Groundwater Evolution, Hydrochemical Facies and Quality Evaluation for Irrigation Use in Akure, Ondo State, Nigeria

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Abstract

Hydrochemical facies, groundwater evolution, and physicochemical reactions between soil or rock and water are of considerable importance when evaluating or predicting the nature of anthropogenic impacts on groundwater quality. In this respect a total of 67 ground water samples were collected randomly in Akure, southwestern, Nigeria from hand pump/dug wells and analyzed for major cations and anions. The domination of cations and anions was in the order of $Ca^{2+} > K^+ > Na^+ > Mg^{2+}$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ respectively. The pH and Eh of the water samples show an acidic condition, with low salinity hazard (generally less than 250 µS/cm). The Piper classification for hydrogeochemical facies indicates carbonate hardness (secondary alkalinity) exceeds 50% that is by alkaline earths and weak acids, with $Ca^{2+} + Mg^{2+} + HCO_3^-$ water-type. This also suggests a meteoric origin of water quality caused by rock-water interaction. The ratio of HCO_3^- and Cl$^-$ is greater than 1 and implies recharge area or upper water flow course of carbonate rocks (interaction of water with aquifer material). The Na$^+$:Cl$^-$ is less than 0.7 signifying loss of Na$^+$ through precipitation of evaporating water; the water is Ca^{2+} rich and Na$^+$ depleted with Mg^{2+}:Ca^{2+} less than 0.5 and Na$^+$:K$^+$ less than 15. The Na$^+$:Ca^{2+} (<1) indicates reverse ionic exchange. The Ca^{2+}:$SO_4^{2-} + HCO_3^-$ for the samples is less than 1.0 suggestive of flow of water through the normal hydrological cycle. The calculated range of values of sodium absorption ratio (1.89 - 26.42), permeability index (42.67 - 170.24), residue sodium carbonate (−1 to 5), magnesium ratio (4 - 53), Kelly ratio (0.04 - 0.84), percent sodium (0.41 - 3.45) suggest good water suitable for irrigation purposes. In addition, the Wilcox plot shows that 98% of the water samples belong to "good to permissible category" for irrigation use.

1. Introduction

Groundwater accounts for about 98 percent of the world's fresh water and is evenly distributed throughout the world. It provides a reasonably constant supply which is not completely susceptible to drying up under natural condition unlike surface water (Shitta, 2007; Fetter, 1993). All over the globe, groundwater has been a very good and important source of water supply for drinking, irrigation, municipal water supply, industrial purposes (Matthess, 1982). It is conveniently available at point of use and possesses excellent quality that requires little or no treatment in most cases. Therefore assessment of ground water for drinking, irrigation, and industrial has become a necessary and important task for present and future ground water quality management (Parker & Foster, 1986; Lloyd & Helmer, 1991) and policy makers, especially the Ondo State government, even as it calls for economy diversification to agriculture/irrigation farming, in order to reduce teeming unemployment rate among the youth in the State.

Ground water quality depends on the quality of recharged water, atmospheric precipitation, inland surface water and subsurface geochemical processes (Freeze & Cherry, 1979; Todd, 1980; Fetter, 1983). Temporal changes in the origin and constitution of the recharged water, hydrologic and human factors may cause periodic changes in ground water quality (Fetter, 1990; Price, 1985). The geology of a particular area has a great influence on quality of water and its environment (Srinivasamoorthy et al., 2008; Raju, 2012; Vasanthavigar et al., 2010). The quality of ground water varies due to a change in chemical composition of the underlying sediments and aquifer (Subba Rao, 2017; Coulibaly & Rodriguez, 2004; Backman et al., 1998). In Ondo State, modern civilization and urbanization, has consequently led to frequent discharging industrial effluent, domestic sewage and solid waste dump which could invariably cause ground water contamination (Thomson & Foster, 1986). The polluted water not only affects water quality but also threatens human health, economic development and social prosperity. Hencecontinuous monitoring/assessment of water quality in relation to various standards around the world has become imperative in determination of suitability of water for various purposes (Satheesh et al., 2017).

Over the past decade there has been tremendous increased research on groundwater quality evaluation in the area of irrigation and hydrochemical facies characterization (Singh et al., 2015; Siddiqui et al., 2005; Srinivasamoorthy et al., 2008; Jain et al., 2010; Alam et al., 2012; Raju et al., 2009; Raju et al., 2011). Singh et al. (2015) evaluated the quality of groundwater and its suitability for

domestic and irrigation uses in parts of the Chandauli-Varanasi region, Uttar Pradesn, India and concluded that Water Quality Index calculated exhibits poor quality in less percentage indicating the effective ion leaching, overexploitation and anthropogenic activities from discharge of effluents from agricultural and domestic uses in both seasons (pre and post monsoon). In addition, based on the classification of irrigation water according to sodium absorption ratio (SAR) and Permeability Index (PI) values, all the sample locations were suitable for irrigation purposes. Satheesh et al. (2017) also carried out groundwater quality assessment and hydrochemical facies evolution of Yeshwanthapur sub-basin, Marangal district, the study reveals that concentrations of the major ions and important physical parameters are within the permissible limits for irrigation SAR values ranged from 0.06 mg/l to 13.9 mg/l and the water falls in the class of "excellent to good category". Percent Sodium values indicate the most of groundwater samples belongs to very good to permissible category for irrigation on Wilcox diagram. Thus, the overall groundwater quality in the sub-basin was fresh and suitable for irrigation use. In this present study an assessment of the ground water quality in Akure metropolis is undertaken for irrigation. The objective is to study the hydrochemical facies, groundwater evolution, major geochemistry and evaluate water's suitability for irrigation purposes in line with the aspiration of the State Government to turn the state into industrial base (hub) and "food basket" of Nigeria.

Description of the Study Area

Akure falls within the basement complex region of Nigeria within Northings (790,796 - 809,322 mN and Eastings 733,683 - 752,092 mE, UTM Minna Zone 31) (Figure 1). It covers an aerial extent of about 320 km². The metropolis is located on a gently undulating terrain surrounded by isolated hills and inselbergs (Ojo et al., 2014). Topographic elevations (Figure 2) vary between 260 and 470 m above sea level (Ojo et al., 2014). The major river in Akure is river Ala and its tributaries
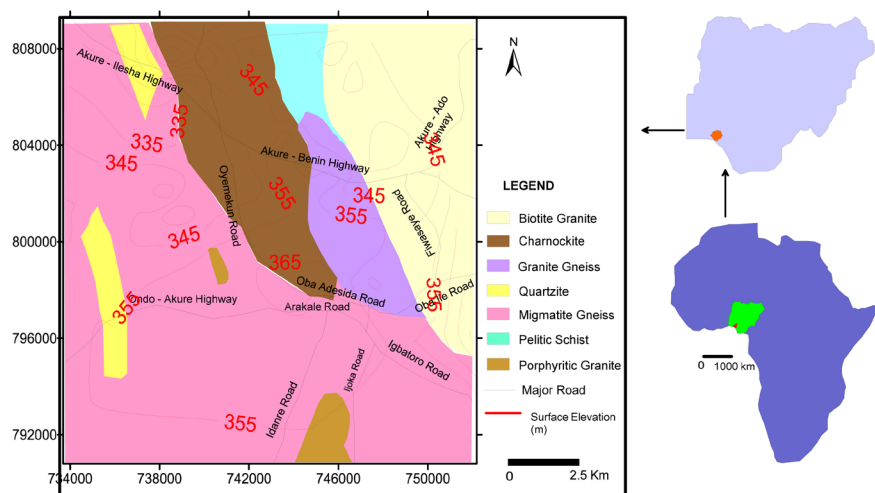

