Journal of Environment and Earth Science
ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online)
Vol.13, No.3, 2023

Hydro-Chemical Studies and Assessment of Trace Elements and Bacterial Contamination of Shallow Groundwater of Oyo Area, Southwestern Nigeria

Olanrewaju Akinfemiwa Akanbi*[1] Oluwagbemileke Samuel Akinola[2] Jeremiah Nwajei[1] Joshua Adegbite[1]
1. Department of Earth Sciences, Ajayi Crowther University Oyo, Oyo Town, Nigeria
2. School of Environment, Geography and Geosciences: University of Portsmouth, United Kingdom
* E-mail of the corresponding author: oa.akanbi@acu.edu.ng

Abstract
Groundwater from shallow hand-dug wells is the only reliable source of water supply in the ancient town of Oyo in the southwestern region of Nigeria. The present work studied the water quality in twenty-five wells across this area by measuring the ancillary parameters, and analyzing the major and trace elements and taking the inventory of the wells as well as assessing the total coliform and Escherichia coliform in sampled water. The field measurement showed that the groundwater is slightly acidic with an average pH of 6.6 and fresh from the total dissolved solids values between 70 and 630 mg/L. From the average concentrations of major ions, the dominance order of the cations constituents in groundwater is in the order- $Mg^{2+} > Ca^{2+} > K^{+} > Na^{+}$ and $HCO^{-} > Cl^{-} > NO_3^{-} > SO_4^{2-}$ for anions. The ranges of trace elements concentrations were; Iron II- 0.01 – 0.06; Chromium VI: 0 - 0.34; manganese 0 – 1.2 in mg/L, while Copper was between 0.38 – 32.7; Cadmium 0.03 – 1.87; lead 0.02 – 3.57; Zinc 0.01 – 7.79; and Arsenic 0.05 – 7.35 in µg/L. The total coliform count ranges from 6 – 1860 cfu/100 mL while Escherichia coliform (E. coli) units was between 2 and 1640 cfu/100 mL with frequency occurrence from nil in three wells representing 12% of the wells, 1 – 50 units (28%), 51 – 100 (20%), 101 – 500 (20%) and > 500 units (20%). The groundwater is grossly contaminated with nitrate and coliform bacteria while four wells were found to be contaminated with manganese and chromium. It is mandatory that the water be treated for metal and bacterial contaminations prior to consumption and public enlightenment on drinking water guidelines be in place.
Keywords: Groundwater. Major ions. Trace elements. Coliform Bacteria.
DOI: 10.7176/JEES/13-3-02
Publication date: April 30th 2023

1. Introduction

The supply of safe drinking water for human communities is essential for good health and well-being of the people, but; sourcing for good quality water involved great financial investment that most governments of the world find challenging particularly in developing nations. In comparison to other fresh water bodies on earth, groundwater is regarded as the cleanest and the most available to man, since it is a renewable resource found beneath the earth surface (Heath, 1983; Edmund and Smedley, 2005; MacDonald, et. al. 2005; Healy, et al. 2007; Tijani, 2016). It is generally assumed that groundwater needs little or no treatment before usage and it is regarded to be less vulnerable to contamination compared to other fresh water bodies such as rivers, lakes and streams. This is because groundwater is regarded to be *free* from suspended particles and pathogenic bacteria (which can cause diseases). In addition, groundwater temperature is more constant than temperatures of surface waters that are controlled by changes in surface environment temperature and its natural occurrence is less affected by seasonal climatic variations. Due to all of these advantages, approximately 50% of world citizens rely on groundwater for domestic, industrial and agricultural utilizations (Siebert, 2010). This is more so in developing countries in sub-Sahara Africa and parts of Asia, where there is continual increase in population, agricultural and industrial growths and the attending need to expand social amenities such as water supply and electricity (Akanbi, 2018; Tijani, 2016).

However, the claim that groundwater is completely free from surface contamination and safe for direct consumption is more of an ideal theory and is often not realistic, most especially in shallow aquifers of crystalline basement complex terrains such as the present study area of Oyo in southwestern (SW) Nigeria. Many groundwater contamination cases have been reported in several parts of SW Nigeria (Oyedele et al, 2019; Tijani and Abimbola, 2003; Abimbola et al., 1999; Ehinola, 2002). Groundwater contamination were attributable to be sourced from inappropriate disposal of liquid and solid wastes and to a lower extent due to agricultural and industrial activities. Generally, natural composition of groundwater is governed by factors that include geology, hydrology and meteorology of that environment. In respect to geology, the lithology/mineral composition of the rock units bears imprint on the chemical signature of the enclosed water. Likewise, the chemistry of recharging waters from the atmosphere and on land surface also contribute immensely to that of the groundwater. Natural occurring constituents in groundwater are the dissolved solids and dissolved solids are elements that may be found at higher or at lower concentrations in groundwater depending on the solubility and relative abundance of such elements in the earth crust, and the residence time of the water. The major ions in groundwater are the cations of sodium, calcium, magnesium, potassium; and anions that include carbonate, chloride, nitrate and sulphate. Elements such as lead, arsenic, mercury, copper, cadmium, zinc, chromium, manganese, cobalt, iron are the trace elements that have high toxic potentials in drinking water. Though, some trace elements including zinc, iron, copper, manganese are essential for proper and balanced human growth; even then, having these essential trace elements at high concentrations in drinking water also endanger health (Calderon, 2000; Mora et al, 2017). Conversely, major ions that occur at higher concentration levels are more tolerable to human. Though, these elements including the major ions are naturally occurring, their concentrations in water are also induced by human inputs and activities. For example, nitrate concentration grows in groundwater from agricultural and industrial activities as well as inputs from domestic effluents. More so, high nitrate in groundwater do facilitate growth of algae and bacteria in water since the bacteria utilize nitrate as an alternative electron acceptor to oxygen and in the process reduce nitrate to nitrite (Kutvonen et al., 2015). Presence of pathogens including bacteria in groundwater is not natural; however, one way or the other these organisms are introduced into groundwater from recharging water. The most commonly found bacteria in well water are the coliform bacteria and the presence of a type of coliform known as Escherichia coliform (E. coli) in groundwater is an indication of contamination from human feces. Hence, total coliform count (TCC) in water represents the total number of bacteria found in both soil and water from human and animal wastes, whereas E. Coli are specifically associated with human digestive/fecal droppings.

Though, some pathogens could be harmless to human but many bacteria are causative agents of water-borne diseases such as cholera and dysentery. Hence, contaminations of groundwater can be chemical and/or biological in nature and the sources of contamination may be from natural and anthropogenic origins (Fawell and Nieuwenhuijsen 2003). For example, the mineral content of groundwater increases as it moves along through the pores and fracture openings in rocks, and if such flow passage is enriched in toxic metals such as trace elements, it is most likely that such water will be contaminated. However, pollution from surface environment through human activities such as improper disposal of both liquid and solid wastes, industrial effluents, and agricultural activities (Tijani, 2016; Akanbi 2020; Kass et al. 2005) are more prevalent in Nigeria than those from lithogenic sources. As a result of this, more attentions are now focused on groundwater quality in Nigeria because most household in urbans (not to mention rural) areas are not connected to piped water supply. Domestic homes largely rely on groundwater, even to a large extent industrial and agricultural activities depend on groundwater source. So, areas and terrains underlain by crystalline rocks where potentials for groundwater occurrences are known to be low (within SW region of Nigeria) are also being exploited (Abiola et al., 2009; Heath, 1983; Danskin, 1998; Offodile, 2002). The fact that the hydrogeology of the crystalline basement terrains of SW Nigeria has been described to be erratic, localized and shallow, and that is largely controlled by seasonal recharge mainly from precipitation (Jones and Hockey, 1964; Egboka, 1987; Tijani and Abimbola, 2003; Oladapo and Akintorinwa, 2007; Jayeoba and Oladunjoye, 2013; Tijani, 2016; Akanbi, 2018) calls for more attention on groundwater quality assessment in this region. The shallow occurrence nature and the recurrent meteoric source of groundwater makes it vulnerable to contamination. An outright pollution of this essential renewable water resource may retard availability of potable water supply in both the urban and rural areas of Nigeria including the ancient town of Oyo-the present study area.

