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**Research article**

# Hydro-geochemical Attributes and Quality Status of Groundwater in Port Harcourt, Eastern Niger Delta

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## Abstract

A hydro-geochemical evaluation of groundwater quality status in Port Harcourt City, Eastern Niger Delta was investigated. This was carried out to assess the quality for human consumption and the processes responsible for the modification of groundwater quality. Thirty two (32) groundwater samples were analyzed for their physical and chemical properties. The average temperature of the groundwater samples is 29$^oC$. The water is acidic to slightly alkaline with pH values ranging from 4.28 – 7.72 while Eh ranges between 26.44 to 197mV. Electrical Conductivity (EC) values ranges from 28µS/cm to 717.40µS/cm. Elevated EC and chloride values in some locations are indicative of high ionic activities as well as salinity and suggest possible pollution of groundwater. Chloride concentrations in some boreholes are up to 710mg/l, which shows saltwater encroachment at those locations with Total Dissolved Solids (TDS) ranging from 12.60mg/l - 401mg/l. The chemical composition of the groundwater is characterized by high chloride concentration and variations in cation concentrations due to the cation exchange reaction between aquifer characteristics and seawater components. Besides pH, Fe, TDS and EC (in some locations), all other parameters fall within the WHO desirable and maximum permissible limits for drinking and other purposes. Thus, the groundwater in the area is low in dissolved constituents, soft and acidic. The analytical results show the abundance of the ions in the following order: Mg > Ca > Na > K = Cl > $SO_4$ > $HCO_3$ > $NO_3$. Chloride is the dominant anion found in the groundwater of the study area. The groundwater is classified into Ca – Mg-Cl-$SO_4$ and Na – K - Cl - $SO_4$ types based on its hydro-geochemical characteristics. This study therefore, provides the basic tool for sustainable groundwater management in the context of quality assessment. It is recommended that regular, systematic, comprehensive and sustainable groundwater quality monitoring in the study area be carried out.

**Keywords:** Groundwater quality, Coastal aquifer, hydro-geochemistry, saltwater intrusion

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## Introduction

Quality of water is an important factor in development and use of groundwater as resources (Kumar and Singh, 2010). The need to ascertain the quality of water used by humans has become very intense in the past decade

(Olatunji *et al*., (2005). The assessment of groundwater quality status is important for socio-economic development of any region of the world. It is therefore difficult to imagine any programme for human development that does not require a readily available supply of water. The quantity, physical, chemical and biological characteristics of water determine its usefulness for domestic, industrial or agricultural purposes (Ariyo *et al*., (2005).

Port Harcourt is a fast growing area faced with increasing demand for water resources due to high population growth rate and growing prosperity. The entire population of the area depends on groundwater for their domestic water supplies because the rivers and creeks are polluted (Udom & Amah, 2006). Water for local consumption and industrial use is extracted mainly from boreholes. Presently, there is no programme by the government to monitor the quality of potable water in the study area.

Several studies have been carried out on the interaction of groundwater with the host rock in parts of the Niger Delta (Amadi *et al.,* 1989; Olobaniyi and Owoyemi, 2006; Edet and Ekpo, 2008, Nganje *et al.,* 2010 and Amadi *et al* 2010). None of the studies have been able to evaluate the hydro-geochemistry of the deep aquifer systems. The hydro-geochemical processes and hydro-geochemistry of the groundwater vary spatially and temporally, depending on the geology and chemical characteristics of the aquifer (Lakshmanan *et al*., 2003; Nwankwoala & Udom, 2011b). Thus, knowledge on hydro-geochemical processes that control groundwater chemical evolution could lead to improved understanding of hydro-geochemical characteristics of an aquifer. Groundwater provides a reasonably constant supply that is not likely to dry up under natural conditions, as surface sources may do. In Rivers State which is rapidly expanding and industrialization going on, coupled with the nearness of the area to the sea, possibilities abound that groundwater quality may be affected. Groundwater quality is normally characterized by different physico-chemical characteristics and these parameters change widely due to the type of pollution, groundwater extraction, etc.

Generally, in groundwater quality studies, many data are required to make meaningful interpretation, advanced procedures must be required, because of the complexities of the regional hydro-geological conditions and hydro-geochemical processes that occur in the aquifers which are difficult to explain and document. This paper therefore examines the quality of groundwater, the hydro-geochemical attributes as well as the factors controlling water quality in the area.

## Geology and Hydro-geological Setting

Port Harcourt is located within latitudes 6$^{o}$ 58$^{'}$ to 7$^{o}$ 6$^{'}$N and longitudes 4$^{o}$ 40$^{'}$ to 4$^{o}$ 55$^{'}$E (Fig.1). It falls almost entirely within the lowland swamp forest ecological zone and is flanked in the east, west and southern limits by mangrove swamp forest (Braide *et al*., 2004; Chindah, 2004). The area experiences heavy rainfall averaging 25000mm/annum. It rains for about eight months (March to October) during the year and even the months considered as dry months are not free from occasional rainfall (Gobo, 1990). The area has an almost flat topography and is underlain by superficial soil that consists of silty clays mixed with silty sands. The water table is less than 10m below ground surface.Geologically, Port Harcourt area is characterized by the Niger Delta sedimentary rocks.

Lithostratigraphically, these rocks are divided into the oldest Akata Formation (Paleocene), the Agbada Formation (Eocene) and the Youngest Benin Formation (Miocene to Recent). Generally, the present knowledge of the geology of the Niger Delta was derived from the works of the following researchers (Reyment, 1965; Short & Stauble, 1967; Murat, 1970; Merki, 1970) as well as the exploration activities of the oil and gas companies in Nigeria. The formation of the so called proto-Niger Delta occurred during the second depositional cycle (Campanian-Maastrichtian) of the southern Nigerian basin. However, the modern Niger Delta was formed during the third and last depositional cycle of the southern Nigerian basin which started in the Paleocene. The geologic sequence of the Niger Delta consists of three main Tertiary subsurface lithostratigraphic units (Short & Stauble, 1967) which are overlain by various types of Quaternary deposits (Table 1).

**Table 1:** Quaternary deposits of the Niger Delta (after Etu-Efeotor & Akpokodje, 1990)

| **Geologic Unit** | **Lithology** | **Age** |
|---|---|---|
| Alluvium | Gravel, Sand, clay, silt | |
| Freshwater Backswamp, meander belt | Sand, clay, some silt, gravel | |
| Saltwater Mangrove Swamp and backswamp | Medium-fine sands, clay and some silt | Quaternary |
| Active/abandoned beach ridges | Sand, clay, and some silt | |
| Sombreiro-warri deltaic plain | Sand, clay, and some silt | |

The major aquiferous formation in the study area is the Benin Formation. It is about 2100m thick at the basin centre and consists of coarse-medium grained sandstones, thick shales and gravels. The upper section of the Benin Formation is the quaternary deposits which is about 40 – 150m thick and comprises of sand and silt/clay with the later becoming increasingly more prominent seawards (Etu-Efeotor & Akpokodje, 1990). The formation consists of predominantly freshwater continental, friable sands and gravel that have excellent aquifer properties with occasional intercalations of claystone/shales (Olobaniyi & Oweyemi, 2006). According to Etu-Efeotor (1981), Etu-Efeotor & Akpokodje (1990), Offodile (2002), Udom *et al* (2002), the main source of recharge is through direct precipitation where annual rainfall is as high as 2000 – 2400mm. The water infiltrates through the highly permeable sands of the Benin Formation to recharge the aquifers. Groundwater in the study area occurs principally under water table conditions. Multi-aquifer systems occur in the study area and the upper aquifers are generally unconfined (Etu-Efeotor, 1981; Offodile, 2002; Edet, 1993; Amadi, 2004; and Udom, 2004).

## Methods of Study

Groundwater samples were collected from boreholes after 5 minutes of pumping to ensure the samples were true representative from the aquifer. The samples were stored in sterilized two-litre containers with tightly fitting covers wrapped in a black polyethylene plastic bag and put in a cooler to ensure constant temperature. The containers were first washed with de-ionized water, and then several times with the sample water before collection in order to avoid any contamination.

Parameters like pH and temperature and electrical conductivity were determined in the field due to their unstable nature. The pH of the water sample was measured with a pH-meter. The glass tube in the kit was sterilized before been filled to its mark with water sample. The tube was then placed in the space provided in the equipment and a knob adjusted for colour matching, the pH was then read and recorded. The temperature was read using a mercury thermometer. The electrical conductivity was measured using a Mark electronic switchgear conductivity meter. After sampling, the lids of the containers were immediately replaced to minimize contamination and escape of gases. The samples were then stored in an ice-packed cooler for analysis within 24 hours. All analyses were carried out at a standardized laboratory using national and international regulatory methods. The evaluation of water quality was in accordance with regulatory standard. The approach ensures that the samples collected were tested in accordance with agreed requirements using competent personnel as well as appropriate equipment and materials. Fig.1 is the map of Port Harcourt showing sampling locations.

