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Spatial assessment of groundwater quality and hydrochemical indices in Ore, Southwestern, Nigeria

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Abstract. Millennium development goals is aimed at having sustainable safe drinking water and basic sanitation. Consequently an assessment of groundwater quality was carried out in Odigbo LGA of Ondo State, Nigeria for drinking, domestic and irrigation uses. Samples from thirty randomly selected ground water sources; shallow wells and boreholes were analyzed using APHA method. The results show that all the parameters are within the permissible limit of World Health Organization. The physicochemical analysis of groundwater samples indicates the dominant major cations are in decreasing order of Na^+ , Ca^{2+} , Mg^{2+} , K^+ and the dominant anions are HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- . The values of water quality index varies suggest a good water (50 - 75) accounts for 70 % of the study area. The dominant groundwater facies are the non-carbonate alkali (primary salinity) exceeds 50 %; and transition zone with no one cation-anion pair exceeds 50 %, while evaporation; rock-water interaction, and precipitation; and silicate weathering process are the dominant processes in the hydrogeochemical evolution of the groundwater. In conclusion, the water in the study area are good/suitable for drinking, domestic and irrigation purposes with low equivalent salinity concentrate and moderate electrical conductivity.

Key words: groundwater quality, water quality index, water-rock interaction, principal component analysis, hydrochemical facies.

1. Introduction

Water is the elixir of life, without it life is impossible. It is known to be an essential resource for industrial, and economic development [1]. Its supply in sufficient quantity and quality at appropriate time is critical to all aspect of life. Over the years, effort to meet these prerequisites have proved difficult even though water is the most abundant substance on the earth surface. Its unique properties make it the

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most important and abundant substance in the universe. Groundwater accounts for about 98 % of the world fresh water and is distributed throughout the world [2]. Groundwater is one of the most significant natural sources and can be used as an alternative to surface water for drinking, irrigation and industry usage. Poor drinking water quality, high cost of water purification, human health problems, and loss of water supply are attributable to groundwater contamination. Accessing quality groundwater has been a major concern for both the rich and the poor most especially in Nigeria as almost 75 % of the entire population depend solemnly on groundwater for consumption [3]. The quality of groundwater is of vital importance, whether for industrial or domestic purposes. The quality of groundwater for different purpose depend largely on its physical, chemical and bacteriological compositions and as a result of these various concerned agencies have set out permissible standards for water usage. According to Davis and Deweist [4], these standards are based on two main criteria, namely; the presence of objectionable tastes, odor and color and; the presence of substances with adverse physiological effects. However, mineral enrichment from underlying rocks can change the chemistry of the groundwater, making it unsuitable for the consumption [5].

Most rural areas in Nigeria depend solemnly on rivers, streams and hand-dug wells for water supply while the urban settlements depend on treated pipe-borne water and boreholes for their water supply. This uncoordinated rationalization has led to slow industrial, agricultural growth in the rural areas [6-7]. Odigbo Local Government of Ondo State is becoming a cosmopolitan city in terms of infrastructural and urban utilities and also connecting Ondo State with Lagos, and Benin, is seriously facing acute water supply over the last decade. Access to quality water supply has become very difficult due to the rapid increase in population with little or no provision for water supply expansion and quality control. Industrial discharges/effluents from petrochemical depots and companies is really contaminating the inadequate existing water sources in the area. The geochemistry of ground water may influence the utility of aquifer systems as sources of water [8-9]. 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. Changes in the concentrations of certain constituents in the water of an aquifer system, whether because of natural or anthropogenic causes, may alter the suitability of the aquifer system as a source of water [10]. Assessing ground-water quality and developing strategies to protect aquifers from contamination are necessary aspects of water-resource planning. Hence, the monitoring of the chemical, physical and biological conditions of groundwater is considered to be critical for the planning strategy for the protection of groundwater quality [11]. The data obtained from this study are valuable for understanding, identifying, and describing modifications in the condition of the groundwater quality. Many researchers have conducted groundwater quality assessment using major ion chemistry analysis [1], [8-10], [12-13]. In this paper, hydrogeochemical

characteristics and physicochemical parameters of groundwater (boreholes and dug wells) were assessed in Ore metropolis for groundwater environmental monitoring purpose.

1.1 Study area

The study area is Odigbo Local Government of Ondo State. The area can be accessed through Akure – Ore Lagos – Benin highways and is located within latitude 715000 – 755000 mN and longitude 664750 – 725000 mE (Fig. 1). Major part of the study area is devoted to agricultural and commercial activities. The study area has a tropical rainforest climate. The average temperature is 25 °C. Relative humidity of the area differs within 70 % to 80 %. The average annual rainfall of the study area is about 1500 mm and 2500 mm. The geology of the area plays a significant role for assessing groundwater potential and quality of the region. The northern area falls within the geologic terrain, underlain by the Precambrian basement complex rocks of southwestern Nigeria, characterized by the migmatite-gneiss complex, older granites, charnockites, quartzite and minor intrusive lithologies [14-15].

The local geology consists of charnockite, fine grained biotite granite and gneiss in the north. Field observation shows that biotite granites in the area occur as large igneous bodies, and largely coarse grained. However the southern parts of the study area is underlain by coastal plain sands of Benin formation; Ewekoro & Akinbo and Abeokuta formations (Fig. 2). The Abeokuta Formation in surface outcrops comprises mainly sand with sandstone, siltstone, silt, clay, mudstone and shale interbeds. It usually has a basal conglomerate which may measure about 1 m in thickness and generally consists of poorly rounded quartz pebbles with a silicified and ferruginous sandstone matrix or a soft gritty white clay matrix. In outcrops where there is no conglomerate, coarse, poorly sorted pebbly sandstone with abundant white clay constitutes the basal bed. The overlying sands are coarse grained, clayey, micaceous and poorly sorted, and indicative of short distances of transportation or short duration of weathering and possible derivation from the granitic rocks located to the north. The Ewekoro Formation overlies the Araromi Formation in the eastern Dahomey basin (Fig. 2). It is an extensive limestone body, which is traceable over a distance of about 320 km from Ghana in the west, towards the eastern margin of the Dahomey basin in Nigeria [16]. Nton and Elueze [17] has reported that the limestone is of shallow marine origin owing to abundance of coralline algae, gastropods, pelecypods, echinoid fragments and other skeletal debris. It is Palaeocene in age. Overlying the Ewekoro Formation is the Akinbo Formation, which is made up of shale and clayey sequence [15]. The claystones are concretionary and are predominantly Kaolinite [17]. The base of the Formation is defined by the presence of glauconitic band with lenses of limestone [15], [18-19]. The Formation is Palaeocene to Eocene in age [20-21]. The area is well drained by rivers and streams that flow in the same direction as the rock strike. These streams take their source from relatively high elevation about 200 m above

the mean sea level (absl.) and flow downhill along the strike into valleys. The topographical variation within the area is between 100 to 200 m absl (Fig. 3).

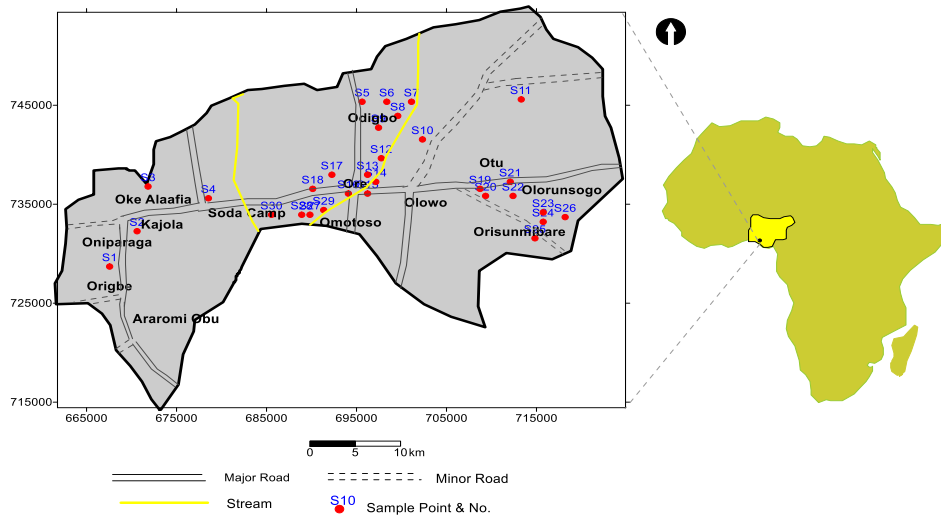


Fig. 1. Location map showing Odigbo Local Government Area and Sampling locations.

