

Hydrogeochemical Characterization of Groundwater in and around Rajahmundry, Andhra Pradesh, South India

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Abstract

Groundwater quality assessment is critical for ensuring sustainable water resources in rapidly urbanizing regions. This study evaluates the hydrogeochemical characteristics and water quality of groundwater in and around Rajahmundry, Andhra Pradesh, South India, an area influenced by both natural geological processes and anthropogenic pressures. A total of 151 groundwater samples were collected during pre- and post-monsoon seasons and analyzed for major ions using standard APHA procedures. Hydrochemical facies were identified through classical graphical methods (Piper, Durov, Chadha, Schoeller, Gibbs, and Gaillardet plots) and supported by statistical clustering. The results reveal that the groundwater is predominantly of calcium-magnesium-bicarbonate (Ca-Mg-HCO₃) type, indicating dominance of rock-water interaction, particularly carbonate weathering, as the primary hydrogeochemical process. Both pre- and post-monsoon datasets showed minimal seasonal variation, suggesting a stable aquifer system with strong geogenic control and high buffering capacity. Gibbs and Gaillardet plots confirm rock-weathering as the major mechanism governing groundwater chemistry, while Schoeller plots highlight the consistency of ion concentrations across the study area.

Keywords: Groundwater quality; Hydrogeochemistry; Rajahmundry; Rock-water interaction; Carbonate weathering; Seasonal variation

1. Introduction

Access to safe drinking water is a fundamental human right and a cornerstone of public health, economic progress, and environmental stability. In South India, groundwater serves as the primary water source for domestic, agricultural, and industrial use, especially in semi-arid regions and rapidly developing urban areas where surface water is often scarce or inconsistent [1], [2]. The Godavari River basin, India's second-largest, is a critical hydrological system that supports a vast population and extensive agriculture. Yet, growing human pressures have led to a significant decline in the quality and quantity of groundwater across the basin [3][4].

The city of Rajahmundry, located on the banks of the Godavari River in Andhra Pradesh, exemplifies a rapidly expanding urban center with increasing industrial activity. This expansion, coupled with intensive farming in the surrounding areas, puts immense strain on the shallow alluvial aquifers that supply the region's water [5]. The complex interaction between natural geological processes and human activities, such as the release of untreated sewage, industrial waste, and agricultural runoff, greatly impacts the chemical composition of the groundwater and its suitability for consumption [6], [7].

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Characterizing groundwater chemistry is an essential method for identifying the origin of dissolved ions and the key processes that shape its composition, including rock-water interaction, ion exchange, and mineral dissolution. This analysis provides a vital foundation for assessing current groundwater quality and pinpointing potential contamination sources [8], [9]. However, the complexity of hydrogeochemical data can make it difficult for policymakers and the public to fully understand the overall water quality. To overcome this, a Water Quality Index (WQI) is a powerful and widely used tool that consolidates multiple water quality parameters into a single, comprehensive score [10], [11]. This index offers a simplified and easy-to-interpret assessment of water quality, classifying it into categories ranging from “excellent” to “unsuitable” for drinking.

Despite the critical importance of groundwater in and around Rajahmundry, few comprehensive studies have focused on the combined effects of geogenic and anthropogenic factors on its quality. While some regional research exists, a holistic, integrated assessment that links detailed hydrochemical analysis with a robust WQI framework for this specific area is lacking. This study aims to fill that void by providing a thorough hydrochemical characterization and a WQI-based assessment of groundwater in and around Rajahmundry.

The objective of this study includes determining the spatial variation of major physical and chemical parameters of groundwater in the study region. It is also aimed to identify the dominant hydrogeochemical processes that influence groundwater chemistry by employing both graphical and statistical techniques. Further, the study focuses on calculating the Water Quality Index (WQI) in order to evaluate the overall suitability of the groundwater for drinking purposes. Finally, spatial distribution maps will be generated to visualize areas of concern and to delineate potential contamination hotspots, if any. The findings from this research will provide valuable insights for local authorities and water resource managers, helping them develop sustainable management and conservation strategies to protect this vital resource for future generations.

