

Hydro-Geochemical Attributes of Quaternary Sands in Warri, Western Niger Delta, Nigeria.

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ABSTRACT

Hydro-geochemical study of the Quaternary Sands of Warri was conducted. The research was purposed to appraise the groundwater quality status in view of human consumption and delineate its attributive hydro-chemical facies and processes. Water samples from eight representative hand-dug wells tapping the formation were analyzed for physical and chemical parameters. Analyses indicate ambient water temperature ranges from 28.6 to 31^oC, P^H ranges from 6.4-7.6 which indicates the water is weakly acidic to weakly alkaline. Electrical Conductivity (EC) values range from 159.4-612 μ S/cm while Total Dissolved Solids (TDS) range from 79 to 306.0mg/l. The maximum chloride content recorded in wells was up to 25.03mg/l which indicates salt water intrusion/contamination is lacking.

Except for high levels of iron in Ubeji, Ejeba, Jakpa, and Airport junction, all analyzed parameters in other areas were compatible with the World Health Organization (WHO, 2006) standards for drinking water. Analytical results show the abundance of major ionic components of the groundwater system appear in the following order; Ca>Mg>K>Na = HCO₃ >Cl >SO₄ >NO₃. Hydro-chemical indices (Mg/Ca, Cl/HCO₃, and Cation Exchange Value (CEV) describe the groundwater as that of Inland origin while delineation of hydro-chemical facies show the system consists dominantly of calcium-chloride facies with minor occurrences of mixed water (Ca-SO₄-Cl/Ca-Cl-HCO₃) and Calcium-bicarbonate/Sulphate facies types.

Further Interpretation of Hydro-geochemical data suggests the groundwater chemistry is attributable to ion-exchange, Natural water recharge, leachate impact, silicate weathering and dissolution following the infiltration of atmospheric/surface water into the aquifer. The study therefore stresses the need for regular water quality assessment as this would guide management decisions against hydro-chemical hazards and quality degradation.

(Keywords: groundwater chemistry, hydrochemical facies, infiltration, dissolution)

INTRODUCTION

Groundwater is that subsurface water that fills the voids of soils and permeable geological formations. It is readily available and cheap to develop, hence a majority of the population in Warri and environs depend on groundwater as a source of potable water supply.

Groundwater quality appraisal is gaining importance due to intense urbanization, industrialization and agricultural activities putting the soil and groundwater to greater risk of contamination (Sayyed and Wagh, 2011; Tiwari, 2011) and this threatens human health and economic development.

The chemistry of groundwater is determined by hydrologic, climatic and hydrogeologic factors Such as the type of aquifer, the mode and source of recharge, the drainage area and permeability of the soil cover (Abam

2001; Amadi et al., 2005; Oseji et al., 2005; Ekundayo, 2006 ; Olobaniyi and Owoyemi, 2006).

The investigation of the hydro-geochemistry of groundwater is predicated in the fact that the usefulness of groundwater to human in a large extent depends on its chemistry. Since groundwater is the major source of water in the study area, the research therefore investigates the hydro-geochemistry of the quaternary sands in Warri and environs with the view to assessing the potability of its water content and delineating the hydro-geochemical processes dictating the groundwater chemistry.

Geomorphology, Hydrology and Geology of the Area

Warri lies between latitude $N005^{\circ}31'$, Latitude $005^{\circ}35'$ and Longitude $E005^{\circ}44'$, Longitude $E005^{\circ}38'$. It is in the Western Niger Delta area of Nigeria (Figure 1) and lies on a flat-gently sloping depositional plain with slopes of about $0 - 4^{\circ}$. It is drained by the tide-influenced River Warri, with numerous small tributaries that describes a dendritic drainage pattern. Sections of the Warri River exhibits anastomosing pattern that is mainly visible during low tides and dry weather.

