ORIGINAL ARTICLE

Hydrochemistry and stable isotopes (^{18}O and ^{2}H) characteristics of groundwater in Lokoja and its environs, central Nigeria

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Abstract

To determine hydrochemical and stable isotope characteristics of groundwater in Lokoja and its environs, 39 samples were collected, analyzed and interpreted. The results of the analyses revealed that pH of the water samples of the area ranged from 5.9 to 8.4 indicating neutral water except few slightly acidic samples. TDS varied between 44 and 1273 mg/L but were generally < 1000 mg/L suggesting fresh water and total hardness of 1.2–360 mg/L classified the water ranging from 'soft' to 'very hard water'. The concentrations of the major cations are in the order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ with average values of 48.5 mg/L, 29.4 mg/L, 15.3 mg/L and 13.0 mg/L, respectively; while that of anions are $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ with average values of 143.3 mg/L, 59.5 mg/L, 35.8 mg/L and 18.3 mg/L, respectively. Groundwater is generally suitable for drinking purposes as most samples fell within the "excellent water" and "good water" categories, while the quality for irrigation ranged from suitable to unsuitable. Five hydrochemical facies were determined: $CaHCO_3$, mixed $CaMgCl$, $NaCl$, $CaNaHCO_3$ and $NaHCO_3$ water types. Several processes such as reverse ion exchange, weathering of silicate minerals and rock–water interactions were main mechanisms controlling ionic constituents of groundwater of the study area. In addition, the results of stable isotopes analyses showed considerable variations, ranging between -3.9 and -1.2% with an average of -2.7% for $\delta^{18}O$ and -23.9 and 11.7% with a mean of 16.9% for δ^2H. The plot of δ^2H vs $\delta^{18}O$ of groundwater system in the study area along global meteoritic water line indicated recent meteoritic recharge. However, all of the samples plotted deviated appreciable from global MWL except a sample from sandstone bedrock that was plotted along the line as defined by this equation: $\delta D = 8 \ \delta^{18}O + 10$. The deviation was a consequence of kinetic evaporative effect as well as rock–water interaction and carbondioxide exchange effects.

Keywords Hydrochemistry · Stable isotopes · Groundwater · Lokoja · Nigeria

Introduction

Groundwater is the most reliable source of fresh water for many communities in Lokoja as government pipe-borne supply system is usually erratic and does not extend across many parts of these communities. Abundant surface water bodies in the area are prone to anthropogenic contamination. The cost of treatment to make it safe for various uses

is usually high. This source of water is readily renewable as the area receives sufficient precipitation which recharges the shallow aquifers. The area is a basement complex–sedimentary transition zone where both crystalline and sedimentary rocks are represented and the aquiferous units are mainly weathered regolith, fractured zone and medium to coarse grained sediments. The aquifers are extensively exploited owing to growing population, increasing industrialization and agricultural activities. The quality of groundwater as determined by its chemical and biological constituents, its dissolved solid contents (TDS) and temperature is of great importance in determining the suitability of a particular groundwater for a certain use (public water supply, irrigation, industrial application, domestic use, etc.). In fact, the quality of groundwater is the resultant of all processes and reactions that have acted on the water from the moment it condensed in the atmosphere to the time it is discharged by

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a well or spring (Todd 2005). There is constant interaction between groundwater and the subsurface medium in which it stagnates or circulates leading to equilibrium between the composition of the soil/rock and that of the water. The chemical composition of groundwater circulating within the rocks is controlled by many factors including the composition of precipitation/recharge, the mineralogy of aquifers, climate, topography and anthropogenic activities (Edmunds 1992). The interaction of groundwater with these factors leads to the formation of differing hydrochemical facies which can be correlated with location, geology, climate and topography.

Stable isotopes have been used in various hydrogeological investigations especially in respect of groundwater recharge and characterization of groundwater flow (Fritz and Fontes 1980; Moser and Rauert 1980). The stable isotopes have the advantage of not only being components of water molecule itself, but also they are inert in the subsurface, and hence serve as ideal tracer in hydrogeochemical evaluation of groundwater systems (Tijani and Abimbola 2003). The application of stable isotope of ^{18}O and ^{2}H based on the principle of thermodynamic equilibrium (Drever 1982) provides information on isotope exchange processes and flow direction. It indicates the direction in which isotope exchanges and groundwater mineralization are taking place and it is the basis for understanding the rate of rock–water interaction involving isotope exchanges in the flow direction (Furi 2011). In addition, water molecule with the least important energy barrier for phase change will evaporate preferentially during evaporation and an increasingly enriched ^{18}O and ^{2}H results from the residual water. This study will provide valuable information about the recharge and hydrochemistry of groundwater of Lokoja which could be useful in understanding the groundwater origin, factors influencing the chemical composition, and distribution of physicochemical properties.

The study area

Location and climate

Lokoja metropolis is the capital of Kogi state in north-central Nigeria. The area lies betweenlatitudes 6°39′–6°46′N and longitude 7°44′–7°52′E (Fig. 1). It is the segment of the basement complex of southwestern Nigeria and part of the Lokoja sub-basin of the Mid-Niger sedimentary basin. The area is characterized by undulating topography with limited flat terrains with elevation ranging from 30 to 400 m above sea level. Mount Patti is the prominent hill in the area and it is capped by indurated and ferruginous sandstones. It is a linear NW–SE ridge parallel to the nearby Agbaja plateau with an altitude of about 400 m both following the basin trend and perpendicular to the main axis of the Benue trough (Omada et al. 2009).

The climate condition of Lokoja is the humid tropical of Nigeria (Iwena 2012) which is characterized by two distinct seasons; the wet and the dry seasons. The wet season lasts for 7 months from April to October with two peak periods in July and September while the dry season last for 5 months from November to March. Average annual precipitation ranges from 1000 to 1500 mm (Meteorological Department, Federal Ministry of Aviation 2007). Daily temperatures in the area vary with the seasons. Minimum average temperatures of about 25–27 °C are recorded mainly during the wet season, while maximum temperature of about 35 °C is experienced during the dry season. Relative humidity in the area ranges from 55 to 65% during the dry season and from 70 to 80% during the wet season (Iloeje 1980). The vegetation of the area is Guinea savanna; it is characterized by the presence of tall grasses and scattered short deciduous trees.

Geology and hydrogeology

The study area is largely underlain by rocks that belong to the precambrian basement complex of southwestern Nigeria. Part of the area is, however, underlain by Cretaceous sediments of the southern Bida basin (Fig. 2). The basement complex rocks comprise migmatite–biotite gneisses and granite with quartz and pegmatite veins as minor intrusives. It was noted from field observation that the mineral contents of these rocks are biotite, quartz and feldspar. Structural features present in these rocks include fractures, foliations, joints and folds. The sedimentary part (southern Bida basin) consists of Lokoja formation which is unconformably overlying the basement complex and the lithologic unit ranges from conglomerates, coarse to fine grained sandstones, siltstones and claystones. The sandstone units are frequently cross-stratified, generally poorly sorted and composed mainly of quartz and feldspar, and are, thus, texturally and mineralogically immature (Ojoh 1992).