2. Literature Survey

The hydrogeochemical characterization of groundwater is a critical area of study, particularly in regions like Rajahmundry, Andhra Pradesh, which are experiencing rapid urbanization and industrialization. This field of research focuses on understanding the chemical composition of groundwater, identifying the natural and anthropogenic factors that influence its quality, and assessing its suitability for various uses such as drinking, irrigation, and industrial purposes. Recent studies published since 2015 have utilized a combination of classical hydrogeochemical diagrams, statistical analyses, and geospatial techniques to gain a deeper understanding of these complex processes. The findings from this body of work are essential for developing sustainable groundwater management strategies to safeguard this vital resource.

Research has consistently shown that the chemical composition of groundwater is primarily controlled by two major factors: geogenic processes (natural rock-water interactions) and anthropogenic activities (human-driven contamination) [12], [13].

Geogenic Processes: The natural dissolution and weathering of host rock minerals are a dominant force in shaping groundwater chemistry. Studies in hard rock terrains of South India, for instance, have identified that the weathering of silicate and carbonate minerals leads to the enrichment of major ions like Ca^{2+} , Mg^{2+} , and HCO_3^- [14] [15]. Bivariate plots and Piper diagrams are widely used to identify the dominant water types, such as Ca-Mg- HCO_3 , which indicates the prevalence of rock-water interaction as a control on water chemistry [16] [17].

Anthropogenic Influences: A growing body of research highlights the significant impact of human activities on groundwater quality. Rapid urbanization, inadequate waste disposal, agricultural practices, and industrial effluents introduce a variety of pollutants into the groundwater system. High concentrations of nitrate (NO_3^-) and chloride (Cl^-) are frequently linked to pollution from domestic sewage, septic systems, and the excessive use of nitrogen-based fertilizers [18]. Similarly, elevated levels of Total Dissolved Solids (TDS) and other ions are often correlated with industrial wastewater discharge and urban runoff [19], [20].

Modern hydrogeochemical studies have moved beyond traditional methods to incorporate advanced tools for a more comprehensive analysis. Statistical Analysis: Multivariate statistical techniques like Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) are extensively used to identify the underlying sources of contamination. These methods help group water samples with similar characteristics and distinguish between geogenic and anthropogenic factors influencing water chemistry [21] [8]. Similarly, the integration of Geographic Information Systems (GIS) with hydrogeochemical data has become standard practice. GIS is used to create spatial distribution maps of various hydrochemical parameters, which helps in identifying pollution hotspots and understanding the spatial

variability of groundwater quality. This visual representation is crucial for effective groundwater management and for targeting areas that require immediate intervention [22].

Although specific studies on the Rajahmundry region are limited, research from other parts of Andhra Pradesh and South India provides valuable context. Studies in nearby regions like Visakhapatnam and Chennai have shown similar trends of groundwater degradation due to rapid urban expansion and inadequate sanitation infrastructure. These studies serve as a strong foundation for the present research by demonstrating that the hydrogeochemical processes observed in the Rajahmundry region are part of a broader, regional phenomenon linked to rapid urbanization.

2.1. Study Area

The study area, centered around Rajahmundry city, is situated in the East Godavari District of Andhra Pradesh, South India (Figure.1). It lies between $16^{\circ}54'00''\text{N}$ to $17^{\circ}08'00''\text{N}$ latitude and $81^{\circ}44'00''\text{E}$ to $81^{\circ}54'00''\text{E}$ longitude, covering approximately 155 km^2 . Administratively, the region encompasses Rajahmundry Urban, Rajahmundry Rural, Rajanagaram, and Korukonda Mandals. The selected settlements for this study include a diverse urban-rural continuum, ranging from fully urbanized cores like Rajahmundry, Dowleswaram, and Kotta Bommuru to semi-urban transition zones such as Morampudi, Torredur, and Kateru, and rural villages including Kolamuru, Namavaram, Gadala, Madhurapudi, and Palacherla. This gradient provides an ideal framework to evaluate the impacts of urbanization on groundwater resources.

