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ResearAch Paper

Groundwater Pollution Assessment for drinking water in Osogbo Area, Southwestern Nigeria using hydrogeochemistry approach.

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ABSTRACT
Assessment of drinking water for pollution was carried out on groundwater samples in Osogbo area southwestern Nigeria to assess the status of pollution, types of pollutants present and mechanisms responsible for the evolution of the chemical composition of the groundwater in the study area. Twenty water samples collected in clean 2 litres plastic bottles for analyses at Iwaloye chemical laboratory. Hydrogeochemical properties analyzed for in each samples includes: EC, pH, TDS, total hardness, Na^{2+}, Mg^{2+}, Ca^{2+}, K^{2+}, PO_4^{3-}, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, As^{3+} , Pb^{2+}, Fe^{2+}, Zn^{2+}, Ba^{2+}, Cr^{6+}. Results showed that Na^{2+} ranged from 0.073 - 0.86 mg/L, Mg^{2+} from 3.30 - 21.70 mg/L, Ca^{2+} from 4.40 - 16.80 mg/L, PO_4^{3-} from 0.002 -1.560 mg/L, HCO_3^- from 2.20 - 34.80 mg/L, SO_4^{2-} from 0.004 - 89.67 mg/L, Cl^- from 10.80 - 78.30 mg/L, NO_3^- from 0.000 - 0.67mg/L, Zn^{2+} from 0.27 - 8.96 mg/L , Fe^{2+} from 0.002 - 1.45 mg/L, As^{3+} from 0.000 - 0.078 mg/L, Pb^{2+} from 0.000 - 0.460 mg/L, Ba^{2+} from 0.000-0.091 mg/L, Cr^{6+} 0.110 - 8.39 mg/L. Water samples in the study area were polluted by chromium, lead, arsenic, iron and zinc. The piper trilinear diagram shows that groundwater hydrogeochemical facies was Na–Mg-HCO3 type. Gibbs diagram shows that dissolved constituents were due to water – rock interaction. In conclusion, since the groundwater have been polluted therefore they should be discarded or treated before use

KEYWORDS: *Pollution, water samples, heavy metals, Nigeria*

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I. INTRODUCTION

A clean an unpolluted source of water supply is essential for high quality of life. Groundwater is a major source of water for both domestic and industrial uses in Nigeria mostly because it is believed to be clean, potable and safer than surface water due to the protective qualities of the soil cover. It has become an indispensable source of drinking water worldwide and especially in developing countries. Groundwater has been considered a vital source of water supply for about one third of the world's population [1] . Groundwater sources have become the preferred means of supplying water to meet the growing demand of the rural and dispersed communities and small urban towns in Nigeria. Generally, the chemical and microbiological quality of groundwater needed to be assessed at interval to avoid pollution. Groundwater supply is usually less expensive to develop than surface water and it is more easily expanded at a future date by simply adding new boreholes [2]. Compared to surface water, groundwater responds more slowly to climate change thereby making it less vulnerable to drought conditions. The high dependence on groundwater stem from the thought that is free from pollution found in surface waters and for this reason, groundwater resource development is the most feasible way forward to meeting the potable drinking water needs in the study area. [3] Noted that groundwater resources as the solution to rural water supply systems is because drought and hot weather condition pose risks for farmers. Hydrogeochemistry is important tool to assess the groundwater pollution in any area in which the groundwater is used for both irrigation and drinking purposes [4]. In view of this, groundwater in Osogbo area were subjected to pollution studies to assess their potability and various dissolved constituents present in them. The international standards for drinking water by WHO was used as guidelines in providing guidance on hazard identification and risk assessment of water samples in the study area. However, groundwater may be susceptible to a variety of pollutants thereby altering the quality and permissible standard resulting in great threat to human health. Water quality can be affected by anthropogenic activities, which may cause the release of harmful materials like hydrocarbon, septic wastes, effluent water, landfills leachates and other industrial wastes that have harmful effects on human health. Researchers that have carried out investigation on water quality includes [5], [6], [7], [8], [9] [10], [11], [12, [13]. They concluded that sometime dissolved constituents are found in higher concentration in groundwater than surface water and may result into pollution

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II. LOCATION, PHYSIOGRAPHY AND GEOLOGY OF THE STUDY AREA

Osogbo the study area is the capital territory of Osun State, Southwestern Nigeria and is situated between latitude 7°46' N and 7°50' N of the Equator and longitude 4°28' E and 4°36' E of the Greenwich Meridian. The area has an elevation of 320m above sea level by its tropical location. The people of Osogbo largely depend on groundwater for their domestic and industrial uses.