Weathered basement rocks and thick saprolite form the basement aquifers. Medium-coarse Cretaceous sediments and recent alluvium constitute the shallow aquifer in sedimentary portion of the area. Groundwater within the alluvial aquifer occurs largely under water table conditions. At outcrops and in some places, it is confined by interstitial clay. The groundwater is recharged by precipitation and direct infiltration of River Niger, River Benue and River Mimi. The groundwater occurrence in the basement area of Lokoja is through the development of secondary porosities or permeabilities as a result of fracturing, jointing, shearing and deep weathering (Oyinloye and Ademilua 2005).
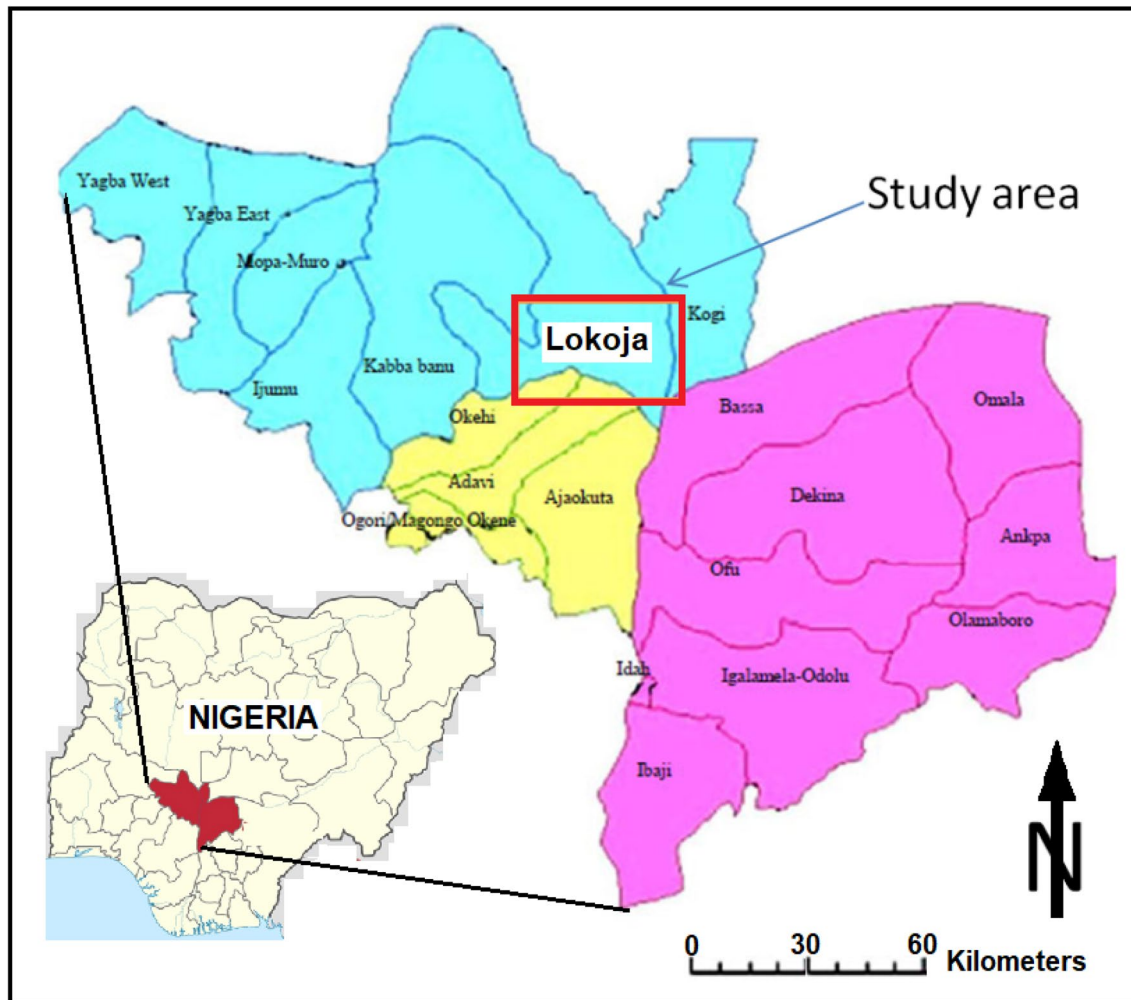
Fig. 1 Location map of the study area

Sampling and analytical procedures

The groundwater samples were collected at 39 locations from hand-dug wells for hydrochemical and stable isotopes analyses during rainy month of June, 2016. At each location, a pair of sample was collected; one for cations and the second for anions analysis. The samples for cations were acidified to pH of < 2.0 with concentrated nitric acid to maintain stability of the oxidation state of the various elements in solution and to prevent precipitation. In addition, another 39 samples were collected for stable isotope analyses of water. The representative water samples were collected in pre-cleaned, 120-mL HDPE plastic bottles that have been rinsed with sample water three times prior to use based on the methods described by APHA (1995) and the precise location of the sample points were determined in the field using global positioning system (GPS) Germain etress 20. Parameters such as temperature, pH, conductivity and total dissolved solids (TDS) were determined at the wellhead using a digital conductivity meter (Hanna HI9861-3) that was calibrated with buffer solutions having pH values of 4 and 7. In situ measurement of these parameters during the sampling operation is necessary to obtain on-the-spot physicochemical data which may not be accurately determined in the laboratory due to possible change during transportation (Tijani and Abimbola 2003).

The hydrochemical analysis for major cations, anions and stable isotopes was analyzed at Water Science Laboratory, University of Nebraska, Lincoln USA. The concentration of major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were analyzed through atomic absorption spectrophotometry (AAS) using a Perkin Elmer Analyst 400 spectrophotometer, while that of major anions (NO_3^-, SO_4^{2-} and Cl^-) were determined by ion chromatography (IC) on a Dionex ICX-90. Alkalinity (primarily as HCO_3^-) was measured by potentiometric titration with standardized sulfuric acid (APHA (American Public Health Association) 1995). Stable isotopes (^{18}O and ^2H) of the samples were determined using mass

Fig. 2 Geology map of the study area
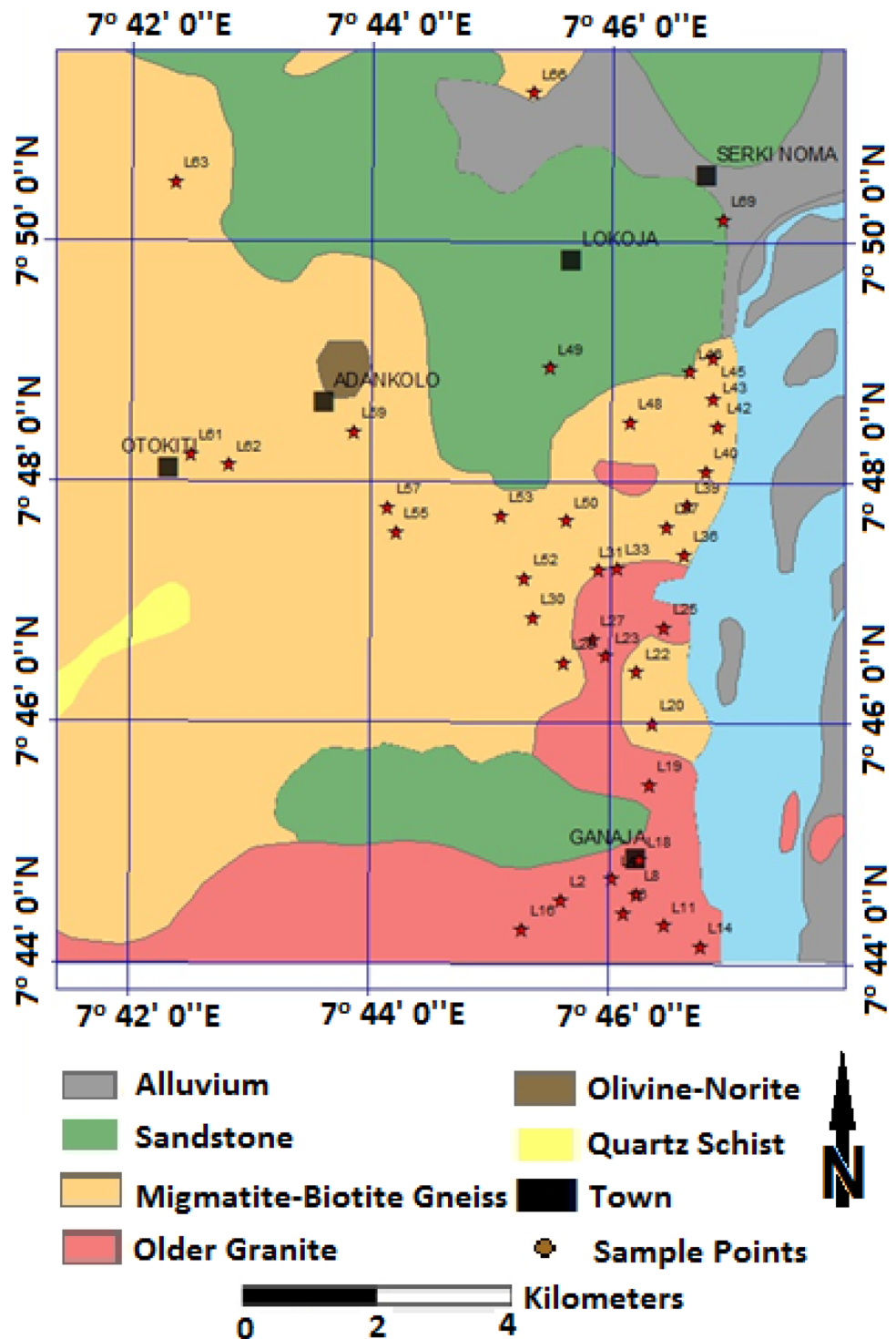
spectrometry method. Deuterium (D) content was determined on a Eurovector EA furnace packed with chromium set at 1040 °C and interfaced with a ISoprime (GV Instruments, Manchester, UK) continuous flow mass spectrometer (Morrison et al. 2001). Helium carried the resultant hydrogen through a gas chromatograph to separate the carbon monoxide peak from H_2 peak. Oxygen isotope composition

