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ASSESSMENT OF NITRATE, TRACE ELEMENTS AND BACTERIAL CONTAMINATION OF GROUNDWATER IN ILORA AREA OF SOUTHWESTERN NIGERIA

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ABSTRACT

Assessments of groundwater pollution parameters were carried out in groundwater samples collected from selected shallow hand-dug wells across Ilora township. The analysed parameters were nitrate, trace elements including, iron, cobalt, chromium, manganese, zinc, arsenic, cadmium and lead, and bacteria count in water; using spectrophotometric method, HM Metalyser 5000 and multiple tube techniques respectively. The pH of the samples was between 6.4 and 7.6 and TDS range was 50 - 640 mg/l. The concentration of nitrate (NO_3) in water was 12.8 - 274 mg/l. For trace elements concentrations in µg/l ; iron (Fe): 150 – 880, Cobalt (Co): 1 – 100, Manganese (Mn): 0.01 - 140, Chromium (Cr): 0.01 – 0.31, Zinc (Zn): 1.86 - 9.97, Arsenic (As): 3.11 - 20.80, Cadmium (Cd): 0.71 - 4.76, Lead (Pb): 1.00 – 6.82. Based on the average concentration of the trace elements the order of abundance was Fe > Co > Mn > As > Zn > Pb > Cd > Cr. Total coliform count (TCC) in groundwater samples were between 18 and 370 cfu/100mL. From the evaluation of the degree of association between the parameters, a moderate to strong positive relationship occurred between Fe/Mn (0.59), Fe/Cr (0.85), Fe/TC (0.56), NO_3/Co (0.56), NO_3/Mn (0.48), NO_3/Cd (0.51) and Mn/Pb (0.85). Presence of coliform bacteria in the groundwater samples indicated fecal contamination from surface environment. Comparing the parameters with guideline standards for drinking water, most of the hand-dug wells are contaminated with nitrate, five wells were contaminated with either arsenic and/or cadmium, while water from some of the wells may have objectionable taste due to high iron content. The high values of cadmium and arsenic in some wells are harmful to human health and appropriate treatment is needed. For bacteria contamination, deeper wells are recommended, and the water should to be treated and boiled prior to consumption.

KEYWORDS: groundwater; hand-dug wells, pollution parameters, guideline standards, portability

NTRODUCTION

Groundwater is the major source of fresh water for the global population (Siebat, 2010; Akanbi et. al., 2022) but the worth of groundwater is its quality and this is determined by the physical, chemical and biological constituents. Naturally groundwater contains dissolved ions that dissolve slowly from soil particles, sediments and rocks as the water travels along mineral surfaces in the pores of the unsaturated zone and within the aquifer. Dissolved solids in groundwater increases as it moves through opening in geologic units which is why deeper and older waters are more mineralized.

Dissolved solids in water are categorized into major, minor and trace elements. Municipal and industrial wastes from human activities also contribute to groundwater chemistry, but most constituents from anthropogenic source are hazardous to human health and render the water unfit for domestic, industrial and agricultural usage. Pollutants from point sources such as septic tanks, industries, agricultural activities and automobile exhausts introduce trace elements and add to the concentrations of naturally occurring ions such as nitrate, sulphate, chloride and other cations. For example, nitrate is released into the environment by nitrogenous fertilizers, organic matter and from

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human and animal waste as well as industrial effluent. This is apart from naturally generated nitrate from atmospheric nitrogen that is released as ammonium (NH_4^+) and amide (NH_2^-) forms which generates nitrate in soil system through mineralization, which is fairly rapid in tropical and subtropical soils. Due to the high solubility of nitrate in water and low retention by soil particles, nitrate is prone to leaching to the subsurface and eventually into the groundwater. This process is enhanced when the groundwater table is shallow and where there is excessive application of nitrogenous fertilizer, manures and irrigation with abundant rainfall. Consumption of nitrate-rich groundwater may lead to health risk causing methemoglobinemia, gastric cancer, genetic mutation, among others.