The study area falls within the tropical region which is characterized by alternating wet and dry seasons. The dry season comes up between November and March while the wet season depicted by heavy rainfall falls between April and October. The vegetation of the area comprises dominantly of lowland tropical rain forest which encourages agricultural activities in the area due to fertile soil. Drainage and relief of the area is as a result of the geomorphological processes that have shaped the area and are controlled largely by the compositions of bedrock and the structures found on them. The area is a low land area with flat lying outcrops and undulating little hills with an elevation of about 320m above sea level. The general drainage pattern in the area is dendritic.

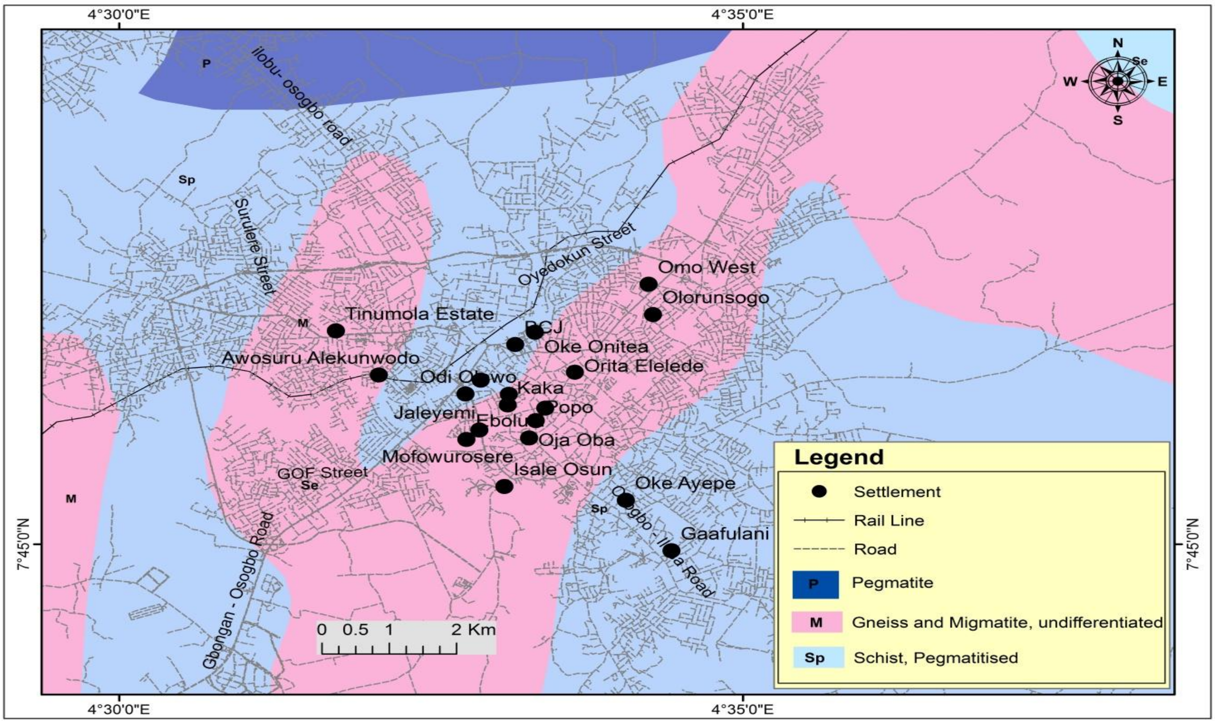

Figure 1.1 Geological maps of Osogbo showing the sample locations
(Source: Department of Geography, Obafemi Awolowo University, Ile-Ife)

The study area is underlain by the Pre – Cambrian Basement complex rocks which outcrop in various places. Rock types includes migmatites, undifferentiated gneiss, schists, associated with quartzite ridges and pegmatites ([14] [15], [16]. The structural features found on rocks include foliation, lineation, folds, faults and joints due to regional metamorphism and deformation during several cycles of orogeny.

