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# Assessment of Groundwater Samples in the Niger Delta Using Chemometric and Geospatial Techniques

Gabriel Erhiga Odesa
Department of Geology, Faculty of Science, Dennis Osadabe University, Delta State Nigeria

*Corresponding Author:
Email: gabriel.odesa@dou.edu.ng

## Article Information

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## Abstract

The Niger Delta, rich in natural resources but facing serious environmental challenges, requires a thorough assessment of groundwater quality for safe drinking water and sustainable practices. This research analyzes the groundwater chemistry in the Benin Formation to evaluate its suitability for domestic and industrial use. The study employs chemometric techniques to assess these characteristics comprehensively. 179 groundwater samples were assessed according to APHA, (2012) criteria for ten physicochemical parameters which include pH, total dissolved solids (TDS), chloride ($Cl^-$), bicarbonate ($HCO_3^-$), sulfate ($SO_4^{2-}$), sodium ($Na^+$), magnesium ($Mg^{2+}$), potassium ($K^+$), and calcium ($Ca^{2+}$). The average concentrations of analytes across the study area are as follows: pH ranged from 4.3-8.9, TDS (4.11-2330), EC (0.45-1163us/cm), $Cl^-$ (0.76-387mg/l), $HCO_3^-$(0.001-164.5mg/l), $SO_4^{2-}$ (0.001-164.5), Na+0.07-306.93mg/l, $Mg^{2+}$ (0.001-123.0), $K^+$ (0.11-153.75) and $Ca^{2+}$ (0.001-126.15mg/l). Notably, approximately 60% of samples exhibited a pH below the recommended minimum of 6.5. The evaluated water quality index ranges from good to excellent for domestic and industrial use. The dominant groundwater types encountered are in the order of Bicarbonate > Chloride >Sulphate. PCA and Rock Source deduction ratios show that the major factors influencing the groundwater chemistry include geogenic factors such as saltwater intrusion and silicate mineral dissolution and anthropogenic factors such as leachate migration and industrial effluent discharge. The study observes that while groundwater is generally suitable for use, pH remediation is necessary and recommends the need for differentiated groundwater usage and treatment based on the varying groundwater types present in the region.

**Keywords**:
Groundwater, Chemometrics, Geospatial, Wilcox.

## INTRODUCTION

Water has a significant impact on the global economy, an essential component of life, and as such the daily need and demand for water is inevitable**.** The significance of water supply to health and the quest for pure water in adequate quantity and quality can be traced back to existence (Park *et al*., 2015). Meteoric water, surface water (stream, river, lake, ocean, etc.,) and groundwater are the three basic sources of water. However, in Nigeria, groundwater is the most reliable source of water, due to aquifer protective measures which make them less vulnerable to biological pollution (Idise and Igborgbor, 2017). This made it the most feasible, economical, and practical source of water delivered to communities (Park *et al*., 2015). When the rate of groundwater extraction exceeds its replenishment, the level of groundwater drops locally, in some cases, it leads to environmental hazards such as seawater intrusion (Eyankware, and Omo-Irabor, 2009).

Across the country, several occurrences of waterborne diseases, streams of novel diseases originating from the complication of hazardous water intake, and cases of loss in aquaculture investment due to poor water quality (Orobator *et al*., 2020; Akpotayire *et al*., 2018), Cases of drop in pH of standardized water for public supply such as sachet and bottled water had also been reported by Acharya *et al*. (2021). This was attributed to the lack of an expiry date clearly not stated in the labels (Acharya *et al*., 2021). However, since pure water is made up of two molecules of hydrogen and one molecule of oxygen, it ought not to have an expiry date. Nevertheless, Since the Influence of water quality varies from place-to-place groundwater facies may also vary from place to place, and temperature changes may have various effects on its chemical constituents, as such, various facies and water types may require different approaches while dealing with issues of water quality. Hydrogeochemical facies also known as groundwater facies refer to distinct chemical zones within groundwater systems, each characterized by the dominance of concentrations of cations and anions, this includes but not limited to chloride, bicarbonate, sulfate, etc. Each facies may encompass various water types depicting the multiple geochemical processes occurring within the aquifer as the groundwater traverses diverse geological formations (Daughney and Reeves, 2005). The knowledge of Groundwater facies is essential for assessing groundwater chemistry as it helps identify the sources of contaminants and the natural variability in groundwater across different regions.

Understanding groundwater chemistry has been a searchlight for scientists for quality health investigation (Olalekan *et al*., 2018; Raimi *et al*., 2022). Various statistical models have been designed and deployed to investigate groundwater suitability for domestic and industrial usage. These include using chemometrics, geospatial modeling, and many other appropriate approaches. Chemometry is the science that deals with the use of mathematical, statistical, and other appropriate methods to select optimal measurement procedures and analyze chemical data to deliver the most relevant information possible, these include calculations involving the determination of water quality index (WQI), rock sources deduction ratios, multivariate statistical analysis (Hierarchical cluster analysis, principal components analysis etc.). However, chemometric and geospatial modeling will be applied in this study.

Some previous studies carried out on groundwater investigation within the basin include leachate migration on groundwater (Idise and Igborgbor, 2017; Nwankwoala and Offor, 2018; Ugbebor and Brownson, 2019, etc.), delineation of heavy metal concentration in groundwater (Ikem *et al*., 2002; Efe *et al*., 2005; Akudo *et al*., 2010; Ighalo and Adeniyi, 2020), microbial loads in groundwater(Okolo *et al*., 2017; Onwuka and Ezugwu, 2019), impacts of crude oil spillage on groundwater (Nganje *et al*., 2010; Akpoborie *et al*., 2014; Lawal *et al*., 2015; Ibezue *et al*., 2018) and Saltwater intrusions (Amadi *et al*., 2012; Olabaniyi and Owoyemi, 2006).

Despite the extensive research on groundwater in the Niger Delta, significant gaps remain in understanding the trends in groundwater chemistry throughout the basin. Analyzing these trends is essential for identifying contamination sources and evaluating water suitability for drinking, irrigation, and industrial applications. This will help in elucidating the underlying geochemical processes responsible for the groundwater chemistry, such as mineral dissolution, ion exchange, and the impact of anthropogenic activities, which are crucial for predicting changes in groundwater quality over time. Furthermore, insights into groundwater chemistry trends will facilitate effective resource management, ensuring that extraction practices do not jeopardize water quality or availability. Consequently, this study aims to assess groundwater chemistry in the Niger Delta sedimentary basin to delineate trends in (i) groundwater quality, (ii) groundwater facies, and (iii) hydrogeochemical evolution, and the factors responsible for the diverse water types present in the region.

## Description of the Study Area

Location, Population, Occupation, Climate, and Vegetation.

The study area is bounded by longitude $4^{0}$00'0" E to $8^{0}$00'0" E and latitude $4^{0}$00'0" to $7^{0}$00'0" (Figure 1), some few kilometers away from the shores of the Atlantic Ocean. The research region is made up of towns, cities, and villages, and it is home to roughly 31 million people who work mostly in agriculture, transportation, trade, and industry (NPC, 2006), having an annual mean temperature of $27^{0}$C and rainfall of 3000 mm (Odesa *et al.*, 2021a). This study area is a prominent center for Agricultural activities within the state. It is virtually re-vegetated by secondary regrowth vegetation such as oil palms (*Elaeis guineensis*), food and cash crops, rubber plantation (*Chromolaena odorata*) etc. (Ohwoghere-Asuma *et al.*, 2017).