1.1 The study area

The study area covered the hub of Oyo town- an ancient and one of the urban areas of Oyo state in SW Nigeria. It lies within latitude 7°49'15" N - 7°51'30" N and longitude 3°53'46" E - 3°56'45''E (Fig. 1). Oyo town has a land mass of about 1,286 square kilometer and present human population is 740,503 based on 3.5% growth rate projection from the 2006 national census. It is bordered by Ogun state in the south, Kwara state in the north and by Osun state to the east. The study area falls within the tropical humid climate region where there are two seasons-the rainy and dry seasons just like any other parts of the south western region of Nigeria. The dry season occurs between November and March and rainy season spans from late March to October when the groundwater bearing zones are normally recharged. mostly between April and October. The mean annual temperature varies from 26.5^{0}C to 27.8^{0}C. The mean annual rainfall is between 1100mm and 1500mm. The relief of the study area is gentle spanning from 260 to 340 m. The landforms are more of flat-lying to gentle rising land. The soils are pale brown in colour and are more of residual lateritic soils of sandy, clayey and gravelly grades. The vegetation of the area is tending towards derived savannah, unlike decades of years ago when this area is reputed to be within the tropical rainforest belt characterized by presence of thick evergreen forest with undergrowth. The vegetation of Oyo town has transited to tall grasses, shrubs and scattered trees that characterized a derived savannah.

1.2 Geology and hydrogeology

Most part od SW Nigeria is underlain by intrusive crystalline rocks of Precambrian age that are collectively referred to as the Basement Complex (NGSA, 2009). Rahaman (1976) grouped the crystalline rocks of the SW Nigeria Basement Complex into four classes namely; Migmatite - Gneiss - Quartzite complex; Schist belt of slightly migmatised to unmigmatised paraschists; Charnockitic rocks, and the Older granite, which include granite, granodiorite, diorites and potassic syenites. The geochronology of these rocks has been dated to be Precambrian age (Jones and Hockey, 1964; Dada 1998).

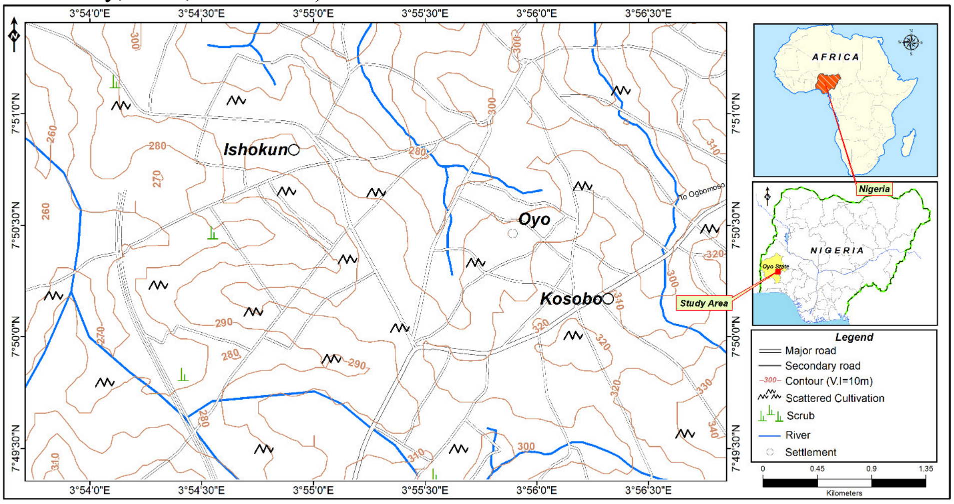

Fig.1 Location, topographic and drainage map of the study area

For the present study area, the underlying rock units are mainly quartzite and quartz schist, undifferentiated schist, migmatite and banded gneiss (Fig. 2). These major rock units are incised by granitic intrusions, quartz and pegmatitic veins. Quartzite and quartz-schist are the dominant major rock units in the area. The quartzites are hard, non-foliated light coloured metamorphic rock that compose mainly of quartz mineral while feldspar appears as accessory mineral in some case. The texture of the quartzite is fine grained, sugary, though there are schistose variety as well. Occurrence of groundwater in quartzite is fair due to predominance of joints and its susceptibility to splits into smaller bits in the crust.

The schists underlie part of the western and small portion in the north-north-eastern parts of the study area. Schists occur in association with other rock units such as gneisses and quartzite; hence the term undifferentiated schist is used. The schist is medium-grained, foliated melanocractic metamorphic rock with high content of platy mineral (biotite) and plagioclase felspars. Streak of light coloured quartz veins are common features within the schist. The schists are typically formed during regional metamorphism that accompanying the process of mountain building (orogeny) and reflects medium grade metamorphism. Lastly, migmatite outcropping sections are also mapped, though just a little exposure was within the present study area. Migmatite is a coarse-grained, heterogenous metamorphic rock made up of intermingled metamorphic and igneous components.

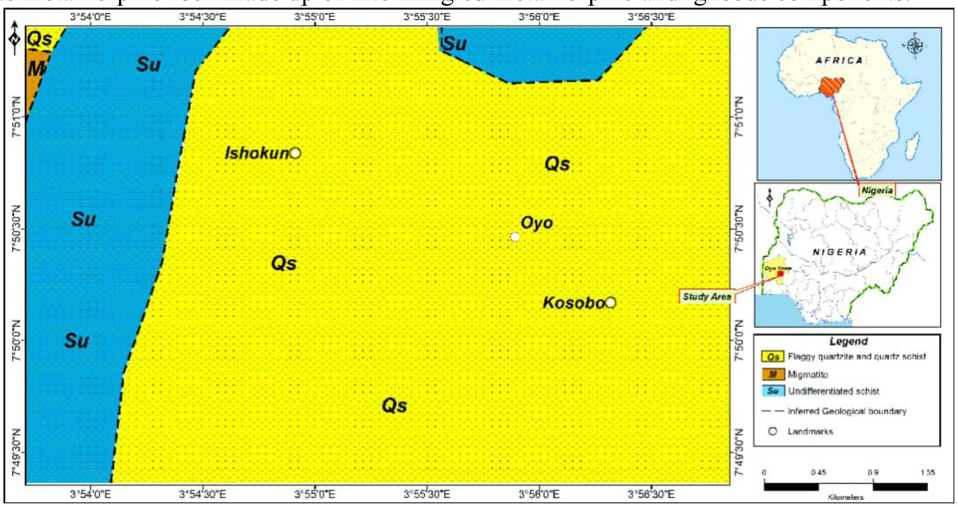

Figure 2: Geological Map of the Study Area

Normally, intrusive crystalline igneous and metamorphic rocks cannot store and transmit water since they are impermeable. However, adequate water bearing zones do develop within the weathered and fractured zones. Hence, the weathered zones and rock discontinuities such as fractures and faults are the potential aquifers in basement terrains. In areas where bedrock fractures are absent, the weathered layer serve an alternative for groundwater supply; though, the weathered aquifers have been described to be largely unsustainable and are characterized by low transmissivity that are mostly below 1.0 m^2 /day (Akanbi, 2018). However, in zones where the weathered layer is thick and coarse grained, prolific aquifers may develop and the yield is better if the bedrock is fractured (Offodile, 2002; Akanbi, 2018). Congruently, because it is known that the weathered layers are porous and do transmit water directly to underlying rock units (Jones, 1985; Acworth, 1987; Chilton and Foster 1995, Singhal and Gupta 1999; Holland, 2011; Akanbi, 2018), the enclosed groundwater is vulnerable to contamination from direct recharge from surface environment, especially when the groundwater bearing zones are in shallow depth as the case in the study area.