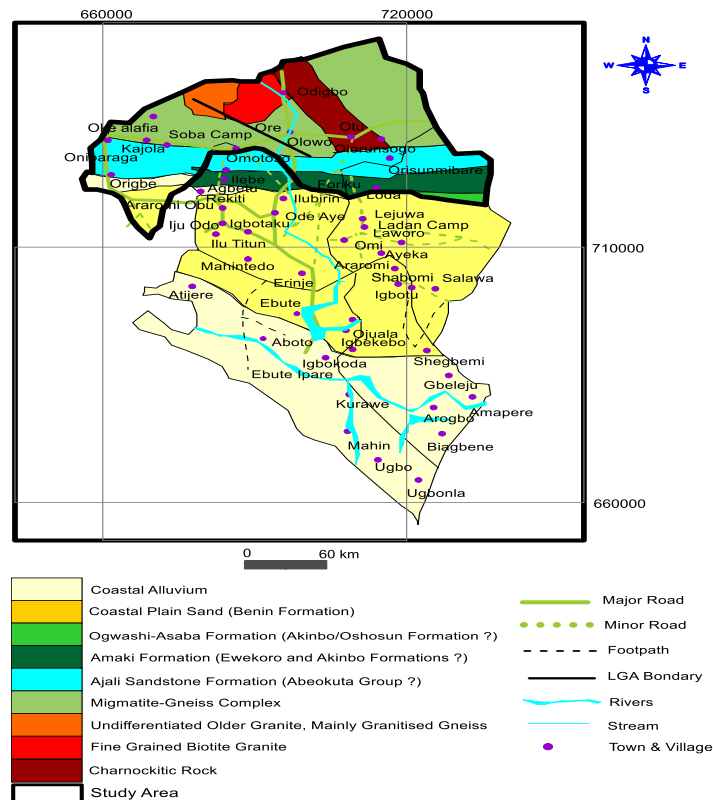


Fig. 2: Geological map of Southern part of Ondo State.

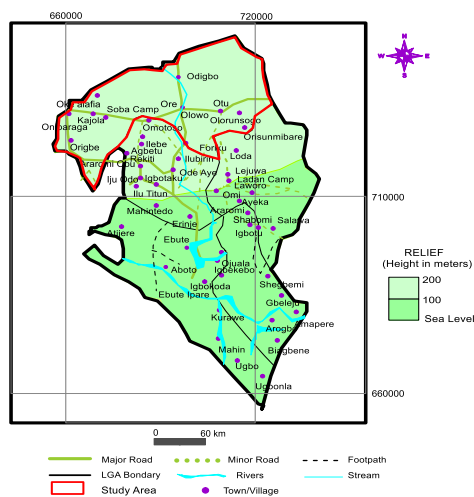


Fig. 3. Topographical variation of the study area.

2. Experimental details

2.1 Water sampling and Analysis

The study involved both field and laboratory activities. The field activity involved collection of water samples randomly [22-23] from different boreholes and hand dug wells. A total of 30 groundwater samples including 16 shallow dug wells and 14 boreholes were taken in the study between the periods of three months (November 2018 - February 2019) before the onset of raining season to ensure the effluents from surface run off were mixed with the sampled water. Fourteen hand-dug well (HDW) and sixteen borehole (BH) water samples were collected randomly (Fig. 1). One-litre plastic bottle was filled with water at each site. The water samples were collected into cleaned plastic bottles which were earlier rinsed with the particular water to be sampled. This was subsequently used in the laboratory for off-site analysis. Samples for bacteriological analysis were collected into 500 ml sterilized bottle and the cap covered with aluminum foil to avoid contamination during sampling in accordance to American Public Health Association method for the examination of water and wastewater [24]. The samples were kept on ice and transported to the Federal Ministry of Water Resources laboratory in Akure, Ondo State for the physico-chemical analysis using American procedures. The bacteriological analyses were carried out immediately on arrival at the laboratory.

2.2 Physico-chemical and bacteriological analysis

In-situ tests of physical parameters were carried out at every sampled site using HANA model HI 83200 multi-parameter ion specific meter. These measurements include temperature, pH, electrical conductivities and total dissolved solids (TDS) while the hardness of the groundwater were calculated. The samples were then

transported to the laboratory and refrigerated prior to further analysis. The samples were analyzed for bicarbonate, chloride, sulphate, nitrate, calcium, magnesium, sodium, potassium, iron, and manganese using standard procedures, according to procedures outlined in the Standard Methods for the Examination of Water and Wastewater [24]. Turbidity was measured with a HACH 2100 P Turbidimeter, colour by visual comparison method comparator, and pH by Suntext Model SP 701 pH Meter.

Conductivity was measured with Cybersan PC 510 conductivity meter, total dissolved solids and suspended solids were measured gravimetrically after drying in an oven to a constant weight at 105°C. Sodium and potassium were measured by flame emission photometry, calcium and magnesium by the EDTA titration, sulphate by the turbidimetric method, bicarbonate by calorimetric and chloride by Argentometric method. Nitrate was determined using hydrazine reduction method. Fluoride was determined by SPADNS method, iron and manganese by Atomic Absorption Spectrophotometry (AAS). Bacteriological analyses involved the determination of total and faecal coliforms by membrane filtration. Statistical analysis was done using SPSS version 19.0 for windows and Microsoft Office Excel 2013. The method of principal components analysis (PCA) of factor analysis was used identify underlying dominant and causal variables among the parameters using varimax rotation method. 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. The WQI The calculation of WQI involve the application of the three (3) fundamental steps as proposed by [25-28]. 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 purpose as propose by Sakati and Sarma, 2007. In this study, a maximum weight of five (5) was assigned to NO_3^- , Fe^{2+} , TDS, Cl^- and F^- ; 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;

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

where, q_i 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 [29]. 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;

$$WQI = \sum_{i=1}^n SL_i \tag{3}$$

Where SL_i is the product of W_i and q_i . Table 5 shows the WQI calculated and their corresponding remarks. 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 [30-31].

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

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

$$RSC = (HCO_3 + CO_3) - (Ca + Mg) \tag{6}$$

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

$$ESC = 0.81Ca + 0.45SO_4 + (Na + Cl) \tag{8}$$

Chloro-alkaline indices (CA) is used in understanding the chemical composition of groundwater along its flow path. Subba Rao et al [32] suggested two chloro-alkaline indices (CA1, CA2) for the interpretation of ion exchange between groundwater and host environment. 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 CA indices are computed using equations 9 and 10.

$$CA1 = Cl^- - Na^+ + K^+ : Cl^- \tag{9}$$

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

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 and discussion

The quality of ground water depends on various chemical constituents and their concentration, which are mostly derived from geology. Industrial and municipal solid wastes have emerged as one of the leading cause of pollution of surface and ground water. The statistical summary of the physical, chemical and bacteriological analyses on the groundwater samples is presented in Tables 1 -3.

