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Geochemical Processes, Groundwater–Rock Interaction and Hydrochemical Evolution of Aquifer Systems in Bayelsa State, Nigeria

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ABSTRACT

Groundwater quality is influenced by physicochemical conditions, dissolved ions and geochemical processes that vary spatially. This study evaluated the physicochemical characteristics, major-ion composition, hydrochemical facies, mineral saturation indices and geochemical relationships of six groundwater samples (GW1–GW6) from Bayelsa State, Niger Delta, Nigeria. Temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), turbidity, hardness, alkalinity, major cations, selected metals and major anions were examined. Hydrochemical interpretation involved ionic charge balance, diagnostic ratios, chloro-alkaline indices, Gibbs ratios, mineral saturation indices and Pearson correlation analysis. Temperature ranged from 27.6 to 28.4 °C, while pH varied from 5.82 to 7.18, indicating acidic to near-neutral conditions. EC ranged from 86 to 684 µS/cm and TDS from 54 to 438 mg/L. Sodium was the dominant measured cation, with concentrations of 12.4–96.5 mg/L, while bicarbonate was the predominant anion by mass, ranging from 34.2 to 153.7 mg/L. Iron and manganese concentrations ranged from 0.13 to 0.42 mg/L and 0.02 to 0.08 mg/L, respectively.

Gw5 consistently exhibited the highest mineralisation-related parameters, whereas GW4 generally recorded the lowest values and the highest iron and manganese concentrations. Charge-balance errors ranged from –2.6% to +6.6%. The reported saturation indices were negative for calcite, aragonite, dolomite, gypsum and halite. EC showed strong positive correlations with most major ions.

Keyword: Groundwater quality; hydrochemical facies; major ions; mineral saturation; Niger Delta; geochemical processes.

1.0 Introduction

Groundwater is an important source of drinking water and domestic supply in many parts of Nigeria, particularly in communities where access to reliable treated water is limited. Its suitability for consumption depends on its physicochemical characteristics, the geochemical composition of aquifer materials and the influence of natural and anthropogenic processes. In the Niger Delta, interactions between groundwater and sediments, together with the region's complex hydrogeological conditions, can influence dissolved-ion concentrations, mineralisation and the distribution of potentially toxic elements. Previous studies have investigated groundwater quality, hydrochemical characteristics and associated health risks in the region, highlighting the importance of evaluating groundwater composition in relation to its intended use [1, 2, 3].

The physicochemical characteristics of groundwater provide essential information about its general quality and the processes controlling its composition.

Parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), turbidity, total hardness and alkalinity indicate acidity, dissolved-ion content, mineralisation and the potential effects of water–rock interaction. Variations in these parameters may reflect differences in aquifer materials, groundwater residence time, mineral dissolution and the influence of external contaminant sources. Previous investigations of groundwater in Nigeria have demonstrated the importance of assessing these parameters when determining water suitability for domestic purposes [4, 5]. Hydrogeophysical studies have also shown that geological structures and aquifer characteristics are important considerations in understanding groundwater occurrence, movement and vulnerability [6, 7].

The chemical composition of groundwater is further determined by the relative abundance of major cations and anions, including calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulphate and nitrate.

Their concentrations and relative proportions provide information about mineral weathering, dissolution, ion exchange and possible anthropogenic influences. Hydrochemical facies classification and ionic ratios are useful for identifying compositional differences among groundwater samples and investigating the processes that may control groundwater chemistry. In coastal aquifer systems, seawater intrusion and other salinity-related processes may influence dissolved-ion distributions. However, such processes cannot be established reliably from individual ionic ratios alone and require interpretation alongside other hydrochemical evidence and the local hydrogeological setting [1,8,3].

Potentially toxic elements, particularly iron and manganese, also warrant consideration in groundwater quality investigations because their concentrations may be influenced by mineral dissolution, oxidation-reduction conditions and interactions between groundwater and aquifer sediments. Although these elements may occur naturally, elevated concentrations can affect water acceptability and indicate geochemical conditions requiring further investigation. Their interpretation should therefore consider pH, mineralisation, major-ion composition and the characteristics of the aquifer materials. Studies of groundwater quality and associated health risks in Nigeria have emphasised the importance of combining chemical measurements with appropriate evaluations of potential human exposure [2,5].

A comprehensive interpretation of groundwater chemistry requires more than comparing individual parameters with drinking-water guideline values. Charge-balance evaluation provides a means of checking the internal consistency of major-ion analyses, while Piper diagrams facilitate the classification of hydrochemical facies and comparison of groundwater compositions. Ionic ratios provide additional evidence for investigating possible ion-exchange and mineral-weathering processes, whereas mineral saturation indices help evaluate whether groundwater is thermodynamically undersaturated or supersaturated with respect to selected minerals. Gibbs diagrams can assist in examining the possible contributions of precipitation, rock-water interaction and evaporation-crystallisation to groundwater chemistry. Nevertheless, the interpretation of these tools must account for their assumptions, the quality of the analytical data and the hydrogeological conditions of the study area. Previous groundwater and hydrogeophysical investigations in Nigeria demonstrate the relevance of integrated approaches to understanding groundwater systems and aquifer vulnerability [6,9,7].