of water was measured after equilibration with 3% carbondioxide (Epstein and Mayeda 1953) measured on a IsoPrep inlet interfaced with a GV2003 continuous flow isotope ratio mass spectrometer (GV instruments, Manchester, UK). After 24 h of equilibration in 12-mL Exetainer vials, headspace gas was autoinjected through a sample loop through a gas chromatograph column to the mass spectrometer where the

carbon and oxygen isotope ratios were determined at masses 44, 45, 46. Both hydrogen and oxygen isotope ratios were measured in triplicate and standards run with each batch of samples. All calibration used International Atomic Energy (IAEA) or US Geological Survey (USGS) reference standards V-SMOW, GISP and SLAP. The measured precision of the deuterium analysis was 0.8 per mil, while the precision of the oxygen isotope analysis was 0.2 per mil.

The suitability of groundwater of the study area for human consumption was assessed using water quality index (WQI) technique. WQI provides the composite influence of individual water quality parameters on the overall quality of water (Mitra and ASABE Member 1998). The WQI for groundwater samples collected and analyzed was evaluated based on method described by Vasanthavigar et al. (2010) and WHO (2006) guidelines for drinking water quality were employed in the calculation of WQI.

Indicators of irrigation quality were determined using sodium adsorption ratio (SAR) and sodium percentage % Na using mathematical relationships as follows:

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}} \qquad (1)$$

$$\%Na = \frac{(Na + K)100}{Ca + Mg + Na + K} \qquad (2)$$

Results and discussion

Hydrochemical characteristics

The physicochemical results of groundwater analyses for this study are presented in Table 1. The pH measured varied from 5.9 to 8.4 and majority of the samples were within a neutral range of 6.5–8.5 except samples L2, L28 and L69 that were less than 6.5 (slightly acidic). The EC ranged from 70 to 1730 μS/cm with an average of 310 μS/cm. TDS varied between 55 and 1273 mg/L with an average of 564 mg/L. Baring values for sample locations L11, L45 and L61 with slightly high TDS, all other samples were classified as fresh (TDS < 1000 mg/L (Hem 1985). The relatively low TDS in the study area indicate mild mineralized groundwater system, low residence time and rock–water interaction (Talabi and Tijani 2012). The total hardness (as $CaCO_3$) of groundwater samples varied from 1.21 to 360 mg/L with an average of 136 mg/L. Soft water represent 15.5% of the sample and most samples (51.3%) were categorized as moderately hard; while 28.2% and 5.1% were classified hard and very hard, respectively (Sawyer and McCarty 1967). Higher values of the total hardness are likely related to lithology of the aquifer matrix, which is mostly formed of weathering products of the surrounding basic and intermediate igneous and metamorphic rocks. These rocks are rich in calcium and magnesium which upon dissolution yield high concentrations of calcium and magnesium that increase total hardness of the groundwater (El-Ahamdi and El-Fiky 2009). The major cations concentrations were generally low and the order of concentration was $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ with average values of 48.5 mg/L, 29.4 mg/L, 15.3 mg/L and 13.0 mg/L, respectively; while that of anions was $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ order with average values of 143.3 mg/L, 59.5 mg/L, 35.8 mg/L and 18.3 mg/L. The results showed that all values for cations were within the WHO (2006) recommended maximum permissible limits for drinking water. Whereas, eight samples for HCO_3^- and one sample for NO_3^- had values above the recommended limits.

Principal component analysis (PCA) was used to statistically reduce the measured physical parameters, major anions and cations in water samples to a smaller number of variables and characterize the groundwater data (Qian et al. 1994). PCA when applied to chemical data helped to establish the different processes that control water chemistry and sources of variation in the data. Twelve input (parameters) in 39 groundwater samples were used for the principal component analysis and four principal components (PCs) were extracted which tested 88% of the total variance. The numbers of significant PCs for interpretation were selected on the basis of the Kaisier criterion with Eigen value higher than one and a total explained percentage variation equal to or greater than 70%. The factor loading, latent root, Eigen value and percentage variation of PC are presented in Table 2. The selection of parameters in each PC was based on their latent roots PC 1 = 6.5, PC 2 = 2.064, PC 2 = 1.209 and PC 4 = 0.822. The first PC (PC 1) explained 54% of the total sample variance and had loading for Ca^{2+}, Mg^{2+}, HCO_3^-, NO_3^-, Cl^-, EC, K^+, Na^+, TDS and TH. PC analysis suggests that much of the chloride (Cl^-) may be anthropogenic and potentially released from the leaching of upper soil layers, which receive wastewater and sewage from domestic activities. Calcium (Ca^{2+}), Na^+, TDS and total hardness are assumed to be indicative of the natural processes and water–rock interaction. The second PC (PC 2) which explained 17.2% of the total variance had high loading for HCO_3^-, Mg^{2+} and TH. PC 3 and PC 4 accounted for 10.1% and 6.85%, respectively, of the total variance of the data set. PC 3 had loading for Cl^-, while PC 4 had loading for K^+ and Na^+.

Groundwater quality for drinking purposes

The calculated WQI values were used to rate groundwater quality for drinking purposes in the study area based on water type classification (Vasanthavigar et al. 2010). The values showed that 59.0% of the groundwater

