac{R_i}{n_i} - N\frac{(N+1)^2}{4}\right] \quad (1)$$

where N is the total number (all *in*) and R_i is the sum of the ranks (from all samples drawn) for the *i*th sample and:

$$S^2 = \frac{1}{N-1} = \left[\sum_{\text{all}} R_{ij}^2 - N\frac{(N+1)^2}{4}\right] \quad (2)$$

Table 4 Summary of physical and chemical properties of groundwater

Parameter	Borehole (deep aquifer)				Dug well (shallow aquifer)				Reference guidelines		Kruskal–Wallis Nonparametric test		
Physical	Mean	Min	Max	SE	Mean	Min	Max	SE	National Standard for Drinking Water Quality (2007)	World Health Organization (2011)	H (chi^2)	Hc (tie corrected)	p (same)
T (°C)	32.4	30	34	5.4	26.8	21.4	31	4.9	Ambient	Ambient	27.1	27.4	< 0.001*
pH	7.9	7.3	8.4	1.3	7.4	6.8	8.1	1.3	6.5–8.5	6.5–8.5	9.8	9.9	0.002**
TDS	180.8	65	394	62.3	142	40	320	50.6	500	1000	0.9	0.9	0.330
EC	363.3	136	796	125.9	95.5	10	260	41.1	1000	1400	21.2	21.2	< 0.001*
TH	76.2	19.4	184.9***	29.2	134.4	63.4	402.8	63.7	150	200	9.015	9.016	0.002**
Cations													
K^+	37.7	32.3	40.7	6.4	42.9	39	78	12.3	–	–	4.0	4.4	0.036
Na^+	3.9	0	9.8	1.5	449.9***	2	598***	94.6	12	200	25.3	25.4	< 0.001
Ca^{2+}	21.9	2.7	129.3	20.4	19.7	1.2	51	8.1	500	75	1.3	1.3	0.256
Cu^{2+}	0.3	0.1	0.6	0.1	0.6	0.1	1.6***	0.3	1	1	1.4	1.4	0.238
Fe^{3+}	0.9	0.1	3.1	0.5	1.6	0.5	2.7***	0.4	2	2	8.7	8.7	0.003**
Zn^{2+}	0.5	0.2	1	0.2	5.3***	2	8.4***	1.3	3	3	29.3	29.4	< 0.001*
Mg^{2+}	19.4***	8.2***	26.8***	4.2	6.6***	1	20***	3.2	0.20	125	22.7	22.7	< 0.001*
Anions													
PO_4^{3-}	0.4***	0.1	0.6***	0.1	18.4***	11***	23***	3.6	0.2	0.2	29.3	29.5	< 0.001*
Cl^-	2.5	0.6	3.5	0.6	188.8	4	888***	140.4	200	250	29.3	29.4	< 0.001*
HCO_3^-	14	0.3	33.3	5.3	176.9***	61	549****	86.8	250	125–130	29.3	29.7	< 0.001*
SO_4^{2-}	131.1	45.1	245.9***	38.9	206.3	67.5	327.1***	51.7	200	250	8.0	8.0	0.005*
NO_3^-	36	12.5	46.8	7.4	42.7	12.6	45.2	7.1	50	50	5.2	5.2	0.022

***Do not follow WHO and/or NSDWQ reference guidelines

*Significant difference between shallow and deep groundwater < 0001; **significant difference between shallow and deep groundwater ≤ 0.005

The null hypothesis of the test is that all k distribution functions are equal. The alternative hypothesis is that at least one of the observations tends to yield larger values than at least one of the other observations (Cruz et al. 2019; Montcoudiol et al. 2019; Morris et al. 2019). Results obtained show that there was no significant difference in TDS, K^+, Ca^{2+}, and Cu^{2+} concentrations between shallow and deep groundwater.

Principal component analysis

One of the major multivariate statistical method used in the interpretation of water chemistry is principal component analysis (Ayoko et al. 2007; Miguntanna et al. 2010). The PCA which is multivariate statistical method is applied to reduce the size of hydrochemical data (Alias et al. 2014; Hildebrandt et al. 2008; Machiwal and Jha 2015; Yidana 2010; Yidana et al. 2018). Reduction of the analytical data of individual sampling location is the primary purpose of applying PCA. The PCA tends to be intercorrelated with a less important set of 'principal components' (PCs) which can be interpreted (Machiwal and Jha 2015). The PC group inter-related absorptions together and can be related to some geogenic processes or pollution from the anthropogenic sources.

Generally, PCA comprises of two steps: standardization of data and extraction of PCs (Machiwal and Jha 2015). While some related data on the variability may be lost via transformation, the explanation of the system is significantly abridged, and it can be envisaged to derive suitable evidence on the relationship between parameters and observations (Hildebrandt et al. 2008). The PCA bilinear model can be rearranged following the matrix decomposition equation (Hildebrandt et al. 2008), and thus,

$$X = TP^T + E \quad (3)$$

where X represents a matrix of data which is compressed into T (scores of matrices) and PT (matrix of loadings), plus E (matrix residual) (Hildebrandt et al. 2008). The extracted PCs in this study showed that groundwater in both shallow and deep aquifers are more influenced by the natural geogenic process as compared to human activities.

Hierarchical cluster analysis

The vital role of HCA is to discrete the parameters in a raw data matrix or PC scores into separate classes designated by

the user without any prior hypotheses. The HCA is an unverified outline identification technique that reveals inherent assembly or recognizing the pattern of a dataset without a prior hypothesis with regard to the data so that the objects of the system can be classified into clusters based on their resemblances (Lin et al. 2012; Machiwal and Jha 2015). The HCA is a widely used method which can form clusters consecutively, beginning with the most identical pair of parameters and forming complex clusters after each step which is repeated until a single cluster comprising all the observations is attained (Lin et al. 2012; Machiwal and Jha 2015). In this study, the Ward's algorithmic gathering technique subsequent to the squared Euclidean distance was employed. This is measured as the most influential means of clustering (Lin et al. 2012; Machiwal and Jha 2015).

Before the clustering analysis, the detected hydrochemical data, x_{ji}, was standardized by z-scale transformation as given below (Machiwal and Jha 2015):

$$Z = \frac{X_{ji-\dot{x}_j}}{Sj}$$

where x_{ji} = value of the jth hydrochemical parameter measured at the ith location, $\dot{x}_j$ = mean (spatial) value of the jth parameter and S_j = standard deviation (spatial) of the jth parameter (Machiwal and Jha 2015). The clustering achieved with standardized data is anticipated to be influenced less by the large and/or small variance of the hydrochemical data matrix. Also, the influence of diverse measurement units of the data can be removed by making the data dimensionless (Machiwal and Jha 2015). In this study, HCA was performed on a subset of 17 selected variables (pH, EC, Temp., TDS, TH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, CO_3^{2-}, HCO_3^{2-}, Cl^{-}, NO_3^{-}, PO_4^{3-}, and SO_4^{2-}), which represented the overall water chemistry outline. The HCA results are presented as a dendrogram (Fig. 10), which offers a graphic summary illustrating an image of the clusters and their closeness with an observed decrease in the dimensionality of original observations. This is measured as a good technique for presenting results of HCA (Lin et al. 2012; Machiwal and Jha 2015). This evidence allowed the construction of a dendrogram as a function of the water quality parameters and sampling locations. Therefore, applying raw data matrix into HCA is an excellent technique which helps classify hydrochemical data based on similarities of sampled parameters across the sampling sites.

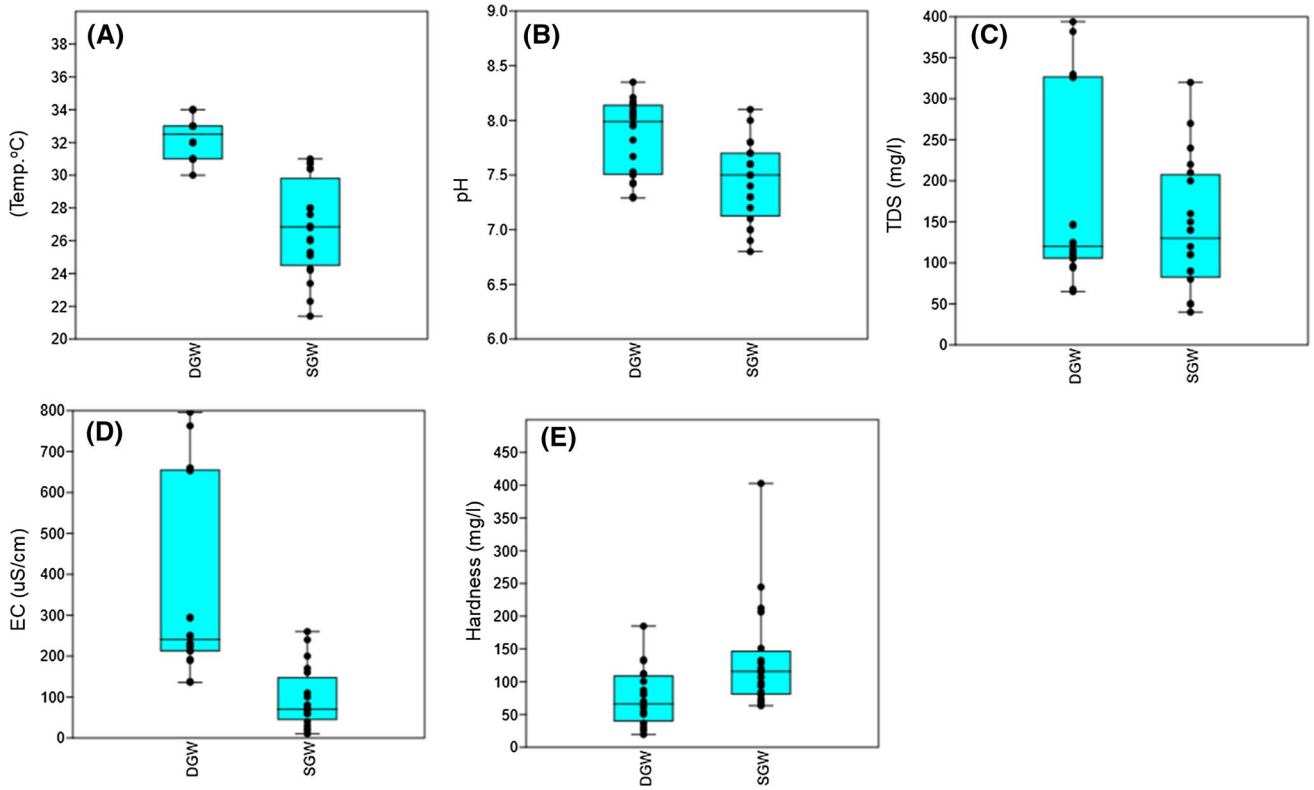


Fig. 5 Variability in physical parameters between deep and shallow groundwater **a** temperature; **b** pH; **c** EC, **d** TDS; and **e** hardness. *DGW* deep groundwater, *SGW* shallow groundwater

Table 5 Groundwater classification based on TDS, hardness, and conductivity

Range	Classification	No. of Samples	% of samples	Sample numbers	
				SGW	DGW
(A) TDS (mg/l) After David and De West (1966)					
< 500	Required for drinking	40	100	1–20	1–20
500–1000	Acceptable for drinking	–	–	–	–
1000–3000	Suitable for drinking	–	–	–	–
> 3000	Unsuitable for drinking and irrigation	–	–	–	–
Total		40	100	–	
(B) Total hardness ($CaCO_3$) After Sawyer and McCarty (1967)					
< 75	Soft	15	37.5	F1, F5, F8, F9, F10; Z2–6, Z9, Z10	F5, F6, F8; Z9
75–150	Moderately hard	21	52.5	F2, F3, F4, F6, F7, Z1, Z5, Z7, Z8	F1, F4, F7, F9, F10; Z1, Z2, Z3, Z4, Z5, Z6, Z7, Z8, Z10
150–300	Hard	3	7.5	–	F2, F3, Z8
>300	Very hard	1	2.5	–	Z4
(C) EC (µS/cm) After Richards (1954)					
<250	Excellent	38	95	F1, F2, F3, F4, F5, F6, F7, F8, F9, F10	F1, F2, F5, F6, F7, F8, F9, F19; Z1, Z2, Z3, Z4, Z5, Z6, Z7, Z8, Z9, Z10
250–250	Good	2	5	–	F3, F4
750–2000	Permissible	–	–	–	–
2000–3000	Doubtful	–	–	–	–
> 3000	Unsuitable	–	–	–	–

DGW deep groundwater, *SGW* shallow groundwater

Table 6 Groundwater classification based on chloride and nitrate

Class	Range	Number of samples	% of samples	Sample number	
				DGW	SGW
(A) Chloride (mg/l) After Stuyfzand (1989)					
Extremely fresh	< 0.14	0	0	0	0
Very fresh	0.14–0.85	0	0	0	0
Fresh	0.85–4.23	30	75	F1, F2, F3, F4, F5, F6, F7, F8, F9, F10; Z1, Z2, Z3, Z4, Z5, Z6, Z7, Z8, Z9, Z10	F1, F2, F3, F4, F5, F6, F7, F8, F9, F10
Fresh brackish	4.23–8.46	1	2.5	0	Z4
Brackish	8.46–28.21	0	0	0	0
Brackish salt	28.21–546.13	9	22.5	0	Z1, Z2, Z3, Z5, Z6, Z7, Z8, Z9, Z10
Hypersaline	> 564.13	0	0	0	0
(B) Nitrate (mg/l)					
Acceptable	< 5	0	0	0	0
Moderate	5–30	9	22.5	F1, F3, F7, F9	F6, F7; Z3, Z5, Z9
Severe	> 30	31	77.5	F2, F4, F5, F6, F8, F10; Z1, Z2, Z3, Z4, Z5, Z6, Z7, Z8, Z9, Z10	F1, F2, F3, F4, F5, F8, F9, F10; Z1, Z2, Z3, Z4, Z6, Z7, Z8

DGW deep groundwater, *SGW* shallow groundwater

Results and discussion

Suitability for drinking

Table 4 summarizes the physicochemical composition of groundwater obtained from boreholes and hand-dug shallow wells. Groundwater composition between the two sources showed a marked variability between the shallow and deep groundwater sources. Groundwater temperature varies significantly ($H = 27.36$, $p = < 0.001$) between shallow and deep aquifers. Temperature variability can be very critical especially where biochemical reactions are concerned. Because an increase in temperature by 10 °C in groundwater aquifer leads to doubling of chemical reactions (EPA 2001), the solubility of gasses, ion exchange capacity, redox reaction, sorption processes, complexation, speciation, EC and pH level are all affected by variations in temperature (Ngabirano et al. 2016).