Likewise, assessment of trace elements in groundwater supply in human communities is of great importance due to industrialization and activities such as agriculture and cattle rearing with the attending high potential for increasing the concentration of several ions and trace elements in groundwater, leading to water quality deterioration (Bardsley *et al.* 2015; Akanbi *et al.* 2020). Studies performed in Pakistan indicate that more than 74 million inhabitants are subjected to health risk from Arsenic, Cadmium, Chromium Iron, Manganese, Nickel and Lead contamination of groundwater (Bhowmik *et al.*2015). Similarly, other studies carried out in highly populated states of Nigeria showed that more than 16 million inhabitants were suggested to be at high risk of developing cancer due to ingestion of groundwater with elevated levels of Cr, Pb, As, and Cd (Ayedun et al. 2015; Aboyeji and Eigbokhan, 2016; Amoo *et al*. 2018; Olubukola *et al*. 2018; Adewoyin *et al.* 2019; Rahman *et al*. 2020). Trace elements are divided into essential and non-essential trace elements. For example, Cobalt, Iron, Manganese, Selenium and Zinc are essential for human growth, so they are called essential trace element, while elements like Bismuth, Cadmium, Lead and Titanium appear to have no metabolic function, so they are called non-essential trace elements (Mora *et. al*, 2017). Non-essential trace elements can induce some pathologies in humans such as neurocognitive impairments, cardiovascular diseases, and several kinds of cancer. Even trace elements that are essential to humans can also cause morphological abnormalities, reduced growth, increased mortality and induce genetic mutation in humans at elevated levels (Calderon, 2000).

Of equal important is the biological components of groundwater, most of which are diseases-causing organisms. Presence of bacteria in groundwater, particularly the coliform units, is an outright confirmation of contamination due to poor sanitary conditions around the wells. Coliform bacteria are known to be associated with fecal droppings of man and animals and originates from the digestive tract of humans and warm-blooded animals. The inclusions of coliform bacteria in groundwater means the water is unsafe for consumption, except it is treated.

For this study, the quality of groundwater at Ilora area of SW Nigeria was evaluated by measuring the physico-chemical parameters, and analysing for nitrate and trace elements concentrations, as well as assessing the total coliform counts (TCC) in the representative groundwater samples from selected hand dug wells across the study area.

The Study Area

Ilora town is located in the present Oyo state and it lies within the basement complex terrain of south-western Nigeria. The study area is within latitude 07°48’0” N and 07°49’15” N, and longitude E03°53’30” and E 03°54’15” E (Fig. 1). It is in Afijio Local Government Area and has a population of about 134.184 people (NBS, 2006). The topography of the area ranges from medium to low terrain above sea level. The northwestern part of the area is a low-lying area. The peak of the topography is at the southwestern part of the area, and is about 325 m. Ilora area is underlain by migmatite gneiss, biotite gneiss and quartzite (Fig. 2). Geological features such as ~~a~~ faults, granitic intrusions, quartz and pegmatite veins are also present.

MATERIALS AND METHODS

A total of fifteen (15) groundwater samples were collected within Ilora, including fourteen hand-dug wells and one borehole. The spread of the sampled wells in the area and on geological map are shown in Figures 1 and 2 respectively. The sampled borehole is at Oja-Oke 3 with sample number L13. The borehole sample is to serve as a control for samples from hand-dug well. The water samples were iced to ensure preservation and stability of dissolved solutes and were taken to the water laboratory of the Federal Ministry of Water Resources at Akure for chemical analyses. Prior to this, supplementary in situ parameters were measured in the field with digital TDS/EC meter. The measured trace elements concentrations include~~d~~ cobalt (Co), manganese (Mn), iron (Fe), zinc (Zn), chromium (Cr), cadmium (Cd), arsenic (As) and lead (Pb). Nitrate concentration was measured using colorimeter while HM Metalyser 5000 was used for measuring trace elements concentrations in the water. The procedure followed the standards of measurements of the laboratory manual of the Federal Ministry of Water Resources (Adeoye and Babalola, 2011). Correlation analyses were done to interpret existing relationship among parameters and concentration contour maps of certain trace elements were drawn to determine their spatial distribution across the area using Surfer 12 and Microsoft tools.