The only visible water supply in Oyo township are the hand-dug wells that penetrated shallow depths ranging between 5 to 20 meters. These wells are dug using axe and diggers by peasants to serve individual households and the yield of most of these wells are susceptible to seasonal changes. The important of these wells to the residents of Oyo mandate the assessment of the major and trace elements as well as enumeration of bacteria counts in collected water samples from representative hand-dug wells across the study area. The aim is to characterize the hydrochemistry and to find out possible contamination of selected trace elements and presence of coliform bacteria in the groundwater of the area which is the only reliable water supply for the residents.

2. Materials and Methods

The method of study involved field work, laboratory analyses and data evaluation. The field work phase involved water sampling, sample preparation and in-situ measurement of physical parameters that included pH, total dissolved solids (TDS) and electrical conductivity of water (EC) using digital TDS/EC meter. The geographical locations of sampled wells and other relevant well inventories such as well depth and well topography were also taken in the field.

2.1 Sampling and preparation

The groundwater sampling involved collection of representative samples from twenty-five (25) hand-dug wells across the study area within the hubs of Oyo town. The locations of individual wells are presented in Fig. 3. These wells are the main visible water source in the communities. The water samples were collected directly from the hand-dug well in new plastic bottle but firstly rinsed with part of the water sample to be collected. The samples were adequately labelled and iced to prevent flocculation and bacteria proliferation prior to laboratory analyses. The chemical and biological analyses were carried out in the water laboratory of the Federal Ministry of Water Resources of Nigeria.

2.2 Analyses

The major elements that were analyzed included calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, sulphate and nitrate. Spectrophotometry method was used to determine the concentrations of most anions except chloride ion where silver nitrate titrimetric method was employed. The parameter to be analyzed for was selected from the test manager of the spectrophotometer. Two 10 ml sample cells were filled with the samples to be tested, 1 pillow of test parameter was added to one of the samples in the sample cell and was shaken, it was then allowed to stay for reaction time depending on the test parameter e.g (0,5,10) minutes. The blank was then placed in the sample chamber to calibrate to zero, then the second sample cell was placed in the chamber, the concentration of the test parameter in mg/L was displayed on the spectrophotometer screen. Chloride was measured using titrimetric methods by adding 2 drops of potassium dichromate (K_2CrO) indicator to each water samples in a conical flask, and titrate with silver nitrate (0.014N AgNO). The end point is the brownish coloration of solution. Carbonate and bicarbonate were determined from alkalinity. Flame Photometry method was used for determining the concentrations of cations. Sample was aspirated into the flame through an inlet hose in which the flame photometer has been calibrated by series of known standard of the tested parameters. The concentration of the tested parameters is displayed on the screen.

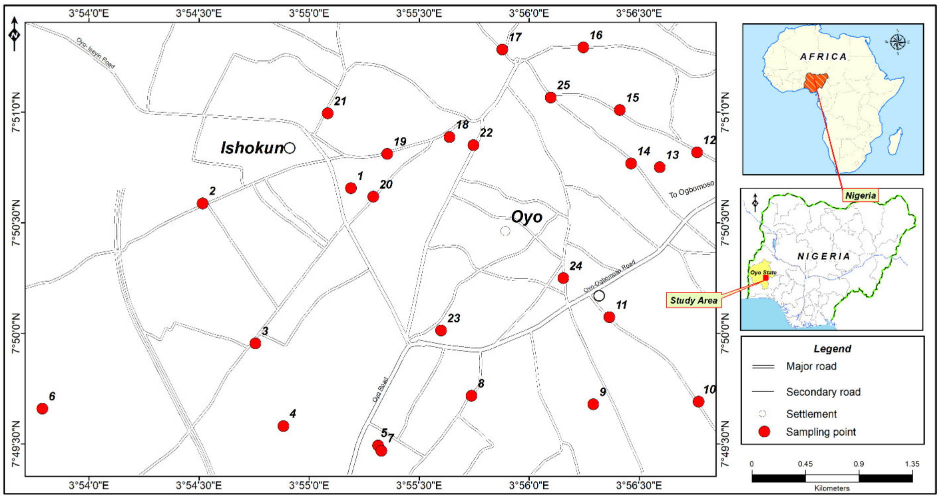

Fig. 3 Map of the study area showing the distribution of sampled hand-dug wells

A total of eight minor/trace elements that included Lead (Pb), Arsenic (As), Copper (Cu), Zinc (Zn), Cadmium (Cd), Chromium (Cr), manganese (Mn) and ferrous iron (Fe^{2+}) were analyzed in the laboratory. HM500 Metalyser was used for the analyses of the first 5 trace elements and the results are presented in microgram per liter (µg/L). Palintest spectrophotometer 7100 was used to analyze Chromium VI (Cr^{6+}), while colorimetry method using DR900 Colorimeter was used for both to analyze Fe^{2+}) and Mn and results reported in milligram per liter (mg/L).

The isolation and enumeration of coliform bacterial in the samples were determined by multiple tube technique using the following materials/apparatus groundwater samples; sample bottles, dilution bottles, pipettes and graduated cylinders, containers for culture medium, culture dishes, test tubes, Durham tubes, incubators, inoculation loop, microscope and light source, Ringer's solution (for sterilization), M- Endo broth, Brilliant green lactose bile broth (BGB) and E. coli broth. The procedure for material sterilization, preparation of culture media and the actual isolation and enumeration of coliform and E. Coli in water samples followed the procedure of the water quality laboratory of the Federal ministry of water resources of Nigeria (Adeoye and Babalola, 2011). Data statistics and evaluation, and correlation analyses were done using Window office tool while Surfer 12 software was employed for generating concentration contour maps of specific chemical and bacteriological parameters.

3. Results and Discussion

The well inventory and the results of analyzed major ion concentrations are presented in Table 1. The trace elements concentrations and bacterial counts are presented in Table 2, while the statistical summary is presented in Table 3.

