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ORIGINAL PAPER

Geochemical and quality assessment of groundwater in some Nigerian basement complex

A. M. Odukoya[1]

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Abstract Fifty samples from hand dug wells and boreholes were collected at Ijebu Igbo and its environs within the basement complex of some part of southwestern Nigeria. The purpose was to establish preliminary baselines for constituents in the groundwater and also to determine the quality for both drinking and irrigation purposes. Physical parameters were determined in situ using the appropriate digital meters, while the analysis of trace elements and cations in water was carried out using inductively coupled plasma optical emission spectrometry at Actlabs, Ontario, Canada. The order of relative abundance for major elements is Na > Ca > K > Si > Mg > P > Fe > Al > S. Al, Fe, Na, K and P were above the EPA 2012 recommended standard for drinking water in 79, 23, 3, 37 and 6 % of the water samples, respectively, and geochemical process is being influenced by both man activities and weathering of silicate minerals. Sodium absorption ratio ranges between 0.12 and 10.43 and falls within excellent and good for irrigation purpose. Only 78 and 22 % of water samples were suitable for irrigation based on the soluble sodium percentage and magnesium adsorption ratio, respectively, while all the water samples were good for irrigation purpose based on Kellys ratio. Concentration of Te and Ti was below the detection limit for all the samples. As, B, Cd, Cr, Cu, Mo, Ni, U and Zn though present in water were below recommended standards for all the samples. Ni and Sb exceeded recommended standard only in sample W24, and Ba exceeded recommended standard in W20 with value as high as 909.76 ppb. Mn and Pb were higher than recommended standard in 12 % of the samples, respectively. The pollution index varied from 0.09 to 1.66 with 8 % of the water samples showing pollution index above 1. Generally, groundwater in the study area is suitable for both domestic and irrigation uses except samples W4, W20, W24, W47 and W49. However, since heavy metals are not biodegradable, they tend to bioaccumulate and biomagnify in the body and eventually become harmful to human health.

Keywords Irrigation · Major elements · Nigeria · Trace element

Introduction

Water is an essential component for survival of life on Earth. It contains minerals which are important for human beings as well as plant and aquatic life. Groundwater is also a major source of freshwater for agricultural and domestic uses, and approximately 97 % of the earth's useable freshwater is stored as groundwater (Delleur 1999). Approximately 40 and 70 % of the total global water resources being used for irrigation and domestic purposes are from groundwater, and these values could be increased due to the continuous decline in the quantity and quality of available surface water resources which are largely caused by increase in global pollution threats, industrialization and urbanization, as well as the effects of the climate change (Qiu 2010).

Hydrogeochemistry of groundwater is determined by its chemical and biogeochemical constituents. The exploration and exploitation of groundwater as a major resource to meet the growing population in some urban cities located

✉ A. M. Odukoya
amodukoya@unilag.edu.ng

[1] Department of Geosciences, University of Lagos, Lagos, Nigeria

in the basement complex rocks of Nigeria have been a subject of discussion (Odukoya and Abimbola 2010; Nagard 2010; Obiefuna and Sheriff 2011; Olorunfemi 1990).

The suitability of a particular groundwater for certain utilities such as public water supply, irrigation, industrial application, cooling, heating, power generation largely depends on sediments, lithologic content, temperature, possible temporal variations caused by climatic conditions as well as water quality (Vetrimurugan et al. 2012). The chemistry of groundwater is due to several processes like soil/rock–water interaction during recharge and groundwater flow, prolonged storage in the aquifer, dissolution of mineral species (Sekabira et al. 2010; Hem 1985). These processes are related to weathering of minerals which generally exerts an important control on groundwater chemistry (Garrels and Mackenzie 1967; Frape et al. 1984; Rogers 1987; Nordstrom et al. 1989; Kenoyer and Bowser 1992; Bullen et al. 1996; Kim 2002). This process generally dominates the concentration of the major cations (Ca, Mg, Na, K) in groundwater (Garrels and Mackenzie 1967; Jacks 1973; Kenoyer and Bowser 1992; Bartarya 1993; Kim 2002, 2003).

The available published works on groundwater quality and chemistry of Nigeria are on specific issues and generally localized in terms of area coverage. There are some published data on groundwater chemistry and quality in Nigeria for some basins including the crystalline basement complex. These researches generated data for saline and coastal groundwater within the basement complex. The water was classified as acidic, fresh and generally hard. The average concentrations of sodium, calcium, magnesium, potassium, chloride and sulfate for the different areas were generally within the limits stipulated by WHO (World Health Organization) (1993) for domestic purposes. However, the average concentration of potassium is high in some area. The geology has been put as the principal factor controlling the chemistry of groundwater in terms of the water types and the processes. The main processes include chloride dissolution for saline and coastal groundwater aquifers and a combination of silicate, carbonate weathering and ion exchange for the different aquifers in the various basins and the basement complex areas. In respect of agricultural uses, groundwater from the different areas were put to be of low-salinity and low-alkalinity hazard, good to excellent quality for irrigation on the basis of Na%, sodium absorption ratio (SAR) and RSC. These studies were documented in the work of Longe et al. (1987), Otezie (1991), Edet (1993), Olarewaju et al. (1997), Udom et al. (1998, 2004), Edet et al. (2011), Ajayi (1998), Ajayi and Obot (1998), Erah et al. (2002), Ahiarakwem and Ejimadu (2002), Ogunbanjo (2004), Olobaniyi and Owoyemi (2004), Ozoko (2004), Adediji and Ajibade (2005), Ofoma et al. (2005), Efe et al. (2005), Edet and Okereke (2002), Alagbe (2006), Abulude et al. (2007), Olobaniyi and Efe (2007), Adekunle et al. (2007), Jatau and Bajeh (2007), Chukwu (2008), Boboye (2008), Adebo and Adetoyinbo (2009) and Nganje et al. (2010).