3.1 Physicochemical and Biological parameters

The appearance of the studied water samples is clear, tasteless and odourless. These can affect positively its marketability for domestic, agriculture and industrial use. The temperature of groundwater governs to a large extent the biological species present and their rate of activity. The temperature of the water samples

ranges from 25.1 to 27.6 °C with an average of 25.5 °C. The water turbidity ranges from 0.9 to 5.9 NTU and average of 3.3 indicating low silt/clay or colloidal content. The TDS ranges from 122 – 810 mg/l with a mean and standard deviation (stdev) of 377 and 189 respectively indicating a fresh water [27, 33]. The spatial distribution of Turbidity and TDS in Figure 4 shows relatively high TDS and turbidity in Ore, Soda camp and Kajola. The electrical conductivity ranges from 120 to 674 $\mu\text{s}/\text{cm}$ (av. 331.4 $\mu\text{s}/\text{cm}$). Chloride varies between 12.5 – 85.2 mg/l with an average of 35.17 and stdev of 21.75 indicating a brackish water type. The spatial distribution of chloride and EC in Figure 4 shows a generally low EC (less than 500 $\mu\text{s}/\text{cm}$) although higher in Ore environment, while chloride is high in Ore, Araromi Obu which is very close to the Atlantic Ocean.

However both EC and Chloride are within the WHO Standard of 500 $\mu\text{s}/\text{cm}$ and 250 mg/l respectively. The pH of the water samples in the study area ranged from 6.4 to 8.2 and an average of 7.1, which indicates that the groundwater is slightly acidic to neutral water types. These values are within the permissible limits of 6.5 – 8.5 set by WHO [29]. The spatial distribution of pH of sampled water is shown in Fig. 4. It is generally less than 7.0 indicating a slightly acidic water type, while Araromi Obu, Onigbe, Ore, Omotoso, Olowo are characterized by slightly alkalinity water type. Bicarbonates varies between 8 and 88 mg/L (av. of 36.13) with a wide stdev of 24.63. This obtained range of values is within the 120 mg/l recommended by WHO. However, values in the range of 5 – 55 mg/l are the most preponderant, while sulphate values varies from 1.1 to 38.2 mg/l with an average of 9.0 mg/l, and high at Soda camp. Consequently sulphate is within the WHO limit of 250 mg/l. Fluoride ranges between 0.01 to 0.87 mg/l with an average concentration of 0.31 and low stdev of 0.22. Nitrate ranges from 1.23 – 15.21 mg/l with a mean of 7.11 and stdev of 4.19. The average value is within the acceptable limit of WHO of 50 mg/l. Spatial distribution of nitrate in the study area in Figure 5 shows relatively high closures in Ore and Orisunmibare (above 13.0mg/l). Sodium, Calcium, Magnesium, and Potassium vary from 3.5 – 55.5 mg/l (av. 23.22 mg/l), 2.36 – 36.8 mg/l (av. 10.52 mg/l), 1.24 – 33.5 (av. 9.87 mg/l), and 1.42 – 14.25 mg/l (av. 5.77mg/l) respectively. Heavy metal concentrations of manganese and iron in the water range from 0.0 to 0.03 mg/l (av. 0.01 mg/l) and 0.0 to 0.03 mg/l (0.01 mg/l). These concentrations of the cations and heavy metals are very low and are within the standard of WHO.

However spatial map of sodium/potassium shows corresponding trend of the ions enrichment in the study area (Fig. 5). The total hardness of the water varies between 40 – 119 mg/l (av. 74.5 mg/l) and stdev of 20.4. The hardness water in Ore is high (> 100 mg/l) and account for just 10 % of the area (Fig. 5). Lead, arsenic, and mineral oil are the major toxic chemicals and contaminants observed in the samples water with concentrations ranging from 0.001 – 0.01 mg/l. The concentrations of these contaminants are within the permissible of 0.01 specified by WHO. This contaminants are noticeable around Ore, Kajola, and Odigbo town which have experienced influx of petrochemical companies and depots.

The biological test recorded E-Coli of 0 Cfu/100 ml and total bacteria count ranging from 0 – 13 (av. 5.45). The values are less than 3 Cfu/100 ml and 10 Cfu/100 ml specified for total coliform and E-Coli respectively. However no trace of *Enterococcus Faecalis* was found in the samples. The values of water quality index varies from 37.06 to 140.20 (Fig. 5). Excellent water types (WQI of 0-50) account for 10 % of the study area including Soda camp and Ore; Good water (WQI of 50-75) accounts for 70 % of the study area; Fair water (WQI of 75-100) common in Ore, Olowo, Olorunsogo account for 12 % of the area, while Bad water (WQI > 100) account 8 % and covers Omotoso, Ore, and Orisunmibare.

Correlation Analyses and Principal Components

The result of correlation analysis using Pearson correlation in Table 4 shows strong positive correlation exists between some of the chemical parameters; pH and Cl ($r = 0.80$), pH and TDS ($r = 0.53$), EC and total hardness ($r = 0.51$), TDS and Nitrate ($r = 0.57$), HCO_3 and NO_3 ($r = 0.64$), Mg and NO_3 ($r = 0.65$), HCO_3 and TDS ($r = 0.69$), Mg and TDS ($r = 0.55$), Fe and TDS ($r = 0.75$), Fe and Na ($r = 0.71$) and Na and EC ($r = 0.60$). The strong positive correlation that existed among these chemical parameters is an indication of similar source. The weak positive correlation between nitrate and chloride ($r = 0.21$) is a clear indication of uncommon anthropogenic source [34].

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 five components analysis (Table 5). The principal component 1 (PC-1) has an eigen value of 2.866 which accounts for 20.5 % of the total variance in the groundwater. This factor is strongly and positively loaded with parameters such as nitrate, manganese, TDS, bicarbonate, and magnesium. 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 are organic matter degradation/anthropogenic pollution. The PC-2 has an eigen value of 2.704 which accounts for 19.3 % of the total variance. This factor is strongly and positively loaded with the following parameters; TDS, calcium, iron, and sodium. This factor could be as a result of weathering and anthropogenic pollution. PC-3 has an eigen value of 1.955 which account for 13.947 % of the total variance. This factor is strongly and positively loaded with pH and Cl, which be result of mixing of saline with fresh water and anthropogenic contamination. The PC-4 has an eigen value of 1.815 with total variance of 12.96 %. Hardness and EC are the major parameters strongly and positively loaded with this factor. PC-5 has an eigen value of 1.888 which accounts for 8.48 % of the total variance.

Only sulphate is strongly and positively associated with this factor. Therefore PC-4 and -5 share the same process of mineral dissolution or precipitation due to contributions from rock-water interactions. The physico-chemical analysis of groundwater samples indicates that the dominant major cations are in decreasing order; Na^+ , Ca^{2+} , Mg^{2+} , K^+ and the dominant anions are HCO_3 , Cl^- , SO_4^{2-} , NO_3^- .