Figure 1. Location map of the study area on the map of Africa and Nigeria.
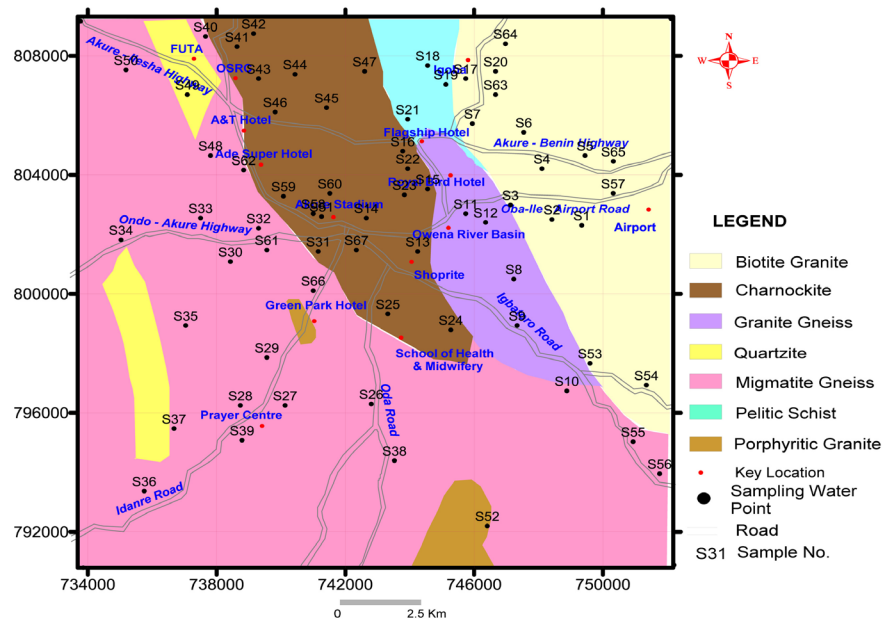
Figure 2. Base Map showing the Sample Nos. and Sampling Points on Geology.

such as Owuruwu river. Rivers such as Otenre river, Omi Atamo, are smaller rivers that serve as runoff in the town, which are tributaries of Ogbese river.

There are seven major different rock units in the area as shown in Figure 3, comprising of Migmatite-Gneiss, Quartzite, Charnokite, Biotite granite, Pelitic Schist, Granite Gneiss, and Granite. The Migmatite Gneiss occupies about 60% of the area with an intrusion of Quartzite and Biotite Granite in some places like Alagbaka-Oda road, Akure-Idanre road. The granite rocks which are member of the older granite suit occupy about 65% of the total area of Akure. Three principal petrographic varieties are recognized, the fine-grained biotite granite, medium to coarse grained, non-porphyritic biotite—hornblende granite and coarse—porphyritic biotite hornblende granite. The classification is based largely on the textural characteristics. Also three main textural types of charnockitic rocks are also distinguished in Akure. These are the coarse-grained variety, massive fine grained and the gneissic fine-grained types. Unlike most of the older granite, the charnokite rocks do not occur in form of smooth rounded boulders and only a few low hills all forming oval to sub-circular and elongated bodies. All the charnockitic in the region are dark-greenish to greenish-grey rocks with bluish quartz are greenish feldspars. The study area exhibits varieties of structures such as foliation, schistosity, folds, faults, joints and fractures. The groundwater in a typical basement complex area like the Akure Metropolis, is contained in two major aquifer units, namely weathered and fractured basement aquifers (Aniya & Shoeneick, 1992). The weathered layer aquifer is derived from chemical alteration processes while the fractured basement aquifer system is as a result of tectonic activities (Ojo et al., 2014). The weathered layer aquifer may occur singly or in combination with the fractured aquifer (Bayode et al., 2006). The direct exposure of the uppermost part of the vadose zone of the weathered layer
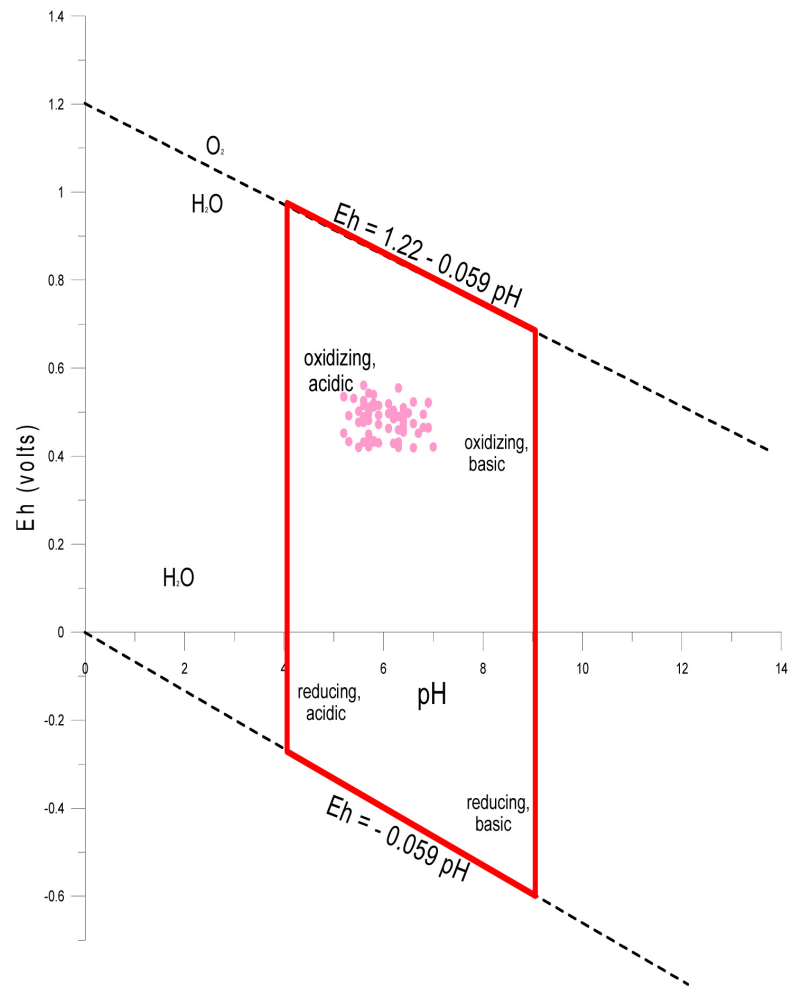
Figure 3. Framework of aqueous Eh-pH field showing a near oxidizing acidic condition for the sampled waters.

aquifer system makes it vulnerable to surface/near surface pollutants such as leachate from waste dump sites and flooding (Ojo et al., 2014).

2. Methodology/Procedures

Groundwater samples were collected at selected locations based on hydro-geomorphology and geology of the area (Driscoll, 1986; Hem, 1989) after hydrogeological investigations have been carried out to know the geochemical behavior (Scalf et al., 1981; Gibb et al., 1981). Consequently the map of the study area was first gridded into different zones (**Figure 2**) from which representative samples were collected and geo-referenced with the use of Global Positioning System (GARMIN 78 12-Channels). Sixty Seven (67) water samples were taken for a period of three (3) months. The samples were collected at depth levels (static water level) varying between 1.1 - 8.0 m and an average (avg.) of 3.7 m. The hydraulic head of the sampled wells ranges between 320.2 and 392.1 m and an average (avg.) of 345.6 m.