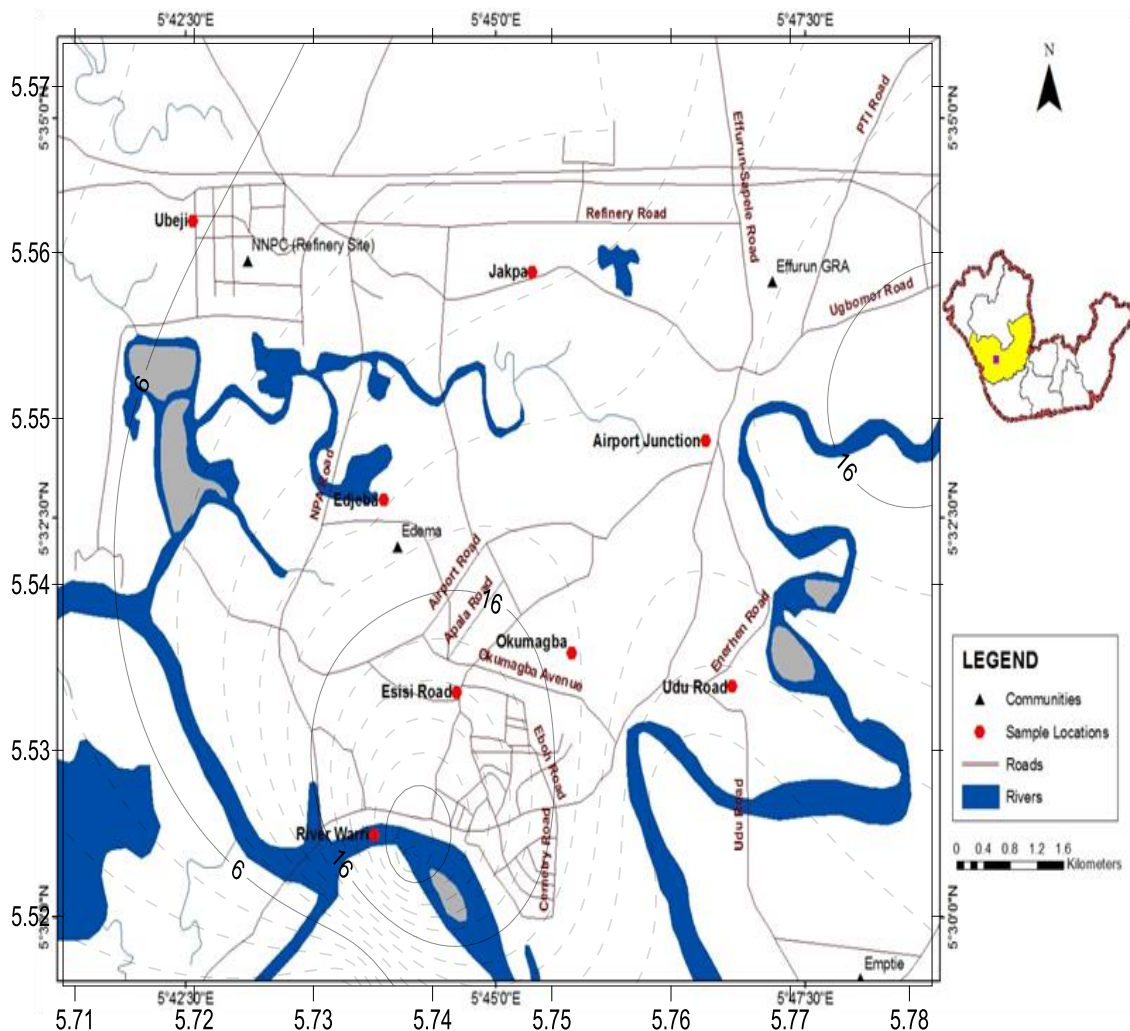


Figure 1: Map of the Study Area Showing the Sample Location. (Inset: Map Of Delta State Showing the study location)

The study area is underlain by Quaternary-recent alluvium known as the Sombreiro-Warri Deltaic plain sands which consist predominantly of unconsolidated fine-medium grained sands, brownish medium stiff-stiff clayey/silty sands or thick organic clays especially at the marshy Nigeria Ports Authority (NPA) areas of Warri, (Wigwe 1975; Avwenagha et al., 2014). This geological unit generally does not exceed 120 meters in thickness and it is predominantly unconfined (Olobaniyi and Owoyemi, 2006).

