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RESEARCH ARTICLE

HYDROGEOCHEMICAL CHARACTERIZATION AND GROUNDWATER QUALITY APPRAISAL IN OKITIPUPA AND ENVIRONS, NIGERIA

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ABSTRACT

The objectives of study was to determine hydrochemistry of groundwater in Okitipupa and environs to assess the quality of groundwater for drinking, domestic and irrigation. A total of 27 groundwater samples were collected randomly from different sources and analyzed for major cations and anions. The domination of cations and anions was in the order of K>Na>Ca>Mg and SO4>Cl >HCO3>NO3. The hydrogeochemical facies indicate three dominant facies: non-carbonate hardness exceeds 50 %; non-carbonate alkali exceeds 50 %; and transition zone with no one cation-anion pair exceeds 50 %, while precipitation is the dominant process in the hydrogeochemical evolution of the groundwater samples. The WQI calculated exhibits good (60 %) and poor (40 %) quality water for drinking and domestic purposes. For irrigation assessment, residual sodium carbonate values revealed good irrigation, permeability index values indicates suitable and marginal class, sodium absorption ratio, Kelly ratio, and %Na indicate good irrigation water. The processes controlling the groundwater chemistry are mixing of saline with fresh water and anthropogenic contamination; weathering and cation exchange; mineral precipitation/anthropogenic pollution; and groundwater dilution and mineral dissolution. Consequently the water is fairly suitable for drinking/domestic, and good for irrigation purposes.

KEYWORDS

Hydrochemical indices, Geogenic origin, Principal component analysis, Toxic metals, Environmental pollution.

1. INTRODUCTION

Water is one of the most important resources of the earth and it's vital for the existence of life (Fetter, 1980). It has a critical function in all spheres of life. Water, which exists as surface (river, stream, lakes, seas, and oceans), groundwater (soil water, spring, artesian, etc.) and rainwater, can be utilized in several ways; generation of electricity, navigational, agricultural, commercial, and domestic purposes. Equally, groundwater is used for sanitation and domestic purposes. Groundwater usually occupies geological formations, fissures and joints in hard rocks, solution cavities, and channels in limestone are examples of void within the masses of rocks and sediments (Freeze and Cherry, 1979). However pollution of groundwater from the source can lead to lack of safe drinking or irrigation water, which consequently can lead to diseases such as cholera, typhoid, malaria, diarrhea etc.

In most urbanized cities in Nigeria, the expectation of the citizenry from the government is to provide adequate water supply devoid of contamination, as part of its social responsibilities. Most often this responsibility is not adequately discharged causing the inhabitants to look elsewhere to meet this special need. This has consequently lead to sinking or construction of boreholes and shallow water wells in any place (in most places closer to septic tanks), irrespective of the yield of such water well. Many times water generated through this "hurry" process are usually pumped out and consumed "raw" without any form of treatment. Although in recent types break down of water borne diseases in many parts of Nigeria have not been critically investigated or linked with indiscriminate sinking of boreholes, which of recent, has become rampart.

In the Okitipupa area part of Ondo State, Nigeria, the population density of the area is increasing geometrically annually due to rapid government infrastructural intervention by provision of good roads, health care facilities, provision of higher school of learning etc. This has attracted a lot of people into the area and also increase indiscriminate siting of boreholes without government restrictions. In most cases, the boreholes are located too close or downstream of latrines or soak away pits belonging to adjoining buildings or very close to municipal and industrial waste dump sites. Hence the quality of water from these boreholes may not be guaranteed except through comprehensive quality water analysis.

Recent studies have confirmed the usefulness of carrying out groundwater quality assessment for domestic, drinking, industrial, and irrigation uses using water quality index, irrigation indices, and multivariate analysis (Singh et al., 2004; Singh et al., 2009; Mohapatra et al., 2011). This has

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helped in providing insight into hydrochemical processes influencing the water quality, identification critical water quality issues and possible sources of pollution or polluting processes interaction of groundwater mixing (Ruiz et al., 1990; Jayakumar and Siraz, 1997; Papatheodorou et al., 2007; Baez-Cazull et al., 2008; Machado et al., 2008; Singh et al., 2005; Kumar and Riyazuddin, 2008; Sargaonkar et al., 2008; Rao et al., 2010; Reghunath et al., 2002). Therefore, in this study, the groundwater quality of Okitipupa and environs was evaluated from various boreholes/water wells to understand the hydro-geochemistry of the aquifers with special attention to the physicochemical, bacteriological, toxic/heavy mineral parameters. In addition, its suitability for domestic and irrigation purposes was also evaluated on the basis of data from 27 hand pump/boreholes/dug wells, using water quality indices, irrigation indices analysis, and principal component statistical analysis.

2. Material and Methods

2.1 Description of Study Area

The study location, Okitipupa and environ is one of the major cities in Ondo State, southwestern Nigeria. It is located between latitudes 704000 to 734000mN and longitudes 682000 to 712000mE (Figure 1). The town lies within the tropical rain forest zone of West Africa. The climate is humid and semi-hot equatorial type. The city usually experiences heavy rainfall, with an average annual rainfall of 2000-2500 mm/yr (Iloje, 1981). particularly during the rainy seasons (April – October). The superficial rainfall distribution is bimodal, with peaks in July and September and a two weeks break in August. The rainy season begins in March and lasts till October or early November. The higher annual rainfall depths and rainfall days encourages large volumes of runoff. Relative humidity alternates between 75% and 90% during the dry and rainy seasons.

Okitipupa area is underlain by the sedimentary rocks of southwestern Nigeria. The zone constitutes the easternmost segment of the extensive Dahomey basin. The area regionally gently undulating southward; topographic elevations vary from 120 m above the mean sea level in the northern part, with gradual slope to a near sea level swamp flat in the coastal area to south (Figure 2). The area is drained by many perennial streams and rivers among which are Ominla, Oluwa, Akeun, Ufara and Oni, while the southern part is particularly characterized by lagoons, coastal creeks, canals and several tributaries to the extensive river Oluwa. The annual temperature ranges from 24 to 27 °C (Iloje, 1981). The area is underlain by the coastal plain sands or Benin formations (Figure 3). The sediments of the coastal plain, deposited during the Late Tertiary-Early Quaternary period, consist of unconsolidated, coarse to medium-fine grained sands and clayey shale in places (Jones and Hockey, 1964; Okosun, 1998). The sands are generally moderately sorted and poorly cemented. The Benin Formation is overlain by lateritic overburden or recent alluvial deposits and underlain by Paleocene Akinbo Formation; this formation is predominantly shale. The Akinbo shale is underlain by the continental Cretaceous sediments of the Abeokuta Group (Omotsola and Adegoke, 1981). The coastal plain sands constitute the major shallow hydrogeologic units in the area. Aquifers are characteristically continental sands, gravels, or marine sands. The lateritic earth overlying the sands as well as the underlying impervious clay/shale member of the Akinbo Formation, constitute protective configuration for the aquifer units.

