



Geochemical Evolution and Irrigation Quality of Groundwater in Ogba-Ikpoba River Catchment Area, Western Niger Delta, Nigeria

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Abstract: Groundwater from coastal plain sand deposit in Ogba-Ikpoba watershed was studied to determine its geochemical origin and suitability for irrigation purpose using analytical tools. Samples of the water were analyzed for pH, TDS, some major cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), anions (Cl^- , HCO_3^- , NO_3^- , SO_4^{2-} , PO_4^{3-}) and trace elements (Pb^{2+} , Fe^{2+} , Mn^{2+}). Irrigation water quality indices were computed using standard formulas. Results of pH test indicated fairly acidic groundwater with low TDS (≤ 407 mg/l) and hardness (5.65 to 379 mg/l). There was a fairly strong positive correlation between TDS and Ca^{2+} (0.737), Mg^{2+} (0.567) and Na^+ (0.556). Nitrate (NO_3^-) correlated strongly with Ca^{2+} (0.613), signifying likelihood of anthropogenic contamination. Piper plot indicated evolving water and predominance of mixed Ca^{2+} - Mg^{2+} - Cl^- hydrochemical facies. Stiff plots showed groundwater mixing and ion exchange with water patterns showing transient groundwater chemistry within short distances. Identical patterns with diminishing ionic concentrations were observed, suggesting dilution along flow direction. Gibb's plot signified rainfall as the pre-dominant mechanism controlling the groundwater chemistry, and possible anthropogenic groundwater contamination. Most of the water samples from the study area are recommended for irrigation based on SAR values, USSS and Wilcox plots.

Keywords: Food security, irrigation, geochemical evolution, hydrochemical facies, Ikpoba, Niger Delta.

I. INTRODUCTION

Water is an indispensable resource for human existence on earth and an essential prerequisite for socio-economic development of any nation. Water and food security are two inseparable daily necessities. The role of groundwater in increasing food security cannot be overemphasized in the sub-Saharan (arid and semi-arid) Africa which is reportedly in food crisis caused by drought (Vilholth and Altchenko, 2016). The phenomenal rise in population coupled with urbanization, increasing industrialization and competition for economic growth have increased water demands thereby overstressing the available global water resources (Foster *et al.*, 1998; Nwankwoala, 2014). The potential risk of a significant global decline in fresh water resources and crop yield at the close of the 21st century has been predicted (Misra, 2014). Sustainability of groundwater to meet the water demands of growing global population is dependent on timely reversal of the projected tendency for shortage. Also, the quality of groundwater resources must be maintained and protected against the risks of contamination (Ali and Young, 2014). Public health control is also essential to secure a continuous supply of water within safe limits (John De Zuane, 1990). Established guidelines and regulatory policies under United Nations (UN) monitoring system by World Health Organization (WHO) and the United Nations Children's Fund (UNICEF) have been playing important roles in this area.

Groundwater may be the key to improved food security in Nigeria. Majority of the ever-growing population in the country is increasingly dependent on groundwater resources, where available, for domestic, industrial, recreational as well as irrigation uses. In the drought-prone Sahelian states of northern parts of Nigeria (such as Adamawa, Borno, Jigawa, Kano, Kebbi, Sokoto, Yobe and Zamfara), many people do not have access to safe potable water. Conversely, in the southern states like Edo, Ekiti, Ondo, Ogun, Osun and Oyo, the situation of accessibility to good drinking water is much better due to improved annual rainfall, surface water and groundwater resources. Benin-City (the study area), a city in Edo State, Southern Nigeria has had a long history of settlement. It became a State capital in 1962. Since then it has been the center of urban migration from other parts of Nigeria. It ranks among the fastest growing cities in the country. The metropolitan city recorded 1.2 million people in 2005 at an annual growth rate of 3.3 percent (Brinkhoff, 2006). More recent estimate gave 1.5% increase (Odjugo *et al.*, 2015). Conservatively, a projected population of two million and per capita demand of 120 l/day have been estimated for Benin-City with the domestic water demand put at about 240,000m³/day (Oteze, 2011). Many people in the area, like some other parts of the Country, rely on groundwater sources for potable water supply and other uses. The residents need good quality water in the cultivation of both food and cash crops which are the main agricultural activities of the rural settlers. Groundwater irrigation could be explored to increase food security in the area. To this end, the current study aimed at determining the geochemical evolution and ascertaining the suitability of groundwater in Ogba-Ikpoba River Catchment, Nigeria for irrigation purpose.

Study area

Ogba-Ikpoba watershed lies within longitudes E005° 30' and E005° 45' of the Greenwich Meridian and latitudes N06° 15' and 6° 30' of the Equator (Figure 1). It covers a land mass of over 950 km² in Edo State, western Niger Delta, Nigeria. The area falls within the tropical climate belt of southern Nigeria. The mean annual precipitation in the area is about 2280 mm (Ezeigbo & Aneke, 1993). The study area lies within the Nigerian tropical rain forest belt characterized by dense vegetation with closed canopy.

Geological setting

The study area is underlain by sedimentary sequences of the western Niger Delta Sedimentary Basin. The Niger Delta basin comprises three main subsurface stratigraphic Formations (Short and Stauble, 1967), viz: (i) Benin Formation - Miocene to Recent, (ii) Agbada Formation - Eocene to Recent, (iii) Akata Formation - Eocene to Recent (Doust & Omatsola, 1990). The Benin Formation is the topmost and youngest in the stratigraphic sequences with type-locality around Benin-City. It consists of massive continental/fluvial sands and gravels (Weber and Daukoru, 1975). It is deposited in the continental facies phase of the Niger Delta (Short & Stauble, 1967). It is characteristically reddish to reddish-brown at the top and generally white sands with clayey and sometimes pebbly intercalations with depth. The top reddish clayey sand is lateritic. The poorly developed clay inter-beds are often discontinuous and occur at various depths in the stratigraphic succession. The geological map of the study area is shown in Figure 2.

II. MATERIALS AND METHODS

Field measurements and laboratory analyses

Total dissolved solids (TDS) and pH were measured on the field at site. Thirty-two (32) groundwater samples were collected for chemical analyses of some dissolved constituents. The standard laboratory methods for chemical analysis of water stipulated by American Society for Testing and Materials (ASTM) Standards were followed. Sodium, potassium, manganese, iron and lead concentrations were determined using atomic absorption spectrophotometer (AAS).