Despite existing research on groundwater quality, hydrochemical processes and environmental risks in Nigeria, site-specific evaluation remains necessary because groundwater composition can vary considerably across sampling locations. Assessing physicochemical parameters, major ions, ionic proportions, charge balance, hydrochemical facies, diagnostic ratios, mineral saturation and relationships among measured variables can provide a more comprehensive understanding of groundwater chemistry and its controlling processes. Such an integrated approach is relevant to the Niger Delta, where groundwater is an important source of domestic water and its suitability must be established through reliable chemical assessment. Therefore, this study aimed to evaluate the physicochemical characteristics and major-ion composition of six groundwater samples from the study area in the Niger Delta, Nigeria.

2.0 Materials and Methods

2.1 Study Design and Sampling

A cross-sectional hydrogeochemical study was conducted to evaluate the physicochemical characteristics, major-ion composition, hydrochemical facies, mineral saturation and geochemical relationships of groundwater in Bayelsa State, Niger Delta, Nigeria. Six groundwater samples, designated GW1–GW6, were investigated to determine spatial variations in water chemistry. The parameters examined included temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), turbidity, total hardness, alkalinity, major cations, selected metals and major anions.



Figure 1. Map of Bayelsa State, Niger Delta, Nigeria, Showing the Six Proposed Groundwater Sampling Locations (GW1–GW6).

2.2 Sample Collection and Preservation

Groundwater samples were collected in pre-cleaned polyethylene bottles. The bottles were labelled according to sampling location and transported to the laboratory in ice-packed containers. Temperature, pH, EC, TDS and turbidity were measured in situ using calibrated instruments. Samples intended for metal analysis were preserved separately by acidification with nitric acid to pH below 2, while samples for anion analysis were kept unacidified and refrigerated until analysis.

2.3 Physicochemical Analysis

Temperature was measured using a calibrated thermometer, while pH was determined using a calibrated pH meter. Electrical conductivity and TDS were measured using a conductivity/TDS meter. Turbidity was determined using a calibrated turbidimeter and expressed in nephelometric turbidity units (NTU). Total hardness was determined by EDTA complexometric titration and expressed as mg/L CaCO_3 . Alkalinity was determined by acid titration and reported as mg/L CaCO_3 .

2.4 Determination of Major Cations and Metals

Calcium and magnesium were determined by EDTA complexometric titration. Sodium and potassium were measured using a flame photometer, while iron and manganese were determined by atomic absorption spectrophotometry. The concentrations of the major cations and metals were expressed in mg/L.

2.5 Determination of Major Anions

Bicarbonate was determined by acid titration, chloride by argentometric titration, sulphate by the turbidimetric method, and nitrate and phosphate by appropriate spectrophotometric procedures. All anion concentrations were expressed in mg/L.

2.6 Quality Assurance and Quality Control

Analytical quality was maintained through instrument calibration, the use of appropriate analytical standards, reagent blanks and replicate measurements. Instruments were calibrated before use, and analytical procedures followed relevant standard methods for water examination. Sample labels and laboratory records were checked to ensure consistency between sampling locations and analytical results.

2.7 Hydrochemical Calculations

Major-ion concentrations were converted from mg/L to milliequivalents per litre (meq/L) using the equivalent weight of each ion. Charge-balance error (CBE) was calculated using the equation:

$$\text{CBE (\%)} = [(\Sigma \text{ cations} - \Sigma \text{ anions}) / (\Sigma \text{ cations} + \Sigma \text{ anions})] \times 100$$

where Σ cations and Σ anions represent the total concentrations of cations and anions in meq/L, respectively. A charge-balance error within $\pm 5\%$ was adopted as the acceptance criterion.

Hydrochemical facies were evaluated using the relative proportions of the major cations and anions expressed as percentages of their respective equivalent totals. The cation groups included Ca^{2+} , Mg^{2+} and $\text{Na}^+ + \text{K}^+$, while the anion groups included HCO_3^- , Cl^- and SO_4^{2-} . These proportions were used to describe the ionic composition of each groundwater sample and prepare the Piper diagram.

Diagnostic ratios, including Ca/Mg , $\text{Ca}/(\text{Ca} + \text{Mg})$, Na/Cl and HCO_3/Cl , were calculated using major-ion concentrations expressed in equivalent units. Chloro-alkaline indices CAI-I and CAI-II were calculated to examine the relationships between alkali and alkaline-earth metals and chloride.

Mineral saturation indices for calcite, aragonite, dolomite, gypsum and halite were evaluated using the relationship between the ion activity product and the mineral solubility product:

$$\text{SI} = \log_{10} (\text{IAP}/\text{Ksp})$$

where SI is the saturation index, IAP is the ion activity product and Ksp is the equilibrium solubility product. Negative, positive and zero values indicate undersaturation, supersaturation and equilibrium, respectively.