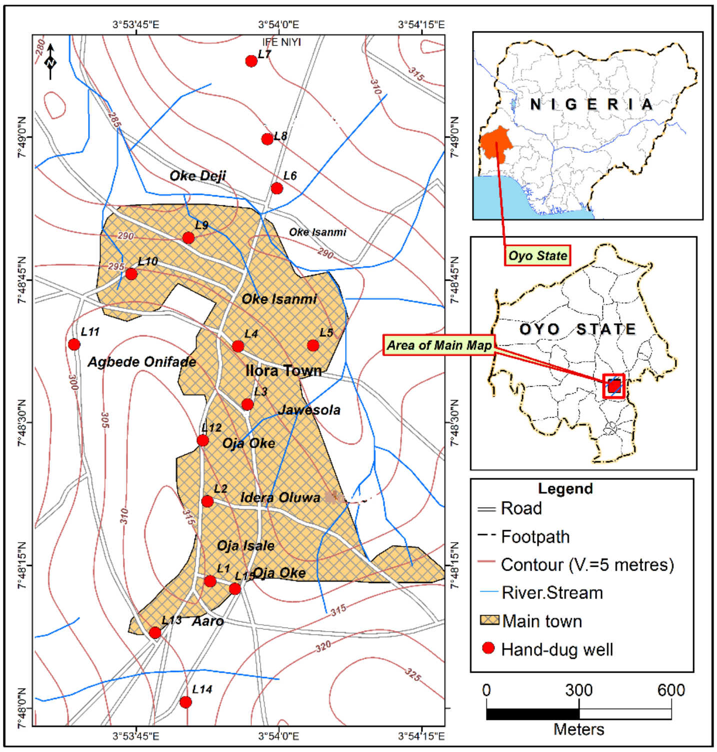

Figure 1: Location map of the study area with sampled borehole points

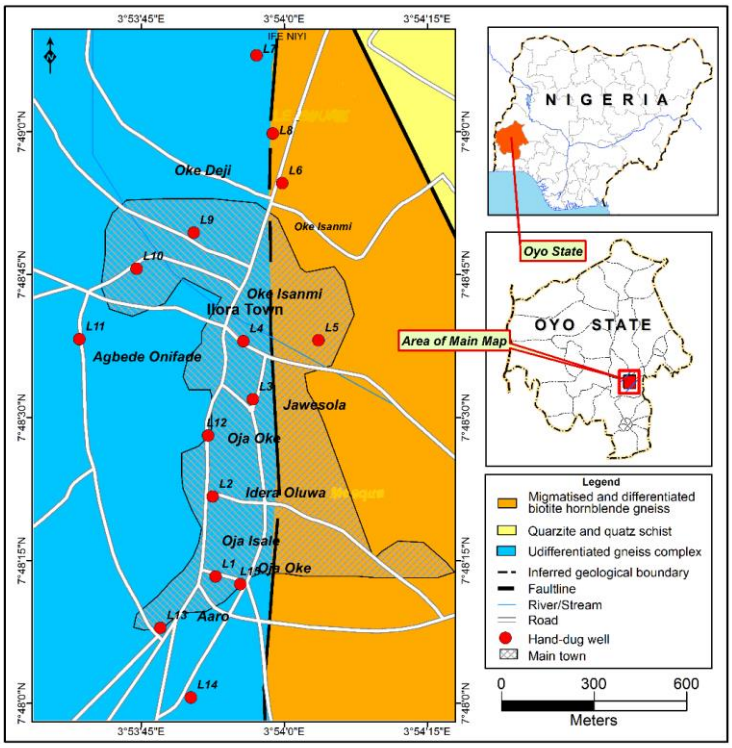

Figure 2: Geological map of the study area, showing also the sampled wells

RESULTS AND DISCUSSION

Location name of the wells as well as the results of the measured physicochemical parameters, trace elements concentrations and coliform count in water samples are presented in Table 1. Statistical summary of parameters is presented along with the national guideline limits of the Nigerian industrial standards given by the Standards Organisation of Nigeria (SON, 2007) and that of the World Health Organization (WHO, 2017) for drinking water quality. From the presented results, the pH spanned from 6.4 to 7.6, with an average (avg.) of 6.8, and the total dissolved solids (TDS) was between 50 and 640 mg/l (avg. 393) and, based on this, the water can be regarded as fresh.

Nitrate and trace elements concentrations

Nitrate concentrations ranged from 12.8 to 274 mg/l, with an average concentration of 131.27 mg/l. The location with the highest concentration of nitrate is L02 (Oja-oke 2) in the southern part of the area and the area with lowest concentration is L08 (Oke-Isanmi 3). Nitrate abundance in most of the hand-dug wells exceeded the permissible limit of 50 mg/l (WHO 2017; SON 2007). Nitrate contamination is widespread in the study area (Fig. 3). The high concentration of nitrate is attributed to improper disposal of human waste and not to agricultural activities because Ilora is mainly a residential town characterized by poor waste disposal system.