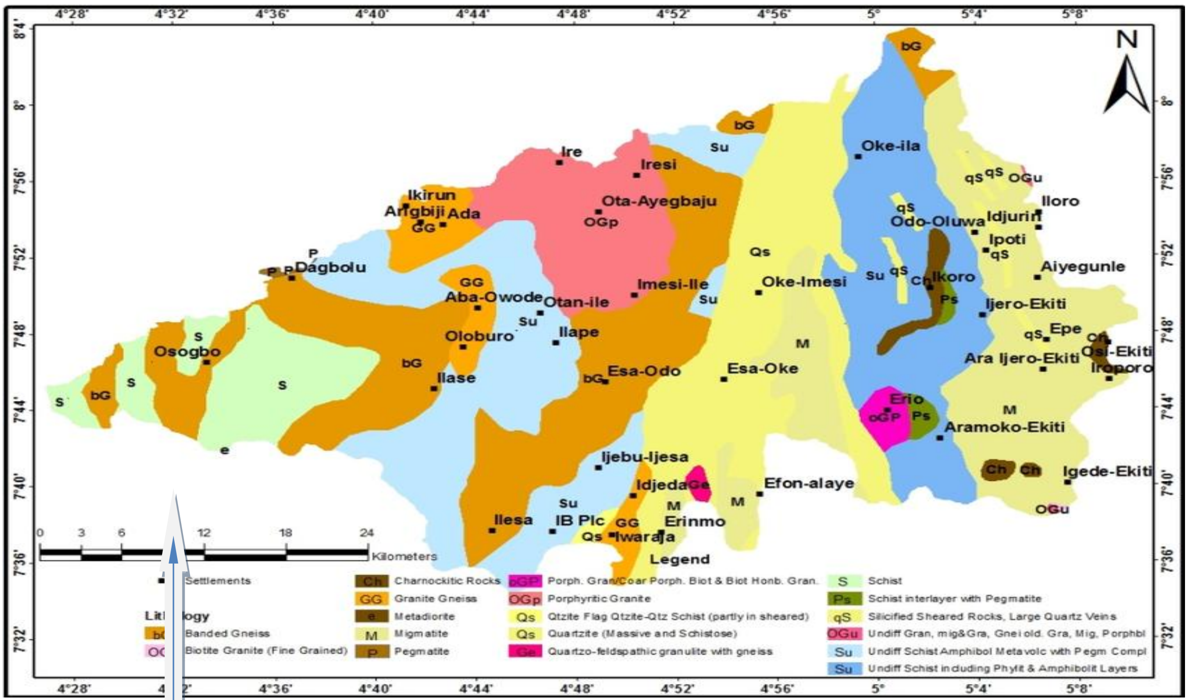

Figure 2.2 Geological Map of Osun State showing the study area (NGSA-2006).

III. MATERIALS AND METHODS

Twenty water samples from 14 boreholes and 6 hand-dug wells were collected in clean 2 litre plastic bottles with cap stoppers aimed at preventing contamination. These bottles were thoroughly washed and rinsed before samples were collected. Water samples from boreholes were taken after water was allowed to run for some minutes to ensure a good representative sample. Samples were refrigerated before analysis at Iwaloye water laboratory in Ibadan. Physical parameters like pH, electrical conductivity and total dissolved solids were measured onsite. Chemical parameters analyzed in the laboratory include total hardness, bicarbonate, calcium, magnesium, chloride, potassium, sodium, lead, sulphate, phosphate, arsenic, barium. Heavy metals concentration were determined by AAS, potassium and sodium by flame photometry and anions by titration using established standard of [17]. Total hardness of the groundwater was calculated as suggested by [18].

IV. RESULTS AND DISCUSSION

The results of physical and chemical parameters of the groundwater from boreholes and hand dug wells in the study area are presented in Table 1. Comparison with World Health Organization (,[19], [20]) Guidelines for drinking water as shown in Table 2.

