Journal of Environment Pollution and Human Health, 2019, Vol. 7, No. 2, 100-106
Available online at http://pubs.sciepub.com/jephh/7/2/5
Published by Science and Education Publishing
DOI:10.12691/jephh-7-2-5

Statistical Investigation of the Spatial and Seasonal Variations of Heavy Metal Contents of Groundwater Sources in Ayedaade Area, Southwestern, Nigeria

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Received September 11, 2019; Revised October 19, 2019; Accepted November 10, 2019

Abstract This study assessed the spatial and seasonal variations in heavy metal concentrations of groundwater sources of Ayedaade LGA. It also assessed the suitability of the investigated groundwater sources for domestic use and compared the water quality with the minimum standard of drinking water provided by the World Health Organization (WHO). Twenty-five sampling stations were established covering the three bedrock types (migmatite gneiss, biotite and undifferentiated schist) identified in the three major towns of the study area. A total of a hundred and fifty (150) water samples were collected from the stations at three monthly intervals over the period of study, and analyzed for cadmium, chromium, iron, lead, nickel, and zinc using Atomic Absorption Spectrophotometric method. The results showed that approximately 60% of the water samples could be classified as soft-moderately hard fresh water type, occurring within the range of Bromothymol Blue indicator (pH 6.0 – 7.6). The result showed that all metals investigated for were present in the water samples. None of the samples analyzed had Zn concentration above the permissible limit, while Fe concentration was above the permissible limit for drinking water by WHO in 82% of the samples. Chromium, Ni, Cd, and Pb exceeded the limit for potable water in 99.7, 91.3, 90.0 and 42.0% respectively of the samples investigated. The study concluded that the water quality fell below minimum standard of drinking water provided by WHO and hence unfit for drinking.

Keywords: *boreholes, contamination, groundwater, hand dug wells, heavy metal, season*

Cite This Article: Abidemi O. Omopariola, and Funso I. Adeniyi, “Statistical Investigation of the Spatial and Seasonal Variations of Heavy Metal Contents of Groundwater Sources in Ayedaade Area, Southwestern, Nigeria.” *Journal of Environment Pollution and Human Health*, vol. 7, no. 2 (2019): 100-106. doi: 10.12691/jephh-7-2-5.

1. Introduction

Heavy metals are naturally occurring elements with a high atomic weight between 63.55 $gmol^{-1}$ and 200.54 $gmol^{-1}$ (Manganese, Copper, Arsenic) and a density at least 5 times greater than that of water. Some heavy metals, e.g. Iron, Zinc are essential trace elements; however, some of them e.g. lead, cadmium and nickel can be toxic to all forms of life at high concentration due to formation of complex compounds within the cell. Urbanization and industrialization have increased the level of trace metals, especially heavy metals in industrial, municipal and urban runoff, and this can be harmful to humans and biotic life [1-4]. Because of the wide range of its application in industrial, domestic, agricultural, medical and technological processes, this has led to their distribution in the environment [5]. Heavy metals exist in colloidal, particulate and dissolved forms in water and their occurrence could be of natural origin, i.e. volcanism, leaching of ore deposits and minerals within sediments or anthropogenic in origin i.e. solid waste disposal, industrial/domestic effluent, [6,7,8]. Human activities have thus increased the concentration of heavy metals in the environment; water, soil, air, fruits and vegetables [9]. Solid wastes from industrial units are being dumped near factories, and on open ground surfaces which react with percolating rain water, surface runoffs and find its way to the ground water [10]. Some of the metals are essential to sustain life, e.g. calcium, magnesium, potassium and sodium must be present for normal body functions. Also, cobalt, copper, iron, manganese, molybdenum and zinc are needed at low levels as catalyst for enzyme activities [7,8], however, excess exposure to heavy metals can result in toxicity and can be harmful to all forms of life and the eco system [9,11]. There are about 35 metals that are of concern due to occupational or residential exposure, of which 23 are heavy metals. These are antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc [9]. Heavy metals can cause serious health effect with varied symptoms depending on the nature and quantity of the metal ingested [7,8]. Some of these known fatal effects of heavy metal toxicity in drinking water include damaged or reduced mental and central nervous function and lower energy level. They also cause irregularity in blood composition; badly affect vital organs such as kidney and liver [4,12]. The long term exposure to these metals result in physical, muscular and neurological degenerative processes that cause Alzheimer's disease (a brain disorder), Parkinson's disease (degenerative disease of the brain), muscular dystrophy (progressive skeletal muscle weakness), multiple sclerosis (a nervous system disease that affects brain and spinal cord). Also, lead is one of the most common heavy metal in drinking water, which if present beyond permissible limit, causes a general metabolic poison effect and inhibits enzyme activities [4,13]. In addition to the symptoms found in acute lead exposure, symptoms of chronic lead exposure could be allergies, arthritis, hyperactivity, mood swings, nausea, numbness, lack of concentration, seizures and weight loss [14]. Heavy metal like copper is an essential trace element but show toxicity when in excess.