The unit overlies the three major subsurface lithostratigraphic units of the Niger Delta (Benin, Agbada and Akata Formations). Hydraulic conductivities of the Quaternary sand vary from 3.82×10^{-3} to 9.0×10^{-2} cm/sec (which indicates a potentially productive aquifer and specific capacities recorded from different areas within this formation vary from 6700lit/hr/m to 13,500lit/hr/m (Offoile 1991). The water table is very close to the ground surface and varies from 0 to 4metres. This limited groundwater level fluctuation reflects the high amount of precipitation recorded in Warri over the greater part of the year with annual average of about 3000mm (Adejuwon, 2012). Classical works on the Geology and geomorphology of the Niger Delta have been presented by authors (Allen, 1965; Reyment, 1965; Short and Stauble, 1967; Assez, 1970; Oomkens, 1974; Akpokodje, 1979, 1987 and Nwajide, 2013).

METHODOLOGY

This study involved measurement of depth to water table in hand dug wells using a water level indicator (Solinst Model 101) with a view to determining the static water levels. Elevation and co-ordinates of representative wells were recorded using the hand-held GARMIN 12 model GPS. Water samples were collected from hand dug wells into sterilized bottles and stored in ice containers at 4°C. Sensitive parameters such as temperature, Conductivity and pH were measured in-situ before samples were transported to laboratory for further physical and chemical analyses. Temperature was measured with a mercury-filled Celsius thermometer, Total Dissolved Solids (TDS) and Electrical Conductivity were estimated with Oakton TDS/Conductivity meter. pH was estimated using the ATI-Orion pH meter. Concentration of Na^+ and K^+ were determined with a flame Emission analyser. Ca^{2+} and Mg^{2+} were determined by EDTA Titrimetry.

Cl^- , HCO_3^- , and CO_3^{2-} were also measured by appropriate titrimetric methods. NO_3^- was measured by Colorimetry while SO_4^{2-} was determined by precipitation using BaCl_2 and measurement of absorbency with a spectrophotometer. Iron concentrations were estimated using model SP2900 Pye-Unicam Atomic Absorption spectrophotometer. Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were determined using the modified Winkler and KmnO_4 methods respectively.

RESULTS AND DISCUSSIONS

The hydro-chemical data of groundwater in Warri and environs were compared with WHO standards for drinking water (Table 1). Groundwater temperatures in the area range from 28.6°C at Ubeji to 31°C at Okumagba Layout, with a mean value of 29.83°C. Groundwater pH values range from 6.4 - 7.6 (mean = 6.47), indicating weakly acidic to weakly alkaline groundwater system.

Total Dissolved Solids (TDS) is a measure of the total solutes in water. It gives a rough index of the suitability of Groundwater for any purpose (Offodile, 2002). It also gives an insight on the rate of infiltration (vertical recharge), travel velocity of groundwater in an aquiferous medium and Depth of the aquifer. TDS values range from 29.80mg/l at River Warri to 306.0mg/l at Jakpa, with a mean value of 167.24mg/l. The relatively low TDS recorded at river Warri could be attributable to direct natural recharge (rainfall) unlike the land locations where natural recharge is slowed-down / interrupted by overburden soils resulting in a higher TDS. All TDS values in the area fall below the stipulated WHO permissible limit for drinking water which indicates potable water in view of this parameter.

According to Richard (1954), water with more than 1000mg/l is good for dyeing of textiles and manufacture of plastic and rayons. Electrical conductivity values vary from 159.4 $\mu\text{S}/\text{cm}$ at Ubeji and reach a maximum of 612 $\mu\text{S}/\text{cm}$ at Jakpa area, with a mean value of 374.204 $\mu\text{S}/\text{cm}$. These values have direct relationship with the Total dissolved solids (TDS) and fall below stipulated standard (WHO, 2006).