Table 1 Physicochemical parameters of groundwater in the study area

ID	PH	EC	TDS	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	NO_3^-	Cl^-	SO_4^{2-}
L2	5.9	350	254	35	7.6	3.9	18.9	13.8	35.5	15.8	15.1	20.6
L4	8.3	680	470	114	32.0	8.2	37.1	8.0	53.3	33.2	41.9	33.4
L6	7.5	630	447	92.2	15.9	12.8	45.2	6.6	77.3	12.0	80.8	14.0
L8	7.6	1020	721	212	58.9	15.9	57.9	11.8	96.4	40.8	95.2	40.6
L11	6.7	1570	1148	309	60.8	38.3	109.2	23.0	284.2	23.4	151.5	62.7
L14	7.1	780	586	208	68.4	9.1	30.7	12.8	207.9	9.3	62.1	38.3
L16	8.1	750	541	133	24.3	17.7	59.7	22.6	309.5	5.5	4.6	26.8
L18	7.1	900	572	90.1	19.2	10.3	44.5	8.3	88.8	16.0	47.3	45.2
L19	7.1	570	410	112	30.5	8.8	35.7	10.8	104	15.6	37.0	40.2
L20	8	580	422	121	20.7	17.0	38.6	2.6	230.8	0.2	27.8	25.6
L22	7.6	440	274	87.6	15.0	12.2	15.0	9.4	121.7	2.3	8.2	31.5
L23	7.4	600	428	99.9	21.9	11.0	39.2	7.3	94	16.6	37.1	50.0
L25	7	710	508	150	32.9	16.6	33.2	6.5	102.7	25.7	49.1	42.1
L27	7.7	830	594	191	44.1	19.6	31.4	1.8	271.3	3.4	39.3	49.6
L28	6.3	430	306	25.9	5.8	2.8	29.4	4.3	34.2	18.3	26.9	6.0
L30	7.4	760	549	193	42.4	21.2	31.5	1.5	254.9	1.8	37.5	55.9
L31	7.8	730	528	131	34.4	10.9	52.5	5.8	235.8	10.2	43.9	43.8
L33	7.3	880	637	180	49.6	13.7	48.6	10.8	195.3	19.7	53.5	54.5
L36	7.8	1250	905	197	46.3	19.8	91.7	28.4	121.9	55.4	98.4	74.5
L37	8.4	1050	753	136	34.8	11.8	32.3	13.2	154.7	25.9	73.9	62.8
L39	7	750	542	140	35.2	12.7	43.9	16.0	96.5	31.6	48.9	49.0
L40	7.3	810	568	184	21.4	32.0	42.4	10.6	319.7	0.5	34.5	7.8
L42	6.9	800	569	118	26.4	12.6	47.6	21.4	66.1	33.2	73.0	43.0
L43	7.2	1060	767	232	48.1	27.2	55.4	14.4	251.1	8.9	128.7	36.6
L45	6.7	1730	1273	176	41.1	17.9	157.7	60.7	111.7	42.2	191.7	70.5
L46	7.8	1320	960	142	37.5	11.7	110.2	57.2	114.2	34.5	139.8	37.9
L48	6	580	417	82.7	23.1	6.1	34.3	15.6	28	25.2	43.8	15.1
L49	7.6	70	55	1.21	0.1	0.2	3.4	1.9	12.7	0.0	1.1	2.0
L50	6.6	700	505	124	24.6	15.2	42.6	2.1	98.9	21.4	51.5	40.3
L52	6.8	810	503	167	21.6	27.5	36.4	5.0	213.1	7.7	42.4	41.3
L53	6.8	640	464	96.4	12.1	16.2	54.0	2.7	175.1	13.4	31.7	27.1
L55	7	950	687	171	51.6	10.3	63.5	18.8	119.2	29.2	75.6	51.5
L57	7.2	550	396	74.7	14.0	9.7	34.2	12.7	43.2	20.4	28.2	24.8
L59	6.9	400	293	59.2	2.7	12.8	20.3	7.3	167.5	0.8	7.4	5.3
L61	7.1	1580	1150	360	50.2	57.1	74.9	15.1	254.9	24.8	180.1	52.4
L62	8	700	487	103	22.6	11.4	50.5	6.6	10.3	33.9	55.9	30.2
L63	6.8	510	362	75.1	12.0	11.0	31.9	4.8	183.5	1.8	17.8	5.5
L66	6.7	690	500	124	20.0	17.9	47.7	6.5	190.3	4.3	75.7	16.5
L69	6.3	680	455	62.9	15.1	6.1	58.3	19.0	56.8	28.1	62.9	22.3

samples represents "excellent water", 33.3% represents "good water" and 7.7% of "poor water" (Table 3). The majority of the water samples represent "excellent water" and "good water" categories. This confirms the earlier assertion that the groundwater in the study area is mildly mineralized with limited migratory history. It was also observed that "poor water quality" recorded in the eastern part of the study area is a reflection of poor hygienic practice in this populated area, and hence the anthropogenic contamination.

Groundwater quality for irrigation purposes

Sodium adsorption ratio (SAR) and sodium percentage (% Na) were employed for the evaluation of groundwater quality for irrigation purposes. SAR can show the degree to which irrigation water tends to participate in cation-exchange reaction in the soil (Jafar et al. 2013). When sodium replaces adsorbed calcium and magnesium, it can potentially damage the soil structure by enhancing compaction, thereby decreasing the soil permeability. The SAR classification (Table 4) shows that

Table 2 Factor loading of each variance

$n=12$	PC1	PC2	PC3	PC4
Ca^{2+}	0.32012	0.00796	−0.1353	−0.48385
Cl^-	0.30981	−0.04624	0.36305	−0.05321
EC	0.38479	−0.03674	0.04079	0.08211
HCO_3^-	0.19256	0.5509	−0.11743	0.2078
K^+	0.21282	−0.35538	−0.07172	0.53474
Mg^{2+}	0.25255	0.43673	0.18085	0.18604
NO_3^-	0.21925	−0.51614	0.00491	−0.12765
Na^+	0.32205	−0.1722	0.0648	0.33647
SO_4^{2+}	0.29016	−0.08059	−0.32027	−0.42036
TDS	0.38612	−0.04237	0.03671	0.08659
TH	0.34553	0.26372	0.02465	−0.18562
pH	0.0535	0.04519	−0.82936	0.21076
Latent roots	6.5	2.064	1.209	0.822
% Variation	54.17	17.2	10.07	6.85

n number of parameters

69.2% of the groundwater samples were suitable for irrigation purposes; while 20.8% of the samples were unsuitable. In Lokoja, % Na ranges from "good" to "unsuitable" with "permissible" and "doubtful" as dominant water categories (Table 4). High % Na in irrigation water with respect to Ca^{2+}, Mg^{2+} and K^+ causes deflocculation and impairment of soil permeability (Glover 1996).

Hydrochemical facies

To identify the groundwater types and percentage composition of different ions, a Piper trilinear diagram (Piper 1944) was plotted from hydrochemical data and is presented in Fig. 3. The cations and anions were plotted in the left and the right triangles as single points. These points were then projected into the central diamond-shaped area parallel to the upper edges of the central area. The points in the diamond-shaped area represent specific hydrochemical facies and water types. For each water sample, a single point was obtained in the diamond-shaped area, which represents a water type. In this study, majority of the groundwater samples were classified into $CaHCO_3$ (33.3%), mixed CaMgCl (38.5%), and NaCl (23.1%) water types while 2.6% each of the samples belong to mixed $CaNaHCO_3$ and $NaHCO_3$ water types and no samples was represented in CaCl water types. The presence of different hydrochemical facies is related to the diversity of geology and geochemical processes in the study area.

Mechanism controlling ionic constituent of groundwater

A broad range of different elements can become dissolved in groundwater as a result of interactions with the atmosphere,

Table 3 Water quality

Sample ID	WQI	Type of water
L2	22	Excellent water
L4	48	Excellent water
L6	39	Excellent water
L8	74	Good water
L11	103	Poor water
L14	56	Good water
L16	46	Excellent water
L18	45	Excellent water
L19	40	Excellent water
L20	36	Excellent water
L22	24	Excellent water
L23	40	Excellent water
L25	51	Good water
L27	53	Good water
L28	25	Excellent water
L30	50	Good water
L31	48	Excellent water
L33	60	Good water
L36	90	Good water
L37	62	Good water
L39	55	Good water
L40	49	Excellent water
L42	55	Good water
L43	70	Good water
L45	105	Poor water
L46	80	Good water
L48	39	Excellent water
L49	03	Excellent water
L50	47	Excellent water
L52	47	Excellent water
L53	41	Excellent water
L55	65	Good water
L57	35	Excellentwater
L59	22	Excellent water
L61	106	Poor water
L62	48	Excellent water
L63	28	Excellent water
L66	43	Excellent water
L69	42	Excellent water

the surficial environment, soil and bedrock. Groundwater tend to have much higher concentrations of most constituents than do surface water, and deep groundwater that have been in contact with rock for a long time tend to have higher concentrations than shallow and or young waters. In order to evaluate the mechanism controlling groundwater chemistry in Lokoja and its environs, bivariate plots were used to investigate silicate weathering, carbonate dissolution and evaporate dissolution (Halim et al. 2010; Srinivasamoorthy

Table 4 Suitability of groundwater for irrigation based on % Na (after Janardhana 2007) and SAR (after Richard 1954)

Quality parameter	Range of values	Description	Number of samples	Percentage of samples (%)
SAR	< 2.0	Suitable	27	69.2
	> 2.0	Unsuitable	12	20.8
% Na	< 20	Excellent	0	0
	20–40	Good	3	7.7
	40–60	Permissible	19	48.7
	60–80	Doubtful	16	41.0
	> 80	Unsuitable	1	2.6
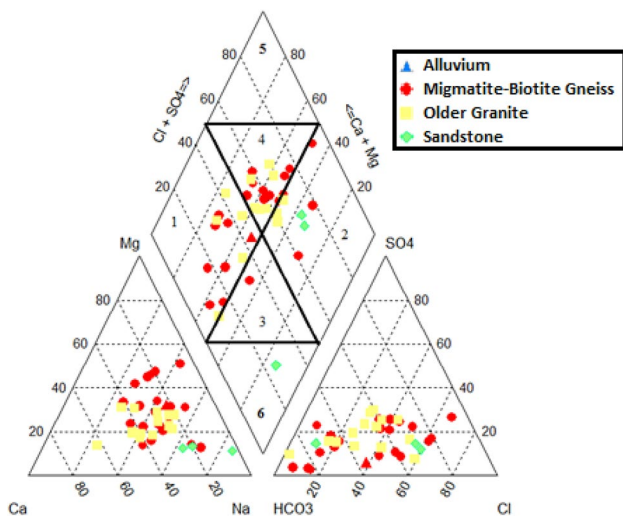
Fig. 3 Piper diagram for Lokoja