Table 1: Locations of hand-dug wells, well inventory and results of analyses of major ions in groundwater samples

Sample No	Location Name	Well Depth (m)	Well Elevation (m)	pH	EC (µs/cm)	TDS (Mg/L)	Major ions (mg/L)								
							Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na+ (mg/L)	K+ (mg/L)	HCO_3 (mg/L)	CO_3^{2-} (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)
HD01	Iseyin Road	15	286	6.6	750	370	24.0	2.67	0.24	0.29	161	*ND	90.5	41.6	92.6
HD02	Cele	20	289	6.4	560	280	32.1	27.2	0.27	0.33	457	ND	77.9	6.36	105
HD03	Ilora	10	286	6.5	160	80	10.4	9.72	0.19	0.22	91.3	ND	7.20	8.91	22.6
HD04	Dakanka	13	302	6.7	200	100	21.25	11.4	0.24	0.29	82.9	ND	7.20	14.6	25.5
HD05	Araromi 1	10	315	5.9	290	140	20.0	6.80	0.25	0.29	24.0	ND	35.0	4.55	72.2
HD06	Araromi 2	10	317	5.8	410	200	25.7	12.6	0.33	0.41	21.6	ND	56.5	0.27	94.0
HD07	Araromi 3	6	306	6.7	150	70	8.02	10.2	0.29	0.56	72.1	ND	9.25	2.73	14.2
HD08	Araromi 4	6	320	6.4	350	170	29.7	18.5	0.31	0.20	135	ND	27.8	14.5	31.5
HD09	Mabolaje 1	6	314	6.4	140	70	7.21	7.78	0.35	0.28	88.9	ND	3.08	8.91	ND
HD10	Mabolaje 2	6	335	6.3	240	120	16.0	10.7	0.29	0.42	72.1	ND	20.8	5.64	39.0
HD11	Mabolaje 3	7	323	6.4	360	170	23.3	13.1	0.28	0.18	98.5	ND	48.0	8.82	35.4
HD12	Akunlemu	10	306	7.2	640	320	31.3	19.9	0.30	0.37	279	ND	62.7	44.7	24.8
HD13	Agboye 1	5	289	6.6	670	280	35.3	22.4	0.25	0.32	159	ND	53.5	37.1	62.0
HD14	Arowoshegbe	8	305	7.3	620	310	28.9	48.6	0.34	0.28	154	ND	139	75.6	77.1
HD15	Adikuta	6	286	6.9	800	400	36.9	38.4	0.22	0.49	226	ND	90.5	53.2	62.5
HD16	Lagbodoko	6	282	7.2	1050	510	30.5	51.5	0.32	0.44	428	ND	141	53.6	24.8
HD17	Okeafin	12	307	6.9	1090	540	25.7	78.7	0.21	0.37	255	ND	102	76.8	117

Sample No	Location Name	Well Depth (m)	Well Elevation (m)	pH	EC (µs/cm)	TDS (Mg/L)	Major ions (mg/L)								
							Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na+ (mg/L)	K+ (mg/L)	HCO_3 (mg/L)	CO_3^{2-} (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)
HD18	Isaleagbala	10	297	6.0	900	450	11.2	64.2	0.34	0.40	111	ND	186	62.0	52.7
HD19	Ile Ekerin	6	290	6.9	930	460	36.9	29.7	0.27	0.78	168	ND	156	77.5	69.1
HD20	Ile Oluwo	12	306	7.4	1050	520	40.9	17.5	0.38	0.62	180	ND	186	67.3	53.1
HD21	Isokun Road	10	299	6.2	230	110	25.7	4.86	0.31	0.58	50.5	ND	29.8	0.55	37.7
HD22	Asogo	9	300	6.4	770	380	19.2	36.5	0.41	0.60	175	ND	106	62.6	58.9
HD23	Adeniran	12	324	6.0	470	230	16.8	27.7	0.24	0.49	50.5	ND	78.1	7.36	78.0
HD24	Durbar	12	321	6.6	780	390	37.7	60.0	0.20	0.35	132	ND	145	75.5	52.3
HD25	Adesina	10	292	7.0	1250	630	44.9	30.6	0.28	0.72	257	ND	179	94.3	81.5

*Not detected

Table 2: Results of trace elements and bacteria counts in water samples

Sample No	TRACE ELEMENTS								BACTERIAL COUNTS	
	Cu (µg/L)	Pb (µg/L)	Zn (µg/L)	Cd (µg/L))	As (µg/L)	Mn (mg/L)	Cr^{6+} (mg/L)	Fe^{2+} (mg/L)	Total coliform (cfu/100ml)	E. Coli (cfu/100ml)
HD01	1.07	0.58	0.30	0.99	0.05	ND	ND	ND	520	470
HD02	0.69	0.95	5.62	0.03	5.20	ND	ND	0.02	94	70
HD03	15.8	1.19	1.92	0.45	0.54	ND	ND	0.03	1460	1280
HD04	0.38	ND	2.82	ND	1.25	ND	ND	0.06	8	5
HD05	2.15	3.57	2.91	0.42	1.27	1.2	0.027	0.05	164	148
HD06	3.76	0.05	0.03	0.42	1.24	ND	ND	0.04	68	58
HD07	ND	0.38	2.23	0.46	0.91	ND	ND	0.03	0	0
HD08	ND	2.29	0.07	1.87	1.13	ND	0.08	0.03	1560	1280
HD09	ND	0.09	2.57	0.03	2.15	0.5	0.34	0.01	96	44
HD10	9.56	0.83	1.87	0.06	1.86	ND	ND	0.06	1860	1640
HD11	13.3	0.05	0.37	0.08	3.52	ND	ND	0.03	96	80
HD12	11.6	0.04	1.01	0.07	0.07	ND	ND	0.02	0	0
HD13	16.9	0.02	1.00	0.05	ND	ND	ND	0.03	1360	1060
HD14	7.77	1.31	0.06	1.78	3.11	ND	ND	0.03	50	32
HD15	0.91	0.06	0.01	0.07	1.6	ND	ND	0.04	504	460
HD16	3.26	0.5	0.02	0.06	2.08	ND	ND	0.06	78	48
HD17	2.73	0.03	3	0.04	0.12	ND	ND	0.04	102	88
HD18	3.38	0.22	2.84	0.36	7.35	ND	ND	0.03	6	2
HD19	10.3	0.27	0.3	0.09	2.22	ND	ND	0.02	0	0
HD20	2.56	0.03	0.08	0.86	1.52	ND	ND	0.04	74	46
HD21	1.38	0.13	0.6	0.08	ND	ND	ND	0.02	164	154
HD22	0.51	0.72	1.31	0.89	1.46	ND	ND	0.04	52	48
HD23	11.8	0.05	7.79	0.07	ND	ND	ND	0.04	84	76
HD24	32.7	1.02	ND	0.59	ND	0.3	ND	0.05	230	188
HD25	16.1	0.12	ND	0.06	0.08	ND	ND	0.03	1240	1060
Detection Limits	0.01	0.01	0.01	0.01	0.01	0.005	0.005	0.005	-	-