Table 1: Hydro-Chemical Data of the Study Area.

S/N	Parameters	WHO (2006)	SAMPLED LOCATIONS								
			UBEJI	EDJEBBA	UDU ROAD	ESISI ROAD	JAKPA ROAD	AIR PORT JUNCTION	OKUMAGBA	WARRI RIVER	MEAN
1	pH	6.5-8.5	6.40	7.60	5.60	6.61	6.40	6.00	6.70	7.50	6.60
2	Temperature (°C)	N/A	28.60	29.00	30.50	28.40	30.70	30.60	31.00	28.20	29.63
3	TDS (mg/l)	500	79.60	122.0	211.00	172.00	306.00	227.00	192.00	29.80	167.43
4	Conductivity (µS/cm)	1400	159.4	244.00	422.00	244.00	612.00	554.00	384.00	59.60	334.87
5	Bicarbonate (mg/l)	-	3.00	18.00	5.00	15.00	32.00	35.00	20.00	9.00	17.13
6	Turbidity (NTU)	5	12.60	13.90	16.90	20.90	16.70	16.10	16.80	61.30	21.9
7	Total Hardness (mg/l)	500	5.84	4.82	5.14	11.00	4.60	4.28	5.62	4.00	5.66
8	Total Acidity (mg/l)	-	22.00	64.00	20.00	0.28	6.60	52.00	164.00	0.36	41.15
9	Total Alkalinity (mg/l)	500	32.40	27.25	8.25	-	36.16	38.10	27.25	-	21.17
10	Carbonate (mg/l)	-	3.86	4.28	3.25	4.30	4.16	3.10	7.25	3.40	4.20
11	Chloride(mg/l)	250	4.50	6.51	14.51	12.90	25.03	12.01	31.53	1.50	13.16
12	Nitrate (mg/l)	50	12.49	10.72	2.70	0.13	1.98	2.38	2.40	0.07	4.11
13	BOD (mg/l)	-	1.10	1.30	1.30	1.40	1.30	1.50	1.40	3.80	1.64
14	COD (mg/l)	-	2.70	2.30	2.90	40.00	2.70	2.40	2.70	30.00	10.7
15	BOD/COD ratio	-	0.41	0.57	0.45	0.04	0.48	0.63	0.52	0.13	0.37
16	Sulphate (mg/l)	250	2.52	2.66	22.04	2.11	14.94	8.44	20.74	19.66	11.64
17	Calcium (mg/l)	75	2.13	2.4	0.80	3.06	1.61	1.18	0.65	2.56	1.79
18	Potassium (mg/l)	10	1.04	1.19	0.54	1.16	1.18	0.71	0.51	0.70	0.90
19	Sodium (mg/l)	200	0.05	0.06	0.06	0.03	0.09	0.08	0.04	0.01	0.05
20	Iron (mg/l)	0.3	3.00	12.00	0.23	0.29	0.39	0.32	0.11	0.13	2.06
21	Magnesium (mg/l)	150	0.14	0.43	0.06	0.28	0.12	0.09	0.04	0.11	0.16
22	TSS(mg/l)	N/A	12.00	10.00	10.00	12.00	10.00	10.00	10.00	20.57	11.57
23	Dissolved Oxygen (mg/l)	-	4.60	2.10	3.80	4.90	3.20	3.10	3.00	3.00	3.47
24	Phosphate (mg/l)	-	0.46	0.68	0.26	0.64	0.28	0.30	0.32	0.05	0.37

ABBREVIATIONS

- TDS- Total Dissolved Solids
- TSS - Total Suspended Solids
- COD- Chemical Oxygen Demand
- BOD- Biochemical Oxygen Demand

Conductivity usually indicates the presence of unstable ions, (Johnson, 1975). According to Klassen et al (2014), groundwater with electrical conductivity and TDS more than 958-2090µS/cm and 621-965mg/l respectively, is 90-95% indication of saltwater intrusion. This implies that saltwater intrusion is lacking in respect of this parameter.