Table 1: Summary of Physical and Chemical parameters in the study area

Loc. No	Sample Type	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Zn^{2+}	Fe	Pb^{2+}	Cr^{+}	Ba^{2+}	Cl^{-}	As^{2+}	$HCO3^{-}$	CO3
1	BH	5.20	3.80	0.08	0.13	0.31	0.00	0.00	0.45	0.00	12.70	0.00	2.70	0.02
2	HDW	8.70	10.60	0.35	0.67	2.32	0.06	0.01	2.65	0.03	51.80	0.02	9.70	0.41
3	BH	7.60	21.70	0.34	0.66	2.26	0.06	0.47	8.39	0.09	50.20	0.08	34.80	0.45
4	BH	5.30	5.20	0.09	0.13	0.33	0.00	0.00	0.15	0.00	12.70	0.00	2.80	0.03
5	BH	6.30	4.50	0.09	0.13	0.42	0.00	0.00	0.57	0.00	13.60	0.00	3.40	0.03
6	BH	6.10	9.50	0.11	0.21	1.08	0.01	0.02	2.67	0.03	23.40	0.02	10.20	0.24
7	HDW	8.30	14.50	0.24	0.39	1.35	0.02	0.29	6.78	0.06	39.60	0.04	23.60	0.34
8	BH	4.70	3.30	0.08	0.12	0.29	0.00	0.00	0.18	0.00	11.20	0.00	2.50	0.02
9	BH	7.30	8.40	0.24	0.38	1.23	0.02	0.01	2.36	0.02	38.60	0.01	7.60	O.28
10	BH	5.40	7.50	0.07	0.12	0.32	0.00	0.00	0.43	0.00	10.80	0.00	8.20	0.02
11	BH	4.90	3.70	0.08	0.12	0.27	0.00	0.01	0.51	0.00	11.50	0.00	2.90	0.02
12	HDW	16.80	12.40	0.52	0.87	8.96	1.45	0.03	2.89	0.05	78.30	0.03	16.30	0.76
13	BH	4.90	4.10	0.08	0.13	0.31	0.01	0.00	0.11	0.00	11.60	0.00	2.20	0.01
14	BH	4.40	8.60	0.86	0.13	0.33	0.01	0.01	0.52	0.00	12.70	0.00	10.40	0.03
15	BH	6.10	6.10	0.08	0.13	0.34	0.00	0.02	0.96	0.02	13.20	0.02	8.90	0.04
16	BH	5.60	6.80	0.08	0.12	0.35	0.01	0.00	0.24	0.00	11.5	0.00	7.50	0.02
17	HDW	5.60	4.60	0.08	0.13	0.36	0.01	0.00	0.24	0.00	13.2	0.00	3.20	0.02
18	HDW	5.70	5.70	0.09	0.09	0.12	0.01	0.02	0.82	0.01	13.4	0.02	7.80	0.04
19	HDW	5.80	4.20	0.08	0.08	0.39	0.00	0.01	0.63	0.01	12.8	0.00	3.60	0.03
20	BH	5.30	7.9	0.83	0.127	0.29	0.009	0.00	0.33	0.00	11.8	0.00	8.70	0.02

Loc No	Loc Name	Sample Type	SO_4^{2-}	PO_4	NO_3^-	pH	EC	TH	TDS
1	Oke-Ayepe	BH	0.01	0.00	0.00	7.02	55.70	9.80	64.40
2	Isale-Osun	HDW	54.31	0.09	0.05	6.89	87.60	15.60	94.20
3	Gaafulani	BH	53.67	0.09	0.67	6.85	85.70	13.80	92.30
4	Popo	BH	0.01	0.00	0.00	7.08	54.60	9.70	62.80
5	BCJ	BH	0.01	0.01	0.00	7.06	57.30	10.20	65.10
6	Oke-Onitea	BH	3.36	0.01	0.05	7.08	67.10	11.30	74.80
7	Tinumola Est	HDW	26.45	0.07	0.28	7.11	75.60	15.40	84.30
8	Awosuru Alekuwodo	BH	0.01	0.00	0.00	6.85	52.70	8.10	60.90
9	Mofowurosere Street	BH	23.45	0.06	0.04	7.13	73.40	13.40	81.30
10	Oja-Oba	BH	0.00	0.00	0.00	7.02	51.80	7.90	59.20
11	Ebolubi Owoope	BH	0.00	0.00	0.00	6.89	53.60	8.30	61.80
12	Kolabalogun	HDW	89.67	1.56	0.07	7.24	96.70	25.70	111.20
13	Omo-West	BH	0.01	0.01	0.00	6.87	52.50	7.80	61.20
14	Orita Elelede	BH	0.01	0.01	0.00	7.05	53.70	7.70	58.80
15	Balogun Agoro	BH	0.01	0.00	0.01	7.02	57.10	9.80	64.60
16	Fagbewesa	BH	0.01	0.01	0.00	6.98	51.50	8.30	58.70
17	Odiolowo	HDW	0.01	0.01	0.00	7.00	55.30	9.40	62.50
18	Jaleyemi	HDW	0.01	0.01	0.01	6.970	56.40	10.30	63.70
19	Araromi Ave	HDW	0.01	0.01	0.00	7.05	56.50	9.70	63.60
20	Kaka	BH	0.00	0.01	0.00	7.03	52.90	8.10	59.20

Table 2: Physico-Chemical analysis of groundwater of the study area and WHO Standard

Parameter	Minimum	Maximum	Mean	**SD**	**WHO (2011& 2017)**
Ca^{2+}	4.40	16.80	6.50	2.69	20
Mg^{2+}	3.30	21.70	7.66	4.51	20
Na^{2+}	0.07	0.86	0.22	0.25	20
K^{+}	0.12	0.87	0.25	0.23	50
Fe^{2+}	0.00	1.45	0.09	0.32	0.30
Pb^{2+}	0.00	0.46	0.04	0.12	0.01
Cr^{6+}	0.11	8.39	1.59	2.26	0.05
Ba^{2+}	0.00	0.09	0.02	0.03	1.30
As^{3+}	0.00	0.08	0.01	0.02	0.01
Zn^{2+}	0.27	8.96	1.09	1.96	3-5
Cl^{-}	10.80	78.30	22.73	18.85	250
NO_3^{-}	0.00	0.67	0.06	0.16	50
HCO_3^{2-}	2.20	34.80	8.85	8.08	200
CO_3	0.00	0.76	0.14	0.21	-
SO_4^{2-}	0.00	89.67	12.55	25.11	400
PO_4^{3-}	0.00	1.56	0.10	0.346	-
pH	6.85	7.24	7.01	0.10	6.5-8.5
TDS	58.70	111.20	70.23	14.72	1000
EC	51.50	96.70	62.39	13.80	1000
Total Hardness	7.70	25.70	11.02	4.25	500