Physico-chemical parameters such as colour, turbidity, odour, taste, appear-

ance, temperature, oxidation potential, pH, total dissolved solid (TDS) and electrical conductivity (EC) were measured in the field by digital meters using the standard procedures (Scalf et al., 1981; Gibb et al., 1981). Sodium (Na^+) and potassium (K^+) were determined by using flame photometer. Calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), hardness, alkalinity and chloride (Cl^-) were analyzed by titrimetric method. Sulfate (SO_4^{2-}), and nitrate (NO_3^-) employed spectrophotometer model. The chemical data of groundwater samples are subjected to compute the ionic-balance-error between the total concentration of cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and total concentration of anions (HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^-) for testing accuracy of chemical analysis of each groundwater samples, before the interpretation of the chemical data is undertaken. The value of the ionic-balance-error is observed to be within the acceptable limit of ±10% (Domenico & Schwartz, 1990) using Equation (1).

$$IBE = \frac{(TCC + TCA)}{TCC - TCA} \times 100 \qquad (1)$$

where,

TCC = total concentration of cations

TCA = total concentration of anions

3. Results and Discussion

3.1. Physical and Chemical Parameters

The chemical composition of groundwater can be used to delineate the recharge and discharge areas on the basis of hydrogeochemical facies and genetic classification (Subba Rao, 2017; Domenico & Schwartz, 1990). The results of the physico-chemical parameters are presented in Table 1 to Table 2. The temperature of the groundwater varies from 25.9°C - 30.8°C with a mean of 27.9°C. This range of values shows a uniformly moderate temperature. All the water samples are colourless, odourless, and tasteless, with clear appearance. The turbidity of water ranges from 0.6 to 9.5 NTU and an average of 3.16 NTU. This indicates that they are characterized with less suspended matter such as clay, silt, fine fragments of organic matter, and similar material. The pH plays a vital role to react with acidic or alkaline. It is controlled by CO_2- CO_3^{2-}- HCO_3^- equilibrium (Subba Rao et al., 2002). The combination of CO_2 with H_2O (water) forms H_2CO_3 (carbonic acid), which affects the pH of water. Water can be classified as acidic and alkaline on the basis of pH, which varies from 1 to 14. The recorded pH varies from 5.2 - 7.8 in the groundwater. As per the classification of pH, the water is characterized by an acidic condition, as H^+ is more than OH^- in the water (Subba Rao, 2017).

The oxidation potential (Eh) shows a positive value (0.4190 - 0.5610 volts) which indicates that the water is an oxidizing type (Fetter, 1990). From Figure 3, it shows a near oxidizing acidic water. Total alkalinity (TA) is a measure of the capacity of water to neutralize acid in terms of calcium carbonate ($CaCO_3$). The TA is in between 40 - 340 mg/l (avg. 123.9 mg/l). The concentration of total

Table 1. Result obtained from the physical parameters measured/examined.

Well No.	Temp (°C)	pH	TDS	EC (μS/cm)	Eh (volts)	Turb. NTU
1	30.8	6.4	100	204	0.483	1.8
2	28.4	5.6	73	145	0.432	1.5
3	30.4	5.5	75	151	0.420	2.5
4	27.6	5.6	65	131	0.477	2.9
5	28.1	6.4	376	754	0.464	8.6
6	29.3	5.8	56	115	0.512	1.2
7	29.4	5.7	50	101	0.511	1.5
8	28.5	5.7	42	83	0.543	2.2
9	29.6	5.6	50	101	0.561	3.4
10	29.2	6.2	91	181	0.485	1.1
11	29.2	5.7	150	303	0.481	1.2
12	30.5	5.6	74	152	0.515	4.6
13	29.6	5.7	66	132	0.505	6.2
14	30.1	6.4	130	61	0.457	5.1
15	29.6	5.7	64	127	0.450	6.5
16	29.8	6.4	50	101	0.475	8.2
17	27.4	6.3	78	156	0.460	4.2
18	28.2	7.0	424	874	0.421	1.2
19	27.0	6.6	281	563	0.419	1.5
20	28.2	6.3	143	286	0.432	2.3
21	27.4	6.6	165	331	0.474	1.8
22	29.5	5.3	40	79	0.492	1.5
23	27.5	5.8	161	323	0.435	1.1
24	28.2	5.6	65	131	0.480	0.8
25	26.8	5.5	62	124	0.477	4.7
26	27.5	5.6	42	84	0.481	1.2
27	26.4	5.2	101	203	0.535	3.5
28	28.5	5.5	83	167	0.502	2.5
29	27.8	5.6	73	146	0.490	1.2
30	28.4	6.3	112	224	0.555	4.4
31	25.7	5.9	57	114	0.493	3.2
32	27.5	5.6	105	210	0.526	5.8
33	27.6	6.8	119	238	0.495	6.9
34	28.1	6.3	123	246	0.490	7.8
35	26.8	6.4	84	169	0.501	0.6
36	26.5	6.5	89	179	0.498	1.2
37	27.7	6.9	101	202	0.521	1.5
38	28.3	5.9	63	127	0.430	1.8
39	27.9	5.8	48	96	0.540	1.2

Continued

40	29.8	6.4	44	89	0.455	1.2
41	27.2	6.2	57	114	0.504	1.3
42	27.6	6.4	103	206	0.490	1.2
43	27.5	6.9	50	101	0.464	1.4
44	27.3	6.4	72	144	0.510	1.6
45	27.1	6.1	78	157	0.519	1.4
46	26.5	6.1	57	115	0.497	2.2
47	27.8	6.9	49	98	0.465	3.2
48	27.5	6.3	46	91	0.420	4.5
49	27.4	6.2	83	166	0.429	6.8
50	27.2	6.8	331	662	0.465	4.8
51	27.8	6.7	125	250	0.452	1.5
52	27.5	5.8	142	285	0.432	1.1
53	27.6	6.1	53	108	0.463	1.4
54	27.7	5.7	62	125	0.421	4.4
55	28.3	5.9	41	83	0.472	5.8
56	27.4	6.3	54	108	0.422	7.9
57	27.9	6.6	115	231	0.523	4.5
58	27.3	6.9	174	348	0.522	2.6
59	26.1	6.2	52	228	0.490	1.2
60	26.5	5.9	89	178	0.515	1.2
61	26.9	6.5	46	53	0.498	1.2
62	27.8	5.8	62	122	0.520	5.5
63	28.4	5.4	78	156	0.531	9.5
64	26.3	5.7	42	98	0.437	6.5
65	26.9	5.3	47	101	0.433	4.2
66	26.1	5.2	150	122	0.452	2.2
67	26.4	5.7	48	65	0.497	1.2
Min.	25.9	5.2	40	53	0.419	0.6
Max.	30.8	7.0	424	874	0.561	9.5
Average	27.9	6.0	96.7	189.8	0.481	3.16

Table 2. Summary of the analyzed chemical parameters.

Well No.	T.A	Acidity	T.H	HCO_3^-	Ca^{2+}	Mg^{2+}	Cl^-	Na^+	K^+	SO_4^{2-}	NO_3^-
1	180	360	228	219.5	52.5	5.72	49.7	5.4	10.5	3.2	1.1
2	210	220	10	120.1	23.3	0.9	5.5	2.5	2.3	0.9	0.9
3	150	200	20	142.2	14.5	0.8	15.5	2.8	4.5	1.2	0.8
4	40	260	55	123.4	21.2	2.2	20.5	2.9	9.5	2.5	4.5
5	340	380	392	214.8	60.9	19.5	74.5	4.2	7.8	4.5	1.3
6	60	280	88	73.2	10.0	3.8	17.7	3.0	5.7	6.0	4.5

