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Hydrochemical and stable isotopic characterization of shallow groundwater system in the crystalline basement terrain of Ekiti area, southwestern Nigeria

Abel O. Talabi · Moshood N. Tijani

Abstract Assessments of hydrochemical quality and recharge source are critical components of sustainable groundwater resources evaluation and management, especially in complex weathered/fractured crystalline bedrock terrains. Assessment of the weathered/fractured basement aquifer of Ekiti area, SW-Nigeria was undertaken with emphasis on hydrochemical quality and stable isotope characterization of shallow groundwater system. The study approach involved field sampling and in situ measurements of physico-chemical parameters followed by hydrochemical and stable isotope analyses of the water samples. In situ measurements revealed EC value of 43–995 μS/cm (av 431.96 μS/cm) and total hardness of 31.3–295.1 mg/L. The pH of the water sample ranged from 7.0 to 8.9 (av 8.00). The concentrations of the major cations are in the order of $Ca^{2+} > K^+ > Na^+ > Mg^{2+}$ with their respective average values of 33.35, 25.61, 24.91 and 8.7 mg/L respectively while that of the anions are in the order of $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ with their respective average values of 165.44, 31.85, 21.27 and 5.44 mg/L respectively. However, the results of stable isotope analyses revealed $\delta^{18}O$ value of −4.2 to −2.1 ‰ and δD of −22.3 to −10.2 ‰, suggesting meteoric water source (recent precipitation water recharging the associated shallow basement aquifer) while the estimated deuterium excess of 6.80–11.00 ‰ (av 9.6 ‰) suggested little or no imprint of kinetic evaporation. Furthermore, the overall hydrochemical profiles revealed the main hydrochemical facies as Ca(Mg)-HCO_3 (dominant) and Na(K)-HCO_3 (minor) water types which can be attributed to dissolution of minerals in the various rock units in the study area. Conclusively, the overall hydrochemical and stable isotope evaluations revealed a recharge predominantly derived from meteoric (rainfall) source while the corresponding low TDS is a reflection of low water–rock interaction and limited migratory history of the shallow groundwater system in the study area.

Keywords Shallow groundwater · Basement terrain · Hydrochemical facies · Stable isotope · Meteoric water

Introduction

Over the years, before the discovery of crude oil in Nigeria, Ekiti area was the least developed and neglected part of the former Western region of Nigeria despite the fact that the area was a major producer of cocoa that formed the backbone of the region's economy. Most of the communities are predominantly rural with the exception of few township areas like Ado-Ekiti (the state capital) and others such as Ikere-Ekiti, Ise-Ekiti, Emure-Ekiti and Ikole-Ekiti. The communities are peasant farmers and depend mostly on shallow groundwater (hand dug wells) and surface waters (rivers, streams and springs) for sustainability of their farming activity and other domestic requirements. Surface waters in form of rivers and streams apart from being prone to contamination from anthropogenic activities are subject to seasonal variation as most of them dried off during the dry season. Hence, the most reliable source of water for the agricultural and domestic purposes in the study area is groundwater. However, the groundwater in the area were found within two major aquiferous units

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(the weathered and fractured layers) and tapped in form of shallow hand-dug wells and shallow hand-pump boreholes (Ademilua and Olorunfemi 2000).

Some of the existing wells were uncovered, unlined and in few cases even were covered with wooden plank or rusting iron sheet. Consequently, the incidences of water-borne diseases (guinea worm, typhoid fever, gastrointestinal diseases, poliomyelitis etc.,) were at times common in the area. Hence, there is need for hydrochemical assessment of the shallow groundwater system of the study area with particular reference to drinking and irrigation quality evaluation.

The groundwater was generally a product of infiltrated rainwater, channel precipitation, overland flow, subsurface baseflow, agricultural drains and even municipal effluents. In many cases, waters from the highlighted different sources usually have a distinct isotopic and geochemical composition. Increased knowledge about the geochemical processes that control groundwater chemical composition in weathered/fractured basement aquifer of Ekiti area could lead to improved understanding of hydrochemical systems in such area. Such improved understanding can contribute to effective management and utilization of the groundwater resources by clarifying relations among groundwater quality, aquifer lithology and recharge type. Furthermore, the spatial changes in the water types can equally be evaluated and used to trace the recharge source(s) to the groundwater system using stable isotopes of water (δ^{18}O and δD). These stable isotopes (unlike other tracers of 'water' such as Cl^- which is still widely used) are ideal tracers of water sources and movement because they are constituents of the water molecules (Akiti 1986). The elements constituting the water molecule, hydrogen and oxygen, undergo changes in the various phases of hydrologic environments; atmosphere, hydrosphere, biosphere and the upper part of the earth's crust. These changes results in isotopic fractionation to give isotopic "fingerprints" due to different physicochemical, biochemical, kinetic and thermodynamic effects (Das et al. 1998). Consequently this study also employed evaluations of stable isotopes to draw conclusions with respect to recharge source(s) and processes of the groundwater system in the study area.

Previously, there were a number of studies relating to chemical quality aspect of shallow groundwater systems in the Basement Complex area of southwestern Nigeria which focussed mostly on the township areas like Abeokuta, Ilesha, Ibadan and Ado-Ekiti (Loehnert 1981; Ako et al. 1990; Malomo et al. 1991; Sangodiyin 1993; Asubiojo et al. (1997); Olayinka et al. 1999; Abimbola et al. 1999; Tijani and Abimbola 2003; Olobaniyi et al. (2007); Omotoyinbo and Okafor 2008). Sangodiyin (1993) found poor bacteriological quality of groundwater close to sites of

waste disposals in Abeokuta area, highlighting the potential for impacts from other pollutants. Asubiojo et al. (1997) carried out a survey of tap water and groundwater quality from various sources in Southern Nigeria and found that most elements investigated are present at concentrations below the respective WHO standard values with exception of Ba, Pb, Ni and Se.

Abimbola et al. (1999) identified the dominant ions in the groundwater of Abeokuta as Ca^{2+} and HCO_3^-, and the water was characterized as Ca-HCO_3 type having low total dissolved solids (TDS). Omotoyinbo and Okafor (2008) worked on the influence of rock mineralogy on subsurface water in Ado-Ekiti and concluded that dissolved minerals from rocks have great influence on the underground water property. The level of the dissolved minerals was within the acceptable limit for water quality standard values by WHO.

All these studies and many others have contributed immensely to groundwater development and management. However, most of the works were restricted to hydrogeochemistry involving major cations and anions with only few given consideration to heavy metals and other trace constituents. Substantial hydrogeological and hydrochemical research works have been carried out in the Basement Complex of southwestern Nigeria, but in the study area these research works were scanty and to a greater extent did not include isotope evaluation of the groundwater. In most cases, the understanding of the hydrochemical properties of the aquifers as a means of establishing the recharge regimes for the better management of the aquifer systems have not been fully exploited. This study integrates both hydrochemical and stable isotope studies to characterize shallow groundwater in a typical weathered basement aquifer terrain of Ekiti area, with the focus on assessment of water quality status, hydrochemical facies and associated geochemical processes as well as recharge source(s) and processes.

Location of the study area

The study area lies within latitudes 7°25′ and 7°52′N and longitudes 4°48′ and 5°30′E covering an approximate area of about 4,344 km^2. Prominent towns and settlements in the area include Ado, Ikere, Ilawe, Ise, Emure, Ifaki, Aramoko, Ikogosi, Iyin, Igede, Ijan, Igbara-Odo, Ijero, Iworoko as well as other smaller settlements (Fig. 1).

Geographically, the area falls within the rainforest in the southwestern part of Nigeria. The topography is generally undulating with most area lying above 250 m above sea level. The landscape is characterized by old plains, broken steep-sided outcrop dome rocks (Inselbergs) that may occur singularly or in crops of ridges. Such outcrops exist mainly
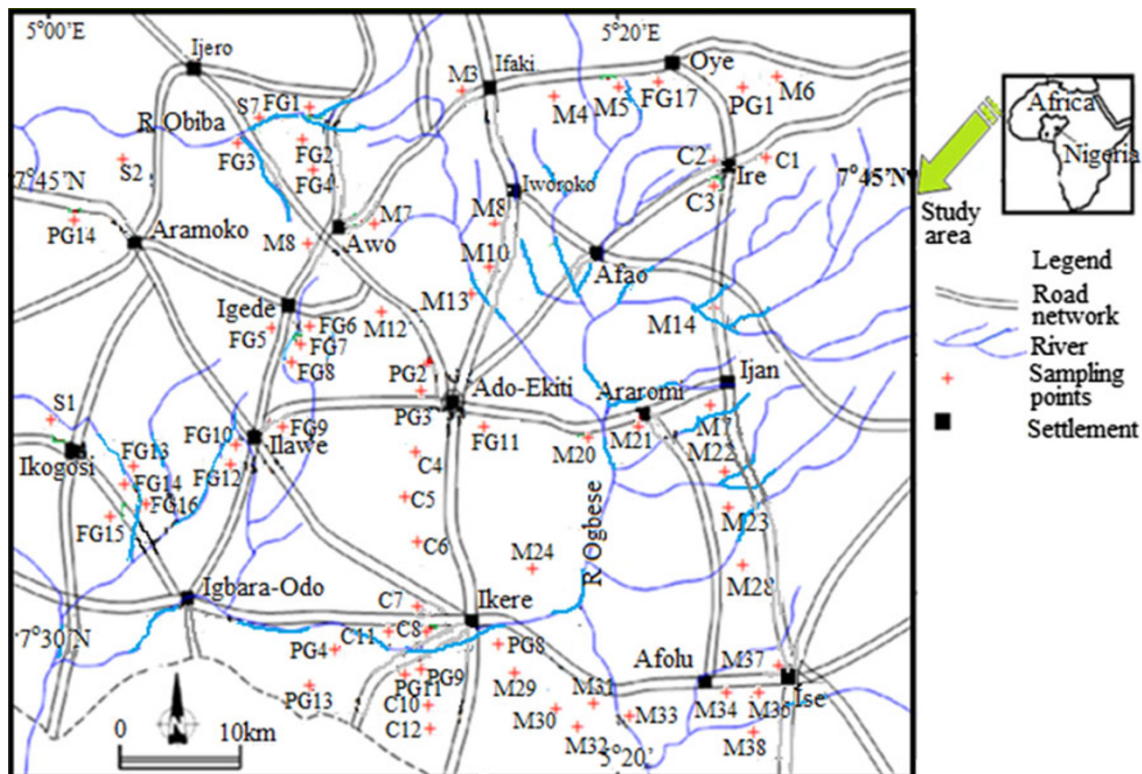
Fig. 1 Location Map of the study area showing sampling points