4.1 pH: is a measure of degree of acidity and alkalinity of water. The pH scale runs from 0 - 14. Water having a pH between 1 and 6 is considered to be acidic, 7 as neutral and above 7 as alkaline. The pH of the water sample in the study area ranged between 6.85 and 7.24. The mean value was 7.0 with standard deviation of 0.1. The pH of the water samples here is within the [20] drinking water standard of 6.5- 8.5.
4.2 Electrical Conductivity: Electrical conductivity in water is as a result of ion dissolving in water. The EC ranged from 51.5 to 96.7 µs/cm with the mean values of 62.4 µs/cm and standard deviation of 13.8 µs/cm. These values are within [19], [20] drinking water standard of 1000 µs/cm. The low electrical conductivity values make the water suitable for irrigation. Conductivity value less than 200 µs/cm are permissible for irrigation [21].
4.3 TOTAL DISSOLVED SOLID (TDS): TDS values ranged between 58.7 and 111.2 mg/L with mean value of 70.2 mg/L and standard deviation of 14.7 mg/L. [19] standard is 1000 mg/L, indicating that the water is fresh [22] .
4.4 TOTAL HANDNESS (TH): may be due to high mineral contents of magnesium (Mg^{2+}) and calcium (Ca^{2+}). Here value ranged from 7.7 mg/L to 25.7 mg/L. The mean value of the samples was 11.0 mg/L and standard deviation was 4.2 mg/L. This is within the [19] drinking water standard of 500 mg/L.
4.5 IRON (Fe^{2+}): The common form of iron in water is the soluble ferrous ion (Fe^{2+}). The minimum iron present was 0.002 mg/L while maximum was 1.45 mg/L. The mean value was 0.085 mg/L and the standard deviation was 0.322 mg/L. The WHO recommended maximum iron concentration for drinking water is 0.3 mg/L. The values of iron in location 12, Kolabalogun exceeds acceptable drinking limits, therefore people living in this area may suffer from laundry staining and unpleasant taste
4.6 CALCIUM (Ca^{2+}): This is a mineral that is highly essential for bone and teeth strengthening. The value of calcium in the study area has a minimum concentration of 4.4 mg/L and maximum of 16.8 mg/L. The mean value was 6.5 mg/L while the standard deviation was 2.7 mg/L. The calcium contents of the water in the study area is far below the WHO limit of 200 mg/L.
4.7 MAGNESIUM (Mg^{2+}): The minimum concentration of magnesium ion in the study area was 3.3 mg/L and 21.7 mg/L as the maximal value. The mean is approximately 7.7 mg/L with a standard deviation of 4.5 mg/L. High concentration of magnesium intake can lead to gastrointestinal, liver or kidney damage.
4.8 SULPHATE (SO_4^{2-}): The value of sulphate ion in the study area has minimum value of 0.004 mg/L and maximum value as 89.7 mg/L. The mean value was 12.6 mg/L and standard deviation was 25.1 mg/L. The low concentration of sulphate ion in water is an indication of absence of salt water intrusion in the area. These values are low when compared to WHO limit of 250 mg/L for drinking water. Concentrations above 250 mg/L may have a laxative effect. Based on the results, the samples are potable and will not cause health hazard.
4.9 SODIUM (Na^{+}): The value of sodium ion in the study area ranged from 0.073 mg/L to 0.860 mg/L. The mean was 0.223 mg/L while standard deviation was 0.246 mg/L. However, the concentration of sodium ion in the study area is relatively low when compared to [19]. [20] limit of 200 mg/L. The sodium concentration is important in classifying irrigation water because it reacts with soil to reduce permeability. Sodium saturated soils support little or no plant growth. The primary source of sodium in groundwater is due weathering of plagioclase feldspar [22] .
4.10 CHLORIDE (Cl^{-}): The value of chloride ion ranged from 10.8 mg/L to 78.3 mg/L. The mean value for chloride content in the study area is 22.7 mg/L with standard deviation of 18.8 mg/L. However, the concentration of chloride ion in the study area is relatively low when compared to [20] limit of 250 mg/L for

drinking water. The low concentration is an indication of absence of salt water intrusion in the study area. Chloride in excess of 100 mg/L gives a salty taste to water. High concentration of chloride results in hypertension.