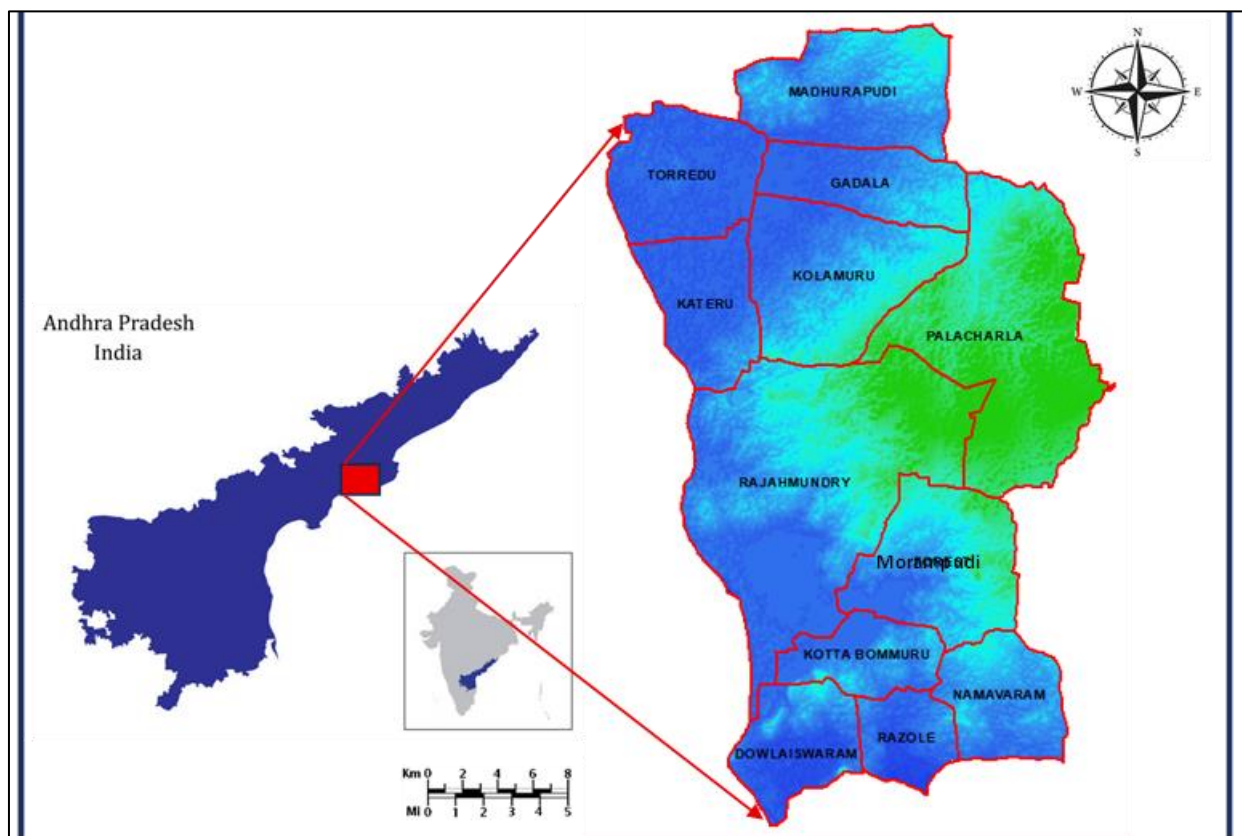


Figure 1 Location Map of the Study Area

2.2. Geographical Extent and Boundaries

The study area is part of the Godavari deltaic plains, characterized by flat to gently undulating terrain with elevations of 10–25 meters above mean sea level. The region is bounded by the Godavari River to the north, which significantly influences groundwater regimes through recharge. To the south lie the agricultural and semi-rural lands of Rajanagaram Mandal. The eastern boundary is marked by semi-urban areas like Torredur and Kateru, while the west is defined by the expanding urban and industrial corridors of Rajahmundry city.