in form of rugged hills at Ado-Ekiti (central part of study area) and Ikere-Ekiti in the southern part. The study area lies within the tropical climatic zone, characterized by alternating wet and dry season and drained by rivers such Elemi, Ureje, Ose, Ogbesse and their seasonal network of tributary and streams forming a somewhat dendritic drainage pattern (Fig. 1). The wet season was from April to October, dominated by heavy rainfall, while the dry season was from November to March. The mean annual rainfall was about 1,500 mm while the mean annual temperature ranged from 25 to 30 °C.

Geologic and hydrogeologic frameworks

Geologically, the study area lies within the Pre-Cambrian Basement Complex of SW-Nigeria which also constitutes part of the Pan-African mobile belt lying east of the West African Craton (Jones and Hockey 1964; Odeyemi 1976; Rahaman and Ocan 1988). The major rocks in the study area include five principal lithologic units; migmatite/ migmatite gneiss, metasediment, Pan-African granite, charnockite and quartzite/quartz-schist (Fig. 2). The migmatite/migmatite gneiss rocks cover more than half of the study area, occurring as highly denuded hills of essentially fine-medium grained textures with closely

spaced alternating bands of leucocratic and melanocratic minerals. They are characteristically low lying and conspicuously foliated with abundance of platy biotite minerals sandwiched into zones that are markedly distinguishable from the light-coloured quartzo-feldspartic portions. Quartzite occurs as ridge of steeply dipping, massively bedded fine-medium grained bodies or an environment characterized by the abundance of quartz rubbles. Granite and charnockite occur as minor intrusive bodies within the migmatite rock. The granite is essentially fine to medium grained and sometimes porphyritic texture acidic rocks. Pegmatite, aplite and quartz veins occur as minor intrusions into the granitic rocks. Field studies indicate that the charnockite occurs as dark greenish grey and greasy, medium to fine grained and weakly foliated with occasional gneissic banding. The rock outcrops are fresh, rough in surface appearance with little signs of weathering. The rock is in contact with migmatite and granite. With the exception of the small hills and inselbergs, the bedrocks are generally covered by weathered regolith composing mainly of clay and sandy materials which are capped by lateritic soil in places depending on the bedrock types.

Hydrogeologically, like in other typical basement complex terrain, unweathered or fresh crystalline rocks have, on their own, hardly any potential in terms of groundwater occurrence and flow. However, the mode of groundwater

Fig. 2 Geological map of the study area
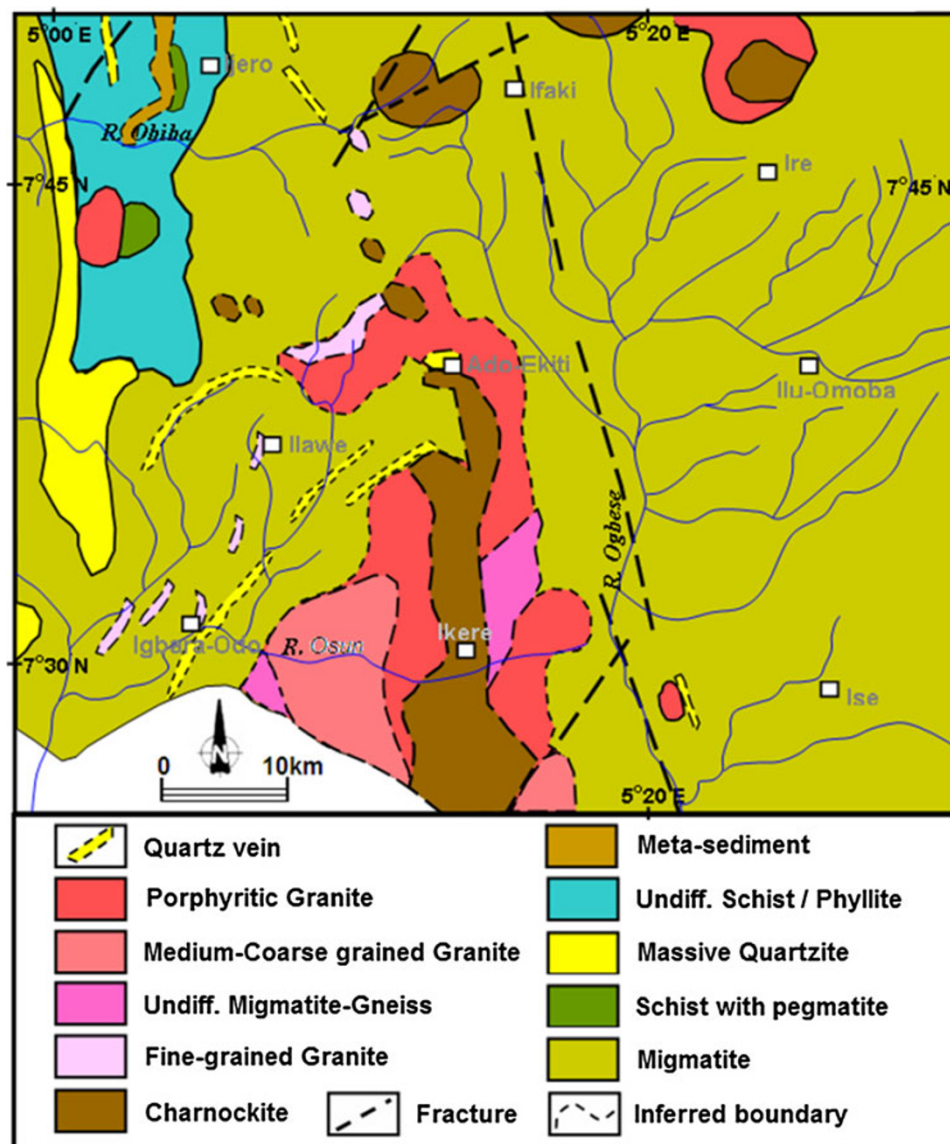
occurrence in the study area is through the development of secondary porosities or permeabilities as a result of fracturing, jointing, shearing and deep weathering (Ademilua and Olorunfemi 2000; Oyinloye and Ademilua 2005). The fractures might have probably developed from transpressive forces during tectonic movement, pressure relief due to erosion of overburden rock, shrinking during cooling of the rock mass and the compression and tensional forces caused by regional tectonic stresses. Most of the groundwater in the study area occur in the weathered regolith/fractured parent rock zone (Fig. 3). Investigation during field work activity in the course of this study revealed that the varied distribution of the rock units in terms of mineralogy and the resulting differential weathering are responsible for the variable thickness of the in situ weathered regolith, which is also responsible for the differences in the groundwater potential at different locations.

In SW-Nigeria, such variations in thickness usually in the range of 2–25 m are controlled by local and regional factors such as bedrock type, the degree of resistance to weathering, intensity and fracture density among others (Ako et al. 1990; Malomo et al. 1991; Tijani and Abimbola 2003).

The overall hydrogeologic setting of the study area, as revealed by the hand-dug wells, is characterised primarily by the weathered regolith or saprolite units with varied thickness ranging from 4.3 to 15 m, located entirely within the saprolite unit with characteristically low yield of 6–246 l/min. Hence, the groundwater in the study area could be said to occur at shallow depths in localised and disconnected weathered regolith aquifers existing mainly as unconfined to semi-confined groundwater table conditions. The variable aquifers are tapped through shallow hand-dug wells that terminate mostly in the saprolite unit.

Fig. 3 Typical weathered soil profile developed on charnockitic bedrock from the study area

This reported hydrogeologic profile is consistent with other research work reported elsewhere within the Basement Complex of SW-Nigeria (Tijani 1994; Tijani and Abimbola 2003).