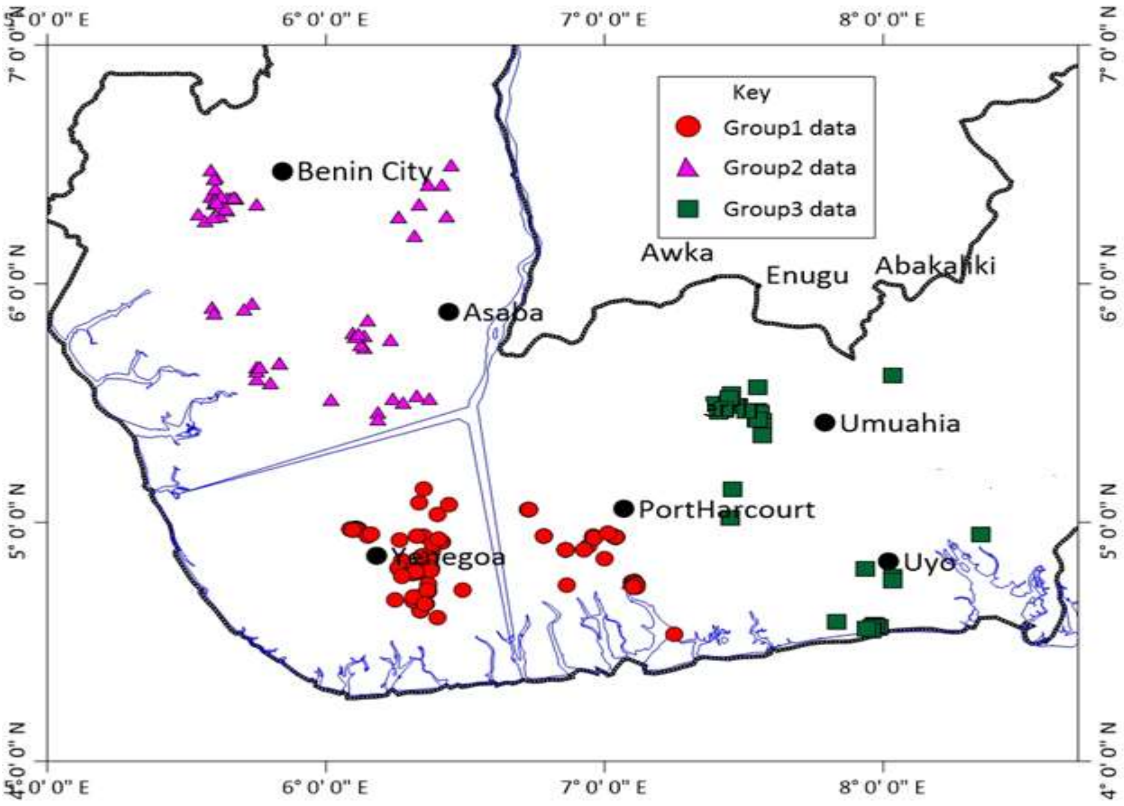


**Figure 1.** Geology Map of the Study Area showing groundwater sampling points.

## Hydrology of the study area

The study area is located within the region occupied by the Benin formation of the Niger Delta Sedimentary Basin, this formation contains the most productive and hence most tapped aquifer in the Niger Delta sedimentary Basin. The Benin formation within the study area has two significant aquiferous units: the Quaternary to Recent coastal plain sand and the Somebreiro-Warri Deltaic Plain Sands (Olabaniyi and Owoyemi, 2006). This unit has a water table very close to the ground surface and varies from 0 to 20 meters with high susceptibility to pollution. Ohwoghere-Asuma *et al.* (2017) observed that the hydraulic conductivities of the sand vary from 3.82 x 10-3 to 9.0 x 10-2 cm/sec, having specific capacities recorded from different areas within this formation which vary from 6700 lit/hr/m to 13,500 lit/hr/m. This indicates a potentially productive aquifer, especially for irrigation.

## MATERIALS AND METHODS

The study made use of 179 groundwater samples obtained from different boreholes across the study area. The groundwater was sampled from October 2023 to March 2024 when there was a decrease in the water level and the concentration of cations and anions was more stable. Precautionary measures were taken by washing the bottles with clean water, followed by cleaning reagents, and finally thoroughly rinsing with distilled, de-ionized water before collecting water samples from the site. Before collecting water samples from the location, precautionary procedures were taken by washing the bottles with clean water, using cleaning agents, and then completely rinsing them with distilled, de-ionized water. Ten (10) physicochemical parameters, including pH, total dissolved solids (TDS), electrical conductivity, chloride ($Cl^-$), bicarbonate ($HCO_3^-$), sulfate ($SO4^{2-}$ mg/l), sodium (Na+), magnesium ($Mg^{2+}$), potassium ($K^+$), and calcium ($Ca^{2+}$), were measured in the samples following the APHA standard. pH was measured in situ using a handheld pH meter. These samples were further analyzed using the following techniques as shown in Table 1.

**Table 1**. Techniques for examining physicochemical parameters

| S/No | Parameters | Analytical Method |
|---|---|---|
| 1 | pH | pH meter HachsensION + PH1 portable pH meter and HachsensION + 5050 T Portable Combination |
| 2 | Total dissolved solids (TDS) | pH Electrode TDS meters (model HQ14D53000000, USA) |
| 2 | Electrical Conductivities (EC) | HACH Conductivity |
| 3 | Magnesium ($Mg^{2+}$) | EDTA titrimetric method |
| 4 | Calcium ($Ca^{2+}$) | Titrimetric method |
| 5 | Chloride ($Cl^-$) | Titrimetric method |
| 6 | Sulphate ($SO_4^{2-}$) | Turbidimetric method using a UV-Vis spectrometer |
| 7 | Potassium ($K^+$) | Jenway clinical flame photometer (PFP7 model) |
| 8 | Sodium ($Na^+$) | Jenway clinical flame photometer (PFP7 model) |
| 9 | Bicarbonate ($HCO_3^-$) | Titrimetric method |

Sampling was done in Six (6) different States, areas within the Niger Delta Sedimentary Basin whose basic hydrological unit is the Benin Formation. The sampling points were randomly chosen across the study areas having a common hydrological unit (Benin Formation).

For easy interpretation, the study subdivided the Niger Delta Sedimentary Basin into three regions, each consisting of two states. Interpretations were done based on states, regions, and the general sedimentary basin at large. The regions under the study include:

1. The Central Niger Delta Sedimentary Basin (River State and Bayelsa State)
2. The Western Niger Delta Sedimentary Basin (Edo State and Delta State)
3. Eastern Niger Delta Sedimentary Basin (Abia and Akwa-Ibom)

The statistical summary of the laboratory results for the groundwater samples is shown in Table 1.

### Structure for Interpretation

### Groundwater Chemistry of the Niger Delta Sedimentary Basin.

Generally, the concentration of Sodium ranged from 0.07 to 306.93mg/L with a mean value of 56.39 mg/l, only about 1% greater than the 200mg/l acceptable limit. Potassium concentration ranged from 0.03 to 120.4mg/L with a mean of 3.76 mg/L. Calcium concentration ranged from 1.05 to 126.15 mg/l with a mean of 15.24 mg/L. Magnesium concentration ranged from 0.001 to 69.1mg/L with a mean of 5.27mg/L. Chloride concentrations ranged from 0.76 to 387 mg/l, about 2% greater than 250 mg/l acceptable values. Sulphate concentrations in the groundwater samples ranged from 0.001 to 164.5 mg/L with a mean value of 7.2 mg/L. The bicarbonate anion concentrations ranged from 0.001 to 447.7mg/L with a mean value of 12.90 mg/L.