2.3. Geomorphology of the Study area

Geomorphologically, the area is composed of several features that directly influence groundwater storage and movement (Figure 2). These include floodplains and deltaic deposits (Rajahmundry, Dowleswaram, Rajavolu), shallow buried pediplains (Kolamuru, Gadala, Namavaram), and urbanized plains with reduced infiltration due to construction (Morampudi, Kotta Bommuru, Kateru). The soils are predominantly alluvial sandy loams and clayey loams, which are generally favorable for agriculture and groundwater percolation.

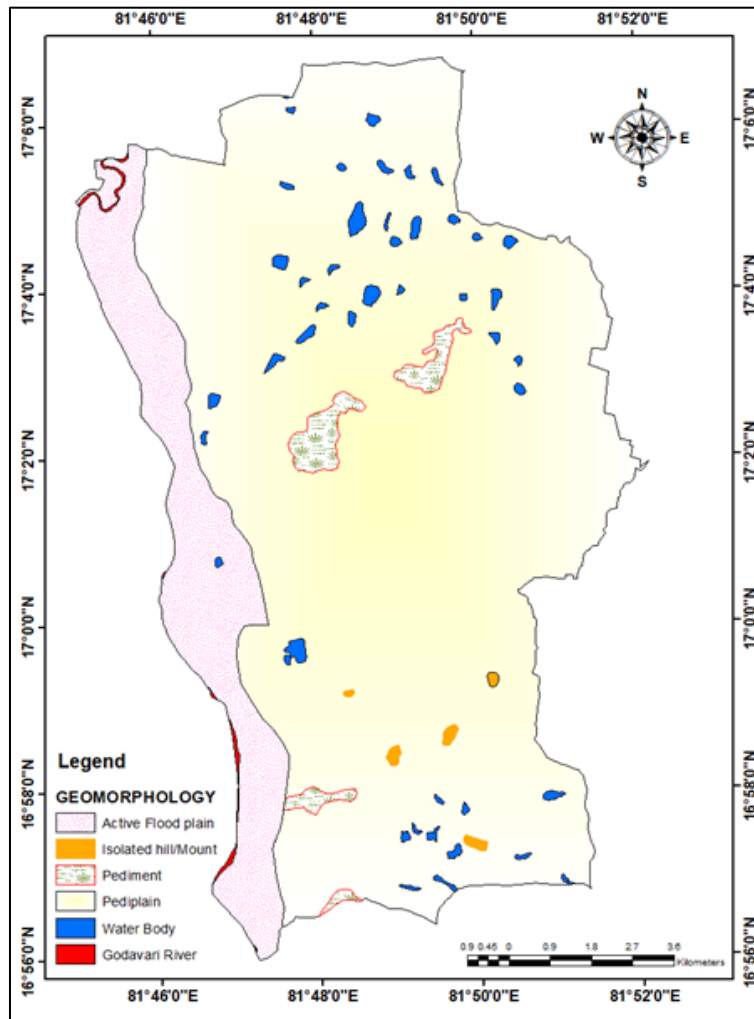


Figure 2 Geomorphology of the Study Area

2.4. Climate and Hydrology

The region has a tropical monsoon climate with hot summers, humid monsoons, and mild winters. The average annual rainfall ranges from 1000 - 1200 mm, with the majority occurring during the Southwest Monsoon from June to September. The mean annual rainfall is about 1270-1300 mm, with the highest monthly rainfall in August. While historically, rainfall and riverine flooding have maintained aquifer recharge, increasing urban impermeable surfaces have reduced natural infiltration pathways, creating imbalances in the hydrologic cycle.

The drainage network of the study area is organized according to the Horton-Strahler classification system. The Godavari River represents the highest stream order (6th order) in the region, acting as the dominant fluvial system that controls regional hydrology. Lower-order streams (1st and 2nd) are abundant in the upland and semi-rural areas, serving as local recharge sources. However, urban growth has modified or blocked many of these lower-order streams, increasing surface runoff and altering natural drainage paths, which can lead to localized flooding.