Similarly, pH differs significantly ($H = 9.86$, $p = 0.002$) between the two sources of groundwater. Groundwater is slightly acidic to alkaline in the study area. While pH has less effect on consumers, it is fundamental to understanding the chemical composition of groundwater. Moderate pH level is required depending on the composition of groundwater and aquifer properties (EPA 2001). No significant difference in TDS concentration ($H = 0.94$, $p = 0.33$), but EC levels differ significantly ($H = 21.15$, $p = < 0.001$)

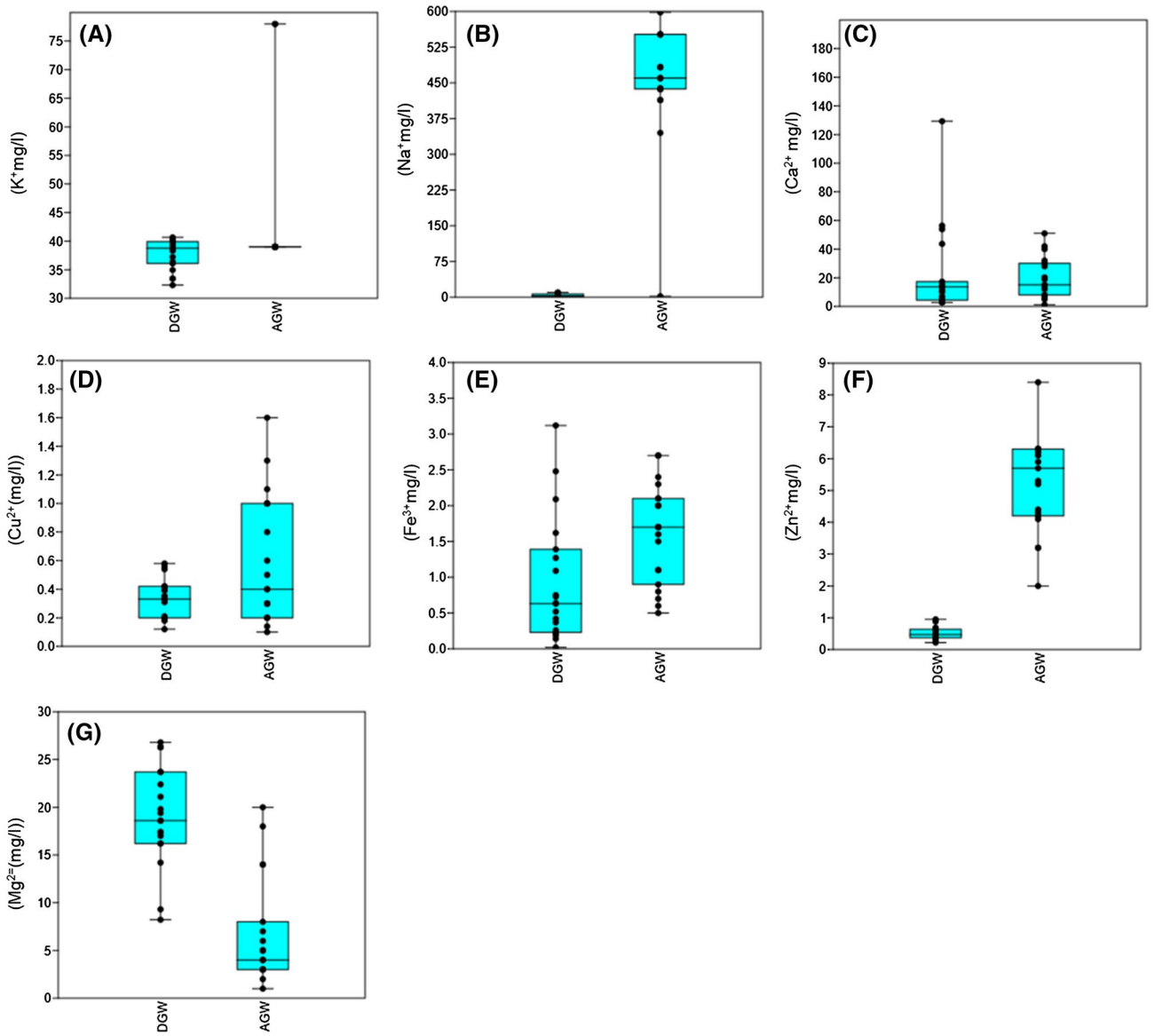


Fig. 6 Variability of cations **a** potassium; **b** sodium; **c** calcium; **d** copper; **e** iron; **f** zinc; and **g** magnesium

between deep and shallow groundwater. Overall, the physical composition of groundwater in the study area indicates water of excellent quality for drinking. Mean pH, TDS, and EC are within World Health Organization (2011) and National Standard for Drinking Water Quality (2007) reference guidelines. Figure 5 illustrates the variability of physical parameters of groundwater in the study area.

Groundwater classification base on TDS, EC, and TH

Table 5 presents the groundwater classification based on TDS, TH, and EC. All the groundwater samples obtained from deep and shallow groundwater sources have TDS concentrations < 500 mg/l. This is especially required for drinking (David and DeWest 1966). Low TDS concentrations have been reported elsewhere in Sokoto Basin (along the Sokoto-Gusau road). Groundwater sources in this area have low TDS—28–79 mg/l (Anderson and Ogilbee 1973; Uma 1993; Alagbe 2006). Groundwater hardness also differs significantly between deep and shallow groundwater ($H = 9.015$, $p = < 0.005$). Further, classification base on hardness showed that most of the groundwater sources are moderately hard (Table 5). Current result concurs with previous reports on hardness in Sokoto Basin. Groundwater obtained from the Rima Group is moderately hard to hard in nature (Anderson and Ogilbee 1973; Uma 1993; Alagbe 2006). Groundwater classification based on EC showed that 95% of water sources fall in excellent class and 5% fall in a good class. The relatively low EC levels in the study area are consequent of low TDS, which is generally low in Sokoto Basin.

Groundwater classification base on chloride and nitrate

Table 6 presents the groundwater classification based on chloride and nitrate pollution in the study area. Based on chloride 75% of water samples fall in fresh class (i.e., 0.85–4.23 mg Cl), 22.5% fall in brackish salt class (i.e., 28.21–546.13 mg Cl) and 2.5% fall in fresh brackish salt (i.e., 4.23–8.46 mg Cl). However, based on nitrate pollution, 22.5% fall in moderate class (i.e., 5–30 mg NO_3) and 77.5% fall in severe class (i.e. > 30 mg NO_3). Since NO_3^- is mainly derived from the oxidation of ammonia and agricultural fertilizer, the observed high NO_3^- levels in both shallow and deep aquifer is perhaps consequent agriculture and/or other human activities (changes in land use, sewage), but new studies are required for further evaluation. Mean NO_3^- concentration is below 50 mg/l in both shallow and deep groundwater. This is an expected outcome since Basement Complex areas are often characterized by one-aquifer system. Therefore, effluents collected in shallow groundwater are transported to deeper groundwater reservoirs.

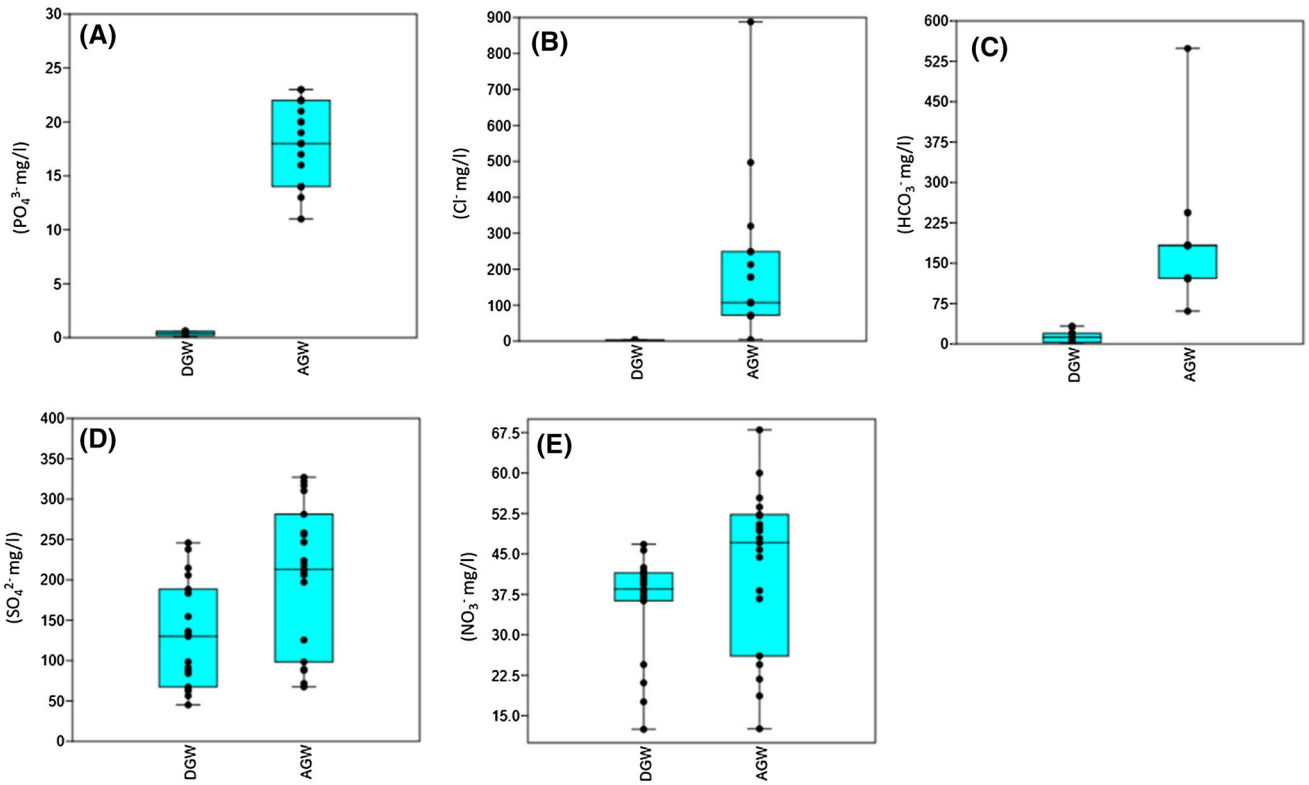


Fig. 7 Variability of anions **a** phosphate; **b** chloride; **c** bicarbonate; **d** sulfate; **e** iron; and **f** nitrate

Elevated NO_3^- levels in drinking water (> 50 mg/l) can be dangerous to infants—blue baby syndrome (EPA 2001; Wali et al. 2018a, b).