The quality of water is now the concern of experts in all countries of the world. Eighty percentage of the diseases and deaths in the developing countries are related to water contamination UNESCO (2007), UNDP (1971). It has been generally agreed that the water delivered to the populace should meet the high requirement of modem hygiene and should at least be free from pathogenic organisms and toxic substance. It is therefore important to carry out water quality assessment for sustainable management of water bodies. Additionally, intense agricultural and urban developments have placed a high demand on groundwater resources worldwide and also directly or indirectly play a major role in regulating groundwater chemistry (Lowrance et al. 1997; Fakir et al. 2002; Cardona et al. 2004). Groundwater contamination due to intense agricultural activities is usually expressed increasing salinity and increasing nutrient concentration (Dash et al. 2006; Perez et al. 2003; Chae et al. 2004). Uncontrolled applications of fertilizers and manure, as well as indiscriminate disposal of domestic wastes and sewage, could further contribute to the degradation of groundwater quality, especially in the developing countries (Oladeji et al. 2012). Similarly, urban development also causes deterioration in groundwater quality (Nkotagu 1996; Stigter et al. 1998; Zilberbrand et al. 2001). Numerous studies have quantified the effect of anthropogenic contamination in groundwater composition (Vetrimurugan et al. 2012).

The rural population in the study area mostly depends on the use of groundwater for cultivation and domestic uses during most period of the year. The common crops grown in this area are cocoyam, maize, cassava, yam, cocoa and others. Occupation of the people in this area is farming, and many people engage in different crop plantation. This research thus focused on the geochemical and quality assessment of groundwater samples in Ago Iwoye, Oru, Awa and Ijebu Igbo area of Ogun southwestern Nigeria to determine the suitability for drinking and irrigation purposes and also to identify major hydrogeochemical processes that are responsible for groundwater chemistry in the study area.

The field work was carried out in April/May 2009 which happens to fall in the period when raining season normally starts to prevent dilution during sampling.

Geographically, the study area which include Oru, Awa and Ijebu Igbo fall within basement complex of the southwestern Nigeria, which occur between Precambrian and lower Paleozoic (Jones and Hockey 1964; Rahaman 1976). It is located in latitude 06°50′–07°00′N and longitude 003°50′–004°00′ (Fig. 1). The area is characterized

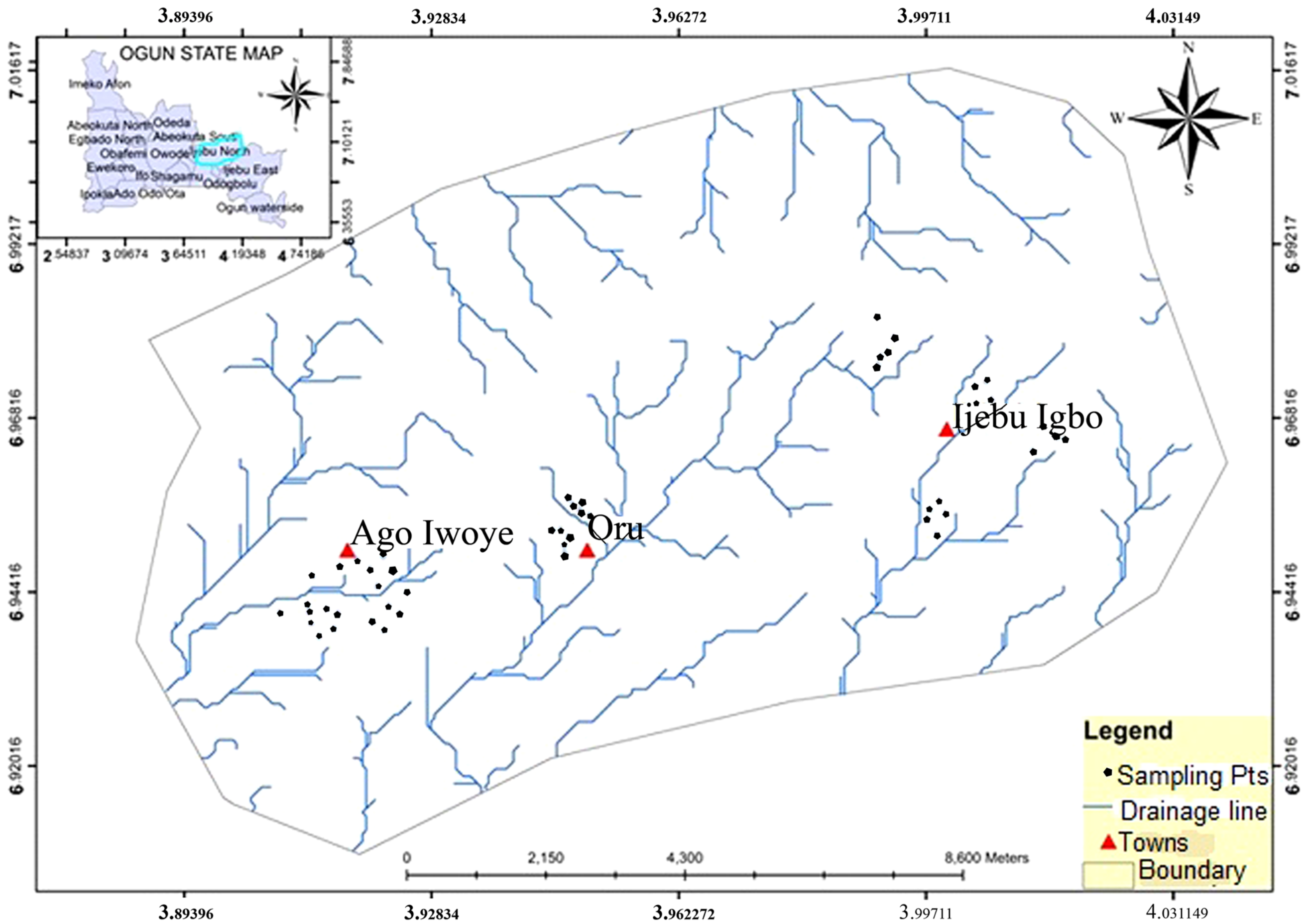

Fig. 1 Location map of the study area

with two types of climate with contest between dry and wet seasons. The average rainfall during the wet season is 750–1000 mm. The study area is within the tropical rain forest, and the natural vegetation consists of multitudes of evergreen trees ranging from tropical hardwood, palm trees and green grasses.