Total iron (Fe) concentrations range from 150 to 1880 µg/l (avg. 397 µg/l). No health baseline value was given for Fe, except that at concentration above 300 µg/l, the water may have an objectionable taste and can stain laundry (WHO, 2017). The average concentration of Fe in water exceeded the limit of 300 µg/l but the actual number of wells with concentrations above this value were four and are at Oja-Oke 1, Oke-Isanmi, Ife Niyi and Aaro. Cobalt concentrations in the groundwater of Ilora range from 1 to 100 µg/l, with an average concentration of 34.2 µg/l. The location with highest cobalt concentrations is L10 (Oke-Deji 1) in the North western part of the area and the location with the lowest cobalt concentration is L14 (Aaro) in the southern part of the area. Cobalt is not found in three wells, two of which are at Oke-isanmi and the third at Aaro. Manganese was not detected in six wells also and it occurred below 10 µg/l in other wells but its concentration was relatively and markedly significant in wells at Oja-oke 2 and Aaro with corresponding values of 130 and 140 µg/l and these concentrations are still far below the national maximum limit of 200 µg/l (Table 2). Chromium enrichment in the wells is comparatively lower against other elements from 0.01 to 0.31 µg/l, with average concentration of 0.08 µg/l. The location with the highest concentration is L14 (Aaro) in the southern part of the area and ahand-dug well with the lowest chromium concentration is L09 (Ile Ewure) in the northern part of the area. The guideline limit of Cr in drinking water is 50 µg/l. Zinc concentration in Ilora ranges from 1.86 to 9.97 µg/l (avg. 3.72 µg/l). Well with the highest concentration is at Okedeji 1 on L10. Zn was not detected in two wells at Ile-Ewure and at Agbede. Zn is an essential trace element with quite a large permissible limit of 3000 µg/l in drinking water. Arsenic (As) and lead are both toxic elements that should not occur beyond 10 µg/l in drinking water. Arsenic concentration ranges from 3.11 to 20.80 µg/l with an average of 10.1 µg/l in the analysed water samples. The concentrations of arsenic exceeded the recommended limit in five wells at Oja-oke 1, Oja Isale, Oke-Isanmi 3, Ile Ewure and Aaro while that of Oja-oke 1 on L01 has the highest concentration. The spread of arsenic concentration in Ilora is presented in Figure 4. However**,** lead occurred below 10 µg/l in all wells. The range of Pb occurrence was between 1.00 and 6.82 µg/l. The highest occurrence of 6.82 µg/l is at Oja-oke 2 and Pb was not detected in four wells across the area. Cadmium is not detected in most wells at Ilora, but it is found in six wells with concentrations spread between 0.71 and 4.76 µg/l (avg. 1.00 µg/l). The location with highest concentrations is Oja-oke 1 on L01 in the southern part of the area. The recommended limit for the concentration of cadmium in groundwater is 3 µg/l, and this means that the concentrations of cadmium in two wells at Oja-Oke i.e.L01 and L02 occur above the recommended limit.

Table 1: Results of physicochemical parameters, trace elements and bacterial count in groundwater samples