## Results and Discussion

The analytical results for groundwater samples from study area are presented in Table 1. Groundwater temperature in the study area ranges from 26.35 – 29.64$^0$C. There is no standard value recommended for groundwater temperature by the WHO (2006). The hydrogen ion concentration (pH) and redox potential (Eh) of the groundwater in the study area ranges from 3.84 – 7.72 and 26.44 – 197.00mV respectively. EC ranges between 28.00µS/cm and 717.40µS/cm. Majority of the samples have values which fall above the WHO (2006) guide values of 500µS/cm, except few low values. The concentration of Total Dissolved Solids (TDS) ranges from 12.60–401.00mg/l. The TDS values correlate well with conductivity values. The highest TDS value (401.00mg/l) recorded had a corresponding high conductivity of 717.40µS/cm in Borokiri (UPE) (BH 5). The concentration of Total Suspended Solids (TSS) ranges from Below Detection Limit (BDL) to 35.00mg/l. TSS is not stated in WHO (2006) guidelines. WHO (1996) stipulates 10mg/l as the desirable level of TSS and a maximum permissible limit of 25mg/l in drinking water. The highest TSS value (35.00mg/l) was recorded in Borokiri Sandfill (BH 14). A comparison of measured TSS value with WHO (1996) standards shows that the water samples are within the maximum permissible limit implying that the water is suitable for drinking/domestic uses, except in Borokiri Sandfill (BH 14) which needs to be treated before use.