2.5. Hydrogeological and Geological Characteristics

The study area is part of the alluvial aquifer system of the Godavari basin, where groundwater is found in unconfined to semi-confined aquifers. The lithology is varied, including unconsolidated alluvium, flood-plain deposits, and older crystalline basement rocks. Major litho-units include basalt, black clay, silty clay, brown silt, coarse sand, and sandstone. While sandy zones are highly productive, clay-dominated stretches show seasonal stress. Over-extraction and pollution are significant challenges, especially in urban areas, leading to declining water tables and a higher risk of contamination from sewage and industrial discharges. In contrast, rural areas still show comparatively stable aquifer conditions. The combined effect of urbanization has resulted in reduced recharge and spatial inequalities in groundwater availability across the urban-rural divide.

3. Materials and Methods

3.1. Sample Collection and Preservation

A comprehensive sampling program was designed to assess the seasonal variations in groundwater quality. A total of 151 groundwater samples were collected from various sources, including bore wells and dug wells, across the study area. The sampling was carried out during two distinct periods, i.e., the pre-monsoon (dry) season in (*March – May*) and the post-monsoon (wet) season in (*October – December*) to capture the hydrochemical variability.

3.2. Analytical Procedures

Physicochemical parameters such as pH and Total Dissolved Solids (TDS) were measured in-situ at the time of sampling using a calibrated portable multi-parameter probe.

In the laboratory, the major ion concentrations were determined following standard analytical methods of American Public Health Association (APHA) [23]

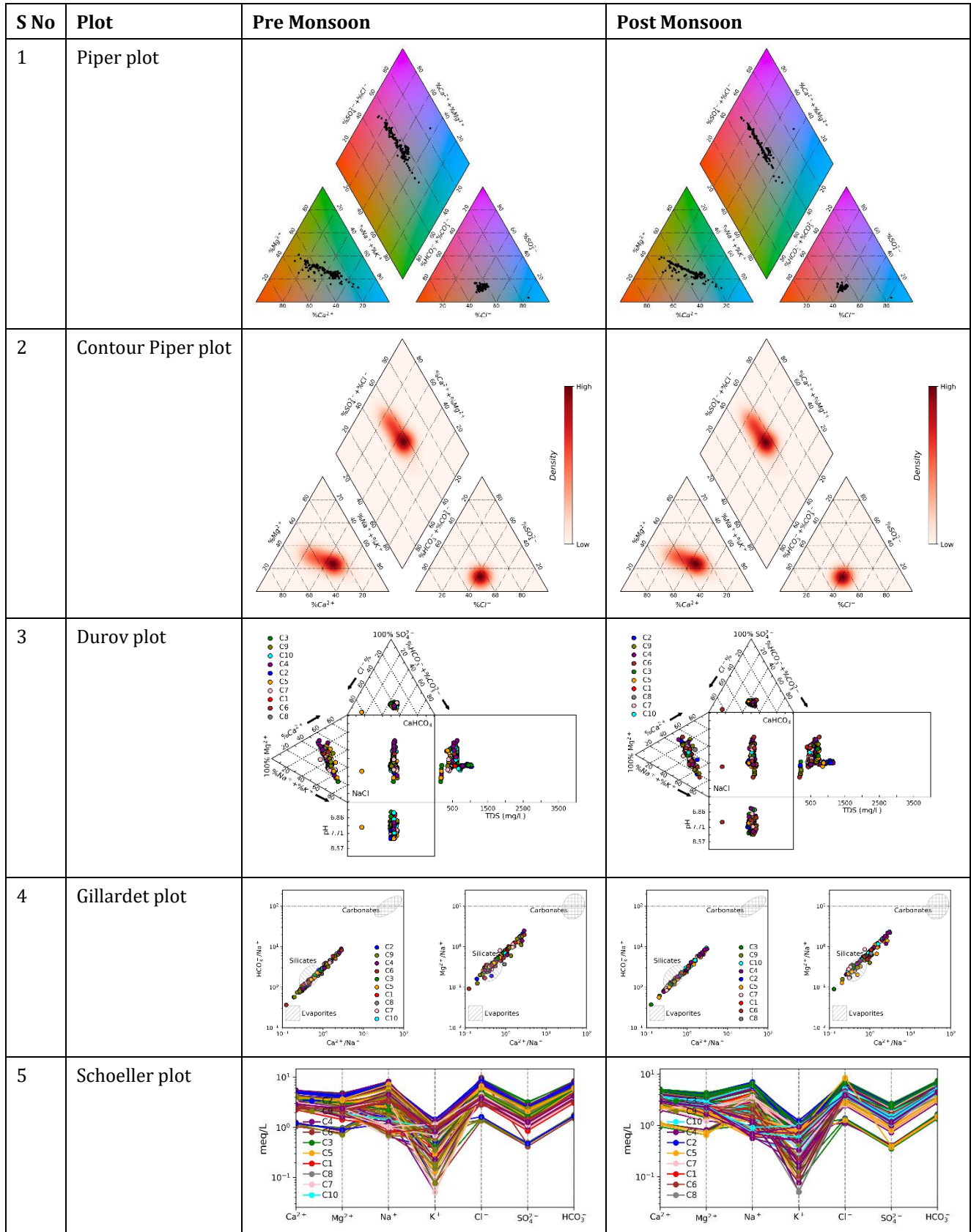
Bicarbonate (HCO_3^-) and Carbonate (CO_3^{2-}) were analyzed by potentiometric titration. Chloride (Cl^-) was determined by silver nitrate titration (Argentometric method). Sulphate (SO_4^{2-}) was measured using a UV-Vis Spectrophotometer. Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) were analyzed using an Atomic Absorption Spectrophotometer (AAS). Sodium (Na^+) and Potassium (K^+) were determined using a Flame Photometer. The analytical precision was verified by calculating the ionic balance error for each sample, which was found to be within the acceptable limit of $\pm 5\%$.