2. Study Area

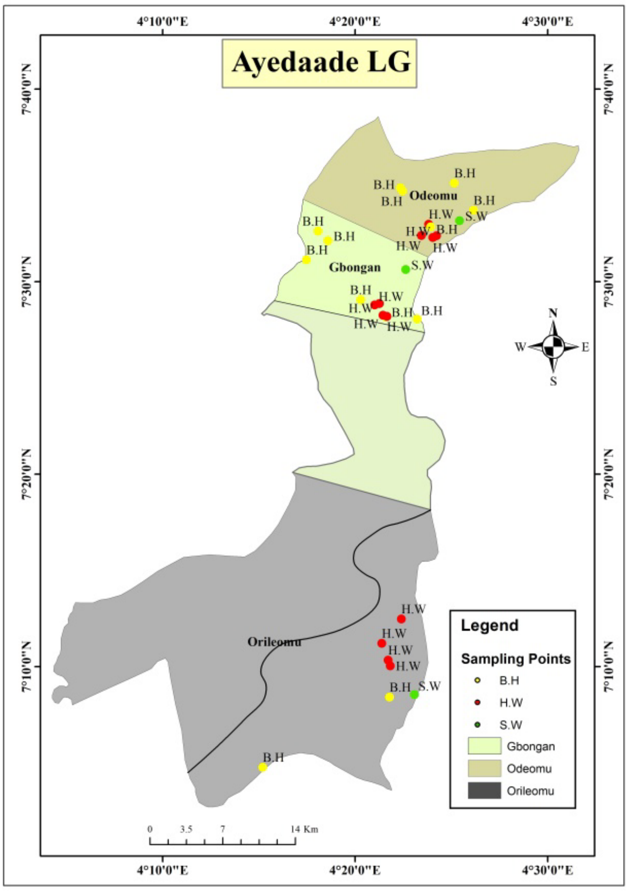

Figure 1. Map of the Study area

The study was carried out in Ayedaade Local Government. It is located within and between Latitudes 07^0 10' 00"- 07^0 47' 7" N, and Longitudes 004^0 12' 02" - 004^0 28' 004" E and covers a land mass of about 1,100 km^2 which falls within the Basement Complex of Nigeria (Figure 1). It is bounded to the West by Isokan, Aiyedire, and Irewole LGAs together with Oyo State, Ede South LGA to the North, Atakumosa and Ife North to the East and Ife South LGA and Ogun State to the South. It is about 43km south of Osogbo, the Osun State capital. The area, experiences two major seasons; dry and rainy seasons. The dry season lasts for about five months (November – March) during this period, the area at times record a minimum temperature of 18.9^{o}C while the Rainy season is experienced for the remaining seven months of the year (April to October). The rainfall distribution pattern is characterized by two peaks, June/July being the first peak while the second peak is in September. The area is underlain by the metamorphic rocks of the Basement Complex and are largely undifferentiated, with two specific rock groups namely; the migmatite complex (including banded magmatic and auguen gneisses and pegmatites); and meta-sediments (schist and quartzite, quartzofelspartic rock, calsilicate, meta-conglomerates, amphibolites and metamorphic iron beds [15,16]. The groundwater occurrence is essentially semi-confined – confined, trapped in the fractures of the basement rock [16]. Majorly, agriculture is the main source of livelihood to the people, depending on farming and permanent cropping which includes cultivation and harvesting of cocoa, plantain, palm oil, timber, cassava and kola-nut amongst many others; and rearing of livestock such as cow, goat, sheep, poultry and pigs. The land use can be divided into built up area, rural area and commercial area.

2.1. Sample Collection and Sample Procedure

A total of a hundred and fifty (150) samples were collected from the study area. The selected sampling points consisting of boreholes and hand dug wells covered the northern part, central area and the south western area of the study area. Sampling was carried out quarterly covering the dry and rainy seasons of the annual cycle. Well labeled 2 liters sample bottles, washed with soap, rinsed in clean water and thereafter with the sample water were used to collect water samples, and tightly closed immediately. The samples were transported at low temperature (4°C) to the laboratory for heavy metal analysis of Cadmium, Chromium, Iron, Lead Nickel, and Zinc using standard methods with adequate quality assurance and quality control measures.

3. Methodology

The samples were analyzed with a PG990 Atomic Absorption Spectrophotometer for metals by flame atomization, using air-acetylene flame and single element hollow cathode lamp and following the equipment procedures (Weltz, 1985 and Beaty, 1988).