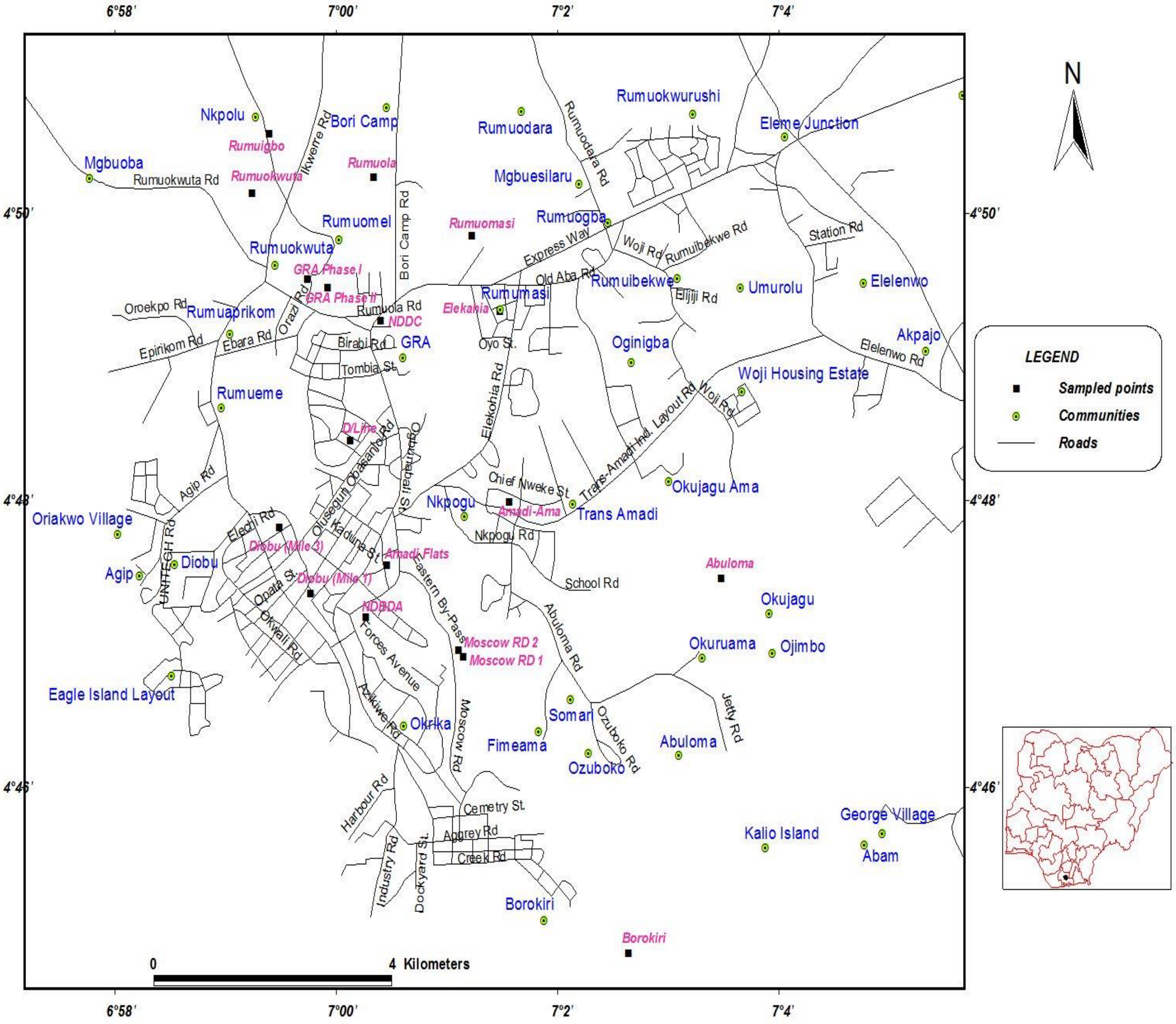


**Figure 1:** Map of Port Harcourt Showing Study Locations

**Table 1:** Hydrogeochemical Data of Groundwater Samples in the Study Area

| BH No. | Location | Temp ($^0C$) | pH | EC (µS/cm) | TDS (mg/l) | TSS (mg/l) | Hardness (mg/l) | $Cl^-$ (mg/l) | Eh (mV) | $SO_4^{2-}$ $^($mg/l) | Fe (mg/l) | Salinity (mg/l) | $NO_3^-$ $^($mg/l) | $HCO_3^-$ (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | Abuloma (GSS) | 27.22 | 55.53 | 573.00 | 250.00 | 1.00 | 28.00 | 710.00 | 122.00 | ND | 1.600 | 116.00 | 0.230 | 18.401 |
| 2. | Amadi-Ama | 26.91 | 6.81 | 421.60 | 370.50 | 5.00 | 8.43 | 250.00 | 131.00 | ND | 0.400 | 511.00 | ND | 21.800 |
| 3. | Moscow Rd 1 (Pumping Station) | 27.02 | 4.50 | 522.00 | 230.60 | 10.0 | 14.50 | 330.00 | 170.00 | ND | ND | 355.00 | 0.201 | 6.701 |
| 4. | Moscow Rd 2(Post Office) | 28.33 | 7.40 | 513.00 | 221.30 | 12.00 | 20.40 | 300.00 | 143.00 | 75.00 | 0.400 | 82.00 | 0.831 | 10.321 |
| 5. | Borokiri (UPE) | 26.51 | 3.84 | 717.40 | 142.70 | 1.00 | 14.00 | 351.00 | 152.00 | 19.30 | 0.020 | 181.00 | 0.510 | 21.010 |
| 6. | Borokiri (Comprehensive Sec. Sch.) | 29.03 | 7.72 | 618.20 | 297.20 | BDL | 36.00 | 410.00 | 191.00 | 90.10 | ND | 163.40 | ND | 54.011 |
| 7. | Eagle Island (NAOC Fence) | 26.35 | 6.50 | 230.00 | 49.00 | 10.00 | 10.40 | 53.00 | 124.00 | 69.13 | 0.200 | 398.60 | ND | 11.000 |
| 8. | Eastern-Bye-P(LNG) | 27.67 | 6.70 | 183.70 | 183.21 | 3.00 | 70.00 | 331.00 | 187.00 | 82.55 | 0.300 | 200.50 | 14.000 | 39.230 |
| 9. | Harley Street(Old GRA) | 29.03 | 7.23 | 195.20 | 55.00 | 1.00 | 142.00 | 300.00 | 192.00 | 96.32 | 0.200 | 85.10 | 34.000 | 23.003 |
| 10. | Forces Avenue (Old GRA) | 29.64 | 7.34 | 181.40 | 59.70 | BDL | 8.00 | 68.00 | 137.00 | 38.31 | 0.400 | 49.31 | 0.100 | 8.190 |
| 11. | Elekahia | 28.28 | 7.30 | 33.50 | 21.00 | 2.00 | 6.00 | 18.00 | 123.00 | 87.15 | 0.500 | 240.11 | 6.500 | 12.110 |
| 12. | Woji | 27.19 | 5.90 | 49.30 | 12.60 | 3.00 | 7.00 | 48.00 | 127.00 | 75.80 | 0.800 | 150.00 | 3.200 | 15.300 |
| 13. | Elijiji Woji | 26.40 | 5.81 | 28.00 | 20.00 | 1.00 | 20.00 | 38.00 | 135.00 | ND | 0.200 | 50.00 | 0.310 | 58.040 |
| 14. | Borokiri Sandfill | 27.92 | 6.23 | 429.30 | 241.00 | 35.00 | 13.5 | 250.00 | 196.00 | 48.00 | 0.020 | 113.21 | 6.300 | 23.171 |
| 15. | Rumuolumeni | 27.51 | 5.90 | 350.60 | 122.70 | 3.00 | 2.50 | 115.00 | 193.00 | 72.96 | 0.820 | 210.32 | 0.600 | 30.000 |
| 16. | Marine Base | 26.83 | 7.11 | 560.00 | 401.00 | 7.00 | 11.00 | 103.50 | 123.00 | 22.03 | 0.000 | 63.70 | 13.000 | 7.110 |
| 17. | Reclamation Rd | 26.33 | 6.02 | 527.00 | 270.00 | 8.00 | 13.00 | 132.00 | 124.00 | 24.70 | 0.100 | 25.00 | 9.311 | 9.500 |
| 18. | Aggrey Rd | 27.04 | 5.83 | 150.00 | 255.00 | 4.00 | 121.32 | 401.00 | 130.00 | 230.11 | 0.020 | 15.60 | 0.500 | 15.210 |
| 19. | Churchill (Harold Wilson Drive) | 28.27 | 5.31 | 160.00 | 218.00 | 14.00 | 78.36 | 390.50 | 185.00 | 9.70 | 0.010 | 62.10 | 0.100 | 20.713 |
| 20. | Rumuagholu | 29.47 | 5.44 | 50.00 | 25.00 | 2.00 | 135.00 | 12.00 | 131.00 | 78.00 | 0.200 | 95.30 | 0.200 | 8.080 |
| 21. | Elelenwo | 28.03 | 5.93 | 35.00 | 25.00 | 3.00 | 132.10 | 35.00 | 192.00 | 65.10 | 0.100 | 26.40 | 0.500 | 10.345 |
| 22. | Rumuibekwe | 28.17 | 6.01 | 56.00 | 59.00 | 4.00 | 12.34 | 38.00 | 194.00 | 74.71 | 0.010 | 62.10 | 0.010 | 11.000 |
| 23. | Mgbuoba (Okilton) | 26.78 | 6.82 | 32.00 | 39.30 | 1.00 | 18.00 | 19.00 | 196.00 | 96.00 | 0.040 | 672.75 | 1.550 | 13.400 |
| 24. | D/Line (Okija Street) | 28.51 | 6.76 | 49.42 | 65.60 | 3.00 | 48.00 | 23.00 | 197.00 | ND | 0.030 | 60.24 | 1.580 | 10.361 |
| 25. | GRA 111(Abacha Rd) | 28.02 | 4.69 | 36.73 | 140.54 | 1.00 | 4.00 | 41.00 | 96.30 | 80.00 | 0.051 | 130.30 | 2.000 | 12.712 |
| 26. | Mile4(Mkt Junction) | 27.30 | 7.71 | 30.21 | 33.60 | 2.00 | 13.13 | 30.80 | 26.44 | 70.00 | 0.400 | 220.50 | 5.320 | 15.170 |
| 27. | Orazi | 28.03 | 6.50 | 74.01 | 36.00 | 1.00 | 12.00 | 50.51 | 27.78 | 78.00 | 0.210 | 120.12 | 0.400 | 12.121 |
| 28. | Rumuigbo | 27.22 | 4.75 | 33.00 | 33.00 | 3.00 | 10.00 | 32.00 | 55.77 | 191.32 | 0.090 | 50.00 | 0.330 | 13.100 |
| 29. | Diobu (Nanka Street) | 28.00 | 6.83 | 45.00 | 35.72 | 4.00 | 30.23 | 16.10 | ND | 126.00 | 0.303 | 10.33 | 0.624 | 29.100 |
| 30. | UST (New VCs Lodge) | 27.11 | 5.73 | 250.13 | 150.10 | 1.00 | 19.31 | 28.00 | 39.22 | 100.00 | 0.400 | 15.11 | 0.666 | 12.000 |
| 31. | Onne | 28.13 | 4.28 | 519.40 | 381.31 | 2.00 | 25.22 | 215.00 | 123.22 | 80.00 | 0.361 | 12.00 | 0.378 | 12.000 |
| 32. | Odili Rd (GTC/Zoo) | 27.10 | 7.00 | 210.28 | 211.00 | 1.00 | 14.12 | 28.13 | 50.00 | 120.30 | 0.111 | 10.00 | 0.507 | 12.300 |
| WHO (2006) Standards | LOCATIONS | NS | 6.5-8.5 | 500 | 500 | NS | 500 | 250 | NS | 250 | 0.3 | NS | 50 | NS |

**Table 1:** Hydrogeochemical Data of Groundwater Samples in the Study Area (Contd.)

| BH No. | $S_r^{2+}$ (mg/l) | $Ca^{2+}$ (mg/l) | $Na^+$ (mg/l) | $Mg^{2+}$ (mg/l) | $K^+$ (mg/l) | $PO_4^{3-}$ (mg/l) | Mn (mg/l) | $F^-$ (mg/l) | $SiO_2$ (mg/l) | $Zn^{2+}$ (mg/l) | $Cu^{2+}$ (mg/l) | Pb (mg/l) | $Br^-$ (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | 4.00 | 3.460 | 2.756 | 2.222 | 0.540 | 0.010 | 0.002 | 1.900 | 2.64 | 0.21 | 0.01 | 0.01 | 20.00 |
| 2. | 3.90 | 4.444 | 3.000 | 2.981 | 0.810 | 0.221 | 0.041 | 2.200 | 4.30 | 0.30 | 0.03 | 0.02 | 76.10 |
| 3. | 3.80 | 7.633 | 1.022 | 0.826 | 0.505 | 0.030 | 0.033 | 2.310 | 0.94 | 0.60 | 0.05 | 0.01 | 18.30 |
| 4. | 4.50 | 4.111 | 0.834 | 4.500 | 0.300 | 0.732 | 0.780 | 0.800 | 0.60 | 0.33 | 0.03 | 0.02 | 29.11 |
| 5. | 1.99 | 2.000 | 0.666 | 2.757 | 0.891 | 0.010 | 0.101 | 1.300 | 5.50 | 0.03 | 0.63 | 0.28 | 11.00 |
| 6. | 2.00 | 6.123 | 3.400 | 0.445 | 0.431 | 0.233 | 0.011 | 0.411 | 4.94 | 0.48 | 0.01 | 0.02 | 12.50 |
| 7. | 2.40 | 8.100 | 1.400 | 0.233 | 0.733 | 0.131 | 0.004 | 0.330 | 5.86 | 0.30 | 0.00 | 0.07 | 63.50 |
| 8. | 2.11 | 11.234 | 1.776 | 2.080 | 0.144 | 0.001 | 0.001 | 0.500 | 6.80 | 0.36 | 0.05 | 0.04 | 80.30 |
| 9. | 2.33 | 5.000 | 1.822 | 1.000 | 0.656 | 0.233 | 0.041 | 0.510 | 6.00 | 0.15 | 0.01 | 0.03 | 93.01 |
| 10. | 2.50 | 4.121 | 0.310 | 3.221 | 0.444 | 0.000 | 0.033 | 1.631 | 1.49 | 0.30 | 0.00 | 0.09 | 16.13 |
| 11. | 2.70 | 5.395 | 0.433 | 0.310 | 0.500 | 0.231 | 0.003 | 0.010 | 5.40 | 1.30 | 0.01 | 0.06 | 18.00 |
| 12. | 4.10 | 7.523 | 1.777 | 0.277 | 0.401 | 0.088 | 0.334 | 2.100 | 3.10 | 0.26 | 0.05 | 0.03 | 7.90 |
| 13. | 0.91 | 12.210 | 2.433 | 0.823 | 0.300 | 0.001 | 0.100 | 2.333 | 4.44 | 0.52 | 0.03 | 0.00 | 71.00 |
| 14. | 3.99 | 4.223 | 2.321 | 1.789 | 0.424 | 0.232 | 0.230 | 2.000 | 0.80 | 0.15 | 0.02 | 0.01 | 79.70 |
| 15. | 4.00 | 3.000 | 1.443 | 5.677 | 0.555 | 0.221 | 0.727 | 1.520 | 4.55 | 0.14 | 0.03 | 0.04 | 31.72 |
| 16. | 3.78 | 8.234 | 2.320 | 2.111 | 0.678 | 0.781 | 0.030 | 0.910 | 6.70 | 0.43 | 0.01 | 0.03 | 15.00 |
| 17. | 3.21 | 9.200 | 1.000 | 4.577 | 0.341 | 0.210 | 0.004 | 0.701 | 9.13 | 0.21 | 0.05 | 0.02 | 63.31 |
| 18. | 4.37 | 6.322 | 2.303 | 8.900 | 0.231 | 0.200 | 0.003 | 0.322 | 5.00 | 0.77 | 0.06 | 0.03 | 17.93 |
| 19. | 2.52 | 18.300 | 1.820 | 7.000 | 0.322 | 0.020 | 0.010 | 0.410 | 0.56 | 0.28 | 0.06 | 0.03 | 9.34 |
| 20. | 0.92 | 4.245 | 2.211 | 2.821 | 0.788 | 0.231 | 0.782 | 0.335 | 0.75 | 0.21 | 0.01 | 0.10 | 81.33 |
| 21. | 4.30 | 2.478 | 0.213 | 0.332 | 0.133 | 0.777 | 0.605 | 0.441 | 0.38 | 0.36 | 0.06 | 0.03 | 18.22 |
| 22. | 4.22 | 13.788 | 0.241 | 4.300 | 0.567 | 0.200 | 0.200 | 0.210 | 4.13 | 0.18 | 0.06 | 0.04 | 61.00 |
| 23. | 3.72 | 5.333 | 1.444 | 2.781 | 0.044 | 0.000 | 0.210 | 0.222 | 9.00 | 0.15 | 0.09 | 0.03 | 88.33 |
| 24. | 2.33 | 6.781 | 2.300 | 4.000 | 0.781 | 0.233 | 0.002 | 0.800 | 2.15 | 0.65 | 0.02 | 0.01 | 19.20 |
| 25. | 1.01 | 5.340 | 1.000 | 8.721 | 0.233 | 0.440 | 0.033 | 0.788 | 10.89 | 0.70 | 0.02 | 0.01 | 11.90 |
| 26. | 2.30 | 6.000 | 3.445 | 3.010 | 0.457 | 0.788 | 0.450 | 0.011 | 4.08 | 0.45 | 0.75 | 1.09 | 83.00 |
| 27. | 3.77 | 7.586 | 2.111 | 2.111 | 0.543 | 0.421 | 0.333 | 0.310 | 2.64 | 0.43 | 0.03 | 0.04 | 93.00 |
| 28. | 4.10 | 2.300 | 0.333 | 6.200 | 0.789 | 0.210 | 0.210 | 0.210 | 60.02 | 0.35 | 0.02 | 0.06 | 66.00 |
| 29. | 0.93 | 5.777 | 2.113 | 5.833 | 0.233 | 0.780 | 0.200 | 0.227 | 2.75 | 10.09 | 0.01 | 0.01 | 75.76 |
| 30. | 2.00 | 4.234 | 0.631 | 4.050 | 0.540 | 0.788 | 0.021 | 0.233 | 0.57 | 0.40 | 0.05 | 0.06 | 14.00 |
| 31. | 3.78 | 8.000 | 1.376 | 2.341 | 0.220 | 0.220 | 0.030 | 0.734 | 0.55 | 0.24 | 0.30 | 0.06 | 19.78 |
| 32. | 4.00 | 6.333 | 0.311 | 3.000 | 0.567 | 0.221 | 0.456 | 0.400 | 0.57 | 1.0 | 0.08 | 0.02 | 12.75 |
| WHO (2006) | NS | 7.5 | 200 | 50 | 200 | 10 | 0.1 | NS | NS | 0.5 | 0.05 | 0.1 | NS |