The cation chemistry

Figure 6 shows the variability in K^+, Na^+, Ca^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, and Mg^{2+} concentrations between shallow and deep groundwater in the study area. Potassium concentration differs significantly ($H = 4.41$, $p = < 0.005$) between deep and shallow groundwater (Table 4). Elevated K^+ level in groundwater is associated with toxicity. K^+ in most aquifers is found in low concentrations and excessive intake is not associated with any health hazard (EPA 2001). Sodium concentration differs significantly ($H = 25.41$, $p = < 0.001$). Na^+ is regulated in drinking water because of the joint effects it exercises with sulfate. High consumption is associated with hypertension (EPA 2001). Na^+ absorption in an aquifer is dependent on the temperature of the solution and the associated anion. No significant difference in calcium concentration ($H = 1.29$, $p = 0.25$). Elevated Ca^{2+} level is often associated with hardness.

Table 7 Correlation matrix of physicochemical parameters of deep groundwater

Para.	*T* (°C)	pH	TDS	EC	K^+	Na^+	Ca^{2+}	Cu^{2+}	Fe^{3+}	Zn^{2+}	Mg^{2+}	PO_4^{3-}	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-
T (°C)	1															
pH	0.13	1														
TDS	0.17	0.39	1													
EC	0.24	0.46	**0.85**	1												
K^+	0.14	0.43	0.27	0.35	1											
Na^+	0.28	0.07	−0.15	−0.22	0.22	1										
Ca^{2+}	0.08	0.48	**0.75**	**0.86**	0.40	−0.26	1									
Cu^{2+}	0.14	0.11	−0.09	0.00	−0.22	0.40	−0.02	1								
Fe^{3+}	0.25	−0.20	−0.22	−0.31	−0.40	0.25	−0.21	**0.63**	1							
Zn^{2+}	−0.40	−0.21	−0.21	−0.15	0.01	0.16	−0.18	−0.16	−0.28	1						
Mg^{2+}	0.05	0.46	0.14	0.04	**0.65**	0.13	0.11	−0.37	−0.44	0.01	1					
PO_4^{3-}	0.03	0.42	−0.10	−0.02	0.34	0.04	0.17	0.09	−0.12	−0.43	0.15	1				
Cl^-	0.13	0.37	**0.57**	**0.63**	**0.59**	0.40	**0.65**	0.06	−0.25	0.09	0.32	0.077	1			
HCO_3^-	−0.19	0.10	0.21	0.31	−0.19	−0.89	0.32	−0.15	−0.22	−0.22	−0.18	0.121	−0.40	1		
SO_4^{2-}	0.01	0.33	0.26	0.20	0.21	−0.19	0.03	−0.04	−0.25	−0.10	0.42	−0.03	0.14	0.08	1	
NO_3^-	−0.01	0.04	−0.12	−0.18	−0.33	0.36	−0.23	−0.03	0.00	−0.06	−0.06	0.079	0.07	−0.44	−0.29	1

Values in bold are significant at ≥ 0.50

Table 8 Correlation matrix of physicochemical parameters of shallow groundwater

Para.	*T* (°C)	pH	TDS	EC	K^+	Na^+	Ca^{2+}	Cu^{2+}	Fe^{3+}	Zn^{2+}	Mg^{2+}	PO_4^{3-}	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-
T (°C)	1															
pH	0.12	1														
TDS	−0.56	−0.23	1													
EC	−0.56	−0.23	1.00	1												
K^+	−0.10	−0.26	−0.13	−0.13	1											
Na^+	0.01	0.29	−0.27	−0.27	0.21	1										
Ca^{2+}	−0.24	−0.26	0.09	0.09	0.12	−0.13	1									
Cu^{2+}	−0.16	0.05	0.06	0.06	0.46	0.23	−0.24	1								
Fe^{3+}	0.23	−0.39	−0.16	−0.16	−0.48	−0.10	−0.06	−0.27	1							
Zn^{2+}	−0.14	−0.64	**0.60**	0.60	0.30	−0.23	0.20	0.14	−0.05	1						
Mg^{2+}	−0.28	−0.02	**0.80**	**0.80**	−0.31	−0.09	0.13	−0.35	−0.20	0.42	1					
PO_4^{3-}	−0.02	−0.15	−0.30	−0.29	−0.14	−0.24	0.26	−0.11	0.19	−0.14	−0.32	1				
Cl^-	0.04	0.03	−0.09	−0.09	0.10	0.20	−0.15	0.04	0.01	−0.17	−0.17	−0.38	1			
HCO_3^-	−0.04	0.34	−0.24	−0.24	−0.25	0.16	−0.27	0.42	−0.09	−0.48	−0.33	0.03	−0.01	1		
SO_4^{2-}	0.38	0.30	−0.56	−0.56	0.01	0.11	−0.47	0.08	−0.03	−0.36	−0.39	−0.19	−0.02	0.34	1	
NO_3^-	−0.61	−0.03	0.13	0.13	−0.02	0.27	−0.04	0.27	0.10	−0.14	−0.15	−0.16	0.41	0.19	−0.06	1

Values in bold are significant at ≥ 0.50

There is no significant difference in Cu^{2+} concentration ($H = 1.39$, $p = 0.23$). Unpleasant tastes can occur at levels above 1 mg/l (EPA 2001). High Cu^{2+} ingestion in drinking water is not harmful to humans, and therapeutic doses of ~ 20 mg/l are occasionally permitted (EPA 2001). There is a significant difference in Fe^{+} concentration ($H = 8.7$, $p = 0.003$). Elevated Fe^{3+} levels in water can be injurious to aquatic animals even though the degree of noxiousness can be reduced by the interactions between other elements. Zinc differs significantly ($H = 29.37$, $p = < 0.001$) between the two aquifers. At concentrations level of about 4 mg/l, the unfriendly taste can occur (EPA 2001). At levels between 3 and 5 mg/l, water might look opalescent and can form an oily film when boiled. There was a significant difference in Mg^{2+} concentration ($H = 22.74$, $p = < 0.001$). The significance of Mg^{+} in drinking water is that magnesium is the second major constituent of hardness ($CaCO_3$) (EPA 2001).

Anion chemistry

Figure 7 shows variability in PO_4^{3-}, Cl^{-}, HCO_3^{-}, SO_4^{2-} and NO_3^{-} between deep and shallow groundwater in the study area. There is a significant difference in PO_4^{3-} concentration ($H = 29.48$, $p = < 0.001$). The relevance of PO_4^{3-} is mainly related to the rate of eutrophication in surface water bodies (EPA 2001). Chloride differs significantly ($H = 29.39$, $p = < 0.001$). Cl^{-} vary widely in natural waters, reaching a maximum level of ~ 35,000 mg/l. Excessive intake does not constitute a health hazard to humans, but at levels above 250 mg/l water will taste salty (EPA 2001). Chloride concentrations ~ 2000 mg/l in drinking water is consumed in arid and semiarid regions. However, elevated Cl^{-} levels in freshwater may render it unfit for irrigation use (EPA 2001). What is important is understanding in a sequence of outcomes from aquifers is that Cl^{-} values are not absolute, rather the relative levels from one sampling point to another. Elevated Cl^{-} levels of ~ 5 mg/l at one location in comparison with other sampling points might lead to the suspicion of groundwater contamination from sewage ejection, especially if ammonia levels are also elevated (EPA 2001). Bicarbonate differs significantly ($H = 29.74$, $p = < 0.001$). HCO_3^{-} in conjunction with Ca^{2+} and Mg^{2+} forms carbonate hardness. When groundwater designates high pH concentrations, it can be a sign of high content of carbonate and bicarbonate ions (EPA 2001). Sulfate concentrations differ significantly ($H = 7.99$, $p = 0.004$). High SO_4^{2-} in drinking water is associated with the emetic effect, particularly when joint together with Mg^{+} or Na^{+}. Nitrate concentration differs significantly ($H = 5.22$,

Table 9 Calculated chemical indices for evaluating rock weathering process

Source type	Deep groundwater			Source type	Shallow groundwater		
	Si	Vi	MR		Si	Vi	MR
DGW1	12.8	0.1	12.8	SGW1	6.4	1.0	5.8
DGW2	13.4	0.1	13.4	SGW2	1.5	0.9	1.4
DGW3	15.6	0.0	15.6	SGW3	0.8	0.9	0.7
DGW4	18.5	0.0	18.5	SGW4	2.2	0.9	2.1
DGW5	13.8	0.0	13.8	SGW5	7.3	1.0	6.7
DGW6	18.9	0.2	18.9	SGW6	2.4	0.9	2.2
DGW7	30.8	0.1	30.8	SGW7	3.0	0.9	2.6
DGW8	13.4	0.1	13.4	SGW8	2.4	1.0	2.2
DGW9	24.8	0.0	24.8	SGW9	4.7	1.0	4.3
DGW10	20.9	0.3	20.9	SGW10	5.5	1.0	5.2
DGW11	16.4	0.2	16.4	SGW11	4.4	0.9	4.1
DGW12	15.2	0.0	15.2	SGW12	4.7	1.0	4.3
DGW13	19.9	0.2	19.9	SGW13	8.2	1.0	7.7
DGW14	20.1	0.0	20.1	SGW14	7.4	1.0	6.8
DGW15	13.4	0.1	13.4	SGW15	10.3	0.0	0.5
DGW16	11.2	0.0	11.2	SGW16	4.2	1.0	3.9
DGW17	15.2	0.2	15.2	SGW17	1.0	0.9	0.9
DGW18	61.9	0.0	61.9	SGW18	5.4	0.9	4.9
DGW19	12.2	0.2	12.2	SGW19	4.4	1.0	4.1
DGW20	19.3	0.2	19.3	SGW20	2.9	1.0	2.7

Si Scholler index, *Vi* Versluy's index, *MR* molar ratio

$p = 0.02$). High NO_3^- in groundwater lead to suspicion of past anthropogenic pollution or high application of composts slurries feast over the land and inorganic fertilizers (EPA 2001).

Mechanisms controlling water chemistry

Geochemical facies

The origin of groundwater and the process which control groundwater chemistry is understood by the relationships between dissolved elements (Tables 7, 8). It is assumed that a sizable portion of HCO_3^- in aquifers originate from the dissolution of carbonate rocks by means of the action of infiltrating rainwaters enriched in CO_2. A Ca-HCO_3^- water type is produced when CO_2 is released into solution by the dissolution of carbonate (Marghade et al. 2010). HCO_3^- and Ca^{2+} were positively correlated in shallow groundwater ($r = 0.32$), suggesting that calcite rocks were a source of Ca^{2+}. The negative correlation between these ions in the deep aquifer ($r = -0.27$) suggests that Ca^{2+} was not exclusively derived from calcite mineral. Other sources of Ca^{2+} in groundwater aquifers are apatite, dolomite, fluorite, gypsum, limestone, and marble. A weak positive correlation between Ca^{2+} and SO_4^{2-} ($r = 0.03$) perhaps indicates that some parts of Ca^{2+} in shallow groundwater is perhaps derived from gypsum. The negative correlation between these ions in deep

Table 10 Geochemical characterization of groundwater samples

Geochemical facies	Characterization of groundwater quality	Water samples		No. of samples	% of samples
		DGW	SGW		
1	Alkaline earth (Ca + Mg) > Alkalis (Na + K)	F1, F2, F3, F4, F5, F6, F7, F8, F9, F10	Z1, Z2, Z3, Z4, Z5, Z6, Z7, Z8, Z9, Z10	20	50
2	Alkalis (Na + K) > Alkaline (Ca + Mg) earths	Z1, Z2, Z3, Z4, Z5, Z6, Z7, Z8, Z9, Z10	F1, F2, F3, F4, F5, F6, F7, F8, F9, F10	20	50

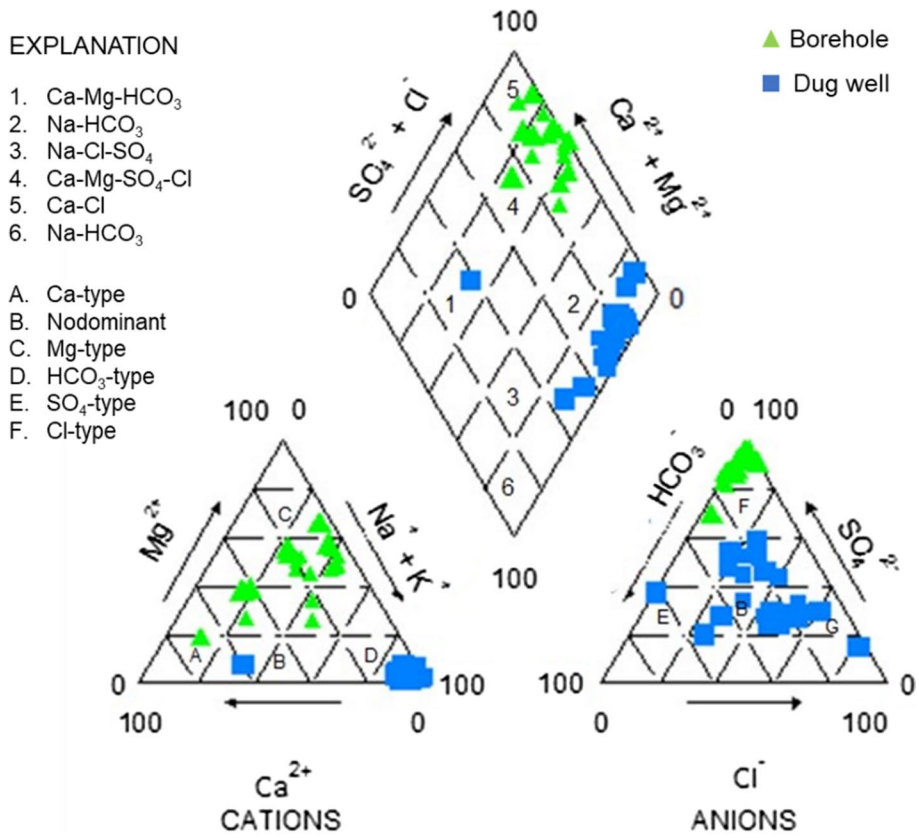


Fig. 8 Piper diagram showing the chemical composition of shallow and deep groundwater

aquifer suggests that Ca^{2+} did not derive from gypsum. TDS correlates significantly with EC, Ca^{2+}, and Cl^{-} in shallow groundwater and was significantly correlated with Zn^{2+} and Mg^{2+} in deep groundwater. Significant correlations between TDS and these ions suggest that large parts of the dissolved solids in the study area are derived from these ions.