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

Location	East	North	Well No.	Temp (°C)	EC (µS/cm)	Turbidity (NTU)	Colour	Odour	Taste	Appearance
LAGOS – ORE RD	667564	728709	1	25.2	260	3.9	Colourless	unobjectionable	Tasteless	Clear
KAJOLA	670613	732276	2	25.3	340	4.3	Colourless	unobjectionable	Tasteless	Clear
OKE ALAFIA	671833	736795	3	25.2	180	3.2	Colourless	unobjectionable	Tasteless	Clear
SODA CAMP	678541	735606	4	25.2	165	2.5	Colourless	unobjectionable	Tasteless	Clear
ODIGBO	695618	745357	5	25.3	260	2.9	Colourless	unobjectionable	Tasteless	Clear
	698363	745357	6	27.2	320	3.4	Colourless	unobjectionable	Tasteless	Clear
	701107	745357	7	27.6	420	1.5	Colourless	unobjectionable	Tasteless	Clear
	699582	743930	8	26.4	154	0.9	Colourless	unobjectionable	Tasteless	Clear
	697448	742741	9	25.1	210	1.2	Colourless	unobjectionable	Tasteless	Clear
	702327	741552	10	25.2	265	3.2	Colourless	unobjectionable	Tasteless	Clear
	713305	745595	11	25.2	247	2.4	Colourless	unobjectionable	Tasteless	Clear
ORE	697753	739649	12	25.5	541	5.8	Colourless	unobjectionable	Tasteless	Clear
	696228	737984	13	25.3	587	5.9	Colourless	unobjectionable	Tasteless	Clear
	697143	737271	14	25.2	623	5.2	Colourless	unobjectionable	Tasteless	Clear
	696228	736082	15	25.5	390	4.0	Colourless	unobjectionable	Tasteless	Clear
	694093	736082	16	25.2	674	5.4	Colourless	unobjectionable	Tasteless	Clear
	692264	737984	17	25.2	410	4.5	Colourless	unobjectionable	Tasteless	Clear
	690129	736557	18	25.2	420	2.5	Colourless	unobjectionable	Tasteless	Clear
OUT	708730	736557	19	25.2	258	3.4	Colourless	unobjectionable	Tasteless	Clear
	709340	735844	20	25.2	269	2.8	Colourless	unobjectionable	Tasteless	Clear
	712085	737271	21	25.3	452	4.4	Colourless	unobjectionable	Tasteless	Clear
	712390	735844	22	25.2	120	2.2	Colourless	unobjectionable	Tasteless	Clear
OLORUNSOGO	715744	734179	23	25.2	187	1.7	Colourless	unobjectionable	Tasteless	Clear
	715643	733228	24	25.3	125	1.6	Colourless	unobjectionable	Tasteless	Clear
	714829	731563	25	25.2	231	1.1	Colourless	unobjectionable	Tasteless	Clear
	718184	733701	26	25.2	230	2.1	Colourless	unobjectionable	Tasteless	Clear
ORE –OKITIPUPA RD	689824	733941	27	25.2	210	4.4	Colourless	unobjectionable	Tasteless	Clear
	688909	733941	28	25.2	350	3.9	Colourless	unobjectionable	Tasteless	Clear
	691349	734417	29	25.3	385	3.4	Colourless	unobjectionable	Tasteless	Clear
	685555	733941	30	25.2	527	5.2	Colourless	unobjectionable	Tasteless	Clear

3.3 Groundwater Classification

Piper trilinear plot [35] was used in classifying the groundwater type (Fig. 6) hydrogeochemical regime of the study area by plotting the major cations and anions in a piper trilinear diagram. This diagram reveals similarities and difference among groundwater samples because those with similar qualities will tend to plot together as groups.

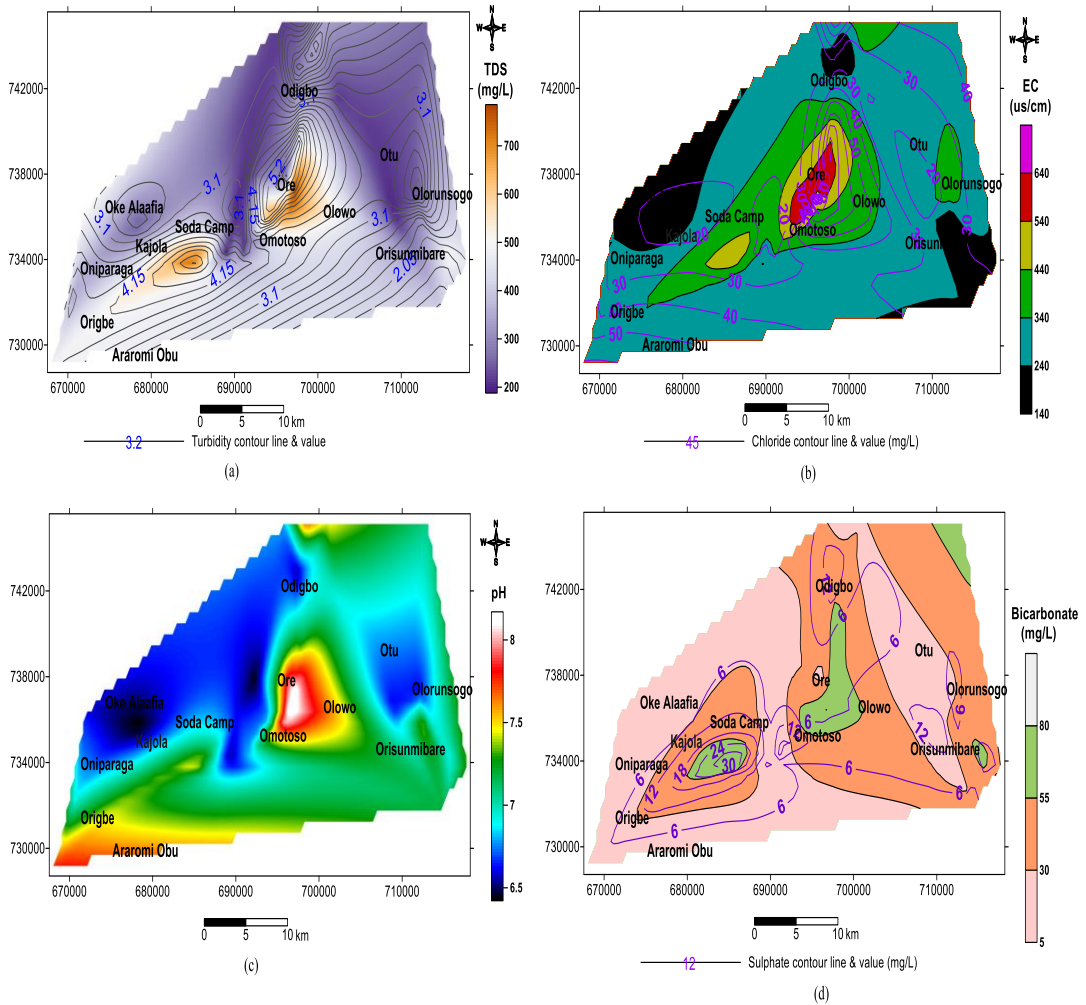


Fig. 4. Spatial Distribution of (a) TDS/Turbidity (b) EC/Chloride (c) pH (d) Bicarbonate/Sulphate