Table 3: Statistical summary of well inventory and analyzed parameters

Parameters	**Minimum**	**Maximum**	**Mean**	**WHO guidelines (2017)**	**National guidelines SON (2007)**
Well Depth (m)	5	20	9.48	-	-
Well Elevation (m)	282	335	303.88	-	-
pH	5.8	7.4	6.59	-	6.5 – 8.5
EC (µs/cm)	140	1250	594.40	1500	1000
TDS (mg/L)	70	630	292.00	600	500
Ca^{2+} (mg/L)	7.21	44.9	25.58	-	-
Mg^{2+} (mg/L)	2.67	78.7	26.45	-	-
Na^{+} (mg/L)	0.19	0.41	0.28	200	200
K^{+} (mg/L)	0.18	0.78	0.41	3000	-
HCO_3^- (mg/L)	21.6	457	157.18	-	-
Cl^- (mg/L)	3.08	186	81.51	250	250
SO_4^{2-} (mg/L)	0.27	94.3	36.20	250	100
NO_3^- (mg/L)	14.2	117	57.65	50	50
Ferrous Iron (mg/L)	0.01	0.06	0.04	*NHC	0.3
Copper (µg/L)	0.38	32.7	7.66	2000	1000
Cadmium (µg/L)	0.03	1.87	0.41	3	3
Lead (µg/L)	0.02	3.57	0.60	10	10
Zinc (µg/L)	0.01	7.79	1.68	4000	3000
Arsenic (µg/L)	0.05	7.35	1.84	10	10
Chromium VI (mg/L)	0.027	0.34	0.11	0.05	0.05
Manganese (mg/L)	0.30	1.20	667	0.1	0.2
Total coliform (cfu/100mL)	6	1860	395	0	1
E. coli (cfu/100mL)	2	1640	334	0	0

*NHC Not of health concern

3.1 Physicochemical parameters

From Table 1, the depths of the hand-dug wells were between 5 and 20 m. the depth range while the average depth is just about 9.5 m depicting the extent of the shallowness of the water table. The pH of the water samples was between 5.8 and 7.4. The average pH is 6.6 and the pH of 80% of sampled hand-dug wells were below the neutral value of 7.0. By this, the groundwater from the wells is generally slightly acidic (Ezeigbo, 1989), though the mean pH is still within the acceptable national limits between 6.5 and 8.5 of standard organization of Nigeria (SON, 2007). The total dissolved solids (TDS) which is the concentration of mineral dissolution in water was between 70 and 630 mg/L. from the mean TDS of 292 mg/L, mineral dissolution in groundwater is low and this indicates low residence time of water in the underground and by this, the water is regarded as freshwater since TDS less than 500 mg/L is generally satisfactory for domestic use and many industrial purposes and the taste of water becomes unpalatable when the TDS exceeds 1,000 mg/L (WHO, 2017). The electrical conductivity (EC) in the study area ranges from 140 - 1250 µs/cm with a mean 594 µs/cm. The maximum limit of EC in drinking water according to WHO (2017) guidelines limit is 1500 µs/cm, therefore all the groundwater samples in the study fell within the acceptable limit.

Statistics of major ions concentrations in water are presented along with other parameters in Table 3. Calcium enrichment in groundwater was between 7.21 - 44.9mg/L and av. 25.58 mg/L. Calcium is one of the most prevalent elements in the earth's crust and in the hydrosphere due to its mobility and there is no guideline as such for calcium due to the fact that its concentrations in water are not really of health concern. However, the desirable limit of Ca^{2+} for drinking water as specified by WHO (2017) is 200 mg/L and all samples were within this limit. The largest occurrence of calium in samples was found at Adeshina in location HD25 at the north-eastern part of the study area. Calcium ions is the second most abundant cations in the groundwater. Based on average concentration of 26.45 mg/L of magnesium ion, it is the most abundant cation in the analyzed water samples. The main source of magnesium in groundwater is from the dissolution of mineral elements such as olivine, biotite, hornblende and augite from the basement rocks in the study area. The well with the highest concentration (HD17) of 78.7mg /L is at the northern area at Oke-Afin closed to well at Adeshina Street with the highest concentration of calcium ion. The desirable limit of magnesium for drinking water as specified by WHO (2017) is 150 mg/L, and the concentrations in all samples lie far below this limit. The concentrations of univalent cations occurred below 1.00 mg/L in all the hand-dug wells. The low occurrence of sodium and potassium ions is probably due to the underlying rock type that is mainly quartzite/quartz schist composed of mostly silica quartz that does not compose of essentially of sodium and potassium.

The results of the concentrations of anions in mg/L are presented as well in Table 1 along with other parameters. Carbonate was not detected in any of the water samples but on the other hand, bicarbonate ions have the highest enrichment in water with concentration range of 21.6 – 457 mg/L and mean 157 mg/L. Locations with exceptional high concentrations of bicarbonate are sampled wells at Cele and Lagbodoko having more than 400 mg/L. The desirable limit of bicarbonate for drinking water is 500 mg/L and concentrations in all samples fell below this limit. Chloride is the second most abundant anion in the well water. Sources of chloride ions in water are attributable more often to anthropogenic origin such as fertilizers, human excrement etc., especially in places with poorly designed waste disposal scheme. In the study area, chloride concentration ranges from 3.08 – 186 mg/L and the mean of 81.51 mg/L. The desirable limit of chloride for drinking water as specified by WHO (2017) is 600 mg/L. Sulphate ions is the least abundant anion and it ranges from 0.27 - 94.3 mg/L with an average of 36.2 mg/L. The low sulphate content in the groundwater is attributable to the fact that the study area is not an industrial hub. Hand-dug well with the highest concentration of 94.3 mg/L sulphate is at Adeshina on location HD25. The desirable limit of sulphate for drinking water is specified by WHO (2017) as 250 mg/L.

In the study area, nitrate concentration ranges from 14.2 -117 mg/L and av. of 57.6 mg/L. The location with the highest concentration is at OkeAfin on HD17 in the Northern section of the area; while Araromi 3 has the lowest nitrate concentration (HD07) with a value of 14.2 mg/L in the southern area of the map. The desirable limit of nitrate for drinking water is 50 mg/L (WHO, 2017). Nitrate concentrations in more than half of the sampled hand-dug wells exceeded 50 mg/L (Table 1) as illustrated in Fig. 4 and the most dominant nitrate concentration spread is 51 – 100 mg/L (Fig. 5). Most often, nitrate sources in groundwater are attributable to both natural origin from atmospheric nitrogen and direct recharge or infiltration of contaminated surface water.