Weak correlation between HCO_3^{-} and Ca^{2+} ($r=0.32$) in shallow groundwater and negative correlation ($r=-0.27$), between these ions in deep groundwater, suggest that dissolution of gypsum may not be the source of Ca^{2+} and SO_4^{2-}. Chloride correlates positively but weakly with Na^{+} in both shallow ($r=0.40$) and deep groundwater ($r=0.20$). Positive correlations between these two ions suggest that some parts of Na^{+} in the study area are derived from halite (Marghade et al. 2010).

Poor correlations ($r=0.11$, $r=0.13$), between Ca^{2+} and Mg^{2+} in both shallow and deep groundwater, suggest that the two ions might not have the same source. SO_4^{2-} and Mg^{2+} were positively correlated in shallow groundwater ($r=0.40$), suggesting that the two ions might likely have the same origin. But deep groundwater the two ions were negatively correlated ($r=-0.36$), indicative that SO_4^{2-} and Mg^{2+} are not derived from the same source. A charge equilibrium occurs between cations and anions when Ca^{2+}, Mg^{2+}, SO_4^{2-}, and $HCO_3^{-}+SO_4^{2-}$ originate from the simple dissolution of gypsum, dolomite, and calcite (Marghade et al. 2010).

Silicate weathering and ion exchange process

Silicate weathering reaction in the study area was evaluated using the Na^{+}/Cl^{-} molar ratio (Table 9). About 55% of the analyzed water samples from deep groundwater sources have a molar ratio greater than 1, whereas 85% of water samples from shallow aquifer have a molar ratio greater than 1. This suggests that some parts of Na^{+} were derived from silicate weathering. However, the process of cation exchange Ca^{2+}, Mg^{2+}, and Na^{+} may produce higher levels of Na^{+}. When groundwater samples have a molar ratio greater than 1, it indicates deficiency in $Mg^{2+}+Ca^{2+}$ which is equivalent to Ca^{2+}–Na^{+} cation exchange process, resulting in softening of water. More so, in aquifers having clay mineral, Na^{+} derived from the exchangeable sites can exchange with Ca^{2+} and Mg^{2+}, causing elevated Na^{+} level (Marghade et al. 2010).

Conversely, Scholler index (Si) (Scholler 1965) can be used to evaluate the ion exchange process (Table 9). Water samples from both deep and shallow groundwater in the study area have positive Si, suggesting overall base exchange reactions in the underlying aquifer. In aquifers where alkaline rock minerals are exchanged with Na^{+} ions, ($HCO_3 > Ca+Mg$) indicates base exchange soft water. Hardened water is formed when Na^{+} ions are exchanged with alkaline rocks ($Ca+Mg > HCO_3$). Similarly, Versluy's index (Versluys 1916), was positive in both shallow and deep groundwater, suggesting overall base exchange reaction in both shallow and deep groundwater (Table 9). Table 10 summarizes the geochemical aspects of groundwater samples (Panaskar et al. 2016). Two faces can be discerned. The alkaline earth (Ca + Mg) is greater than the alkalis in shallow groundwater, whereas the alkalis (Na + K) are greater than the alkaline earth in deep groundwater.

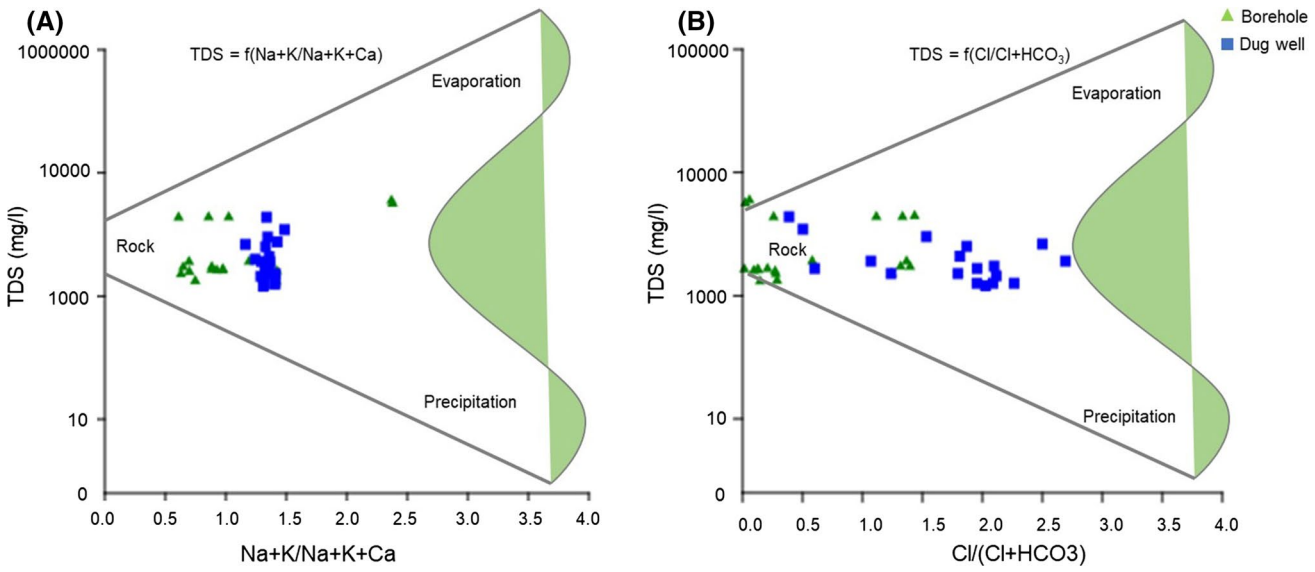


Fig. 9 Gibbs plot showing major natural mechanisms controlling groundwater chemistry

Hydrogeochemical faces

The Piper trilinear diagram (Fig. 8) (Piper 1944), shows that samples derived from deep groundwater fall in the class of Ca–Mg–SO_4–HCO_3, and Mixed Mg–Na–K–SO_4 water type, whereas in the shallow aquifer, groundwater falls in Ca–Na–K–Cl–HCO_3 and mixed HCO_3–Cl–SO_4 water type. The hydrogeochemical faces in Sokoto Basin are mainly of two types: Ca–Mg–HCO_3 and Ca–Mg–SO_4–Cl. These faces perhaps are derived from dissolution of Ca^{2+} and Mg^{2+} carbonates (Anderson and Ogilbee 1973; Uma 1993; Alagbe 2006). The observed slightly variability in the faces can be related to geology, as most previous reporting of groundwater, faces come from the Cretaceous and Tertiary section of the basin. But new studies comparing groundwater faces between the Basement Complex and Cretaceous and Tertiary sections of the Sokoto Basin are required for further evaluation.

Gibbs model

The mechanism controlling water chemistry was further evaluated using a plot of weight ratio of TDS versus [Na + K]/Na + K + Ca] and [Cl]/[Cl + HCO_3] for cations and anions, respectively (Fig. 9). The model reveals that rock weathering is the dominant mechanism controlling groundwater chemistry in the study area (Gibbs 1970; Rakotondrabe et al. 2018). The observed mechanism is perhaps derived from the Geology and Geography of the study area, which is in the Sokoto Basin (semiarid). The lithology here is mainly comprised of sands and clays of different textural classes overlying a crystalline basement complex (CBC). The lithologic logs from CBC in southern parts of Kebbi State show the lithology is mainly comprised of gneisses, granites, quartzite, and schist (Anderson and Ogilbee 1973; Kogbe 1986; Offodile 2002).

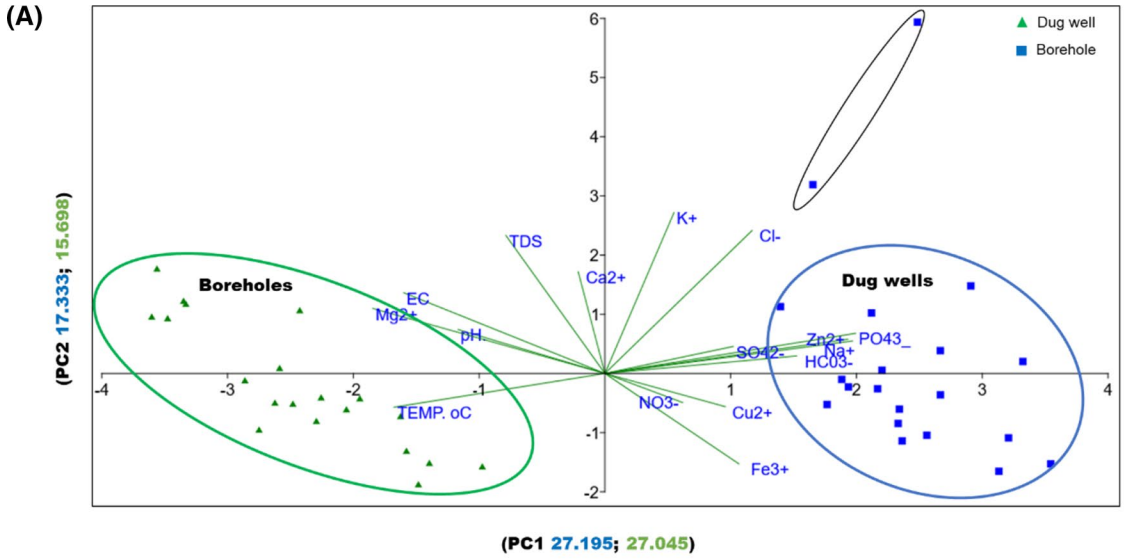
Anthropogenic inputs

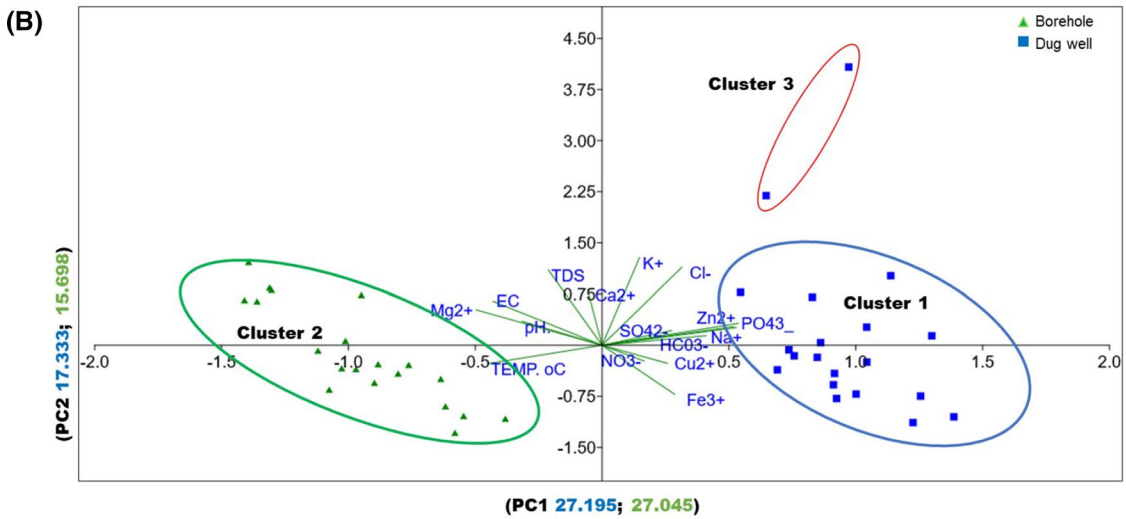
Variations of TDS in groundwater are due to contamination from anthropogenic sources (Marghade et al. 2010). Ions including Na^+, Cl^-, SO_4^{2-}, and NO_3^- are mainly derived from anthropogenic sources—sewage ejections from municipal and industrial sources as well as the application of chemical fertilizer and manure. Correlations between Na^+, Cl^-, SO_4^{2-}, and NO_3^- with TDS indicates how anthropogenic activities accelerate changes in groundwater composition (Marghade et al. 2010). TDS correlates positively with Na^+, Cl^-, Ca^{2+}, $SO4^{2-}$, and NO_3^-. Negative correlations between TDS and Na^+ in shallow and deep groundwater informs silicate weathering reaction was not the source of Na^+ (Tables 7, 8). Municipal and industrial sewage and effluents from mining and engineering works can result in a positive correlation between Na^+ and TDS (Dragon 2008). Significant correlations between TDS and Cl and positive correlation between TDS and SO_4 in shallow groundwater suggest input from anthropogenic origins. Negative correlations between TDS and NO_3^- in both shallow and