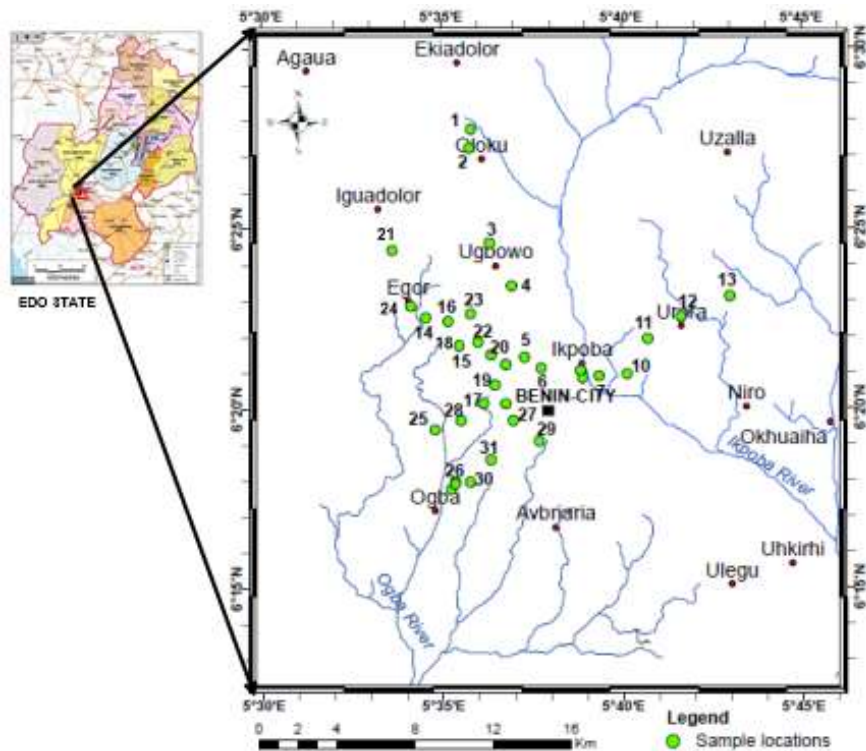


Fig. 1: Drainage map of the study area showing sampling locations.

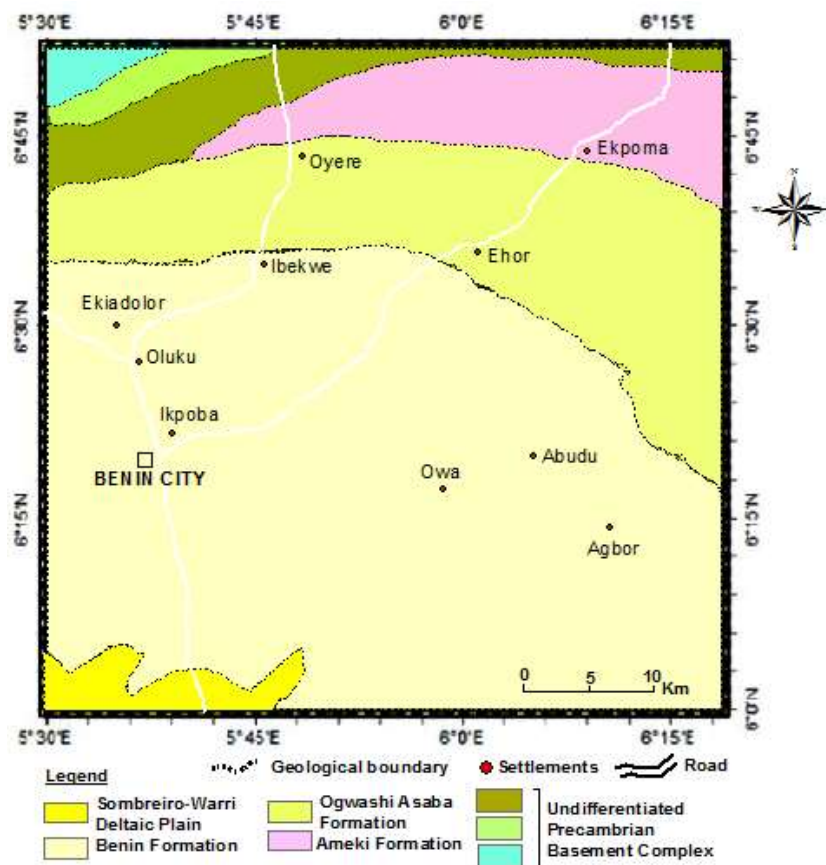


Fig. 2: Geological map of the study area (Adapted from Nigerian Geological Survey Agency, 2006).

Calcium, magnesium, chloride and bicarbonate were analyzed using EDTA titrimetric method. Sulphate, phosphate and nitrate were determined using ultra-visible spectrometry method.

Computational analyses

Ionic concentrations were converted from milligram per litre (mg/l) to milliequivalent per litre (meq/l) for the purpose of the calculations. Ionic balance calculation was done as a means of reliability check of the analytical results (Equation 1).

$$\% \text{ Ionic Balance} = \left(\frac{\text{meq (cations)} - \text{meq (anions)}}{\text{meq (cations)} + \text{meq (anions)}} \right) \times 100 \quad \dots\dots\dots (1)$$

Total hardness (TH) in mg/L of CaCO_3 and electrical conductivity (EC) were calculated using equation (2) according to Todd (1980) and equations (3) as follow:

$$TH = 2.497 (\text{Ca}^{2+}) + 4.115 (\text{Mg}^{2+}) \quad \dots\dots\dots (2)$$

$$EC (\mu\text{S}/\text{cm}) = TDS/0.67 \quad \dots\dots\dots (3)$$

where all ionic concentrations are expressed in milligrams per litre (mg/L).

Equation (4) was used to compute Sodium Adsorption Ratio (SAR) as proposed by the United States Salinity Laboratory (Richards, 1954). The ratio of sodium to the total cations in the groundwater samples which defines sodium hazard for irrigational purpose was evaluated as Soluble Sodium Percent (SSP) using equation (5) according to Wilcox (1955). The chloro-alkaline index (CAI) which indicates ion exchange process between groundwater and its environment was computed using the formula by Schoeller (1965), (Equation 6). Kelley ratio was computed according to equation (7) (Kelly, 1963). Permeability Index (PI) was calculated according to Doneen (1964), equation (8). The Residual Sodium Carbonate (RSC) which represents the relative proportion of excess sodium carbonate present in the groundwater samples was determined using equation (9) following Eaton (1950) and Ragunath (1987). The Residual Sodium Bicarbonate (RSBC) was calculated using Gupta & Gupta (1987) according to equation (10).

$$SAR = \frac{\text{Na}^+}{\sqrt{[(\text{Ca}^{2+} + \text{Mg}^{2+})/2]}} \quad \dots\dots\dots (4)$$

$$SSP = \frac{(\text{Na}^+ + \text{K}^+) \times 100}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)} \quad \dots\dots\dots (5)$$

$$CAI = \frac{[\text{Cl}^- - (\text{Na}^+ + \text{K}^+)]}{\text{Cl}^-} \quad \dots\dots\dots (6)$$

$$KR = \frac{\text{Na}^+}{(\text{Ca}^{2+} + \text{Mg}^{2+})} \quad \dots\dots\dots (7)$$

$$PI = \frac{\text{Na}^+ + \sqrt{[\text{HCO}_3^- \times 100]}}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+} \quad \dots\dots\dots (8)$$

$$RSC = (\text{CO}_3^{2-} + \text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+}) \quad \dots\dots\dots (9)$$

$$RSBC = \text{HCO}_3^- - \text{Ca}^{2+} \quad \dots\dots\dots (10)$$

$$MAR = \frac{(\text{Mg}^{2+}) \times 100}{(\text{Ca}^{2+} + \text{Mg}^{2+})} \quad \dots\dots\dots (11)$$

Where all ionic constituents are in milliequivalents per litre (meq/l)

III. RESULTS AND DISCUSSION

Table 1 showed the results of water analysis which suggested that the water in Ogba-Ikpoba area was of low mineralization, considering the low values of total dissolved solids ($\text{TDS} \leq 407 \text{ mg/l}$) obtained.