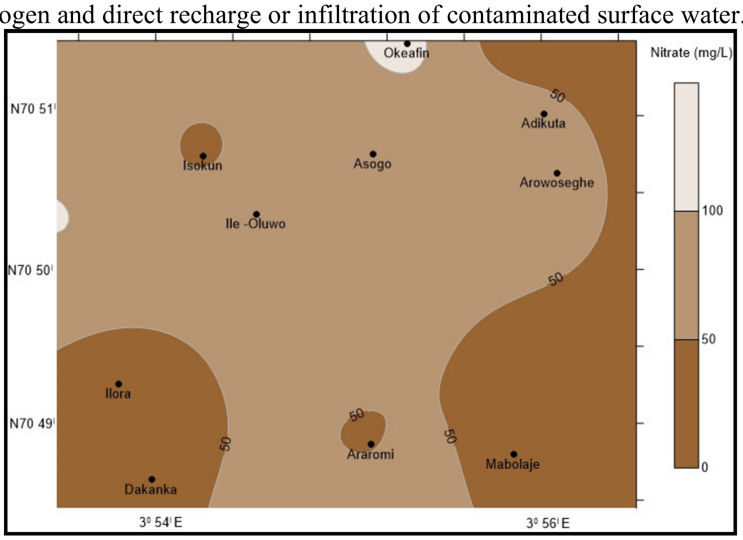

Figure 4: Nitrate concentration map across the study area

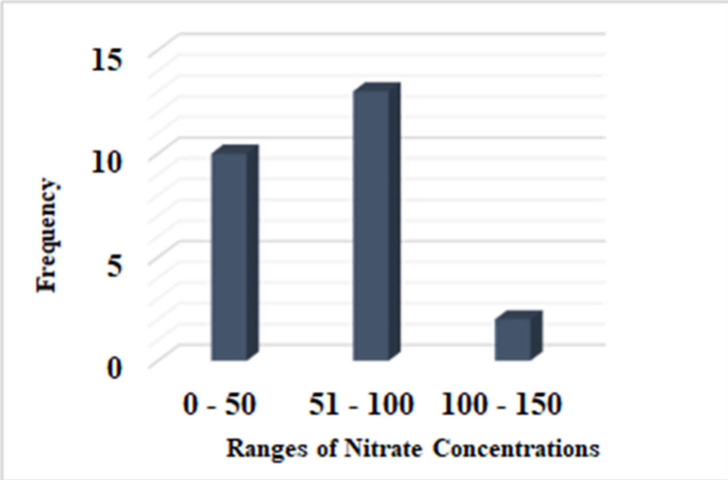

Figure 5: Frequency of Nitrate concentrations in hand-dug wells

Also, it is expected that nitrate concentration should decrease with increasing well depth provided that there is no direct recharge or the extent of direct recharge reduces with well depth. However, the plots of nitrate concentrations in hand-dug wells versus well depth (Fig. 6) showed that the relationship is positive and significant with R = 0.52. This can only mean that the nitrate input in hand-dug wells is still very much significant even as well depth exceeds 20 m. The plots also revealed evidence of direct recharge through the overlying regolith in the study area. This is a frequent issue with the overlying regolith across the basement terrains of Nigeria. It has been widely reported that the water – bearing zones are shallow and semi-confined and the weathered layers are somewhat permeable to direct infiltration of contaminated water from the surface environment, which is a threat to the quality of the groundwater – bearing zones (Acworth, 1987; Egboka, 1987; Tijani and Abimbola, 2003; Oladapo and Akintorinwa, 2007; Jayeoba and Oladunjoye, 2013; Akanbi, 2016). From the average concentrations of major ions in the shallow hand-dug wells of the study area, the dominance order of occurrence of cations is $Mg^{2+} > Ca^{2+} > K^{+} > Na^{+}$, while anionic concentrations decline in the order of $HCO_3^- > Cl^- > NO_{3-} > SO_4^{2-}$.

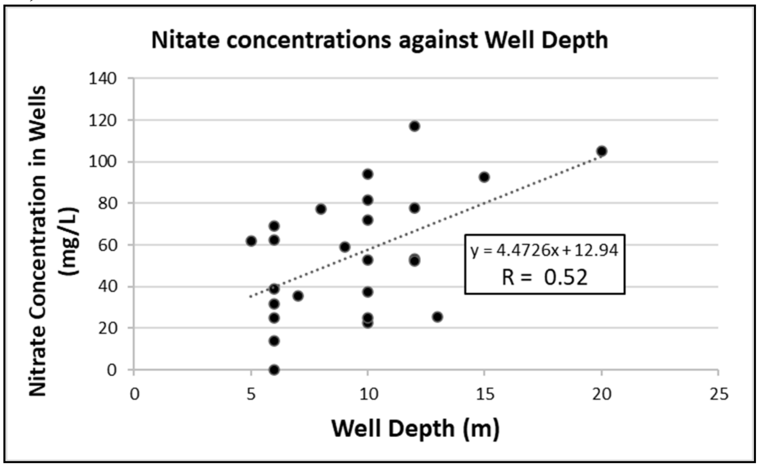

Figure 6: Plots of nitrate concentrations and well depths

3.2 Trace elements concentrations in groundwater

Eight trace elements were analyzed and the results of their concentrations are presented in Table 2. The non-essential trace elements that were analyzed included lead (Pb), Arsenic (As) and Cadmium (Cd). The occurrence of lead in water was between 0.02 and 3.57 µg/L and the average was 0.60 µg/L. Lead occurrence is found in all wells except in HD04. Lead concentrations in five wells were found to occur above 1.00 µg/L and location with the Pb enrichment is HD05- at Araromi 1. HD05 well is sited close to the main inter-state road, which is the busiest road network in the entire region (Fig. 3). So, exhausts from vehicular combustion engines may be the point source for lead enrichment in this well. Nevertheless, lead concentration in this location is still far below the guideline limit of 10 µg/L in drinking water (Table 2), but there is need to exercise caution when the likely sources of contamination of toxic elements such as lead are known. Arsenic, which is a known potent highly toxic non-essential trace element occurred below the detection limit of 0.01 µg/L in three hand-dug wells at Agboye (HD13), Adeniran (HD23) and Durbar (HD24). The highest concentration of As is found in well HD18 at Isaleagbala.

However, a nearby well at Asogo- HD22 has a rather low concentration of 1.46 µg/L depicting a local source for the high concentration in HD18. The recommended limit of As in drinking water is 10 µg/L. Arsenic is carcinogenic and had been linked to be responsible for mental retardation in infants (Wasserman et al. 2014; Muehe and Kappler 2014; Mayer and Goldman 2016). Concentration of arsenic in other wells was from 0.05 to 7.35 µg/L and the mean was 1.84 µg/L. Just like Arsenic, Cadmium is also not detected in sample- HD04 at Dakanka but the concentration lies between 0.03 and 1.87 µg/L in other wells. None of the concentration was above the guideline limit of 3 µg/L. The mean concentration of cadmium in the groundwater was 0.41 µg/L. Chromium VI ion which is also known to be carcinogenic (WHO, 2017) occurred below detection limits of 0.005 mg/L in most of the wells. However, it is found and detected in in three wells sampled at Araromi and Mabolaje, HD05, HD08 and HD09 with respective concentrations of 0.027, 0.08 and 0.341 mg/L. Concentrations of groundwater in wells at Araromi 3 and Mabolaje 1 occurred beyond the acceptable limit of WHO, 2017.

Zinc is one of the essential trace elements just like Cu, Mn and Fe needed by human for effective body metabolism that was analysed in the groundwater samples. High concentration of these essential trace elements can also trigger other health issue in the body and human tolerance for Zn in drinking water is 4.0 mg/L (4000 µg/L). This concentration limit is higher than most other essential trace elements in drinking water. For the present work, Zinc concentration in sampled water was between 0.01 and 7.79 µg/L with an av. of 1.68 µg/L while Copper concentration in was in between 0.38 and 32.7 µg/L. The average concentration of Cu was 7.66 µg/L and this is far below the guideline limit of 2000 µg/L. Even then, location with the highest abundance of 32.7 µg/L at Durbar area of Oyo is a concern considering the fact that other wells have far lower abundance of copper. Like most of the essential trace elements, the concentration of manganese (Mn) found in natural water including groundwater is most of the time is not of health concern. However, occurrence beyond 0.1 mg/L will give water an offensive taste and may precipitate out to form scales in pipes as well as cause stains in laundry. Mn occurred below detection limit of 0.05 mg/L in most of the samples, except in three wells located at Araromi 1 (HD05), Mabolaje 1 (HD09) and durbar (HD24) with concentrations of 1.2 mg/L, 0.5 mg/L and 0.3 mg/L respectively. These concentrations are well above the acceptable limit for domestic usage. Lastly, just like Mn, iron II (Fe^{2+}) has lower potential toxicity as well (Mora et. al., 2017). The concentration of Fe^{2+} found in most underground water has no health effect except for the offensive taste and laundry stains when the concentration exceeds 0.3 mg/L (WHO, 2017). Fe^{2+} was found to occur above the detection limit of 0.005 mg/L in all wells; but the concentration, which was between 0.01 and 0.06 mg/L is far below the guideline limit for domestic utilization.