3.1. Atomic Absorption Spectrophotometry Principle

The Atomic absorption spectrometric technique made use of the flame as the atomizer. The sample solution was aspirated into the flame and the sample element was converted into atomic vapour, the flame thus contains atoms of the element. Some were thermally excited by the flame but most remained in the ground state where they absorbed radiations given off by a special 'source' made from that element. The wavelength of radiation given off by the source was the same as those absorbed by the atoms in the flame. The wavelength for the determination of the elements were 228.8 nm, 357.6 nm, 248.3 nm, 217.0 nm, 232.0 nm, and 213.9 nm for cadmium, chromium, iron, lead, nickel and zinc respectively. This absorption follows Beer-Lambert's law which states that the absorbance is directly proportional to the path length in the flame and to the concentration of atomic vapour in the flame. Both of these variables are difficult to determine but the path length can be held constant and the concentration of atomic vapour in the flame is directly proportional to the concentration of the analyte in the solution being aspirated into the flame. This procedure was used to prepare a calibration curve of concentration in the solution versus absorbance.

3.1.1. Calibration Curve

In preparing the calibration curve for the metals analysis, different concentrations of each metal was prepared from the stock solution (1000 mg/L) for each cation. These were used in preparing a linear curve, passing through zero, for each of the metals.

4. Results and Discussions

The overall pH values ranged from 5.60 to 8.57 pH unit with a mean value of 7.39 ± 0.64. The lowest pH value of 5.6 pH was slightly acidic, while the highest value 8.57 pH was (alkaline) and recorded from boreholes while 5.90 to 8.37 pH unit range was recorded in hand dug wells in the study area (Table 1). The overall range and mean value of electrical conductivity was from 99.40 to 1375 μScm^{-1} and 483.13 ± 219.22 μScm^{-1}. The electrolytic conductivity of borehole water ranged from 99.40 to 1375.00 μScm^{-1} with its mean value as 470.75 ± 38.52 μScm^{-1} On the other hand, the values from hand dug wells ranged from 169.80 to 1230.00 μScm^{-1} with a mean value of 515.82 ± 26.68 μScm^{-1}.The range and mean value concentration of TDS was 66.10 to 920 mgL^{-1} and 327.15 ± 150.25 mgL^{-1} respectively. The overall range and mean values of water samples from HDW were 110.00 to 892.00 mgL^{-1} and 349.94 ± 18.45 mgL^{-1}. Water samples from boreholes ranged from 66.10 to 920.00 mgL^{-1} with a mean value of 306.11 ± 16.08 mgL^{-1}.The overall concentration of iron ranged from 0.20 to 8.43 mgL^{-1} with a mean value of 1.35 ± 1.58 mgL^{-1}(Table 1). The highest concentration value of 8.43 mgL^{-1} occurred in water sample recorded from a borehole source at station 25 (BH25). In HDW source, iron concentration values ranged from 0.22 to 5.15 mgL^{-1} with a mean value of 1.24 ± 0.15 mgL^{-1}Fe (Table 2). The overall zinc concentration in groundwater source ranged from 0.01 to 1.67 mgL^{-1} with a mean value of 0.24 ± 0.02 mgL^{-1} which occurred in HDW at station 15. In borehole water source, the range and mean values were 0.01 to 0.80 mgL^{-1} and 0.23 ± 0.02 mgL^{-1} while the range and mean values in hand dug well source were 0.07 to 1.67 mgL^{-1} and 0.25± 0.03 mgL^{-1} respectively (Table 2). Overall cadmium concentration ranged from 0.00 to 0.03 mgL^{-1} with a mean value of 0.02 ± 0.00 mgL^{-1}. The highest concentration value was recorded in station 23, a hand dug well aquifer type. The overall concentrations of chromium in groundwater source ranged from 0.05 to 0.28 mgl^{-1} with a mean value of 0.15 ± 0.00 mgL^{-1}. The range and mean value of samples from borehole source were 0.05 to 0.28 mgL^{-1} and 0.15 ± 0.00 mgL^{-1} while the values in HDW source ranged from 0.07 to 0.25 mgL^{-1} with mean value of 016 ± 0.00 mgL^{-1}. The range and mean values of lead were 0.00 to 0.21 mgL^{-1} and 0.03 ± 0.00 mgL^{-1} respectively. The overall nickel concentration range and mean values were 0.02 to 0.63 mgL^{-1} and 0.20 ± 0.01mgL^{-1} respectively. The highest concentration value (0.63 mgL^{-1}) was recorded at station 7 from a borehole.