Table 1: Water Analysis Results

Sample ID	TDS (ppm)	Cond. (µm/s)	pH	Na ⁺ (mg/l)	K ⁺ (mg/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Cl ⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	PO ₄ ³⁻ (mg/l)	NO ₃ ⁻ (mg/l)	Fe ²⁺ (mg/l)	Mn ²⁺ (mg/l)	Pb ²⁺ (mg/l)
S01	5	11	5.16	0.86	1.12	0.64	1.92	28.4	24.4	0	0.12	0	0.52	0	0.02
S02	5	10	4.77	1.42	1.85	0.64	1.28	42.6	18.3	0	0.8	0	0.65	0	0.01
S03	25	51	4.6	4.53	5.89	3.2	5.77	28.4	12.2	0	0	0.32	0	0	ND
S04	5	11	5.37	2.15	2.79	0.64	3.21	42.6	18.3	0.26	0	0.08	0.12	0	0.02
S05	152	303	4.53	17.08	2.22	40.32	28.2	113.6	12.2	0	0.3	1.02	0.65	0	ND
S06	54	108	4.21	10.64	13.83	7.04	7.05	42.6	18.3	0	0.1	0.3	0.12	0	0.01
S07	164	332	4.33	16.75	21.78	33.38	22.4	99.4	18.3	0	0.08	0.58	0.65	0.03	ND
S08	407	814	6.59	16.56	21.52	67.84	51.3	198.8	311.2	0	0	0.72	0.12	0.2	ND
S09	6	11	5.84	2.39	3.11	3.84	3.21	42.6	24.4	1	0.9	0	0.25	0	ND
S10	23	46	4.41	5.23	6.8	3.2	1.92	56.8	18.3	0.56	0.44	0.34	0.25	0	ND
S11	31	63	4.42	7.48	9.72	3.2	4.49	56.8	18.3	0	0	0.08	0.25	0.08	ND
S12	9	17	4.6	4.08	5.3	3.84	2.6	28.4	24.4	0	0	0.12	0	0	ND
S13	3	7	5.18	1.34	1.74	3.2	1.28	42.6	18.3	0	0	0	0.12	0	ND
S14	3	7	5.54	1.23	1.6	0.64	1.55	42.6	18.3	0.08	0	0	0.03	0	2
S15	20	40	4.49	5.02	6.53	5.82	3.8	42.6	18.3	0.04	0	0.88	0.01	0	1.09
S16	4	8	4.73	0.9	1.17	1.62	0.39	42.6	12.2	0.2	0	0.98	0.03	0	0.18
S17	64	126	5.02	11.96	15.55	12.18	10.11	42.6	18.3	0	0	1.28	0.03	0.03	ND
S18	86	172	4.28	14.46	18.8	16.26	5.83	99.4	12.2	0.3	0	0.5	0.04	0.03	ND
S19	64	130	4.76	9.55	12.42	8.98	10.11	56.8	12.2	0.76	0.04	0.4	0	0	1.09
S20	97	194	4.25	0.43	0.56	10.9	1.8	85.2	24.4	0	0.06	0.4	0.03	0	1.09
S21	1	2	4.89	4.53	5.89	1.28	2.72	42.6	12.2	0	0	0	0.06	0	1.09
S22	12	25	4.65	6.47	8.41	1.28	0.39	28.4	18.3	0	0.04	0.3	0.06	0	1.09
S23	8	17	5.39	0.78	1.01	2.41	0.78	42.6	18.3	0	0.02	0	0.04	0	ND
S24	34	68	4.51	2.76	3.59	2.56	4.28	42.6	18.3	0	0.08	0	0.04	0	0.18
S25	4	8	4.72	6.5	8.45	0.64	1.56	42.6	12.2	0.78	0.02	0	0.01	0	1.09
S26	32	64	4.5	8.06	10.48	3.85	3.11	42.6	24.4	0	0.18	0	0.09	0.15	ND
S27	101	204	5.2	15.4	20.02	19.24	9.33	71	24.4	0.36	0.08	0	0.04	0.01	0.18

S28	54	108	4.37	10.16	13.21	8.34	6.22	42.6	18.3	0	0	0.1	0.01	0	2
S29	109	218	4.36	15.69	20.39	13.47	11.28	71	12.2	0	0.08	0.5	0.04	0.08	1.09
S30	51	25	4.5	6.26	8.14	3.85	3.5	42.6	12.2	0	0	0	0.01	0	1.09
S31	44	89	4.38	9.38	12.19	7.05	5.06	28.4	12.2	0	0.26	0.1	0.03	0	2
S32	17	35	5.18	8.06	10.48	0.64	0.39	42.6	12.2	0	0.06	0	0.01	0	ND

The values of correlation coefficient among water quality variables are presented in Table 2. TDS had fairly strong positive correlation with Ca^{2+} (0.737), Mg^{2+} (0.567) and Na^+ (0.556). NO_3^- was quite strongly correlated with Ca^{2+} (0.613) and may indicate anthropogenic contamination.

Groundwater Chemistry in the Study Area

Total dissolved solids (TDS) and Ph

Total dissolved solids (TDS) values recorded in recharge areas were generally very low, ranging from 1.0 to 164 mg/l. This low trend may be credited to effect of low solubility of quartz (the main constituent of the loose sand aquifer of the area) at normal groundwater temperature. Also, it may indicate direct perennial recharge of groundwater by rainfall (supported by Gibbs diagrams on mechanisms controlling groundwater chemistry, discussed later). This is consistent with Akpoborie and Efobo (2014), Akpoborie *et al.*, (2015a) and (Akpoborie *et al.*, 2015b). Conversely, relatively higher TDS value (up to 407.0 mg/l) was recorded within discharge area around Ikpoba slope in proximity to some dumpsites where the highest pH (6.59), Ca^{2+} (67.84 mg/l), Cl^- (198.80 mg/l) and HCO_3^- (311.20 mg/l) also occurred. However, all the water samples are desirable for drinking (Davis and DeWiest, 1966) (Table 3). The importance of pH in water supplies with respect to water softening, chemical coagulation, disinfection and corrosion control cannot be overemphasized (Sawyer *et al.*, 2003). The pH values of the groundwater samples ranged from 4.21 to 6.59, indicating a fairly acidic condition which is consistent with earlier reports on groundwater in the western Niger Delta area (Akpoborie and Efobo, 2014; Aliyu *et al.*, 2006; Akpoborie, 2011; Akudo *et al.*, 2010). This may be attributed to anthropogenic activities such as municipal waste and sewage disposal.