ND = Not Determined, NS = Not Stated BDL = Below Detectable Limit

## Distribution of Ionic Ratios and Abundance

Results show the abundance of ions in the following order: Mg > Ca > Na > K and Cl > $SO_4$ > $HCO_3$ > $NO_3$. Chloride is the dominant anion found in the groundwater of the study area. Its concentration is generally higher than 12mg/l. Sulphate is equally found in considerable amount (9.70 – 230.11mg/l), with mean value of 68.76mg/l, followed by Bicarbonate (3.003 – 58.040mg/l), with mean value of 16.68mg/l. $NO_3$ values ranges from 0.010 – 34.000mg/l, with mean value of 3.24mg/l. Magnesium dominate the cations with a mean value of 3.16mg/l, followed by Calcium, with mean value of 3.02mg/l. Next to calcium is sodium with mean value of 1.58mg/l, followed by potassium with mean value of 0.47mg/l.

The Na/Cl ratios of the saline groundwater probably result from ion exchange of Na for Ca and Mg in clays, which is common in saline groundwater. In addition, the simultaneous enrichment in both ions indicates dissolution of chloride salts or concentration by evaporation process (Jalali, 2005). This is responsible for the relatively high $Na^+$ and $Cl^-$ in the saline groundwater and in coastal aquifers. The dissolution of halite in groundwater releases equal concentration of Na and Cl in the solution due to dissolution of salt horizons (Uma, 1998; Uma *et al*., 1990, Ekwere and Ukpong, 1994; Tijani *et al*., 1996; Tijani, 2008) and coastal groundwater affected by sea water intrusion (Amadi *et al*., 1989; Edet and Okereke, 2001; Frank-Briggs, 2003; Nwankwoala & Udom, 2011a; Nwankwoala & Udom, 2008; Edet, 2010; Edet *et al*., 2011). The molar ratio of Na/Cl ranges from 0.0014 to 0.1843. All the samples have Na/Cl molar ratio lessthan 1, which indicates that ion exchange is the major process. The Mg/Ca ratio ranges from 0.0290 to 2.6961. All boreholes except BH 28 (2.6961) are generally lessthan 2, indicating the dissolution of silicate minerals, which contributes calcium and magnesium to the groundwater. Figures 2 - 9 show the relationships of the ratios of anions and cations.

**Table 3.12:** Hydrogeochemical Indices, Ionic Ratios and CEV of Groundwater in the Area

| S/N | $HCO_3$/Cl | Na/Ca | Na/Cl | Ca/Cl | Mg/Cl | K/Cl | $SO_4$/Cl | Mg/Ca | Ca/$SO_4$ | Ca/$HCO_3$ | CEV |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | 0.0259 | 0.7965 | 0.0039 | 0.0049 | 0.0031 | 0.0008 | 0.0000 | 0.6420 | 0.0000 | 0.1880 | 0.99 |
| 2. | 0.0872 | 0.6751 | 0.0120 | 0.0178 | 0.0119 | 0.0032 | 0.0000 | 0.6710 | 0.0000 | 0.2039 | 0.98 |
| 3. | 0.0173 | 0.1339 | 0.0031 | 0.0231 | 0.0025 | 0.0015 | 0.0000 | 0.1080 | 0.0000 | 1.3389 | 0.99 |
| 4. | 0.0344 | 0.2029 | 0.0028 | 0.0137 | 0.0150 | 0.0010 | 0.2500 | 1.0951 | 0.0548 | 0.3983 | 0.99 |
| 5. | 0.0599 | 0.3330 | 0.0019 | 0.0070 | 0.0079 | 0.0025 | 0.0549 | 1.3790 | 0.1036 | 0.0952 | 0.99 |
| 6. | 0.1317 | 0.5553 | 0.0083 | 0.0057 | 0.0011 | 0.0011 | 0.2198 | 0.0730 | 0.0679 | 0.1134 | 0.98 |
| 7. | 0.2075 | 0.1728 | 0.0264 | 0.0149 | 0.0044 | 0.0138 | 0.3043 | 0.0290 | 0.1172 | 0.7363 | 0.95 |
| 8. | 0.1182 | 0.1581 | 0.0054 | 0.1528 | 0.0063 | 0.0004 | 0.2494 | 0.1850 | 0.1361 | 0.2864 | 0.99 |
| 9. | 0.0767 | 0.3644 | 0.0061 | 0.0339 | 0.0033 | 0.0022 | 0.3211 | 0.2001 | 0.0519 | 0.2174 | 0.99 |
| 10. | 0.1204 | 0.0752 | 0.0046 | 0.0160 | 0.0474 | 0.0065 | 0.5634 | 0.7822 | 0.1076 | 0.5032 | 0.98 |
| 11. | 0.6778 | 0.0803 | 0.0241 | 0.0606 | 0.0172 | 0.0278 | 4.8417 | 0.5750 | 0.0619 | 0.4455 | 0.94 |
| 12. | 0.3188 | 0.2362 | 0.0370 | 0.2997 | 0.0058 | 0.0084 | 1.5792 | 0.37000 | 0.0992 | 0.4917 | 0.95 |
| 13. | 1.5274 | 0.1993 | 0.0640 | 0.1567 | 0.0217 | 0.0079 | 0.0000 | 0.6730 | 0.0000 | 0.2004 | 0.93 |
| 14. | 0.0927 | 0.5496 | 0.0093 | 0.3213 | 0.0072 | 0.0017 | 0.1920 | 0.4240 | 0.0879 | 0.1823 | 0.98 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 15. | 0.2609 | 0.4767 | 0.0125 | 0.0169 | 0.0494 | 0.0048 | 0.6344 | 1.8920 | 0.4011 | 0.1000 | 0.98 |
| 16. | 0.0687 | 0.2816 | 0.0224 | 0.0261 | 0.0203 | 0.0066 | 0.2139 | 0.2563 | 0.3738 | 0.0581 | 0.97 |