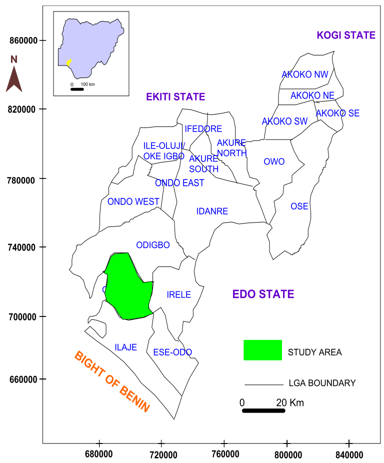

Figure 1: Location Map of the Study Area

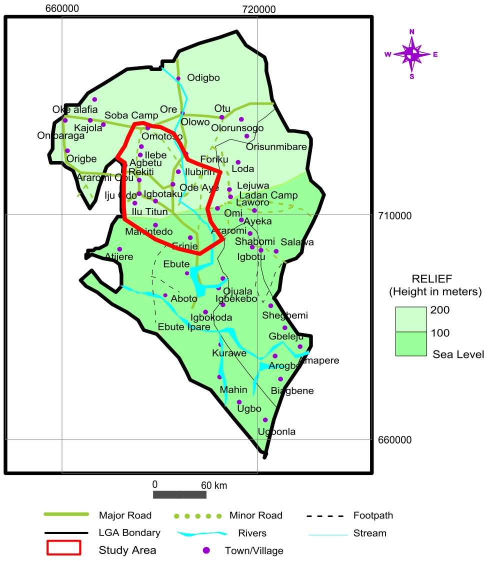

Figure 2: Surface Relief Map of the Study Area

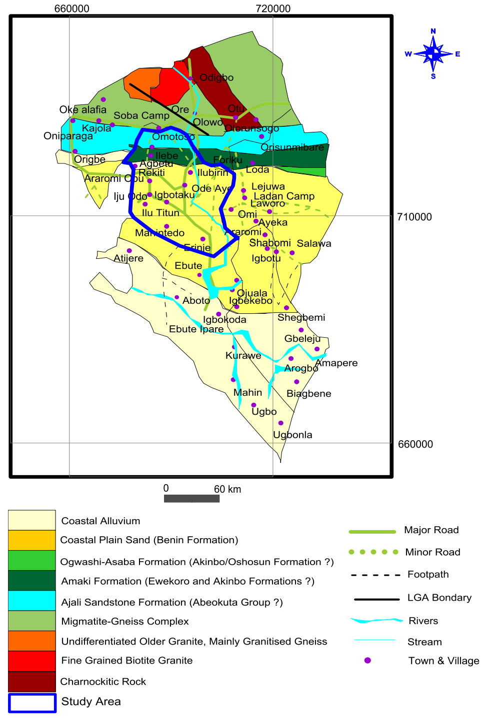

Figure 3: Geology Map of the Study Area

2.2 Groundwater Sampling, laboratory Analysis and Interpretation

A total of twenty-seven (27) water samples were collected randomly, from Ondo state water corporation, privately drilled boreholes, hand pump wells and dug water wells (Figure 4). The samples were collected in the months of November 2018 – February 2019. In places where borehole samples were taken, boreholes were allowed to pump for about 10 minutes before sampling in order to remove the interference of standing water in the metal casing and to stabilize the electrical conductivity (Saroj et al., 2010; Subramani et al., 2005). Water samples were collected in a clean 500ml capacity plastic bottle, prior to sampling; the plastic bottles were thoroughly rinsed with the water samples to prevent contamination. A separate sub-sample was collected and acidified with two drops of nitric acid (HNO_3) for the analysis of dissolved metals such as Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, Fe^{2+}, and Mn^{2+}. The groundwater samples were kept in cooler and transported immediately to laboratory for chemical analyses.

In-situ tests of physical parameters were carried out at every sampled point using HANA model HI 83200 multi-parameter ion specific meters. These measurements include temperature, pH, electrical conductivities and total dissolved solids (TDS) while the hardness of the groundwater was calculated. The samples were then transported to the laboratory and refrigerated prior before analysis. The samples were analyzed for bicarbonate, chloride, sulphate, nitrate, calcium, magnesium, sodium, potassium, iron, and manganese using standard procedures recommended by APHA and suggested precautions were taken to avoid contaminations (APHA, 2005). Metal analyses such as Ca^{2+}, Mg^{2+}, Fe^{2+}, and Mn^{2+} were carried out using Atomic Absorption Spectrometric method while Na^{+} and K^{+} concentrations were determined using Flame Spectrophotometry, while HCO_3 -, NO_3 - and Cl^{-} concentrations were determined by titrimetric method.