Total hardness (TH)

Calcium and magnesium are the chief hardness-causing cations in association with respective relevant anions (HCO_3^- and SO_4^{2-}) in natural waters (Sawyer *et al.*, 2003). In the current study, the observed groundwater hardness varied from 3.20 to 379.93. According to Sawyer and McCarty (1967), over 84% of the groundwater samples were soft (3.20 mg/l to 71.90 mg/l), about 6.25% were moderately hard (79.92 mg/l to 86.35 mg/l), while 6.25% were hard (175.29 to 216.42 mg/l), and 3.12% were very hard (379.93 mg/l) (Table 3).

Alkaline earths (Ca^{2+} and Mg^{2+})

Dissolved Ca^{2+} concentration level ranged from 0.64 to 67.84 mg/l. In natural groundwater, calcium ions may result from dissolution of rocks (limestone, gypsum, dolomite or apatite), minerals (calcite and feldspar) and construction materials (cement and brick lime). Dissolved calcium ions in the groundwater samples might have evolved from anorthite (plagioclase), ferromagnesian minerals or anthropogenic sources. Magnesium concentrations varied from 0.39 to 51.30 mg/L. Common sources of magnesium (Mg^{2+}) in groundwater include dolomite, magnesite or detrital minerals such as plagioclase feldspar, pyroxene, amphibole and mica. For the study area, Mg^{2+} in the groundwater samples probably came from detrital sources.

Alkalies (Na^+ and K^+)

The concentration levels of Na^+ in the groundwater samples varied from 0.43 to 17.08 mg/l. Na^+ in natural groundwater may be derived from rock weathering (of sodic silicates), rock-salt, hot saline waters, road salt, and anthropogenic sources (such as animal wastes and discharges from sewage and dumpsites). Longer residence time may have enhanced water-rock interactions and led to dissolution of substantial amount of sodium ion in deeper aquifers in localities like 2nd East Circular where total depth of about 135 metres was observed. However, anthropogenic sources may include the municipal dumpsite leachates.

Table 2: Correlation matrix of physicochemical parameters of groundwater in the study area

	pH	TDS (mg/l)	TH (mg/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	K ⁺ (mg/l)	Na ⁺ (mg/l)	Cl ⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	PO ₄ ²⁻ (mg/l)	NO ₃ ⁻ (mg/l)	Fe ²⁺ (mg/l)	Pb ²⁺ (mg/l)	Mn (mg/l)
pH	1														
TDS	-0.473	1													
TH	-0.164	0.679	1												
Ca	-0.250	0.737	0.930	1											
Mg	-0.081	0.567	0.950	0.815	1										
K	-0.070	0.442	0.593	0.595	0.673	1									
Na	-0.088	0.556	0.706	0.711	0.779	0.890	1								
Cl	-0.021	0.471	0.560	0.620	0.501	0.355	0.494	1							
HCO ₃	0.206	-0.101	0.095	0.092	-0.034	-0.110	-0.205	0.015	1						
SO ₄	0.173	-0.253	-0.140	-0.087	-0.063	-0.004	0.064	0.197	-0.071	1					
PO ₄	-0.035	0.123	0.083	0.065	0.030	-0.008	0.111	0.086	0.158	0.021	1				
NO ₃	-0.195	0.383	0.546	0.613	0.502	0.317	0.444	0.395	-0.156	0.003	-0.160	1			
Fe	0.135	0.013	0.043	0.011	0.074	-0.083	0.057	0.311	0.337	-0.113	0.492	-0.061	1		
Pb	-0.158	-0.109	-0.058	0.544	0.529	0.658	-0.121	-0.199	-0.246	0.125	-0.094	-0.112	-0.408	1	
Mn	0.059	0.350	0.508	0.544	0.529	0.658	0.596	0.535	0.225	-0.123	-0.066	0.278	0.246	-0.351	1

Table 3: Suitability of groundwater for drinking based on TDS (Davis and DeWiest, 1966) and hardness (Sawyer and McCarthy, 1967)

		Class	Number of samples	% of sample
TDS (mg/l)	< 500	Desirable for drinking	32	100
	500 - 1000	Permissible for drinking	0	0
	1000 - 3000	Useful for irrigation	0	0
	> 3000	Unfit for drinking and irrigation	0	0
TH (mg/l)	< 75	Soft	27	84.38
	75 - 150	Moderately hard	2	6.25
	150 - 300	Hard	2	6.25
	> 300	Very hard	1	3.12

Potassium (K^+) concentration levels in the groundwater varied from 0.56 to 21.78 mg/l. Dissolved K^+ in groundwater may be from weathering of K-feldspar and mica. Anthropogenic source may also include leaching of fertilizer. Potassium in the groundwater may have resulted from both anthropogenic and rock-water interaction sources in shallow and deep aquifers respectively.

Trace elements (Fe^{2+} , Pb^{2+} and Mn^{2+})

Excessive iron concentration level in groundwater can make it objectionable to end-users (Sawyer *et al.*, 2003). Its values ranged from 0 to 0.65 mg/l in the study area and compared well with concentration values obtained by earlier workers (Akujize and Irabor, 2014; Ehiowemwenguan *et al.*, 2014). Majority of the samples (about 91 %) had values less than 0.30 mg/l. Lead is potentially carcinogenic and has potential for kidney impairment and mental retardation (Sawyer *et al.*, 2003). Anthropogenic sources of lead include solder used for connecting copper pipes. Its levels in the samples analyzed ranged from 0 to 2.0 mg/l. About 94 % of the water samples had Pb^{2+} concentrations less than 0.05 mg/l. The amount of dissolved Mn^{2+} observed in the study area varied from 0 to 0.2 mg/l. About 93.75 % of the water samples had Mn^{2+} levels which are well below 0.1 mg/l.

Major anions (Cl^- , HCO_3^- and NO_3^-)

Chloride was the predominant major anion in the groundwater samples and its concentration level varied from 28.4 to 198.8 mg/l. It occurs naturally in groundwater through weathering of sedimentary rocks and soils, and dissolution of rock-salt. In the study area, Cl^- ions are more likely from domestic and municipal effluents from dumpsites and sewage discharges. Bicarbonate concentrations ranged from 12.20 to 311.20 mg/l. Contrary to usual expectation in a continental environment, chloride predominated the anions rather than bicarbonate in the study area. This is however consistent with earlier findings from the same Benin Formation in other parts (such as Sapele, Effurun-Warri, Abraka, Ughoton and Ndokwa) of the western Niger Delta area (Akpoborie, 2011a & 2011b; Akpoborie & Aweto, 2012; Akpoborie & Efobo, 2014; Akpoborie *et al.*, 2015a; Akpoborie *et al.*, 2015b). Nitrate was not detected in about 41 % of the groundwater samples. Where detected, the values (0.08 to 1.28 mg/l) were well below the WHO recommended concentration limit of 50 mg/l for drinking purpose.