3.3. Data Interpretation and Hydrogeochemical Analysis

The hydrogeochemical characteristics of the groundwater were assessed, and the processes controlling its chemistry were identified using a combination of graphical and statistical methods. The concentrations of major ions were used to generate a series of established hydrogeochemical diagrams such as: 1) Piper plot [24] to classify the hydrogeochemical facies (water types) and understand the relative abundance of ions, 2) Chadha plot [25], to further classify water types based on the differences between alkaline earths and alkali metals, and strong and weak acids; 3) Schoeller plot [26] to visualize the absolute concentrations of major ions and compare different water samples; 4) Gibbs Diagram [27] to identify the dominant natural mechanisms (precipitation, rock weathering, or evaporation) controlling the groundwater chemistry, 5) Gaillardet Plot [28] to evaluate the relative contribution of carbonate versus silicate rock weathering to the dissolved ionic load, 6) Durov Diagram [29] to provide a composite view of water chemistry and identify key hydrogeochemical processes such as mixing, dissolution, and ion exchange. The dataset was also subjected to cluster analysis using K-Nearest Neighbors (KNN) algorithm [30] using Python to group samples with similar chemical characteristics, which were then visualized on the hydrogeochemical plots.

4. Results and Discussion

The hydrogeochemical data of the study area were analyzed using various graphical plots mentioned in the preceding section to understand the major ion chemistry, identify the dominant water types, and elucidate the controlling hydrogeochemical processes. The geochemical data and diagrams reveal a distinct seasonal variation in the groundwater chemistry of your study area. The following sections detail the findings from these analyses and discuss the key factors influencing the groundwater chemistry in the region. All the diagrams mentioned above are provided in Figure. 3