Methodology

A total number of 73 water samples were collected mainly from domestic hand-dug wells within the study area for hydrochemical analysis, out of which 27 samples were selected for stable isotope analysis. The sampled locations are shown in Fig. 1. For the hydrochemical analysis, 73 samples were categorized into five classes based on rock formations, namely migmatite (30), porphyritic granite (11), fine to medium grained granite (17), quartzite (4) and charnockitic bedrock (11) settings while the isotope samples in the same order of bedrocks were eleven (11), four (4), seven (7), two (2) and three (3). All water samples were collected in 50-ml preconditioned polyethylene bottles. They were conditioned by rinsing initially with 10 % nitric acid and followed by several rinsing with distilled water to ensure that the sample bottles were free from any impurities.

At each sampling location, samples were collected into polyethylene bottles in triplicate. Two sets of samples were used for cation and anion analyses and 27 selected samples, the third set, for stable isotope analyses. Samples for cations analysis were acidified with concentrated nitric acid. Prior

to this, field in situ parameters (pH, temperature and electrical conductivity) were measured using Multi-parameter Testr^{Tm} 35 series Meter. The samples were then preserved in a refrigerator prior to the laboratory analyses. The cation metals were analysed using the 36-element Inductively Coupling Plasma Oxygen Emission Spectrometer (ICP-OES) analytical method at ACTLABS Laboratory, Canada while the major anions were analysed at the Federal Ministry of Water Resources Laboratory, Alagbaka Akure, Nigeria using Ion Chromatography method. The analyses of the stable isotopes (^{18}O and D) of the 27 water samples were carried out at Hydroisotop Laboratory, Schweitenkirchen in Germany using mass spectrometry method. The δ^{18}O of groundwater samples from the study area were determined by equilibrating $CO_{2(g)}$ with water at 25 °C (Epstein and Mayeda 1953). The ^{18}O/^{16}O ratio of the $CO_{2(g)}$ was then measured on a Micromass MS903 mass spectrometer and the δ^{18}O reported as per mil (‰) deviation from the Vienna Standard Mean Ocean Water (VSMOW) using the delta (δ)-scale with measurement accuracy of ±0.15. The mass ratio of deuterium in the groundwater samples of the study area was determined by reduction of the water molecules to gas following the Zn-reduction procedures outlined in Coleman et al. (1982). Water reacts with zinc at high temperature (400–450 °C) which proceeds by the following reactions:

$$H_2O \ + \ Zn \rightarrow H_2 + \ ZnO \tag{1}$$

Having gasified the hydrogen elements in the samples, consequently, the masses of hydrogen isotopes were

determined by supplying the obtained hydrogen gas into a Micromass 602 mass spectrometer with the δD reported as ‰ relative to V-SMOW.

Result of the hydrochemical data were subjected to graphical evaluation using Piper (1944) and Gibbs (1970) to define the various chemical evolution of groundwater in the study area. Furthermore, scatter plot of $\delta^{18}O$ versus δD with respect to Global Meteoric Water Line (GMWL) was employed to determine the source of groundwater in the study area.

Results and discussion

Hydrochemical profiles

The results of the physico-chemical field measurements are presented in Table 1 while those of the hydrochemical analyses are shown in Table 2. The overall summary is presented in Table 3 along with WHO (2004) standard for drinking water quality. The pH of groundwater varied from 7.0 to 8.9 with a mean of 8.0. The temperature varied from 25.4 to 30.2 °C with a mean of 28.2 °C, which reflects the average air temperature during the sampling period (dry season) while the pH values revealed that the groundwater in the study area is neutral to slightly alkaline. Temperature and pH influence dissolution and precipitation of minerals in groundwater. Thus, the average pH value (av 8.0) is indicative of the presence of free CO_2 and that the dissolved anions exist almost entirely in HCO_3 ion form (Freeze and Cherry 1979). The electrical conductivity (EC) ranges between 109 and 939 μS/cm with a mean of 431.96 μS/cm while the total dissolved solid (TDS) values were generally less than 1,000 mg/L, ranging from 32.25 to 746.25 mg/L with an average value of 323.97 mg/L. The low TDSs are indications of low mineralized water with limited migratory history and water–rock interactions.

The total hardness (TH) varied from 31.28 to 295.10 mg/L with an average value of 128.49 mg/L. The guidelines for Canadian drinking water quality hardness (Health Canada 2012) divided hardness in equivalent concentration of $CaCO_3$ into the following categories: Soft, <60 mg/L; Medium hard, 60 mg/L to <120 mg/L; Hard, 120 to <180 mg/L and Very hard, 180 mg/L or greater. Based on this classification, the groundwater system in the study area can be classified as soft to very hard water with about 70 % of the sample locations having TH > 60 mg/L which is the limit of soft water. The probable source of hardness in the groundwater of the study area could be from the weathering of calcium bearing minerals in most bedrocks of the area. However, hard water is mainly of aesthetic concern because of the unpleasant taste that a high concentration of calcium and other ions give to water.

It also reduces the ability of soap to produce lather, and causes scale formation in pipes and on plumbing fixtures. The pH and TH have positive correlations with HCO_3 with correlation coefficients of 0.50 and 0.94 respectively, while pH and TH are equally positively correlated with correlation coefficient of 0.56. These positive correlation values are clear indication of the interdependency and control of pH on the CO_2 dissolution process in the groundwater system of the study area.

Calcium is the dominant cation with its values ranging from 1.5 to 106 mg/L (av 33.20 mg/L), while magnesium ranges from 0.4 to 39.2 mg/L (av 8.77 mg/L) in the study area. With respect to the alkali metals, the concentrations of Na ranged from 1.1 to 91.5 mg/L (av 25.21 mg/L) while that of K varied from 1.6 to 133 mg/L with an average of 25.13 mg/L. Bicarbonate is the dominant anion with concentration of 17.69–456.28 mg/L and average value of 164.85 mg/L. This is followed by Cl concentrations ranging from 2.8 to 61.5 mg/L with an average value of 32.9 mg/L. Sulphate has concentrations in the range of 1.5–76.10 mg/L with an average value of 21.06 mg/L, while NO_3 concentrations ranged between 1.4 and 19 mg/L with an average value of 5.6 mg/L.

Furthermore, the cation concentrations was in the order of $Ca^{2+} > K^+ > Na^+ > Mg^{2+}$ while that of the anions was $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$. The higher concentration of Ca^{2+} and $(K^+ + Na^+)$ in the groundwater of the study area may probably be due to the dissolution of plagioclase feldspars. HCO_3^- might have been generated in the soil zone en route to the groundwater zone as a result of decomposition of organic matter, which releases carbon dioxide that reacts with water in the soil zone. The reaction generates weak carbonic acid (H_2CO_3) that aids the breakdown of minerals in the rocks resulting in dissolution and the release of the ions into the groundwater which was responsible for its hydrochemical characteristics.

Chemical character and groundwater quality

All over the world, water chemistry is controlled by some few salient factors which include precipitation, mineral weathering/dissolution as well as evaporation–recrystallisation processes (Gibbs 1970). In addition, the concentration of dissolved ions in groundwater samples are generally governed by lithology, nature of geochemical reactions and solubility of interacting rocks (Nosrat and Asghar 2010). In many cases, water within the various phases of the hydrological cycle is affected differently by these controlling processes. Apart from this, other processes such as cation–anion exchange and mixing processes may also exert some considerable influence on the groundwater chemistry (Tijani and Abimbola 2003). Thus, water–rock interaction contributes significantly to evolved chemical