Sulphate and Phosphate (SO_4^{2-} , PO_4)

When excessive in concentration level, sulphate ions are known for bad odour and sewer corrosion under reducing anaerobic conditions. Sulphate (SO_4^{2-}) was non-detectable in a large proportion (69 %) of the water samples analyzed. Where detected, the concentration levels were very low (0.04 to 1.00 mg/l). Phosphate ions were not detectable in about 49 % of the water samples. Where detected, the concentrations ranged from 0.02 to 0.9 mg/l.

Geochemical Evolution of Groundwater

Piper trilinear diagram

Results of hydrochemical analyses plotted on Piper (1944) diagram (Figure 3) enhanced our understanding of, (i) basic water type, (ii) mixing patterns, and (iii) likely ion exchanges. Most of the water samples plotted near the top of the diamond field of the Piper diagram, indicating that the water samples are rich in $Ca^{2+} + Mg^{2+}$ (> 50%) and Cl^- (> 70%). Therefore, the groundwater in the study area is predominantly mixed Ca^{2+} - Mg^{2+} - Cl^- hydrochemical facies type. The dominance of calcium indicates continental materials as expected. Common sources of calcium ions include dissolution of limestone, gypsum, dolomite and apatite. Calcium could also dissolve from detrital minerals such as plagioclase feldspar, pyroxene, amphibole and mica. They may also come from construction materials like cement and brick lime. In the current study area where $Ca^{2+} \gg SO_4^{2-}$, calcite/dolomite or silicate (i.e. plagioclase feldspar, pyroxene, amphibole and mica) is most probably the main source of dissolved calcium ions in the groundwater samples. However, the expected change in composition of rainwater, the main source of groundwater recharge, from sodium chloride-rich near the ocean to calcium

sulphate or calcium carbonate-dominance further inland, in such environment was not observed. Hence, the observed non-predominance of bicarbonate as expected in such continental environment suggests silicate weathering rather than carbonate weathering. It then follows that calcium might have evolved from anorthite (plagioclase) or ferromagnesian minerals. Otherwise, anthropogenic sources may be responsible for calcium enrichment in the area. The latter is most probable from the viewpoint of chloride dominance instead of bicarbonate and may point to influence of leachate contamination from waste dumps (located in places like Army Barracks, Temboga road, Post Pprimary Education Board area, off Ikpoba road and near Nigeria Prison) and sewage discharges in the area. Some of the water samples (from Uwasota Street, Oluku and Envoy motel (off Airport Road) plotted on a straight line on the upper right-hand side of the diamond field. This is indicative of similarity in chemical composition and may suggest same source. Likewise, samples from north of Ugbowo, new Benin market and Plymouth Street (off Adesogbe), plotted linearly, signifying common chemistry and possibly same source. From the anion triangle, the groundwater samples all plotted linearly towards the chloride apex which implied chloride ion dominance (> 70%) among the anions in the groundwater samples. In contrast, the cation triangle indicated some mixing patterns. By interpolation on the cation triangle, the alignment of groundwater samples from 2nd East Circular through 2nd Obasohan, off Oko Road to NNPC station, Ogba suggested evolving water by cation exchange of Ca^{2+} and Mg^{2+} for Na^+ .

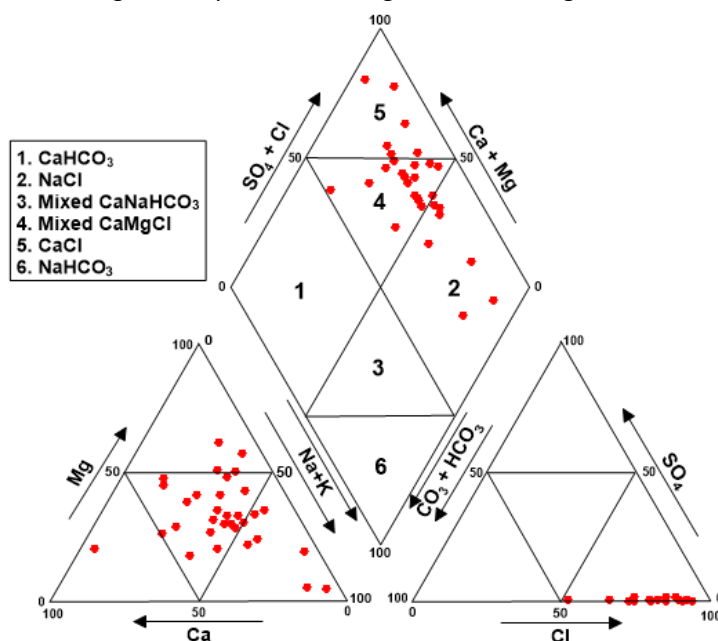


Fig. 3: Piper trilinear plot of the samples

Stiff plots

Based on the spatial trends and forms of the Stiff (1951) plots, there were indications of groundwater mixing and ion exchange among the alkaline earth and alkali metallic ions (Ca^{2+} , Mg^{2+} , Na^+ , and K^+). The water patterns revealed transient characteristics of groundwater chemistry within short distances (Figures 4). This is consistent with ion exchange reactions typical of shallow Benin Formation elsewhere as reported by Akpoborie and Efobo (2014) and Akpoborie *et al.* (2015a). The groundwater samples from north of Ugbowo and north of Uselu shared similar pattern which indicated similar chemical composition ($\text{Mg}^{2+} > \text{Na}^+ + \text{K}^+ > \text{Ca}^{2+}$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$). This suggests common source with southward decrease in cation concentrations and increase in anionic loadings. However, there was a decrease in TDS from north of Ugbowo to north of Uselu. In contrast, groundwater sample from Otufure and Oluku exhibited slightly different patterns with similar chemical composition ($\text{Mg}^{2+} > \text{Na}^+ + \text{K}^+ > \text{Ca}^{2+}$ and $\text{Na}^+ + \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$ respectively) but indicating cation exchange of $\text{Na}^+ + \text{K}^+$ for Mg^{2+} or Ca^{2+} probably caused by the waste dumps in the area, with marginal decrease in TDS (0.9 mg/l). Identical Stiff patterns also characterized groundwater samples from Egor, Asowata Street off upper Siluko

road and south of Uwelu off power line with diminishing cations and anions concentrations suggestive of dilution along flow direction.

Gibbs plot

From Gibbs (1970) plot, there was indication that rainfall was chiefly responsible for the chemical evolution of groundwater in the area (Figure 5). The groundwater samples that showed effects of rock weathering were essentially from localities with deep boreholes like New Benin (146.3 m), Omosogbe area (132.3 m), second Uzama road (128 m) and second East Circular Road (131.1m). At such depths, the resident time for water molecules could have enhanced more dissolution. Groundwater samples which plotted outside the three fields of dominant processes may imply anthropogenic sources such as leachate from waste dumps, sewages and septic pits.