Gibbs ratios were calculated as $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$, using equivalent concentrations. The ratios were examined against TDS to compare the hydrochemical characteristics of the groundwater samples and prepare the Gibbs diagrams.

2.8 Statistical Analysis

Descriptive statistics, including minimum, maximum, mean and standard deviation, were used to summarise the physicochemical parameters, major ions and selected metals. Pearson correlation coefficients were calculated to examine the linear relationships of EC and pH with the major dissolved constituents. Correlation coefficients were interpreted descriptively because the analysis comprised six groundwater samples. Statistical significance was set at $p < 0.05$.

3.0 Results

3.1 Physicochemical characteristics

The physicochemical characteristics of the six groundwater samples showed variations in acidity, mineralisation and turbidity (Table 1). Temperature ranged from 27.6 to 28.4 °C, with a mean of 28.0 ± 0.3 °C, indicating relatively stable thermal conditions. The pH ranged from 5.82 at GW4 to 7.18 at GW5, with GW1, GW2 and GW4 exhibiting acidic conditions below pH 6.6. EC and TDS ranged from 86 to 684 $\mu\text{S}/\text{cm}$ and 54 to 438 mg/L, respectively. GW5 recorded the highest EC, TDS, turbidity, total hardness and alkalinity, whereas GW4 had the lowest values for these parameters. Total hardness ranged from 31.2 to 148.6 mg/L as CaCO_3 , while alkalinity varied from 28.0 to 126.0 mg/L as CaCO_3 . These variations indicate differences in

Table 1: Physicochemical parameters

Parameter	GW1	GW2	GW3	GW4	GW5	GW6	Mean $\pm$ SD
Temperature (°C)	27.8	28.1	27.6	28.4	28.0	27.9	28.0 ± 0.3
pH	6.21	6.54	6.87	5.82	7.18	6.63	6.54 ± 0.48
EC ($\mu\text{S}/\text{cm}$)	186	248	412	86	684	326	323.7 ± 209.2
TDS (mg/L)	119	159	264	54	438	209	207.2 ± 134.2
Turbidity (NTU)	1.42	1.86	2.13	1.17	3.21	1.74	1.92 ± 0.72
Total hardness (mg/L as CaCO_3)	42.6	57.8	96.4	31.2	148.6	74.5	75.2 ± 42.8
Alkalinity (mg/L as CaCO_3)	38.0	52.0	84.0	28.0	126.0	67.0	65.8 ± 35.6

3.2 Major cations and metals

Sodium was the dominant measured cation, with concentrations ranging from 12.4 to 96.5 mg/L, followed by calcium (7.8–42.6 mg/L), potassium (1.8–9.6 mg/L) and magnesium (1.4–10.3 mg/L) (Table 2). GW5 recorded the highest concentrations of all four major cations, while GW4 had the lowest calcium, sodium and potassium concentrations. Iron ranged from 0.13 to 0.42 mg/L and manganese from 0.02 to 0.08 mg/L. Both metals were highest at GW4 and lowest at GW5, contrasting with the distribution of the major cations. Iron concentrations at GW1 (0.31 mg/L) and GW4 (0.42 mg/L) were above 0.30 mg/L, highlighting differences in metal distribution across the groundwater samples.

Table 2: Major cations and metals (mg/L)

Parameter	GW1	GW2	GW3	GW4	GW5	GW6	Mean $\pm$ SD
Ca^{2+}	14.8	19.6	31.7	7.8	42.6	24.3	23.5 ± 12.4
Mg^{2+}	1.4	2.2	4.2	2.8	10.3	3.4	4.0 ± 3.2
Na^+	28.4	36.8	64.7	12.4	96.5	48.2	47.8 ± 29.7
K^+	3.2	4.1	6.8	1.8	9.6	5.3	5.1 ± 2.8
Fe	0.31	0.24	0.18	0.42	0.13	0.21	0.25 ± 0.10
Mn	0.06	0.04	0.03	0.08	0.02	0.04	0.05 ± 0.02

3.3 Major anions

Bicarbonate was the predominant anion by mass, ranging from 34.2 to 153.7 mg/L, followed by chloride (18.6–132.4 mg/L), sulphate (7.4–31.6 mg/L) and nitrate (2.1–11.7 mg/L) (Table 3). All four anions recorded their highest concentrations at GW5 and lowest at GW4.

Phosphate concentrations were comparatively low, ranging from 0.14 to 0.37 mg/L. The consistent distribution of the major anions indicates higher dissolved-ion concentrations at GW5 and lower concentrations at GW4.

Table 3: Major anions (mg/L)

Parameter	GW1	GW2	GW3	GW4	GW5	GW6	Mean $\pm$ SD
HCO ₃ ⁻	46.4	63.4	102.5	34.2	153.7	81.7	80.3 $\pm$ 43.5
Cl ⁻	31.4	43.7	78.3	18.6	132.4	56.2	60.1 $\pm$ 41.0
SO ₄ ²⁻	9.8	14.6	21.8	7.4	31.6	17.2	17.1 $\pm$ 8.8
NO ₃ ⁻	3.2	5.8	8.4	2.1	11.7	6.4	6.3 $\pm$ 3.5
PO ₄ ³⁻	0.18	0.22	0.31	0.14	0.37	0.25	0.24 $\pm$ 0.08

3.4 Ionic composition and charge balance

The equivalent concentrations of the major ions revealed sodium as the dominant cation, ranging from 0.54 meq/L at GW4 to 4.20 meq/L at GW5 (Table 4).