The geology of the study area consists of igneous and metamorphic rocks typical of basement complex. The rocks occur either directly exposed or covered by shallow mantle of superficial deposits and consist of granites–gneiss, minor amphibolites, schists, quartzite, pegmatite, migmatite with minor intrusions. Granites–gneiss account for about 70 % of the study area. They include a very highly metamorphosed coarse-grained banded rock. They are characterized by alternating bands of minerals such as chlorite, biotite, muscovite and quartz. Associated with granite, gneisses are intrusions such as concordant and discordant pegmatite and quartz vein as well as minute joint and fractures. Most of the outcrops are highly weathered and strongly foliated. There are two types of aquifer system in the study area. These are the fracture basement complex rocks and weathered basement rocks. These two types usually occur together in the same place, although they cannot be said to be mutually exclusive because at times only one form occur in a place. The fracturing of the crystalline rocks to store, allow movement and yield chiefly depends on the extent, size openness and continuity of fracture and on the degree to which the fractures are hydrogeologically connected. Ogun River is the largest river in this area, and most of the rivers in Ijebu Igbo are linked to Ogun River. There are other rivers like Odobotu and Alapata. The drainage pattern is dendritic.

Materials and methods

Based on detailed well inventory survey in Ago Iwoye, Oru Awa and Ijebu Igbo area of Ogun southwestern Nigeria, 50 representative groundwater samples (boreholes and wells) were selected for geochemical analysis (Fig. 1). Most of these wells are shallow in nature and have been used for agricultural and domestic purposes. The samples were collected in 1-L high-density cleaned polythene containers and rinsed 3–4 times before sampling using the water to be sampled. Collected samples were stored at 4 °C before transported to the laboratory. Several sensitive parameters of water such as total dissolved solids (TDSs) and pH were determined during the on-the-spot sampling using the appropriate digital meters (e.g., water treatment work (WTW)-conductivity meter model L/92 and WTW-pH meter model pH/91). Water samples collected for major and trace element analysis were preserved by acidifying with 3 mL of analytical grade HNO_3 acid to achieve a pH of 2. All the major cations and other trace elements which include 36 elements were analyzed using ICP–OES (PerkinElmer Elan 6000) at the ACME laboratory, Ontario, Canada. To check the accuracy, activation laboratories (Ontario, Canada) employed two internal standards (each run twice) and found that the errors were consistently minimal. The analytical precision for the total measurements of ions was checked by calculating the ionic balance errors and was generally within ±5 %.

Parameters such as sodium adsorption ratio (SAR), soluble sodium percentage (SSP), magnesium adsorption ratio (MAR), Kellys ratio (KR) were also calculated from the result to determine the suitability of the water for irrigation purpose using the equation in Oladeji et al. (2012). Results were further compared with recommended standards and pollution index, and other hydrogeochemical parameters were calculated to determine the water geochemistry and its quality for both drinking and irrigation purposes.

Results and discussion

The summary of the concentrations of physical properties and dissolved elements in groundwater around Ago Iwoye, Oru, Awa and Ijebu Igbo, southwestern Nigeria is given (Tables 1, 5). Analytical results for significant elements were compared with United State Environmental Protection standards and World Health Organization standards. The standards include maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs) established by the (USEPA 2012) and (WHO 2012). MCLs are enforceable standards that specify the highest level of a contaminant that is allowed in public water.

The pH of groundwater of the study region varied from 6.6 to 8.3 with an average of 7.3 which indicates that water samples fall within slightly acidic to alkaline based on the classification by (Ezeigbo 1989). Low pH value of <8 is said to be an indication of the presence of free CO_2, and that the dissolved carbonates exist almost entirely in HCO_3 ion form (Freeze and Cherry 1979). All the water samples fall within EPA 2012 standard for drinking and irrigation. The TDSs were between 67 and 450 mg/L with an average of 245 mg/L. According to TDS classification (Freeze and Cherry 1979), all the groundwater samples belong to freshwater category (Table 2). They also fall within low-saline and moderate-saline water and were within safe and safe under certain condition for irrigation purposes according to Richards (1954) (Table 2). The physical parameters of water met the EPA 2012 standard for both drinking and irrigation purposes. pH and TDS showed large variation between minimum and maximum value and also expressed high standard deviation. This inference suggests the influences of complex contamination sources and geochemical process as well as inhomogeneous water chemistry in the study area (Table 1)

The order of relative abundance for major elements with their mean values is Na (40,485.95 ppb) > Ca (250, 96.69 ppb) > K (19,165.4 ppb) > Mg (8649.7 ppb) > Si (11,192.03 ppb) > P (513.53 ppb) > Fe (428.87 ppb) >

Table 1 Summary of some parameters in groundwater

Major elements	Min	Max	Mean	SD	Median	Recommended standards	% above recommended standard
pH	6.6	8.3	7.3	24.52	7.2	6.5–8.5	
TDS (ppm)	67	450	245	1432.32	387	500	
Fe	0	22,450	428.87	2159.49	58	300	23
K	81	561,600	19,165.4	55,599.16	5286	12,000	8
Mg	196	71,049	8649.66	12,824.31	3465.5	150,000	
Na	1147	646,396	40,485.95	73,665.54	20,949.5	200,000	3
P	0	15,841	513.13	2134.89	89	25	8
S	0	97	6.22	12.97	6		
Ca	511	100,420	25,096.69	23,964.9	15,894.5	200,000	
Al	0	2686	98.47	294.92	16	200	5
Si	3282	41,968	11,192.03	8094.61	8037.5		

All major elements in ppb

Table 2 Suitability of irrigation water based on the EC values (Richards 1954)

S/N	Electrical conductivity/total dissolved solids	Water type	Suitability for irrigation
01	<250	Low-saline water	Entirely safe
02	250–750	Moderate saline	Safe under most conditions
03	750–2250	Medium to high saline	Safe only with permeable soil and moderate leaching
04	2250–4000	High salinity	Unfair for irrigation
05	4000–6000	Very high salinity	
06	>6000	Excessive salinity	

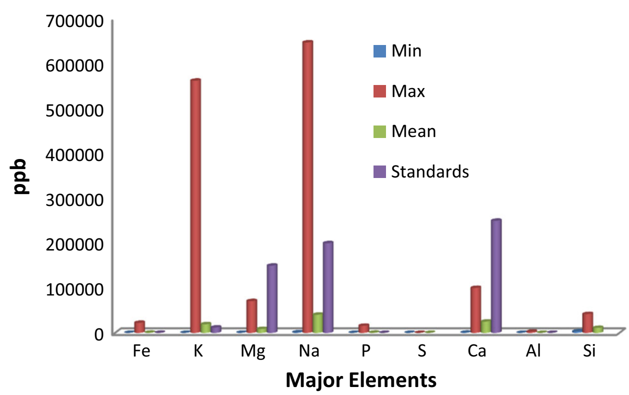

Fig. 2 Summary of major elements

Al (98.465 ppb) > S (6.22 ppb) (Fig. 2). Calcium, magnesium, silicon and sulfur were all within recommended standard for both drinking and irrigation purposes. Aluminum, iron, sodium, potassium and phosphorus were above the EPA 2012 recommended standard for drinking water in 5, 23, 3 and 8 % of the water samples, respectively, (Table 1).