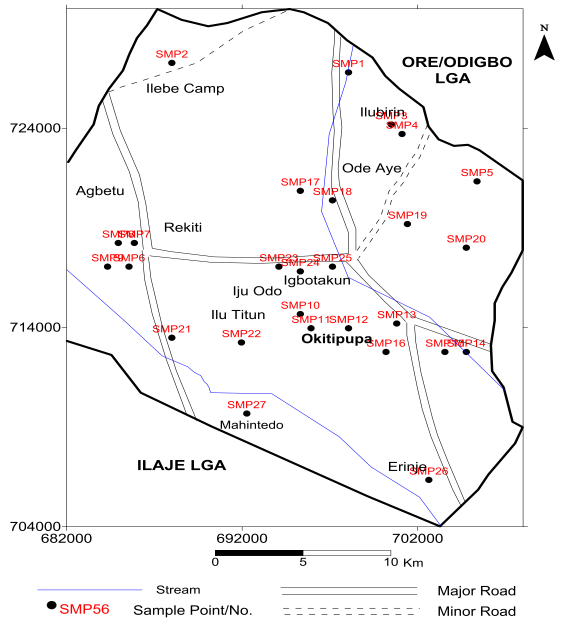

Figure 4: Data Acquisition Map for Study

The heavy metal contents were determined using Atomic Absorption Spectrometer (AAS) unicam series model 969 with air acetylen flame after digestion with perchloric nitric and HCl, conducted at the Federal Ministry of Water Resources, Akure, Ondo State. All values were recorded in mg/l. Application of various multivariate tools and diagrams were used to understand the interdependency of groundwater parameters. Bacteriological analyses involved the determination of total and faecal coliforms by membrane filtration. The method of principal components analysis (PCA) of factor analysis was used to identify underlying dominant and causal variables among the parameters using varimax rotation method (Chen et al., 2007). The aim of PCA is construction of new variables called principal components out of a set of existing original variables. The new variables are a linear combination of the existing variables. The PCA is performed to reduce the large data set of variables into few factors called the principal components which can be interpreted to reveal underlying data structure.

2.3 Water Quality Index

The calculation of WQI (WQI) involves the application of three (3) fundamental steps (Horten, 1965; Li et al., 2010; Sudhakar et al., 2014; Srinivas and Nageswararao, 2013). The first step is the assignment of weight (w_1) to each parameter measured in the water samples according to their relative importance in the overall quality of water for drinking (Kakati and Sarma, 2007). In this study, a maximum weight of five (5) was assigned to NO_3^-, Fe^{2+}, TDS, $Cl^-$and Fl^-; four (4) to pH, EC and Mn^+; three (3) was assigned to Ca^{2+}, Mg^{2+}, HCO_3^-; while Na^+ and Total Hardness (TH) assigned a weight of two (2). The second step involves the determination of the relative weight (W_i) using the formulae;

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \quad (1)$$

where, W_i is the relative weight, w_i is the weight of each parameter and n is the number of parameters. The third step is the calculation of the quantity rating scale (q_i) for each parameter by applying the equation;

$$q_i = {C_i}/{S_i} * 100 \quad (2)$$

where, qi is the quality rating, $C_i$is the concentration of each chemical parameter in each water sample in milligrams per liter, S_i is the WHO standard for each chemical parameter in milligrams per liter according to the guidelines of the World Health Organization Standard (WHO, 2011). The ideal value of pH was taken to be 7 because at pH 7, water is neither acid nor basic. On the other hand, the values for the other parameters is taken to be zero (0) because pure water is assumed to be free from impurities. The final stage of the experiment is the calculation of WQI by applying the formulae;

$$WQI = \sum_{i=1}^{n} SLi \quad (3)$$

Where SLi is the product of W_i and q_i. Table 5 shows the WQI calculated and their corresponding remarks.

2.4 Irrigation Indices

For irrigation purpose, percentage sodium (% Na), sodium absorption ratio (SAR), residual sodium carbonate (RSC), permeability index (PI), equivalent salinity concentration (ESC), Kelly ratio (KR), and magnesium ratio (MR) were determined and rated according to standard (Raju et al., 2011; Raju, 2012).

$$Na\ \% = \frac{(Na+K)*100}{(Ca+Mg+Na+K)} \quad (4)$$

$$SAR = {Na}/{\{(Ca+Mg)/2\}0.5} \quad (5)$$

$$RSC = (HCO_3 + CO_3) - (Ca + Mg) \quad (6)$$

$$PI = {Na + (HCO_3)^2)}/{Ca + Mg + Na * 100} \quad (7)$$

$$ESC = 0.81Ca + 0.45SO_4 + (Na + Cl) \quad (8)$$

Chloro-alkaline indices (CA) is used in understanding the chemical composition of groundwater along its flow path (Gibbs, 1970). Some researchers suggested two chloro-alkaline indices (CA1, CA2) for the interpretation of ion exchange between groundwater and host environment (Rao et al., 2002). A positive CA index indicates the exchange of Na^+ and K^+ from the water with Mg^{2+} and Ca^{2+} of the rocks, and is negative, when there is an exchange of Mg^{2+} and Ca^{2+} of the water with Na^+ and K^+ of the rocks. The indices are computed using equations 9 and 10.

$$CA1 = Cl^- - Na^+ + K^+ : Cl^- \quad (9)$$

$$CA2 = Cl^- - Na^+ + K^+ : Cl^- : SO_4^{2-} + HCO_3^- + NO_3^- \quad (10)$$

Kelly ratio (KR) is used to classify the irrigation water quality, which is the level of Na^+ measured against Ca^{2+} and Mg^{2+} (where the concentrations of ions are in meq/l). If the KR is less than one, it is suitable for irrigation, and if it is more than one, it is unsuitable. Magnesium ratio (MR) is the ratio of magnesium (Mg^{2+}) to alkaline earths (Ca^{2+} + Mg^{2+}) and expressed in percentage (%).

3. Results

The results of the physico-chemical, heavy metal concentrations, toxic/contaminants concentrations and bacteriological parameters of the study area are presented in Tables 1 - 4. The EC value of the samples ranges from 10 to 184 µS/cm with an average value of 56.93 µS/cm. Total hardness ranges from 19 – 63mg/l and average of 34.52mg/l, with an average values of Mg-hardness and Ca-hardness concentrations of 18.45 and 16.59 mg/l respectively. The pH value of the samples ranges from 6.5 to 7.5 with an average value of 6.99 and turbidity ranging from 0.2 – 4.5 NTU and average (av.) of 1.88. The mean value of TDS of studied groundwater samples is 35.65mg/l. The chloride concentration in study area ranges from 6.02 to 125.5mg/l with mean value of 27.63mg/l.