3.3 Bacterial counts in the groundwater

There is no bacterial contamination in three wells located at Araromi 3, Akunlemu and Ile-ekerin; even though, the well depths are shallower than most other sampled wells. For most other wells, coliform counts ranged between 6 and 1860 cfu/100 m and hand-dug wells with the least bacterial contamination count of 6 cfu/100 ml was sampled at Isaleagbala (HD18) while the highest count of coliform of 1860 cfu/100 ml was obtained in well HD10 at Mabolaje 2. Five other wells have exceptional high coliforms count that exceeded 1000 cfu/100 mL and these are those sampled at Ilora, Araromi 4, Mabolaje 2, Agboye and Adeshina areas.

The amount of E. coli in water was between 2 and 1640 cfu/100 ml, and this accounts for between 33 and 90 % of the total coliform in water. Wells with more than 80% Escherichia coliform against the total coliform were 14 out of the total 25 sampled hand-dug wells. This indicated that E. coli bacteria are the major coliform bacteria in the water sampled. It also showed that fecal pollution is one of the main sources of bacterial contamination of underground water in Oyo town. Ranges of E. coli abundance in water is illustrated in Fig. 7 and the range within 1 – 50 counts is 28 %. Higher abundance greater than 50 units amounted to 60 % collectively (Fig. 7). The interpretation is that fifteen hand-dug wells have E. coli counts beyond 50. This is an indication of gross bacterial contamination in water and a reflection of the unhygienic sanitary conditions of the surface environment. Locations with exceptional high E. coli counts of more than 500 are found in four wells at Ilora, Araromi 4, Mabolaje 2, Agboye, and Adeshina areas (Fig 8).

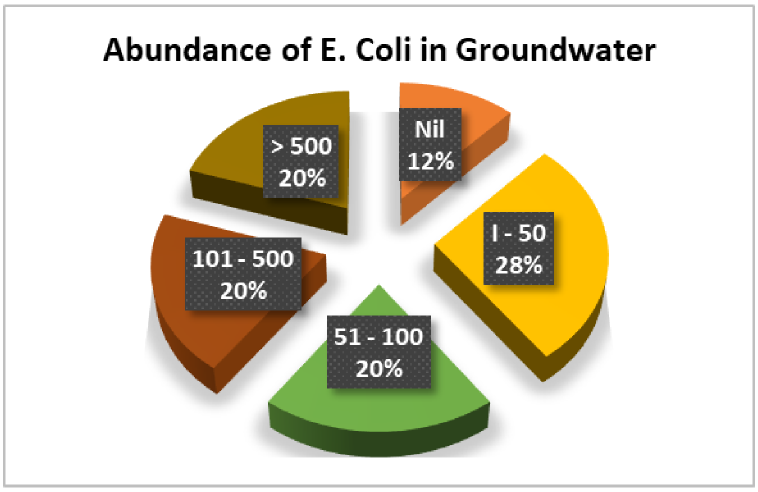

Fig. 7 Abundance of E. coli in sampled hand-dug wells

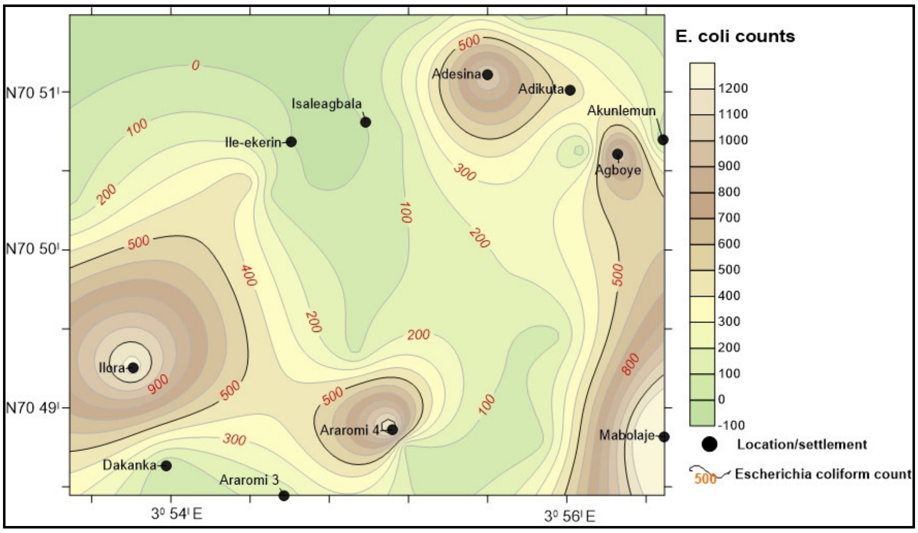

Fig 8 Map of the spread of Escherichia coliform in groundwater across the study area

3.4 Relationships between groundwater parameters

The results of correlation analyses of groundwater variables conducted to reveal the type and degree of relationships existing among the analyzed and measured parameters are presented in Table 4. Further elaborations of inter-relationships between groundwater parameters were illustrated in cross-plots presented in Fig. 9. From the results of correlation analyses, strong relationships existed between TDS and most major ions, with coefficients of correlation (R) greater than 0.50. This is an indication that groundwater mineralization denoted by the TDS is largely controlled by ionic dissolution of these major elements. This is buttressed by the cross-plots of dominant cations (Ca+Mg) and anions (HCO_3+Cl) versus (Vs.) TDS where the R values are respectively 0.82 (Fig. 9a) and 0.83 (Fig. 9b). From the plots of Nitrate/TDS in Fig. 9c, R = 0.49 indicating that nitrate also contribute to groundwater mineralization moderately. This is corroborated further by the fact that nitrate has positive correlation with most other major ions (Table 4), though the degree of the significant is low. However, from the plots of representative trace elements Vs. TDS (Fig. 9d), the linear relationship is close to zero (R = 0.08) depicting that there is no correlation between groundwater mineralization (TDS) and trace elements and meaning that trace elements and other major ions are not likely from the same source(s). This is further confirmed in Table 4, whereby major ions are negatively correlated with trace elements and R values approaching zero in many cases. Also, there is little or no relationship from the plots of nitrate against trace elements (Fig. 9e) with R = 0.06. This confirmed that the trace elements may be from different sources unlike nitrate which has closer affinity with major ions than trace elements. Also, the plots of nitrate against E.coli with R = - 0.10 (Fig. 9f) is indirect and insignificant as well, while E.coli /trace element (Fig. 9g) is positive but with little significant (R = 0.21). Lastly, from the cross-plots of E.coli/TDS (Fig. 9h), there is little or no relationship with R = - 0.15. From the foregoing, it can be summed that trace elements and E.coli have greater affinity than with major ions and even nitrate. Hence,