Continued

7	85	210	65	54.5	11.2	2.8	20.5	2.8	10.2	5.5	3.2
8	60	260	84	73.2	13.4	2.9	14.2	2.4	8.8	12.5	0.9
9	60	460	68	73.2	10.9	2.5	12.4	2.1	9.8	7.5	1.1
10	90	320	68	63.4	22.1	8.2	24.3	2.2	4.6	2.4	3.5
11	120	250	112	51.2	22.3	4.4	18.9	3.4	6.8	0.9	8.2
12	140	180	84	170.8	15.1	2.7	23.8	4.3	7.0	13.5	3.4
13	180	290	45	111.2	11.4	3.3	25.5	10.1	9.2	3.3	3.2
14	140	260	52	170.8	20.9	0.9	33.7	2.4	4.5	5.5	5.9
15	140	240	42	85.3	9.5	1.1	14.2	9.8	4.6	1.2	8.2
16	100	200	88	122.1	16.8	2.9	14.2	2.0	4.4	8.5	7.4
17	140	200	152	170.8	25.2	5.2	17.5	2.8	7.3	12.2	0.9
18	60	380	96	73.2	25.3	1.9	28.4	2.6	11.8	4.7	0.8
19	40	320	83	40.3	20.2	1.2	30.2	6.5	15.2	4.1	0.9
20	70	300	62	20.3	11.2	1.3	33.2	8.8	12.2	2.3	1.1
21	260	340	264	317.2	57.9	7.9	10.6	5.2	7.9	2.5	1.2
22	100	400	60	122.1	11.7	1.9	12.4	10.2	6.1	13.7	1.9
23	190	380	48	68.3	14.5	1.4	42.2	2.9	4.4	3.3	2.2
24	60	220	84	73.2	31.6	0.8	14.2	11.5	6.0	4.5	1.5
25	80	410	92	44.9	16.5	1.1	32.1	14.2	6.2	9.9	3.1
26	40	400	38	48.8	15.4	0.9	12.3	3.8	8.7	9.5	0.8
27	200	360	116	244.0	25.3	3.1	23.8	4.6	4.2	11.5	3.4
28	70	260	55	33.5	23.3	5.6	12.2	5.0	5.8	8.4	2.3
29	300	500	292	366	54.1	16.5	44.3	4.9	6.9	12.2	4.5
30	100	290	165	15.2	22.3	2.2	5.5	6.9	12.3	6.2	1.2
31	60	340	108	73.2	18.5	3.6	12.3	2.7	10.1	15.7	0.9
32	80	340	152	97.6	21.7	5.7	23.8	3.7	8.8	6.5	1.2
33	82	310	182	18.3	20.4	4.4	2.5	8.8	5.5	2.2	1.4
34	110	300	122	20.2	18.2	2.2	3.9	19.5	3.2	2.4	3.8
35	150	310	145	22.5	18.4	1.3	8.8	12.2	4.2	3.5	5.6
36	320	420	140	390.4	23.5	4.7	10.5	2.3	9.3	8.1	6.2
37	100	320	25	42.2	22.4	9.4	18.2	4.1	10.2	5.5	0.9
38	140	300	28	33.2	10.2	4.1	20.1	3.9	11.1	1.8	0.8
39	80	450	35	45.0	8.8	6.0	14.3	3.8	10.5	1.1	0.8
40	60	400	44	90.1	14.5	1.5	21.1	10.1	6.2	4.2	0.9
41	60	420	72	73.2	14.1	2.0	10.6	3.0	10.6	9.5	1.6
42	40	340	63	122.1	30.1	1.8	15.2	9.4	5.2	6.5	4.5
43	160	300	132	195.2	25.3	4.4	12.3	10.7	10.2	3.7	4.4
44	80	400	71	82.2	33.2	6.2	13.4	8.5	8.1	7.3	3.3

Continued

45	100	420	136	122.0	25.3	4.2	23.8	2.5	11.5	4.5	3.4
46	200	440	92	244.0	18.5	2.6	7.1	2.1	10.9	5.5	4.8
47	160	380	80	195.2	15.4	2.7	10.5	11.9	8.3	3.2	8.7
48	120	400	45	56.6	14.2	7.2	8.8	2.9	4.4	1.3	8.4
49	100	410	62	54.4	20.1	8.6	8.2	2.6	3.3	1.5	4.4
50	60	350	60	38.2	19.9	9.9	12.5	3.4	2.2	2.6	6.5
51	200	200	164	244.0	18.5	6.7	23.8	3.2	7.8	4.1	1.5
52	40	300	113	24.5	17.7	1.5	19.0	3.5	10.1	2.8	1.6
53	120	380	72	146.4	15..2	2.0	10.5	2.8	4.9	8.5	3.2
54	80	220	63	56.8	18.5	6.2	19.0	4.4	6.3	8.9	1.9
55	100	380	76	122.1	20.9	1.9	12.2	6.5	10.0	3.0	0.9
56	110	240	44	44.2	9.8	3.3	18.1	3.4	3.3	4.5	3.4
57	200	580	292	244.0	37.1	11.8	15.9	3.1	10.5	3.5	1.3
58	200	380	244	244.2	47.1	7.9	8.8	3.1	7.7	4.2	1.2
59	210	250	182	25.8	10.5	4.1	15.2	9.5	2.9	9.8	1.8
60	250	310	120	55.5	12.2	1.0	12.2	2.9	4.2	3.6	4.4
61	120	240	52	146.4	18.4	0.8	13.2	3.2	5.9	1.4	4.2
62	120	300	42	92.2	16.4	3.2	39.4	2.6	4.1	2.5	1.7
63	120	420	135	145.2	23.5	4.5	14.3	2.8	10.5	1.1	5.7
64	100	300	72	122.1	22.7	1.5	20.2	3.9	4.8	1.4	5.9
65	100	300	64	122.1	21.8	1.5	22.3	2.9	23.6	2.5	6.5
66	40	200	52	55.8	10.0	3.2	20.1	4.4	10.6	3.5	7.8
67	80	180	68	97.6	20.1	1.2	39.5	1.4	6.3	1.7	8.2
Min	40	180	10	15.2	8.8	0.8	2.5	1.4	2.2	0.9	0.8
Max	340	580	392	390.4	60.9	19.5	74.5	19.5	23.6	15.7	8.7
Mean	123	323	101	112.1	21.3	4.0	19.2	5.1	7.7	5.2	3.2

hardness (TH) varies between 10 and 392 mg/l, and acidity ranging from 180 mg/l to 580 mg/l. The concentration of Ca^{2+} varies from 8.8 - 60.9 mg/l with average of 21.3 mg/l. The Mg^{2+} ranges from 0.8 - 19.5 mg/l (avg. 4.0 mg/l). Sodium (Na^+) ranges from 1.4 - 19.5 mg/l with an average value of 5.1 mg/l. The concentrations of Na^+ in the samples is generally low and could be attributed to less influence of anthropogenic activities on the groundwater and it ranges from 1.4 - 19.5 mg/l. The potassium (K^+) is in between 2.2 mg/l and 23.6 mg/l (avg. 7.7 mg/l), important sources include orthoclase feldspar, nepheline, leucite and biotite (Subba Rao, 2017; Back, 1960; Collins & Jenkins, 1996).

The bicarbonate (HCO_3^-) varies from 15.2 - 390.4 mg/l (avg. 112.1 mg/l). Soil CO_2 is the likely main source of HCO_3^- in the groundwater (Fetter, 1983). In addition decay of organic matter could also releases carbon dioxide for dissolution. The analyzed water samples contain sulfate (SO_4^{2-}) in the range of 0.91 - 15.7 mg/l (avg. 5.2 mg/l). The Chloride (Cl^-) is dissolved from rocks and soils in

the study area, and its values range from 2.5 - 74.5 mg/l.