Water chemistry is determined by reactions between groundwater and aquifer minerals which are also useful to understand the genesis or origin of groundwater (Cederstorm 1946) as well as anthropogenic impacts. Since the study region experiences wet and dry climatic condition which promote weathering, this may largely contribute to water chemistry in the study area. Correlation plots between Si and all other major elements showed strong negative values except with Fe which showed weak positive correlation (Fig. 3a, b). This may be due to the facts that the SiO_2, which is the most stable mineral, will not easily weathered and dissolved in water like other major elements; hence, its presence is not predominant in the groundwater which resulted in its poor correlation with them. Correlation between other major elements showed strong positive values except Fe and Ca which showed negative correlation (−0.386) (Fig. 4c). Na and K showed strong positive correlation with other elements compared with Ca which showed low positive correlation. The *P* values for correlation analysis between K and Na, Mg and Na, P and Na and S and P were 0.64, 0.85, 0.55 and 0.86, respectively (Fig. 4a–c).

The principal source of these major elements in groundwater is the interaction between rocks in the study area and aquifer (geogenic). This involved the weathering of silicate minerals like albite, plagioclase, pyroxenes and other igneous rocks typical of the study area in the geochemical processes, which contributed more of sodium, magnesium and potassium ions than calcium to the groundwater (Stallard and Edmond 1983; Sarin et al. 1989). The calcium-bearing rocks are not as widespread as sodium-bearing rocks in the study area. Sodium-bearing minerals like albite and other members of plagioclase feldspars are widespread or abundant. Weathering of these minerals releases primarily sodium-soluble products. The typical ionic concentration ratios are shown in Table 3. The Na/Ca ratio ranged from 2.24 to 6.44, while the Ca/Mg ratio ranged from 1.41 to 2.61. This also confirmed the dominance of sodium ion over calcium ion in the water sample. Figure 5 also confirms that $Na^+ + K^+$ contributed more to water chemistry than $Ca^+ + Mg^+$. The high concentration of Fe, Al, Na, K and P which were above recommended standards in some water samples could also be linked to anthropogenic sources which include waste dumpsites, agricultural activities and sewage that are common in the study area. The concentrations of these ions are important in agricultural and human pathology, but their acute effects may include nausea, vomiting, convulsions, muscular pains and cerebral and pulmonary edema in humans and poor crop yield in plants. The concentration of sodium is important in agricultural and human pathology. Soil permeability can be disturbed by a high sodium concentration.

Dispersion pattern showing the level of variation of parameters is shown in Fig. 6. The highest concentrations for all the major elements were recorded in locations 2, 12, 13, 17, 18, 24 and 27 which are mostly hand dug wells that were not well constructed and were close to the areas with high impact of domestic wastewater, dumpsites, sewage and sewage pits. The presence of detergents in the

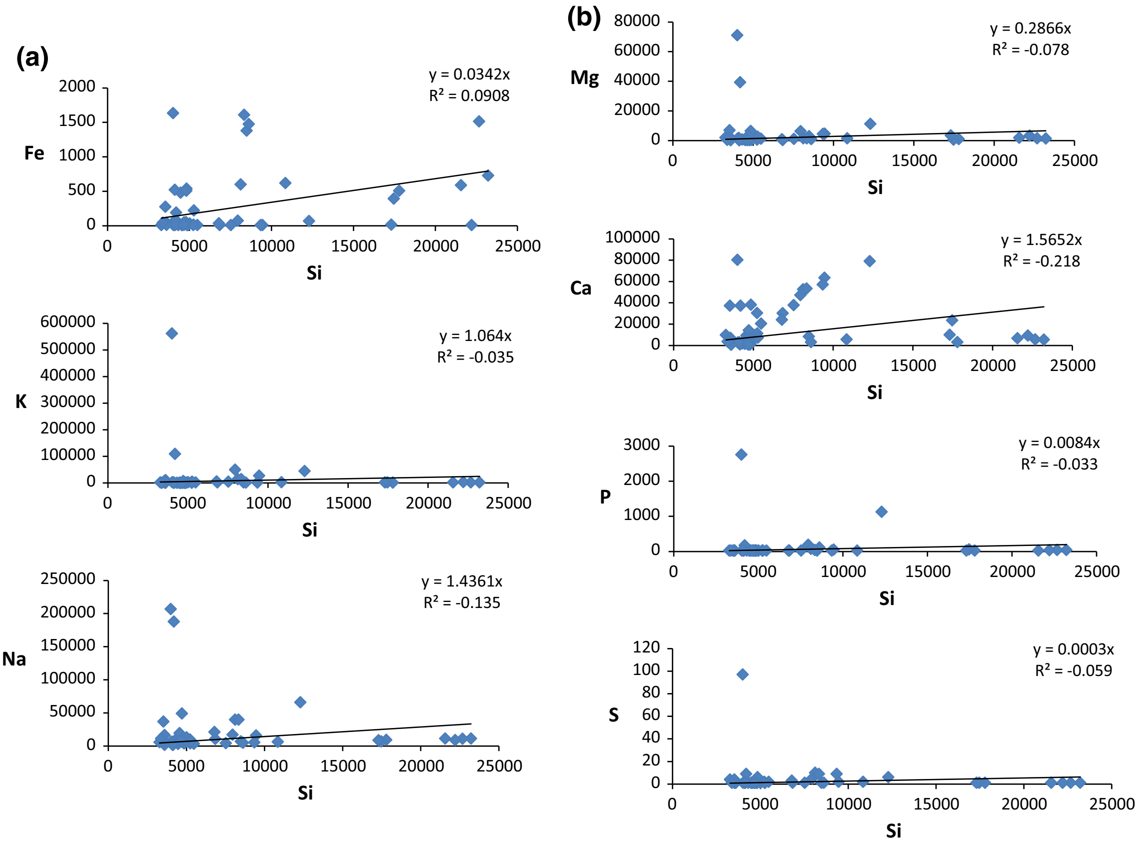

Fig. 3 Plot of major elements against Si

wastewater may enhance concentrations of sodium, potassium and chloride in the groundwater (Juang et al. 2009). The high concentration of potassium in the study area may be due to sources of surface contamination since potassium is not expected to be high because of the resistance of potassium minerals to decomposition by weathering and also the fixation of potassium in clay minerals formed due to weathering. Irrigation return flow and application of synthetic fertilizers and farm manures also have strong influences on groundwater quality in the study region. The lowest values for all the major elements except Si and Fe were recorded in sample W39 which is a borehole located in a cleaner environment.