Table 1 Physico-chemical parameters analysed in water samples

Sample ID	Location	Temperature (°C)	pH	EC	TDS	TH	TDW	SWC
M-3	Ifaki	28.20	7.30	663.00	497.25	118.56	13.4	2.4
M-4	Ayegbaju	27.40	8.30	879.00	659.25	243.43	14.5	2.7
M-5	Oye	28.60	8.10	194.00	145.50	75.59	12.45	1.85
M-6	Igbodo	26.70	7.80	43.00	32.25	10.45	6.1	1.1
M-7	Eyio	27.20	8.30	808.00	606.00	239.49	11.45	1.75
M-8	Iworoko	27.10	8.50	903.00	677.25	195.84	5.1	0.4
M-9	Awo	28.60	8.30	939.00	704.25	213.30	7.25	1.75
M-10	Olora-farm	28.60	7.90	407.00	305.25	100.56	4.1	0.1
M-11	Are	28.80	8.40	763.00	572.25	211.65	6.4	0.4
M-12	Araromi-iyin	29.00	7.40	67.00	50.25	15.18	9.2	0.2
M-13	Ilokun	28.60	7.30	126.00	94.50	37.42	7.7	0.2
M-14	Igbemo	29.50	8.30	637.00	477.75	180.97	6.7	2.5
M-17	Ilumoba	28.30	7.50	150.00	112.50	40.02	5	1.2
M-19	Erifun	27.50	8.20	854.00	640.50	225.34	4.6	0.1
M-20	Ayoko	29.00	8.80	710.00	532.50	162.17	7.7	0.2
M-21	Agoologunja	27.20	7.80	315.00	236.25	99.27	6.7	0.1
M-22	Asoajegunle	27.90	7.60	270.00	202.50	82.81	7.5	0.5
M-23	Abaoyan	27.10	7.10	658.00	493.50	216.82	8	0.7
M-24	Ilupeju-ijan	28.80	7.00	736.00	552.00	119.80	7	0.8
M-26	Abaefon	25.40	8.30	233.00	174.75	86.25	6.9	0.7
M-27	Kajola-ise	29.20	6.00	699.00	524.25	132.63	7.2	0.6
M-28	Igbaraodo	28.50	8.20	587.00	440.25	238.56	6.3	0.7
M-29	Okoisa	27.00	7.70	152.00	114.00	42.50	7.5	2.9
M30	Abapopoola	27.90	8.40	548.00	411.00	169.53	5.5	1.2
M-31	Ogbese	30.10	8.00	626.00	469.50	221.55	4.2	0.4
M-33	Ogbese	26.80	8.70	220.00	165.00	72.40	4.5	0.1
M-34	Obada-ise	28.00	6.90	121.00	90.75	14.40	7.6	0.2
M-35	Ise	27.50	8.00	384.00	288.00	73.34	5.8	0.8
M-37	Orun	30.50	8.20	591.00	443.25	112.33	7.2	1.2
M-38	Okoo	29.60	7.90	227.00	170.25	73.33	5.2	0.9
PG-1	Itapa	28.30	8.10	644.00	483.00	179.80	11.5	1.5
PG-2	Oshin	28.70	8.60	335.00	251.25	124.04	12.6	1.1
PG-3	Ado	28.00	7.10	101.00	75.75	11.02	7.3	1.1
PG-4	Ado	28.50	7.60	755.00	566.25	173.06	8.1	0.6
PG-5	Ikere	27.60	7.50	365.00	273.75	54.12	3.6	0.6
PG-6	Ikere	28.50	7.30	293.00	219.75	39.44	5.5	1.7
PG-8	Eruobodo	27.00	8.00	267.00	200.25	67.02	3.91	0.01
PG-9	Eruobodo	26.80	8.80	224.00	168.00	83.22	9.2	7.6
PG11	Ikere	27.90	7.40	1041.00	781.00	82.70	7.2	0.1
PG-13	Ikere	28.50	8.60	323.00	242.25	128.88	5.9	1.1
PG-14	Ikere	27.20	7.50	109.00	81.75	42.87	5.8	0.1
S-1	Erio	27.10	8.60	850.00	637.50	249.21	4.6	0.9
S-2	Erio	29.40	8.00	484.00	363.00	131.43	5.8	2.1
S-4	Aramoko	27.50	8.10	834.00	625.50	180.12	5	0.2
S-7	Ikogosi	28.00	8.80	312.00	234.00	120.85	15	0.4
FG-1	Epe	26.80	8.00	847.00	635.25	231.08	5.2	0.9
FG-2	Osi	25.50	7.10	191.00	143.25	55.85	5.3	1.1
FG-3	Araromi-iyin	27.00	8.40	936.00	702.00	349.59	5.4	1.1

Table 1 continued

Sample ID	Location	Temperature (°C)	pH	EC	TDS	TH	TDW	SWC
FG-4	Ara-ijero	25.60	8.00	219.00	164.25	61.90	6.2	1.8
FG-5	Iropora	25.90	8.90	686.00	514.50	196.54	4.3	1.1
FG-6	Igede	29.70	8.10	687.00	515.25	206.66	2.7	1.6
FG-7	Iyin	28.10	7.90	153.00	114.75	61.37	11.3	0.8
FG-8	Igede	26.50	8.10	316.00	237.00	114.67	1.6	0.6
FG-9	Iyin	27.50	7.50	456.00	342.00	116.26	11.3	1.5
FG-10	Odo	26.50	7.50	142.00	106.50	42.71	6.7	0.9
FG-11	Ilawe	26.70	8.20	380.00	285.00	151.76	11.1	1
FG-12	Ijelu	26.80	8.40	525.00	393.75	191.47	5.8	2.8
FG-13	Ilawe	26.10	8.80	995.00	746.25	295.10	1.5	0.3
FG-14	Temidire-asa	29.00	7.60	144.00	108.00	31.28	4.7	0.3
FG-15	Kajolaoriokuta	29.80	7.40	88.00	66.00	22.82	8	2.8
FG-16	Aba-Alawaye	29.10	8.50	275.00	206.25	118.13	9	2
FG-17	Aba-Oshun	30.20	8.30	203.00	152.25	37.53	9.1	0.1
C-1	Ilupeju	28.80	8.40	226.00	169.50	68.37	6.6	0.1
C-2	Ire	27.20	7.80	532.00	399.00	131.28	5.4	0.2
C-3	Ire	28.00	7.90	185.00	138.75	60.24	9.3	1
C-4	Afao	29.70	8.90	914.00	685.50	192.29	5.3	1
C-5	Ajebandele	27.80	7.80	187.00	140.25	59.37	10.7	1.2
C-6	Ajebandele	28.50	7.40	96.00	72.00	10.88	10	1.4
C-7	Fagbohun	28.40	7.40	123.00	92.25	40.05	10.8	0.2
C-9	Ikere	27.80	8.10	267.00	200.25	79.15	12.1	0.2
C-10	Ikere	28.40	8.40	630.00	472.50	237.76	2.5	1.6
C-11	Ikere	29.00	7.60	157.00	117.75	13.75	7.9	0.3
C-13	Igbole	25.30	6.40	135.00	101.25	8.27	13.7	2.2

EC Electrical conductivity in µS/cm, *TDS* Total dissolved solids in mg/L, *TH* Total hardness in mg/L CaCO₃, *TDM* Total depth of well in metre, *SWC* Saturated water column in metre

composition of the groundwater system in the study area in addition to contribution from precipitation. Results of hydrochemical analysis in the study area (Tables 1, 2) clearly reflect varied chemical composition with respect to the measured parameters which is a reflection of the varied lithologic units in the area as well as differential weathering/dissolution in such bedrocks.

Strong correlation exists among the major cations and TDS with correlation coefficients >0.60 (Table 4) which is a clear indication of the contribution of these ionic components to the overall mineralisation (TDS). Similarly, with the exception of NO_3^- versus TDS ($r = -0.17$), all the major anions also have positive correlation coefficients ($r > 0.70$) (Table 4). This observed chemical character suggested that NO_3^- concentration in the groundwater system was from different source possibly from anthropogenic contamination (household contaminants and waste pits). Hence, most ionic input into the groundwater system of the study area was mostly from geogenic source. However, few cross plots of the groundwater ionic parameters in the study area as indicated in Fig. 4(a–f)

signify distinctly two types of water. The first type of water has low TDS while the second type has fairly high TDS values. Hudson and and Golding (1997) pointed out that the concentrations of sodium, magnesium, calcium and silica in groundwater system of any area are controlled by mineral weathering of the bedrocks. This was clearly demonstrated in the study that the percolated CO_2-charged rain water turned to weak carbonic acid initiating water–rock interactions during which weathered minerals released cations (Ca, Mg, Na and K) that reacted with the weak carbonic acid to produce bicarbonate waters. However, the low TDS in the groundwater system of the study area was a reflection of the general characteristics of groundwater in basement terrain. The groundwater in such basement terrain has limited migratory history and its composition was controlled by recharge water from rainfall and mineral dissolution from slow weathering of the minerals constituting the bedrocks (Tijani 1994).

Furthermore, a plot of TDS against $Na^+/(Na^+ + Ca^{2+})$ ratio referred to as Gibbs plot (Fig. 5) assessed the functional source of dissolved ions in waters as evaporation