Excessive concentrations of dissolved ions in the irrigation water affect plants and agricultural soil physically and chemically through lowering of osmotic pressure in the plant structural cells. This prevents water from reaching the branches and leaves, thus reducing the agricultural productivity (Fetter, 1993). Salinity hazard, sodium, percent sodium (%Na^+), permeability index (PI), residual sodium carbonate (RSC), magnesium ratio (MR) and Kelly ratio (KR) are widely used for the assessment of water quality for irrigation. **Figure 4** shows the trilinear diagram of the water samples, which is an effective tool for segregating data for critical study with respect to the sources of dissolved ions in water and modifications in water character (Piper, 1944). Generally the water in the study area fall within zone 5 which comes under carbonate hardness or fresh water type (**Table 3**). They are characterized by Ca^{2+} and Mg^{2+} of HCO_3^- and CO_3^{2-} over Na^+ and K^+ of Cl^- and SO_4^{2-}. Only few samples (about 5%) belongs to mixed type (transition zone) where no cation-anion pair exceeds 50%. The mechanism controlling the groundwater quality for the water samples determined using Gibb's diagrams, by relating the ratio of the cations ($Na^+ + K^+$:$Na^+ + K^+ + Ca^{2+}$) and ratio of anions (Cl^-:$Cl^- + HCO_3^-$) which are plotted against TDS, for understanding the mechanisms that control the groundwater chemistry with respect to atmospheric precipitation (rainfall), rock-water interaction and evaporation. From **Figure 5**, the chemistry of the water falls in the precipitation domain, indicating a meteoric origin. Hence the soil/rock-water interaction is responsible for the source of dissolved ions.
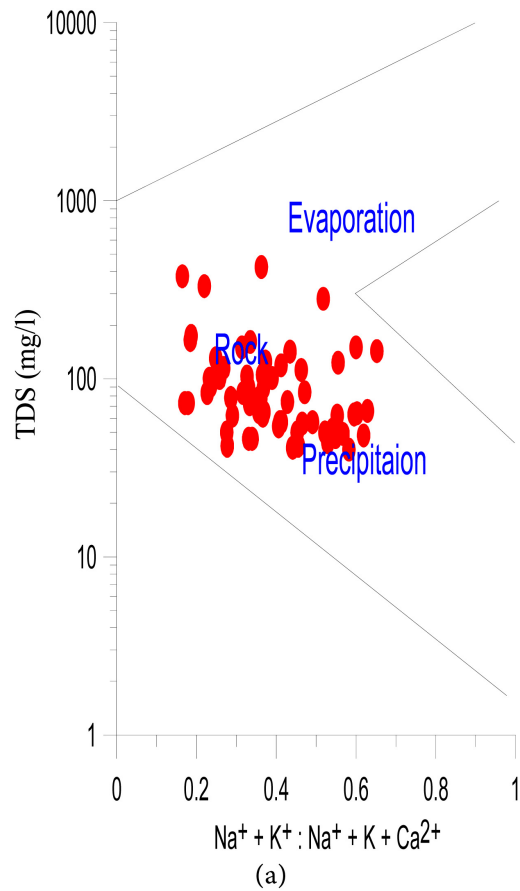

(a)

(b)
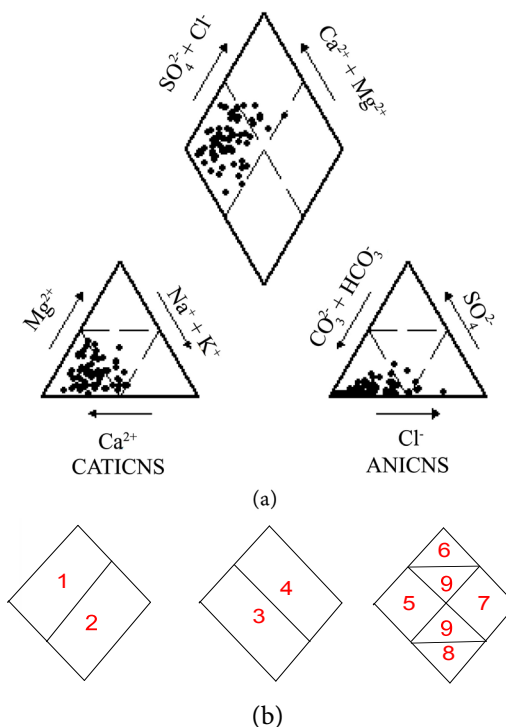
Figure 4. (a) Piper's trilinear diagram for water samples (b) showing a predominant zone 5 water type.
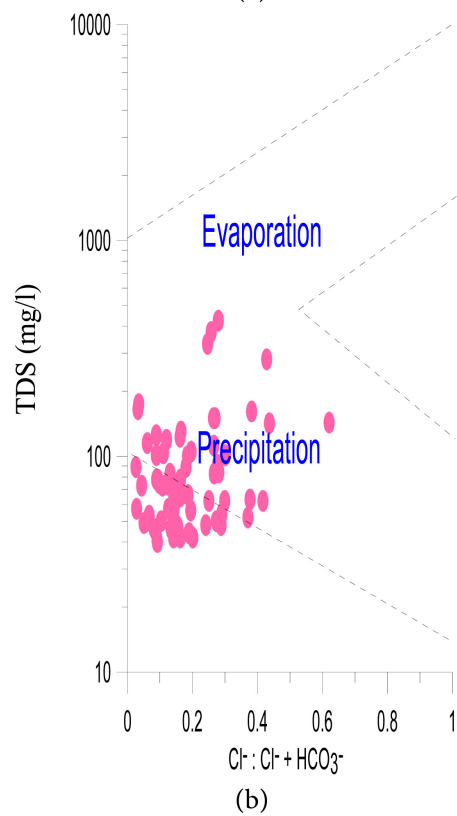
Figure 5. Mechanisms controlling groundwater chemistry in the study area.

Table 3. Characterization of water quality using interpreted trilinear diagram.

Zone	Characterization of water quality
1	Alkaline earths ($Ca^{2+} + Mg^{2+}$) exceed alkalies ($Na^+ + K^+$)
2	Alkalies exceed alkaline earths
3	Weak acids $HCO_3^- + CO_3^{2-}$ exceed strong acid $Cl^- + SO_4^{2-}$
4	Strong acids exceed weak acids
5	Carbonate hardness (secondary alkalinity) exceeds 50% that is by alkaline earths and weak acids
6	Non-carbonate hardness (secondary salinity) exceeds 50%
7	Non-carbonate alkali (primary salinity) exceeds 50%
8	Carbonate alkali (primary alkalinity) exceeds 50%
9	Mixed type (transition zone)-No cation-anion pair exceeds 50%

Consequently since the value of TDS is less than 1000 mg/l in the samples, the origin of the ions in the water samples is presumed to be the rock units in the area (geogenic origin).

3.2. The Groundwater Evolution

The evolution of groundwater quality is represented in Langelier and Ludwig's graphical diagram, as shown in Figure 6. The groundwater samples fall in Group I, relating to $Ca^{2+} + Mg^{2+} + HCO_3^-$ Type, which indicates a meteoric origin of water quality, caused by rock-water interaction. This implies that the chemistry of the groundwater is controlled by geogenic process and not anthropogenic sources. None of the samples fall to Group II where $Na^+ + K^+$ and $Cl^- + SO_4^{2-}$ over $Ca^{2+} + Mg^{2+}$ and $HCO_3^- + CO_3^{2-}$. The HCO_3^- and Cl^- distinguish between fresh and brackish water environments respectively.

3.3. Hydrochemical Facies Characterization

Hydrogeochemical facies describes the distribution and genesis of principal groundwater types (Back, 1960). The facies also provide information on progressive ion enrichment during stay of groundwater on the basis of residence time of water in subsurface and the extent of rock-water interaction (Subba Rao, 2017). The facies are arranged by taking the ionic percentages in relative decreasing order of their abundances. The facies can be classified with respect to residence time of water in aquifer material and topography as shown in Table 4. The water in the area is dominantly Type I—Recharge Water emanating from high topography.