The cations analyzed include Iron (Fe²⁺), Calcium (Ca²⁺), Magnesium (Mg²⁺), Sodium (Na⁺) and potassium (K⁺). Calcium concentration ranges from 0.65 -3.06mg/l with a mean concentration of 1.63mg/l. The relatively high concentration of calcium at Esi Road may be traceable to leachates from the major dump site nearby. The

Calcium concentration also falls within the acceptable limits of WHO (2006). Other cations (Na⁺, K⁺, Mg²⁺ and Fe²⁺) have mean concentration levels of 0.06, 0.09, 0.17 and 2.33, respectively. Except for Ubeji, Edjeba, Jakpa, and Airport Junction, iron concentrations in other locations fall within the WHO (2006) permissible limit for drinking water.

Unacceptably high levels of iron recorded in these areas (Figure 2), could be attributed to weathering of Iron-bearing minerals (such as Limonite, Goethite and Haematite) which abundantly characterize the Quaternary sands in the area, thereby liberating Ferrous ions (Fe²⁺) which infiltrate the groundwater system.

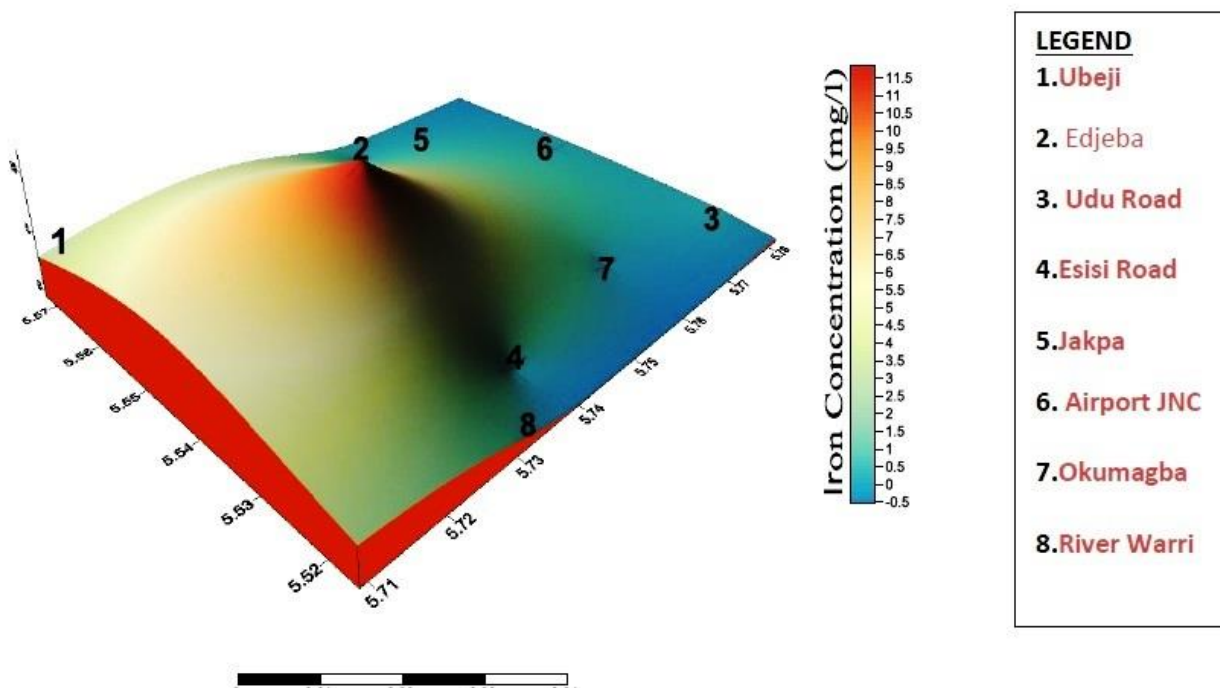


Figure 2: Iron Distribution Model for the Study Area.