Water analysis data obtained in the present study have been utilized for understanding the suitability of water for agricultural purpose. There are various parameters, which help in determining the quality of water for irrigation such as SAR, Kellys ratio (KR), magnesium absorption ratio (MAR) and SSP (Table 3).

Sodium adsorption ratio (SAR) is a measure of the suitability of water for use in agricultural irrigation, as determined by the concentrations of solids dissolved in the water. It is also a measure of the sodicity of soil, as determined from analysis of water extracted from the soil.

The formula for calculating SAR is:

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{\frac{1}{2}\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)}} \quad (1)$$

where sodium, calcium and magnesium are in milliequivalents/liter.

The SAR in water samples range from 0.12 to 10.43 and fall within excellent and good for irrigation purpose (Tables 3, 4). The higher the SAR, the less suitable the amendments to prevent long-term damage to the soil. As a rule, water that has an SAR below 3 is safe for irrigating turf and other ornamental landscape plants (Harivandi 1999). Water that has an SAR >9, on the other hand, can cause severe permeability problems when applied to fine-textured soils such as silty clay loam and should be avoided. Coarse-textured (sandy) soils typically are less susceptible to permeability problems Bryan et al. (2007) (Table 5). For those types of soils, the irrigation water SAR can be a bit higher than for fine-textured soils. The Na% also ranged from 21.6 to 44.18 % which were higher than 15 % for all the samples (Table 3). Water samples were higher than recommended standard for irrigation based on Na%. If irrigation water with a

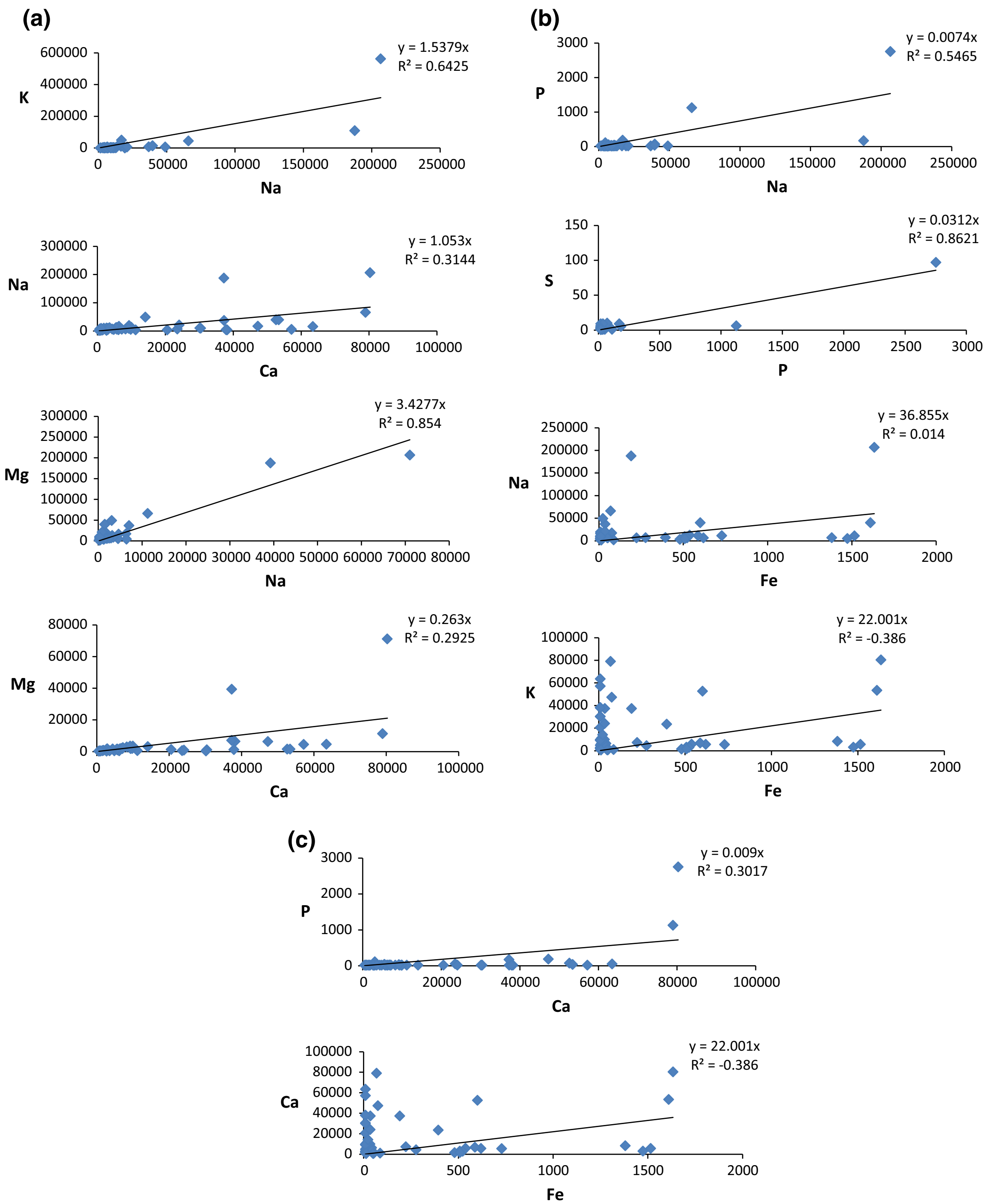

Fig. 4 Correlation plots between major elements

high SAR is applied to a soil for years, the sodium in the water can displace the calcium and magnesium in the soil. This will cause a decrease in the ability of the soil to form stable aggregates and a loss of soil structure. This will also lead to a decrease in infiltration and permeability of the soil to water leading to problems with crop production.