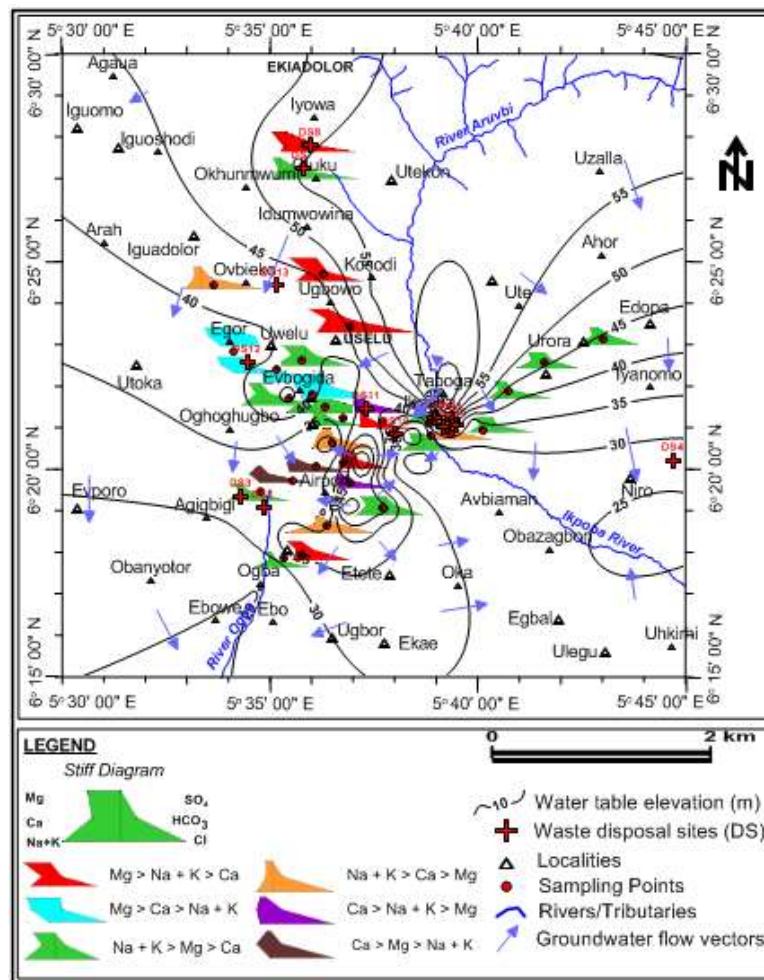


Fig. 4: Water Table map with mixing patterns from Stiff (1951) plots

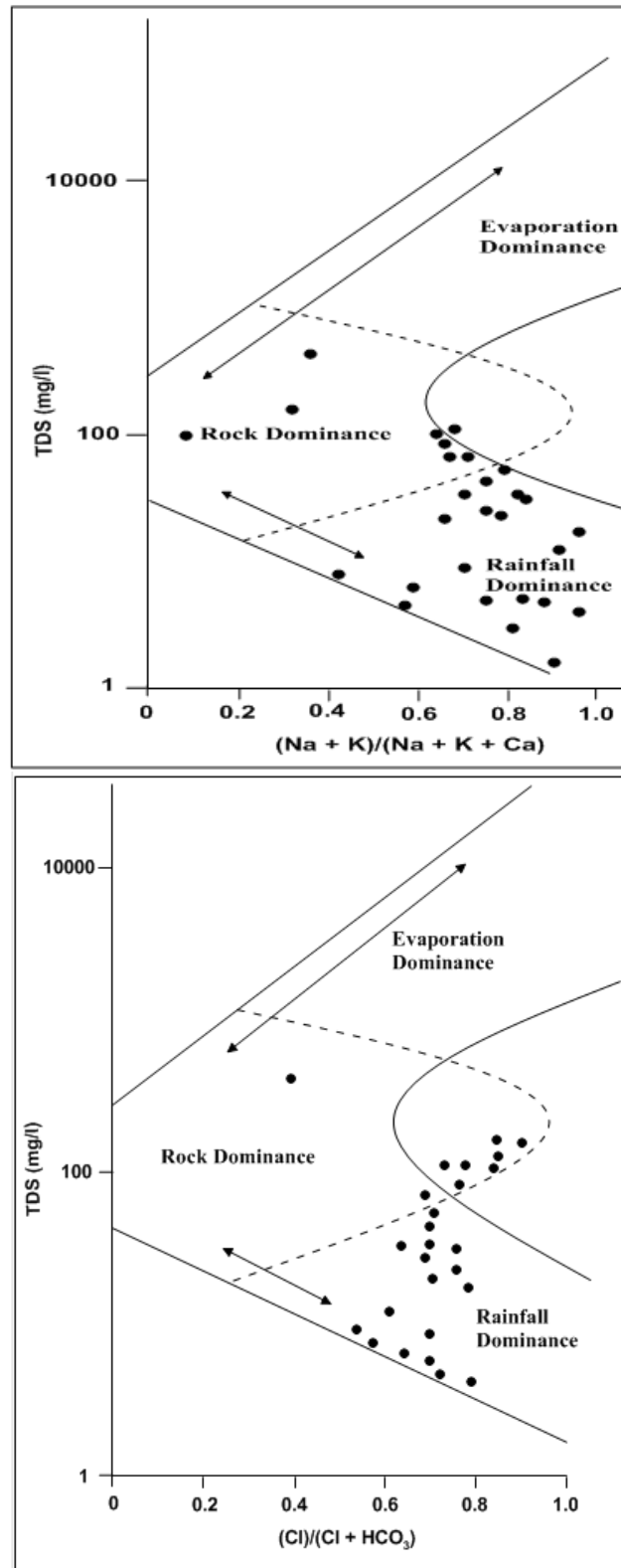


Fig. 5: Gibbs plots showing mechanisms governing groundwater chemistry (a) Major cations versus TDS (b) Major anions versus TDS

Groundwater Suitability for Irrigation in the Study Area

Table 4 showed the summary of the computed irrigation water indices for groundwater in the study area.

Sodium Absorption Ratio (SAR) and USSL diagram

SAR is a fundamental parameter in determining the acceptability of water for irrigation. Over-utilization of water characterized by high SAR for irrigation leads to soil structure breakdown and consequent drop in crop yield (Nagarajah, *et al.*, 1988). The groundwater samples investigated were excellent based on SAR criterion (Table 5). According to the classification scheme of Richards (1954) using the USSL diagram (Figure 6), most of the groundwater samples (93.75%) fall under C1-S1 (low salinity-low sodium hazard) category, while only 6.25% belonged to C2-S1 (medium salinity-low sodium hazard) category. The water samples are therefore safe for irrigation with no fear of sodium or salinity hazard.