Table 2 Hydrochemical parameters analyzed in water samples

Sample ID	Location	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO$_3$ mg/L	Cl mg/L	SO$_4$ mg/L	NO$_3$ mg/L
M-3	Ifaki	34.50	7.90	22.60	80.00	195.81	52.00	36.75	3.60
M-4	Ayegbaju	74.00	14.30	22.10	101.00	340.99	76.00	42.00	1.80
M-5	Oye	18.10	7.40	3.80	3.60	57.34	13.00	18.20	2.30
M-6	Igbodo	3.20	0.60	2.70	3.00	17.69	1.50	2.80	ND
M-7	Eyio	53.80	25.60	16.60	83.70	303.78	47.50	57.75	1.40
M-8	Iworoko	54.10	14.80	36.10	101.00	355.63	36.20	58.80	ND
M-9	Awo	61.10	14.80	23.80	133.00	367.22	43.60	59.50	3.60
M-10	Olora-farm	23.00	10.50	23.30	23.80	134.20	17.80	34.65	4.90
M-11	Are	63.90	12.70	26.00	52.30	253.76	28.50	60.20	14.00
M-12	Araromi-iyin	4.60	0.90	6.10	4.00	21.35	4.50	3.50	8.00
M-13	Ilokun	8.90	3.70	4.90	7.60	46.36	1.50	4.55	14.00
M-14	Igbemo	46.00	16.10	12.50	64.90	192.76	36.00	61.95	8.60
M-17	Ilumoba	7.80	5.00	11.30	2.70	56.12	1.50	9.10	9.40
M-19	Erifun	62.30	17.00	65.20	18.10	347.09	20.50	53.20	11.00
M-20	Ayoko	47.20	10.80	63.20	24.30	260.47	24.50	60.55	5.40
M-21	Agoologunja	23.80	9.70	22.40	3.00	101.87	12.50	35.00	7.20
M-22	Asoajegunle	17.70	9.40	10.80	14.10	89.67	12.00	24.85	3.50
M-23	Abaoyan	22.30	39.20	30.30	15.60	217.77	49.50	54.25	ND
M-24	Ilupeju-ijan	20.00	17.00	91.50	10.00	323.91	10.00	37.80	1.80
M-26	Abaefon	26.00	5.20	13.60	5.00	93.94	12.00	21.00	3.20
M-27	Kajola-ise	16.90	22.00	62.10	32.20	254.98	29.50	46.90	2.60
M-28	Igbaraodo	67.60	17.00	23.40	12.20	242.17	22.00	61.25	ND
M-29	Okoisa	11.10	3.60	19.00	2.90	59.78	10.00	18.20	3.20
M-30	Abapopoola	36.80	18.90	42.80	8.60	198.86	36.00	45.85	9.40
M-31	Ogbese	35.40	32.40	44.10	1.60	245.22	38.00	52.85	4.30
M-33	Ogbese	18.80	6.20	13.60	7.20	68.93	21.00	19.25	6.80
M-34	Obada-ise	3.30	1.50	16.60	3.40	46.36	12.00	2.80	ND
M-35	Ise	17.20	7.40	45.10	5.30	157.38	10.50	25.20	2.80
M-37	Orun	35.30	5.90	17.10	84.50	200.08	13.50	52.50	5.20
M-38	Okoo	22.80	4.00	16.90	7.40	105.53	6.40	16.45	2.40
PG-1	Itapa	56.90	9.20	20.70	49.70	226.92	35.00	46.90	ND
PG-2	Oshin	42.30	4.50	24.90	3.00	159.21	12.00	25.90	2.30
PG-3	Ado	3.10	0.80	14.20	3.40	37.21	9.50	3.50	1.40
PG-4	Ado	54.20	9.20	74.90	16.90	308.66	12.00	46.90	ND
PG-5	Ikere	15.10	4.00	48.30	10.00	128.71	12.50	36.40	1.50
PG-6	Ikere	10.70	3.10	40.50	8.00	104.31	10.00	28.35	2.00
PG-8	Eruobodo	20.60	3.80	26.50	3.30	99.43	9.00	24.15	5.00
PG-9	Eruobodo	23.30	6.10	14.20	3.40	84.18	32.00	11.55	ND
PG-11	Ikere	28.70	2.70	27.00	7.80	120.78	11.00	31.50	2.00
PG-13	Ikere	38.80	7.80	19.20	5.80	128.71	19.00	35.00	3.20
PG-14	Ikere	15.70	0.90	2.70	3.50	34.77	3.00	5.60	16.00
S-1	Erio	75.00	15.10	54.30	60.40	397.11	32.50	58.45	2.40
S-2	Erio	41.80	6.60	33.20	21.90	168.36	31.00	41.65	2.10
S-4	Aramoko	53.90	11.10	53.30	71.20	314.15	41.00	58.45	4.30
S-7	Ikogosi	36.90	7.00	3.20	24.60	134.20	19.50	18.90	2.70
FG-1	Epe	70.70	13.30	35.10	72.80	344.04	44.00	50.75	ND
FG-2	Osi	15.30	4.30	7.50	9.80	59.78	10.50	17.50	ND
FG-3	Araromi-iyin	106.00	20.70	41.80	18.50	400.77	47.00	60.20	0.90

Table 2 continued

Sample ID	Location	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO₃ mg/L	Cl mg/L	SO₄ mg/L	NO₃ mg/L
FG-4	Ara-ijero	16.90	4.80	11.60	16.60	115.29	2.00	8.05	ND
FG-5	Iropora	64.60	8.60	30.60	55.10	259.86	36.50	51.80	11.00
FG-6	Igede	55.80	16.40	19.40	58.60	230.58	40.00	61.25	6.20
FG-7	Iyin	21.30	2.00	6.70	2.90	57.95	10.00	15.05	ND
FG-8	Igede	33.60	7.50	19.00	8.60	121.39	13.50	36.40	1.70
FG-9	Iyin	28.80	10.80	36.60	9.10	172.63	11.50	41.65	ND
FG-10	Odo	13.00	2.50	8.40	3.00	53.07	10.50	7.35	ND
FG-11	Ilawe	48.30	7.60	19.50	6.20	229.97	13.50	33.25	2.60
FG-12	Ijelu	54.00	13.80	36.40	25.90	245.83	33.50	50.05	ND
FG-13	Ilawe	95.70	13.70	50.90	83.10	456.28	42.00	59.50	5.40
FG-14	Temidire-asa	7.10	3.30	9.90	9.30	46.36	12.00	3.50	4.80
FG-15	Kajolaoriokuta	7.50	1.00	8.20	4.20	26.84	9.00	5.95	7.40
FG-16	Aba-Alawaye	45.70	1.00	8.60	7.10	106.75	10.00	24.15	5.20
FG-17	Aba-Oshun	12.90	1.30	16.00	14.80	61.00	11.50	15.40	9.00
C-1	Ilupeju	21.80	3.40	12.30	12.60	65.27	17.50	24.50	5.60
C-2	Ire	33.50	11.60	38.80	25.40	190.93	23.50	46.90	ND
C-3	Ire	16.40	4.70	10.10	3.20	61.61	9.00	17.50	ND
C-4	Afao	56.80	12.30	50.70	99.60	358.07	58.00	53.20	ND
C-5	Ajebandele	20.50	2.00	5.40	15.60	70.15	1.50	19.95	4.20
C-6	Ajebandele	3.70	0.40	6.50	12.00	25.62	6.30	6.65	5.20
C-7	Fagbohun	14.90	0.70	3.10	10.70	35.38	9.00	7.70	13.00
C-9	Ikere	24.80	4.20	1.10	8.10	57.95	18.00	14.35	7.50
C-10	Ikere	74.20	12.80	46.20	14.80	291.58	32.50	57.40	3.00
C-11	Ikere	3.70	1.10	14.80	13.70	36.60	10.00	5.25	19.00
C-13	Igbole	1.50	1.10	18.60	4.10	48.19	6.80	3.85	2.10

ND below detection limit

Table 3 Descriptive summary of hydrochemical data in the study area

Parameters	Min	Max	Mean	Median	Stdev
Temperature (°C)	25.30	30.50	27.94	28.00	1.18
pH	7.00	8.90	8.00	8.00	0.49
ECμS/cm	43.00	995.00	431.96	329.00	280.17
TDS mg/l	32.25	746.25	323.97	246.75	210.12
TH	31.28	295.10	128.49	118.35	70.43
TDW(m)	0.10	15.00	6.98	6.70	3.00
SWC	0.01	7.60	1.06	0.90	1.09
Ca (mg/L)	1.50	106.00	33.20	24.80	23.67
Mg (mg/L)	0.40	39.20	8.77	7.40	7.51
Na (mg/L)	1.10	91.50	25.21	19.40	19.09
K (mg/L)	1.60	133.00	25.13	10.70	30.80
TDS (mg/L)	50.25	637.50	283.23	234.00	180.91
Cl (mg/L)	2.80	61.95	32.19	33.25	19.98
NO₃ (mg/L)	1.40	19.00	5.60	4.30	4.12
SO₄ (mg/L)	1.50	76.00	21.06	13.50	15.83
HCO₃ (mg/L)	17.69	456.28	164.84	128.71	115.62

TDW Total depth of well in metre, *SWC* Saturated water column in metre

Table 4 Correlation matrix of major ions in groundwater of the study area

Parameters	Ca	Mg	Na	K	HCO$_3$	SO$_4$	Cl	NO$_3$	TH	pH	EC	TDS
Ca^{2+}	1.000											
Mg^{2+}	0.537	1.000										
Na$^+$	0.454	0.513	1.000									
K$^+$	0.607	0.373	0.227	1.000								
HCO$_3^+$	0.882	0.706	0.727	0.698	1.000							
SO$_4^{2-}$	0.719	0.692	0.353	0.741	0.753	1.000						
Cl$^-$	0.326	0.761	0.640	0.629	0.336	0.727	1.000					
NO$_3^-$	−0.129	−0.178	−0.192	−0.064	−0.210	−0.179	−0.162	1.000				
TH	0.946	0.732	0.535	0.594	0.923	0.793	0.904	−0.164	1.000			
pH	0.622	0.146	0.043	0.343	0.402	0.392	0.425	0.032	0.515	1.000		
EC	0.820	0.689	0.679	0.715	0.934	0.766	0.894	−0.170	0.871	0.331	1.000	
TDS	0.820	0.690	0.680	0.715	0.933	0.766	0.894	−0.169	0.871	0.331	1.000	1.000

dominance, rock dominance (dilution and weathering) and precipitation dominance which controls the water chemistry (Gibbs 1970). The chemical data of the groundwaters from the study area plotted mainly around the weathering zone and therefore indicate that the chemical compositions of these waters were controlled primarily by rock dominance (weathering reactions). Therefore, the waters of the study area have their chemistry controlled by the weathered materials derived from the underlying bedrocks.