**Table 2:** Statistical comparison between the primary NDSB

| Parameters | Edo State ( n=21) | | Delta State (n= 30) | | Bayelsa state (n=52) | | River State (n=40) | | Akwa-Ibom State. (n=13) | | Abia State (n=23) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | Range | Mean | Ranges | Mean | Range | Mean | Range | Mean | Range | mean | Range |
| pH | 5.2 | 4.3-6.7 | 6.3 | 4.9-8.9 | 6.5 | 5.1-7.9 | 5.65 | 4.1-9.2 | 5.6 | 4.4-6.5 | 6.7 | 6.4-7.5 |
| TDS | 98.45 | 13.54-124.67 | 343.31 | 15.2-2330.00 | 168.78 | 4.11-1125.00 | 72.36 | 3.57-643.33 | 26.31 | 2.28-71.00 | 225.17 | 42.59-1428.00 |
| *E.cond.us/cm* | 115.257 | 12.85-1163 | 41.48 | 0.45-254.7 | 121.614 | 34.9-234.6 | 152.3 | 1.85-1010 | 43.36 | 7.14-106.50 | 251.20 | 11.19-351.70 |
| $Cl^-$ (mg/l) | 14.42 | 9.97-42.6 | 98.22 | 21.05-387.09 | 26.382 | 2.6-113.24 | 33.27 | 0.76-114.3 | 5.01 | 1.31-2.80 | 152.64 | 8.14-302.70 |
| $HCO_3$ *(mg/l* | 72.81 | 25.7-447.7 | 11.19 | 0.001-110.4 | 74.403 | 11.7-35.7 | 55.08 | 40.5-69.65 | 21.23 | 5.30-38.00 | 88.44 | 76.12-172.00 |
| $SO_4^{2-}$ *mg/l* | 6.73 | 1.29-7.5 | 28.14 | 0.06-164.5 | 2.621 | 0.22-8.84 | 6.90 | 0.001-69.98 | 5.04 | 1.31-19.58 | 4.23 | 0.01-12.50 |
| $Na^+$ | 6.65 | 0.1-34.99 | 7.162 | 0.14-13.675 | 20.59 | 6.43-39.45 | 24.96 | 0.07-188 | 60.88 | 2.67-306.93 | 26.69 | 2.49-57.35 |
| $Mg^{2+}$ | 2.79 | 0.03-26.73 | 27.16 | 0.001-123.0 | 3.406 | 0.23-13.03 | 3.81 | 0.001-69.1 | 4.21 | 1.21-26.90 | 3.00 | 1.50-9.10 |
| $K^+$ | 32.96 | 1.36-120.42 | 28.98 | 5.28-153.75 | 14.610 | 5.93-41.12 | 18.05 | 0.47-35.63 | 1.60 | 0.11-4.31 | 5.01 | 0.54-8.34 |
| $Ca^{2+}$ | 17.20 | 1.12-126.15 | 6.26 | 4.91-8.9 | 3.7253 | 1.01-9.01 | 2.84 | 0.001-23.69 | 7.52 | 1.05-37.25 | 8.39 | 2.50-22.78 |

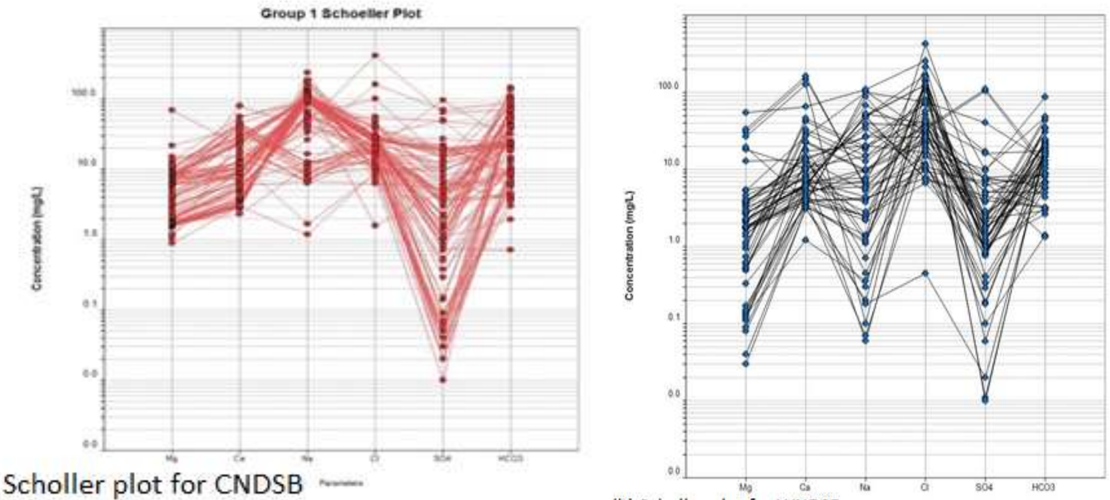
**Table 3:** Rock source deduction

| Equations | Value | Class | Rivers (%) | Bayelsa (%) | Edo (%) | Delta (%) | Abia (%) | Akwa-Ibom (%) |
|---|---|---|---|---|---|---|---|---|
| $WQI = \left( \sum_{n=1}^{i=n} q_i w_n \right)$<br>Ramasubramanian *et al*., (2004)<br>Equation (1) | >50 | Excellent water | 97 | 88 | 100 | 76 | 100 | 60 |
| | 50-100 | Good water | 3 | 10 | | 18 | | 40 |
| | 100-200 | Poor water | | | | 6 | | |
| | 200-300 | Very poor water | | 2 | | | | |
| | >300 | Water unsuitable for drinking | | | | | | |
| $Na^{+}+K+-Cl-/$<br>$Na^{+}+K^{+}-Cl-+Ca^{2+}$<br>(Hounslow 1995)_ Equation (2) | >0.2 and <0.8 | Plagioclase weathering is possible. | 5.5 | 27.5 | 0 | 22 | | |
| | <0.2 or >0.8 | Plagioclase weathering is unlikely. | 94.5 | 72.5 | 100 | 78 | | |
| $Cl^{-}/$<br>$Sum of Anions$<br>(Stallard and Edmond, 1983)_____<br>Equation (3) | >0.8 TDS >500 | Sea water, brine or | 38 | 45.8 | | | | |
| | >0.8 TDS <100 | evaporate | | 5.8 | 8.7 | | | |
| | <0.8 | Rock weathering | 62 | 49.4 | 82.6 | 85.7 | 100 | 100 |
| $r1=(Na^{+}-Cl^{-})/SO_{4}^{2-}$<br>$r2=[(Na^{+}+K^{+})-Cl/SO_{4}^{2-}$<br>(Soltan, M. E. 1999) ____<br>Equation (4) | $r1<1$ and $r2<1$, | Groundwater sources are of $Na^{+}$–$SO_4^{2-}$ and deep meteoric type. | 2.7 | 4.3 | 96 | 52.9 | 54.2 | 87 |
| | $r1>1$ and $r2>1$ | indicates the sources are of $Na^{+}$– $HCO_3^{-}$ and shallow meteoric type | 97 | 95.7 | 4 | 47.1 | 45.8 | 23 |
| Na/Cl<br>(Elango *et al*., 2003)________Equation (5) | >1.15 | Silicate weathering | 61 | 62.5 | 5 | 27.2 | 32.7 | |
| | 0.8-1.15 | Ionic exchange | 13.9 | 30.5 | 95 | 72.3 | 67.3 | 100 |
| | >0.8 | Other sources Cl | 25.1 | 17 | | | | |
| Cl/HCO3<br>(Martos, et al., 1999; Kim et al., 2003)______ Equation (6) | < 0.2 | Unaffected salinization process. | 13.9 | 2.9 | 4 | 3.1 | 78.3 | 14.3 |
| | 0.4 – 4.1 | moderately affected | 33 | 91 | 45.8 | 60.6 | 21.7 | 85.7 |
| | > 4.1 | strongly affected | 2.8 | 21.7 | 50..2 | 36.3 | | |