On exposure to air, ferrous ion (Fe^{2+}) is oxidized to insoluble Fe^{3+} which precipitates as red colored ferric hydroxide [$\text{Fe}(\text{OH})_3$] that causes stains on white porcelain enamel wares, fixtures and sundry plumbing works. High concentration of iron could trigger the growth of iron bacteria which causes dark-colored slime layers on inner walls of pipe system resulting in dirt build-up and blockage of plumbing lines. High levels of iron in groundwater had been noticed in parts of Rivers State, Eastern Niger Delta by UDOM et al. (1998, 1999 and 2002) and Udom and Acra (2006). Nevertheless, deficiency in groundwater quality with respect to iron levels in these areas could be remedied by controlled aeration which is one of the most cost-effective, environmentally friendly and commonly used method for oxidizing iron, coupled with filtration to separate the insoluble ferric ions.

Total hardness varied between 4.28 -11.0mg/l with an average of 5.7mg/l which is within the WHO (2006) limit of 500mg/l. Classification of water based on hardness according to Freeze and

Cherry (1979), indicates groundwater in the area is Soft, hence suitable for domestic use with respect to total hardness.

The anions studied are chloride (Cl^-), Sulphate (SO_4^{2-}), Bicarbonate (HCO_3^-), Nitrate (NO_3^-), and Phosphate (PO_4^{3-}). The Chloride content ranges from 1.5mg/l at River Warri to 25.03mg/l in Jakpa, with mean value of 13.16mg/l. Comparison of the chloride values with the stipulated (WHO, 2004) limit of 250mg/l for potable water confirms the water is suitable for domestic use. Chloride content is also a reliable tool for judgment on saltwater intrusion because it is the most stable macro-element in seawater and the most sensitive to saltwater intrusion (Zesheng, 1992). Chloride content greater than 130-484.0mg/l in groundwater is 90-95% indication of saltwater intrusion (Klassen et al., 2014). The low chloride content in the study area therefore indicates the groundwater is not impacted by saltwater intrusion. Bicarbonate (HCO_3^-)

concentration in the water ranges from 3 - 25mg/l with an average of 17.12mg/l. Other anions that were analyzed also fall within the permissible limit for drinking water.

Biochemical Oxygen Demand (BOD) is a very important parameter in determining the quality status of any water. It is an indirect index of the presence of organic matter. It is the amount of oxygen required to cause biological decomposition of organic matter (Karanth, 1987).

When oxidation is complete and no oxygen is required, BOD is zero. The BOD is reported to be a fair measurement of cleanliness of any water on the basis that values less than 1 - 2mg/l are considered clean, 2-3mg/l fairly clean, 5mg/l doubtful and 10mg/l definitely bad and polluted, (Moore and Moore, 1976). BOD values obtained in this study range from 1.30 - 3.80mg/l with a mean value of 1.66 which is less than the doubtful value of 5mg/l. Comparison of the BOD value with FEPA (1991) permissible limit of 50mg/l for drinking water also confirms the water is potable.

Major Ion Chemistry and Abundance

Major ions constitute a significant part of the total dissolved solids in groundwater. The concentration of ions in groundwater depends on the hydro-geochemical processes that take place in the aquifer system, Lakshmanan et al. (2003). These processes occur when the groundwater moves towards equilibrium in major ionic concentration, Nwankwoala and Udom (2011). Therefore the study of major ionic concentration is useful in evaluating geochemical processes operating in groundwater system.

From Table 1, the concentration of major ions in the system occur in the following order of dominance; $Ca > Mg > K > Na = HCO_3 > Cl > SO_4 > NO_3$. Calcium is the dominant cation while Bicarbonate, is the dominant anion. The cationic dominance of calcium could be attributed to ion-exchange of Na^+ for Ca^{2+} and Mg^{2+} . The molar ratio of Mg/Ca is less than 2, indicating the dissolution of minerals which introduce Ca^{2+} and Mg^{2+} into the groundwater. On the other end, rainwater charged with carbon (IV) oxide (CO_2) may have resulted in the dominance of Bicarbonate ion in the anionic sequence.