Table 1. Descriptive statistics of the heavy metal parameters of groundwater

Parameters (unit)	N	Minimum	Maximum	Mean	Standard Deviation
Total Heavy Metal parameters					
pH (pH Unit)	150	5.60	8.57	7.39	0.64
Conductivity(μScm^{-1})	150	99.40	1375.00	483.13	219.22
TDS(mgL^{-1})	150	66.10	920.00	327.15	150.25
Iron (mgL^{-1})	150	0.20	8.43	1.35	1.58
Zinc (mgL^{-1})	150	0.01	1.67	0.24	0.20
Cadmium (mgL^{-1})	150	0.00	0.03	0.02	0.01
Chromium(mgL^{-1})	150	0.05	0.28	0.15	0.04
Lead (mgL^{-1})	150	0.00	0.21	0.03	0.04
Nickel (mgL^{-1})	150	0.02	0.63	0.20	0.11

Table 2. Descriptive statistics of the heavy metal parameters of groundwater (boreholes and hand dug wells) quality

Parameters (unit)	N	Minimum	Maximum	Mean	Median	Standard Deviation
Boreholes Heavy Metal parameters						
Iron (mgL^{-1})	78	0.20	8.43	1.45	0.73	1.80
Zinc (mgL^{-1})	78	0.01	0.80	0.23	0.17	0.16
Cadmium (mgL^{-1})	78	0.00	0.03	0.02	0.02	0.01
Chromium (mgL^{-1})	78	0.05	0.28	0.15	0.15	0.05
Lead (mgL^{-1})	78	0.00	0.21	0.02	0.01	0.04
Nickel (mgL^{-1})	78	0.04	0.63	0.21	0.16	0.12
HDW Heavy Metal parameters						
Iron (mgL^{-1})	72	0.22	5.15	1.24	0.56	1.30
Zinc (mgL^{-1})	72	0.07	1.67	0.25	0.18	0.24
Cadmium (mgL^{-1})	72	0.00	0.03	0.02	0.02	0.01
Chromium (mgL^{-1})	72	0.07	0.25	0.16	0.16	0.04
Lead (mgL^{-1})	72	0.00	0.20	0.03	0.01	0.05
Nickel (mgL^{-1})	72	0.02	0.47	0.19	0.15	0.11

4.1. Trace/Heavy Metals of Groundwater Quality

The investigated heavy metals were Iron (Fe), Zinc (Zn), Cadmium (Cd), Chromium (Cr), Lead (Pb) and Nickel (Ni). The order of dominance of trace/heavy metals in water from boreholes in the dry season was Fe > Zn > Ni > Cr > Cd > Pb while the order in the rainy season was Fe > Zn > Ni > Cr > Pb > Cd. Variations in their concentration values over the period of sampling is shown in Figure 3. In water from hand dug wells, the order of dominance in the dry season was Fe > Ni > Zn > Cr > Cd > Pb and in the rainy season the order of dominance was