### Dominant Ionic Concentration across the Study Area.

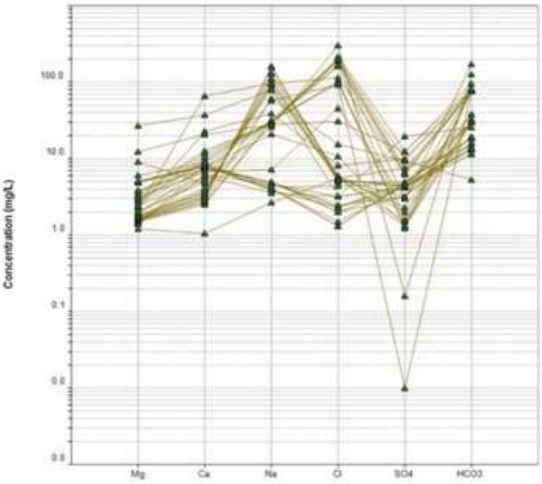
The trend in the magnitude of the various ionic concentrations across the three regions which make up the Niger Delta Sedimentary Basin is shown in the Scholler Diagrams in Figure 2.

A comparison of the Scholler plots reveals the trend in the concentrations of the various ions across the regions. For Central Niger Delta Sedimentary Basin, the plots reveal the order of Na> Ca>Mg for the cations, while $HCO_3$>Cl>$SO_4^{2-}$, for the anions. In the Western Niger Delta Sedimentary Basin, the trend follows Ca>Na>Mg; for the cations, while Cl>$SO_4^{2-}$> $HCO_3^-$ for the Anions. The Eastern Niger Delta sedimentary Basin is in the Order of Na>Ca>Mg for the cations and Cl>$HCO_3^-$>$SO_4^{2-}$ for the anions. The Scholler plots are based on the average concentrations of the major elements involved.



(a) Scholler plot for CNDSB

(b) Scholler plot for WNDSB



(c) Scholler Plot for ENDSB

**Figure 2**: Scholler plots comparison revealing the trend in dominant ionic concentration across the Niger Delta Sedimentary Basin (a) Central Niger Delta Sedimentary Basin (b) western Niger Delta Sedimentary Basin (c) Eastern Niger Delta Sedimentary Basin.

## Groundwater Quality in Benin Formation of the Niger Delta Sedimentary Basin.

The average concentration of the parameters is within the WHO (2011) acceptable limit with few exceptions such as the pH and TDS. pH concentrations range from 4.1 to 9.2. 75% of the locations have pH less than 6.5 WHO (2011) acceptable minimum limit, while 2% fell above the 8.5 maximum acceptable limit, and only about 23% fell within the 6.5-8.5 acceptable range. TDS ranges from 2.28 to 2330mg/l, and only about 9.95% fell above the 500mg/l permissible limit. Data from various locations within the Asari-Toru LGA of Rivers State has TDS ranging from about 501.23-1139mg/l and pH of 6.2- 7.04, Various locations in Warri and Agbarho in Delta State have pH ranging from 7.035-7.50 and TDS of 685.54-778.86. Multiple locations in Amassoma LGA of Bayelsa State also have TDS ranging from 345-600mg/l with pH ranging from 6.1-6. The study attributed low pH within the study area can be attributed to both anthropogenic and geogenic factors such as recharge from acidic rain, industrial effluent, and leachate migration. The environmental effects of low pH in water range from reproductive failure, mortality of aquatic lives, and mobilization of minerals and heavy metals in groundwater flow regime thus leading to heavy metal poisoning, etc.

The distribution of the groundwater quality across the study area shows that > 95% of the groundwater locations in the study area can be used for domestic activities with pH remediation. The study also shows that the groundwater within the study area can be divided into two zones; The fresh groundwater zone (TDS < 1000mg/L) and the slightly salty groundwater zone (>TDS 1000 mg/L < 2500mg/L) with more than 90% of the groundwater location indicating fresh water this information can be useful for the local groundwater development and management.

The water quality criteria calculated based on the parameters used, across the various locations as evaluated using equation 1 in Table 2 shows the groundwater quality varies from poor water to excellent categories. In CNDSB, 88.4% of locations reveal excellent water categories, 7% belong to good water categories and 1% belong to very poor water categories. In WNDSB, about 89% of groundwater locations fell in the field of excellent water categories, 11 % in the field of good water categories, and only 4% in the field of permissible to doubtful. In ENDSB, 82% fell in the excellent water categories, and 18% in the field of good water categories.

## Geochemical Evolution and Trend of Major ions in Groundwater within the study area.

### Principal Component Analysis

PCA is an essential tool designed to demonstrate how the variables are connected to identify the most likely sources of groundwater contamination in the study area by reducing the likelihood to four components.

Table 4 shows that PC1 has about 34.34% of the total variance having high loading for TDS, Ca$^{2+}$, Na$^{+}$ Cl$^{-}$and SO$_4^{2-}$suggesting influence of saline water, PC2 has 26.28% of the total variance having high factor loading Na$^{+}$ and K$^{+}$ indicating weathering of silicate minerals (dissolution of Albite). PC3 has 14.12 % of the total variance, having high factor loading for Cl and SO$_4^{2-}$ which suggests possible anthropogenic influence. PC4 has 6.65% of the total variance having a high factor load for TDS and SO4, this again suggests the influence of anthropogenic activities.

This accounts for 81.39% of the total variance. The findings from this study align with previous observations from research carried out within the study area. Earlier, Amadi *et al.* (2012) conducted a comprehensive evaluation of groundwater in the Eastern Niger Delta using Principal Component Analysis (PCA).