4.11 NITRATE (NO_3^{2-}): Nitrate concentration ranged from 0.00 mg/L to 0.67 mg/L. The mean value was 0.059 mg/L and standard deviation as 0.157 mg/L. However, nitrate level in water samples from the study area is relatively low when compared [20] limit of 50 mg/L for drinking water. The low concentration is an indication of absence of salt water instruction in the study area. Infants below six months, who drink water containing nitrate in excess of 10 mg/L will suffer from blue baby disease/methaemoglobianemia.

4.12 POTASSIUM (K^+): The value of potassium ion in the study area ranged from 0.118 mg/L to 0.867 mg/L and the mean value of 0.25 mg/L with standard deviation of 0.23 mg/L and this is low to [20] limit of 50 mg/L. The potassium concentration is important in classifying irrigation water because it reacts with soil to reduce permeability. Potassium saturated soils support little or no plant growth.

4.13 PHOSPHATE (PO_4^{3-}): This ranged between 0.002 mg/L and 1.56 mg/L. The mean was 0.098 mg/L and standard deviation was 0.35 mg/L.

4.14 LEAD (Pb^{2+}): The value of lead was between 0.00 mg/L and 0.46 mg/L. The mean value was 0.04 mg/L and standard deviation was 0.12 mg/L. Water samples in areas like Gaafulani with lead concentration of 0.46 mg/L, Tinumola Estate with lead concentration of 0.29 mg/L and Kolabalogun having lead concentration as 0.34 mg/L exceeds that of the acceptable standard for drinking water thereby causing public health hazard making water samples unsuitable for drinking. Lead can occur naturally, or result from industrial contamination, or be leached from lead pipes in some water systems. Lead is a cumulative poison which is highly difficult to distinguish in its early stages from minor illness. Early reversible symptoms include abdominal pains, decreased appetite, constipation, fatigue, sleep disturbance, and decreased physical fitness. Long term exposure to lead may cause kidney damage, anaemia, and nerve damage including brain damage and finally death.

4.15 BICARBONATE (HCO_3^-): Bicarbonate ion in the study area has the minimum concentration of 2.2 mg/L and maximum as 34.8 mg/L. The mean value was 8.85 mg/L and standard deviation was 8.08 mg/L. Bicarbonate higher than 200 mg/L in drinking water when ingested may cause severe illnesses.

4.16 CHROMIUM (Cr^{6+}): The value of chromium ion in the study area ranged from 0.11 mg/L to 8.39 mg/L. The mean value was 1.59 mg/L with the standard deviation of 2.26 mg/L. The recommended drinking water limits for chromium is 0.05 mg/L (WHO, 2011& 2017). In the study area level of chromium concentration is higher than the recommended limit in all the water samples, indicating that the water here are polluted by chromium. Chromium is known to produce lung tumours when inhaled.

4. 17 BARIUM (Ba^{2+}): Barium has the minimum value of 0.00 mg/L and maximum value as 0.09 mg/L. The mean value for the ion was 0.016 mg/L and has standard deviation of 0.025 mg/L. WHO limits for barium is 1.3 mg/L. High levels of barium can have severe toxic effects on the heart, blood vessels, and nerves.

4.18 ZINC (Zn^{2+}): The level of zinc concentration in the study area ranged from 0.27 mg/L to 8.9 mg/L. The mean was 1.09 mg/L and standard deviation as 1.95 mg/L. The WHO standard is 5 mg/L. It was observed that the zinc concentration in location 12 (Kolabalogun) is greater than acceptable drinking limits. High concentration of zinc in the water can lead to different illnesses like nausea, cramps, diarrhoea, and associated headaches.

4.19 CARBONATE (CO_3^{2-})

The minimum value of carbonate is 0.0014 mg/L while the maximum is 0.760 mg/L. the mean value for carbonate ion in the water samples is 0.141 Mg/L and standard deviation is 0.207 mg/L.

4.20 ARSENIC (As^{3+}): Concentration of arsenic in the study area ranged from 0.00 mg/l to 0.078 mg/L. The mean value was 0.012 mg/L and standard deviation as 0.019 mg/L. The WHO guideline for drinking water has a standard of 0.05 Mg/L. The concentration of arsenic ion in the water samples in some of the study area all fall below the standard proportion for drinking water thereby making them suitable for drinking. Meanwhile, Gaafulani, Tinumola Estate, Kolabalogun and Balogun Agoro has the high concentration of arsenic of (0.078 mg/L), (0.042 mg/L), (0.028 mg/L), (0.023 mg/L) respectively and these are higher than the drinking limits of 0.05 mg/L for arsenic. Arsenic is responsible for black foot diseases when ingested at concentration higher than 0.05 mg/L.