Fe > Ni > Zn > Cr. Figure 3, show seasonal variation in the mean values of the heavy metal content of sampled groundwater's. The range value for iron (Fe) concentration was 0.20 to 1.94 mgL^{-1} with a mean value of 0.75 ± 0.06 mgL^{-1} in the dry season. The iron value in the rainy season ranged from 0.22 to 8.43 mgL-1 with a mean value of 1.95 ± 0.23 mgL^{-1}. The mean value in the rainy season was higher (1.95 ± 0.23 mgL^{-1}) than the mean value obtained in the dry season (0.74 ± 0.53 mgL^{-1}) and showed a very highly significant difference ($p \leq 0.001$) between the two seasons of the annual cycle. The range and mean value of Zinc in the rainy season for groundwater sources were 0.07 to 1.67 mgL^{-1} and 0.25 ± 0.03 mgL^{-1} respectively and were higher than the range values of 0.01 to 0.51 mgL^{-1} with the mean values of 0.23 ± 0.01 mgL^{-1} obtained in the dry season. The mean values did not show any significant difference ($p \geq 0.05$) over the two seasons of the annual cycle. There was no significant difference ($p \geq 0.05$) between the mean values of the two types of water sources (borehole and hand dug well) too (Table 4). The range values of cadmium during the rainy season was from 0.00 to 0.03 mgL^{-1} with a mean value of 0.01 ± 0.00 mgL^{-1} which was very significantly different ($p \leq 0.001$) from the mean value of 0.02 ± 0.00 mgL^{-1} in the dry season with range values from 0.01 to 0.03 mgL^{-1}. The range and mean values of groundwater for chromium during the rainy season were 0.05 to 0.23 mgL^{-1} and 0.14 ± 0.00 mgL^{-1} respectively, while the value for dry season ranged from 0.09 to 0.28 mgL^{-1} with mean value of 0.16 ± 0.00 mgL$^{-1.}$ The mean value in the dry season was significantly higher than in the rainy season. In waters from migmatite rock type during the dry season, the range was 0.09 to 0.28 mgL^{-1} with mean value of 0.17 ± 0.01 mgL^{-1} while in the rainy season the values were 0.05 to 0.21 mgL^{-1} and 0.15 ± 0.01 mgL^{-1}. Water samples from biotite rock type ranged from 0.10 to 0.17 mgL^{-1} with a mean value of 0.13 ± 0.01 mgL^{-1} during the dry season while in the rainy season, the value ranged from 0.07 to 0.22 mgL^{-1} with a mean value of 0.13 ± 0.02 mgL^{-1}. In the undifferentiated schist aquifer area, water sample ranged from 0.10 to 0.24 mgL^{-1} with its mean value as 0.16 ± 0.01 mgL^{-1} in the dry season while the rainy season range and mean values were 0.06 to 0.23 mgL^{-1} and 0.14 ± 0.01 mgL^{-1} respectively. There was a significant seasonal difference ($p \leq 0.05$) between the mean values, and a significant difference in the mean values of the two water sources. In the rainy season, the range value of Pb was 0.00 to 0.21 mgL^{-1} with a mean value of 0.04 ± 0.00 mgL^{-1} while the dry season range and mean values were 0.01 to 0.03 mgL^{-1} and 0.01 ± 0.00 mgL^{-1} respectively. The highest concentration value of 0.21 mgL^{-1} occurred in migmatite gneiss area at (station BH17) during the rainy season. The mean values for the two seasons were highly significantly different ($p \leq 0.001$). The range and mean values of nickel in groundwater source in the rainy season were 0.02 to 0.63 mgL^{-1} and 0.18 ± 0.01 mgL^{-1} while the corresponding values for the dry season were 0.07 to 0.50 mgL^{-1} and 0.23 ± 0.01 mgL^{-1}respectively. There was a highly significant difference ($p \leq 0.001$) between the mean seasonal values.

4.1.2. Spatial Variation in Heavy Metal Content of Groundwater among the Sampling Station

The mean value of Iron (Fe) was lowest (0.96 ± 0.41 mgL^{-1}) at Station 14HDW from migmatite rock type and highest mean value of 2.13 ± 1.27 mgL^{-1} at Station BH25 from biotite aquifer. Zinc (Zn) had its lowest mean value of 0.16 ± 0.02 mgL^{-1} at Station 10HDW in an undifferentiated schist rock aquifer while its highest value of 0.48 ± 0.24 mgL^{-1} was at Station 15HDW in the migmatite gneiss aquifer. Cadmium (Cd) at Station 12HDW recorded the lowest mean value of 0.01 ± 0.00 mgL^{-1} from migmatite gneiss aquifer and the highest mean value of 0.02 ± 0.00 mgL^{-1} at Station 17BH also a migmatite gneiss rock aquifer. The lowest mean value recorded for Chromium (Cr) was lowest 0.11 ± 0.01 mgL^{-1} at Station 6BH from the biotite aquifer type and the highest value of 0.17 ± 0.01 mgL^{-1} was at Station BH18 in the undifferentiated schist rock type. The mean value of lead (Pb) was lowest 0.01 ± 0.00 mgL^{-1} at Station 12HDW and the highest mean value of 0.05 ± 0.00 mgL^{-1} at Station BH17 both occurred from the migmatite gneiss aquifer. The mean value of Nickel was lowest 0.13 ± 0.02 mgL^{-1} at Station 4HDW in undifferentiated rock type while its highest mean value 0.28 ± 0.07 mgL^{-1} was at Station 25BH from biotite rock type. Figure 3 shows the variation in the heavy metal content of the groundwater samples from the investigated station.