Table 2. Summary of the Analyzed Chemical Parameters

Well No.	pH	Cl ⁻ (mg/L)	Ca Hardness (mg/L)	Mg Hardness (mg/L)	Total Hardness (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	Mn (mg/L)	TDS (mg/L)	HCO ₃ ⁻ (mg/L)	Mg ²⁺ (mg/L)	Ca ²⁺ (mg/L)	Na ⁺ (mg/L)	Fe ²⁺ (mg/L)	Fl ⁻ (mg/L)	K (mg/L)
1	7.9	65.5	50	23	73	1.2	6.22	0.02	495	12	8.12	5.23	44.5	0.01	0.12	3.20
2	6.9	30.1	42	24	66	2.5	2.56	0.01	350	8	11.32	5.21	26.5	-	0.30	4.99
3	6.6	23.3	24	16	40	3.4	4.87	0.00	555	16	3.25	2.36	33.2	0.01	0.08	3.34
4	6.4	14.5	35	47	82	1.2	5.69	0.01	230	22	14.25	6.65	14.4	-	0.04	1.42
5	6.8	28.0	38	61	99	5.9	6.23	0.02	215	34	6.98	6.31	12.5	-	0.01	4.50
6	7.8	74.4	22	48	70	5.4	4.12	0.03	236	21	5.47	2.58	5.9	-	0.36	4.22
7	7.5	38.8	32	22	54	10.2	9.40	0.01	340	29	12.45	2.59	9.8	-	0.57	2.69
8	7.0	25.3	27	55	82	9.5	7.44	0.01	350	33	5.66	7.54	6.5	0.01	0.25	2.87
9	6.5	22.1	31	36	67	18.5	6.33	0.01	258	44	8.87	7.25	12.3	-	0.12	2.86
10	6.9	18.6	36	18	54	2.6	1.23	0.01	210	20	7.58	6.36	10.4	-	0.08	5.10
11	7.1	46.7	18	65	83	9.4	8.36	0.00	260	70	2.36	9.87	14.8	-	0.22	4.10
12	7.2	85.1	22	75	97	3.5	3.44	0.02	444	74	2.22	15.25	3.5	-	0.87	3.66
13	7.9	44.5	24	95	119	3.5	4.25	0.01	250	21	4.25	13.77	52.3	0.01	0.25	8.94
14	8.2	85.2	60	23	83	5.8	15.21	0.01	810	66	26.21	25.32	50.5	0.03	0.60	4.87
15	8.2	81.4	62	20	82	3.4	12.34	0.02	720	87	17.02	18.20	45.3	0.03	0.58	3.33
16	6.8	24.2	52	56	108	1.5	10.11	0.03	690	68	15.32	23.21	42.8	0.02	0.44	4.32
17	6.4	20.4	40	41	81	1.1	4.25	0.02	222	28	8.25	15.25	22.5	0.01	0.32	8.64
18	6.6	18.5	22	24	46	2.2	3.66	0.00	195	15	2.36	11.32	44.3	0.01	0.25	6.21
19	6.6	12.5	38	28	66	10.2	9.89	0.00	198	9	1.24	36.80	9.8	-	0.24	3.21
20	6.8	20.4	48	32	80	18.7	5.36	0.00	201	8	6.98	3.33	19.5	-	0.02	4.87
21	6.6	21.5	32	22	54	3.5	10.47	0.03	252	25	11.84	8.74	24.8	-	0.03	4.45
22	7.4	28.8	23	32	55	4.8	14.25	0.03	316	48	12.40	9.58	17.9	-	0.25	11.32
23	6.9	34.3	24	25	49	15.4	13.99	0.03	520	69	33.50	2.41	13.2	0.01	0.58	10.26
24	7.0	22.2	51	29	80	11.3	12.35	0.01	440	44	8.77	4.40	12.4	0.01	0.35	14.25
25	7.2	23.7	42	15	57	3.5	8.87	0.00	410	32	9.65	2.36	10.2	0.01	0.11	9.98
26	7.4	33.2	22	44	66	9.9	2.36	0.00	449	20	5.98	8.87	9.8	0.01	0.30	11.40
27	6.6	22.9	26	32	58	2.5	1.87	0.00	412	25	7.60	10.25	8.6	0.01	0.21	8.62
28	6.5	18.5	34	27	61	16.6	1.28	0.02	122	11	6.02	7.87	7.8	-	0.54	4.28
29	6.8	16.4	38	66	104	23.4	2.25	0.02	185	13	3.25	3.21	42.4	0.02	0.36	3.34
30	7.5	26.6	47	62	109	38.2	12.33	0.02	780	88	11.90	15.23	55.5	0.02	0.58	3.85
WHO	8.5	250	-	20	500	250	50	0.4	500	120	50	75	200	3	1.5	12
Min	6.4	12.5	18	15	40	1.1	1.23	0	122	8	1.24	2.36	3.5	0	0.01	1.42
Max	8.2	85.2	62	95	119	38.2	15.21	0.03	810	88	33.5	36.8	55.5	0.03	0.87	14.25
Mean	7.08	35.17	35.69	39.78	74.50	9.00	7.11	0.01	377	36.13	9.87	10.52	23.22	0.01	0.31	5.77
S.D.	0.53	21.75	12.09	20.11	20.40	8.27	4.19	0.01	189	24.63	6.97	7.89	16.41	0.01	0.22	3.01

Table 3. Summary of the Analyzed Toxic Chemicals and Contaminants

Well No.	Toxic Chemicals							Contaminants					Microbiological analysis	
	Lead (mg/L)	Cyanide (mg/L)	Cadmium (mg/L)	Arsenic (mg/L)	Barium (mg/L)	Mercury (mg/L)	Pesticide (mg/L)	Mineral oil (mg/L)	Ammonia (mg/L)	Phenol (mg/L)	Detergent (mg/L)	Radionuclides (Bq/L)	Total Bacteria count	E. Coli
1	0.008	ND	NL	0.004	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	12	0
2	ND	ND	NL	0.010	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	8	0
3	0.007	ND	NL	ND	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	5	0
4	0.004	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	8	0
5	0.001	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	8	0
6	0.010	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	4	0
7	0.002	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	3	0
8	0.005	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	1	0
9	0.002	ND	NL	ND	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	1	0
10	0.001	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	5	0
11	0.001	ND	NL	ND	ND	ND	NIL	0.003	ND	NIL	NIL	NIL	12	0
12	0.001	ND	NL	0.006	ND	ND	NIL	0.002	ND	NIL	NIL	NIL	13	0
13	ND	ND	NL	ND	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	8	0
14	ND	ND	NL	0.001	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	12	0
15	ND	ND	NL	0.003	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	10	0
16	ND	ND	NL	0.001	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	5	0
17	ND	ND	NL	0.003	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	8	0
18	ND	ND	NL	ND	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	1	0
19	ND	ND	NL	0.001	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	0	0
20	ND	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	0	0
21	ND	ND	NL	0.001	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	0	0
22	0.006	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	0	0
23	0.005	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	1	0
24	0.003	ND	NL	ND	ND	ND	NIL	NIL	ND	NIL	NIL	NIL	8	0
25	0.003	ND	NL	ND	ND	ND	NIL	0.002	ND	NIL	NIL	NIL	1	0
26	0.003	ND	NL	ND	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	12	0
27	0.001	ND	NL	ND	ND	ND	NIL	0.002	ND	NIL	NIL	NIL	5	0
28	0.001	ND	NL	0.007	ND	ND	NIL	0.001	ND	NIL	NIL	NIL	1	0
29	0.009	ND	NL	0.007	ND	ND	NIL	0.005	ND	NIL	NIL	NIL	5	0
30	0.008	ND	NL	0.006	ND	ND	NIL	0.005	ND	NIL	NIL	NIL	12	0
WHO, Standard	0.01	0.01	0.003	0.01	0.05	0.00	0.005	0.01	0.05	0.001	0.01	0.1	0	0

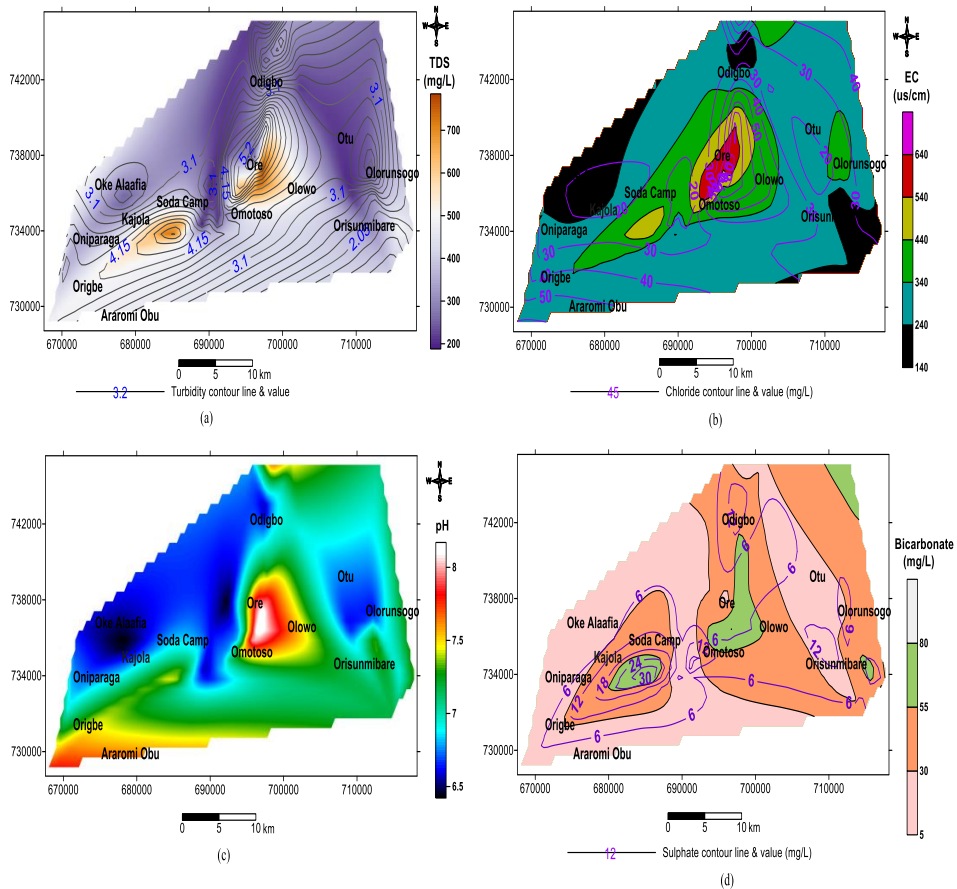


Fig. 4. Spatial Distribution of (a) TDS/Turbidity (b) EC/Chloride (c) pH (d) Bicarbonate/Sulphate