Bicarbonate ranges from 6 and 21 mg/l with an average value of 11.97 mg/l (Table 2). Sulphate ranges from 12.2 to 71.5mg/l and an average of 40.87mg/l. Nitrate recorded in the groundwater varies from 0.24 to 18.9

mg/l (av. 4.17 mg/l). Calcium values range from 1.2 – 9.8 mg/l (av. 5.37 mg/l). The concentrations of iron, potassium, sodium and manganese range from 0 – 0.98 mg/l (av. 0.37 mg/l), 8.2 – 35.81 mg/l (av. 14.13 mg/l), 2.44 – 32.65 mg/l (av. 10.18 mg/l) and 0 – 0.018 mg/l (av. 0.01 mg/l) respectively. The values of water quality index vary from 33 to 84 (Fig. 7c). From the bacteriological analysis, the total coliform ranges from 0 to 8 cfu/100ml. The Principal component one (PC-1) has an eigen value of 2.472 which accounts for 19.02 % of the total variance in the groundwater. The PC-2 has an eigen value of 2.414 which accounts for 18.57 % of the total variance. PC-3 has an eigen value of 2.209 which account for 16.991 % of the total variance. The PC-4 has an eigen value of 1.956 with total variance of 15.04 %.

The calculated values of %Na range from 14.43 to 86.20 and an average of 53.75. The SAR values in groundwater samples range from 0.08 to 0.86 (av. 0.39). The RSC varies from −0.67 to 0.09 (av. -0.37). The calculated PI value ranges from 57.43 to 129.13 with an average of 86.89 meq/l. The magnesium ratio (MR) of the water samples varies from 36.83 to 83.99 meq/l and average of 53.64 meq/l (Table 6). The KR values calculated for the water samples is in between 0.2 and 4.7, with a mean of 0.94. The groundwater samples shows CA1 and CA2 in the range of -0.34 to 2.2 (av. 1.26) and -0.09 to 3.65 (av. 0.73) respectively.

4. Discussion

4.1 Physicochemical and Bacteriological Parameters Assessments

The geochemistry of groundwater may influence the utility of aquifer systems. The types and concentrations of dissolved constituents in the water of an aquifer system determine whether the resource, without prior treatment is suitable for drinking-water supplies, industrial purposes, irrigation, livestock watering, or other uses (Singh et al., 2015; Siddiqui et al., 2005). The total hardness (av. 34.52 mg/l) is suggestive of soft water (Rao, 2017). However, both EC and total hardness are within World Health organization standard of 1400 µS/cm and 100 mg/l (WHO, 2011). Figure 5a shows a dominant EC and hardness range of 120-170 µS/cm and 20-50mg/l respectively in Erinje and Mahintedo. Acid pH of water may be due to dissolved carbon dioxide and organic acids such as fulvic and humic acids which are derived from decay and subsequent leaching of plant materials; pH is mainly influenced by volume of water, and soil type. Acceptable range of pH for drinking water is 6.5-8.5 (WHO, 2011). In the present study, pH was within this limit. Low pH of groundwater can cause gastrointestinal disorders especially hyperacidity, ulcers and burning sensation. Water having pH below 6.5, causes corrosion of metal pipes, resulting in the release of toxic metals such as zinc, lead, cadmium, copper etc.

Table 1: Result obtained from the Physical Parameters measured/examined

Location	East	North	Well No.	EC (µS/cm)	Turbidity NTU	Colour	Odour	Taste	Appearance
ILUBIRIN	698058	726806	1	10	1.2	Colourless	Odourless	Tasteless	Clear
	687995	727282	2	12	1.0	Colourless	Odourless	Tasteless	Clear
	700497	724190	3	18	0.9	Colourless	Odourless	Tasteless	Clear
	701107	723714	4	22	1.5	Colourless	Odourless	Tasteless	Clear
	705376	721336	5	12	0.2	Colourless	Odourless	Tasteless	Clear
IJU ODO	685555	717055	6	26	0.8	Colourless	Odourless	Tasteless	Clear
	685860	718244	7	11	1.1	Colourless	Odourless	Tasteless	Clear
	684945	718244	8	10	1.3	Colourless	Odourless	Tasteless	Clear
	684335	717055	9	18	2.5	Colourless	Odourless	Tasteless	Clear
OKITIPUPA	695313	714676	10	85	2.7	Colourless	Odourless	Tasteless	Clear
	695923	713963	11	82	2.2	Colourless	Odourless	Tasteless	Clear
	698058	713963	12	78	2.9	Colourless	Odourless	Tasteless	Clear
	700802	714201	13	69	3.4	Colourless	Odourless	Tasteless	Clear
	704766	712773	14	82	1.8	Colourless	Odourless	Tasteless	Clear
	703547	712773	15	92	1.6	Colourless	Odourless	Tasteless	Clear
	700192	712773	16	90	2.1	Colourless	Odourless	Tasteless	Clear
ODE AYE	695313	720860	17	85	1.8	Colourless	Odourless	Tasteless	Clear
	697143	720384	18	80	2.7	Colourless	Odourless	Tasteless	Clear
	701412	719195	19	50	1.4	Colourless	Odourless	Tasteless	Clear
	704766	718006	20	55	0.5	Colourless	Odourless	Tasteless	Clear
ILUTITUN	687995	713487	21	12	0.8	Colourless	Odourless	Tasteless	Clear
	691959	713249	22	15	1.2	Colourless	Odourless	Tasteless	Clear
IGBOTAKUN	694093	717055	23	42	2.2	Colourless	Odourless	Tasteless	Clear
	695313	716817	24	36	2.4	Colourless	Odourless	Tasteless	Clear
	697143	717055	25	12	1.0	Colourless	Odourless	Tasteless	Clear
ERINJE	702632	706352	26	169	4.5	Colourless	Odourless	Tasteless	Clear
MAHINTEDO	692264	709682	27	184	4.0	Colourless	Odourless	Tasteless	Clear

Higher values of pH hasten scale formation in water heating apparatus and decrease germicidal potential of chlorine. TDS is an important parameter which imparts a peculiar taste to water and reduce its portability. Desirable limit of TDS is 500 mg/l and maximum allowable limit is 1500 mg/l. From Figure 5, the TDS is low across the area ranging from 6.8 and 122.6 mg/l (Figure 6c) which indicates a fresh water, with relatively higher values in southern part of the study area, especially in Erinje and Mahintedo (Fetter, 1980). All the values obtained are much lower than these limits. Chloride is an important quality parameter that affects the aesthetic property of water including taste and renders it unsuitable for drinking purpose if present in high concentration. Subsequently, the Cl- values in the present study are on lower side considering WHO maximum permissible limit of 200mg/l for drinking and domestic uses (WHO, 2011).