Regarding water quality for potability and usability, all the various chemical components of the groundwater system in the study area fell within the WHO (2004) acceptable limits for drinking water standard. The irrigation quality assessment was carried out using EC (μS/cm), SAR (Richards 1954), Kelly ratio (Kelly 1963) and magnesium adsorption ratio (MAR) (Paliwal 1972). Detailed formula employed in estimating irrigation quality parameters is highlighted below with ionic concentrations in meq/L:

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

$$KR = \frac{Na}{Ca + Mg} \qquad (3)$$

$$MAR = \frac{Mg^{2+}}{(Ca^{2+} + Mg^{2+})} \qquad (4)$$

Fifty-nine (59) samples out of total seventy-three (73) samples, representing about (81 %) of the water samples, have EC < 700 μS/cm except for one sample with EC > 1,000 μS/cm viz., PG11, 1,041 μS/cm. Normally, irrigation water with an EC < 700 μS/cm causes little or no threat to most crops while EC > 3,000 μS/cm may limit their growth (Tijani 1994). Esimated Kelly ratio <1 for all water samples implies groundwater suitability for irrigation

(Raihan and Alam 2008), MAR for the water samples ranges from 3.41 to 46.17 which is within permissible limit of 50 (Paliwal 1972). Mandel and Shiftan (1991) stated that water with SAR < 10 can be applied on all soil for irrigation usability and the groundwater system in the study area fell into this category. Thus, based on these evaluations, groundwater in the study area was suitable for agricultural purposes.

Hydrochemical facies

The Piper trilinear diagram (1944) is used to infer hydrogeochemical facies. These plots include two triangles, one for plotting cations and the other for plotting anions. The cation and anion fields are combined to show a single point in a diamond-shaped field, from which inference is drawn on the basis of hydrogeochemical facies concept (Back and Hanshaw 1965). The trilinear diagram is useful in bringing out chemical relationships among groundwater samples in more definite terms compared to other convectional plotting methods. The concept of hydrochemical facies was developed to understand and identify the water composition in different classes. Facies are recognizable parts of different characters belonging to any genetically related system. Hydrochemical facies are distinct zones that possess cation and anion concentration categories (Rajendra Prasad et al. 2009).

Plots of the hydrochemical parameters of the water samples on the Piper (1944) trilinear diagram (Fig. 6) classified the groundwater system in the study area into Ca(Mg)HCO$_3$ (dominant) and Na(K)HCO$_3$ (minor) waters. Ca(Mg)HCO$_3$ water facies represent about 89 % of total water samples from the study area. The two main water facies cut across the entire bedrocks of the area except in the Na(K)HCO$_3$ water where only water samples from migmatite, quartzite and fine-medium grained granite
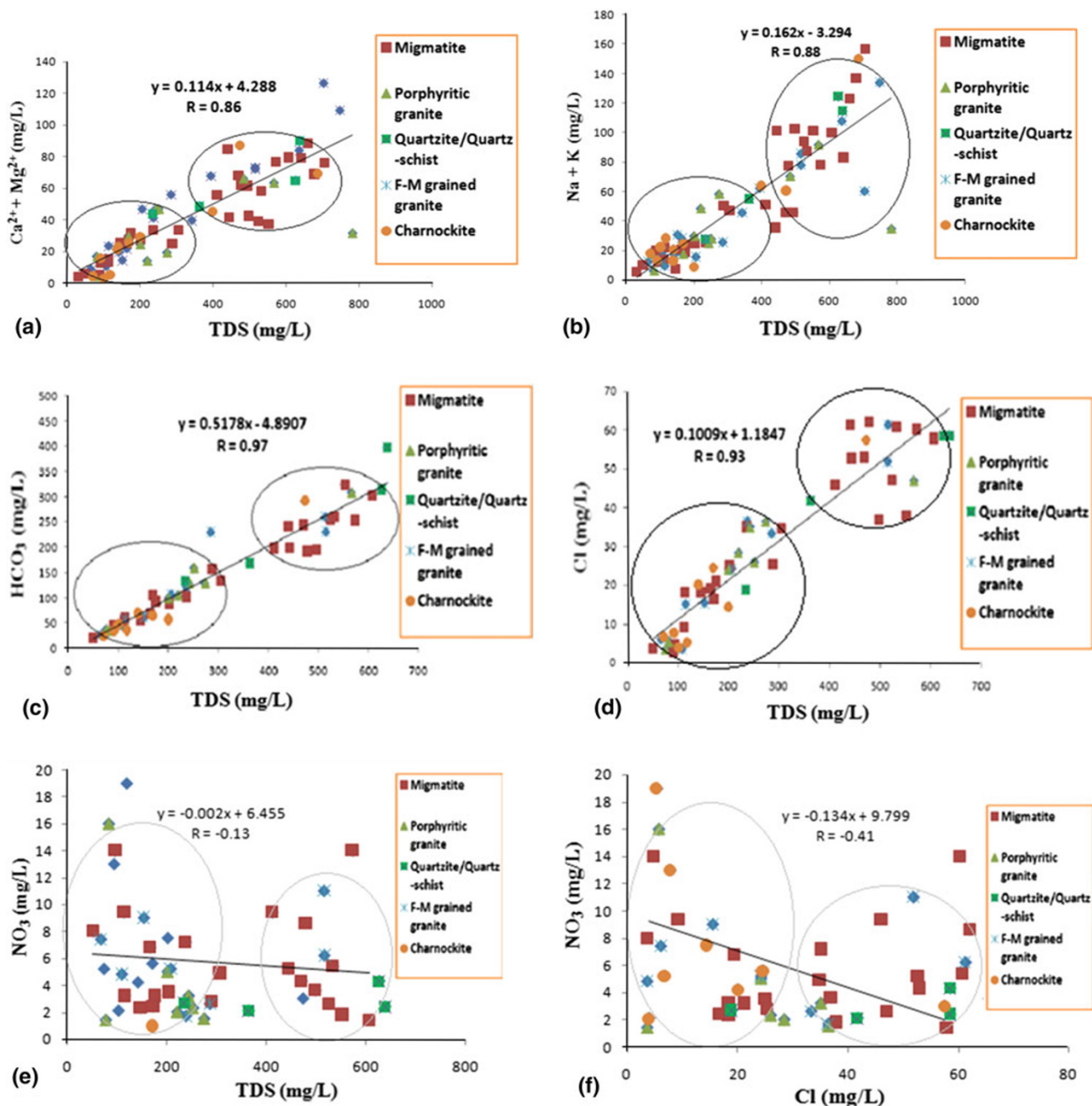
Fig. 4 Cross plots of major ionic parameters in the analysed groundwater samples from the study area

bedrocks were represented. The mineralogical composition of the various rocks especially (migmatite and granite) in the study area could easily weather to produce CaMgHCO$_3$ water type. However, since the study area is located in the rain forest zone where total annual rainfall is about 1,500 mm, the granites weathered to form thick layers of clay deposit and as such cation–anion exchange reactions were therefore suspected to contribute to the groundwater evolution of the study area.

Stable isotopes profiles (δ^{18}O and δD ‰)

Isotope techniques can be used to solve problems such as identification of the origin of groundwater, determination of its age, flow velocity and direction, interrelations between surface waters and groundwaters, possible connections between different aquifers, local porosity, transmissivity and dispersivity of an aquifer (Faure 1998). Stable isotopes of ^{18}O and Deuterium are ideal tracers of
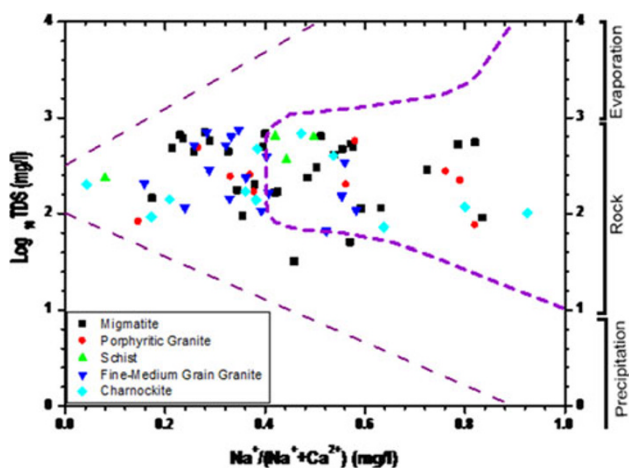
Fig. 5 Controlling mechanisms for groundwater quality in the study area (after Gibbs 1970)

water sources and movement because they are constituents of the water molecules (Akiti 1986). In addition, ^{18}O and Deuterium undergo changes in the various phases of hydrologic environments, resulting in isotopic fractionation that gives isotopic "fingerprints" (Das et al. 1998).

The isotopic composition of oxygen and hydrogen is reported in terms of differences of ^{18}O/^{16}O and D/H

(^{2}H/^{1}H) ratios relative to a standard called Standard Mean Ocean Water (SMOW) (Craig 1961).

$$\delta^{18}O = \frac{\left(^{18}O/^{16}O - ^{18}O/^{16}O_{SMOW}\right) \times 10^3}{^{18}O/^{16}O_{SMOW}} \quad (5)$$

$$\delta D = \frac{\left(^2H/^1H - ^2H/^1H_{SMOW}\right) \times 10^3}{^2H/^1H_{SMOW}} \quad (6)$$

Consequently, positive values of δ^{18}O and δD indicate enrichment of the sample relative to δ^{18}O and δD as compared to SMOW, whereas negative values imply depletion of these samples relative to the standard. On the basis of large numbers of meteoritic water collected at different latitudes, it has been shown that δ^{18}O and δD values of meteoritic water are linearly related and can be represented by the equation $\delta D = 8\delta^{18}O + 10$ (Craig 1961). Data plotted on this suggest that such water is derived from the meteoritic origin. Large deviations also imply either enrichment or depletion.