Hydrogeochemical Indices

Hydro-geochemical indices [(Mg/Ca, Cl/ HCO_3 , Cation exchange value, (CEV) = $(Cl - [Na^+ + K^+]/Cl)$] were used to assess the salinity and origin of groundwater in the study area. Mg/Ca values are less than 2, ranging from 0.002 to 0.179 (Table 2). Interpretation of this index implies the groundwater in the study area is of Inland origin because water under marine influence would have values of about 5, Morell et al. (1986), except where other processes such as cationic exchange intervene and if this happens, the values could be 4 or less.

Cl/ HCO_3 ratios range from 0.36 to 2.90 which also implies the groundwater is of Inland origin as values of this index (Cl/ HCO_3) for Inland waters and Sea waters are between 0.1 - 5.0 and 20-50 respectively, (Custudio, 1987). In general, CEV for seawater ranges from +1.2 to +1.3 (Custudio, 1983), whereas low-salt inland waters give values close to zero either positive or negative. The CEVs of the groundwater are less than 1.0 (ranging from 0.53 - 0.98), this also indicates that the groundwater is inland.

Hydrochemical Facies

The diagnostic character of water solution in a hydrosystem is determined by the application of the concept of hydro-chemical facies, (Back, 1966). They reflect the impact of the interplay of geochemical processes between minerals in the subsurface rocks and the groundwater. Hydrochemical facies will therefore give a better insight into the chemical processes dictating the groundwater chemistry in the area. The Piper Trilinear plot was used in delineating these facies. Results of chemical analyses were used to characterize groundwater in the area, based on the predominance of major ionic components in the Piper's plot (Figure 3).

From the plot, groundwater in the area is predominantly characterized by Calcium-Chloride facies while the Mixed Water types (Ca- SO_4 -Cl/Ca-Cl- HCO_3) and Calcium-Sulphate/ Bicarbonate facies are the least dominant Facies.

Table 2: Hydro-Geochemical Indices of the Study Area.

Mg/Ca	Cl/HCO ₃	CEV = Cl-(Na ⁺ +K ⁺)/Cl
0.066	1.50	0.758
0.179	0.36	0.808
0.075	2.90	0.960
0.002	0.86	0.908
0.075	0.78	0.950
0.076	0.38	0.934
0.061	1.58	0.983
0.043	0.17	0.530