Sample No	Location name	pH	TDS Mg/L	EC µS/cm	$N0_3^-$	Fe	Co	Mn	Cr	Zn	As	Cd	Pb	TCC
					(mg/l)	µg/L								(cfu/100 ml)
L01	Oja-oke 1	6.6	560	1140	168	340	22	ND	0.08	2.79	20.80	4.76	ND	72
L02	Oja-oke 2	7.6	640	1280	274	220	90	130	0.04	1.86	7.46	4.55	6.82	32
L03	Jawesola	6.9	550	1100	97.5	200	60	10	0.04	4.55	ND	ND	2.28	130
L04	Oja Isale	7.3	490	1000	126	210	1	1	0.01	6.47	12.80	ND	1.13	54
L05	Idera-Oluwa	6.5	340	700	124	200	23	ND	0.04	3.72	6.27	2.20	ND	18
L06	Oke-Isanmi 1	6.6	50	115	19.5	310	10	10	0.23	2.06	6.37	ND	1.27	24
L07	Oke-Isanmi 2	6.4	90	190	32.8	210	ND	ND	0.04	0.00	7.97	ND	1.68	32
L08	Oke-Isanmi 3	7.0	150	310	12.8	1180	ND	10	0.19	3.15	19.7	ND	4.04	390
L09	Ile Ewure	6.9	580	1170	183	150	46	ND	ND	ND	16.1	ND	ND	36
L10	Okedeji 1	6.9	460	930	189	220	100	10	0.04	9.97	6.11	ND	1.86	40
L11	Okedeji 2	6.4	390	780	175	190	50	0.01	0.02	4.65	6.11	ND	ND	18
L12	Agbede	6.4	410	830	158	230	71	ND	0.05	ND	3.11	1.17	1.85	48
L13	Oja-oke 3	7.2	370	740	74.4	215	30	5	0.02	4.11	8.70	0.71	1.00	0
L14	Aaro	7.4	290	600	174	1880	ND	140	0.31	4.52	10.4	ND	5.71	110
L15	Oja-oke 4	6.5	520	1060	161	200	10	ND	0.03	8.00	9.94	1.60	2.41	118

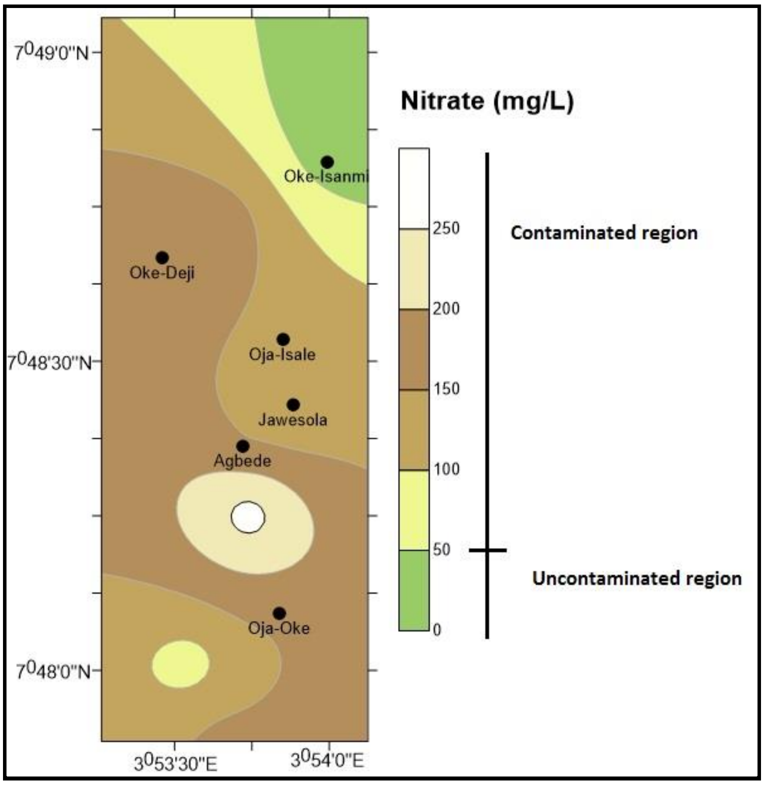

Figure 3: Spread of nitrate concentration at Ilora

Table 2: Statistical summary of measured and analysed parameters with guideline limits

Parameters	Minimum	Maximum	Mean	Guideline limits WHO (2017)	Guideline limits SON (2007)
pH	6.4	7.6	6.8	-	6.5 - 8.5
TDS (mg/l)	50	640	393	600	500
EC µS/cm	115.0	1280.0	796.3	-	1000.0
NO_3 (mg/l)	12.8	274	131.27	50	50
Fe (µg/l)	150	1880	397	-	-
Co (µg/l)	1	100	34.2	-	-
Mn (µg/l)	0.01	0.14	21.1	100	200
Cr (µg/l)	0.01	0.31	0.08	50	50
Zn (µg/l)	1.86	9.97	3.72	3000	3000
As (µg/l)	3.11	20.8	10.1	10	10
Cd (µg/l)	0.71	4.76	1.00	3	3
Pb (µg/l)	1.00	6.82	2.10	10	10
TCC (cfu/100mL)	18	370	80	0	10