Table 4: Major ions (meq/L) and charge balance

Sample	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Σ cations	Σ anions	CBE (%)
GW1	0.74	0.11	1.24	0.08	0.76	0.89	0.20	0.05	2.17	1.90	+6.6
GW2	0.98	0.18	1.60	0.10	1.04	1.23	0.30	0.09	2.86	2.67	+3.5
GW3	1.58	0.34	2.81	0.17	1.68	2.21	0.45	0.14	4.91	4.48	+4.7
GW4	0.39	0.23	0.54	0.05	0.56	0.52	0.15	0.03	1.21	1.27	-2.6
GW5	2.13	0.84	4.20	0.25	2.52	3.73	0.66	0.19	7.41	7.10	+2.2
GW6	1.21	0.28	2.10	0.14	1.34	1.59	0.36	0.10	3.72	3.39	+4.7

3.5 Hydrochemical facies

The relative proportions of the major ions, expressed as percentages of their respective equivalent concentrations, demonstrated the predominance of sodium and potassium over the combined calcium and magnesium contribution at most sampling locations (Table 5). Na⁺ + K⁺ accounted for 59.6–60.8% of the cation composition at GW1, GW2, GW3, GW5 and GW6. At GW4, this proportion decreased to 48.4%, while calcium and magnesium contributed 32.2% and 19.4%, respectively. GW4 therefore exhibited a more substantial relative contribution from the divalent cations than the other samples.

The anion composition showed a less pronounced distinction between chloride and bicarbonate. Chloride contributed 41.2–52.6% of the anion equivalents, while bicarbonate accounted for 35.5–44.0%. Chloride was the largest individual anion fraction at five locations, with its highest proportion at GW5. At GW4, bicarbonate accounted for 44.0%, exceeding the chloride contribution of 41.2%. Sulphate represented a smaller fraction, ranging from 9.3% to 12.1%. These distributions indicate predominantly sodium-rich groundwater with variable chloride and bicarbonate contributions. The comparatively larger calcium and magnesium fractions at GW4 distinguish its ionic composition from the stronger sodium dominance observed elsewhere. The Piper diagram (Figure 1) will provide a graphical representation of these relationships.

Table 5: Relative proportions of major-ion groups (% meq/L)

Sample	Ca ²⁺	Mg ²⁺	Na ⁺ + K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
GW1	34.1	5.2	60.7	40.0	46.6	10.7
GW2	34.2	6.2	59.6	38.9	46.2	11.4
GW3	32.2	7.0	60.8	37.5	49.3	10.1
GW4	32.2	19.4	48.4	44.0	41.2	12.1
GW5	28.7	11.4	59.9	35.5	52.6	9.3
GW6	32.6	7.4	60.0	39.6	46.8	10.6

Calcium and magnesium contributed additional cation equivalents, while potassium occurred at lower concentrations. Among the anions, chloride exceeded bicarbonate at five locations, whereas GW4 showed a slightly higher bicarbonate concentration on an equivalent basis. GW5 had the highest total concentrations of both cations and anions, consistent with its elevated EC and TDS. Conversely, GW4 recorded the lowest overall ionic concentrations.

The calculated charge-balance error (CBE) ranged from -2.6% at GW4 to +6.6% at GW1. Five samples fell within the commonly applied acceptance range of $\pm 5\%$, while GW1 exceeded this range slightly. The positive CBE values at GW1, GW2, GW3, GW5 and GW6 indicate that the reported sums of cation equivalents exceeded those of anion equivalents, whereas GW4 had a negative CBE.

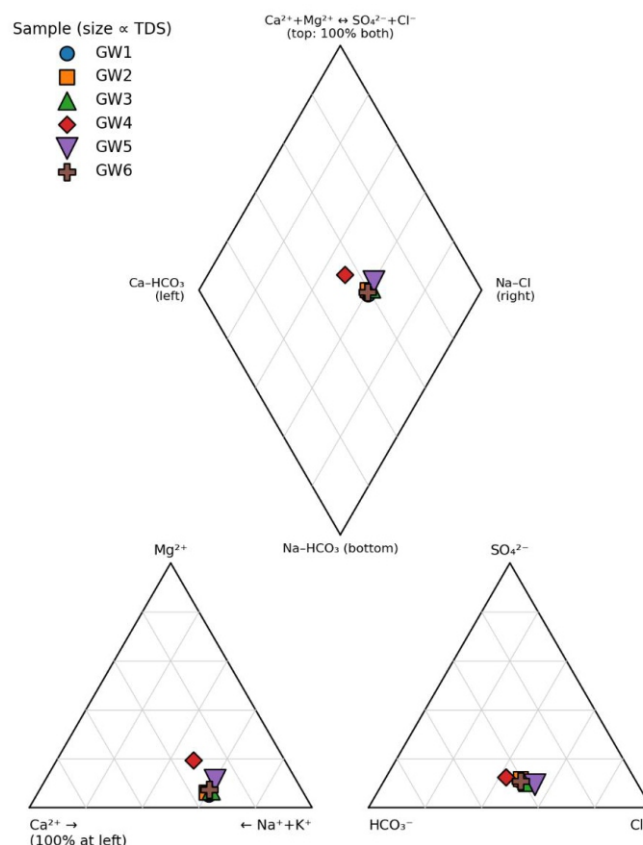


Figure 1: The Piper diagram showing the graphical representation of these relationships.