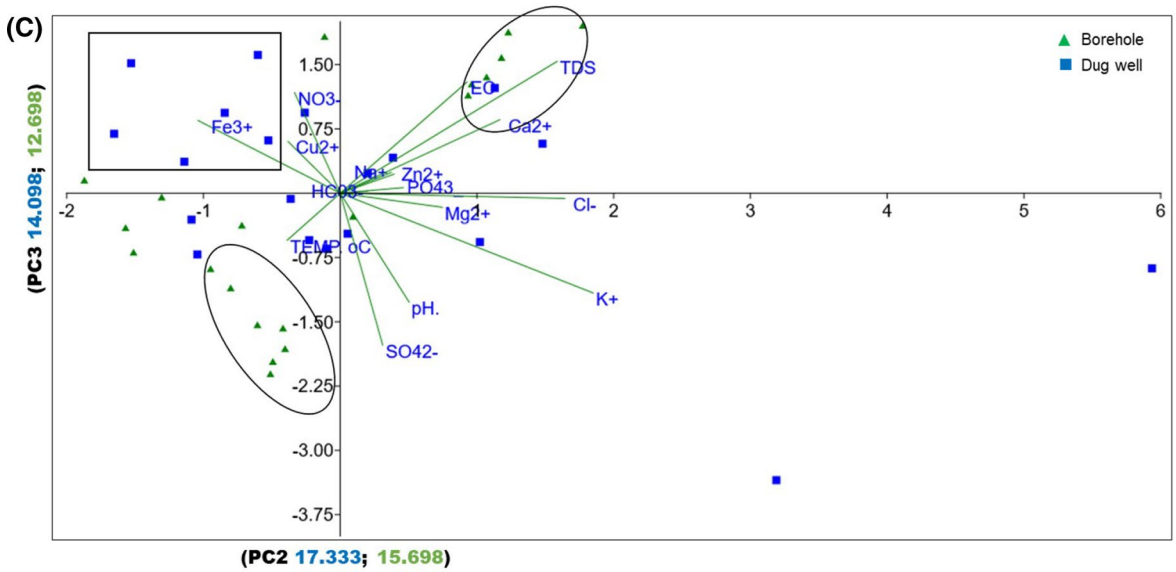
Table 11 Varimax rotated R-mode factor loadings matrix

Parameters	Shallow groundwater			Deep groundwater		
	PC1	PC2	PC3	PC1	PC2	PC3
T (°C)	0.377	0.242	−0.378	−0.563	0.138	−0.409
pH	**0.688**	0.044	0.134	−0.042	**0.773**	0.07
TDS	**0.784**	−0.283	0.026	**0.951**	−0.228	0.069
EC	**0.848**	−0.34	0.002	**0.951**	−0.228	0.068
K^+	**0.596**	0.24	**0.533**	−0.308	−0.558	**0.649**
Na^+	0.091	**0.955**	−0.12	−0.175	0.291	**0.479**
Ca^{2+}	**0.832**	−0.336	0.007	0.066	−0.543	−0.154
Cu^{2+}	0.122	0.267	−0.719	−0.113	−0.043	**0.765**
Fe^{3+}	−0.176	0.214	−0.815	−0.161	−0.011	−0.482
Zn^{2+}	−0.34	0.179	**0.560**	0.418	−0.73	0.069
Mg^{2+}	0.332	0.248	0.694	**0.879**	−0.033	−0.239
PO_4^{3-}	0.28	0.057	−0.023	−0.362	−0.269	−0.394
Cl^-	**0.766**	0.37	0.212	−0.028	0.198	0.385
HCO_3^-	0.036	−0.948	−0.04	−0.185	**0.588**	0.253
SO_4^{2-}	0.272	−0.154	0.335	−0.508	**0.590**	0.065
NO_3^-	−0.133	**0.520**	−0.108	0.197	0.193	**0.556**
Eigenvalues	4.351	2.773	2.256	4.327	2.512	1.957
% of variance	27.195	17.333	14.098	27.045	15.698	12.232
Cumulative%	27.195	44.529	58.627	27.045	42.742	54.975

Values in bold showed high positive loadings at ≥ 0.65


(A)
Dug well
Borehole
Boreholes
Dug wells
TDS
K+
Cl-
Ca2+
EC
Mg2+
pH.
Zn2+
PO43_
Na+
SO42-
HC03-
NO3-
Cu2+
TEMP. oC
Fe3+
(PC2 17.333; 15.698)
(PC1 27.195; 27.045)


(B)
Borehole
Dug well
Cluster 3
Cluster 1
Cluster 2
TDS
K+
Cl-
Ca2+
Mg2+
EC
pH.
Zn2+
PO43_
SO42-
Na+
HC03-
NO3-
Cu2+
TEMP. oC
Fe3+
(PC2 17.333; 15.698)
(PC1 27.195; 27.045)


(C)
Borehole
Dug well
TDS
EC
NO3-
Fe3+
Ca2+
Cu2+
Na+
Zn2+
HC03
PO43
Cl-
Mg2+
TEMP. oC
K+
pH.
SO42-
(PC3 14.098; 12.698)
(PC2 17.333; 15.698)

◂**Fig. 10** **a** PCA biplots for examining relationships between groundwater quality parameters from 40 groundwater sources. **b** Biplot of PC1 versus PC2 of hydrochemical data matrix (*y*-mean centered) for 17 parameters analyzed from 40 groundwater samples. **c** Biplot of PC2 versus PC3 of hydrochemical data matrix for seventeen parameters analyzed from 40 groundwater samples

deep groundwater (Tables 7, 8) suggest that groundwater in the study area is less influenced by anthropogenic activities.

However, the topographical setting of the study area may reduce the anthropogenic impact, since effluents may be washed off by a single storm. So, impurities may be transported downhill to the nearby river floodplains and transported downstream. Since Basement Complex aquifers are primarily recharged along cracks and other openings, the chances of getting contaminants may be low if the recharge zones are located away from the source of pollutants. This perhaps explains the low anthropogenic inputs in the study area. Yet new studies are required for further evaluation. Positive correlations between TDS and SO_4^{2-} also indicates contamination from the anthropogenic origin in the absence of geological inputs and this cannot be totally ruled out in the study area, owing to its geology. SO_4^{2-} and NO_3^- correlate negatively ($r=-0.29$; $r=-0.06$) in shallow and deep groundwater suggesting the different origin of the two ions, perhaps derived from both the rock mineral and anthropogenic activities (Dragon 2008). Weak correlations between Cl^- and NO_3^- ($r=0.07$; $r=0.41$) in both the shallow and deep groundwater suggest that the two ions might have originated from a different source. Negative correlations between Ca^{2+} and NO_3^- ($r=-0.23$; $r=0.04$), NO_3^- and SO_4^{2-} ($r=-029$; $r=-0.06$) and weak positive correlation between Cl^- and NO_3^- ($r=0.07$; $r=0.41$) in both shallow and deep aquifers made it very difficult to relate these ions to anthropogenic inputs.

Principal component analysis

In this paper, PCA was carried out using two sets of groundwater quality data, comprising of 20 groundwater samples each from shallow and deep groundwater sources, to identify and describe the factors that affect groundwater chemistry of the two groundwater environments. PCA was performed on a subset of 17 selected water quality variables, namely: Temperature, EC, pH, TDS, TH, K^+, Na^+, Ca^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Mg^{2+}, Cl^-, HCO_3^-, PO_4^{3-}, NO_3^-, and SO_4^{2-}, which characterized the overall groundwater chemistry outline. The PCA results comprising the loadings, eigenvalues, and percentages of total variance are summarised in Table 11. The extraction of three factors each from shallow and deep groundwater was built on the proportion of variance accrued, which included a percentage greater than 80% (Lin et al. 2012; Selvakumar et al. 2017). The computed data indicate these three factors explained 58.63% and 54.98% of the total variance within the data matrix in shallow and deep groundwater, respectively. Based on 'scree test,' the three factors with typical factor loadings suggest three different noticeable contributions were involved in controlling the composition of shallow and deep groundwater in the study area. Factor 1 explained 27.195% and 27.045% of the variability of groundwater data in shallow and deep groundwater, respectively. In shallow groundwater, Factor 1 has corresponded to high positive loadings on pH, TDS, EC, K^+, Ca^{2+}, and Cl^- as well as TDS, EC, and Mg^{2+} in deep groundwater. Factor 1 can be related to rock weathering since all the parameters having high positive loading on these factors have a geologic origin.

Potassium, for instance, is derived from many minerals through the weathering process. Such minerals include microcline and orthoclase feldspars, chlorine minerals, sylvite, carnalite, and clay minerals. Calcium in groundwater is primarily derived from rock minerals such as apatite, calcite, dolomite, fluorite, gypsum, limestone, and marble. In most natural aquifers, Cl^- occurs as a key ion, yet Cl^- is continuously added in freshwaters by anthropogenic activities in many receiving glasses of water (Gregory et al. 2015). Factor 2 explained 17.33% and 14.09% of the variability in shallow and deep groundwater, respectively. The factor corresponded to high positive loadings on Na^+ and NO_3^- in shallow groundwater, pH, HCO_3^- and SO_4^{2-} in deep groundwater. A large part of Na^+ comes from rocks and soil, whereas, NO_3^- is derived in aquifers from agriculture via runoff and oxidation of ammonia. Bicarbonate comes from carbonates dissolution and like nitrate, and SO_4^{2-} can be derived from both geogenic and anthropogenic sources. Therefore, Factor 2 can be related to both geogenic and anthropogenic influence. High positive loadings on HCO_3^- in deep groundwater inferred that it is expected to control the character of other parameters (Lin et al. 2012). Factor 3 corresponded to high positive loadings on K^+ and Zn^{2+} in shallow groundwater, K^+, Na^+, and NO_3^- in deep groundwater water. Factor 3 can be related to rock weathering in shallow groundwater since both Na^+ and Zn^{2+} are derive from rock weathering and soil. In deep groundwater, this factor can be related to both geologic and anthropogenic influence. However, negative loading on pH in PC1 in the deep aquifer was deemed reasonable since pH attained a converse relationship with rocks of carbonate origin (Lin et al. 2012).