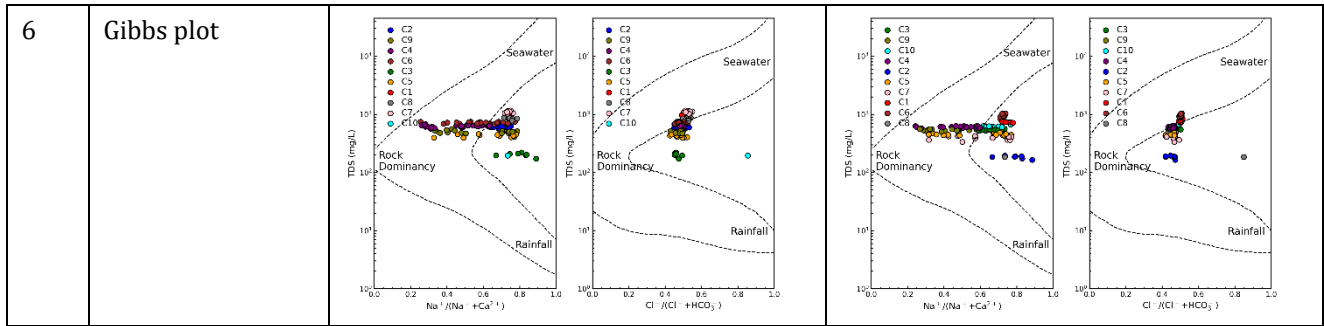


Figure 3 Hydrogeochemical Facies and Water-Rock Interaction Plots for sample groups

4.1. Piper plots

The pre-monsoon samples are primarily calcium-magnesium bicarbonate waters. This water type is common in fresh groundwater that has undergone limited water-rock interaction. The high concentration of bicarbonate suggests that the water has interacted with carbonate minerals, such as calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), which are dissolved in the water. This is typical for groundwater in regions with limestone or dolomite geology. The relatively low presence of chloride and sulfate suggests limited influence from sources like saltwater intrusion or industrial pollution.

The post-monsoon samples also fall into the calcium-magnesium bicarbonate water type. The striking similarity between the pre- and post-monsoon diagrams suggests that the water chemistry hasn't undergone a significant change due to monsoon rainfall. This could imply a few things mentioned below.

- **Recharge Source:** The monsoon rain is recharging the same aquifer that was sampled before the monsoon. The chemistry of the rainwater is likely diluted, but the primary water-rock interaction with the geological formation dictates the final water type, which remains a bicarbonate type.
- **Limited Seasonality:** The hydrochemical processes (like mineral dissolution) in this area are stable and not significantly impacted by the seasonal change in rainfall. The residence time of the groundwater might be long enough that a single monsoon event does not drastically alter the overall hydrochemistry.
- **Low Mineralization:** The rainwater itself might have very low total dissolved solids (TDS), and its addition to the groundwater simply dilutes the existing concentrations without changing the dominant ion types.

Hence, Pre- and Post monsoon diagrams of Piper illustrate that the dominant hydrochemical facies in the studied area is calcium-magnesium bicarbonate. This indicates that rock-water interaction, specifically the dissolution of carbonate minerals like calcite and dolomite, is the main process controlling the water chemistry. There is no significant seasonal variation in the water chemistry between the pre-monsoon and post-monsoon periods, suggesting a stable hydrogeological system.

To visualize the concentration of data points, making them more effective for large datasets, Contour Piper diagrams for pre-monsoon and post-monsoon seasons, which are a variation of the standard Piper diagram are used with density contours.

The use of contours reinforces the findings from the previous Piper and Gibbs diagrams:

- **Dominant Water Type:** The primary hydrochemical facies is consistently calcium-magnesium bicarbonate. This indicates that the water's chemistry is governed by the dissolution of carbonate minerals, such as calcite and dolomite, from the geological formations.
- **Lack of Seasonal Variation:** The contour plots for both seasons are strikingly similar, showing that the monsoon rainfall does not significantly alter the overall hydrochemistry of the groundwater. The dominant water type remains stable throughout the year. This suggests that the aquifer system is well-buffered and the influence of rainfall is limited compared to the ongoing rock-water interaction.

Hydrochemical Uniformity: The tight clustering and clear contouring of the data points indicate a high degree of hydrochemical uniformity in the sampled water, meaning the water quality is consistent across the study area during both seasons.

4.2. Durov plots

A hydrochemical plotting technique similar to a Piper diagram but with a central square plot that provides additional insights. The diagram consists of two triangular plots (one for cations and one for anions) and a central square plot that represents the projection of the two triangular plots.

The majority of the data points from both pre-and post-monsoon dataset, are clustered in the lower-left quadrant of the central square (Figure.3). The lower-left quadrant represents water dominated by calcium-bicarbonate (Ca-HCO_3) ions. This indicates that the water's chemistry is primarily controlled by the dissolution of carbonate minerals, such as calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). This is a common characteristic of fresh groundwater in areas with carbonate rock formations.