4.2: PIPER'S DIAGRAM: This diagram [23] consists of three distinct fields including two triangular fields and a diamond-shaped field. The cations expressed as percentage of total cations in meq/l as a single point on the left triangle while anions plot in the right triangle. Each point is then projected into the upper field along a line parallel to the upper margin of the field and the point where the extension intersects indicates the character of the water. From the tri linear plot (Figure 3) water type in the study are is Na – Mg HCO_3

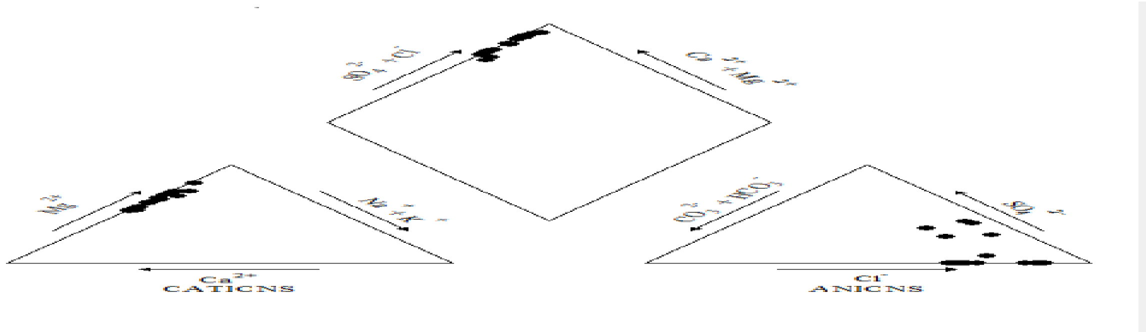

Figure 3: Piper's diagrams in the study area

4.3: GIBBS DIAGRAMS: Gibbs [24] diagram is widely used to establish the relationship of water composition and aquifer lithological characteristics. Three distinct fields such as precipitation, evaporation and rock dominance are shown in the Gibbs diagram. Gibbs diagrams were plotted for cations and anions respectively as shown in Figures 4 and 5 respectively. Here water chemistry indicates influence of geologic formation that served as aquifers for groundwater as a result of water – rock interaction.