The range of values obtained for bicarbonate is within the recommended limit of 100mg/l. In Figure 5, relatively high values are found in southern part of the study area, including Ilubinrin and Ode Aye (Figure 7a) which are underlain by hard rocks. The values of sulphate obtained is within the 250 mg/l recommended (WHO, 2011). Notable relative higher values greater than 50 mg/l are also observed in the southern area (Figure 7b). Nitrate has human health impacts, primarily in infants. Nitrate affects haemoglobin in the blood and reduces the babies' ability to transport oxygen. There is also a 'suspected link between exposure to nitrate and cancer in human (WHO, 2004). Spatial distribution of Nitrate shows relatively high values between 10 – 20 mg/l in the southern part, while concentration in the range of 1-10 mg/l accounts for 90% of the study area (Figure 6a). The most common origin of nitrate in groundwater within the study area are agricultural activities and disposal of untreated human waste especially into drainages and open channels. The general acceptable limit of calcium in water is usually 75 mg/l whereas its maximum permissible limit is 300 mg/L (WHO, 2011).

Table 2: Summary of the Analyzed Chemical Parameters

Well No.	pH	Cl^-	Mg Hardness	Ca Hardness	Total Hardness	SO_4^{2-}	NO_3^-	Mn	TDS	HCO_3^-	Mg^{2+}	Ca^{2+}	Fe^{2+}	K^+	Na^+
1	6.8	10.10	15	20	35	52.2	9.42	ND	22.1	10	4.45	5.6	ND	10.10	5.36
2	6.8	14.12	10	18	28	40.2	8.55	ND	20.3	12	3.25	6.4	ND	9.10	3.21
3	7.0	8.23	10	15	25	32.3	4.42	0.018	14.5	18	3.21	2.3	0.21	8.36	4.26
4	7.5	6.22	12	14	26	24.5	2.36	0.009	45.8	10	2.25	4.4	0.36	8.86	2.87
5	7.4	8.25	10	35	45	12.8	1.65	ND	6.8	10	3.28	5.2	0.87	9.27	4.10
6	7.2	6.02	15	36	51	29.7	2.58	0.009	6.9	11	4.25	3.9	0.21	8.20	2.44
7	6.9	6.22	11	21	32	52.5	8.44	ND	15.4	16	4.69	5.7	ND	8.84	4.20
8	6.9	7.85	12	8	20	41.7	3.25	0.010	8.8	17	3.77	7.4	0.44	8.58	5.80
9	6.8	9.90	10	10	20	38.8	0.58	0.015	24.2	10	3.82	1.2	0.89	8.99	3.75
10	7.2	11.11	17	12	29	62.1	0.55	ND	50.2	8	3.50	5.4	ND	11.10	4.40
11	7.1	15.16	19	10	29	63.2	0.69	ND	44.5	12	4.94	5.5	0.44	8.32	4.23
12	7.4	17.50	20	14	34	42.1	2.36	ND	20.2	16	2.88	6.4	0.23	8.55	9.23
13	6.9	12.20	25	12	37	25.3	0.57	ND	35.7	12	3.19	5.2	0.65	8.44	15.30
14	6.6	11.87	22	15	37	19.4	0.41	ND	33.5	8	4.40	4.9	0.69	9.20	10.90
15	7.2	18.79	15	13	28	55.5	1.22	ND	45.9	8	3.95	4.7	0.57	9.63	8.60
16	7.2	19.36	18	14	32	63.7	1.36	0.012	55.1	21	3.33	5.6	0.22	15.60	11.41
17	6.8	8.95	11	8	19	45.8	0.58	0.013	52.4	11	4.25	3.5	0.18	35.81	26.80
18	7.1	9.25	19	12	31	69.2	0.98	0.017	25.4	19	1.25	2.3	0.36	34.60	23.50
19	7.4	28.65	13	10	23	40.2	1.25	0.004	20.1	8	2.25	3.2	0.78	28.50	32.65
20	6.6	15.58	12	15	27	48.7	6.34	ND	12.2	6	1.45	4.1	0.98	8.20	29.10
21	6.6	64.21	44	19	63	33.4	4.92	ND	6.8	10	2.36	4.4	ND	9.50	4.68
22	6.8	25.89	22	14	36	15.8	4.23	0.015	6.9	10	4.21	9.8	ND	8.20	4.90
23	6.8	29.30	32	8	40	17.9	0.24	0.018	10.5	8	4.58	7.8	ND	8.50	5.10
24	7.5	70.20	24	9	33	12.2	0.87	0.012	55.3	7	3.69	6.3	0.57	8.80	5.68
25	7.1	65.32	16	15	31	25.6	0.99	ND	25.4	8	5.87	5.9	0.18	9.90	4.55
26	6.5	125.5	26	28	54	71.5	18.90	ND	122.6	15	3.61	9.1	0.35	30.5	12.80
27	6.6	120.3	22	32	54	65.3	14.10	ND	116.9	19	5.22	8.5	0.48	32.2	10.32
Min.	6.5	6.02	10	8	19	12.2	0.24	0	6.8	6	1.25	1.2	0	8.2	2.44
Max.	7.5	125.5	44	36	63	71.5	18.9	0.018	122.6	21	5.87	9.8	0.98	35.81	32.65
Mean	6.99	27.63	18.48	16.59	34.52	40.87	4.17	0.01	35.65	11.97	3.62	5.37	0.37	14.13	10.18

Table 3: Summary of the Analyzed Toxic Chemicals and Contaminants

	Toxic Chemicals						Contaminants					
Well No.	Lead	Cyanide	Cadmium	Arsenic	Barium	Mercury	Pesticide	Mineral oil	Ammonia	Phenol	Detergent	Radionuclides (Bq/L)
1	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
2	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
3	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
4	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
5	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
6	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
7	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
8	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
9	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
10	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
11	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
12	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
13	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
14	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
15	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
16	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
17	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
18	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
19	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
20	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
21	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
22	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
23	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
24	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
25	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
26	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
27	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL

Table 4: Summary of the Bacteriological Analysis

Well No.	Presumptive coliform	Enterococcus faecalis	E. Coli	Total coliform
1	00	00	00	07
2	00	00	00	05
3	00	00	00	06
4	00	00	00	06
5	00	00	00	06
6	00	00	00	07
7	00	00	00	00
8	00	00	00	00
9	00	00	00	00
10	00	00	00	08
11	00	00	00	07
12	00	00	00	00
13	00	00	00	00
14	00	00	00	00
15	00	00	00	00
16	00	00	00	00
17	00	00	00	00
18	00	00	00	00
19	00	00	00	00
20	00	00	00	00
21	00	00	00	00
22	00	00	00	00
23	00	00	00	00
24	00	00	00	00
25	00	00	00	00
26	00	00	00	05
27	00	00	00	00

In the present study, the result shows that the magnesium in the water samples varies from 1.25 - 5.87 mg/l. The minimum acceptable limit of magnesium in water is 50 mg/l. All the samples are above the recommended limit. The average concentrations of iron (av. 0.37 mg/l), potassium (av. 14.13 mg/l), sodium (av. 10.18 mg/l) and manganese (av. 0.01) are within the permissible limits of 0.3 mg/l, 10 mg/l, 50 mg/l and 0.3 mg/l respectively of WHO standard (WHO, 2011). Consequently from the results of WQI, good water types (WQI of 50-75) account for 60 % of the study area which extended from the north to the central part; while bad water (WQI of 50-75) accounts for 40 % of the study area, and generally observed in the east and southern part (Erinje and Mahintedo). This areas are also characterized by equivalent salinity concentration greater than 3 mg/l (Figure 6a).

4.2 Toxic contaminants and Bacteriological Characteristics

Furthermore, the results showed that all water samples contain no trace of toxic chemicals such as lead, cyanide, cadmium, arsenic, barium, and mercury. In addition no pesticide, mineral oil, ammonia, phenol, detergent, radionuclides (Table 3). From the bacteriological analysis, the total coliform ranges from 0 to 8 cfu/100ml (sample 10). This is still within the acceptable limit of 10 cfu/100ml for potable water. However, no indication of faecal contamination in sampled water. In addition, no trace of E. coli was recorded in the samples (Table 4). Effects of the presence of E. coli in water include: Urinary tract infections, bacteremia, meningitis, diarrhea, (one of the main cause of morbidity and mortality among children), acute renal failure and hemolytic anaemia (WHO, 2004).

4.3 Principal Component Analysis

Principal component (PC) analysis is performed on groundwater data for better understanding of their interrelationships and probable source of major ions. The data set were subjected to four components analysis (Table 5). PC-1 factor is strongly and positively loaded with parameters such as Cl, TDS, and K. This association showed that all these variables have common source which accounts for their precipitation in the water samples. The processes assigned to this factor is mixing of saline with fresh water and anthropogenic contamination. PC-2 factor is strongly and positively loaded with the following parameters; Mg, Ca, Fe, and Na. The processes assigned to this factor is weathering and cation exchange. PC-3 factor is strongly and positively loaded with pH, hardness, nitrate, and manganese. The process assigned to this factor is mineral precipitation/anthropogenic pollution, while sulphate, bi-carbonate, and iron are the major parameters strongly and positively loaded with PC-4 factor. This factor could be as a result of groundwater dilution and/or mineral dissolution. The physico-chemical analysis of groundwater samples indicates that the dominant major cations are in decreasing order; K^+, Na^+, Ca^{2+}, Mg^{2+} and the dominant anions are SO_4^{-2}, Cl^-, HCO_3^-, NO^-_3.

4.4 Groundwater Facies Characterization

Piper trilinear plot show the dominant groundwater facies revealed in this study are the non-carbonate hardness (secondary alkalinity) exceeds 50 %; non-carbonate alkali (primary salinity) exceeds 50% (zone 7); and transition zone with no one cation-anion pair exceeds 50 % (zone 9) (Piper, 1944). Zones 6 and 7 are the most dominant. From the Gibbs diagram (Figure 8), precipitation are the dominant processes in the hydrogeochemical evolution of the groundwater samples (Figure 9) (Gibbs, 1970). Since the study area is also dominated by silicate rocks and minerals, the silicate weathering process is more than carbonic weathering (Figure 9c).

4.5 Evaluation of the Groundwater for Irrigation

The concentration and composition of dissolved constituents in groundwater determine its quality for irrigation use. The suitability of groundwater for irrigation is liable on the effects of the mineral constituents in the water on both the plants and soil (Raju et al., 2011). Higher salt content in irrigation water causes an increase in soil solution osmotic pressure. Effect of salts on soil causing changes in soil structure, permeability and aeration in directly affect plant growth (Collins and Jenkins, 1996).