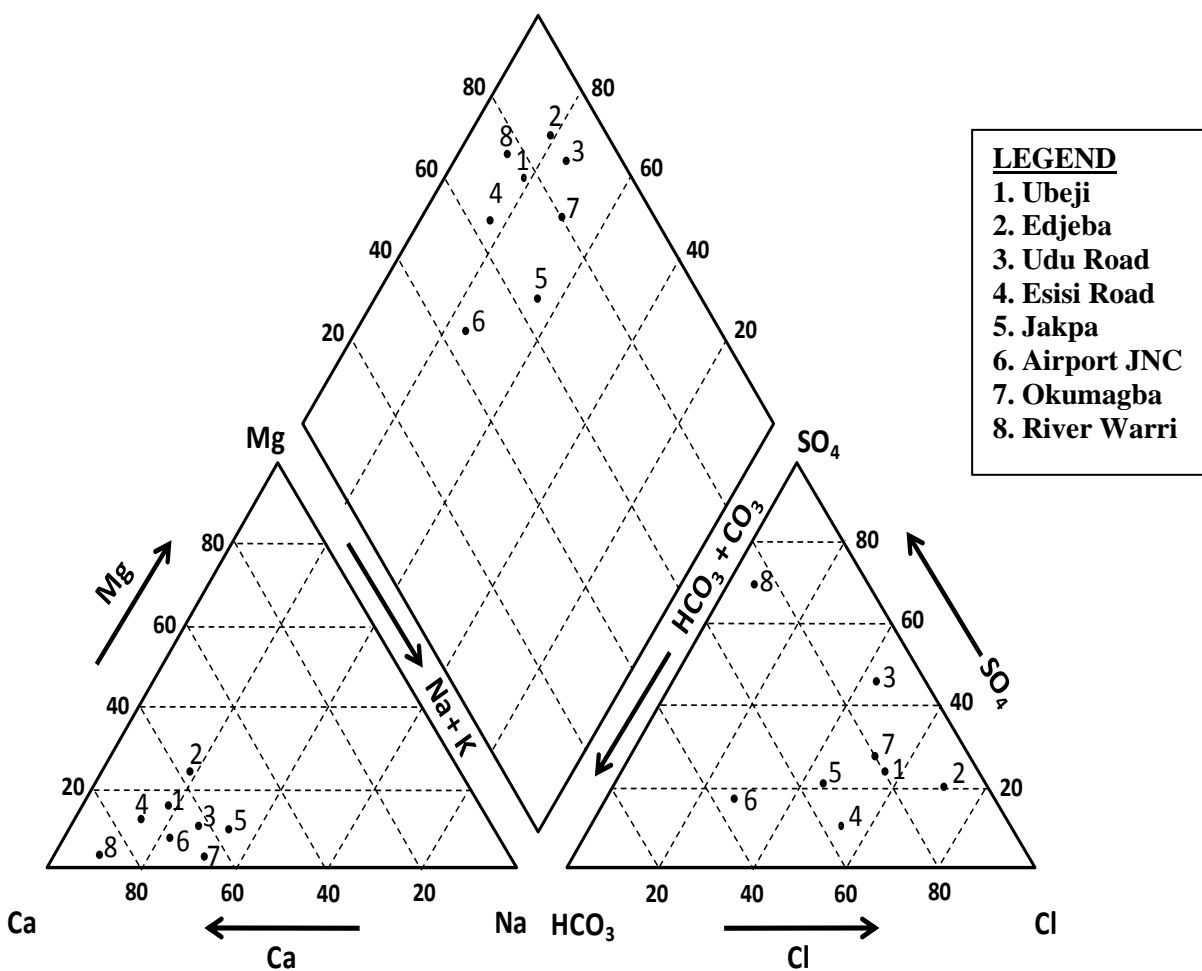


Figure 3: Piper Trilinear Diagram of Groundwater Characterization in the Study Area.

The calcium chloride facies account for about 50% of the groundwater samples while the mixed water and Calcium-Sulphate/ Bicarbonate facies account for 25% each.

Chloride is a useful parameter for evaluating atmospheric and marine influence on groundwater (Appelo and Postma, 1993; Klassen et al 2014). The chloride levels in the groundwater fall below saltwater intrusion bench mark of 130mg/l, according to Klassen et al (2014), which implies the absence of marine influence. Therefore, the dominance of the calcium-chloride type facies could be attributed to a combination of atmospheric precipitation charged with chloride ion, leachates from surrounding dumpsites (Akpoborie et al., 2014) and silicate weathering. The calcium-bicarbonate/sulphate facies type are most probably a reflection of rain water precipitation charged with Carbon (IV) oxide and sulphate ion.

CONCLUSION

A hydro-geochemical investigation of the Sombreiro-Warri Deltaic plain sands has been conducted. Except for unacceptable levels of dissolved iron in wells within Ubeji and Edjeba areas, all physio-chemical parameters of groundwater were compatible with the World Health Organization (WHO, 2006) standard for drinking water.

Interpretation of hydro-geochemical indices indicates the groundwater is of Inland origin. Analysis of spatial display diagram (Piper plot) reveals the groundwater is dominated by Calcium-Chloride facies with subordinate mixed water (Ca-SO₄-Cl/Ca-Cl-HCO₃) and Calcium-Bicarbonate/ Sulphate facies types. This study, therefore, has provided a basic geochemical data for groundwater quality management; hence it is recommended that regular, coordinated and intensive groundwater quality monitoring be conducted in the area.

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