3.6 Diagnostic ratios and chloro-alkaline indices

The diagnostic ratios revealed differences in the relative contributions of calcium, magnesium, sodium, chloride and bicarbonate among the groundwater samples (Table 6). The Ca/Mg ratio ranged from 1.66 at GW4 to 6.54 at GW1, indicating that calcium exceeded magnesium throughout the study locations, although the relative difference was smallest at GW4.

The Ca/(Ca + Mg) ratio followed a similar pattern, varying from 0.62 at GW4 to 0.87 at GW1. These ratios highlight the stronger relative contribution of calcium at GW1 and the more substantial magnesium contribution at GW4.

Na/Cl ratios exceeded unity at all six locations, ranging from 1.03 at GW4 to 1.39 at GW1. This indicates that sodium concentrations were proportionally greater than chloride concentrations when compared on the equivalent basis used for the ratio. In contrast, $\text{HCO}_3^-/\text{Cl}^-$ was below unity at five locations, with values between 0.67 at GW5 and 0.86 at GW1, but reached 1.07 at GW4. Thus, chloride was relatively dominant over bicarbonate at most locations, whereas GW4 displayed a slightly greater bicarbonate contribution. Both chloro-alkaline indices, CAI-I and CAI-II, were negative throughout the study area. CAI-I ranged from -0.49 to -0.12, while CAI-II ranged from -0.42 to -0.08. GW4 had the values closest to zero for both indices, whereas GW1 recorded the most negative values.

Table 6: Diagnostic ratios and chloro-alkaline indices

Sample	Ca/Mg	Ca/(Ca+Mg)	Na/Cl	$\text{HCO}_3^-/\text{Cl}^-$	CAI-I	CAI-II
GW1	6.54	0.87	1.39	0.86	-0.49	-0.42
GW2	5.52	0.85	1.30	0.84	-0.38	-0.33
GW3	4.59	0.82	1.27	0.76	-0.35	-0.34
GW4	1.66	0.62	1.03	1.07	-0.12	-0.08
GW5	2.52	0.72	1.12	0.67	-0.19	-0.21
GW6	4.39	0.81	1.32	0.84	-0.41	-0.36

3.7 Mineral saturation indices

The reported mineral saturation indices were negative for all six samples with respect to calcite, aragonite, dolomite, gypsum and halite (Table 7). Within the reported calculations, this pattern indicates undersaturation relative to the specified mineral phases. Calcite saturation indices ranged from -3.09 at GW4 to -0.46 at GW5, while aragonite values ranged from -3.23 to -0.60. The proximity of the GW5 values to zero indicates that this sample was comparatively closer to equilibrium with calcite and aragonite than the other samples. GW4 had the most negative values for both minerals.

Dolomite saturation indices ranged from -6.27 at GW4 to -1.19 at GW5, showing the same spatial ordering as calcite and aragonite. Gypsum values varied from -3.40 at GW4 to -2.22 at GW5, while halite indices ranged from -8.16 to -6.46. Halite had the most negative saturation indices across the samples, whereas calcite and aragonite were comparatively closer to equilibrium. The consistent differences between GW4 and GW5 correspond to their contrasting mineralisation levels, with GW5 having the highest EC and TDS and GW4 the lowest.

Table 7: Saturation indices

Sample	Calcite	Aragonite	Dolomite	Gypsum	Halite
GW1	-2.31	-2.45	-5.31	-3.04	-7.58
GW2	-1.74	-1.88	-4.10	-2.77	-7.33
GW3	-1.03	-1.17	-2.60	-2.45	-6.85
GW4	-3.09	-3.23	-6.27	-3.40	-8.16
GW5	-0.46	-0.60	-1.19	-2.22	-6.46
GW6	-1.47	-1.61	-3.45	-2.63	-7.11

3.8 Gibbs ratios

The Gibbs ratios showed variation in the relative contributions of sodium and calcium, and chloride and bicarbonate, across the six groundwater samples (Table 8). The cation ratio $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ranged from 0.58 at GW4 to 0.66 at GW5, while the anion ratio $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ ranged from 0.48 to 0.60.

Both ratios were lowest at GW4 and highest at GW5, indicating that GW5 had the strongest relative sodium and chloride contributions among the sampled locations, whereas GW4 had comparatively lower proportions of these ions.