**Table 3.12:** Hydrogeochemical Indices, Ionic Ratios and CEV of Groundwater (Continued)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17. | 0.0719 | 0.1086 | 0.0076 | 0.0796 | 0.0347 | 0.0026 | 0.1871 | 0.4980 | 0.3725 | 0.9684 | 0.98 |
| 18. | 0.0379 | 0.2818 | 0.0057 | 0.0697 | 0.0222 | 0.0006 | 0.5738 | 1.4082 | 0.0275 | 0.4156 | 0.99 |
| 19. | 0.0530 | 0.0995 | 0.0047 | 0.0158 | 0.0179 | 0.0008 | 0.0248 | 0.3831 | 1.8866 | 0.8835 | 0.99 |
| 20. | 0.6733 | 0.5208 | 0.1843 | 0.0469 | 0.2351 | 0.0657 | 6.5000 | 0.6658 | 0.0544 | 0.5254 | 0.75 |
| 21. | 0.2956 | 0.0859 | 0.0061 | 0.3538 | 0.0095 | 0.0038 | 1.8600 | 0.1345 | 0.0381 | 0.2395 | 0.99 |
| 22. | 0.2895 | 0.0175 | 0.0069 | 0.0708 | 0.1132 | 0.0149 | 1.9660 | 0.3120 | 0.1846 | 1.2535 | 0.97 |
| 23. | 0.7053 | 0.2708 | 0.0380 | 0.3628 | 0.1464 | 0.0023 | 5.0526 | 0.5210 | 0.0556 | 0.3979 | 0.92 |
| 24. | 0.4505 | 0.3392 | 0.1211 | 0.2807 | 0.1734 | 0.0339 | 0.0000 | 0.5894 | 0.0000 | 0.6545 | 0.86 |
| 25. | 0.3100 | 0.1873 | 0.0435 | 0.2948 | 0.2127 | 0.0057 | 1.9512 | 1.6330 | 0.0668 | 0.4201 | 0.96 |
| 26. | 0.4925 | 0.5742 | 0.0840 | 0.1302 | 0.0977 | 0.0148 | 2.2727 | 0.5022 | 0.0857 | 0.3955 | 0.87 |
| 27. | 0.0024 | 0.2783 | 0.0685 | 0.1948 | 0.0418 | 0.0108 | 0.0154 | 0.2780 | 0.0973 | 0.6250 | 0.95 |
| 28. | 0.4094 | 0.1447 | 0.0066 | 0.0015 | 0.1938 | 0.0247 | 5.9786 | 2.6961 | 0.0120 | 0.1756 | 0.96 |
| 29. | 1.8075 | 0.3658 | 0.0660 | 0.0719 | 0.3646 | 0.0145 | 7.8261 | 1.0090 | 0.0458 | 0.1985 | 0.85 |
| 30. | 0.4286 | 0.1490 | 0.0392 | 0.3588 | 0.1446 | 0.0193 | 3.5714 | 0.9570 | 0.0423 | 0.3528 | 0.96 |
| 31. | 0.0558 | 0.3249 | 0.0491 | 0.1512 | 0.0109 | 0.0088 | 0.3721 | 0.2933 | 0.1000 | 0.6667 | 0.99 |
| 32. | 0.4373 | 0.3249 | 0.0014 | 0.0372 | 0.1066 | 0.0202 | 4.2766 | 0.4740 | 0.0526 | 0.5149 | 0.97 |

## Hydrochemical Indices and Facies

The following ionic relationships were studied to check the salinity and origin of the groundwater in the study area. These includes: Mg/Ca, $Cl/HCO_3$, and the Cationic Exchange Value (CEV = [Cl – (Na + K)]/Cl). Mg/Ca values were all less than 2.0 (Table 3.12) ranging from 0.029 – 1.892. According to the interpretation of this index, the groundwater in the study area appears to be slightly of inland origin, because waters under marine influence would have values of about 5 (Morell *et al.*, 1986) except where other processes such as cationic exchange intervene. If this happens, the values could be 4 or less.

The $Cl/HCO_3$ values range from 0.553 – 49.250. Values of this hydrogeochemical index given for inland waters are between 0.1 and 5 and for seawater between 20 and 50 (Custodio, 1987). In general, the CEV for seawater ranges from +1.2 to +1.3 (Custodio, 1983), where low-salt inland waters give values close to zero, either positive or negative. The CEV values for groundwater of Port Harcourt area are generally below 1.0 (Table 3.12), ranging from 0.75 – 0.99, indicating that the groundwater is inland in some locations with respect to provenance. This results agrees with the findings of Bolaji (2009).

Piper (1944) trilinear diagram for the study area shows that there is a mixture of two types of water with variable concentrations of major ions. These are Ca – Mg – Cl – $SO_4$ type and Na + K – Cl – $SO_4$ type water. The second water type is also influenced by $NO_3$.

The Schoeller semi-logarithmic plots (Fig.3.8) of the data further confirmed this water type. The peaks indicate the dominant ions in the water samples while the trough indicates the less dominant ions. In this study, the dominant ions are $Cl^-$, $SO_4^{2+}$ with $HCO_3^-$ ions following.