Magnesium absorption ratio (MAR) can be calculated using this formula;

$$\mathrm{MAR} = \frac{\mathrm{Mg} \times 100}{\mathrm{Mg} + \mathrm{Ca}}. \quad (2)$$

Calcium and magnesium in water are generally, "in the state of equilibrium." Magnesium content of water is

Table 3 Summary of water irrigation criteria

Water irrigation parameter	Min	Max	Mean
Na%	21.68	44.18	38.23
Na/Ca	2.24	6.44	1.61
Ca/Mg	1.41	2.61	2.9
SAR	0.12	10.43	1.54
KR (meq/L)	0.00057	0.0047	0.001
SSP (%)	62.79	90.32	62.79
MAR (%)	0.89	87.94	31.58

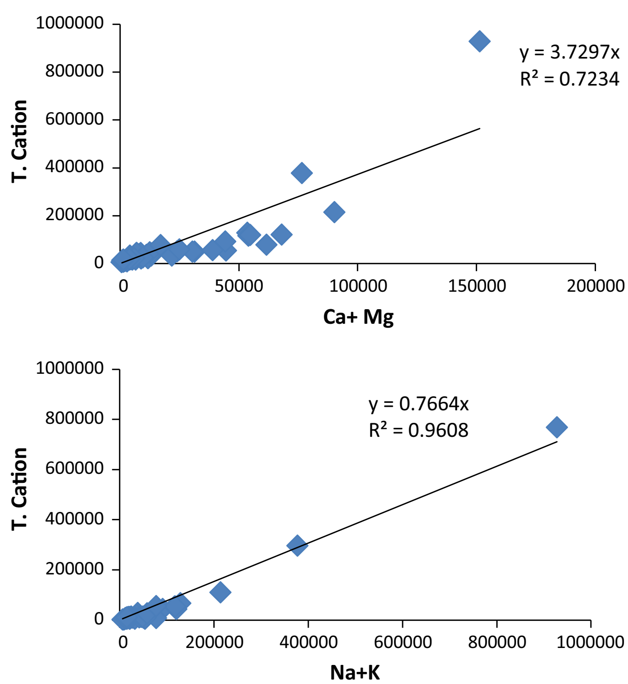

Fig. 5 Plots of total cations against Na + K and Ca + Mg

considered as one of the most important qualitative criteria in determining the quality of water for irrigation. More magnesium in water will adversely affect crop yields as the soils become more saline (Joshi et al. 2009).

The presence of large amount of magnesium in water adversely affects soil quality. It converts the soil into alkaline in nature, thus reducing its crop yield. Magnesium ratio of more than 50 % in a water body will make the water poisonous to plants. The values obtained for the MAR within the study area vary between 0.89 and 87.94 %. Increasing amount of magnesium in water will also increase the salinity of the water and therefore decline the crop yield Schoeller (1965). According to Schoeller (1967), 22 % of the water samples fall within 50 % considered suitable with no hazardous effects to the soil based on MAR (Table 3). The high magnesium in water also causes heart diseases.

Soluble sodium percentage (SSP) is frequently used in the determination of the suitability of water for irrigation purpose and can be calculated using this formula

$$SSP = \frac{(Na + K) \times 100}{Ca + Mg + Na + K}. \quad (3)$$

It can be defined as the tendency for a water to enter into cation-exchange reactions and is commonly evaluated in terms of the "sodium percentage" which is the percentage of total cations made up by sodium. Because divalent cations usually are preferentially held in exchange position on clay minerals, the extensive displacement of "Ca and Mg by Na" is unlikely unless the sodium percentage is considerably higher than 50 or the total concentration of solutes is large (Hem 1985). In this work, the values obtained for the SSP parameter ranged between 62.79 and 90.32 %. According to Stallard and Edmond (1983), 78 % of the water samples fall within fair classification of 80 % and the remaining samples fall within poor (>80 %) for the purpose of irrigation (Table 3).

Twenty-seven trace elements were analyzed for in the water samples. Concentrations for gold, beryllium, mercury, indium, iridium, niobium, osmium, palladium, platinum, rhenium, rhodium, ruthenium, antimony, selenium, tantalum and tellurium were all below the detection limit for inductively coupled plasma optical emission spectrometry (ICP-OES) and therefore are not listed in Table 6. Arsenic, boron, beryllium, cadmium, chromium, copper, molybdenum, selenium, uranium, vanadium and zinc were below Environmental Protection Agency (EPA) (2012) and WHO (2012) recommended standard for drinking water with maximum values of 9.4, 443, 0.37, 0.56, 30.8, 86.6, 24.8, 15.7, 20.9, 1.85, 15.3 and 302.9 ppb, respectively. Nickel and antimony exceeded recommended standard only in sample W24 with the following values 15.7 and 7.78 ppb, respectively. Barium also exceeded recommended standard in W20 with value as high as 909.76 ppb. Manganese and lead were higher than recommended standard in 12 % of the samples with the following ranges <0.5–356.1 and <1–20.5, respectively (Table 6).

Trace element deficiency or excess (toxicity) causes a wide range of environmentally related health problems. Toxicity may affect more than one organ in the system. Lead is toxic to both plant and animal life; lead toxicity depends on its solubility, and this, in turn, depends on pH and is affected by hardness.

Manganese and selenium are vital micronutrient for both plants and animals. When they are not present in sufficient quantities, plants exhibit a yellowing of leaves (chlorosis) or failure of the leaves to develop properly. Inadequate quantities of manganese in domestic animal food result in