The dominant groundwater facies revealed in this study are the non-carbonate alkali (primary salinity) exceeds 50 % (zone 7); and transition zone with no one cation-anion pair exceeds 50 % (zone 9). Zone 7 means primary salinity i.e combined concentrations of alkali metals, sulfate and chloride are greater than 50 percent of the total meq/l. Very concentrated waters of this hydrochemical facies are considered brackish or (in extreme cases) saline. Zone 9 implies that no specific cation-anion pair exceeds 50 percent of the total dissolved constituent load. Such waters could result from multiple mineral dissolution or mixing of two chemically distinct ground-water bodies. Na, Ca, HCO₃, and Cl are the dominant cations and anion occurring in the waters. Hence, the area is dominated by alkali metal/alkaline earth-bicarbonate groundwater facies.

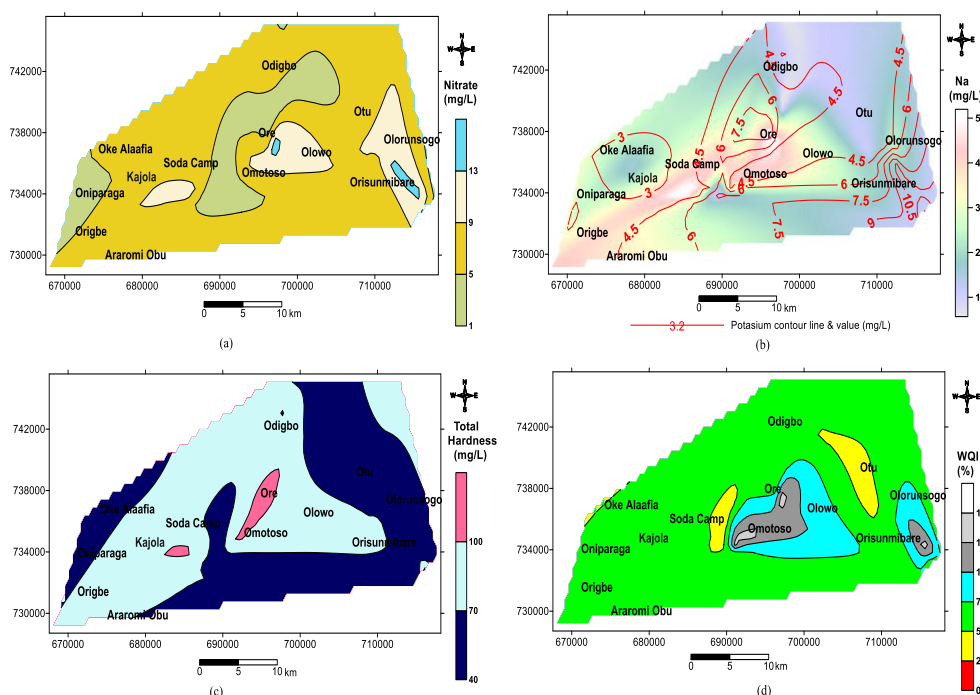


Fig. 5. Spatial Distribution of (a) Nitrate (b) Na/K (c) Total Hardness (d) Water Quality Index (WQI)

This confirms that the groundwater contributions of alkaline earth metals (Ca + Mg) and alkali metals (Na + K) and more of weak acids (HCO_3) than strong ones ($\text{SO}_4 + \text{Cl}$). It has been revealed that the hydrogeochemistry of the groundwater systems is influenced by the hydrogeological setting, geology, chemical weathering, ionic exchange, and agricultural inputs. From the Gibbs [36] analysis/diagram (Fig. 7), evaporation, rock–water interaction, and precipitation are the dominant processes in the hydrogeochemical evolution of the groundwater samples (Fig. 7a&b). Since the study area is also dominated by silicate rocks and minerals, the silicate weathering process is more than carbonic weathering (Fig. 7c).

3.4 Water Quality Studies for Irrigation

Electrical Conductivity: The electrical conductivity of the water ranges from 120 to 674 $\mu\text{s}/\text{cm}$ with an average of 331 $\mu\text{s}/\text{cm}$ which corresponds to moderate (medium salinity). However, from the map, the water in the study area shows variation of low salinity to medium salinity. However the area is generally of low salinity (95 % coverage) except small closure of high EC observed in Ore area.

Na Percentage: The structure of the soil is considerably affected by the presence of Sodium. Na concentration is important in classifying water for irrigation purposes.

The % Na of the samples varies between 20.67 and 81.86 and an average of 46.10. This suggests suitable irrigation water since the mean value is less than 60 %. Figure 8(a) shows that the area generally falls within “permissible irrigation rating” and occupies about 65%, while “Good” and “Doubtful” account for 20 % and 15 % respectively of the study area. Excess sodium concentration in groundwater produces the undesirable effects because sodium reacts with soil to reduce its permeability and support little or no plant growth. Higher Na% in Omotoso, Soda camp and parts of Ore may be dissolution of minerals from lithological composition, and the addition of chemical fertilizers by the irrigation waters [37].

Sodium Absorption Ratio (SAR): The important chemical parameter for estimating the degree of suitability of water for irrigation as sodium content or alkali hazard for crops, which is expressed in sodium adsorption ratio (SAR). SAR is calculated from the ratio of sodium to calcium and magnesium. Calcium and magnesium ions are important since they are tending to counter the effect of sodium. Higher concentration of SAR leads to breakdown in the physical structure of the soil. Sodium is adsorbed and become attached to soil particles. The soil then become hard and compact when dry and impervious to water penetration. Sodium replacing adsorb calcium and magnesium is a hazard as it causes damage to the soil structure. The degree to which irrigation water tends to enter into cation exchange reaction in soil can be indicated by the SAR. The SAR values of the studied water samples vary from 0.22 to 3.99 with a mean of 1.39 with relatively low SAR in the eastern flange of the study area (Fig. 8b). The values are within 0 - 10 specified by Singh [38] as excellent water for irrigation purpose. There is a close relationship between SAR values in irrigation water and the extent to which Na is absorbed by soils. If water used for irrigation is high in Na and low in Ca, the ion-exchange complex may become saturated with Na, which destroys soil structure, because of dispersion of clay particles. As a result, the soils tend to become deflocculated and relatively impermeable. Such soils can be very difficult to cultivate

Table 4. Correlation Matrix of Chemical Parameters in Water Samples from the Study Area

Parameter	pH	Cl	Hardness	SO ₄	NO ₃	Mn	TDS	HCO ₃	Mg	Ca	Fe	K	Na	EC
pH	1													
Cl	0.800	1												
Hardness	0.272	0.223	1											
SO ₄	-0.033	-0.224	0.255	1										
NO ₃	0.371	0.213	0.037	0.161	1									
Mn	0.168	0.246	0.224	0.046	0.300	1								
TDS	0.534	0.471	0.188	0.090	0.566	0.142	1							
HCO ₃	0.385	0.465	0.351	0.218	0.642	0.344	0.687	1						
Mg	0.258	0.223	-0.093	0.038	0.645	0.409	0.552	0.489	1					
Ca	0.126	0.172	0.312	-0.074	0.309	-0.019	0.296	0.308	0.040	1				
Fe	0.462	0.318	0.344	0.123	0.370	0.084	0.749	0.467	0.400	0.339	1			
K	0.061	-0.147	-0.155	-0.094	0.166	-0.042	0.043	0.029	0.157	-0.142	0.068	1		
Na	0.398	0.199	0.402	0.113	0.231	0.129	0.492	0.216	0.187	0.291	0.707	-0.140	1	
EC	0.320	0.371	0.518	0.013	0.065	0.282	0.341	0.313	0.121	0.488	0.428	-0.248	0.595	1