Fig. 4 Plot of $Ca^{2+} + Mg^{2+}$ versus $HCO_3^- + SO_4^{2-}$
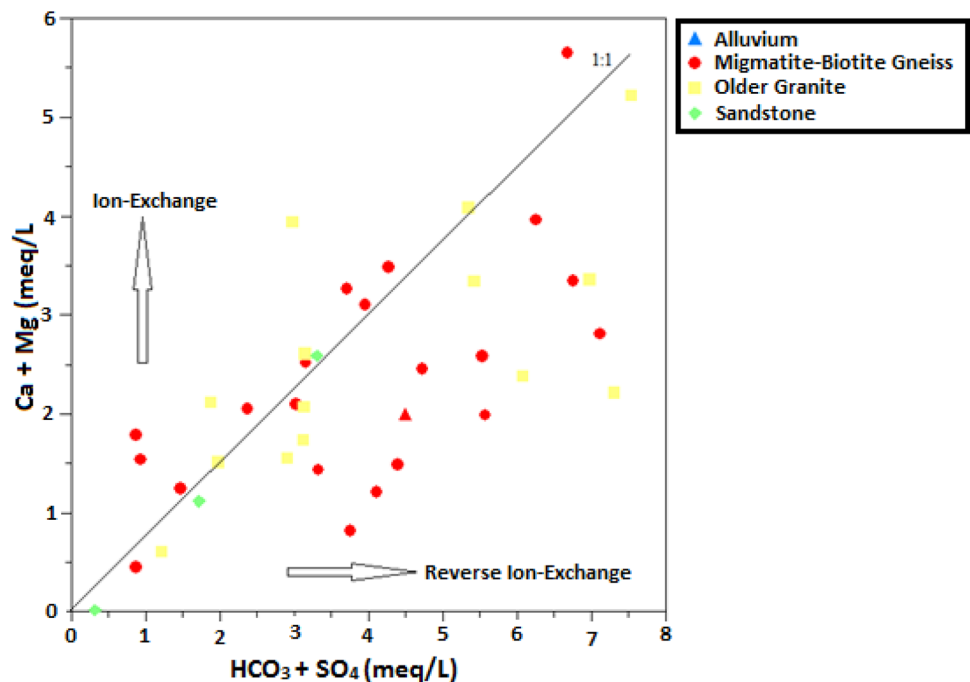
et al. 2011; Hallouche et al. 2017). Bivariate plots of major ions provide additional information about the groundwater chemistry of the study area. The relative importance of weathering processes and ion exchange were examined using a plot of $Ca^{2+} + Mg^{2+}$ versus $HCO_3^- + SO_4^{2-}$ (Fig. 4). A stoichiometry of $Ca^{2+} + Mg^{2+}$ to $HCO_3^- + SO_4^{2-}$ should exist if Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- are influenced by dissolution of dolomite, gypsum and calcite (McLean et al. 2000). Excess of $Ca^{2+} + Mg^{2+}$ over $SO_4^{2-} + HCO_3^-$ results in ion exchange and the points on the plot are shifted to the left and if the points shift to the right due to large excess of $Ca^{2+} + Mg^{2+}$ over $SO_4^{2-} + HCO_3^-$, the process is reverse ion exchange. Twenty-four groundwater samples representing 61.5% of the total samples scattered below the 1:1 line indicating reverse ion exchange, while 38.5% (15 samples) were scattered above the line suggesting an ion exchange and in this process, Na^+ and K^+ must balance part of the $HCO_3^- + SO_4^{2-}$. The plot of alkaline earth ions $Ca^{2+} + Mg^{2+}$ versus HCO_3^- (Fig. 5) showed that samples were scattered along 1:1 equiline. Evaluation of the slope of the plot indicated that carbonate minerals and silicate weathering were responsible for HCO_3^- (Srinivasamoorthy et al. 2011).

The Ca^{2+} versus HCO_3^- plot (Fig. 6) showed that Ca:HCO_3 ratio (0.20) is an indicator of simple dissolution of carbonate (Zhang et al. 1995). The exchange of calcium and magnesium in water by sodium in clay, enrichment of HCO_3^- from silicate weathering and cation exchange were probably responsible for the low molar ratio (< 0.5) in groundwater (Drever 1997). Groundwater chemistry especially in hard rock aquifers is controlled by geochemical processes and key of which is silicate weathering (Kumar

Fig. 5 Plot of $Ca^{2+} + Mg^{2+}$ versus HCO_3^-

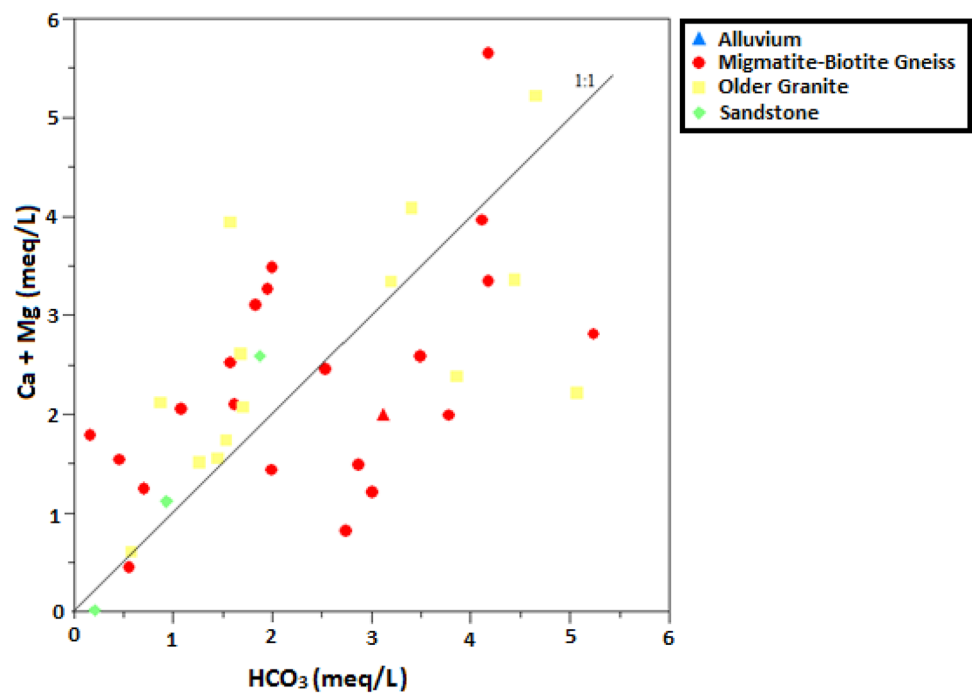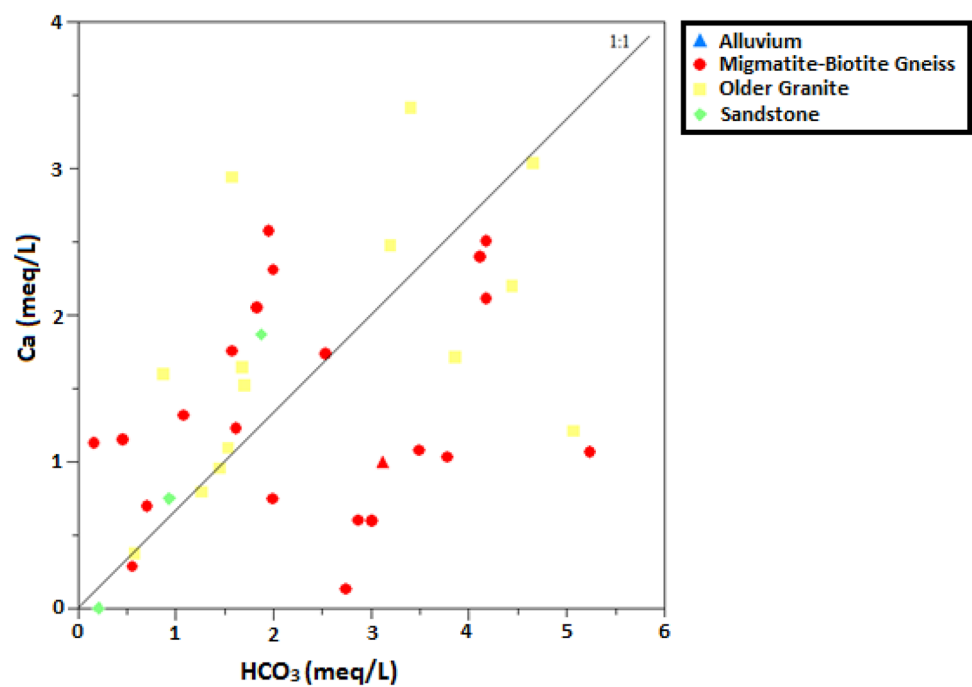**Fig. 6** Plot of Ca^{2+} versus HCO_3^-