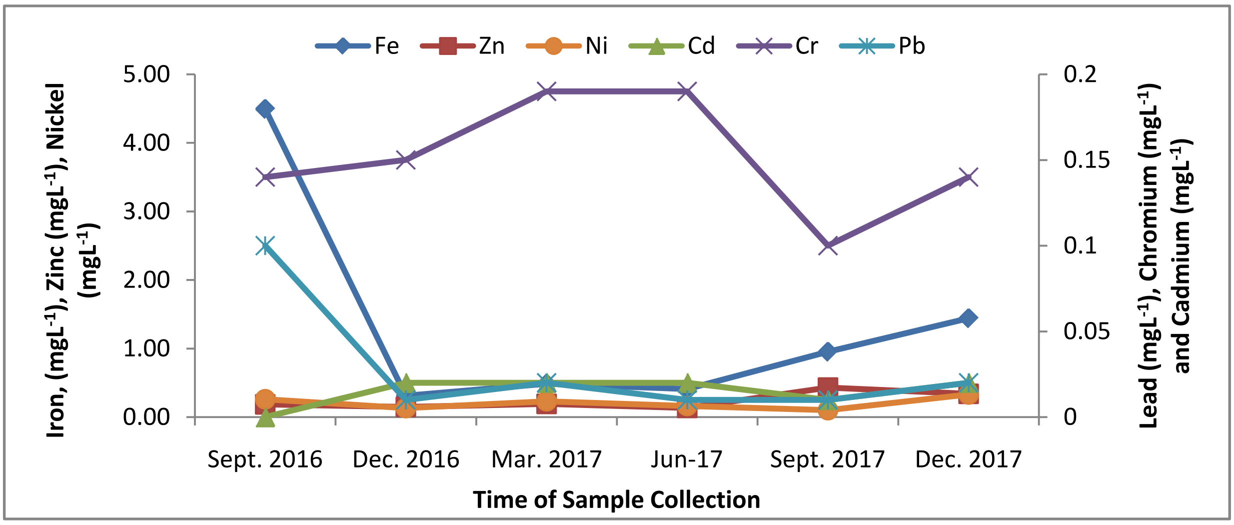

Figure 2. Seasonal variations in the heavy metal parameters of groundwater quality

Table 3. T-test statistics of the seasonal variation in the heavy metal parameters of groundwater quality

Parameters (unit)	N	Seasons		T-Test	
		Dry Season Mean ± S.E	Rainy Season Mean ± S.E	t	P
Heavy Metal parameters					
Iron (mgL^{-1})	75	0.75 ± 0.06	1.95 ± 0.23	5.031	1.395x10^{-6}***
Zinc (mgL^{-1})	75	0.23 ± 0.01	0.25 ± 0.03	0.5909	0.556
Cadmium (mgL^{-1})	75	0.02 ± 0.00	0.01 ± 0.00	5.7456	5.040x10^{-8}***
Chromium (mgL^{-1})	75	0.16 ± 0.00	0.14 ± 0.00	2.5469	0.0012**
Lead (mgL^{-1})	75	0.01 ± 0.00	0.04 ± 0.00	4.3758	2.272x10^{-5}***
Nickel (mgL^{-1})	75	0.23 ± 0.01	0.17 ± 0.01	3.2925	0.001**

N.B:* = Significant difference ($p \leq 0.05$) ** = Highly significant difference ($p \leq 0.01$) *** = Very highly significant difference ($p \leq 0.001$).

Table 4: ANOVA Statistics of the heavy metal Quality of the Different Groundwater Source (Boreholes and Wells)

Parameters	Statistics	Source Type		ANOVA	
		Boreholes (N=78)	Hand Dug Wells(n=72)	F	P
Heavy Metals					
Iron (mg L^{-1})	Range	0.20-8.43	0.22-5.15		
	Mean ± s.d	1.45±1.80	1.24±1.30	0.608	0.437
Zinc (mgL^{-1})	Range	0.01-0.80	0.07-1.67		
	Mean ± s.d	0.23±0.16	0.25±0.24	0.534	0.466
Cadmium (mgL^{-1})	Range	0.00-0.03	0.00-0.03		
	Mean ± s.d	0.02±0.01	0.02±0.01	0.0654	0.799
Chromium (mgL^{-1})	Range	0.05-0.28	0.07-0.25		
	Mean ± s.d	0.15±0.00	0.16±0.04	2.558	0.055
Lead (mgL^{-1})	Range	0.00-0.21	0.00-0.20		
	Mean ± s.d	0.02±0.04	0.03±0.05	0.848	0.359
Nickel (mgL^{-1})	Range	0.04-0.63	0.02-0.47		
	Mean ± s.d	0.20±0.01	0.19±0.11	0.755	0.386

N.B:*= Significant difference ($P \leq 0.05$) ** = highly significant difference ($P \leq 0.01$*** = Very highly significant difference ($P \leq 0.001$).