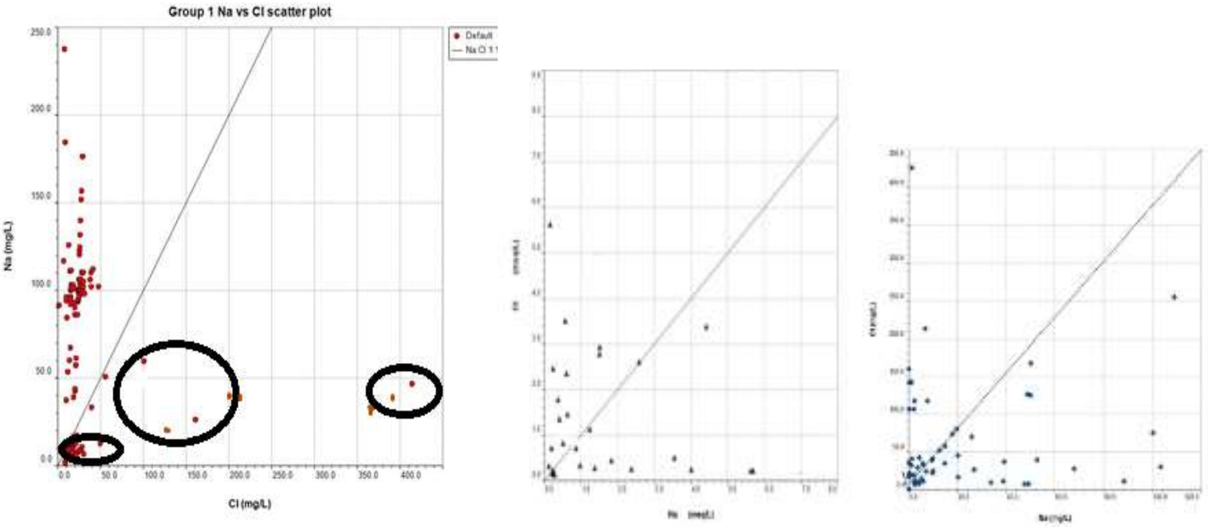
**Table 4:** Factor Loadings after Varimax Rotation

| Variables | Factor1 | Factor2 | Factor3 | Factor4 |
|---|---|---|---|---|
| tds | 0.75476 | -0.0065 | 0.03854 | 0.43733 |
| Ca2 | 0.85975 | 0.01427 | -0.271 | -0.0651 |
| Mg2 | -0.0706 | -0.3504 | 0.0655 | 0.20829 |
| Na | 0.76943 | 0.78028 | -0.0392 | -0.1002 |
| K | -0.0274 | 0.83831 | 0.10766 | 0.19619 |
| HCO3 | 0.23354 | 0.26116 | 0.79132 | 0.17744 |
| Cl | 0.60303 | 0.5567 | 0.83067 | -0.2982 |
| SO4 | 0.51025 | -0.2687 | 0.16983 | 0.6408 |
| Eigen Value | 1.98 | 1.13 | 0.62 | 1.26 |
| Variance (%) | 34.34 | 26.28<br>14.12 | 6.65 | |

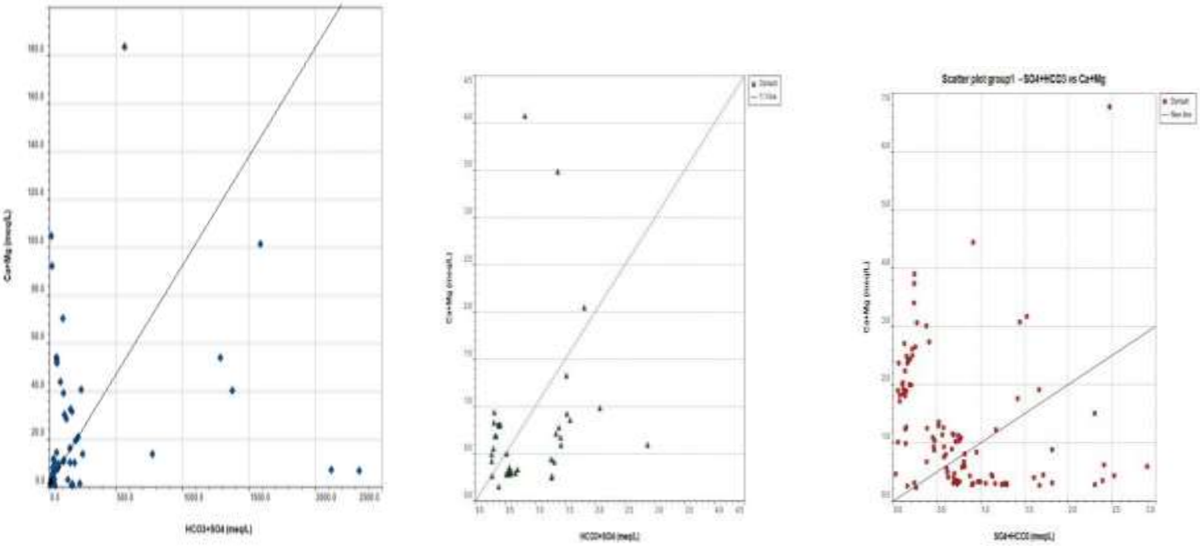
The study identified saline intrusion, chemical weathering, mineral leaching, and anthropogenic activities as the primary geochemical processes influencing groundwater chemistry. Similarly, Raimi *et al.* (2021) investigated groundwater contaminants and the factors contributing to groundwater pollution in an oil-producing wetland in Rivers State. The study highlighted mineral dissolution and human activities as significant determinants of groundwater quality. In a related study, Akpan *et al.* (2023) performed a water variables analysis using PCA in the Etim Ekpo River area of the Niger Delta. Their findings also pointed to the substantial impact of anthropogenic activities on water quality.

The PCA result from the current study has demonstrated the influence of both natural processes and human activities on groundwater chemistry in the study area. These findings highlight the critical need for effective monitoring and management strategies, emphasizing the importance of a comprehensive approach that takes into account both natural and anthropogenic factors to protect the groundwater resource in the Niger Delta region.

However, scatter plots in (Figure 4) further reveal the trend in processes responsible for the sources of ions across the study area.



(ai) CNDSB (aii) WNSB (aiii)ENDSB



(bi) CNDSB (bii) WNSB (bi) ENDSB

**Figure. 3:** Scatter plot showing the trend in the evolution of major ions across the basin (a) $Na^+$ vs $Cl^-$ (b) Scatter plot of Ca+Mg vs $SO_4^{2-}$+$HCO_3$.

**Central Niger Delta Sedimentary Basin**, the $Na^+$ vs $Cl^-$ scatter plots show about 64.5% plotted above the 1:1 equiline which indicated $Na^+$, enrichment, and 20.1% plotted below the equiline which indicates Cl enrichment suggesting Na and Cl obtained from sources other than saline water. The graph also shows about 15.4% clustering around the equiline which in turn suggests the presence of saline water and the calculated ratio of Cl/HCO3 as well as the presence of saline water within this region. The findings validate the observations of (William *et al.*, 2018) who observed the presence of salt water along three different profiles at various depths within the subsurface in Opobo town in Nkoro L.G.A, Rivers State, Nigeria.

The $Na^+$ vs $Cl^-$ scatter plots in the **Eastern Niger Delta Sedimentary** Basin reveal about 37% of the locations plotted far above the 1:1 equiline which indicated additional sources of $Cl^-$, 37% plotted below the equiline indicating chloride enrichment while about 25% plotted around the equiline which indicate the presence of saline intrusion.

Meanwhile, in the **Western Niger Delta Sedimentary Basin**, $Na^+$ vs $Cl^-$ scatter plots reveal about 14% Cl- enrichment, 46% Na+ enrichment, and about 39% plotted around the 1:1 equiline, indicating saline water's presence.