Soluble Sodium Percentage (SSP) and Wilcox diagram

Excessive dissolved Na^+ in irrigation water can reduce soil permeability, and modify soil structure and physical properties (Janardhana Raju *et al.*, 1992; Asiwaju-Bello *et al.*, 2013). When too much of Na^+ concentration and high EC characterize any irrigation water, objectionable effects like low osmotic activity, slow water and nutrient uptake by plants are expected. Ultimately, low crop yield may ensue. Based on the modified Wilcox classification system (Todd, 1980), the SSP values obtained indicated that 9.38 %, 40.63 %, 40.63 %, 3.13 % and 6.25 % of the groundwater samples were excellent, good, permissible, doubtful and unsuitable for irrigation respectively (Table 5). This implies that about 90.62 % of the groundwater samples are suitable for irrigation use. Also, Wilcox (1955) diagram shows that 96.87 % and 3.13 % of the water samples fall under excellent to good and good to permissible categories for irrigation respectively (Figure 7).

Residual Sodium Carbonate (RSC) and Magnesium Adsorption Ratio (MAR)

Irrigation water should have lower concentration of $\text{CO}_3^{2-} + \text{HCO}_3^-$ than $\text{Ca}^{2+} + \text{Mg}^{2+}$ expressed in meq/l to be adjudged desirable. Otherwise, CaCO_3 will be precipitated in the soil and cause rise in Na^+ concentration in the water (Sharma *et al.*, 2017). Eventually, this will produce detrimental effects like soil clogging, reduced soil water infiltration, stunted growth of plants, and at the end low crop yield may be observed. Based on Lloyd and Heathcote (1985), all the water samples recorded RSC values less than 1.25, indicating good quality and suitability for irrigation use (Table 5). For Magnesium Adsorption Ratio, about 25% of the water samples fall within the suitable class ($\text{MAR} < 50$ %). Up to 75 % of the samples attained $\text{MAR} > 50$ % and may therefore be unsuitable for irrigation.

Table 4: Irrigational quality parameters

Sample ID	EC ($\mu\text{S}/\text{cm}$)	SAR (meq/l)	SSP (meq/l)	CAI (meq/l)	KR (meq/l)	PI (meq/l)	RSC (meq/l)	MAR (meq/l)
S01	7.46	0.121	25.80	0.83	0.20	28.02	0.17	83.18
S02	7.46	0.236	44.28	0.82	0.45	27.84	0.12	76.73
S03	37.31	0.350	35.40	0.13	0.31	5.61	-0.06	74.83
S04	7.46	0.243	35.77	0.73	0.32	14.32	0.12	89.21
S05	4.48	0.189	37.19	0.84	0.34	25.96	0.12	79.97
S06	11.94	0.112	24.47	0.90	0.18	25.28	0.03	34.79
S07	29.85	0.397	38.98	0.36	0.36	6.94	-0.14	51.84
S08	50.75	0.245	30.62	0.65	0.25	9.33	0.02	73.38
S09	25.37	1.959	90.62	-0.03	5.47	11.65	0.07	50.12
S10	1.49	0.519	54.72	0.42	0.68	9.63	0.04	77.80
S11	5.97	0.165	37.95	0.88	0.35	29.68	0.02	28.41
S12	17.91	1.284	83.80	-0.24	2.93	15.27	0.09	33.44
S13	226.87	0.505	15.58	0.50	0.17	1.03	-1.91	53.56
S14	80.60	0.678	46.71	-0.36	0.50	4.26	-0.20	62.28

S15	128.36	0.783	46.22	0.21	0.49	2.66	-0.71	37.15
S16	150.75	0.720	40.61	-0.18	0.39	2.92	-0.76	44.43
S17	162.69	0.763	42.93	-0.20	0.43	2.26	-0.57	57.99
S18	144.78	0.032	4.55	0.97	0.03	8.92	-0.34	21.40
S19	95.52	0.613	38.93	-0.53	0.36	3.06	-0.46	57.78
S20	80.60	0.649	45.66	-0.30	0.48	4.32	-0.27	55.15
S21	5.97	0.998	75.68	0.17	1.76	10.73	0.07	80.07
S22	65.67	0.658	48.37	-0.80	0.53	4.15	-0.25	54.19
S23	95.52	0.519	36.41	0.08	0.32	2.88	-0.35	64.99
S24	76.12	0.556	50.02	0.20	0.57	6.31	-0.09	59.98
S25	47.76	0.740	57.99	-0.03	0.78	8.36	0.01	57.11
S26	244.78	0.550	26.81	0.08	0.21	17.14	-1.52	52.53
S27	607.46	0.369	14.31	0.55	0.09	1.46	-0.83	55.49
S28	8.96	0.218	28.70	0.69	0.23	2.80	0.01	57.95
S29	34.33	0.571	55.82	0.50	0.72	10.47	-0.01	49.73
S30	46.27	0.632	52.03	0.28	0.61	6.79	-0.01	69.82
S31	13.43	0.394	43.56	0.22	0.44	11.15	0.01	52.75
S32	4.48	0.160	27.94	0.83	0.22	11.48	-0.01	39.74

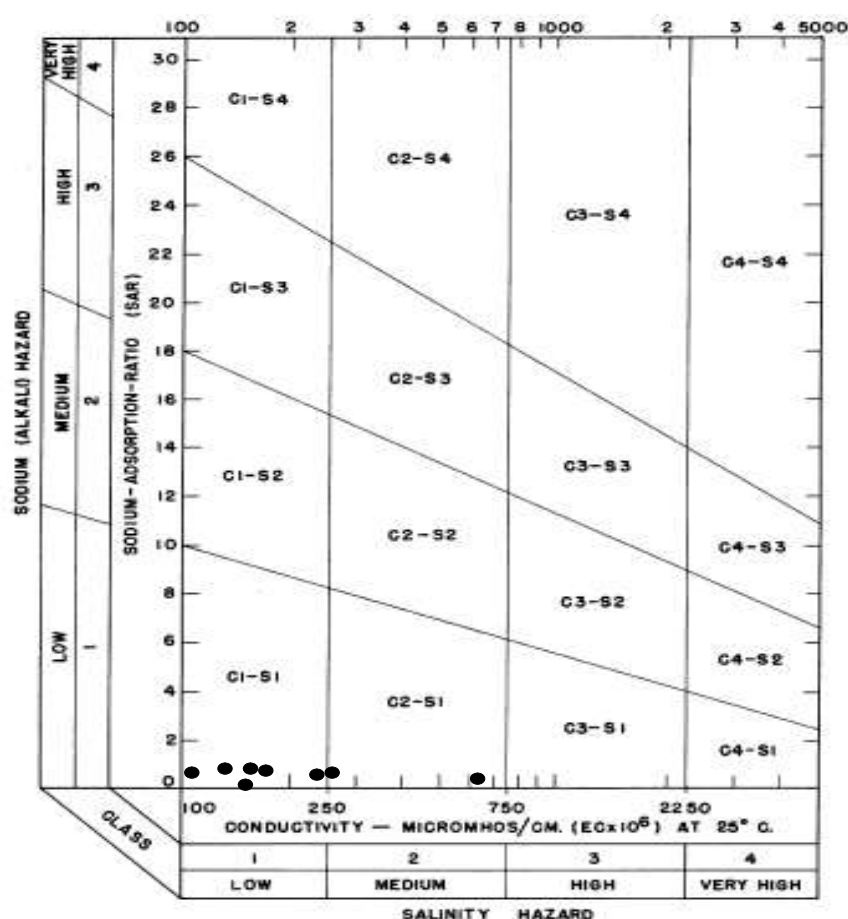


Fig. 6: USSL diagram representing sodium (alkali) and salinity hazard (After Richards, 1954).