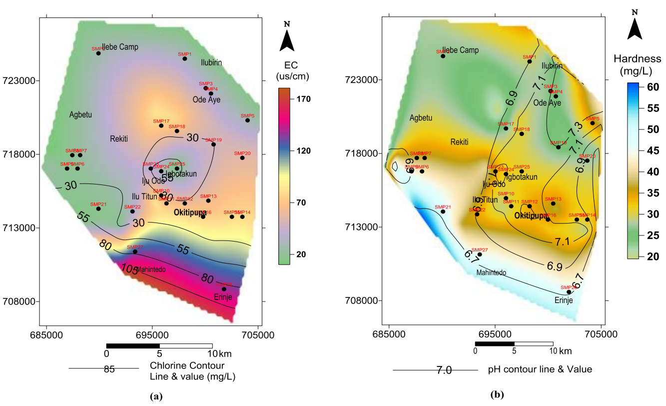

Figure 5: Spatial Distribution of: (a) EC and Chloride (b) Hardness and pH

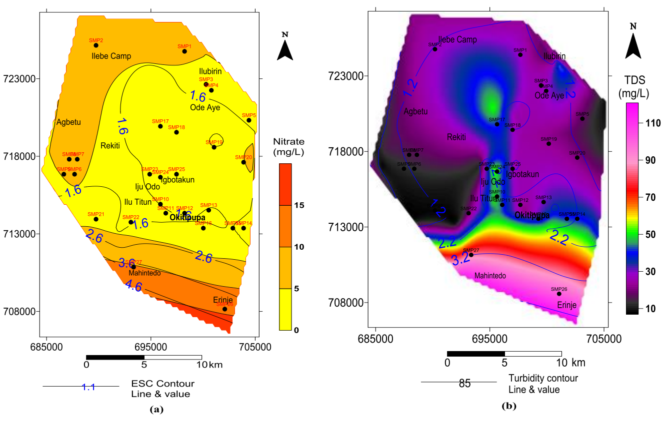

Figure 6: Spatial Distribution of: (a) Nitrate and ESC (b) TDS and Turbidity

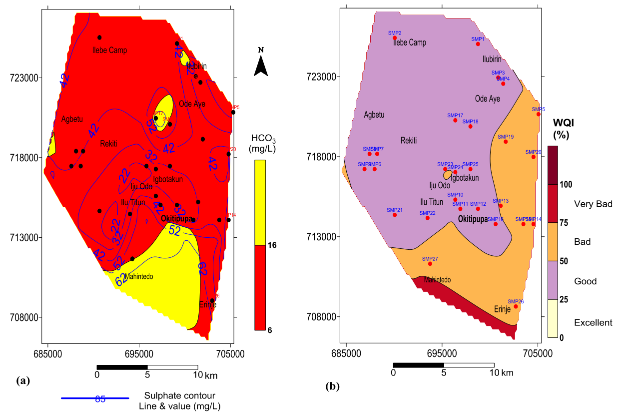

Figure 7: Spatial Distribution of: (a) HCO_3 and Sulphate (b) WQI

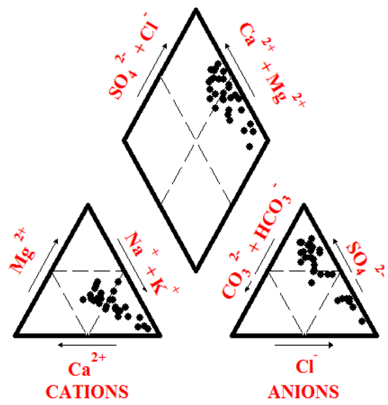

Figure 8: Trilinear piper diagram of the studied samples

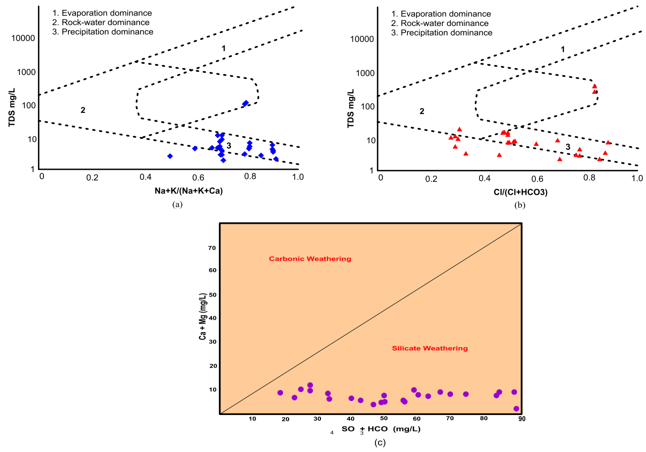

Figure 9: (a) Gibbs diagram for cations (b) Gibbs diagram for anions (c) Scatter plot for carbonate weathering versus silicate weathering

The important chemical parameter for judging the degree of suitability of water for irrigation are sodium (%Na), sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and permeability index (PI). Generally, % Na should not exceed 60 % in irrigation waters. Consequently the mean value obtained is lower than 60 %, hence safe for irrigation. The % Na was higher may be dissolution of minerals from lithological composition, and the addition of chemical fertilizers by the irrigation waters (Collins and Jenkins, 1996). Relatively high % Na (60 - 100) are observed in the eastern part, and accounts for 40 % of the study area, while doubtful/unsuitable water has 60 % coverage in the area (Figure 10d).

Higher concentration of SAR leads to breakdown in the physical structure of the soil. The sodium hazard is expressed in terms of classification of irrigation water as low (S1: <10), medium (S2: 10 to 18), high (S3: 18 to 26) and very high (S4: >26). The SAR value (av. 0.39) indicating that all the groundwater samples are suitable for irrigation purposes. Spatial distribution of SAR is shown in Figure 6. Low values in the range of 0.1 – 0.5 accounts for 70 % of the study area and observed in the central part and a small closure in the south (Figure 10a).

The relative abundance of sodium with respect to alkaline earths and the quantity of bicarbonates and carbonate in excess of alkaline earths also influence the suitability of water for irrigation. RSC is an important parameter to evaluate the suitability of irrigation water (Raju et al., 2009). Generally, >2.5 meq/l of RSC is unsuitable for irrigation purposes. The RSC value in ground water sample range from −0.67 to 0.09 (av. -0.37) indicating a good water for irrigation.

Table 5: Varimax orthogonal rotated factor loadings from PCA of the analyzed parameters

Variable	Factor 1	Factor 2	Factor 3	Factor 4
pH	-0.077	0.027	**-0.631**	-0.242
Chloride	**0.803**	-0.209	0.411	-0.006
Hardness	0.261	-0.323	**0.602**	-0.045
Sulphate	0.258	0.306	0.258	**0.695**
Nitrate	0.375	-0.126	**0.707**	0.383
Manganese	-0.027	-0.078	**-0.738**	0.266
TDS	**0.861**	-0.012	0.194	0.209
Bicarbonate	0.141	-0.071	-0.066	**0.827**
Magnesium	0.259	**-0.700**	0.012	-0.103
Calcium	0.381	**-0.616**	0.346	0.016
Iron	0.201	**0.626**	-0.049	**-0.503**
Potasium	**0.678**	0.424	-0.051	0.444
Sodium	0.268	**0.839**	-0.034	0.073
Eigen value	2.472	2.414	2.209	1.956
% Variance	19.015	18.566	16.991	15.043
Cumulative % variance	19.015	37.581	54.573	69.616
Interpretation of process	**Mixing of saline and fresh water and anthropogenic pollution**	**Weathering and cation exchange**	**Mineral precipitation /anthropogenic pollution**	**Dilution of groundwater /Mineral dissolution**

Soil permeability is affected by long-term use of irrigation water with high salt content as influenced by Na^+, Ca^{2+}, Mg^{2+}, and HCO_3 contents of the soil. The PI values >75 % comes under class I and indicates that the excellent quality of water for irrigation. The PI values between 25 % - 75 % comes under class II indicates that the good quality of water for irrigation and the PI value less than 25% comes under class III indicates that the unsuitable nature of water for irrigation. According to the permeability index, the groundwater comes under class I (PI > 75 %) category and under class II (PI ranges from 25 % to 75 %) category and account for 55 % and 45 % respectively (Figure 10b). For magnesium ratio, 50% of the groundwater samples are suitable while 50 % are unsuitable for irrigation, as magnesium damages the soil structure, which affects crop yield. The range of values obtained for KR is within the suitable range of less than 1 (Rao, 2017). Areas with low KR less than 0.1 are observed in the east and southern part (Figure 10c).