For this study, 27 locations were sampled and analysed for the stable isotopes (^{18}O and Deuterium). The results and statistical summary of the stable isotopes compositions in δ-notation are presented in Table 4 with all values

Fig. 6 Water type classification using the Piper trilinear diagram (Back and Hanshaw 1965). A Calcium type, B sodium or potassium type, C magnesium type, D no dominant type, E bicarbonate type, F chloride type, G sulfate type, H no dominant I = Ca + Mg type, J = HCO$_3$ + CO$_3$ type, K = Na + K type, L = Cl + SO$_4$ type M = Ca(Mg) HCO$_3$ type, N = Ca(Mg) Cl SO$_4$ type, O = Na(K) HCO$_3$ type, P = Na(K) Cl(SO$_4$) type
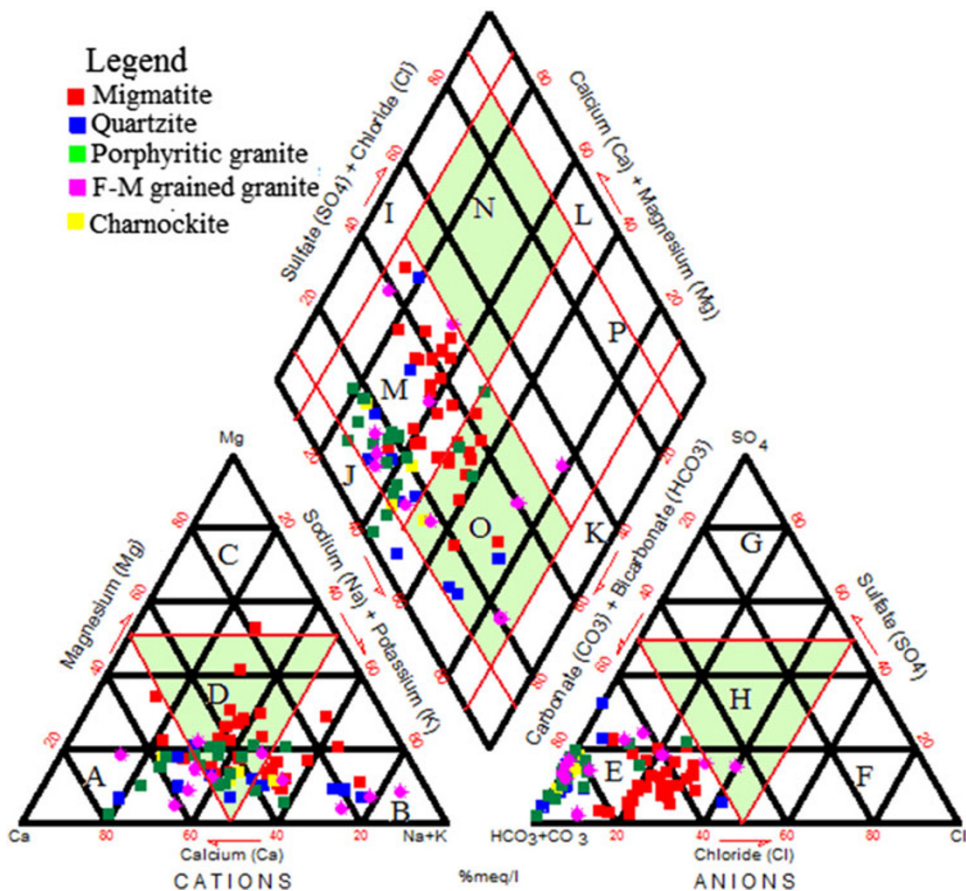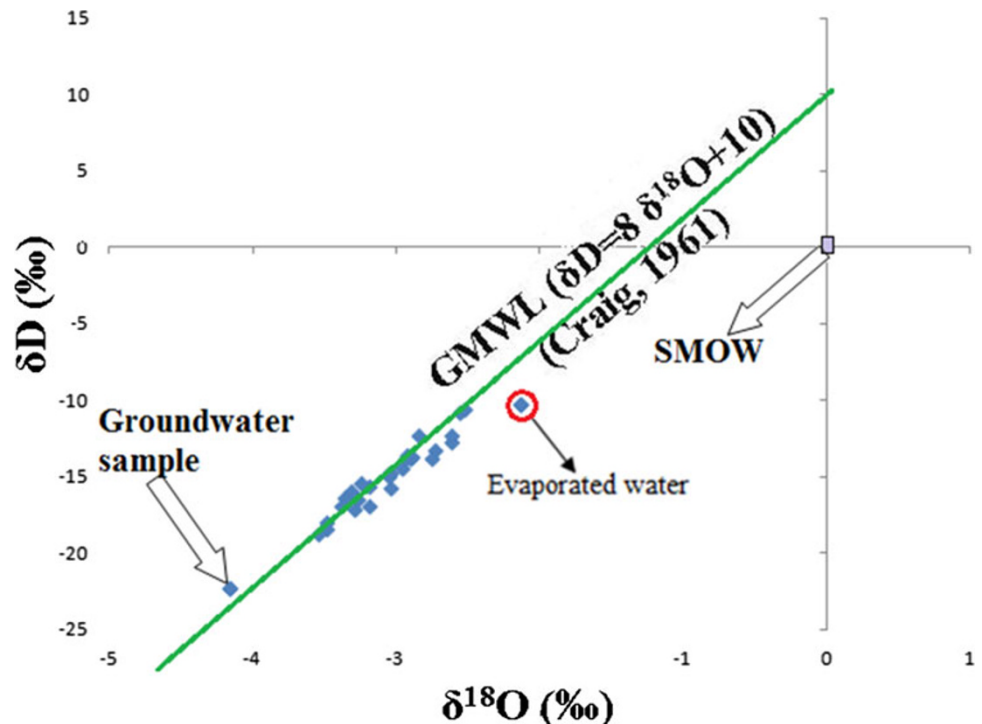
Fig. 7 Stable isotopes of Ekiti groundwaters

reported in per mil (‰) in reference to V-SMOW and measurement accuracy of ± 0.15 for both δD and $\delta^{18}O$. The relationship between δD and $\delta^{18}O$ in the classical δD versus $\delta^{18}O$ plot (Fig. 7) alongside with the global meteoric water line (GMWL) defined by Craig (1961) usually reveals indications about origin and recharge source(s) of groundwater system as well as possible evaporation effect (Murherjee et al. 2007).

The measured δD values of the analysed water samples range from -22.3 to -10.2 ‰ with an average value of -15 while that of $\delta^{18}O$ range from -4.2 to -2.1 ‰ with an average value of -3.1 (Table 5). With the exception of location C2 on charnockite bedrock that deviate slightly from GMWL, all sampled water do not only show depletion compared to that of the sea water ($\delta D = 0$ ‰; $\delta^{18}O = 0$ ‰) but also plotted along the GMWL as defined by the equation $\delta D = 8\delta^{18}O + 10$ (Fig. 7). The general implication of this is that the origin of groundwater in the study area is related to meteoric source, i.e. recent precipitation water recharging the associated shallow basement aquifer, with little or no imprint of kinetic evaporation. This result is further supported by the fact that deuterium excess (d-excess) values are generally in the range of 10 ± 2, i.e. close to 10 which support the observation of recent precipitation with little or no imprint of kinetic evaporation (Table 5). Similar isotopic signature had been reported for shallow groundwater in other parts of the Basement Complex of southwestern Nigeria (Loehnert 1988; Tijani and Abimbola 2003).

The observed isotopic signature was in agreement with the early conclusion from hydrochemical data, i.e. evolution of the groundwater was related to infiltration of CO_2-charged precipitation with limited migratory history characterised by low TDS. The shift of the sample on location C2 slightly away from GMWL with d-excess of 6.8 can be the result of limited degree of kinetic evaporation before or during infiltration process. Furthermore, as shown in Fig. 7, the groundwater samples appeared to group in a narrow range signifying a well mixed system with relatively constant isotopic composition. This observation indicates that the meteoric water recharging the groundwater system in the study area is relatively homogenous with evaporation playing insignificant role on the infiltrated water.