et al. 2006). The ratio estimate between $Na^+ + K^+$ and total cations (TZ) can be a guide to understanding silicate weathering. The majority of the samples were plotted near the equiline (Fig. 7) and Na + K:TZ ratio of 0.6 indicates the involvement of silicate weathering in the geochemical processes, which contributes mainly sodium and potassium ions to the groundwater (Stallard and Edmond 1983).

Results of ^{18}O and ^2H isotopes

Isotope hydrological methods have been employed in various hydrogeological investigations especially in respect of groundwater age dating and characterization of groundwater system (Fritz and Fontes 1980; Moser and

Fig. 7 Plot of Na$^+$ + K$^+$ versus TZ
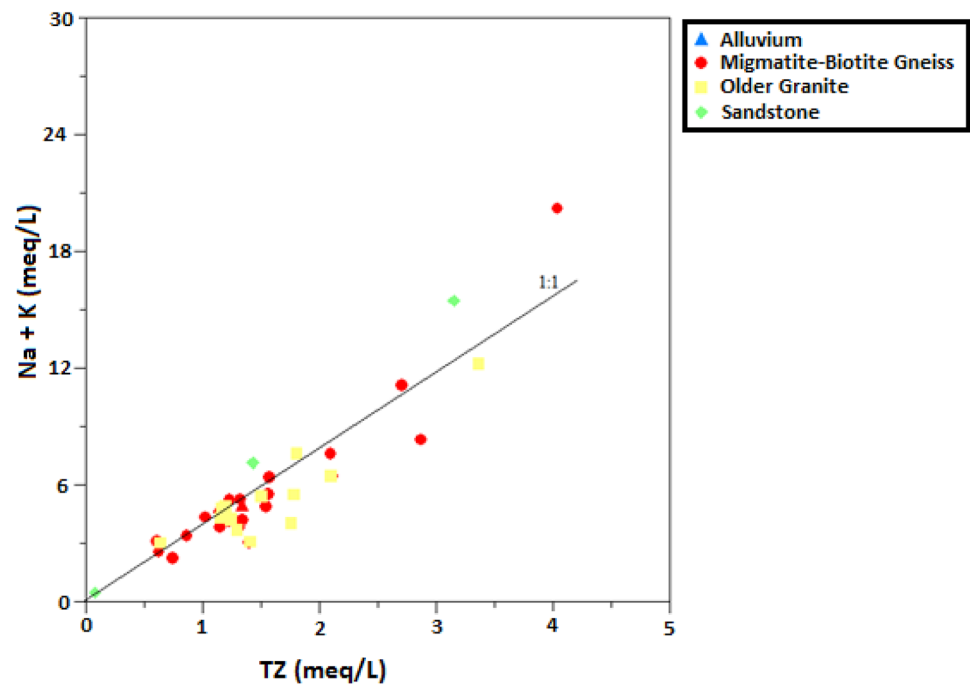
Rauert 1980). However, the use of stable isotopes have the advantage of not only being components of water molecule itself, but also they are inert in the subsurface, and hence serve as ideal tracer in hydrogeochemical evaluation of groundwater systems (Tijani and Abimbola 2003). The application of stable isotope of ^{18}O and ^{2}H based on the principle of thermodynamic equilibrium (Drever 1982) provides information on recharge, isotope exchange processes and flow direction; it indicates the direction in which isotope exchanges and groundwater mineralization are taking place. Further, it helps to establish the basis for understanding the rate of rock–water interaction and isotope exchange (Furi 2011).

For this study, a total of thirty-nine (39) groundwater samples were collected for stable isotope analysis. The results of the analyses are presented in Table 5. The results showed considerable variations, ranging between − 3.9 and − 1.2% with an average of − 2.7% for δ^{18}O and − 23.9% and 11.7% with a mean of 16.9% for δ^2H. The plot of δ^2H against δ^{18}O data for water samples provided the framework for identifying the isotope processes that were at work in the study area. Deviations in isotopic compositions away from the meteoric water line are a consequence of various processes: evaporation from open surfaces, exchange with rock minerals, H$_2$S exchange, hydration of silicate, CO$_2$ exchange and condensation. All of the samples plotted deviated appreciable from Global GMWL except a sample (L69) from sandstone bedrock that was plotted along the line (Fig. 8) as defined by this equation: δD = 8δ ^{18}O + 10. The plot of δD versus δ^{18}O shows that most of the groundwater samples were plotted on the right side of the meteoric water

line (Craig 1961) and the slope of 5.3 indicated an evaporative slope of between 4 and 6 in semi-arid areas (Giggenbach 1990; Clark and Fritz 1997; IAEA 2007a, b). This is also an indication of a predominantly local precipitation source of recharge with isotope enrichment as a result of intense kinetic evaporative effect as well as rock–water interaction and carbondioxide exchange effects. The evaporative effect was thought to be the consequence of intense temperature and heat usually experience in the study area.

The stable isotopes are conventionally transported in many groundwater systems because they represent the water molecule itself and not dissolved solutes in water, hence useful as tracers. Though water–rock interactions, exchange reactions, sorption, biotransformation significantly influence the solutes. A positive correlation between EC and δ^{18}O indicates groundwater undergoing evaporation (Gibrilla et al. 2010). The plot of EC versus δ^{18}O (Fig. 9) showed positive correlation coefficient of $r = 0.4$ which corroborate the earlier assertion that most of the samples plotted to the right of the GMWL and it is an indication of relatively higher evaporative effect before recharge. EC range of between 400 and 100 μS/cm and δ^{18}O of − 3.9% and − 1.2% indicated mild mineralization accompanied with enrichment of δ^{18}O.

Nitrate concentrations were quite variable and likely indicative of anthropogenic sources. Nitrate of groundwater is controlled by several factors especially by the water recharging the aquifer through the unsaturated zone and the lateral flow from the surrounding areas (Talabi and Tijani 2013). Soil organic nutrients and precipitation cannot be the main origins of NO$_3^−$ in shallow groundwater of the study area, since NO$_3^−$ concentration of most samples are

Table 5 Results of stable isotopes analysis in the study area

ID	$\delta^{18}O$	δD	d-excess
2B	− 3.9	− 22.4	8.8
4B	− 3.4	− 21.2	5.8
6B	− 2.3	− 19.3	− 1.1
8B	− 1.9	− 21.6	− 6.3
11B	− 2.1	− 15.4	1.1
14B	− 2.1	− 12.5	4.7
16B	− 3.6	− 12.9	16.2
18B	− 2.3	− 16.2	2.3
19B	− 2.2	− 14.0	3.4
20B	− 3.8	− 17.1	13.3
22B	− 1.4	− 11.8	− 0.4
23B	− 2.8	− 17.3	4.7
25B	− 2.1	− 16.0	0.4
27B	− 1.5	− 16.5	− 4.1
28B	− 3.2	− 18.3	7.5
30B	− 3.5	− 14.7	13.0
31B	− 1.7	− 16.0	− 2.4
33B	− 2.1	− 15.2	1.6
36B	− 1.2	− 15.6	− 6.1
37B	− 2.9	− 18.5	4.3
39B	− 2.2	− 16.6	1.4
40B	− 3.7	− 23.9	6.1
42B	− 2.7	− 17.9	3.8
43B	− 3.1	− 21.2	3.7
45B	− 2.2	− 16.4	1.3
46B	− 2.6	− 18.5	2.7
48B	− 2.4	− 18.1	1.1
49B	− 3.5	− 23.0	5.1
50B	− 1.8	− 16.9	-2.4
52B	− 2.9	− 17.5	5.6
53B	− 2.9	− 18.4	5.1
55B	− 3.0	− 17.5	6.7
57B	− 3.1	− 20.0	4.6
59B	− 3.5	− 14.8	13.5
61B	− 2.6	− 14.5	6.3
62B	− 2.2	− 11.7	6.3
63B	− 3.2	− 12.5	13.0
66B	− 3.5	− 14.8	13.1
69B	− 3.0	− 13.2	10.6
MIN	− 3.9	− 23.9	− 6.3
MAX	− 1.2	− 11.7	16.2
MEAN	− 2.7	− 16.9	4.5