TDS varied from 54 mg/L at GW4 to 438 mg/L at GW5. The correspondence between the Gibbs ratios and TDS demonstrates that the groundwater samples differed in both total dissolved material and the relative ionic composition. GW1, GW2 and GW6 showed relatively similar anion ratios of 0.54, while GW3 had a higher value of 0.57. GW4 stood apart with the lowest ratios for both cations and anions, whereas GW5 consistently recorded the highest. When plotted against TDS, these ratios will provide a visual comparison of the samples' hydrochemical positions on the Gibbs diagrams (Figure 2).

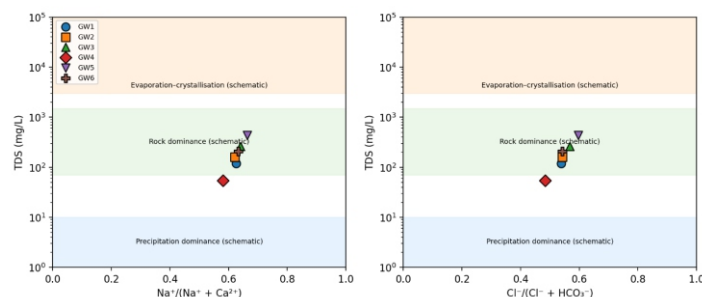


Figure 2: Gibbs diagrams

Table 8: Gibbs ratios and TDS

Sample	TDS (mg/L)	$\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$	$\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$
GW1	119	0.63	0.54
GW2	159	0.62	0.54
GW3	264	0.64	0.57
GW4	54	0.58	0.48
GW5	438	0.66	0.60
GW6	209	0.63	0.54

3.9 Correlation analysis

The Pearson correlation coefficients showed strong positive relationships between EC and the major dissolved ions across the six groundwater samples (Table 9). EC correlated with calcium ($r = 0.99$), sodium ($r = 1.00$), bicarbonate ($r = 1.00$), chloride ($r = 1.00$) and sulphate ($r = 0.99$). Magnesium had a comparatively lower correlation with EC ($r = 0.91$). These relationships indicate that samples with higher conductivity generally had higher concentrations of the measured major ions. The strong correlations are consistent with the elevated ionic concentrations recorded at GW5 and the lower concentrations at GW4.

The correlation between EC and TDS was 1.00, consistent with the reported proportional relationship between these parameters, given that TDS was derived from EC. pH also showed positive correlations with calcium ($r = 0.98$), sodium ($r = 0.96$), bicarbonate ($r = 0.95$), chloride ($r = 0.93$) and sulphate ($r = 0.96$). Its correlation with magnesium was weaker ($r = 0.74$).

Table 9: Correlation of EC and pH with major parameters @

Parameter	Ca^{2+}	Mg^{2+}	Na^+	HCO_3^-	Cl^-	SO_4^{2-}
EC	0.99	0.91	1.00	1.00	1.00	0.99
pH	0.98	0.74	0.96	0.95	0.93	0.96

4.0 Discussion

The groundwater samples exhibited spatial variation in physicochemical characteristics, major-ion composition and trace-metal concentrations, indicating differences in the degree of mineralisation and the geochemical conditions influencing groundwater quality across the sampling locations.

Temperature ranged from 27.6 to 28.4 °C, with a mean of 28.0 ± 0.3 °C, showing relatively little variation among samples. The pH ranged from 5.82 to 7.18, with a mean of 6.54 ± 0.48 , indicating acidic to near-neutral conditions. GW4 had the lowest pH (5.82), whereas GW5 recorded the highest (7.18). The acidic conditions at some locations are relevant because low pH can promote metal mobilisation from aquifer materials and increase the corrosiveness of water. The observed range is comparable to the pH of 5.2–6.8 reported by Ebikienmo et al. (2026) [6] for groundwater around Epie Creek, Yenagoa, Bayelsa State. Amuka et al. (2026) [4] also investigated seasonal groundwater quality in Bori, Rivers State, providing a relevant regional comparison for assessing variability in groundwater chemistry. The pH values below 6.5 fall outside the commonly applied operational range of 6.5–8.5 for drinking water. The acidic conditions at GW4 and other locations with pH below 6.5 warrant attention because they may influence metal solubility and the acceptability of water for domestic use.

Electrical conductivity (EC) ranged from 86 to 684 $\mu\text{S}/\text{cm}$, while total dissolved solids (TDS) ranged from 54 to 438 mg/L, with mean values of 323.7 ± 209.2 $\mu\text{S}/\text{cm}$ and 207.2 ± 134.2 mg/L, respectively. GW5 recorded the highest EC and TDS, whereas GW4 had the lowest values. This consistent pattern indicates that GW5 was the most mineralised sample and GW4 the least mineralised. The variation may reflect differences in water–rock interaction, mineral dissolution, groundwater residence time and the contribution of dissolved constituents from the surrounding environment. Similar regional investigations have examined the spatial and seasonal variability of groundwater quality in the Niger Delta [4, 6]. All TDS values were below 600 mg/L, indicating relatively low dissolved-solids concentrations. The maximum EC of 684 $\mu\text{S}/\text{cm}$ reflects a greater concentration of mobile dissolved ions at GW5. Turbidity ranged from 1.17 to 3.21 NTU, with a mean of 1.92 ± 0.72 NTU. All samples were below 5 NTU, a commonly used operational benchmark, although lower turbidity is desirable for effective disinfection. The higher turbidity at GW5 may reflect differences in suspended particles or colloidal material.