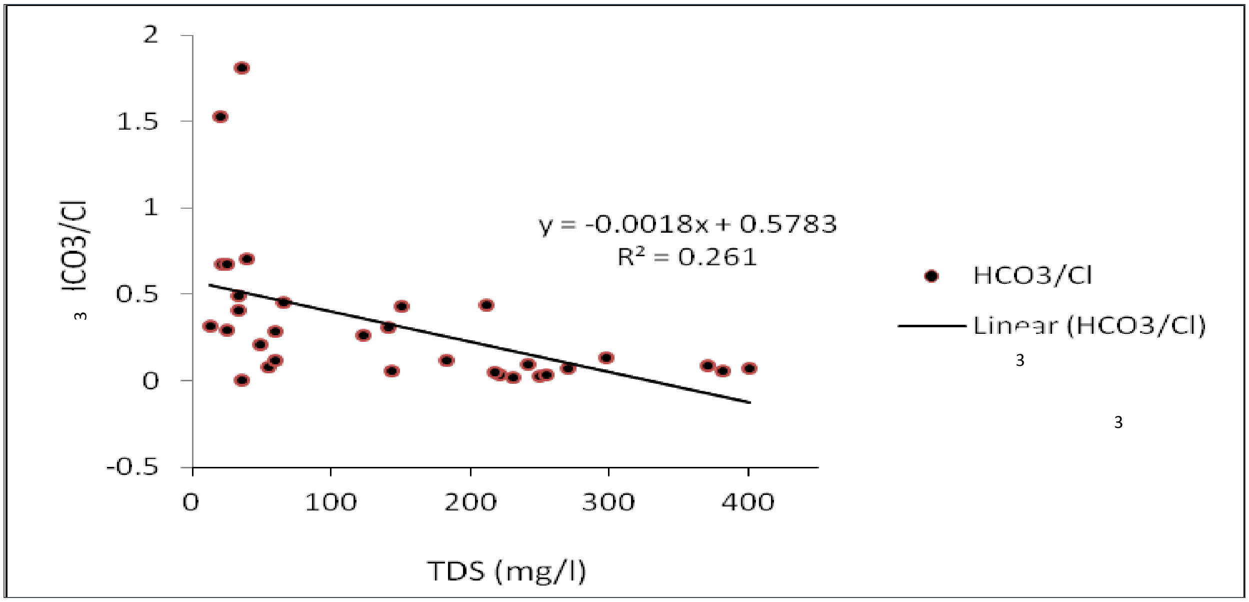


**Figure 2 :** Ionic ratio of $HCO_3/Cl$ Versus TDS

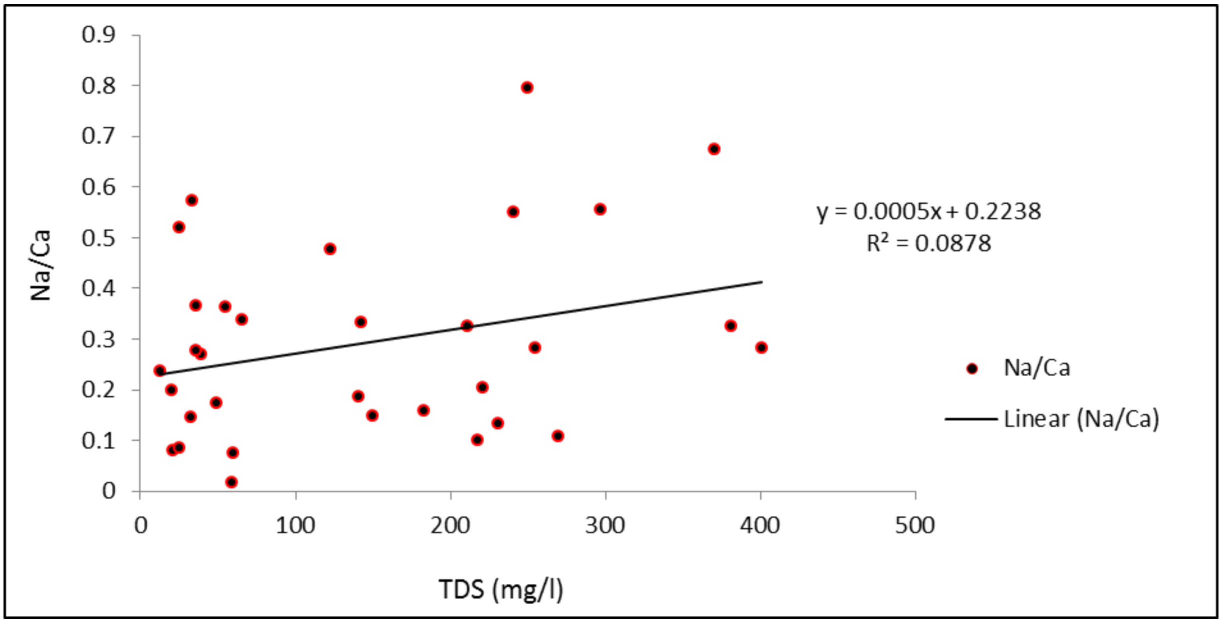


**Figure 3:** Ionic Ratio of Na/Ca Versus TDS

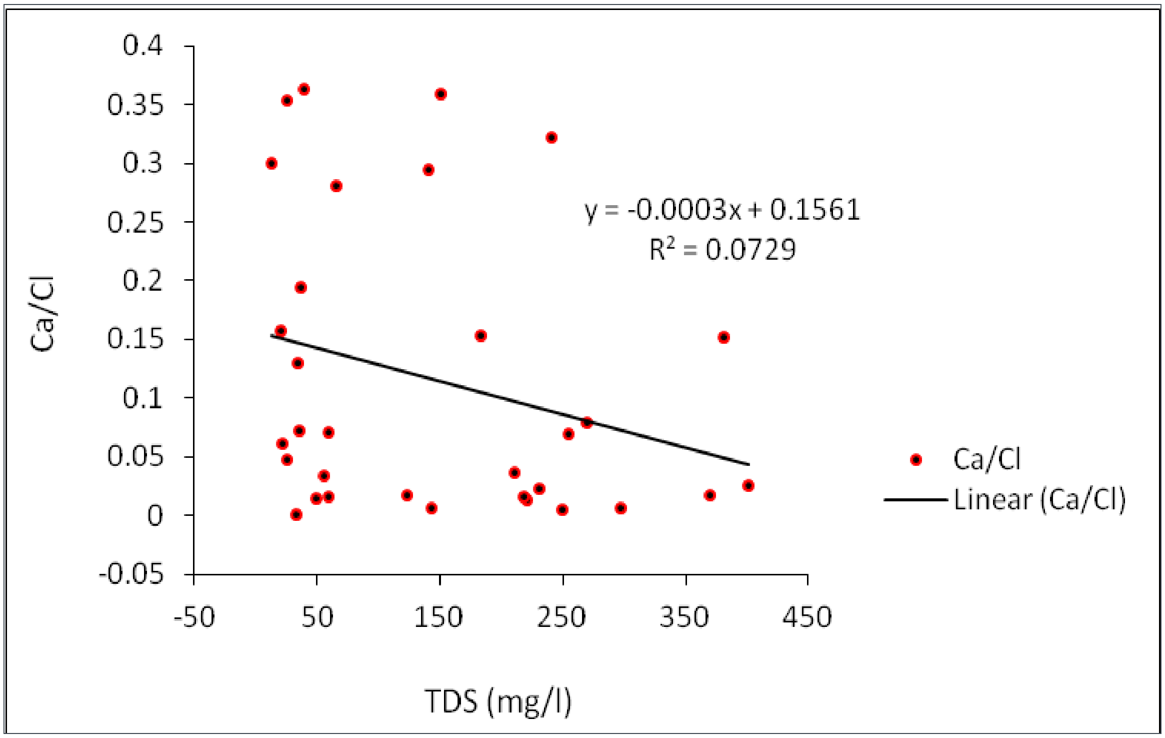


**Figure 4 :** Ionic ratio of Ca/Cl Versus TDS

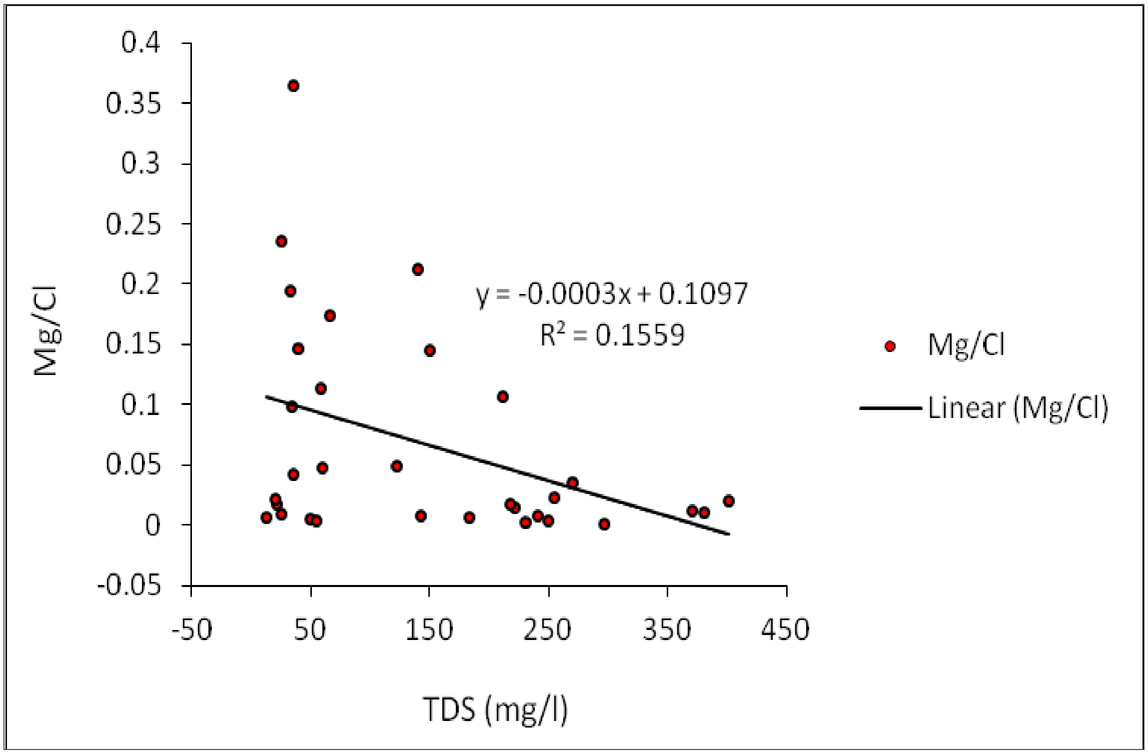


**Figure 5:** Ionic ratio of Mg/Cl Versus TDS

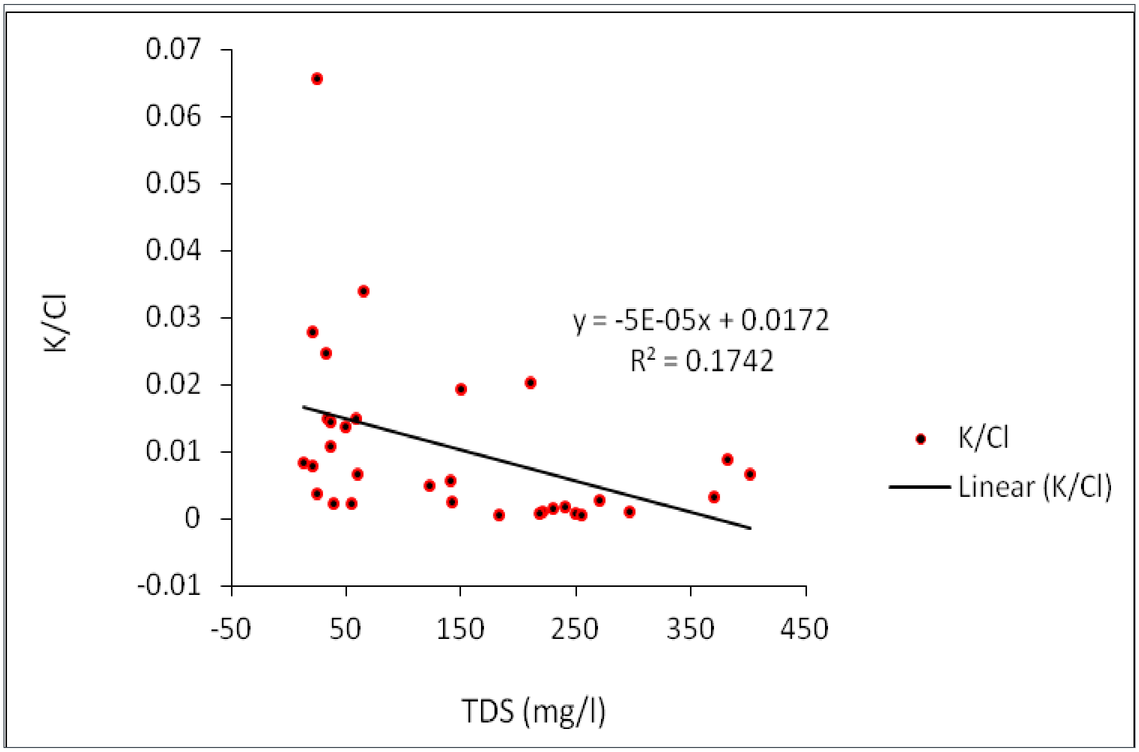


**Figure 6 :** Ionic ratio of K/Cl Versus TDS

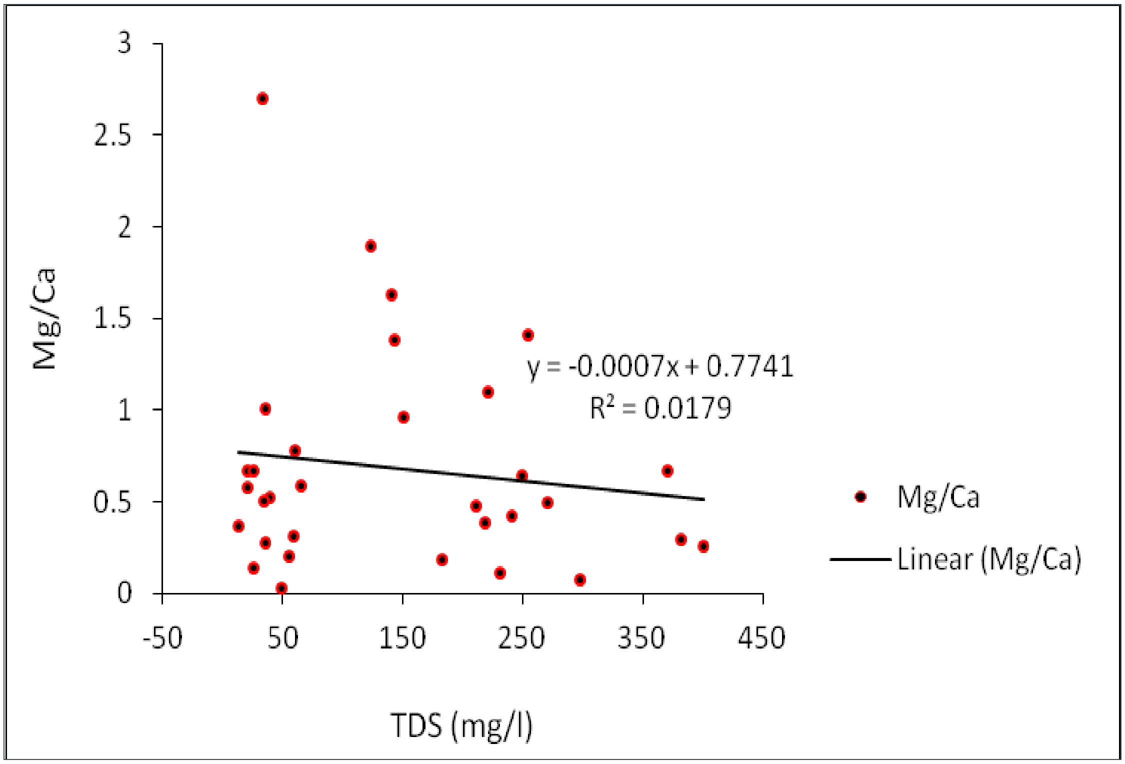


**Figure 7 :** Ionic ratio of Mg/$SO_4$/Cl Versus TDS

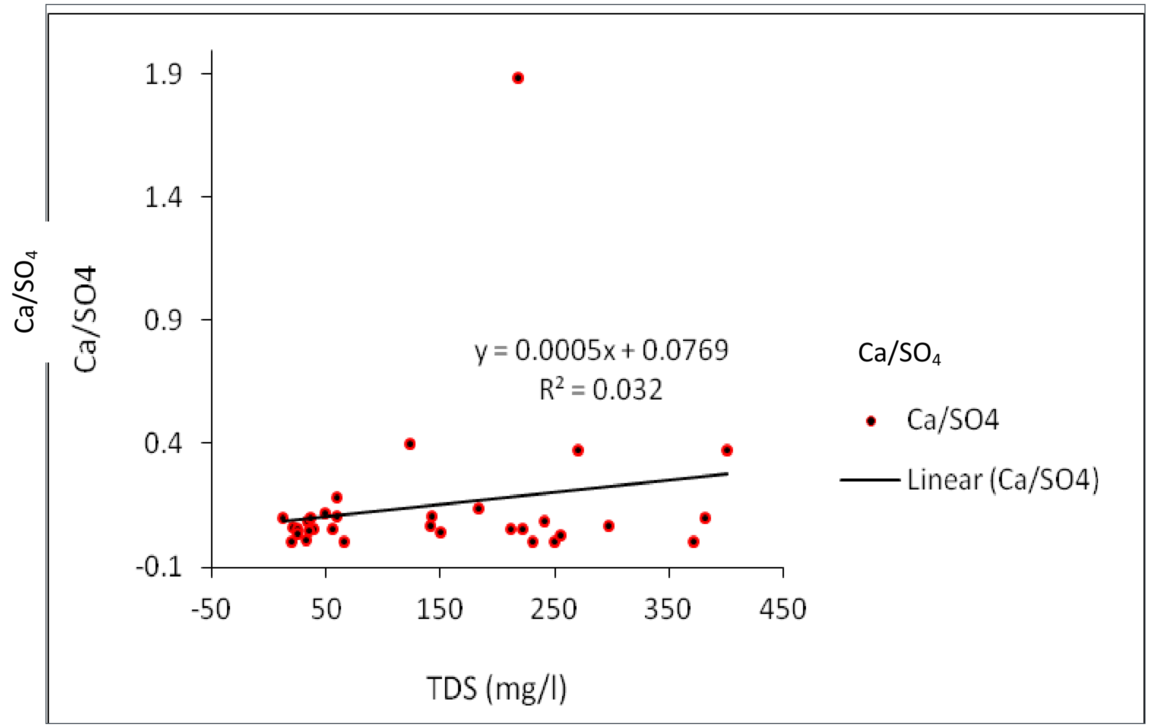


**Figure 8 :** Ionic ratio of Ca/$SO_4$ Versus TDS

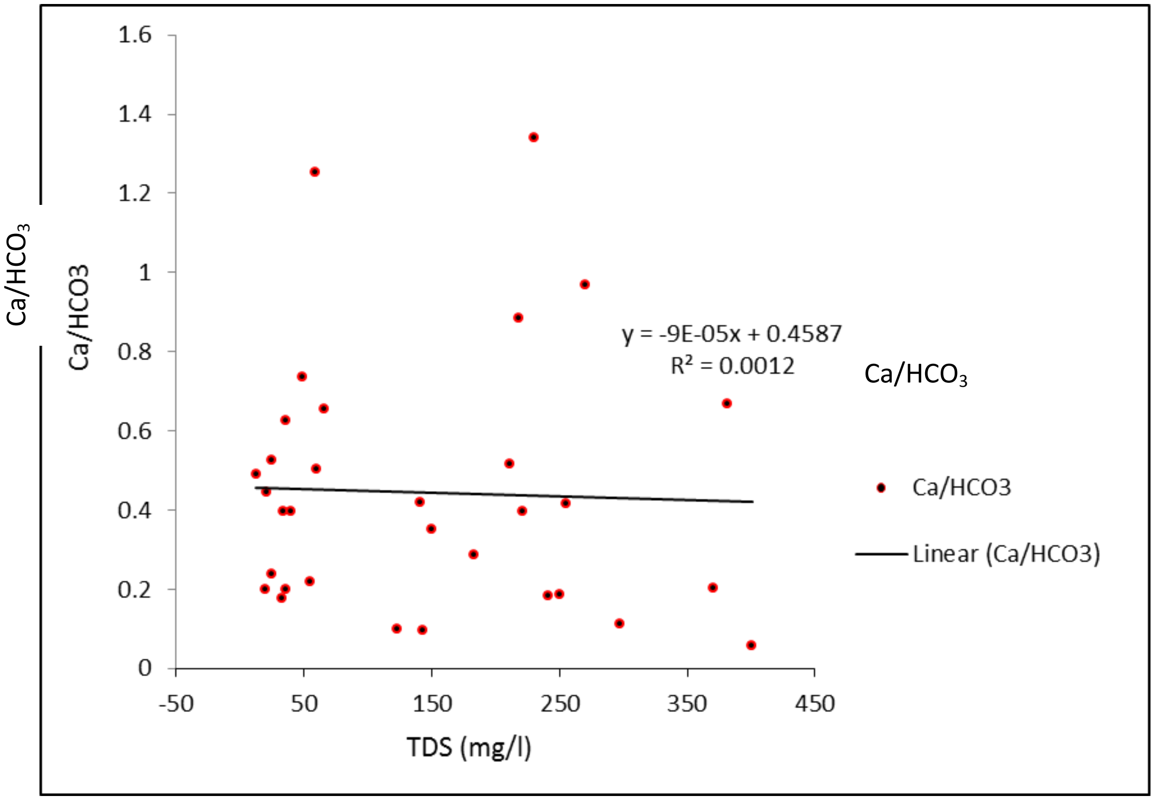


**Figure 9:** Ionic ratio of Ca/$HCO_3$ Versus TDS

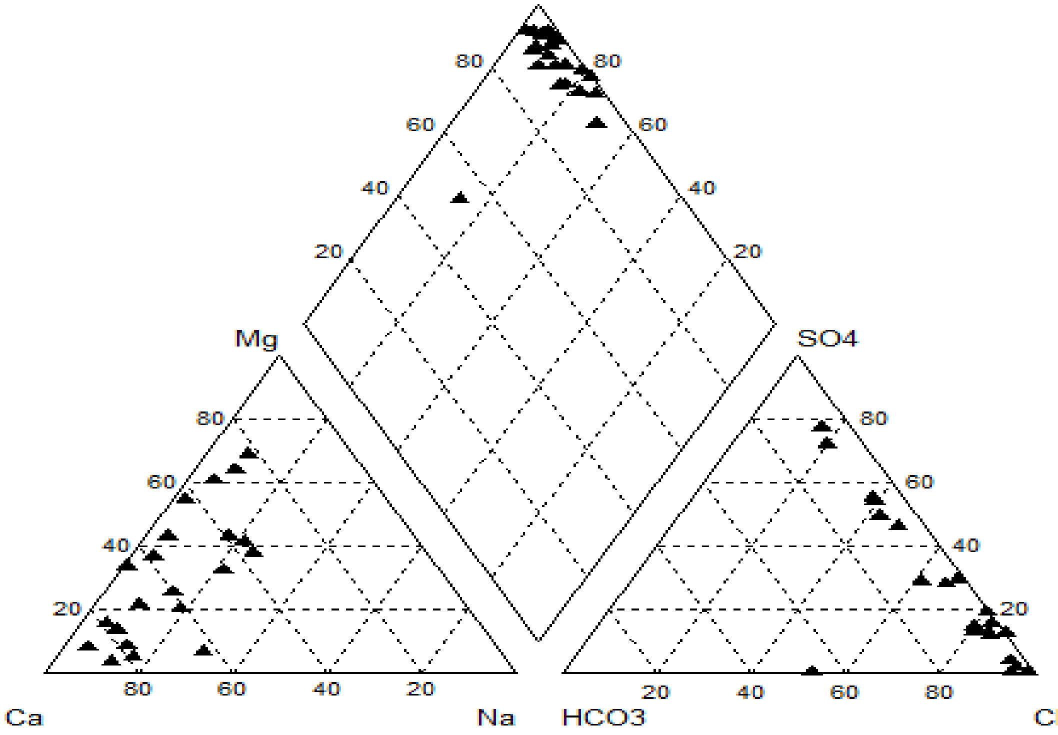
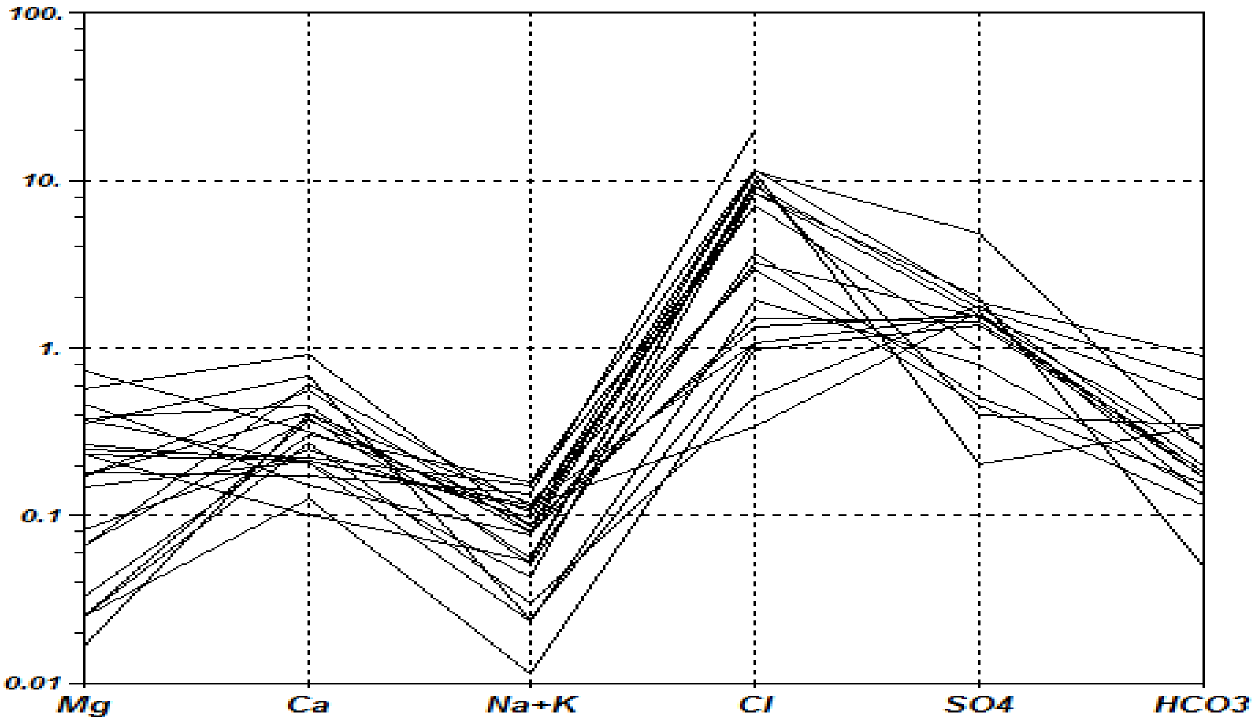