Despite the variability in water table depths, groundwater composition in the study area is controlled by rock weathering. Using scatter plot, water quality parameters cluster nicely along the spectrum of shallow and deep groundwater, respectively, in a biplot of PC1 and PC2 (Fig. 10a, b). The two components joint together explained 58.626% (shallow groundwater) and 54.975% (deep groundwater) of the variability within the data set. Interestingly the results are

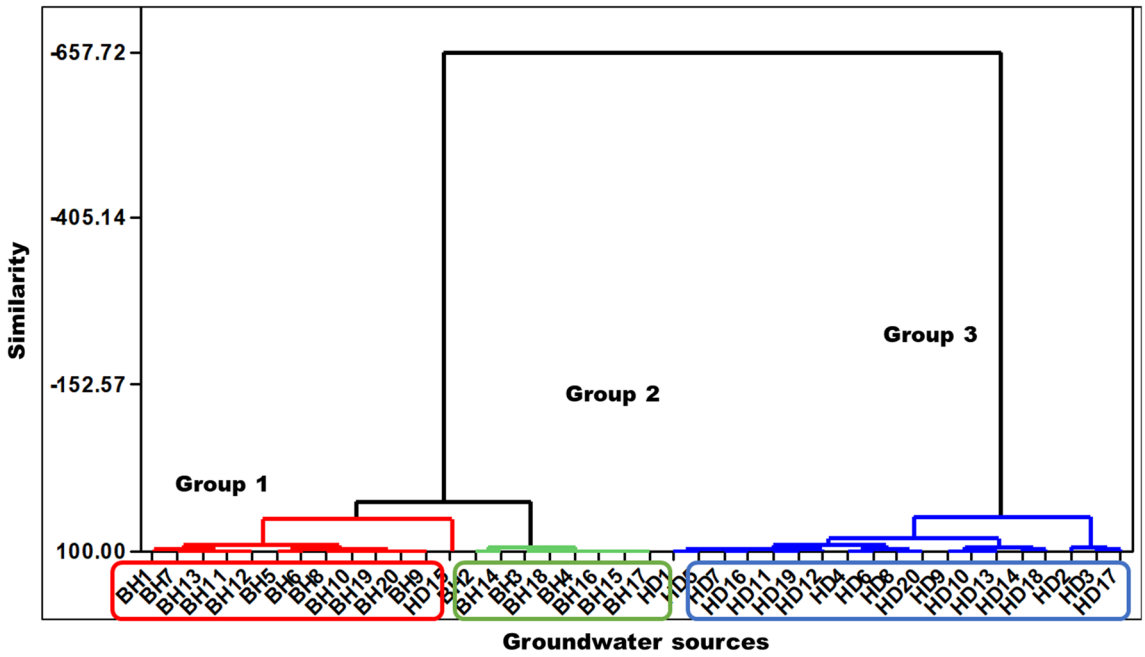


Fig. 11 Dendrogram produced from cluster analysis based on sampling boreholes to understand the most important hydrochemical physiognomies in Basement Complex areas of southern Kebbi State. Three groups were distinguished viz. Group 1 (BH1, BH7, BH11, BH12, BH5, BH6, BH8, BH10, BH19, BH20, BH9 and HD15), Group 2 (BH2, BH14, BH3, BH18, BH4, BH16, BH15, BH17and HD1) and Group 3 (HD5, HD7, HD16, HD11, HD19, HD12, HD4, HD66, HD8, HD20, HD9, HD10, HD13, HD14, HD18, HD2, HD3 and HD17)

remarkable as the parameters form a comparatively tight cluster around the water sources. All the 17 originally analyzed variables (or parameters) are clearly visible on the biplot, even though these elements are selected on the basis of their absolute size (i.e., high elemental absorptions) which was established by reference to the raw data matrix. As a result, the significance or otherwise of these parameters is identified from this plot (Kokot et al. 1994, 1998; Kokot and Stewart 1995; Olsen et al. 2012; Zhang et al. 2015). Although a good clustering is observed in the biplot of PC1 and PC2, the biplot of PC2 and PC3 (Fig. 10c) indicates wide dispersity of groundwater quality parameters, making it difficult to identify any pattern. It is not clear which of these later components is important.

Hierarchical cluster analysis

The vital role of HCA is to discrete the parameters in a raw data matrix into separate classes designated by the user without any prior hypotheses. The HCA is an unverified classification technique that reveals inherent assembly or recognizing the pattern of a dataset without a prior hypothesis with regards to the data so that the objects of the system can be classified into clusters based on their resemblances (Lin et al. 2012; Machiwal and Jha 2015). In this study, Ward's algorithmic clustering technique subsequent to the Euclidean distance was used. This is considered as the most powerful grouping tool (Dou et al. 2008; Shyu et al. 2011; Lin et al. 2012), because it is capable of minimizing the misrepresenting effect or sum of squared distances of centroids from two theoretical groups produced at each step (Lin et al.

Table 12 Summary of chemical indices used in determining groundwater suitability for irrigation

Parameter	Formula for Calculation	Source
Kelly index (Ki)	$Na/(Ca+Mg)$	Kelly (1940)
Magnesium hazard (MH)	$Mg\times100/(Ca+Mg)$	Szablocs and Darab (1964)
Permeability index (Pi)	$Na+\sqrt{HCO_3}/(Ca+Mg+Na\times100)$	Doneen (1962)
Sodium adsorption ratio (SAR)	$Na^+/\sqrt{Ca+Mg/2}$	Ayers and Westcot (1976)
Sodium percent (SP)	$Na^+\times100/(Ca+Mg+Na+K)$	Wilcox (1955)
Versluys index (Vi)	$Na/(Na+Ca+Mg)$	Versluys (1916)

Table 13 Summary of chemical indices of shallow and deep groundwater in the study area

Source type	Shallow groundwater					Source type	Deep groundwater				
	Ki	SAR	SP	MH	PI		Ki	SAR	SP	MH	PI
DGW1	0.1	0.5	4.1	60.8	14.6	SGW1	23.0	97.6	87.9	27.8	2024.4
DGW2	0.1	0.8	5.6	23.6	30.6	SGW2	11.8	71.8	85.2	13.5	2148.6
DGW3	0.0	0.0	0.1	33.2	2.6	SGW3	9.2	74.2	80.7	21.5	2575.7
DGW4	0.0	0.0	0.1	90.8	3.1	SGW4	16.3	84.5	86.9	29.6	2144.2
DGW5	0.0	0.2	1.6	48.0	5.1	SGW5	21.0	100.7	88.6	13.0	87.9
DGW6	0.3	1.4	9.6	36.0	30.5	SGW6	16.7	96.1	88.5	9.1	1963.6
DGW7	0.1	0.6	4.4	85.3	14.8	SGW7	11.5	72.7	79.6	50.0	1909.4
DGW8	0.2	0.7	4.7	79.7	15.0	SGW8	32.5	133.9	90.8	29.4	2064.4
DGW9	0.0	0.2	1.3	58.1	6.2	SGW9	21.9	100.4	88.5	4.8	2033.2
DGW10	0.4	1.9	12.9	72.7	67.9	SGW10	55.2	174.6	91.8	30.0	2848.6
DGW11	0.2	1.3	9.4	59.6	31.3	SGW11	13.2	76.1	85.9	54.5	1809.6
DGW12	0.0	0.2	1.3	55.1	5.6	SGW12	24.2	105.5	88.8	73.7	1901.8
DGW13	0.3	1.4	10.0	74.9	71.5	SGW13	61.3	184.0	92.0	22.2	2602.9
DGW14	0.0	0.2	1.5	13.0	14.4	SGW14	23.0	105.4	89.0	28.6	1911.9
DGW15	0.1	0.6	4.7	60.3	31.0	SGW15	0.0	0.3	2.4	7.0	2163.5
DGW16	0.0	0.0	0.0	60.4	19.7	SGW16	34.5	119.5	89.0	33.3	2630.8
DGW17	0.3	1.8	12.2	85.6	46.6	SGW17	8.9	62.4	83.2	14.3	2249.2
DGW18	0.0	0.4	2.7	35.2	17.3	SGW18	11.1	62.0	83.1	9.7	2415.2
DGW19	0.2	0.8	5.8	85.0	86.2	SGW19	36.4	126.2	89.5	33.3	2031.9
DGW20	0.2	1.3	9.8	62.5	52.5	SGW20	92.9	211.8	91.6	76.9	2528.7

Ki Kelly's index, *SAR* sodium adsorption ratio, *MH* magnesium hazard

2012). Using HCA, groundwater sources with comparable hydrochemical physiognomies can be grouped into the same cluster. The graphics collection of the clustering processes in this study is offered as a dendrogram. Base on the dendrogram (Fig. 11), three groups of groundwater sources can be distinguished.

Group 1 (BH1, BH7, BH11, BH12, BH5, BH6, BH8, BH10, BH19, BH20, BH9 and HD15), Group 2 (BH2, BH14, BH3, BH18, BH4, BH16, BH15, BH17and HD1) and Group 3 (HD5, HD7, HD16, HD11, HD19, HD12, HD4, HD66, HD8, HD20, HD9, HD10, HD13, HD14, HD18, HD2, HD3 and HD17).Generally, the lithology of these boreholes is comprised of clay, ironstone, schists, and sands of different textural groups. Group 1 is characterized by a higher temperature, magnesium, pH, TDS, EC, and calcium. Group 2 corresponded to groundwater sources having higher potassium, chloride, sodium, sulfate, phosphate, zinc and bicarbonate. Group 3 is comprised of water sources having higher concentrations of copper, iron, and nitrate. Group 1 can be related to natural geogenic processes as it is comprised of ions derived primarily from rock minerals (notably Ca^{2+}). Similarly, Group 2 can be related to natural geogenic processes. Lastly, Group 3 can be related to both anthropogenic (notably NO_3^- pollution) and rock weathering.

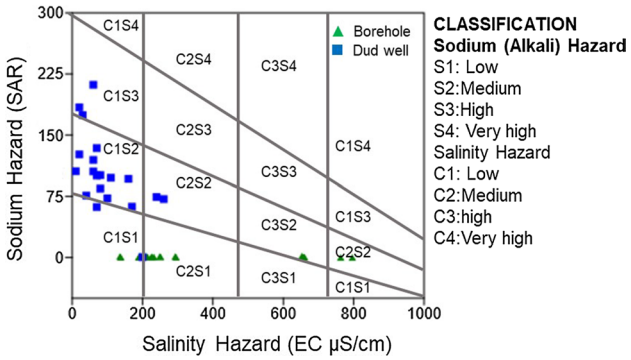


Fig. 12 USSL classification of groundwater samples from shallow and deep aquifers

Suitability for irrigation use

The suitability of groundwater for irrigation can be evaluated using a total concentration of soluble salts (SAR) which is express in terms of specific conductance (Sadashivaiah et al. 2008; Rakotondrabe et al. 2018). Sodium percent was calculated following Kumar et al. (2014) and Rakotondrabe et al. (2018). Soil often reacts with sodium to decrease soil permeability, which results in high sodium concentration. This causes cation exchange between Mg^{2+} and Ca^{2+} in soil under wet conditions. Water and air circulations are reduced as a consequent to this process. In the same vein, Kelly's

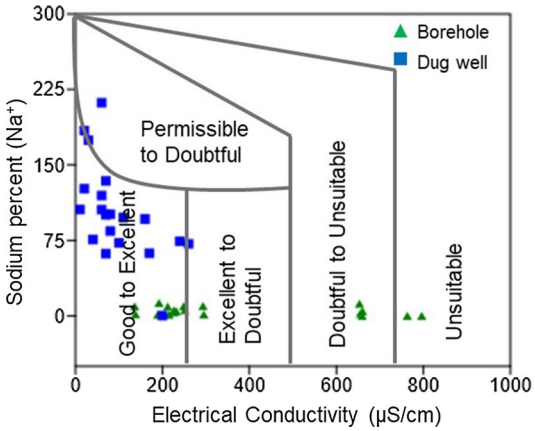


Fig. 13 Wilcox diagram showing groundwater classification for irrigation use

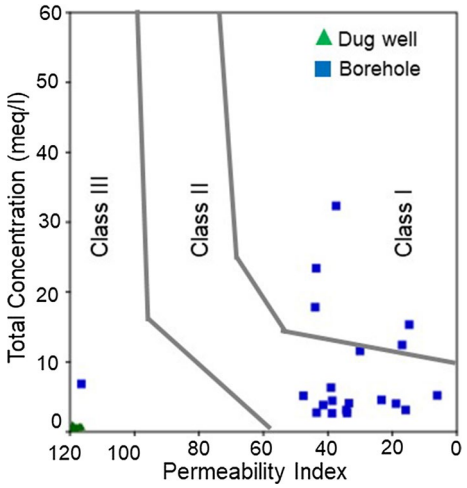


Fig. 14 Doneen's chart showing groundwater classification of irrigation water based on PI

index and magnesium adsorption ratio (MAR) were also calculated. Kelly's index value greater than 1 designates water of excellent quality for irrigation use. However, index value less than 1 designates water which is unsuitable for irrigation, because of alkali hazard to crops (Kelly 1940). 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 (Kumar et al. 2014). Also, values of MAR less than 50 in irrigation water are considered appropriate for irrigation use. Often in groundwater, 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, which destroys soil structure, and consequently, reduces its productivity (Goswamee et al. 2015).

The chemical composition of groundwater for irrigation farming affects the soil quality and crop yield (Table 12). The suitability of groundwater for irrigation use hinges on the composition and concentration levels of ions in groundwater (Panaskar et al. 2016). To assess this, the properties of groundwater play an important role including (1) comparative amount of sodium to other cations, (2) total absorption of soluble salts, (3) the bicarbonate absorption in relation to the absorption of Ca + Mg (USSL 1954; Panaskar et al. 2016). Using this, an assessment of groundwater appropriateness for irrigation uses has been carried out in the study area using numerous salinity indices viz. sodium adsorption ratio (SAR), sodium percentage (Na%), Kelly's ratio, magnesium ratio, residual sodium carbonate (RSC), and USSL diagram among others (Panaskar et al. 2016). Table 13 presents the calculated indices from the shallow and deep groundwater in the study area.