The geochemical signatures/ratios are widely used to assess the origin of water as shown in Table 5. The HCO_3^- is a dominant ion in groundwater, while Cl^- is an abundant ion in seawater. The ratio of HCO_3^- and Cl^- is greater than 1 and implies Organic matter and/or CO_2 or recharge area or upper water flow course of carbonate rocks (interaction of water with aquifer material). From the results
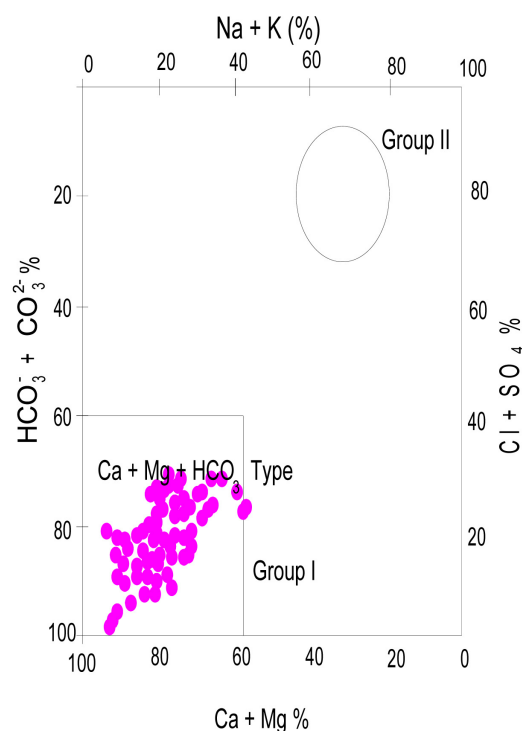
Figure 6. Evolution of groundwater quality of water samples showing prominent Ca^{2+} + Mg^{2+} + HCO_3^- type.

Table 4. Hydrochemical facies in relation to residence time of water and topography.

Hydrogeochemical facies	Types	Water Type	Topography
$Ca^{2+} > Mg^{2+} > Na^+: HCO_3^- + SO_4^{2-} > Cl^-$	I	Recharge	High
$Mg^{2+} > Ca^{2+} > Na^+: HCO_3^- + CO_3^{2-} > SO_4^{2-} > Cl^-$	I	Recharge	High
$Na^+ > Mg^{2+} > Ca^{2+}: SO_4^{2-} > Cl^- > HCO_3^-$	II	-	-
$Na^+ > Mg^{2+} > Ca^{2+}: Cl^- > SO_4^{2-} > NO_3^- > HCO_3^-$	III	-	-
$Na^+ > Mg^{2+} > Ca^{2+}: Cl^- > SO_4^{2-} > HCO_3^-$	IV	Discharge	Low

Table 5. Geochemical signatures (Subba Rao, 2017).

GS	Range	Influence of
$HCO_3^-:Cl^-$	>1.0	Organic matter and/or CO_2 or recharge area or upper water flow course of carbonate rocks
	<1.0	Lower water flow course of carbonate rocks
	<0.2	Saline water and brines
$Na^+:Cl^-$	0.876	Seawater
	<0.876	Replacement of Na^+ by Ca^{2+} or Mg^{2+}
	<0.7	Loss of Na^+ through precipitation of evaporate rocks
	>0.1	Waste flow through crystalline or volcanic rocks
$Mg^{2+}:Ca^{2+}$	0.5 - 0.7	$CaCO_3$ rocks
	0.7 - 0.9	$CaMg(CO_3)_2$ rocks

Continued

	>0.9	Mg^{2+} rich rocks or seawater mixture
	<0.5	Ca^{2+} rich water
$Na^+:K^+$	15 - 25	Natural recharge area
	50 - 70	Lower water flow course
	>70	Volcanic rocks
	<15	Na^+ depleted water
$Ca^{2+} + Mg^{2+}:Na^+:K^+$	>1.0	Upper water flow course of carbonate rocks or precipitation of NaCl from brine or exchange of Na^+ and K^+ against Ca^{2+} and/or Mg^{2+}
	<1.0	Lower water flow course of carbonate rocks
$Na^+:Ca^{2+}$	>1.0	Base ion exchange
	<1.0	Reverse ion exchange
$Ca^{2+}:SO_4^{2-} + HCO_3^-$	<1.0	Normal hydrological cycle
	>1.0	$Ca^{2+} - Cl^-$

obtained, the $Na^+:Cl^-$ is less than 0.7 signifying loss of Na^+ through precipitation of evaporate water; the water is Ca^{2+} rich and Na^+ depleted with $Mg^{2+}:Ca^{2+}$ less than 0.5 and $Na^+:K^+$ (<15) respectively. The $Na^+:Ca^{2+}$ (<1) indicates reverse ionic exchange. The $Ca^{2+}:SO_4^{2-} + HCO_3^-$ for the samples is less than 1.0 suggesting the flow of water through the normal hydrological cycle.

Chloro-alkaline indices (CA) is used in understanding the chemical composition of groundwater along its flow path. Subba Rao (2017) 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 Equation (2) and Equation (3).

$$CA1 = Cl^- - Na^+ + K^+:Cl^- \qquad (2)$$

$$CA2 = Cl^- - Na^+ + K^+ : Cl^- : SO_4^{2-} + HCO_3^- + NO_3^- \qquad (3)$$

The groundwater samples show CA1 and CA2 in the range of −14.8 - 70.4 and −0.56 - 1.05. Only samples 33, 34, 35, and 47 show negative 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.

## 3.4. Groundwater Evaluation for Irrigation Purpose

Excessive concentrations of dissolved ions in the irrigation water affects plants and agricultural soil physically and chemically through lowering osmotic pressure in the plant structural cells. Hence salinity hazard (C), sodium hazard, percent sodium (%Na^+), permeability index (PI), residual sodium carbonate (RSC), magnesium ratio (MR) and Kelly ratio (KR) are widely used for the assessment of water quality for irrigation.

The salinity hazard (C) is computed in terms of electrical conductivity. **Figure 7** shows the spatial distribution of EC in the area. It shows a predominant range of 0 - 250 μS/cm (low salinity hazard) which covers about 80% of the area. This type of water is good for irrigation. The moderate-high salinity hazard water forms small closure especially in the northern part of the area. The high salinity hazard has less than 5% aerial dominance. The sodium hazard is computed in terms of sodium absorption ratio (SAR) as well as in terms of percent sodium (%Na⁺) where the ions are expressed in meq/l using Equation (4) and Equation (5).

$$SAR = \frac{Na^+}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}} \tag{4}$$

$$\%Na^+ = \frac{\left(Na^+ + K^+\right)}{\left(Ca^{2+} + Mg^{2+} + Na^+ + K^+\right)} \times 100 \tag{5}$$

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 (Subba Rao et al., 2002). 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. SAR of the studied water samples varies from 1.89 to 26.42. The values are generally within 0 - 18 specified by (Singh et al., 2015) as excellent
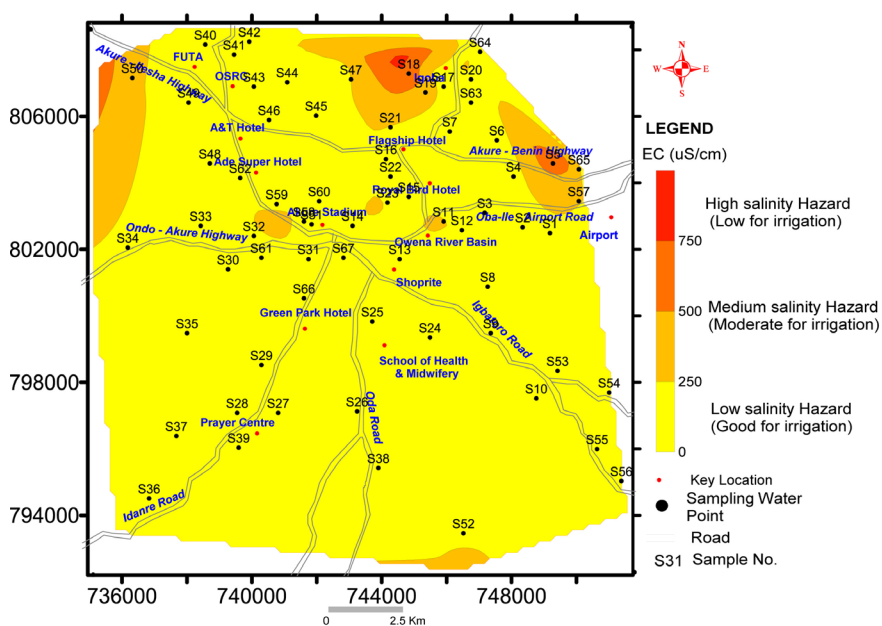
Figure 7. Spatial distribution of electrical conductivity (salinity hazard) in the study area.

water for irrigation purpose (**Figure 8**). The % Na$^+$ is inversely proportional to permeability of soils. The %Na$^+$ obtained ranges from 0.41 - 3.45 and the spatial distribution of %Na$^+$ in **Figure 9** shows dominant values in the range of 1.4 - 2.4. In addition the Wilcox plot (Wilcox, 1955) of the water samples (**Figure 10**) shows "excellent to good" irrigation water.