much higher than the natural NO_3^- concentration of about 4.4 mg/L. Characterizing biogeochemical processes in groundwater is a key issue to understand the sources and behavior of NO_3^-. Microbial denitrification can decrease NO_3^- concentration and cause significant alterations of the isotopic composition of NO_3^-. There was week positive

correlation (0.4) between $\delta^{18}O$ and NO_3^- in shallow groundwater (Fig. 10). This indicates the higher extent of denitrification in the deep groundwater than that in the shallow groundwater. The correlation coefficient also showed that the wells were recharged by evaporated precipitation infiltrating through contaminated soil to the groundwater system. Plot of Cl and $\delta^{18}O$ (Fig. 11) showed two water types. The first water type (A) is the water samples plotted at $Cl^- > 140$ mg/L in which mild leaching of salts leads to increased salinization of groundwater. The second water type (B) are samples with chloride content < 100 mg/L showed a linear correlation between Cl and $\delta^{18}O$ values which indicated little leaching of salts hence low salinization.

Furthermore, deuterium-excess (d-excess) which is a measure of relative proportions of ^{18}O and ^2H in the water is defined as $d = \delta^2H - 8\delta^{18}O$ (Dansgaard 1964). It is an index of deviation from GMWL in which the value is usually close 10% for meteoritic waters on a global scale. In the study area, the calculated d-excess ranged between − 6.3 and 16.2% with an average of 4.5%. It was observed from Fig. 12 that the enrichment of $\delta^{18}O$ resulted in gradual decrease of d-excess, hence indicative of evaporative effects on the groundwater system. The negative d-excess values recorded in sample 6B (− 1.1), 8B (9 − 6.3), 22B (− 0.4), 27B (− 4.1), 31B (− 2.4) and 26b (− 6.1) were as a result partial evaporation of the samples, either as the precipitation falls from the cloud or during storage. However, the significant variation occurred in the d-excess values in this study and this can be attributed to evaporation from unsaturated zone during recharge as well as water–rock interaction and CO_2 exchange (Allison and Hughes 1983).

Conclusion

The analyses and interpretation of hydrochemical data indicated little or no anthropogenic contamination of groundwater and majority of the samples were within neutral of 6.5 − 8.5 pH baring few samples that were slightly acidic. The water ranged between moderately hard and hard, while values for total dissolved solids were generally < 1000 mg/L which suggested mild mineralized groundwater. Groundwater is generally suitable for drinking purposes as most samples fell within the excellent water and good water categories based on WQI; while the quality for irrigation based on SAR ranges from suitable to unsuitable and good to unsuitable based on % Na. The groundwater samples were classified into $CaHCO_3$, mixed CaMgCl, NaCl, $CaNaHCO_3$ and $NaHCO_3$ water types. The presence of these different hydrochemical facies is related to the diversity of geology in the study area. Reverse ion exchange, weathering of silicate minerals and rock–water interactions are the mechanism controlling

Fig. 8 Plot of ^{18}O vs. D of groundwater samples in Lokoja area

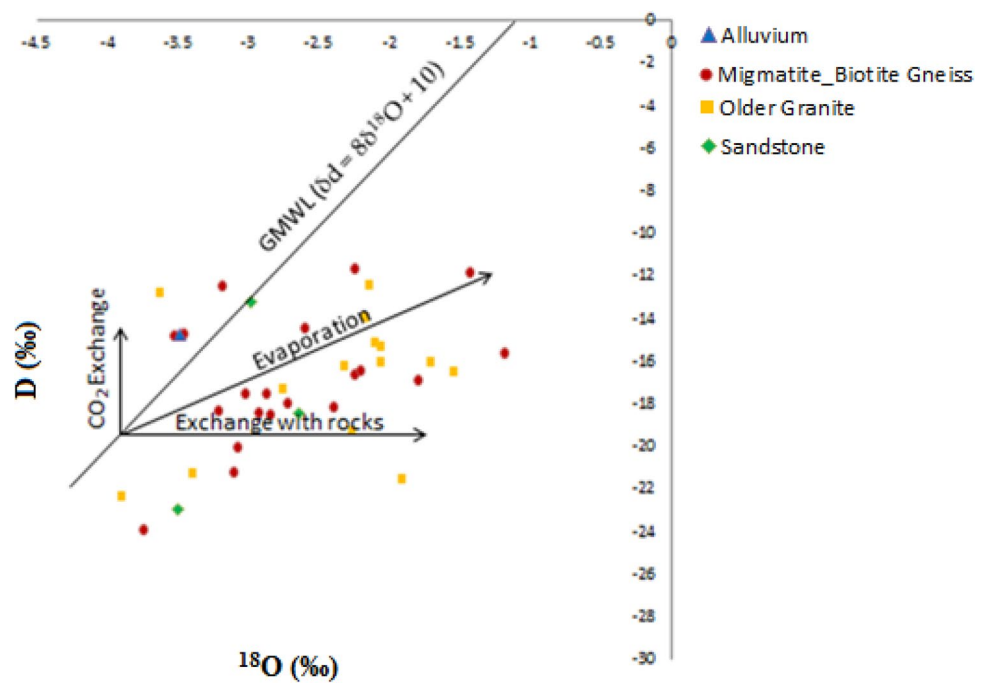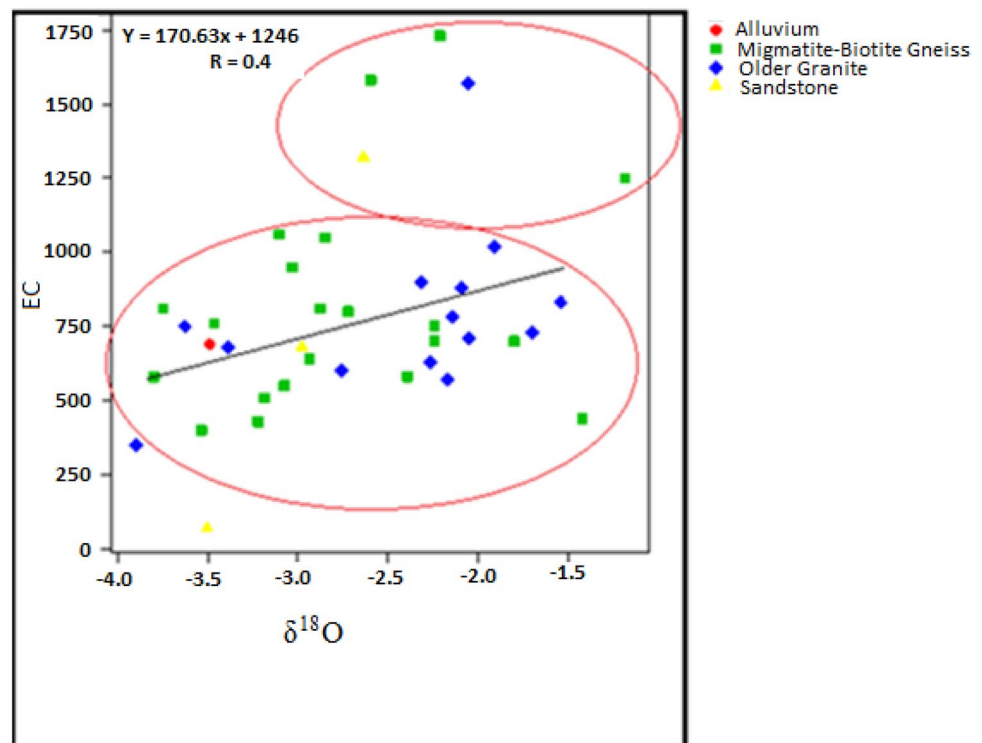**Fig. 9** Plot of EC vs. δ^{18}O of groundwater in the study area

ionic constituent of groundwater of the study area. The plot of Deuterium versus oxygen-18 of groundwater system in the study area along global meteoric water line indicated recent meteoritic recharge. The recharge was affected with kinetic evaporative effect as well as rock–water interaction and carbondioxide exchange effects.