Groundwater undergoing evaporation will have a positive correlation between $\delta^{18}O$ and electrical conductivity (Gibrilla et al. 2010). In Fig. 8a showing the plot of $\delta^{18}O$ versus EC, it was observed that a positive correlation of $r = 0.54$ supports earlier observations that few of the groundwater samples plotted slightly away from the GMWL, which are indicative of possible mild evaporation prior to recharge or kinetic interaction with the subsurface medium. With EC < 300 μS/cm, $\delta^{18}O$ (‰) changed minimally as shown by samples in circle B. Samples in circle A illustrate evaporative effects with mineralization accompany enrichment of $\delta^{18}O$ (‰) (Fig. 8a). Nitrate content in the groundwater at any point or area in the saturated aquifer is controlled by the water recharging through the unsaturated zone and the lateral flow from

Table 5 Result of stable isotopes in the study area

Sample ID	Location	$\delta^{18}O$ ‰	δ^2H ‰	d-excess ‰
M1	Oye	−3.36	−16.4	10.5
M2	Eyio	−3.29	−17.1	9.2
M3	Awo	−2.9	−13.8	9.4
M4	Are	−2.62	−12.7	8.3
M5	Ilokun	−3.19	−15.6	9.9
M6	Ayoko	−2.89	−13.7	9.4
M7	Aso Ajegule	−3.49	−18.4	9.5
M8	Ilupeju-Ijan	−2.73	−13.3	8.5
M9	Aba-Efon	−3.31	−15.9	10.6
M10	Igbaraodo	−2.96	−14.4	9.3
M11	Ogbesse	−2.75	−13.8	8.2
PG1	Itapa	−3.38	−16.9	10.1
PG2	Ado	−2.62	−12.3	8.7
PG3	Ikere	−3.27	−16.5	9.7
PG4	Ikere	−3.19	−16.9	8.6
S1	Erio	−2.56	−10.8	9.7
S2	Ikogosi	−4.16	−22.3	11
FG1	Epe	−3.04	−15.7	8.6
FG2	Ara-Ijero	−3.05	−14.8	9.6
FG3	Iropora	−2.52	−10.6	9.6
FG4	Iyin	−3.49	−18	9.9
FG5	Temidire-Asa	−2.84	−12.3	10.4
FG6	Aba-Alawaye	−2.94	−13.8	9.7
FG7	Aba-Oshun	−2.93	−13.6	9.8
C1	Ire	−3.54	−18.7	9.6
C2	Afao	−2.13	−10.2	6.8
C3	Fagbohun-Ado	−3.25	−15.4	10.6
Min.		−4.2	−22.3	6.8
Max.		−2.1	−10.2	11
Mean		−3.1	−15	9.5
Median		−3	−14.8	9.6
Standard deviation		0.4	2.8	0.9

surrounding areas. Therefore, depending on the recharge/infiltration characteristics and the period of stay of water on the land surface (and thereby subjected to evaporation) at different locations, some kinds of correlation are expected between $\delta^{18}O$ and NO_3^- contents of groundwater (Akiti 1986). It is observed from Fig. 8b that correlation coefficient of 0.25 is obtained from the plot of $\delta^{18}O$ versus NO_3^-. In circle I of Fig. 8b, enriched $\delta^{18}O$ signifies evaporation while that of circle II indicates low nitrate groundwater associated with depleted $\delta^{18}O$ water implying anaerobic conditions at deeper levels in the soil profile (Datta et al. 1997). Some of the wells were recharged by significant quantities of evaporated (^{18}O enriched) rainwater infiltrating along with NO_3^- salts from the soil to the groundwater system. In circle III, fairly constant $\delta^{18}O$ with relatively high NO_3^- values

support argument of surface source of NO_3^-. Finally, assessment of the deuterium excess (d-excess) reflects the conditions that lead to kinetic isotope fractionation between water and vapour during primary evaporation in the oceans (Dansgaard 1964). It shows the extent of deviation of a given sample from the Global meteoric water line. The calculated deuterium excess of the groundwater was found ranging from 6.80 to 11.00 ‰. As the $\delta^{18}O$ increases (more enriched), the deuterium excess in most of the samples decreases gradually (Fig. 8c and Table 5) signifying the slight evaporative effects on the groundwater system. However, the fact that the groundwater samples plot in close range to GMWL imply a modern recharge source to the groundwater system of the study area.

Conclusion

Assessment and evaluation of the hydrochemical data from the study area have thrown light on the hydrochemistry, quality and stable isotope characterisation of shallow groundwater system from the weathered basement aquifer of Ekiti area, southwestern Nigeria. The physical and chemical parameters of all sampled water fell within the WHO (2004) guideline values for drinking water and revealed that the groundwater was potable. Further, evaluation of the hydrochemical results showed that the groundwater system in the study area was fresh ($32.25 \leq$ TDS ≤ 746.25 mg/L), low mineralised with limited water–rock interactions. The groundwater system was soft to moderately hard ($31.28 \leq$ TH ≤ 295.10 mg/L) and slightly alkaline ($7.0 \leq$ pH ≤ 8.9). Quality evaluation in terms of agricultural uses revealed that the estimated irrigation indices using SAR, MAR and Kelly's ratio indicated that the groundwater was suitable for irrigation purposes.

The principal source of the dissolved chemical species in the groundwater system of the study area was from mineral weathering/dissolution process facilitated by the action of infiltrating rain water rich in atmospheric and/or biogenic CO_2. This mineral weathering/dissolution was the main process responsible for the hydrochemical evolution of the groundwater system in the study area. This was further supported with the fact that most water samples plotted in the rock dominance part of the Gibb's diagram. The principal hydrochemical facies in the study area were Ca-(Mg)-HCO_3 and Na-(K)-HCO_3 waters. Ca-(Mg)-HCO_3 water represents geogenic characters of the shallow groundwater system in the study area which was the result of weathering/dissolution of aluminosilicate minerals. This is also consistent with the results of stable isotope analysis which revealed meteoric source of groundwater recharge

Fig. 8 Cross-plots of $\delta^{18}O$ (‰) versus EC(μS/cm), NO$_3$(mg/L) and d-excess
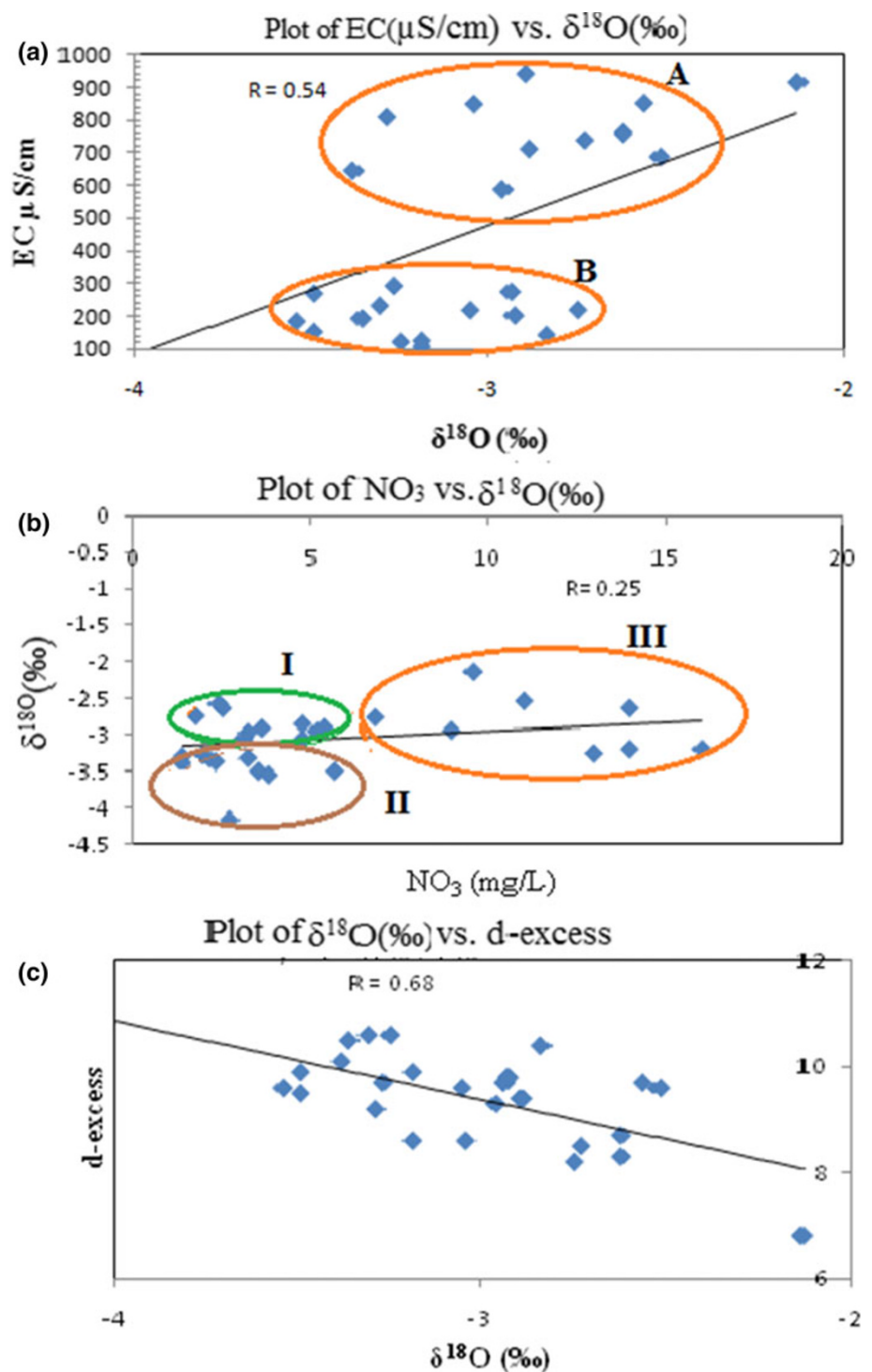
(i.e. recent precipitation with insignificant degree of kinetic evaporation recharging the associated shallow basement aquifer).

Finally, the fact that the aquifers in the study area are shallow and localised and that recharge is primarily from infiltrating precipitation, warrants the need for proper design and construction of sewage pits to forestall anthropogenic pollution due to seepage/leakage that may arise from possible hydraulic connection with the shallow groundwater system in the study area.r

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