Table 5. Varimax orthogonal rotated factor loadings from PCA of the Analyzed parameters

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
pH	0.198	0.332	0.843	0.000	0.005
Chloride	0.212	0.117	0.864	0.217	-0.223
Hardness	-0.007	0.387	0.169	0.608	0.342
Sulphate	0.136	0.149	-0.226	0.089	0.850
Nitrate	0.842	0.241	0.026	-0.125	-0.008
Manganese	0.592	-0.308	0.217	0.455	0.149
TDS	0.556	0.611	0.342	-0.088	0.005
Bicarbonate	0.731	0.282	0.233	0.170	0.117
Mg	0.827	0.089	0.119	-0.168	-0.012
Ca	0.221	0.549	-0.239	0.415	-0.474
Fe	0.299	0.816	0.242	-0.029	0.098
K	0.156	0.048	0.007	-0.655	0.009
Na	0.065	0.762	0.185	0.236	0.133
EC	0.105	0.493	0.191	0.666	-0.104
Eigen value	2.866	2.704	1.955	1.815	1.188
% Variance	20.475	19.313	13.964	12.965	8.484
Cumulative % variance	20.475	39.788	53.752	66.717	75.201
Interpretation of process	Organic matter degradation/ anthropogenic pollution	Weathering and anthropogenic pollution	Mixing of saline and fresh water and anthropogenic pollution	Mineral dissolution	Mineral precipitation

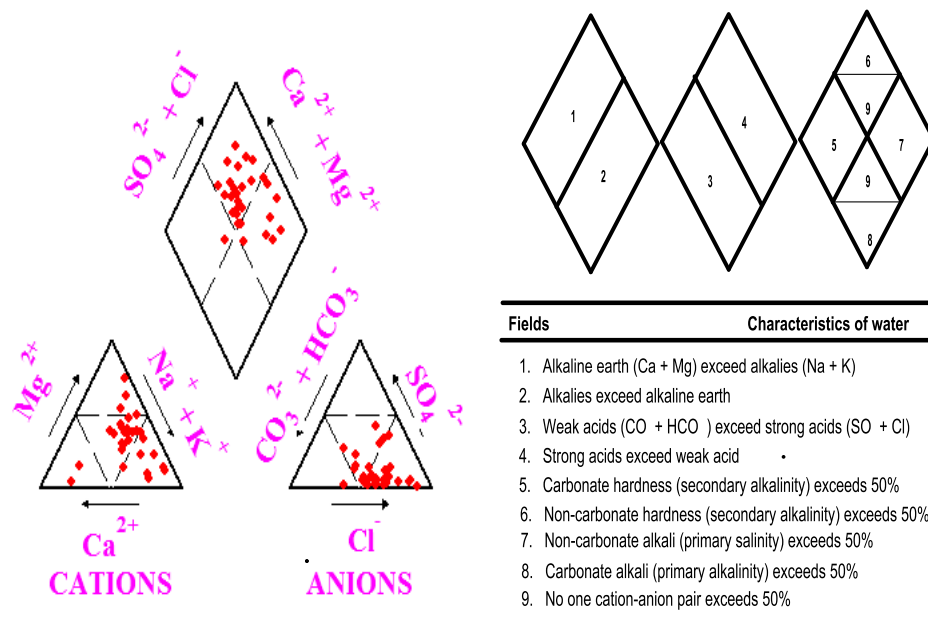


Fig. 6. Piper Trilinear diagram of groundwater in the study area with dominant zones of 7 and 9.

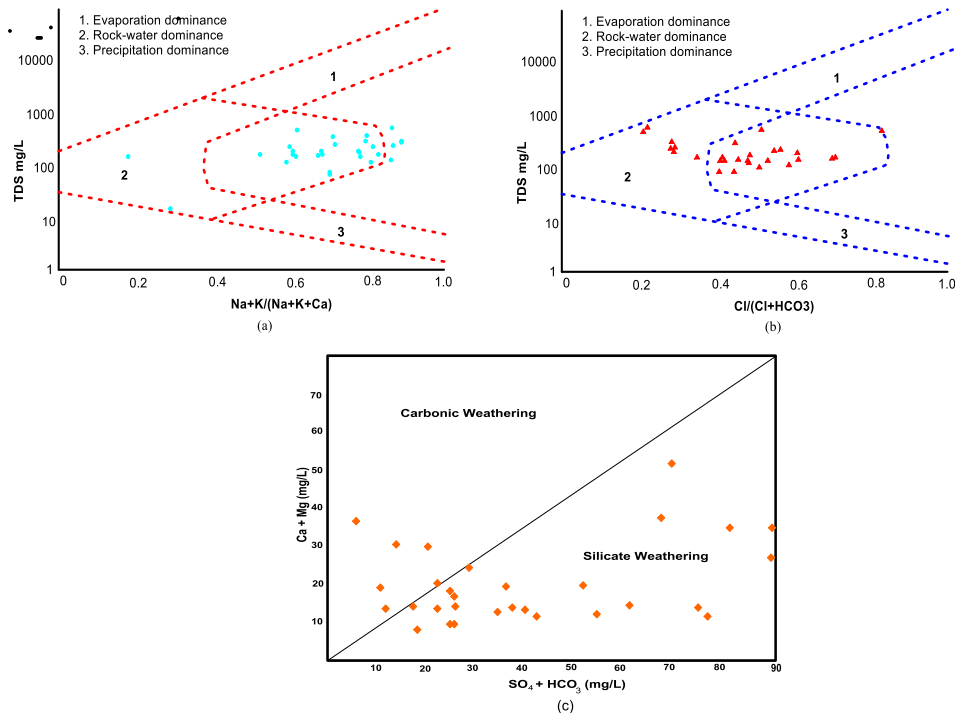


Fig. 7. (a) Gibbs diagram for cations (b) Gibbs diagram for anions (c) Scatter plot for carbonate weathering versus silicate weathering

Permeability Index: Permeability index is a major function, which has influence over the Utility of water for agriculture. 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 an excellent quality of water for irrigation. The PI value 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. The calculated PI value ranges from 34.27 to 128.90 and an average of 79.56 meq/l. According to Figure 8c, 68 % of area falls within class I while 32 % falls under class II category.

Equivalent Salinity Concentration: The equivalent salinity values range from minimum of 1.24 mg/l (Olorunsogo) to maximum of 5.68 mg/l (Ore) with a mean of 2.50 mg/l. The ESC is generally low (less 5 mg/l) across the study area. The equivalent salinity map (Fig. 8d) shows that high values were obtained from Ore, Omotoso, Olowo, and extended to Kajola down to Onigbe.

Residual Sodium Carbonate (RSC): The Residual Sodium Carbonate (RSC) values ranges between -2.34 and $+0.46$, with an average of -0.70 (Table 6) which agrees with less than 2.5 specified by Singh [38] for the purpose of irrigation. The excess sum of carbonate and bicarbonate in groundwater over the sum of calcium and magnesium influences the suitability of groundwater for irrigation. When the excess

carbonate concentration becomes too high, the carbonate combines with calcium and magnesium to form solid materials which settles out of the water. 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.