Fig. 10 Plot of $\delta^{18}O$ vs. NO_3 of groundwater in the study area
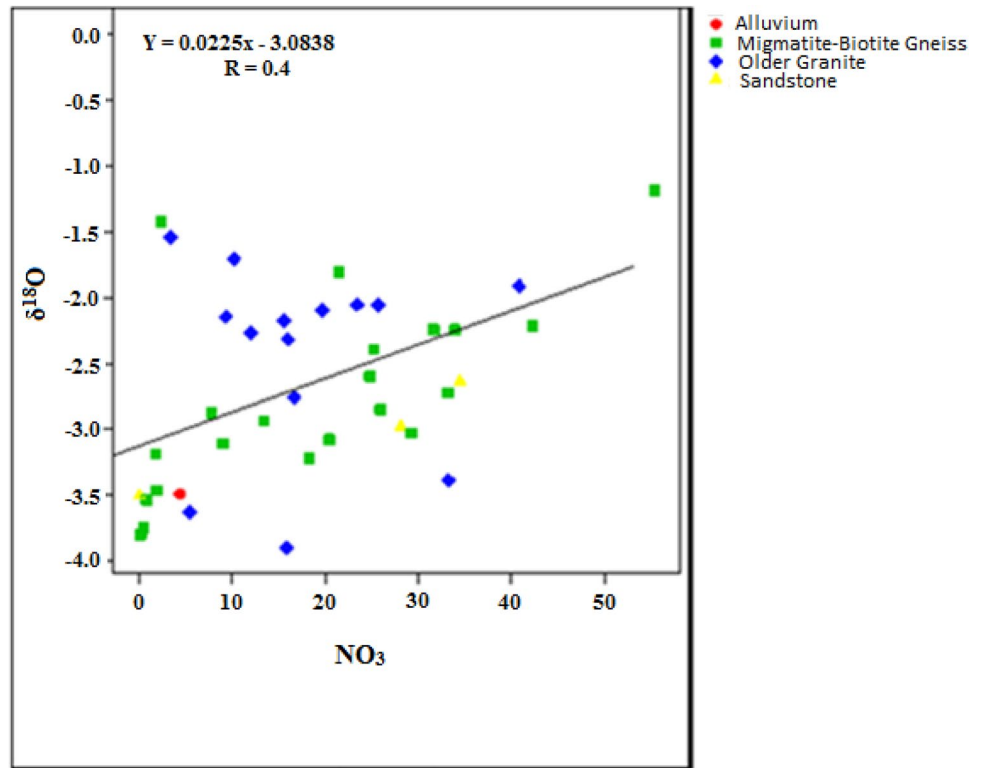
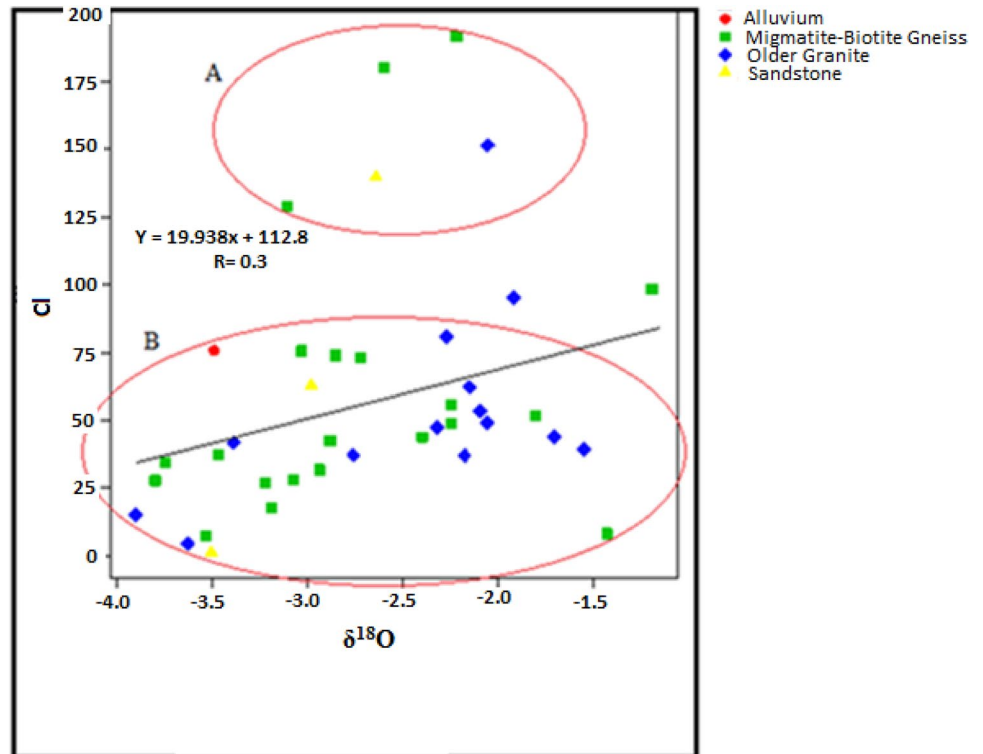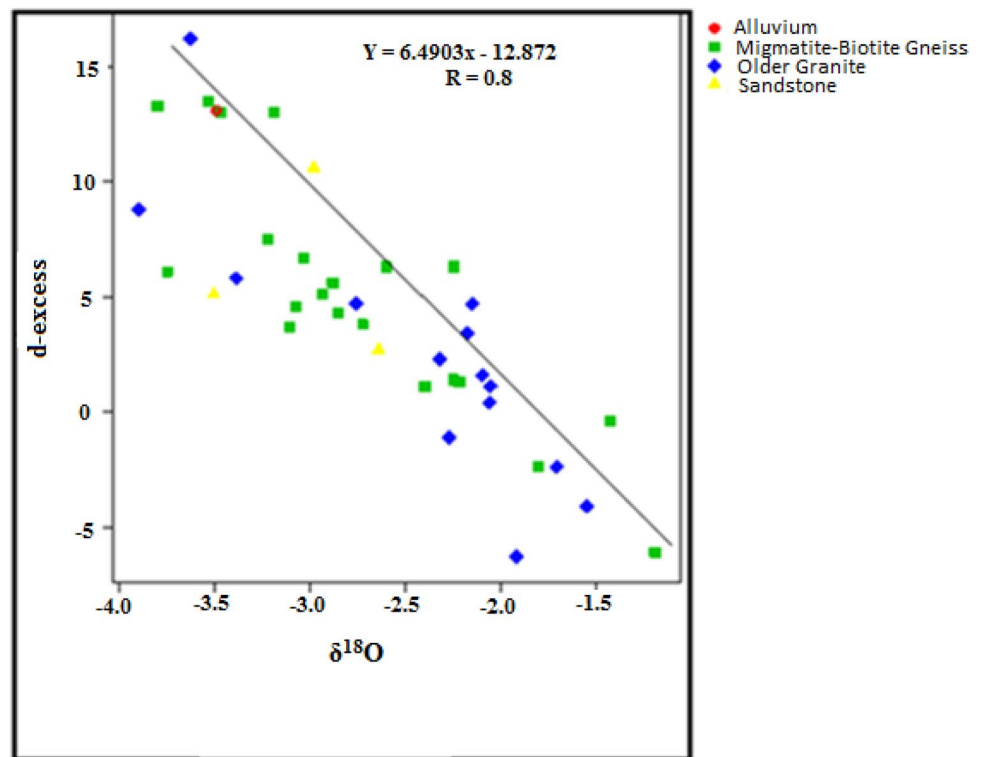**Fig. 11** Plot of Cl vs. $\delta^{18}O$ of groundwater in the study area

Fig. 12 Plot of d-excess vs. $\delta^{18}O$ of groundwater in the study area

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