**Fig. 2: Piper Trilinear Diagram of Groundwater Characterization in**

**Figure 10:** Piper Diagram of groundwater characterization in the Area



## Conclusion

The results of the study show that pH values reveal slightly acidic to slightly basic groundwater in the area. At locations where pH values are less than 6.50, the water should be treated to raise the value to the acceptable standard of 6.50 – 8.50. Base Exchange method with dolomite is suitable for treating the parameter. Acidic groundwater are aggressive, hence boreholes in the area should be constructed with PVC pipes and other non-corrosive materials. This is imperative because if pH and iron are treated for at locations where they exceed their limits, the water will be potable and suitable or drinking and other domestic purposes. Regular flushing of boreholes and distribution systems can help remove buildup of ferruginous material deposits.

Iron values are exceptionally high in some locations. This can be treated by encouraging the iron to precipitate when the water is exposed to the air. The ferric hydroxide precipitate is then filtered out to have potable water. Iron bacteria can then be removed from groundwater with water filters. Treatment with alkaline hydrogen peroxide is one surest way of removing dissolved iron from borehole waters. This method, according to (Orjiekwe, *et al*., 2006) is preferable than most conventional methods because it is fast, cost effective, environmentally friendly and does not require external coagulant. Also, slightly high chloride concentration and high concentration of TDS indicates saltwater encroachment in the area at the depths investigated. It is recommended that regular flushing of boreholes and distribution systems can help remove buildup of ferruginous material deposits in areas affected. More importantly, hydrogeochemical studies in the area should be carried out regularly to detect any future degradation of the water.

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