These observations are also in line with findings from the Na/Cl and $Cl/HCO_3$ of Equations 5 and 6 in Table 2. The Factor Analysis. Scatter plots and ionic ratios reveal the presence of saline water. The presence of saline water observed in some locations across the study area aligns with the findings from previous authors within the study area including (Ukpong and Peter, 2012; ENDSB, Anomohanran and Akporido, 2015; Ohwoghere- Asuma and Essi, 2017; Odesa *et al*., 2021b)

**In CNDSB** inferences from the scatter plot in Figure 5b show That, about 36% of the bicarbonate region plotted around fresh recharge, meanwhile about 64% of the excess $HCO_3^-$indicated areas undergoing ionic exchange. Meanwhile in **ENDSB**, The plot of $Ca^{2+}$ + $Mg^{2+}$ versus $HCO_3^-$ +$SO_4^{2-}$shows that about 29% of the locations are over the 1:1 equiline, indicating that alkali earth is more commonly formed by silicate weathering as observed in equation 2 and 5 in Table 2. The bicarbonate zone has representations of about 55.9% revealing the prevalence of recent recharge to silicate weathering. However, about 63% of the bicarbonate enriched region plotted around fresh recharge while about 37% indicated areas undergoing ionic exchange. In **WNDSB,** the plot of $Ca^{2+}$ + $Mg^{2+}$ versus $HCO_3^-$ +$SO_4^{2-}$ shows about 40% of the locations are over the 1:1 equiline zones indicating that alkali earth is more commonly favored by silicate weathering as also observed in equation 2 and 5 in Table 2. The bicarbonate zone has representations of about 38.5% which also indicates a recent recharge area. This is again in consonance with the findings from PCA 3 and 4 in Table 4 which reveals the dissolution of silicate is a factor responsible for the major ion in the groundwater. Previously, similar reports have also been reported across the study area (Okiongbo and Ohimain, 2014; Eyankware and Omo-Irabor 2019; Abadom and. Nwankwoala, 2018).

## Trend in Groundwater Facies within the Benin Formation of the Niger Delta Sedimentary Basin.

The piper plots and Chadli Diagram in Figure 5 below shows the distribution of groundwater facies across the study area, this helps delineate the possible geochemical processes within the groundwater across the Benin formation of the Niger Delta Sedimentary Basin.

### Facies Encountered

The Piper diagram in Figure 5 generally characterized the groundwater into six distinct categories, group 1 represents CNDSB, group 2 represents WNDSB, and group 3 represents ENDSB.

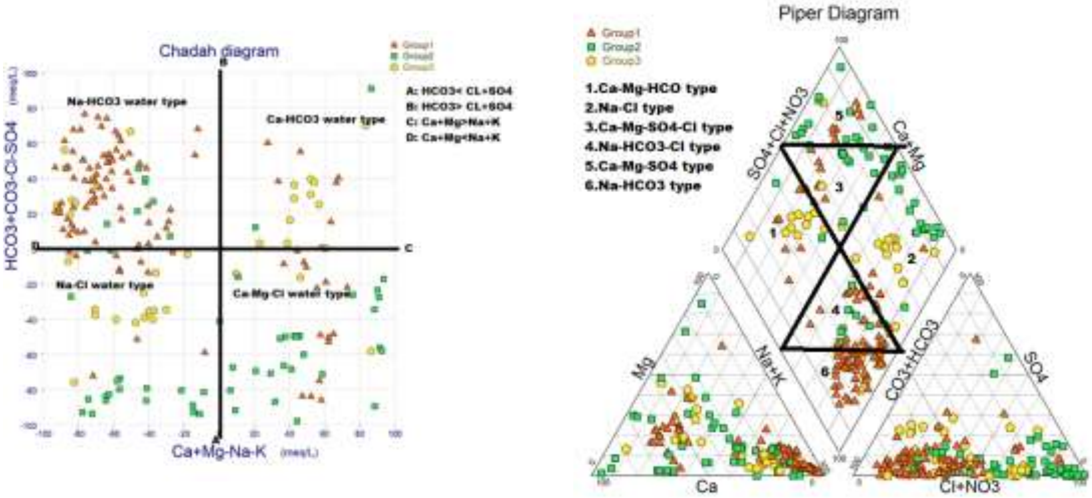


**Figure 4:** Integrated Piper and Chadah Diagram showing the various groundwater types in each region (a) Chadha Diagram (bii) Piper Diagram Group 1(CNDSB), Group 2(WNSB), Group 3(ENDSB)

**Categories 1: Ca+Mg-HCO3 type:** this indicates fresh recharge areas. The Ca+Mg-HCO3 water type is recognized as suitable for human consumption due to its balanced mineral composition, which provides essential nutrients such as calcium and magnesium. The presence of bicarbonate ions plays a crucial role in neutralizing acidity within the body, thereby contributing to potential health benefits, including enhanced digestion and improved metabolic function. In agricultural contexts, Ca-Mg-HCO3 significantly improves soil structure by alleviating compaction, augmenting water retention capacity, and maintaining optimal soil pH levels, which facilitates nutrient availability (Dikeogu *et al*., 2014). Furthermore, this water type stabilizes ion concentrations, thereby supporting the health and vitality of aquatic organisms, including fish.

The analysis of the Pier and Chaldhi plots (Figure 4a and 4b) indicates that this category includes 32% CNDSB, 3.8% WNDSB, and 6.67% ENDSB, collectively constituting 10.8% of the total water types identified within the study area.

**Category 2: Na-Cl Type**

This category indicates the occurrence of seawater incursion. Excessive consumption of this water type can exacerbate conditions such as chronic congestive heart failure, hypertension, neurological disorders, and kidney damage (WHO, 2015). Nonetheless, this water type is beneficial for applications such as water softening and the regeneration of ion exchange resins. Sodium chloride effectively removes hardness ions like calcium and magnesium, thereby enhancing water quality for both industrial and residential purposes. This category constitutes 5.6% of CNDSB, 26.9% of WNDSB, and 38% of ENDSB, representing 20% of the total water types within the study area.

**Category 3: Ca-Mg-SO4-Cl**

This category represents a mixed water type where bicarbonate has been substituted by sulfate ($SO_4^{2-}$) and chloride ($Cl^-$), indicating a transitional zone between freshwater and saline water. The Ca-Mg-$SO_4$-Cl water type is suitable for agricultural irrigation, particularly in managing soil salinity, and can be employed in industrial processes that require specific ionic compositions. However, elevated concentrations may lead to soil salinization, adversely affecting plant growth and agricultural productivity (Fawzi *et al*., 2010; Oliveira, 2018). This category comprises 11.4% of the overall water types, with WNDSB locations accounting for approximately 21%, while ENDSB and CNDSB contribute about 6.4% and 5.6%, respectively.

**Category 4: Na-$HCO_3$-Cl**

This group also signifies a mixed water type in which calcium has been replaced by sodium through sorption processes (both adsorption and desorption), whereby $Ca^{2+}$ ions are absorbed by clay minerals and subsequently replaced by sodium from saline sources. This water type is ideal for culinary applications as a leavening agent and is also utilized in medical contexts to treat acidosis; it is applied in water treatment processes to adjust pH levels. However, excessive consumption may lead to metabolic alkalosis and disrupt electrolyte balance within the body. This category comprises approximately 28.9% of CNDSB, 17.3% of WNDSB, and 7.5% of ENDSB, contributing to 22.9% of the total groundwater types identified in the study.

**Category 5: Ca-Mg-$SO_4$ Type**

The Ca-Mg-$SO_4$ category indicates the presence of sulfate ions likely derived from sulfate minerals such as anhydrite and gypsum. However, the scarcity of these minerals within the Miocene deposits of the Niger Delta sedimentary basin suggests that anthropogenic sources are the primary contributors to sulfate levels in groundwater. This category contains 28% from WNDSB, 7.7% from CNDSB, and 7.55% from ENDSB areas, comprising 13.1% of the total groundwater types identified in the study area.