Permeability is greatly influenced by Na$^+$, Ca^{2+}, Mg^{2+}, HCO$_3^-$ and Cl$^-$ contents of the soil. It plays an important role in the growth of plants. If the permeability is low in the soil zone, it does not support plant growth. The degree of permeability condition in the soil is expressed in terms of permeability index (PI) computed using Equation (6). The concentrations of ions are expressed in meq/l.

$$PI = \frac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+} \times 100 \qquad (6)$$

The PI of the water samples varies from 42.67 to 170.24. According to classification of PI in **Table 6**, the groundwater samples fall within "marginal-suitable" category, and from **Figure 11(a)**, suitable irrigation area are widespread in the central zone. This area is also characterized by low values of RSC (less than 1.25). Residual sodium carbonate (RSC) is the difference between carbonates (HCO$_3^-$ + CO$_3^{2-}$) and alkaline earths (Ca^{2+} + Mg^{2+}) which is expressed in meq/l. Carbonates have an effect on water quality through precipitation of alkaline earths, thereby increasing the % of Na$^+$. This is more when the concentration of carbonates is in excess than that of alkaline earths. The excess carbonates combine with Na$^+$ to form NaHCO$_3$, which affects soil structure. The RSC values
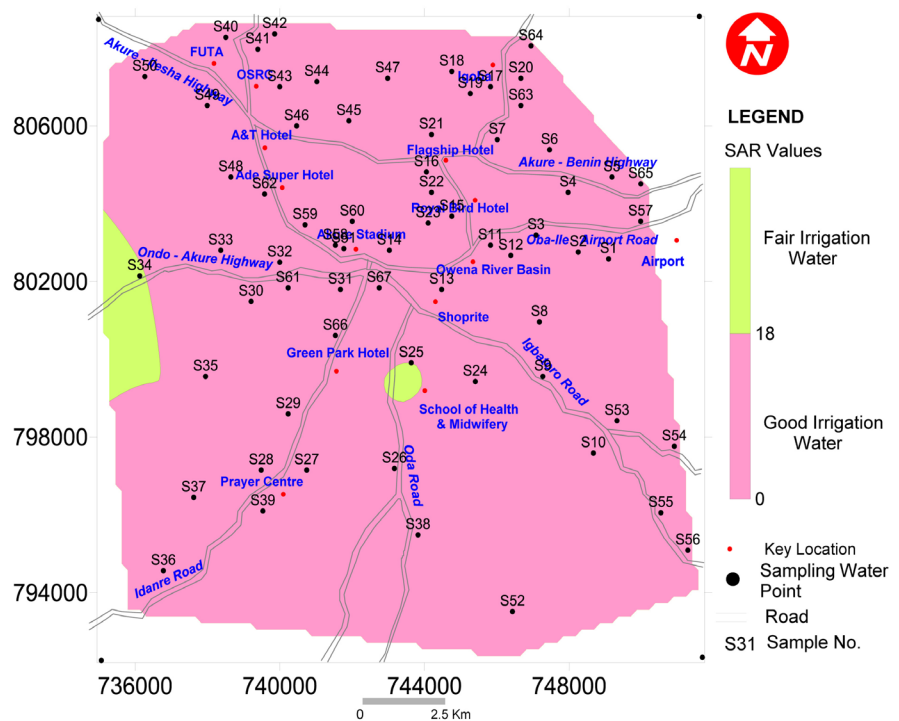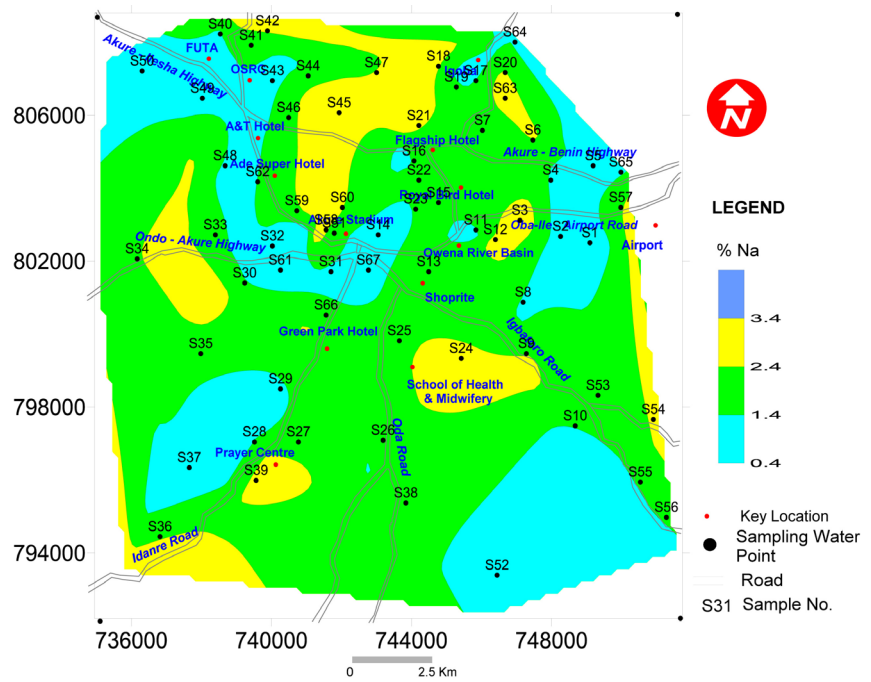

Figure 8. Spatial distribution of SAR.