Sodium adsorption ratio (SAR)

The foremost index applied for evaluation of groundwater suitability for agricultural purposes in relation to Na^{+} absorption which affect soil structure and permeability is SAR (Marghade et al. 2010; Panaskar et al. 2016). SAR is used to measure sodium and/or alkali hazards to crops (Table 13). It provides a clue relating to the magnitude of sodium adsorption by soil. Calcium and Mg^{2+} in the soil can be displaced as a result of the prolonged application of high Na-rich water. This causes damage to the soil structure and reduced crop yields (Marghade et al. 2010; Panaskar et al. 2016). SAR in deep groundwater ranged from < 0.001 to 1.9 with a mean value of 0.7, whereas, in shallow groundwater, it varies between 0.3 and 211.8 with an average value of 103.26. Figure 12 shows the variability in SAR levels between shallow and deep groundwater in the study area.

Groundwater samples having SAR value within the range of 10 and 18 are classified as a good category; however, most of the groundwater samples derived from deep aquifer have SAR value > 18, with one groundwater sample (SAR < 18), classified as good.

Sodium percent (Na%)

Another index employed to identify the concentration of soluble sodium level in irrigation water is sodium percent (Na%). It is applied to reveal sodium hazard to crops (Panaskar et al. 2016). Calcium is replaced by sodium by

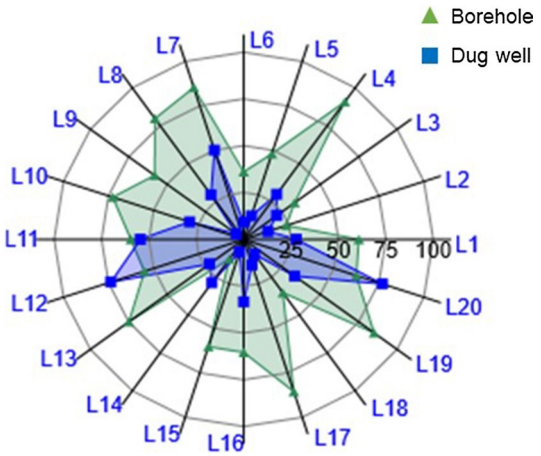


Fig. 15 Radar chart showing the variability of magnesium adsorption ratio between shallow and deep groundwater

process of base exchange which destroys soil structure and consequently reduces soil permeability (Table 12). Using Wilcox plot (Fig. 13), groundwater samples showed marked variability with shallow groundwater samples falling in good to excellent class. Whereas deep groundwater samples vary between good to excellent class and unsuitable to doubtful class, two samples from deep groundwater fall in unsuitable class. Generally, samples from shallow groundwater have very low to high sodium class. However, irrigation water of very low SAR and low salinity (< 200 µS/m) affects the rates of water infiltration into soils (Graham et al. 2006).

Permeability index (PI)

Prolonged application of irrigation water can interfere with soil permeability which is affected by bicarbonate, calcium, magnesium, and sodium (Li et al. 2016; Panaskar et al. 2016). Doneen (1962) developed a standard for evaluating irrigation water suitability using permeability index which is defined as contained (Fig. 14).

Values are express in meq/l. Shallow groundwater classification showed that PI values ranged from 2.6 to 86.2 with a mean value 29.8. In deep groundwater, PI values vary between 0 and 1.9 with an average value of 0.74. Based on permeability index, three classes can be discerned: Class I is classified as excellent for irrigation; Class II is classified as acceptable; Class III is categorized as unsuitable (Li et al. 2016). All the shallow groundwater samples fall in Class III. This is deemed reasonable since the prolonged application of irrigation water of very low salinity is related to poor permeability (Graham et al. 2006). In deep groundwater, 1 sample falls in Class III, 14 samples fall in Class II, and 5 samples fall in Class I. Water samples from deep aquifer can be used for irrigation with little permeability problem, but such water of high SAR level destroys soil structure (Li et al. 2016; Panaskar et al. 2016).

Kelly's index (KI)

Kelly's index is employed to measure the concentration of Na^+ against Ca^{2+} and Mg^{2+} (Table 13). It is vital to evaluate groundwater suitability for agricultural use. Elevated Na^+ level in aquifers produces an objectionable impact on changing characteristics of soil and its permeability; thus, extreme Na^+ is used as an indicator of alkali hazard (Wagh et al. 2016). Kelly's index is greater than 1 in deep groundwater, whereas, in shallow groundwater, indices are less than 1 (Table 13). Values less than 1 are considered suitable for irrigation, whereas KI values are greater than 1 in irrigation water can be classified as unsuitable for irrigation use (Wagh et al. 2016). KI values in shallow groundwater ranged from 0 to 0.4 with a mean value of 0.13. KI values are extremely high in shallow groundwater and vary between 0 and 92.9 with an average value of 28.06. The possible reasons for higher KI values in shallow groundwater need to be unveiled as it presents a serious environmental problem.

Magnesium adsorption ratio (MAR)

Magnesium hazard is also used to characterize groundwater and assess its suitability for irrigation use by revealing the amount of Mg^{2+} over Ca^{2+} (Ragunath 1987; Wagh et al. 2016). The MAR ratio as calculated in Table 13 shows that MAR values ranged from 13.0 to 90.8 with a mean value of 58.3 in shallow groundwater. In deep groundwater, MAR values vary between 4.8 and 76.9 with an average value of 30.17. Based on mean MAR, shallow groundwater in the study area is unfit for irrigation use. Usually, magnesium and calcium occur in a state of equilibrium in groundwater sources. The concentration of magnesium beyond calcium in irrigation water fast-tracks the magnitude of Mg^{2+} saturation and consequently damages soil structure and reduces crop yields. High magnesium in irrigation water impacts soil quality by converting it to alkali which eventually reduces its productivity. The variability of MAR in the study area is further illustrated using a radar chart (Fig. 15). Overall, groundwater evaluation shows deep aquifers in the study area hold water of good quality as compared to shallow groundwater sources.

Implications for groundwater quality in Sub-Saharan Africa

Characterization of groundwater in the study area showed marked variability between aquifers. Groundwater

Table 14 Compilation of the literature report of physical and chemical properties of groundwater in some parts of sub-Saharan Africa

Country	Location	*T* (°C)	EC	pH	TDS	K^+	Na^+	Cl^-	HCO^{3-}	Ca^{2+}	Cu^{2+}	Fe^{3+}	Zn^2	Mg^{2+}	NO_3^-	SO_4^{2-}	PO_4^{3-}	Source
Benin	Lagbe		282.5	**5.6**				28.9							26.1	1.0		Fantombi et al. (2012)
Benin	Coastal lower aquifer (P15)		931.0	7.0	491	22.6	**76**	69.2	209.0	47.5		0.3		**11.1**	10.7	45.3	BD	Boukari et al. (1996)
Benin	Coastal upper aquifer (U23)		931.0	6.9	245	4.8	**43.7**	42.4	81.7	21.8		0.4		**7.9**	5.9	36.8	BD	Boukari et al. (1996)
Cameroon	Semiurban Douala		164.6	**4.7**		3.7		16.7	12.9	9.3				1.4		14.2		Takem et al. (2010)
Cameroon	Douala		101	**6.3**		1.8	4.9	3.5	55.0	16.0				2.4	1.7	10.2		Eneke et al. (2011)
Cameroon	Banana Plain	27.6	173.3	**5.8**	147.6	5.5	6.8	5.6	75.6	11.4				**5.5**	17.3	8.0		Ako et al. (2011)
Congo	Brazzaville		253.5	**5.2**	135.7	20.2	10.8	20.2	31.9	16.0				**8.5**	1.8	7.8		Laurent et al. (2010)
Congo	Brazzaville (wet season)		213.5	**4.7**	111.2	7.9	**31.4**	13.5	38.9	20.2		0.4		**12.5**	1.4	9.7		Matini et al. (2012)
Congo	Brazzaville (dry season)		169.1	**4.6**	89.8	5.4	**125.1**	12.3	36.9	16.5		0.4		**9.1**	1.4	8.3		Matini et al. (2012)
Ethiopia	Wollega Zone		381.8	6.6	232.5	4.1	**21.7**	4.3	245.2	35.6		0.3		0.2	0.5	16.1		Ali et al. (2015)
Ethiopia	Tigray	18.6	817	6.9	393.5	0.9	**50.3**	23.8	**420.4**	94.2				**17.3**	1.4	66.2		Gebrehiwot et al. (2011)
Ghana	Ga East	22.5	505.9	**5.7**	257.6	24.5	**116.6**	116.2	68.4	3.6		0.9	0.03	**2.4**	**302.8**	36.3		Ackah et al. (2011)
Ghana	Obuasi		178..4	**5.0**	146.0	8.6	9.6	6.4	76.7	9.2		0.4		**5.0**			**1.0**	Fianko et al. (2007)
Ghana	Densu Basin	28.9	**1129.5**	6.7		4.8	**64.0**	28.3	191.5	45.3				**37.4**	0.04			Tay and Kortatsi (2008)
Ghana	Northern Ghan		391	6.7	214.4	6.5	**22.9**	9.2	199.2	16.0		0.7		**14.8**	37.9	6.6		Anku et al. (2008)
Malawi	Zombawa-Phalombe Plain		448.5	6.8			**16.8**	8.1		15.0		0.5			4.2	0.7		Hellens (2013)
Malawi	Basement aquifers		687.2	7.1	378.9	3.9	**26.2**	96.0	175.4	3.9		0.5		**19.3**	0.4	16.2		Wanda et al. (2011)
Namibia	Windhoek	24.0	24.0	7.8	161			24.0		11.0				**11.0**	0.3	4.9		Tredoux et al. (2009)
Nigeria	Port Harcourt	27.7	245.8	7.7	145.5	0.5	1.6	161.5	16.7	3.0	0.1	0.3	**0.7**	3.2	3.2	68.8	**0.3**	Nwankwoloa et al. (2014)
Nigeria	Kaltungu		387.6	7.9	221.5	5.4	3.6	74.0	**342.6**	62.0		**4.7**		**49.8**	**103.6**	23.2		Abdulkareem et al. (2011)
Nigeria	Ede Area		330.0	**5.8**		4.8	11.6			26.0				**5.5**		7.2		Adediji and Ajibade (2005)
Nigeria	Akur		284.6		142.0	1.6	**31.6**	43.5	223.0	27.3				**6.7**				Duvbiama and Egbuna (2013)
Nigeria	Akwa Ibom	29.2	10.5	**4.6**	4.5			0.2		72.0	0.1	0.1	BD	**24.0**	BD	3.0	BD	Ukpong (2011)
Nigeria	Ibadan	27.6	207.2	**6.2**	349.3	12.5	**37.5**	79.5	69.8	19.5		0.3		**9.1**	14.0	29.5	0.2	Ajibade and Ogungbesan (2013)
Nigeria	Konduga		160.0	7.1	80.0	11.0	8.9	2.0	218.3	6.5		0.2		2.5	2.3	1.2		Dammo et al. (2013)
Nigeria	Patigi	32.0	**1678**	6.7	460	312	**230**	**260**		268	0.9	0.4	**2.0**	0.0	0.3	**500**		Musa and Ahanonu (2013)

Table 14 (continued)