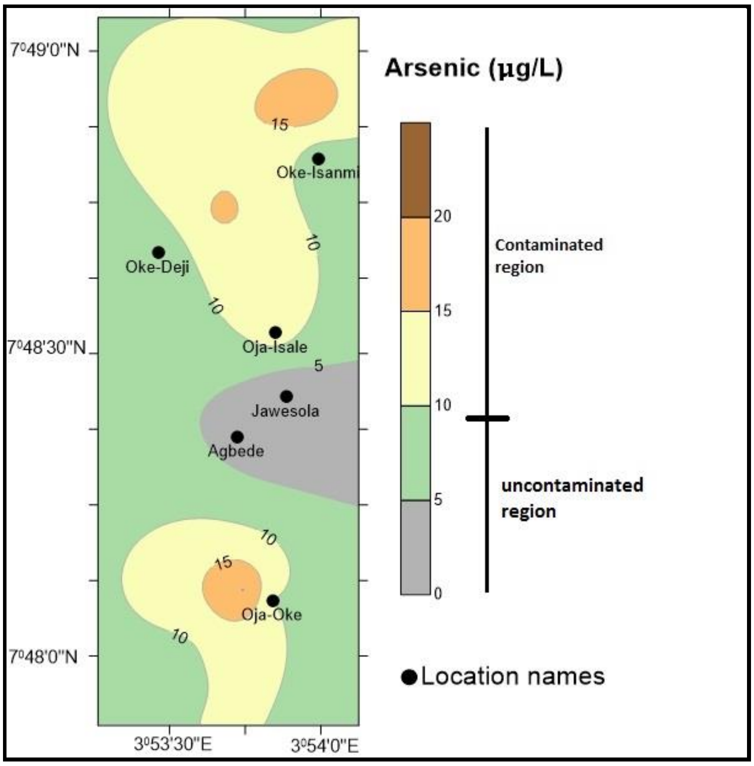

Figure 4 Concentration map of Arsenic in Ilora groundwater

Bacteria contamination assessment

Presence of coliform bacteria in water is an indication of pollution and inadequate water treatment (Ashbolt et, al., 2001; WHO, 2017), and these bacteria are found in faeces of human and animals and they multiply in water and soil environments. Coliform bacteria are diseases-causing organism. The total coliform count (TCC) in the sampled hand-dug well were between 18 and 390, with an average count of 75 cfu/100 ml. The location with the outrageous coliform count of 390 cfu/100 mL is at Oke-Isanmi 3 on L08 and in this well, the pH is neutral, TDS is low-just 150 mg/L; nitrate is equally low with a value of 12.8 mg/l, but total iron and arsenic are comparatively quite higher than most other wells. Locations with the lowest concentrations of bacterial count are at Idera-Oluwa L05 and Oke-deji 2 on L11 with 18 cfu/100ml. The only sample that is free of bacterial contamination is at Oja-Oke 3 well with location number L13. This well is the only borehole among all the sampled wells and with this result, it is obvious that water from deep wells could be free from coliform bacteria in the area. Also, poor hygienic condition of the surface environment through open defecation introduced coliform bacteria to the shallow well in sampled hand-dug well at Ilora. The most widespread coliform unit range is 1 – 50 cfu/100 mL while the TCC in just one well exceeded 200 cfu/100 mL, representing about 7%. (Figure 5).