Table 4 Correlation matrix of chemical and bacteriological parameters

Parameters	pH	TDS	Ca^{+2}	Mg^{+2}	Na^{+}	K^{+}	HCO_3^-	NO_3^-	Cl^-	$S0_4^{2-}$	Fe^{2+}	Cu	Cd	Pb	Zn	As	E. coli.
pH	1.00																
TDS	0.53	1.00															
Ca^{2+}	0.54	0.65	1.00														
Mg^{2+}	0.28	0.68	0.25	1.00													
Na^{+}	0.06	0.09	-0.08	-0.06	1.00												
K^{+}	0.24	0.49	0.34	0.11	0.28	1.00											
HCO_3^-	0.57	0.60	0.50	0.43	0.02	0.12	1.00										
NO_3^-	-0.13	0.49	0.30	0.32	-0.12	0.09	0.21	1.00									
Cl^-	0.43	0.91	0.57	0.65	0.23	0.50	0.42	0.36	1.00								
$S0_4^{2-}$	0.64	0.90	0.59	0.70	0.08	0.43	0.43	0.29	0.86	1.00							
Fe^{2+}	-0.01	0.11	0.04	0.20	-0.19	-0.06	-0.05	-0.11	0.07	0.05	1.00						
Cu	0.07	0.03	0.03	0.14	-0.39	-0.09	-0.13	-0.20	0.10	0.21	-0.04	1.00					
Cd	0.14	-0.04	0.04	0.00	0.30	-0.26	-0.17	-0.05	0.10	0.14	0.04	-0.08	1.00				
Pb	-0.26	-0.31	-0.12	-0.15	-0.12	-0.40	-0.17	-0.05	-0.24	-0.22	0.27	-0.04	0.48	1.00			
Zn	-0.42	-0.20	-0.41	0.09	-0.30	-0.07	-0.01	-0.01	-0.17	-0.33	0.00	0.03	-0.35	0.04	1.00		
As	-0.30	0.03	-0.17	0.33	0.29	-0.12	0.12	0.06	0.29	-0.03	-0.19	-0.18	-0.07	-0.04	0.34	1.00	
E. coli	-0.08	-0.15	0.05	-0.24	-0.26	-0.16	-0.10	-0.16	-0.25	-0.12	0.14	0.34	0.10	0.22	-0.15	-0.29	1.00

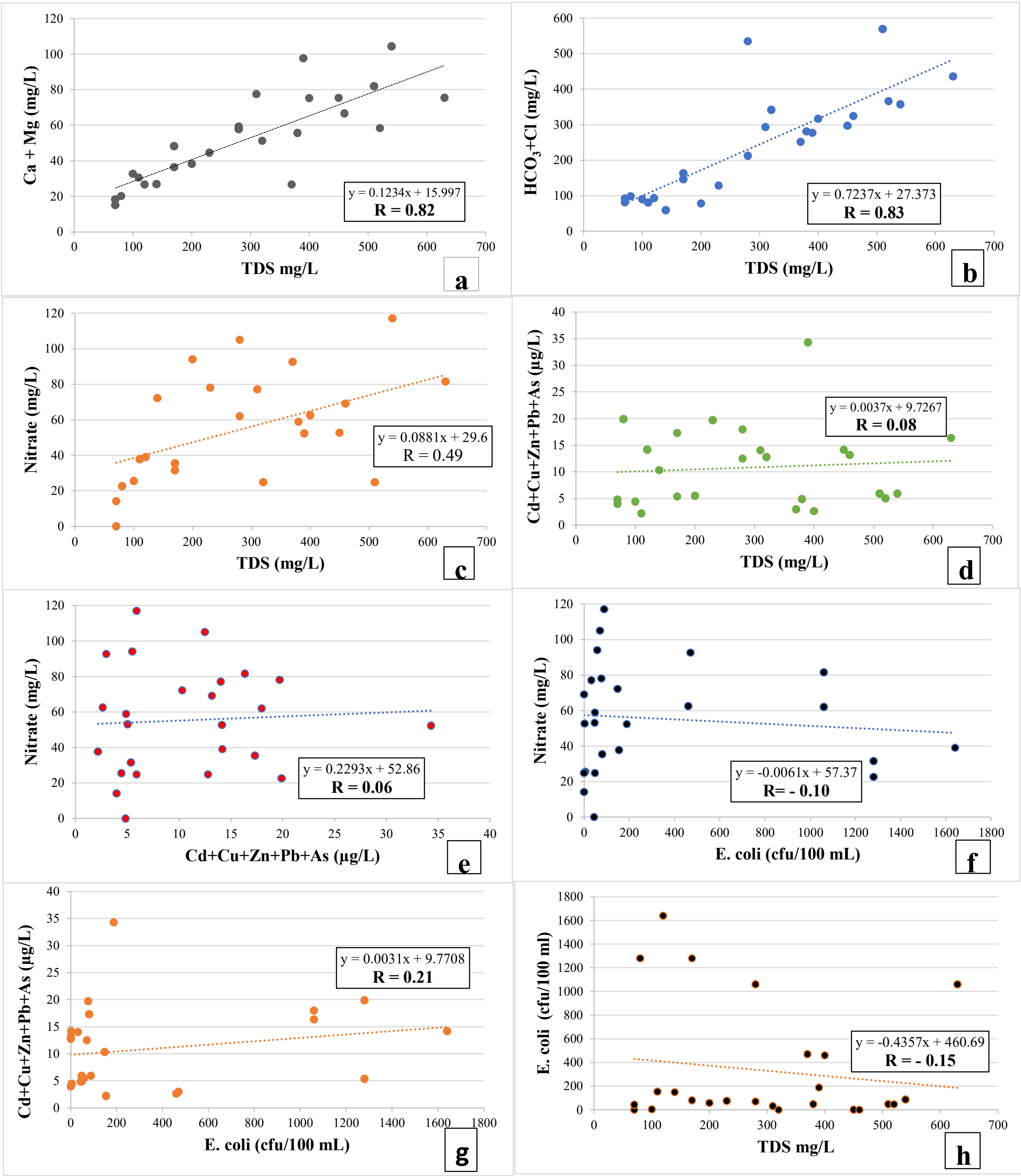

Fig. 9 Cross-plots of groundwater chemical and bacterial parameters

nitrate pollution may be attributable to natural sources from nitrogen fixing processes and perhaps anthropogenic sources as well. However, the abundant E.coli in the groundwater of the area is regarded to be from anthropogenic sources since it is already known to be associated with fecal droplet and to a large reasonable extent trace elements sources are likewise from human sources and not from natural rock dissolution, though; they may be from other human activities such as exhaust from locomotive engines, open incineration of wastes and similar activities in the surface environment.

4 Conclusion

Poor sanitary condition, unregulated industrial processes as well as other human and agricultural activities have always been linked to contamination of the groundwater. The study area is mainly a residential area with poor hygienic conditions. The large amount of colony forming coliform units including E. coli in the groundwater is an indication of sewage and fecal contacts with the underground water. The occurrence of most trace elements below alarming concentrations and toxic levels in the area buttressed the fact that Oyo town is not an industrial area, hence this work revealed that trace elements contamination is largely sourced from industrial activities and not from domestic household discharge. Notwithstanding, the occurrence of chromium and manganese in five wells above the guideline limits at the southeastern part of Oyo town is a call for concern and the point source(s) should be the subjects of further investigations.

The sampled hand-dug wells are presently serving individual households and there is no other alternative water supply, except the common nylon-packaged water that the local peddlers normally display in shops for sale. Most residents that could not afford treated packaged water resolve to water supply from the numerous household hand-dug wells. Therefore, the present work is to stare up the appropriate authority and governmental agencies for effective mobilization of providing clean and safe water supply for the populace, organizing public enlightenment lectures on groundwater quality standards, enforcement of environmental laws and rendering assistance to households in providing water purification kits.

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