Country	Location	*T* (°C)	EC	pH	TDS	K^+	Na^+	Cl^-	HCO^{3-}	Ca^{2+}	Cu^{2+}	Fe^{3+}	Zn^2	Mg^{2+}	NO_3^-	SO_4^{2-}	PO_4^{3-}	Source
Nigeria	Kaduna,	22.1	5.0	6.5	500.0					200.0	0.1	1.0	5.0	0.2			**5.0**	Muhammad (2012)
Nigeria	Kaduna		351.0	6.5	0.3			50.0			0.6	**1.7**					**3.9**	Ugya et al. (2015)
Nigeria	Lagos State		628.6	6.5	321.9			70.8				0.6	8.6	**25.1**				Soladoye and Ajibade (2014)
Nigeria	Calabar	27.5		6.9			2.1	0.3								1.7		Eni et al. (2011)
Nigeria	Sokoto-Rima (Dug well)					4	4	3.7	6.4	0.64				**11.3**	12.2		**23.5**	Graham et al. (2006)
Nigeria	Sokoto-Rima (Borehole)					1.1	2.1	3.7	4.4	0.8				1.9	8.3		**6.4**	Graham et al. (2006)
Nigeria	Uyo	26.9	99.7	**4.2**	47.3		0.1	8.7		0.5	0.3	0.1	BD	1.0				Adetoyinbo et al. (2010)
Rwanda	Huye	21.8	87.3	6.9							0.02	0.3			6.5	1.0	**1.0**	Nsengimana et al. (2012)
Sierra Leone	Bombali-IDA	27.5	88.3	7.2	41.9			10.0		12.0	0.05	0.2				2.0		Ibemenuga and Anaoja (2014)
Senegal	Linguere	39.5		7.0	**789.1**	8.0	**140.0**	33.0	245.2	48.6		0.6		**22.0**		290		Kane et al. (2012)
Senegal	Thiaroye area							182		68					**310.5**	45.0		Faye et al. (2004)
Senegal	Diourbel	39.1		7.9	**1534.7**	8.0	**480.0**	**500.0**	**492.9**	4.1		**4.0**		2.7		43.0		Kane et al. (2012)
Senegal	Kaffrine	37.0		7.9	**932.9**	11.0	**274.0**	**224.0**	**360.0**	13.6		0.3		**4.6**		45.1		Kane et al. (2012)
Senegal	Kaolack	39.0		7.7	**1262.0**	15.6	**400.2**	**386.2**	**390.4**	11.2		2.9		2.7		52.8		Kane et al. (2012)
Sierra Leone	Bombali-Msorie	28.2	336.0	6.9	168.0			32.0		4.0	0.3	0.02				2.0		Ibemenuga and Anaoja (2014)
South Africa	Western Karoo	18.6	159	7.3	**1053**	2.7	**159.4**	1.3	**312.8**	107.2	0.01	1.3	0.1	**40.0**	4.7	147.8		Adams et al. (2001)
South Africa	North mine					1.1	10.9	36.3	**330.4**	172.2				**96.6**	2.1	0.0		Love et al. (2004)
South Africa	Eastern Cape		381.8	6.6	232.5	4.1	**21.7**	4.3	245.2	35.6		0.3		**18.3**	0.5	16.1		Ali et al. (2015)
Togo	Gulf region aquifer	27.2	1977	6.2	**992.8**	0.8	10.6	12.5	2.6	2.3		0.2		2.2	0.9	2.3		Mande et al. (2012)
Uganda	Kampala city	24.3	102.0	**4.6–5.6**				12.4						**26.0**				Haruna et al. (2005)
Uganda	Kampala	21.8	26	**4.7**				2.5							2.0			Kulabako et al. (2007)
Zimbabwe	Harare (Well 11)		208	6.6		6.0	**24.6**			0.4	0.07	**12.0**	**0.4**	0.4				Love et al. (2006)
Zimbabwe	Harare (BH 1)		**1920**	**5.8**				7.9				**11.0**	0.06		16.6			Love et al. (2006)
Zimbabwe	Matsheumhlope well field	23.4	**1179**	7.0				151.0			0.01	1.2			0.04	143.0	**1.6**	Mangore and Taigben (2004)
Reference guidelines		–	1000	6.5–8.5	500	–	12	200	250	75–200[a]	2	0.3	4	0.3–0.5[a]	50	200	0.2	World Health Organization (2011)
Reference guidelines		–	1000	6.5–8.5	500	–	12	200	250	–	1	0.3	3	0.2	50	100	0.2	National Standard for Drinking Water Quality (2007)

Values in bold do not follow WHO and NSDWQ reference guidelines

[a]EPA (2001)

Table 15 Summary of chemical indices of groundwater in some Sub-Saharan Africa

Country	Location	Si	Vi	Ki	SAR	SP	MAR	MR
Benin	L1	ND	ND	ND	ND	ND	ND	ND
Benin	L2	8.9	0.5	1.1	9.1	45.2	0.4	6.8
Benin	L3	6.1	0.5	1.0	6.7	47.9	0.9	5.5
Cameroon	L4	2.6	ND	ND	ND	ND	ND	ND
Cameroon	L5	2.8	0.6	1.4	2.6	48.0	ND	2.0
Cameroon	L6	2.2	0.5	1.2	2.9	38.0	ND	1.2
Congo	L7	3.6	0.3	0.5	2.4	21.1	ND	1.3
Congo	L8	3.1	0.7	2.3	8.4	59.0	2.9	2.5
Congo	L9	14.3	0.9	9.9	35.1	87.4	3.1	13.7
Ethiopia	L10	129.0	0.8	4.7	10.1	71.4	6.5	108.5
Ethiopia	L11	3.0	0.7	2.1	10.3	67.1	0.0	2.9
Ghana	L12	58.8	0.5	1.0	10.8	45.2	0.8	48.6
Ghana	L13	3.6	0.6	1.4	3.7	38.4	5.9	1.9
Ghana	L14	1.8	0.7	2.3	12.0	65.9	0.0	1.7
Ghana	L15	2.0	0.7	2.3	7.3	58.3	7.1	1.5
Malawi	L16	0.0	0.7	2.0	5.7	66.1	5.8	ND
Malawi	L17	1.6	0.2	0.3	2.7	20.7	0.5	1.4
Namibia	L18	ND	ND	ND	ND	ND	ND	ND
Nigeria	L19	0.7	ND	ND	0.1	1.0	0.2	0.5
Nigeria	L20	0.2	ND	ND	0.4	4.1	6.0	0.1
Nigeria	L21	3.0	1.0	ND	ND	70.7	ND	2.1
Nigeria	L22	5.0	0.4	0.7	4.8	41.2	0.0	4.7
Nigeria	L23	ND	ND	ND	ND	ND	33.3	ND
Nigeria	L24	5.5	0.3	0.5	4.2	28.9	0.4	4.1
Nigeria	L25	8.0	0.8	4.0	6.0	40.3	9.1	3.6
Nigeria	L26	ND	0.5	0.9	14.3	28.7	0.2	ND
Nigeria	L27	ND	ND	ND	ND	ND	100.0	ND
Nigeria	L28	ND	ND	ND	ND	ND	3.3	ND
Nigeria	L29	ND	ND	ND	ND	ND	0.8	ND
Nigeria	L30	0.0	0.0	7.0	3.8	87.5	0.0	ND
Nigeria	L31	0.7	0.5	1.1	2.1	34.2	0.0	0.4
Nigeria	L32	1.7	0.4	0.6	1.1	30.4	0.0	1.1
Nigeria	L33	0.1	0.0	0.0	0.0	1.1	1.1	0.1
Rwanda	L34	ND	ND	ND	ND	ND	ND	ND
Sierra Leone	L35	0.0	0.0	0.0	0.0	0.0	2.0	0.0
Senegal	L36	6.7	0.8	4.2	24.2	77.1	1.8	6.4
Senegal	L37	ND	ND	ND	ND	ND	ND	ND

Table 15 (continued)

Country	Location	Si	Vi	Ki	SAR	SP	MAR	MR
Senegal	L38	180.7	0.5	1.0	21.4	48.4	0.8	177.8
Senegal	L39	62.0	0.5	1.2	18.3	53.8	0.1	59.6
Senegal	L40	154.0	0.5	1.0	20.3	49.7	0.7	148.2
Sierra Leone	L41	ND	ND	ND	ND	ND	ND	ND
South Africa	L42	4.1	1.0	61.3	98.9	96.8	50.0	4.0
South Africa	L43	0.1	0.2	0.3	1.8	22.6	0.0	0.1
South Africa	L44	1.4	0.8	4.7	10.1	71.4	6.5	1.2
Togo	L45	5.2	0.5	0.8	3.0	44.0	1.6	4.8
Uganda	L46	ND	ND	ND	ND	ND	ND	ND
Uganda	L47	ND	ND	ND	ND	ND	ND	ND
Zimbabwe	L48	76.5	0.7	2.1	7.1	57.7	100.0	61.5
Zimbabwe	L49	ND	ND	ND	ND	ND	58.2	0.0
Zimbabwe	L50	ND	ND	ND	ND	ND	0.8	ND

SI Scholler index, *Vi* Versluy's index, *KI* Kelly's index, *SAR* sodium adsorption ratio, *MAR* magnesium adsorption ratio, *MR* molar ratio, *ND* no data

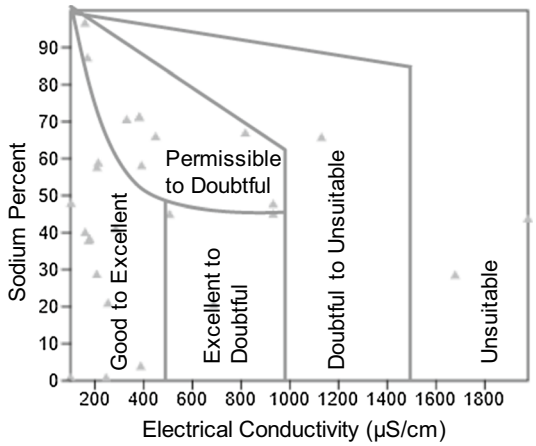


Fig. 16 Wilcox plot showing irrigation water classification in sub-Saharan Africa

parameters showed marked variability between the shallow and deep groundwater. To better understand the composition of groundwater in the rest of SSA, data from 50 locations from the literature was compiled (Table 14). Further Table 14 shows that evaluation of groundwater quality in SSA is constrained by lack of data. Results from the patchy data derived from the literature indicate that 16.7% ($n=24$) of groundwater in SSA have temperatures above 30 °C, 90.0% ($n=40$) have EC values above WHO reference guidelines (1000 µS/cm). At least, 38.6% ($n=44$) of groundwater sources in SSA are acidic to alkaline in nature. Scholler and Versluy's indices are positive, indicating overall base exchange reactions in aquifers underlying SSA. Kelly's index is greater than 1 in about 10 locations, indicating water which is unsuitable for irrigation use.

Sodium percent is greater than 20 in most locations in SSA (Table 15). The high rates of sodium indicate the absence of ion exchange reaction between Ca^{2+} and Na^{2+}. Wilcox plot indicates that most of the groundwater sources in SSA are suitable for irrigation use (Fig. 16). However, some parts of Na^{+} in groundwater aquifers across SSA were not derived from silicate weathering, because the molar ratio is greater than 1 in most locations. Therefore, groundwater in SSA is not deficient in $Mg^{2+}+Ca^{2+}$. As a result, groundwater sources may be hard in most parts of the continent. Magnesium hazard is less than 50 in most locations.

Conclusion

The literature is unanimous on the importance of evaluation and understanding of the hydrochemical composition of groundwater under different environments. This study reveals that:

1. The concentrations of Fe^{3+}, Zn^{2+}, Mg^{2+}, Na^{+}, PO_4^{3-}, and SO_4^{2-} are above World Health Organization (2011) and National Standard for Drinking Water Quality (2007) reference guidelines. Groundwater in the study area is acidic to alkaline in nature;
2. There is a significant difference in concentrations of temperature, pH, EC, hardness, Na^{+}, Zn^{2+}, Mg^{2+}, PO_4^{3-}, Cl^{-}, HCO_3^{-}, SO_4^{2-}, and NO_3^{-} between shallow and deep groundwater sources;
3. Groundwater classification using TDS showed that water sources are suitable for drinking and irrigation use;
4. Groundwater classification base on hardness showed that most of the groundwater sources are moderately hard;
5. Groundwater classification based on EC showed that most of the water sources fall in excellent class. The relatively low EC levels in the study area are consequent of low TDS, which is generally low in Sokoto Basin;
6. Groundwater classification based on chloride revealed that most of the water samples fall fresh class, but most groundwater sources fall in severe class based on NO_3^{-} classification;
7. Evaluation of geochemical faces showed that groundwater composition is controlled by rock weathering, even though little inputs were derived from anthropogenic sources. This was further confirmed by the Gibbs model;
8. Result of Na+/Cl- molar ratio indicates that most of the sampling locations have molar ration greater than 1, which suggests that some parts of Na^{+} were derived from silicate weathering;
9. Most groundwater samples have positive Scholler index, suggesting overall base exchange reactions in the underlying aquifer;
10. Groundwater classification based on Piper diagram revealed two types of faces: Ca–Mg–HCO_3 and Ca–Mg–SO_4–Cl;
11. Significant correlations between TDS and Cl^{-}, and positive correlation between TDS and SO_4 in shallow groundwater suggest input from anthropogenic sources;
12. Groundwater evaluation using PCA, showed water sources are more influenced by rock mineral as compared to anthropogenic inputs;
13. Groundwater analysis using HCA showed that Group 1 and 2 can be related to natural geogenic processes as it corresponds to ions of natural geogenic origin. Group 3 can be related to both anthropogenic (notably NO_3^{-} pollution) and rock weathering;
14. Most of the groundwater samples derived from deep aquifer have SAR value > 18, whereas, all the groundwater samples from shallow aquifer have SAR < 18;
15. Base on Na^{+}% samples from shallow groundwater fall in very low to high sodium class, whereas, deep groundwater samples vary between good to excellent;
16. Based on Doneen's chart, permeability indices are excellent in deep groundwater, whereas, in shallow groundwater, PI indices are affected by low salinity water type;
17. The possible reasons for higher KI values in shallow groundwater need to be revealed as it presents a serious environmental problem; based on mean MAR, shallow groundwater in the study area is unfit for irrigation use;
18. Many sources of groundwater in SSA are acidic in composition; Scholler and Versluy's indices suggest an overall base exchange reaction in aquifers underlying SSA; and
19. Kelly's index is less than 1 in most locations in SSA, indicating water which is suitable for irrigation use. MAR is less than 50 in most locations.

Despite the significant difference in water quality parameters and chemical indices, evaluation of shallow and deep groundwater in the study area indicates that groundwater composition is more a product of rock weathering than anthropogenic inputs.

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