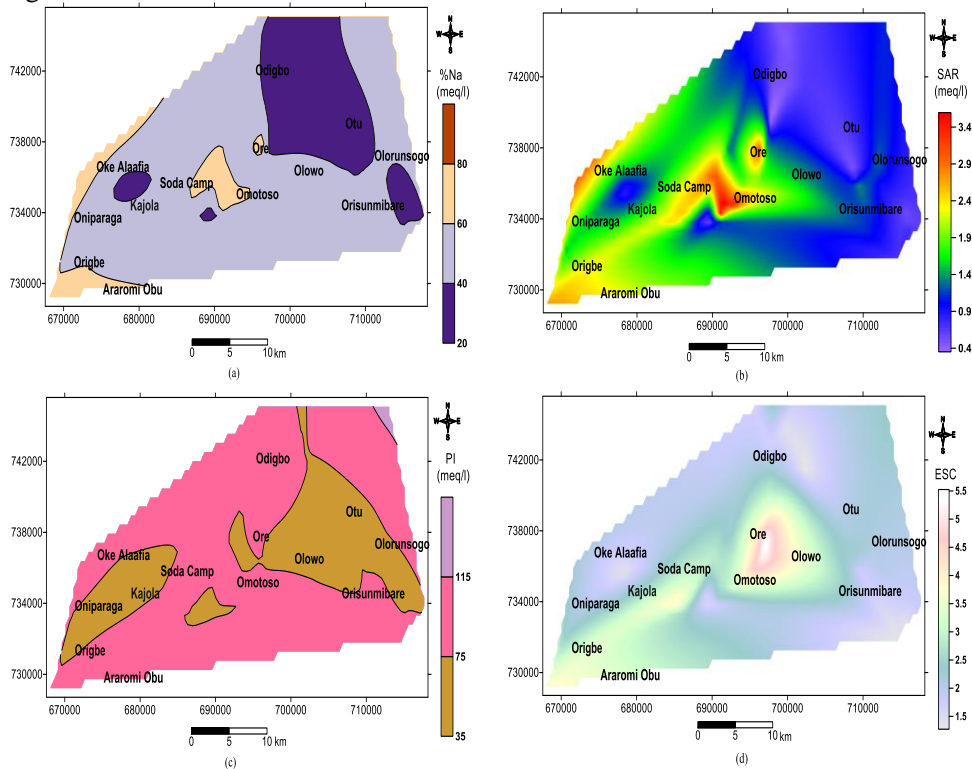


Fig. 8. Spatial Distribution of (a) %Na, (b) SAR, (c) PI, and (d) ESC.

Magnesium ratio and Kelly's ratio: Magnesium ratio (MR) is the ratio of magnesium (Mg^{2+}) to alkaline earths ($Ca^{2+} + Mg^{2+}$) and expressed in percentage (%). Magnesium damages soil structure, when water possesses more Na^+ and high salinity. In equilibrium more Mg^{2+} can affect soil quality by rendering it alkaline, thus it affects crop yields [30, 38]. The MR of the water samples varies from 5.26 to 77.94 and average of 46.90 (Table 6) suggesting a suitable water for irrigation. 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. The KR values calculated for the water samples is in between 0.16 and 3.31, with a mean of 0.94 and still within the suitable range of less than 1.

Chloro-alkaline indices (CA): This is used in understanding the chemical composition of groundwater along its flow path. Subba Rao et al [33] suggested two chloro-alkaline indices (CA1, CA2) for the interpretation of ion exchange between groundwater and host environment.

Table 6. Summary of Calculated Chloro-alkaline indices and irrigation indices

Well No.	CA1	CA2	RSC	MR	KR
1	0.37	1.25	-0.73	61.91	1.08
2	0.29	0.66	-1.06	68.17	0.97
3	-0.28	-0.27	-0.12	69.42	2.75
4	0.10	0.05	-1.14	77.94	0.42
5	0.71	0.43	-0.33	54.58	0.61
6	0.98	2.38	-0.23	67.75	0.44
7	0.82	0.65	-0.68	35.79	0.37
8	0.86	0.43	-0.30	35.31	0.34
9	0.57	0.18	-0.37	46.85	0.49
10	0.72	0.56	-0.61	34.27	0.48
11	0.77	0.41	0.46	28.27	0.94
12	1.00	1.05	0.27	19.35	0.16
13	0.03	0.04	-0.69	33.72	2.19
14	0.46	0.45	-2.34	43.05	0.64
15	0.48	0.38	-0.88	40.65	0.85
16	-0.59	-0.18	-1.30	42.11	0.77
17	0.32	0.20	-0.98	37.14	0.68
18	-1.06	-0.94	-0.51	25.58	2.54
19	0.47	0.20	-1.79	5.26	0.22
20	0.28	0.18	-0.61	67.56	1.15
21	0.05	0.03	-1.00	59.07	0.77
22	0.77	0.33	-0.71	58.09	0.52
23	0.91	0.32	-1.75	65.82	0.2
24	1.08	0.36	-0.22	56.67	0.57
25	0.99	0.53	-0.39	57.08	0.49
26	1.05	1.08	-0.61	42.64	0.46
27	1.00	0.78	-0.73	45.11	0.33
28	0.81	0.52	-0.71	45.77	0.38
29	-1.38	-0.59	-0.21	52.53	3.31
30	-0.94	-0.18	-0.30	40.29	1.39
Min	-1.38	-0.94	-2.34	5.26	0.16
Max	1.08	2.38	0.46	77.94	3.31
Average	0.35	0.40	-0.70	46.90	0.94

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 CA1 and CA2 in the range of -1.38 to 1.08 (av. 0.35) and -0.94 to 2.38 (av. 0.40). Both indices have an average positive values, confirming predominant cation-anion exchange reaction (Table 6), in which ion exchange of Na^+ and K^+ from the water with Mg^{2+} and Ca^{2+} of the rocks. Wilcox's [39] diagram is adopted for the classification of groundwater for irrigation, wherein the EC is plotted against % Na. Data of the groundwater samples of the area are plotted in the Wilcox's diagram in Figure 9, all

the samples plotted within the “excellent. The agricultural yields are generally high in lands irrigated with waters belonging to excellent to good categories. This is probably due to the absence of excess sodium salts, which cause osmotic effects on soil-plant system. When the concentration of sodium is high in irrigation water, sodium ions tend to be adsorbed by clay particles, displacing Mg and Ca ions by base-exchange process. This exchange process of Na in water for Ca and Mg in soil reduces permeability and eventually results in soil with poor internal drainage [40].

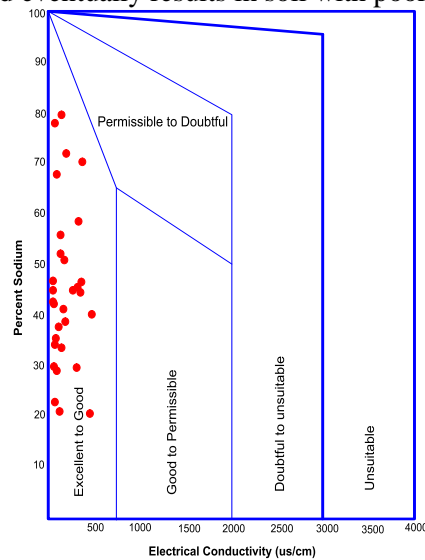


Fig. 9. Classification of the irrigation waters

4. Conclusion

The following main conclusions are drawn from the present study:

- (i) The different parameters analyzed were within the permissible limit recommended by World health organization. The WQI of water samples show a predominant Good water Type (WQI of 50-75) accounts for 70% of the study area.
- (ii) The chemical analysis of groundwater samples indicates that the dominant major cations are in decreasing order; Na^+ , Ca^{2+} , Mg^{2+} , K^+ and the dominant anions are HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- .
- (iii) The processes inferred from the five factors (PCA) are organic matter degradation, anthropogenic pollution, weathering, mixing of saline with fresh water, mineral dissolution and/or precipitation. The dominant groundwater facies revealed are the non-carbonate alkali (primary salinity) exceeds 50% (zone 7); and transition zone with no one cation-anion pair exceeds 50% (zone 9).
- (iv) Evaporation, rock-water interaction, and precipitation are the dominant processes in the hydrogeochemical evolution of the groundwater samples with the silicate weathering process more than carbonic weathering.
- (v) Based on irrigation indices, all the water samples are good/suitable for irrigation purposes with low equivalent salinity concentrate and moderate electrical conductivity.

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