Total hardness ranged from 31.2 to 148.6 mg/L as CaCO_3 , with a mean of 75.2 ± 42.8 mg/L, while alkalinity ranged from 28.0 to 126.0 mg/L as CaCO_3 , averaging 65.8 ± 35.6 mg/L. GW5 recorded the highest hardness and alkalinity, whereas GW4 had the lowest values for both parameters. Based on conventional hardness classification, the groundwater ranged from soft to moderately hard. The greater hardness at GW5 is consistent with its elevated calcium and magnesium concentrations, while the higher alkalinity indicates a greater capacity to neutralise added acids. The relationship between hardness, alkalinity and major-ion concentrations suggests that mineral dissolution and water–rock interaction contribute to groundwater chemistry [1, 2, 5, 7].

Sodium was the dominant measured cation, ranging from 12.4 to 96.5 mg/L, with a mean of 47.8 ± 29.7 mg/L. Calcium ranged from 7.8 to 42.6 mg/L, potassium from 1.8 to 9.6 mg/L and magnesium from 1.4 to 10.3 mg/L. GW5 had the highest concentrations of calcium, sodium and potassium, whereas GW4 generally recorded the lowest concentrations of these ions. Magnesium differed slightly, with its minimum at GW1. The predominance of sodium suggests that groundwater chemistry is influenced by processes beyond the dissolution of calcium-bearing minerals alone.

Potential mechanisms include weathering of sodium-bearing minerals, ion exchange between groundwater and aquifer sediments, and the contribution of saline water. Umueni et al. (2026a) [26] examined hydrochemical evolution and seawater intrusion in coastal aquifers of the Niger Delta, providing relevant regional context for considering salinity-related processes. Calcium-to-magnesium ratios ranged from 1.66 to 6.54. GW1 recorded the highest ratio, whereas GW4 had the lowest.

The higher ratios at GW1, GW2 and GW3 indicate a greater relative contribution of calcium than magnesium, while the lower ratio at GW4 suggests a comparatively greater magnesium contribution relative to calcium. These differences may reflect variations in aquifer mineralogy, mineral dissolution and cation-exchange processes. Their interpretation alongside measured calcium and magnesium concentrations, alkalinity, hydrochemical facies and geological characteristics provides a more comprehensive understanding of groundwater chemistry. This integrated approach is consistent with regional investigations combining hydrochemical evidence with aquifer and geological information [10, 27].

Iron concentrations ranged from 0.13 to 0.42 mg/L, with a mean of 0.25 ± 0.10 mg/L, while manganese ranged from 0.02 to 0.08 mg/L, averaging 0.05 ± 0.02 mg/L. GW4 recorded the highest concentrations of both metals despite having the lowest EC, TDS, hardness and alkalinity. Conversely, GW5 had the lowest iron and manganese concentrations despite exhibiting the greatest overall mineralisation. This contrast indicates that iron and manganese distribution differed from the pattern observed for the major dissolved ions. Redox conditions, pH, aquifer mineralogy and the dissolution of metal-bearing phases may influence their concentrations. The low pH at GW4 may contribute to metal mobilisation by promoting mineral dissolution and influencing metal sorption. The observed variation in iron concentrations is consistent with the importance of examining groundwater chemistry across different locations in the Niger Delta [6].

The iron concentrations at GW1 (0.31 mg/L) and GW4 (0.42 mg/L) exceeded the commonly applied aesthetic benchmark of 0.3 mg/L. Iron above this level may cause staining, discolouration and unpleasant taste, reducing the acceptability of water for domestic use. Manganese reached 0.08 mg/L at GW4, equal to the World Health Organization's provisional guideline value of 0.08 mg/L. The elevated iron concentrations at GW1 and GW4 also indicate the need to consider appropriate treatment measures.

Bicarbonate was the dominant anion by mass concentration, ranging from 34.2 to 153.7 mg/L, with a mean of 80.3 ± 43.5 mg/L. Chloride ranged from 18.6 to 132.4 mg/L, sulphate from 7.4 to 31.6 mg/L, nitrate from 2.1 to 11.7 mg/L and phosphate from 0.14 to 0.37 mg/L. GW5 recorded the highest concentrations of all measured anions, while GW4 recorded the lowest. The bicarbonate concentrations are consistent with the measured alkalinity and indicate the importance of the carbonate system in controlling groundwater chemistry. Bicarbonate may originate from carbon dioxide dissolved in recharge water and subsequent interaction with soil and aquifer minerals. Chloride was the second most abundant anion by mass concentration and reached its maximum at GW5. Its distribution may reflect natural mineral sources, recharge inputs or anthropogenic contributions.