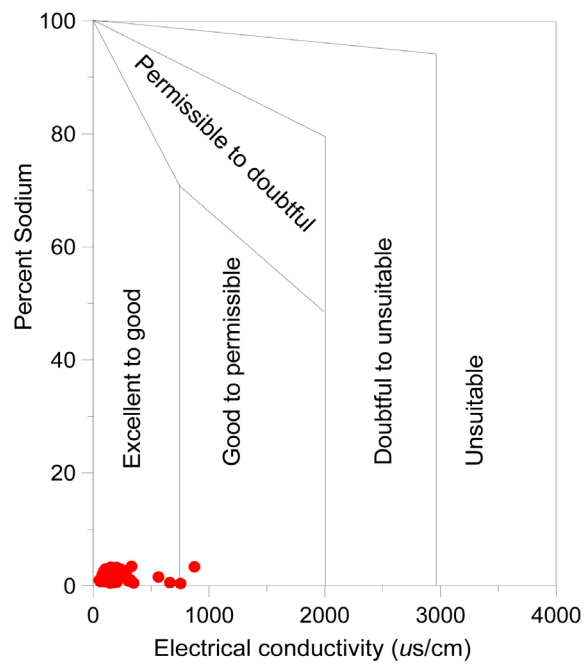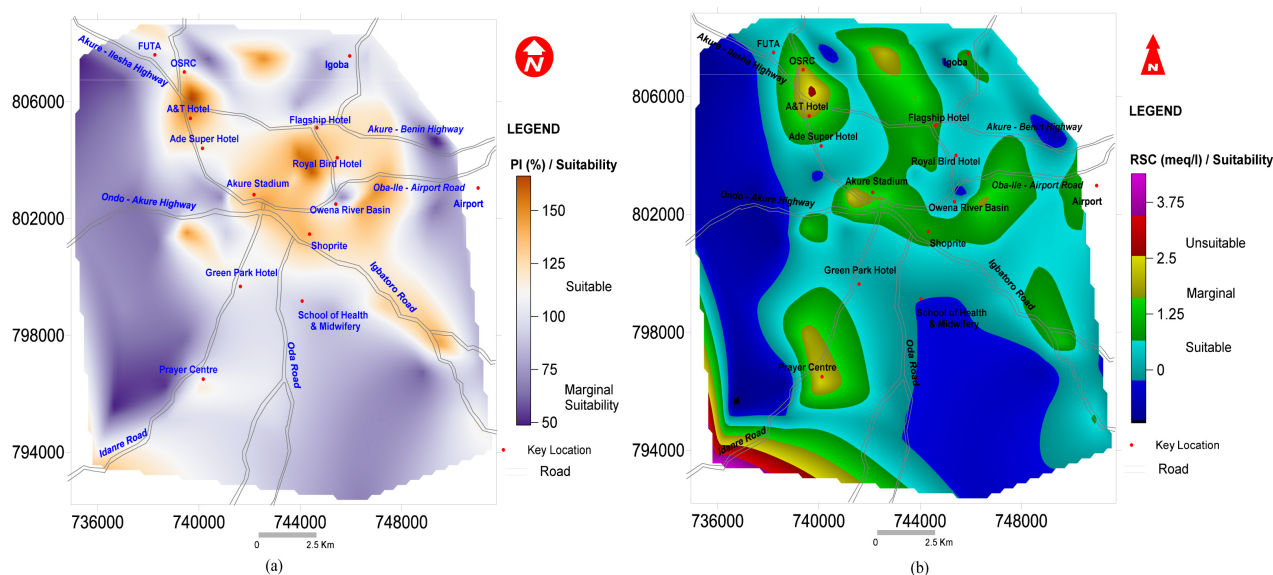**Figure 9.** Spatial distribution of %Na$^+$ in the study area.

Figure 10. Wilcox's diagram for the water samples.

Table 6. Classification of PI for irrigation.

Classification of PI	Permeability	Suitability
1	Above 75%	Suitable
II	25% to 75%	Marginal
III	Less than 25%	Unsuitable

Figure 11. Spatial distribution of: (a) PI and (b) RSC.

range between −1 to 5. Spatial distribution of RSC in the study area shows very high RSC (>2.5) in the southwest (**Figure 11(b)**). However the irrigation water quality in the area is generally "marginal/suitable" (**Table 7**). 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 (Collins & Jenkins, 1996). The MR of the water samples varies from 4 to 53. The values of MR progressively increase radially from the central part of the study area (**Figure 12**).

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 (**Table 7**). The KR values calculated for the water samples are in between 0.04 and 0.84. **Figure 12** shows that area with high values of KR have high MR and vice versa.

4. Conclusion

Hydrochemical facies characterization and groundwater quality evaluation of Akure, Ondo State, Nigeria have been studied. The pH and Eh of the water samples show an acidic condition. Generally the water in the study area falls within zone 5 which comes under carbonate hardness or fresh water type. They are characterized by Ca^{2+} and Mg^{2+} of HCO_3^- and CO_3^{2-} over Na^+ and K^+ of Cl^- and SO_4^{2-}. Only few samples (about 5%) belong to mixed type (transition zone) where no cation-anion pair exceeds 50%. The chemistry of the water falls in the precipitation domain, indication a meteoric origin. Hence the rock-water interaction is responsible for the source of dissolved ions (geogenic origin).

Table 7. Classification of RSC, MR, and KR for irrigation [14].

RSC (meq/l)	Suitability
<1.25	Suitable
1.25 - 2.50	Marginal
>2.50	Unsuitable
MR	
>50	Suitable
<50	Unsuitable
KR	
>1.0	Good
<1.0	Not Good
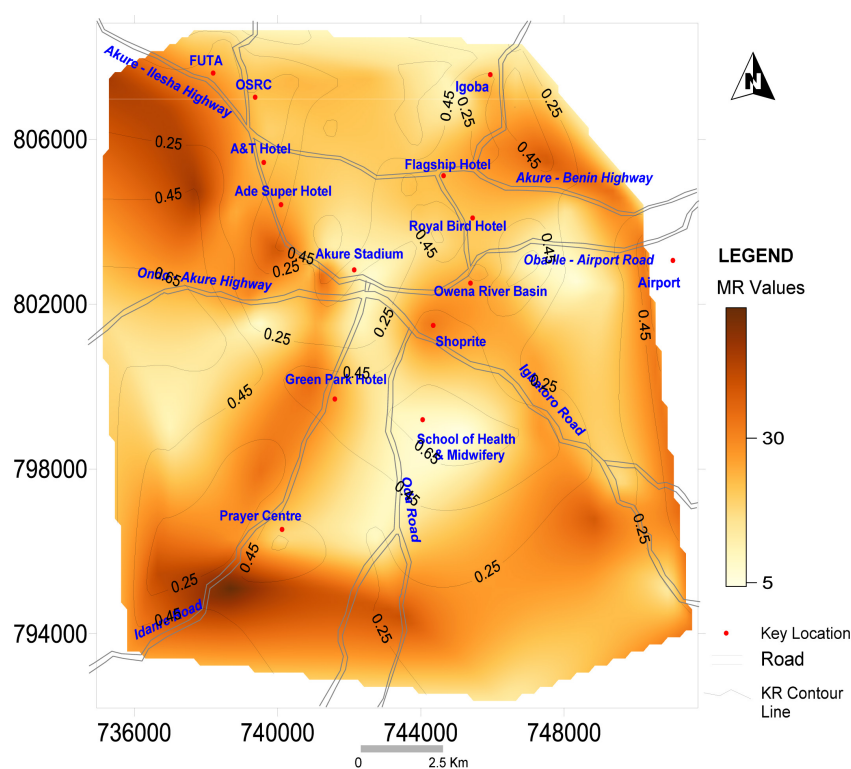
Figure 12. Spatial distribution of MR and KR.

The geochemical signatures show Na^+:Cl^- is less than 0.7 signifying loss of Na^+ through precipitation of evaporate water; the water is Ca^{2+} rich and Na^+ depleted with Mg^{2+}:Ca^{2+} less than 0.5 and Na^+:K^+ (<15) respectively. The Na^+:Ca^{2+} (<1) indicates reverse exchange. The major ion chemistry data revealed that the ground water in the study area is fresh in nature. The Ca^{2+}:SO_4^{2-} + HCO_3^- for the samples is less than 1.0 suggesting the flow of water through the normal hydrological cycle. The water in the area is dominantly Type I—Recharge Water emanating from high topography. Chloro-alkaline indices (CA) confirms 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 of 0 - 250 μS/cm (low salinity hazard) covers about 80% of the area. Based on the classification of irrigation water according to SAR, PI, RSC, MR, KR, %Na values, all the sample locations are generally suitable for irrigation purposes. In addition, based on the Wilcox classification, 1% of the water samples belong to good to permissible category for irrigation use due to the presence of excess sodium salts that cause deflocculating and reduce the permeability of soil.

Acknowledgements

Conflicts of Interest

The authors declare that no conflict of interest exists.

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