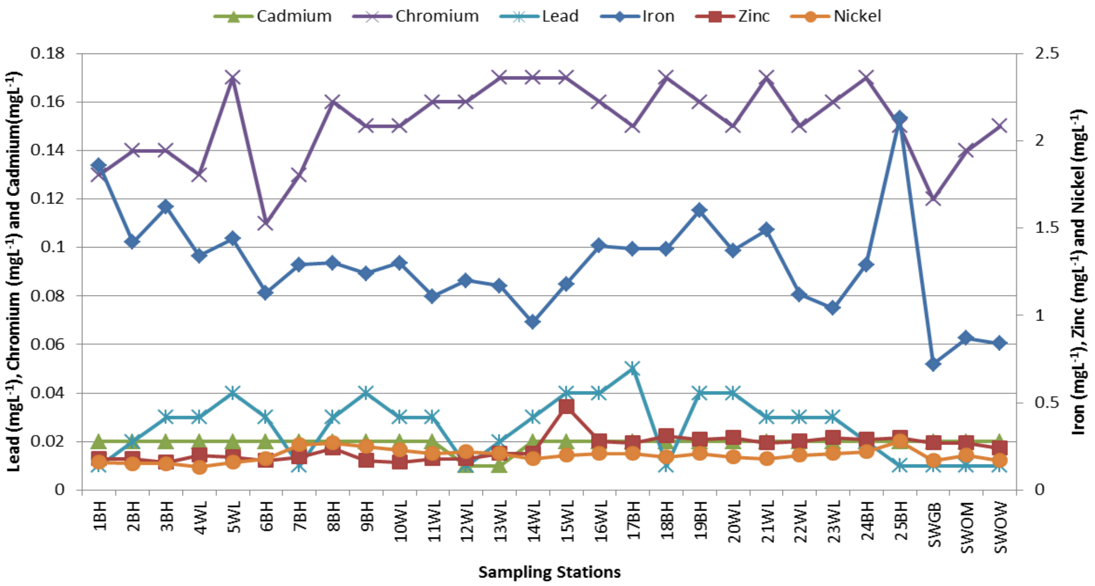

Figure 3. Variation among the trace/heavy metals of groundwater from the investigated sampling stations

Table 5: ANOVA statistics of horizontal variation in the heavy metal parameters of groundwater quality along the major zones

Parameters (unit)	Gbongan (n=66)		Ode-Omu(n=48)		Orile-Owu(n =36)		Anova	
	Range	Mean ±S.E	Range	Mean ±S.E	Range	Mean ±S.E	F	P
Heavy Metal parameters								
Iron (mgL^{-1})	0.22-7.91	1.37±0.20	0.20-6.10	1.28±0.20	0.30-8.43	1.41±0.29	0.069	0.933
Zinc (mgL^{-1})	0.01-0.44	0.18±0.01	0.11-1.67	0.28±0.04	0.09-0.83	0.29±0.04	4.988	0.008 **
Cadmium (mgL^{-1})	0.00-0.03	0.02±0.00	0.00-0.03	0.02±0.00	0.00-0.03	0.02±0.00	0.337	0.714
Chromium (mgL^{-1})	0.05-0.28	0.14±0.01	0.11-0.26	0.16±0.01	0.09-0.25	0.16±0.01	4.310	0.015 *
Lead (mgL^{-1})	0.00-0.18	0.03±0.00	0.00-0.21	0.03±0.01	0.00-0.17	0.03±0.01	0.086	0.918
Nickel (mgL^{-1})	0.02-0.63	0.19±0.01	0.02-0.43	0.20±0.02	0.08-0.50	0.21±0.02	0.259	0.772

N.B: *= Significant difference ($p \leq 0.05$) ** = highly significant difference ($p \leq 0.01$) *** = Very highly significant difference ($p \leq 0.001$).

4.1.3. Variation in Heavy Metal Contents of Groundwater Quality along the Three Zones

The Fe, Zn, Cr, and Ni concentration values of water samples had highest mean values of 1.41 ± 0.29 mgL^{-1} Fe; 0.29 ± 0.04 mgL^{-1} Zn; 0.16 ± 0.01 mgL^{-1} Cr; 0.21 ± 0.02 mgL^{-1} Ni respectively recorded at Orile-owu. The concentrations decreased through Odeomu to Gbongan with lowest concentration mean values of 0.18 ± 0.01 mgL^{-1} for Zn, 0.14 ± 0.01 mgL^{-1} for Cr and 0.19 ± 0.01 mgL^{-1} for Ni respectively, with the exception of Fe, which had the lowest mean value of 1.28 ± 0.20 mgL^{-1} recorded in Ode-omu. Cadmium ion showed comparable concentration values of 0.02 ± 0.00 mgL^{-1} across the three zones while Pb concentration mean values was lowest at Gbongan (0.19 ± 0.01 mgL^{-1}) and highest (0.21 ± 0.01 mgL^{-1}) at Orile-owu (Table 5). Zn and Cr showed significant differences in their mean values across the zones at $p < 0.01$ and $p < 0.05$ while other investigated heavy metals did not ($p > 0.05$).