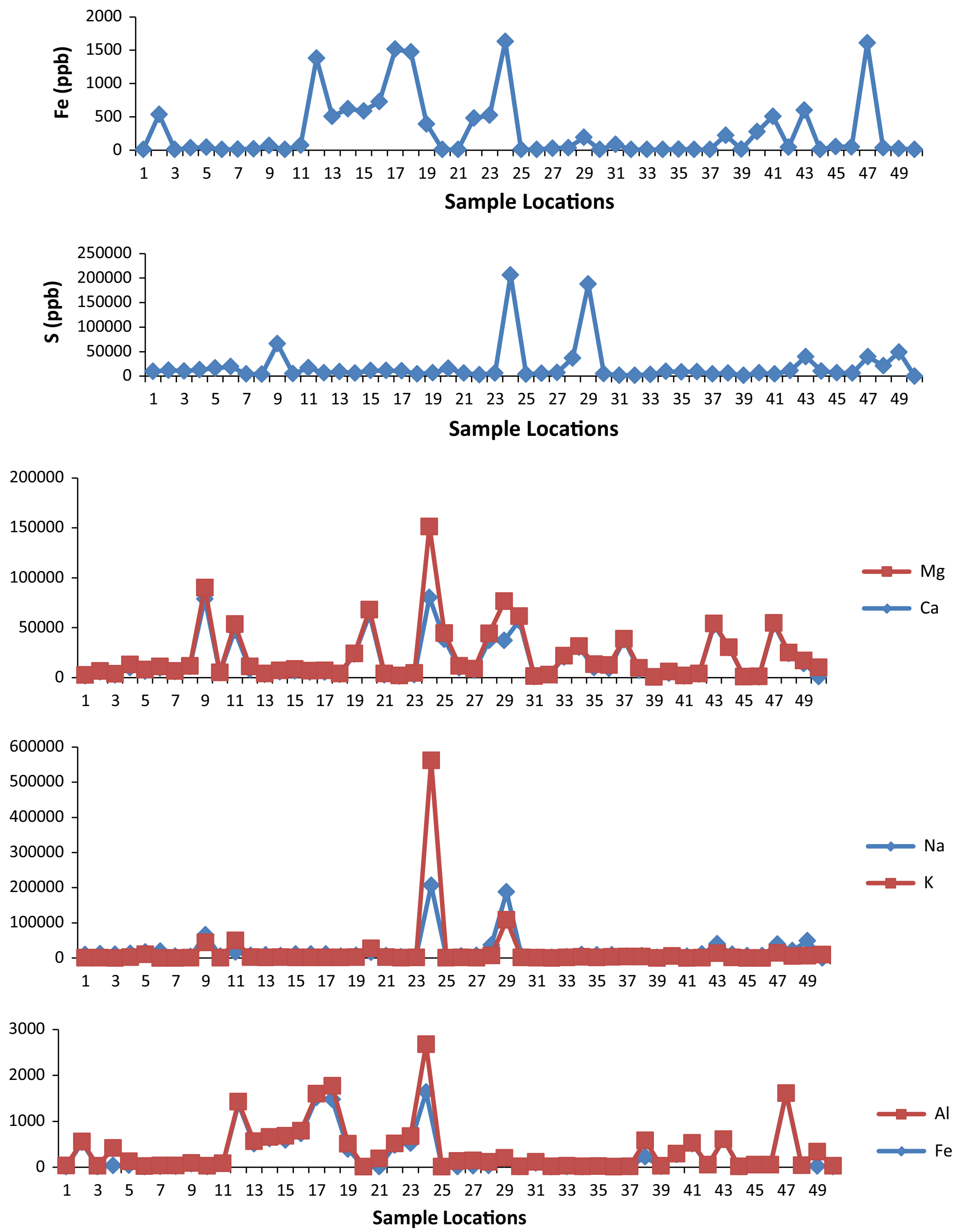

Fig. 6 Variation plots of major elements

Table 4 Some parameter indices for rating the sustainability of groundwater quality for irrigation (Ayers and Westcot 1985; Wilcox 1948)

Class	TDS (mg/L)	RSC (mg/L)	SAR	SSP (%)	Sustainability for irrigation
I	<117.51	<1.25	<10	<20	Excellent
II	117.51–508.61	1.25–2.5	10–18	20–40	Good
III	>503.61	>2.5	18–26	40–80	Fair
IV	–	–	>26	>80	Poor

reduced reproduction and deformed or poorly maturing young. In humans, very large doses ingested these ions can cause some diseases and liver damage. High dose of lead can cause kidney and liver diseases, hypertension, neurological, IQ (children) and anemia; high dose of selenium can cause liver necrosis, muscular dystrophy and Kaschin–Beck diseases (Bowman et al. 2003).

The toxicity of antimony is a function of the water solubility and the oxidation state of the antimony species under consideration (Elinder and Friberg 1986; Fowler and

Table 5 SAR hazard of irrigation water

	SAR	Notes
None	<3.0	No restriction on the use of recycled water
Slight to moderate	3.0–9.0	From 3 to 6 care should be taken to sensitive crops
		From 6 to 8 gypsum should be used. Not sensitive crops
		Soils should be sampled and tested every 1 or 2 years to determine whether the water is causing a sodium increase
Acute	>9.0	Severe damage. Unsuitable

Table 6 Summary of trace elements in groundwater

Trace elements (ppb)	Min	Max	Mean	SD	Median	EPA (2012)		WHO (2012)	% above standard
						MCLG	MCL		
As	<0.5	9.4	2.97	2.97	1	0	10	10	
B	<5	443	25.72	73.86	8			2400	
Ba	5.48	909.76	79.32	153.29	37.26		700	700	2
Be	<0.05	0.37	0.2	0.21	0.12			12	
Cd	<0.05	0.56	0.17	0.16	0.1	5	5	3	
Ce	<0.01	7.5	1.37	2.08	0.44				
Co	<0.02	5.17	1.01	1.13	0.6				
Cr	<0.5	30.8	5.32	6.39	2.4		50	50	
Cu	0.1	86.6	10.07	17.58	1.65	1300	1000	2000	
Li	<1	6.5	1.38	1.06	1				
Mn	<0.05	356.1	59.8	86.01	28.64		50		12
Mo	<0.1	24.8	3.45	7.25	0.2			70	
Ni	<0.2	15.7	2.15	3.23	1			20[a]	2
Pb	<0.1	20.5	4.15	5.38	1.4	0	10	10	12
Sb	0.11	7.78	0.94	1.29	0.77	6	6	6	2
Se	<0.5	20.9	5.65	7.66	2.24	50	50	40	
Tl	<0.01	0.14	0.03	0.03	0.02				
U	<0.02	1.85	0.16	0.32	0.05			30	
V	<0.2	15.3	1.27	2.55	0.6				
W	<0.02	2.27	0.62	1.1	0.09				
Zn	1.8	302.9	39.17	53.26	17.8		5000	1000	

[a] National primary drinking water standard

Goering 1991). The inorganic compounds are more toxic than the organic compounds (Stemmer 1976). Soluble antimony salts can cause gastrointestinal mucosa and trigger sustained vomiting after oral uptake. Other effects include abdominal cramps, diarrhea and cardiac toxicity (Elinder and Friberg 1986).