4.6 Chloro-Alkaline Indices

Chloro-alkaline indices (CA) are used in understanding the chemical composition of groundwater along its flow path. Subba Rao [36] suggested two chloro-alkaline indices (CA1, CA2) for the interpretation of ion exchange between groundwater and host environment (Rao, 2017). A positive CA index indicates the exchange of Na^+ and K^+ from the water with Mg^{2+} and Ca^{2+} of the rocks; and is negative, when there is an exchange of Mg^{2+} and Ca^{2+} of the water with Na^+ and K^+ of the rocks. The groundwater samples shows average CA1 and CA2 of 1.26 and 0.73 respectively. Both indices have an average positive values, confirming predominant cation-anion exchange reaction, in which ion exchange of Na^+ and K^+ from the water with Mg^{2+} and Ca^{2+} of the rocks. Wilcox's diagram is adopted for the classification of groundwater for irrigation, wherein the EC is plotted against % Na (Wilcox, 1948). Data of the groundwater samples of the area are plotted in the Wilcox's diagram in Figure 11, all the samples plotted within the "excellent irrigation water".

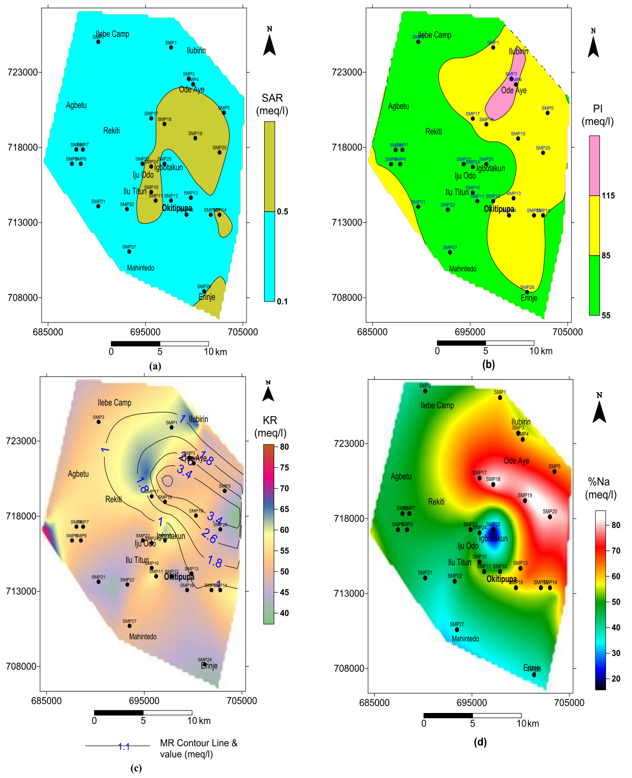

Figure 10: Spatial Distribution of some of the irrigation indices calculated (a) SAR, (b) PI, (c) KR, and (d) %Na

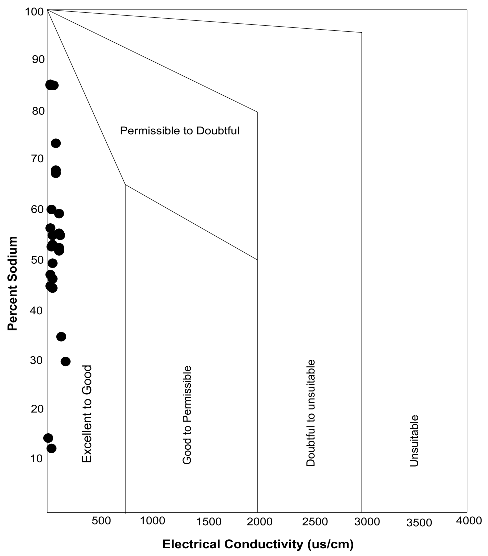

Figure 11: Wilcox Plot of the Water samples

5. Conclusion

The study has provided significant information on the development of ground water quality in Okitipupa and environs. The major ion chemistry data revealed that the ground water in the study area is soft and fresh in nature. All the parameters analyzed are within the permissible limit of World Health Organization. The sequence of the abundance of the major ions is in the following order of K^+> Na^+> Ca^{2+}> Mg^{2+} and the dominant anions are SO_4^{-2}> Cl^-> HCO_3^-> NO^-_3. Three dominant facies that characterized the water are: non-carbonate hardness (secondary alkalinity) exceeds 50%; non-carbonate alkali (primary salinity) exceeds 50%; and transition zone with no one cation-anion pair exceeds 50%, while precipitation is the main dominant process in the hydrogeochemical evolution of the groundwater samples. WQI calculated exhibits good (60 %) and poor (40 %) quality. Based on the classification of irrigation water, all the sample locations are suitable for irrigation purposes. The processes responsible for contamination in areas with poor water quality are mixing of saline with fresh water and anthropogenic contamination; weathering and cation exchange; mineral precipitation/anthropogenic pollution; and groundwater dilution and/or mineral dissolution. It is therefore recommended that future researchers should concentrate their study on morphometric analysis, watershed analysis and hydraulic parameters measurement in order to elucidate more on the quality of the aquifers in the area.

Declaration of Interest

The author declares that no financial and personal relationships with other people or organizations that could inappropriately influence (bias) this study/work.

Submission Declaration and Verification

The author declares that this research work has not been published previously and that it is not under consideration for publication elsewhere. If accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright holder.

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The author declares no competing interest exists

Authors Contribution

Author OOF designed, wrote the protocol, arranged experimental processes, and managed the literature searches. Author VA analyzed and interpreted the data. Both authors OOF and VA prepared and approved the manuscript

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