**Category 6, Na-$HCO_3$,** indicates two potential reactions. Firstly, it suggests anionic exchange, wherein the chloride from NaCl is substituted by $HCO_3$. Alternatively, it may represent a base exchange process in which calcium from Ca-$HCO_3$ is replaced by sodium through sorption to clay minerals. This category constitutes 22.3% of the total water types identified in the study area.

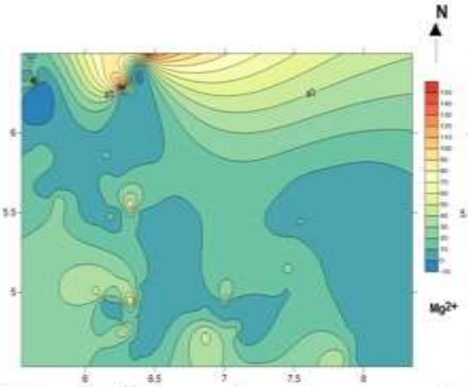
The facies observed across the study area can be ranked by magnitude as follows: chloride, bicarbonate, and sulfate. The $HCO_3$ type groundwater, which signifies high-quality water, is suitable for both domestic, industrial, and irrigational usage, having m*et al*l necessary criteria for portability. Conversely, $SO_4^{2-}$ groundwater types are advantageous for agricultural and industrial applications. The hydrochemical differences among various regions within the basins provide valuable insights for more detailed hydrogeological modeling and further groundwater resource assessments. Consequently, this study supports the effective utilization and management of differentiated water types.

Base ionic exchange and reverse ionic exchange are the primary hydrochemical reactions that contribute to the formation of the diverse groundwater types and facies throughout the basin, as demonstrated by the Sultan ionic ratio presented in Table 3.

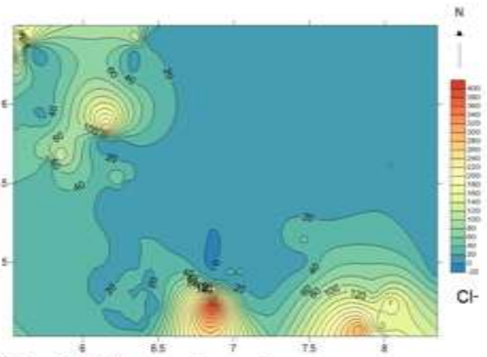
These observations are consistent with previous research by Abi-Bezam and Egboka (2010), who identified three anion facies in the groundwater system of the Port Harcourt area: Cl–SO4, Cl–SO4–HCO3, and HCO3–Cl–SO4. Similarly, Eyankware *et al*. (2022) reported Na-Cl facies in the coastal region of Port Harcourt, attributing this to seawater intrusion. Additionally, Owoyemi *et al*. (2019) identified CaHCO3, NaHCO3, NaCl, and CaMgClSO4 ionic facies in the groundwater of Delta State, which they linked to silicate weathering, ion exchange processes, and tidal flushing from seawater.

The various facies identified within this study highlight the complex geochemical processes affecting groundwater quality and availability. This understanding will aid in accurate groundwater resource assessment, enabling tailored management practices which include monitoring and mitigation strategies against contamination sources and sustainable extraction practices to prevent overexploitation and subsequent saline intrusion. The findings also suggest the need for optimizing groundwater resource allocation based on quality, as different water types can be allocated for specific uses.

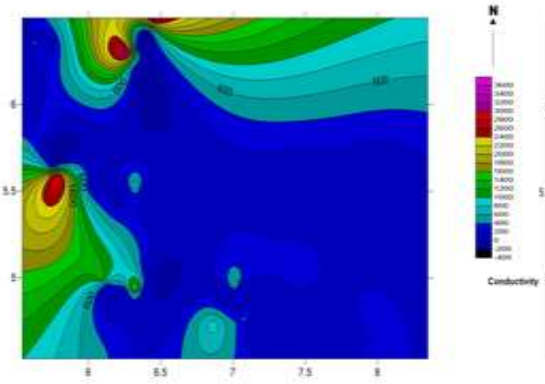
## Geospatial distributions of the analyzed parameters



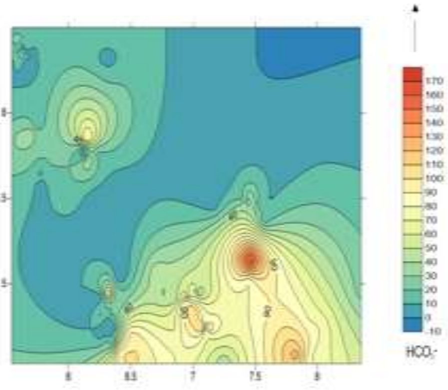
(a)Trend in $Mg^{2+}$ across the study area



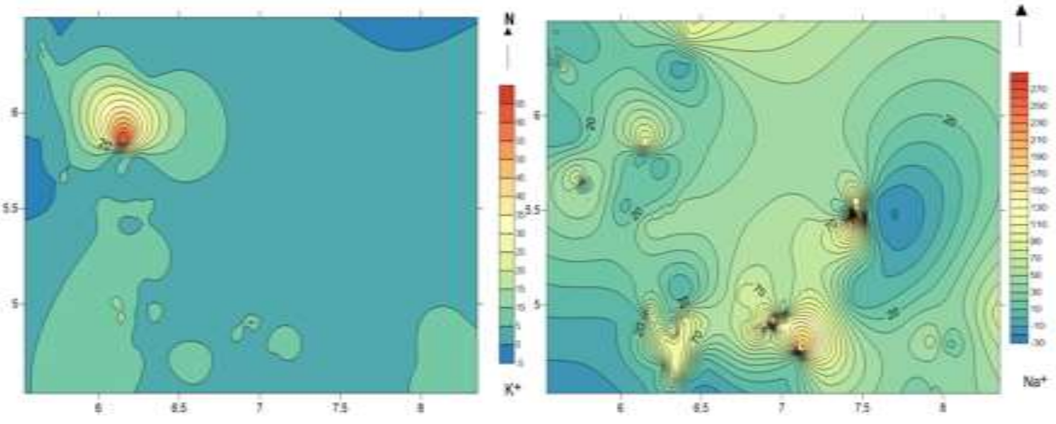
(b) Trend in $Cl^-$ across the study area



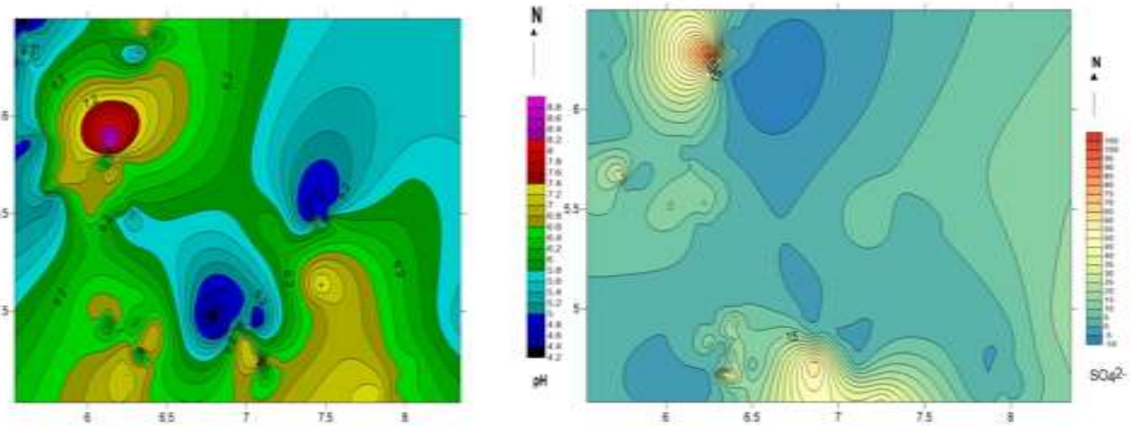
(c) Trend in conductivity across the study area