5. Discussion

The pH overall range values were 5.60 to 8.57 pH unit. This pH range occurred in the rainy season in BH18 obtained from undifferentiated schist aquifer and BH24 was obtained from migmatite rock aquifer. The mean pH value of 7.72 pH unit in the dry season was statistically higher than the 7.02 pH unit in the rainy season. This observation revealed that some values were acidic while others were alkaline in nature. The reason for this could be that the free carbon dioxide from the atmosphere interacts with the rain water as it percolates the groundwater and thus reduces the pH of the water towards acidity [17]. In addition, the corrosive effect that was observed in some of the connecting iron rods used in the boreholes may have also contributed. However, the pH range values in the dry season (6.84 - 8.40) also suggest an alkaline water type. These pH values are similar to what is obtainable from groundwater within other Basement complex areas in Nigeria [18]. Only 11.3% of the values obtained were not within the permissible limit for drinking water. Iron, zinc, and lead mean concentration values were higher in the rainy season than in the dry season while cadmium, chromium and nickel had higher values in the dry season than in the rainy season. All trace metals investigated for showed a very high significant difference ($P \leq 0.001$) between the two seasons with the exception of zinc. High concentration of iron above 0.3 mgL^{-1} indicates that the water is contaminated, 90% of the water samples had values that exceeded the permissible limit recommended by WHO [19] (Table 6). The study further showed that the lower pH values in groundwater held Fe in higher concentrations, thus there was a strong negative relationship between the pH and Fe in groundwater. Zinc was detected in all the water samples at concentrations below the permissible limit for drinking water by WHO. The highest concentration of zinc (0.51mgL^{-1}) may meet up with the daily concentration required for human growth and normal body function, however, too little concentration during growth period can cause damage to epidermal, gastrointestinal, central nervous and reproductive organs [20]. The mean concentration of Cd observed in the two seasons exceeded the permissible limit of the Nigeria standard for drinking water as well as the WHO standard.

Cadmium is not of any nutritional value to man, it is toxic and of adverse health effect even at extremely low concentration, [21]. The high concentration may also be linked with the geology of the parent rock, as cadmium is rich in feldspar minerals [17,22]. Other source could include the possibility of exhaust emission from the diesel powered engine used in oil palm production, which is common place in the study area [23,24,25]. Cadmium intake is detrimental to human health as it causes liver, kidney and bone damage. The mean value of lead was statistically higher in the rainy season than in the dry season while the mean value for nickel was significantly higher in the dry season than the rainy season. Lead concentration values obtained in the dry season exceeded the 0.01mgL^{-1} permissible limit for drinking water by the Nigeria standard and WHO for drinking water. This value further increased in the rainy season, an indication of contamination in the groundwater of the study area. Lead and cadmium are among the inorganic chemicals of major public health concerns by Word Health Organization. These chemicals are regulated in drinking water for their toxicity and classified as a human carcinogen. The high concentration of lead in the study area may be attributed majorly to domestic sources such as coal burning, burning of agricultural waste, vehicular fumes, and fumes from diesel powered plants. Lead has no essential function in the body but rather an adverse effect especially on children [26] as it interferes with a number of body processes and toxic to many organs and tissues, including the central nervous system [27]. The order of heavy metal dominance was Fe> Zn> Ni> Cd> Cr>Pb. According to [28] previous studies have suggested that low coefficient of variation (< 10%) indicates the low degrees of anthropogenic contribution while on the other hand; a high coefficient of variation (90%) indicates a high degree of anthropogenic situation. Therefore, in this present study, the percentage coefficient of variation (% CV) of Fe, Zn, Ni, Cr, Cd, and Pb were 117.18, 84.23, 56.99, 28.79, 47.13 and 152.09 respectively, this implies that most of the heavy metals have been affected by human activities to moderate degrees while Fe, Zn and Cd had high degree of anthropogenic contribution.

Table 6. Comparison of the groundwater sources with standard for drinking water and general uses

Parameter (Unit)		* WHO 2011	**NSDWQ 2007	Range values of samples	% of samples within permissible level
Trace/Heavy metals	Iron Fe^{2+} (mgL^{-1})	0.3	0.3	0.20-8.43	18*
	Zinc (mgL^{-1})	NG	3	0.01-1.67	100*
	Cadmium (mgL^{-1})	0.003	0.003	0.00-0.03	10*
	Cr (mgL^{-1})	0.05	0.05	0.05-0.28	0*
	Lead (mgL^{-1})	0.01	0.01	0.00-0.21	58*
	Nickel (mgL^{-1})	0.07	0.02	0.02-0.63	9*

6. Conclusion

Maintaining the purity of water for the purpose of dinking and other uses is not only limited to regular monitoring of its physico-chemical constituents or microbiological characteristics but also its heavy metal contents should be of concern. In the present study, the heavy metal concentrations were found to be higher than the Nigeria and WHO standards for drinking water. However, the toxic heavy metal levels suggest a significant health risk given the toxicity of theses metals hence the water is unfit for the inhabitants of the areas.

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