Permeability Index (PI) and Kelly Ratio (KR)

Permeability index is another key factor for assessing the quality and suitability of irrigation waters. Based on Doneen (1964), none of the samples fall under class I ($PI > 75\%$). About 15.6% of the water samples belonged

to class II (PI = 25 to 75%) while majority of the samples (about 84.4%) were in class III (PI < 25%). Based on permeability index, a greater proportion of the water samples are unsafe for irrigation purpose (Table 5). Similarly, 3.1%, 6.2% and 90.7% of the water samples are suitable, marginally suitable and unsuitable respectively going by Kelly Ratio (KR) values.

Chloro-Alkaline Indices (CAI)

Scholler (1995) has expressed the degree of Base exchange during water-rock interaction as chloro-alkaline indices (CAI). Most of the samples (up to 72 %) indicated direct ion exchange of $\text{Na}^+ + \text{K}^+$ in groundwater with $\text{Ca}^{2+} + \text{Mg}^{2+}$ in the host aquifer materials with positive CA1 values. Conversely, few of the samples (about 28 %) showed reverse ion exchange of $\text{Ca}^{2+} + \text{Mg}^{2+}$ from groundwater with $\text{Na}^+ + \text{K}^+$ of the rocks with negative CA1 values (Table 4). Therefore, direct ion exchange is a key process controlling the chemistry of groundwater in the area.

IV. CONCLUSION

In the sub-Saharan Africa, groundwater irrigation has the potential to increase food security where quality and suitability is ascertained. In Ogba-Ikpoba River catchment area, groundwater showed relative abundance of major ions in the following order: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ and $\text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^{2-}$. Groundwater in the study area is predominantly mixed Ca-Mg-Cl hydrochemical facies type. The groundwater was fairly acidic and low in hardness.

Table 5: Suitability of groundwater for irrigation

Parameter	Range	Groundwater class	No. of samples	% of samples
EC (Freeze & Cherry, 1979)	< 250	C1 (Excellent or low)	31	96.9
	250 - 750	C2 (Good or medium)	1	3.1
	750 - 2,250	C3 (Permissible or high)	-	-
	2,250- 5,000	C4 (Unsuitable or very high)	-	-
SAR (USDA, 1954)	< 10	Excellent	32	100
	10 - 18	Good	-	-
	18 - 26	Fair	-	-
	> 26	Unsuitable	-	-
Na % (Wilcox, 1955; Todd, 1980)	< 20	Excellent	3	9.5
	20 - 40	Good	13	40.6
	40 - 60	Permissible	13	40.6
	60 - 80	Doubtful	1	3.1
	> 80	Unsuitable	2	6.2
RSC (Lloyd and Heathcote, 1985)	< 1.25	Suitable	32	100
	1.25 - 2.5	Marginally suitable	-	-
	> 2.5	Unsuitable	-	-
PI (Doneen, 1964; Ragunath, 1987)	>75	Safe	-	-
	25 - 75	Moderate	5	15.6
	<25	Unsafe	27	84.4
KR (Kelly, 1963)	< 1	Suitable	29	90.7
	1 - 2	Marginally suitable	1	3.1
	> 2	Unsuitable	2	6.2
MAR (Paliwal, 1972)	< 50	Suitable	8	25
	> 50	Unsuitable	24	75

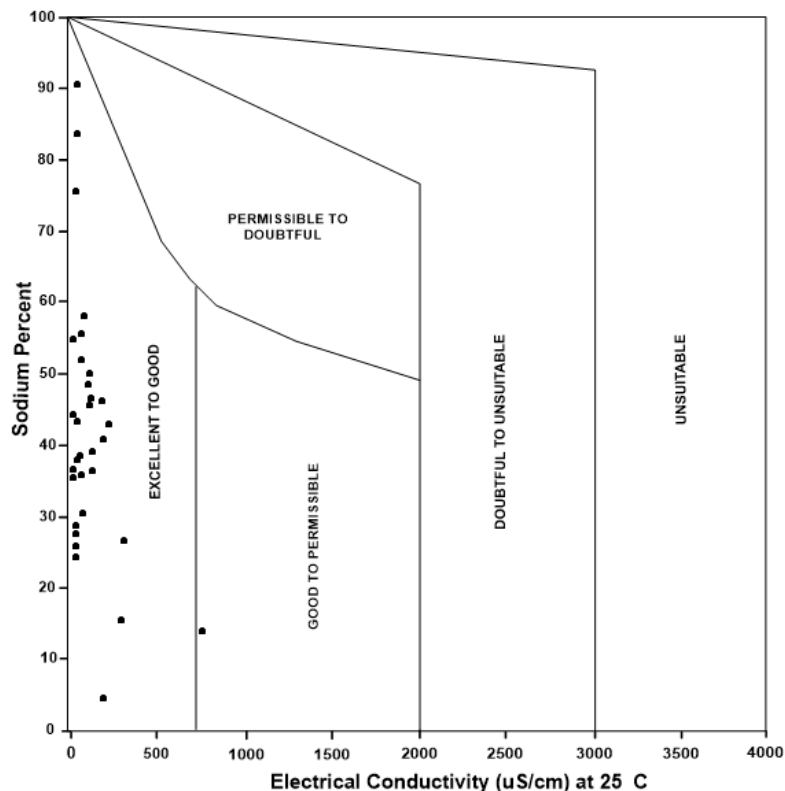


Fig. 7: % Na and Electrical conductivity plot (After Wilcox, 1955)

There were indications of similarity in chemical composition and source of groundwater samples. Evolving water by cation exchange of Ca^{2+} and Mg^{+} for Na^{+} was also exhibited. Groundwater chemistry in the area was predominantly controlled by rainfall. Groundwater mixing was observed. The water patterns also revealed transient characteristics of groundwater chemistry within short distances which is consistent with ion exchange reactions typical of shallow Benin Formation. Diminishing cations and anions concentrations are suggested dilution along flow direction. Based on pH, TDS, TH, Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , NO_3^{-} , Cl^{-} and HNO_3^{-} , almost all the groundwater samples are safe for drinking (WHO, 1984, 1993 and 2011). Most of the samples (93.75%) fit in to C1-S1 category, implying that groundwater in the area is expected to pose low salinity-low sodium hazard when used for irrigation. According to Wilcox diagram, 96.87 % of the water samples belong to excellent category for irrigation purpose. Also, values of residual sodium carbonate signified good quality and suitability for irrigation. However, results on Permeability index, magnesium adsorption and Kelly ratios implied non-suitability for irrigation.

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