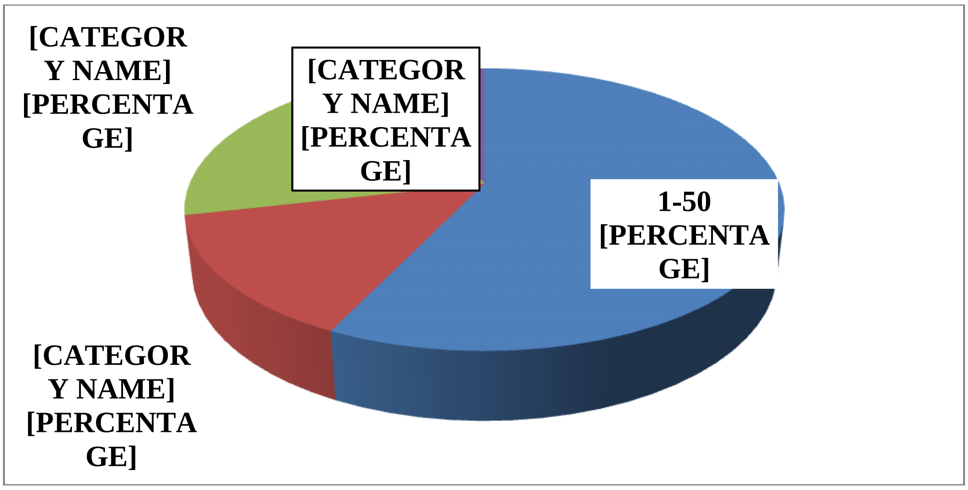

Figure 5: Frequency of occurrence of coliform bacteria in sampled wells

Statistical relationship among parameters

From the results of correlation analyses as presented in Table 3, the type and degree of association existing between the parameters are clearly seen. Positive and moderate associations occurred between total iron and manganese and lead, that is Fe/Mn (R = 0.59) and Fe/Pb (R = 0.58). Likewise, moderately significant positive relationships occurred between nitrate, cadmium and cobalt; NO_3/Co, (R = 0.56) and NO_3/Cd (R = 0.51). A moderately significant relationship occurred between total coliform and iron and total bacteria count; TC/Fe (R = 0.56) and TC/TBC (0.51) A strong positive relationship occurred between iron and chromium, and between manganese and lead; Fe/Cr (R = 0.85) and Mn/Pb (R = 0.85) have strong positive relationship with the degree of relationship being 0.85 and 0.85 respectively. The strong positive relationship between iron and chromium indicates that their sources in the groundwater system are probably similar, likewise for manganese and lead.

Table 3: Results of correlation analysis

	Fe	**Co**	**Mn**	**Cr**	**Zn**	**As**	**Cd**	**Pb**	**TC**	**$N0_3$**
Fe	1.00									
Co	-0.46	1.00								
Mn	0.59	0.06	1.00							
Cr	0.85	-0.54	0.48	1.00						
Zn	0.03	0.28	-0.02	-0.07	1.00					
As	0.32	-0.32	-0.05	0.18	-0.10	1.00				
Cd	-0.19	0.09	0.25	-0.17	-0.15	0.23	1.00			
Pb	0.58	0.02	0.85	0.47	0.02	-0.05	0.16	1.00		
TC	0.56	-0.33	0.02	0.42	0.08	0.44	-0.16	0.38	1.00	
$N0_3$	-0.11	0.62	0.48	-0.29	0.18	-0.06	0.51	0.25	0.36	1.00

CONCLUSION

The present work has studied the pollution parameters in the shallow groundwater of Ilora by analyzing for nitrate, trace elements and bacteria count in the sampled hand-dug wells. Most of the hand-dug wells are contaminated with nitrate with concentrations exceeding the guideline limit of 50 mg/l. Among the eight trace elements that were analysed just two, namely, cadmium and arsenic were found at contamination levels exceeding 3 µg/l and 10 µg/l respectively in five hand-dug wells and these hand-dug wells were located at Oja-oke, Oja Isale, Ile Ewure, Oke-Isanmi and Aaro area of Ilora. The presence of coliform bacteria in all the hand-dug wells is an indication of human contamination since these organisms do not occur naturally in water. this is also buttressed by the fact that the only sample from borehole (deeper well) at Oja-oke 3 was found to have no coliform bacteria count. Apart from depth influence, boreholes are not manually operated like the hand-dug wells whereby there is direct human contact with the water during water fetching.

People of Ilora community have to be enlightened about groundwater quality standard and that water does not have to be muddy before it is considered unfit for drinking. It is also recommended that the water from the hand-dug wells be subjected to boiling or chlorination before drinking to rid the water of bacteria. Also, construction of new hand-dug wells should be as far as possible from soak-aways pits, septic tanks and pit latrines. Groundwater from wells that are contaminated with trace elements should not be served as potable water; else it should be properly treated by appropriate purification methods such as adsorption technique by activated carbon incorporated with iron for arsenic and cadmium contamination. Lastly, other nearby wells in the surrounding areas of contaminated wells at Oja-Oke, Oja Isale, Oke-Isanmi 3, Ile Ewure and Aaro that were not analysed should be subjected to quality assessment to ascertain the suitability of the water for drinking purposes and further studies on the sources of arsenic and cadmium in some of the wells are recommended.

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