Barium is not considered to be an essential element for human nutrition (Schroeder et al. 1972). At high concentrations, barium causes vasoconstriction by its direct stimulation of arterial muscle, peristalsis as a result of the violent stimulation of smooth muscles and convulsions and paralysis following stimulation of the central nervous system (Stockinger 1981). The prevalence of dental caries has also been linked to high dose of barium. Death may occur in a few hours or a few days depending on the dose and solubility of the barium salt. The health effect of excess nickel in water includes skin irritation and hypersensitivity. It can also be carcinogenic (WHO 2005).

Manganese is an essential element for man. Excess intake of Mn in water can lead to neurological effects (Canavanet et al. 1934; Cook et al. 1974; Roels et al. 1999; ATSDR 2000). Exposure to high levels of manganese can also lead to a disease called manganism which is characterized by a Parkinson-like syndrome including weakness, anorexia, muscle pain, apathy, slow speech, monotonous tone of voice, emotionless masklike facial expression and slow clumsy movement of limbs.

The pollution index was used in this study to evaluate the degree of trace metal contamination in water samples (Subramani et al. 2010; Todd 1980; U.S. Environmental

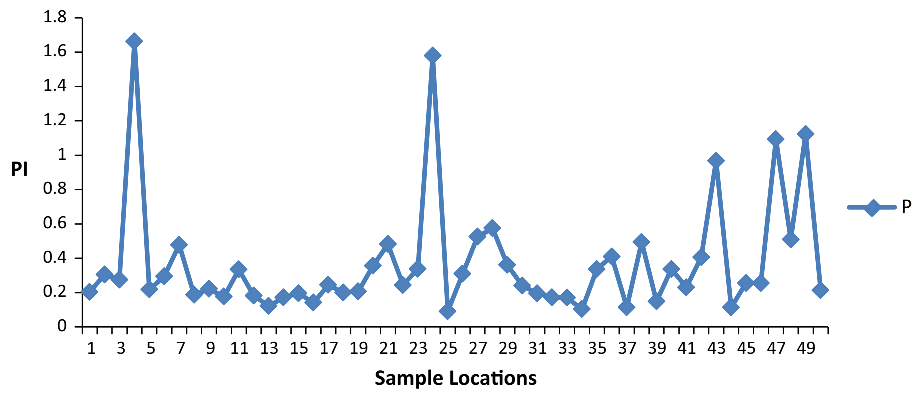

Fig. 7 Plots of pollution index against sample locations

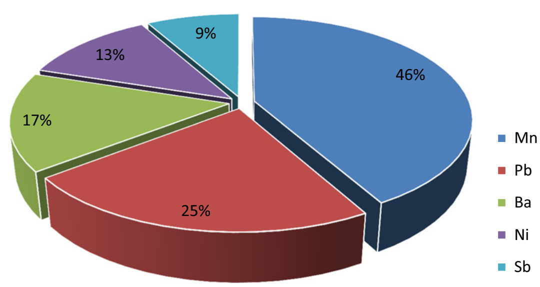

Fig. 8 Percentage of contaminated trace elements

Protection Agency 2002, 2008, 2009). The tolerable level is the element concentration in the water considered safe for human consumption. The tolerable level given by Wilcox (1948) and U.S. Environmental Protection Agency (2012) was used for water, and the pollution index can be calculated by the formulae:

$$PI = (\text{Heavy metal concentration in water}/\text{Tolerable level})/\text{Number of heavy metals}. \quad (4)$$

The PI among all sites varied from 0.09 to 1.76 with a mean value of 0.37 (Fig. 7). Water sample with pollution index >1 is regarded as being contaminated although the water is generally contaminated as much as there is any kind of contamination in it. Eight percentage of the water samples which include W4, W24, W47 and W49 showed pollution index above 1 (Fig. 7).

Mn contributed the highest percentage (46 %) to the pollution index. This was followed closely by Pb which contributed 25 %. Ba, Ni and Sb contributed 17, 13 and 9 %, respectively (Fig. 8). These trace elements just like major elements were from both geogenic and anthropogenic origin.

Conclusion

Fifty samples from hand dug wells and boreholes were collected within Ijebu Igbo and its environs, southwestern Nigeria. The purpose was to establish preliminary baselines for constituents in the groundwater and also to determine the quality for both drinking and irrigation purposes.

The pH and TDS of groundwater showed that the water varied within slightly acidic to basic and fresh, respectively. Ca, Mg, Si and S were all within recommended standard for both drinking and irrigation purposes. Al, Fe, Na, K and P were above the EPA 2012 recommended standard for drinking water in 79, 23, 3, 37 and 6 % of the water samples, respectively.

There is involvement of silicate weathering in the geochemical processes, which contributed mainly calcium, magnesium and potassium ions to the groundwater. $Na^+ + K^+$ contributed more to water chemistry than $Ca^+ + Mg^+$. The high concentration of Fe, Al, Na, K and P which were above recommended standards could also be linked to anthropogenic sources which include waste dumpsites, agricultural activities and sewage that are common in the study area.

SAR in water samples ranged from 0.12 to 10.43 and can be classified as excellent and good for irrigation. MAR varied between 0.89 and 87.94 %. The values obtained in only 22 % of the water samples were <50 % considered suitable with no hazardous effects to the soil. The values obtained for the SSP parameter ranged between 62.79 and 90.32 %. Seventy-eight percentage of the water samples fall within fair classification of 80 %, and the remaining samples fall within poor (>80 %) for the purpose of irrigation. Kellys ratio (KR) obtained for the water samples was 0.008–0.08 meq/L. The values obtained were lower than the permissible limit of 1.0 for all the samples. Water samples were also above 15 % recommended standard for irrigation water based on Na%.

Trace element analysis showed that the concentration of Te and Ti was below detection limit for all the samples. As, B, Cd, Cr, Cu, Mo, Ni, U and Zn though present in water were below recommended standards for all the samples. Ni and Sb exceeded recommended standard only in sample W24, and Ba exceeded recommended standard in W20 with value as high as 909.76 ppb. Mn and Pb were higher than recommended standard in 12 % of the samples. The pollution index varied from 0.09 to 1.66 with 8 % of the water samples showing pollution index above 1.

Generally, groundwater in the study area is suitable for both domestic and irrigation uses except samples W4, W24, W47 and W49. However, since heavy metals are not biodegradable, they tend to bioaccumulate and biomagnify in the body and eventually become harmful to human health.

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