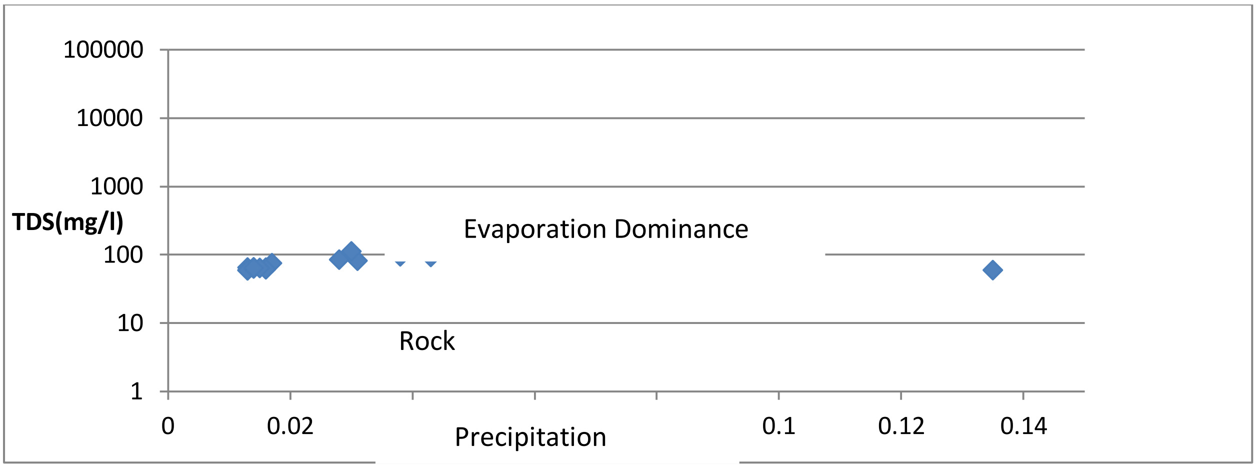

Figure 4: Gibbs diagrams for cations in the study area

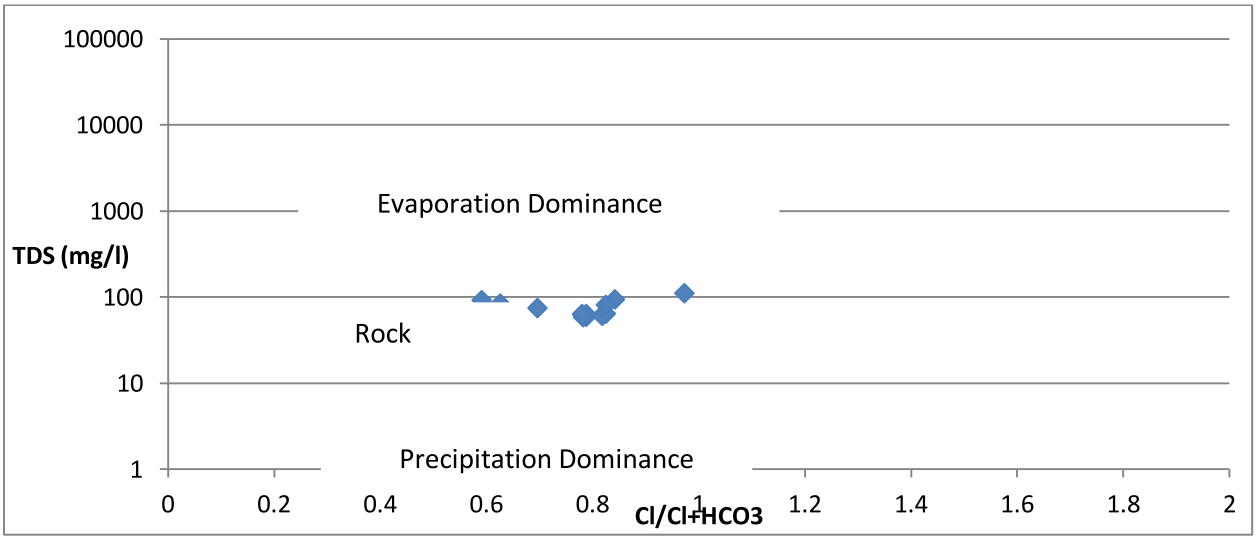

Figure 5: Gibbs diagrams for aions in the study area

4.4 Pie chart: the pie chart of the major ions are presented in Figure 6 bellow. Chloride has the highest mean concentration value, while sodium has the lowest mean value. This water is dominated by magnesium chloride salts.

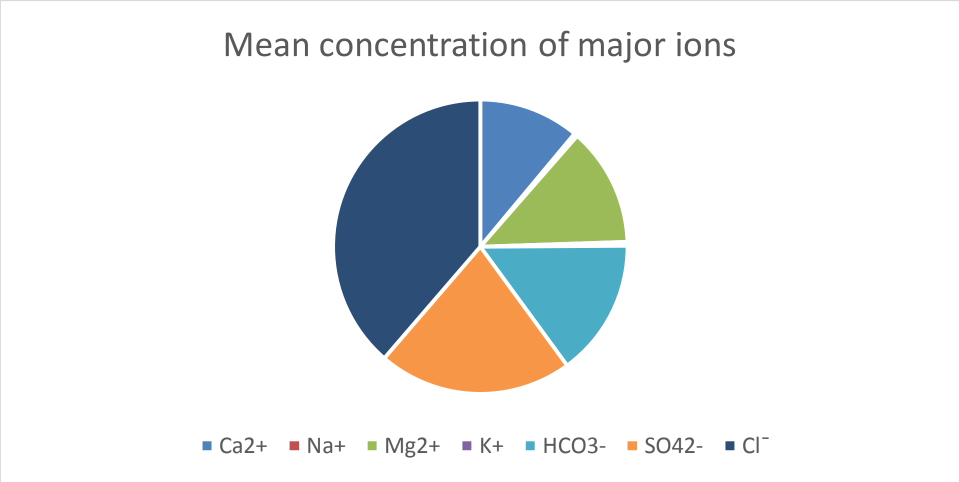

Figure 6: Pie chart of major ions

V. CONCLUSION

From the Gibbs diagrams, the chemistry of the groundwater is strongly dependent on the geology of the area. The geological and climatic factors have influenced either directly or indirectly on the type and content of the chemical constituents of the water in the study area as well as their distribution. However, the chemistry of rain which is the primary source of groundwater changes as it passes through the geologic formation. From the Piper's diagram water type in the study area is Na - Mg-HCO_3 type; this may due to dissolution of some minerals from granite and gneissic rocks. Water in the areas is slightly acidic to alkaline in nature.. Groundwater in the study area are not potable because they were polluted by chromium, iron, lead, zinc and arsenic at harmful level. The source of pollution was caused by the presence of these heavy metals in the bedrock that served as aquifers for groundwater as a result of water – rock interaction. It is therefore recommended that groundwater in the study area should be discarded or be treated before consumption.

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