(d) Trend in $HCO_3^-$ across the study area



(e) Trend in K⁺ across the study area (f) Trend in Na⁺ across the study area



(g) Trend in pH across the study area (h) Trend in pH across the study area

**Figure 5:** Distribution of the Physicochemical Parameters across the study area

## Prediction of Groundwater Chemistry across the Niger Delta Sedimentary Basin Using Multiple Linear Regression (MLR)

MLR is a convenient and precise technique that gives conditions connecting between a reliant variable and a bunch of autonomous factors that go about as indicators. It has the advantage of producing an equation compared to other methods (Hasda *et al*., 2020). MLR was used to develop an equation for predicting electrical conductivity, pH, and WQI in the study area as shown in Equ 9 to 11.

Ec = K +a ($Cl^-$) + b ($HCO3^-$) +c ($SO_4^{2-}$) + d (Na+) + e ($Mg^{2+}$) +f ($K^+$) +g($Ca^{2+)}$) +€ __________ Eqn.7

pH= K +a ($Cl^-$) + b ($HCO3^-$) +c ($SO_4^{2-}$) + d (Na+) + e ($Mg^{2+}$) +f ($K^+$) +g($Ca^{2+)}$) +h(EC)+€ ___Eqn. 8

WQI=K + a(pH) + b($Cl^-$) + c($HCO3^-$) + d($SO_4^2$) + e($Na^+$)+f($Mg^{2+}$)+g($K^+$)+h($Ca^{2+)}$+i(EC)+ €__Eqn. 9

Where k = regression constant, € = error, a, b, c, d, e, f, g are coefficient of predictors in the Model while Ec, Cl-, HCO3-, SO42-, Na+, Mg2+, Ca2+ are input parameters.

MLR-predicted equations for the prediction of pH and EC in the Study area are presented below:
Prediction of groundwater level of electrical conductivity across the study area is presented in equation 4-6.
Ec = 24.8923 +2.0680 ($Cl^-$) + 0.6503 (HCO3-) - 0.1540 (SO42-) + 3.3670 ($Na^+$) + 0.0514 ($Mg^{2+}$) - 1.0892 ($K^+$) -0.0461($Ca^{2+}$) + 71.4804. ___ Eqn. 9
Prediction of groundwater level of Acidity/alkalinity across the Niger Delta sedimentary basin is presented in equation 5.4 below
pH =5.952 -0.001 ($Cl^-$ ) -0.003 ($HCO_3^-$ ) + 0.004 (SO42- ) -0.005 ($Na^+$) - 0.035 ($Mg^{2+}$ ) + 0.011 ($K^+$) +0.080 ($Ca^{2+}$) + 0.001(EC)+ 0.858.______ Eqn. 10
The prediction of groundwater quality across the Niger Delta sedimentary basin is presented in

Equation 5.5

$$WQI = 0.4567+0.112\,(pH) - 0.0013(EC) + 0.01168(CL^{-}) + 0.0107(HCO_3-) - 0.0009(SO_4^{2-}) + 0.003(Na^{+}) - 0.003(Mg^{2+}) + 0.002\,(K^{+}) - 0.017(Ca^{2+}) + 0.5282 \quad \underline{\hspace{6cm}} \text{ Eqn. 11.}$$

Findings from the study showed that:

1. The groundwater quality for domestic and industrial usage ranges from good to excellent, nevertheless, appropriate remediation of pH is needed to upgrade its quality for industrial and domestic use.
2. Inferences from various ionic ratios and charts indicate both geogenic and anthropogenic factors as the sources of the major ions in groundwater within the study area. An on-set of aquifer contamination from wastewater, leachate migration other human activities mobilize the major ions to groundwater. The Geogenic factors include saltwater intrusion, precipitation of meteoric water (rain), and dissolution of silicate minerals such as Biotite, Albite, and Anorthite.
3. Great variation exists in the composition of the analytes reviewed across the regions: In the Western Niger Delta sedimentary Basin, the concentration of most analytes is far lower in Edo relative to Delta state; the same was experienced with Abia and Akw-Ibom State in Eastern Niger Delta sedimentary Basin, Abia having lower concentrations relative to Akwa-Ibom State. These variations can be attributed to the difference in the Depth of the aquifer and the difference in aquifer properties that existed in those states. In the central Niger Delta Sedimentary Basin which comprised of Bayelsa State and Rivers State, there was no significant variation in magnitude of the reviewed analyte concentrations.
4. The groundwater facies encountered include the chloride facies (Na-Cl, Ca-Mg-SO4-Cl, Na-HCO3-Cl water types), the bicarbonate facies (Ca-Mg-HCO3, Na-$HCO_3^-$, Cl, Na- $HCO_3^-$ water types) and the sulphate facies (Ca-Mg-SO4, Ca-Mg-SO4-Cl). The Western and Eastern Niger Delta Sedimentary Basin is dominated by Bicarbonate facies, meanwhile, the Central Niger Delta Sedimentary Basin is predominantly the mixture of Bicarbonate and Chloride facies. This implies that the groundwater flow towards the Central Niger Delta Sedimentary Basin. The study, therefore, observed that the groundwater in the study area in terms of water types is consistent with the known evolutionary trend from recharge to discharge along its flow line, presenting with Bicarbonates dominant recharge area (young) and chloride (oldest) discharge area chemistry. However, since the groundwater facies varies significantly from place to place, change in temperature, redox reactions and UV-radiation may have diverse effects on its chemical constituents when exposed to the surface. This could be a possible reason for the fluctuation in pH readings on harvested groundwater within the region. This therefore implies each water type in its natural state may be suitable for different usage and require different treatment approach.
5. Dissolution of minerals and ionic (Base Exchange and reverse ionic exchange) are the basic hydrogeochemical processes that determine the groundwater chemistry in the study area.

**Implication:**

This study provides empirical evidence on:

- The implications of society's unfriendly operations and its attendant effects on the state of the groundwater.
- The need for a differentiated groundwater treatment and usage.
- The localised factors responsible for the groundwater chemistry across the region.
- This will be useful in policy formulation, evaluation, monitoring and implementation especially on issues relating to groundwater management within the Niger Delta Region.

## RECOMMENDATIONS

1. The study advocates for the treatment of groundwater to modify its pH levels, which is essential for preserving groundwater quality and mitigating corrosion within the affected area. This can be achieved through the adoption of pH-neutralizing filters and other appropriate mechanisms.
2. The study also recommends and emphasizes the necessity of tailored groundwater usage and treatment strategies that consider the specific facies present.
3. This study recommends further evaluation on heavy metal contents and biological

composition of the localized groundwater for its wholesome acceptability.

4. The study, therefore, recommends periodic groundwater quality monitoring across the region. This will enable constant updates on objective evidence necessary for sound decisions on managing groundwater resources within the basin.
5. Proper waste management system and treatment of effluent before release: These may further slow the release of these contaminants and may help reverse the pollution trend with time.

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**Data Availability:** My manuscript has associated data in a data repository.

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