Nitrate concentrations were below the World Health Organization guideline of 50 mg/L as nitrate ion, indicating that nitrate did not exceed this benchmark during the sampling period. The low phosphate concentrations may reflect sorption, precipitation and interactions with iron- and aluminium-bearing minerals.

The ionic charge-balance errors ranged from -2.6% to +6.6%. Five samples were within the commonly applied acceptance range of $\pm 5\%$, while GW1 recorded +6.6%, slightly exceeding this limit. The results indicate general consistency between the major-ion analyses for most samples. A positive charge-balance error indicates that measured cation equivalents exceed measured anion equivalents, whereas a negative value indicates the reverse.

The relative ionic proportions showed that sodium and potassium together contributed 48.4–60.8% of the total cation equivalents. Their contribution was lowest at GW4 and highest at GW3. Calcium accounted for 28.7–34.2%, while magnesium contributed 5.2–19.4%. Among the anions, chloride accounted for 41.2–52.6%, bicarbonate for 35.5–44.0% and sulphate for 9.3–12.1%. Chloride represented more than half of the anion equivalents only at GW5, whereas bicarbonate had the greatest proportional contribution at GW4. These results indicate a broadly sodium-dominated composition with variable chloride–bicarbonate characteristics across the sampling locations. GW5 exhibited a relatively stronger chloride contribution and higher overall mineralisation, while GW4 showed a greater relative bicarbonate contribution and lower dissolved-ion concentrations [21–25].

The Na/Cl ratios ranged from 1.03 to 1.39, remaining above unity in all samples. This indicates that sodium concentrations were proportionally greater than chloride concentrations on a molar-equivalent basis. Possible explanations include weathering of sodium-bearing minerals and cation exchange. The HCO_3/Cl ratios ranged from 0.67 to 1.07, with GW4 the only sample exceeding unity. This finding agrees with the relative ionic proportions, which showed a stronger bicarbonate contribution at GW4 and a greater chloride contribution at the other locations. The chloro-alkaline indices were negative at all locations, ranging from -0.49 to -0.12 for CAI-I and from -0.42 to -0.08 for CAI-II. Negative values are conventionally associated with exchange processes involving dissolved sodium and potassium and calcium and magnesium associated with the aquifer matrix. GW4 had values closest to zero, while GW1 showed the most negative indices [2, 6, 18, 24].

The calculated saturation indices were negative for calcite, aragonite, dolomite, gypsum and halite in all six samples. These values indicate undersaturation with respect to the specified minerals under the conditions used in the calculations. GW5 had the indices closest to zero, particularly for calcite (-0.46) and dolomite (-1.19), whereas GW4 showed the greatest undersaturation for these minerals. This pattern corresponds broadly to the higher mineralisation at GW5 and the lower dissolved-ion concentrations at GW4. The saturation indices provide information on the thermodynamic relationship between groundwater and the specified mineral phases and contribute to the interpretation of groundwater–rock interaction [11, 15, 17, 25].

The Gibbs ratios also varied among the sampling locations. The $\text{Na}/(\text{Na} + \text{Ca})$ ratio ranged from 0.58 to 0.66, while the $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ ratio ranged from 0.48 to 0.60. Both ratios were highest at GW5 and lowest at GW4, reinforcing the contrast between the most mineralised and least mineralised samples.

These ratios provide additional evidence of spatial differences in ionic composition and help evaluate the possible influence of rock weathering, recharge and coastal hydrogeological processes. Umuenu et al. (2026a) [26] provide a relevant regional comparison for interpreting groundwater chemistry in relation to coastal aquifer processes.

The correlation analysis revealed strong positive relationships between EC and calcium ($r = 0.99$), magnesium ($r = 0.91$), sodium ($r = 1.00$), bicarbonate ($r = 1.00$), chloride ($r = 1.00$) and sulphate ($r = 0.99$). These relationships are consistent with the contribution of dissolved ions to electrical conductivity. The strong correlations indicate that samples with higher ionic concentrations generally had higher conductivity. The positive correlations between pH and the measured ions ($r = 0.74–0.98$) also indicate associations between pH and ionic composition within the dataset.

Conclusion

The study revealed spatial variations in the physicochemical and hydrochemical characteristics of groundwater across the six sampling locations in Bayelsa State, Niger Delta, Nigeria. Groundwater pH ranged from acidic to near-neutral, while EC and TDS indicated differences in dissolved mineral content. Sodium was the dominant measured cation, whereas bicarbonate was the predominant anion by mass. GW5 exhibited the highest EC, TDS, hardness, alkalinity and major-ion concentrations, while GW4 generally recorded the lowest mineralisation and the highest iron and manganese concentrations.

The hydrochemical ratios and ionic proportions demonstrated sodium-dominated groundwater with variable chloride and bicarbonate contributions. Negative chloro-alkaline indices and the reported negative mineral saturation indices provided additional information on the ionic relationships and calculated saturation states. The strong positive correlations between EC and most major ions further demonstrated the close association between electrical conductivity and dissolved constituents in the sampled groundwater.

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