The stability of this water type across both seasons strongly suggests that the primary mechanism influencing water quality in the study area is geogenic, meaning it is controlled by the natural dissolution of rock minerals. There is no evidence from these diagrams of a major shift in water chemistry due to other factors like saltwater intrusion or significant anthropogenic pollution. This finding is consistent with the interpretations from the Piper and Gibbs diagrams, which also pointed to rock-water interaction as the dominant process.

4.3. Chada plot

Another variant of the Piper diagram used to classify water types and identify hydrogeochemical processes is Chada plots (Figure 3) They are created by plotting the difference in meq% between alkaline earths and alkali metals on the x-axis and the difference in meq% between weak acidic anions and strong acidic anions on the y-axis. This results in a square or rectangular plot with four main quadrants, each representing a distinct hydrochemical facies or process. In this diagram, data points concentrated in the lower-left quadrant for both pre-and post monsoon seasons which are highly consistent.

The Chadha diagrams for both seasons confirm the findings from the Piper, Durov, and Gibbs (discussed in later sections) diagrams. The data consistently falls within the rock-water interaction zone, specifically the calcium-magnesium bicarbonate facies. This indicates that the geology of the area, rather than seasonal rainfall, evaporation, or other processes, is the primary control on the water chemistry. The stability of the hydrochemical facies across both seasons highlights the robustness of this geological influence.

4.4. Gaillardet plots

This is a hydrogeochemical plotting method used to understand the origin of dissolved ions in water. These diagrams plot two key ratios to determine if the water chemistry is controlled by the weathering of specific rock types:

Carbonate weathering: The ratio of $\text{Ca}^{2+}/\text{Na}^+$ vs. $\text{HCO}_3^-/\text{Na}^+$

Silicate weathering: The ratio of $\text{Mg}^{2+}/\text{Na}^+$ vs. $\text{HCO}_3^-/\text{Na}^+$

The Gaillardet diagrams for both seasons provide conclusive evidence that carbonate weathering is the main process controlling the hydrochemical composition of the groundwater. The data is not influenced by silicate or evaporite weathering to any significant extent. This finding is highly consistent with the results from the Piper, Gibbs, Durov, and Chadha diagrams, all of which point to a stable calcium-magnesium bicarbonate water type resulting from rock-water interaction. The Gaillardet diagram provides a more specific confirmation of the rock type (carbonate) that is responsible for this hydrochemical signature.

4.5. Schoeller plots

This is a hydrochemical plot that displays the concentrations of major ions on a semi-logarithmic scale. It's particularly useful for comparing multiple water samples and identifying similarities or differences in their chemical composition.

The curves in the diagram during pre-and post-monsoon seasons consistently show an identical and specific pattern of ion concentrations. Bicarbonate (HCO_3^-) and Calcium (Ca^{2+}) consistently have the highest concentrations among all major ions. The concentrations of Chloride (Cl^-) and Sulfate (SO_4^{2-}) are generally the lowest. The concentrations of Sodium (Na^+) and Magnesium (Mg^{2+}) fall in the middle range. The lines representing each sample follow a similar, nearly parallel trend, indicating a consistent hydrogeochemical signature across the entire dataset.

The Schoeller diagrams provide a visual confirmation of the findings from the other hydrochemical plots (Piper, Gibbs, Durov, and Chadha). The consistent parallel patterns and the clear dominance of calcium and bicarbonate ions in both seasons lead to the following conclusions.

Dominant Water Type: The water is consistently of a calcium-bicarbonate facies. **Controlling Process:** The chemistry is controlled by a common hydrogeochemical process, which is the dissolution of carbonate minerals. This is evident from the high concentrations of both Ca^{2+} and HCO_3^- .

Seasonal Stability: The remarkable similarity between the pre- and post-monsoon diagrams indicates a stable groundwater system where the influence of rock-water interaction far outweighs any potential dilution or change caused by monsoon rainfall. This suggests that the aquifer has a high buffering capacity or that the residence time of the groundwater is long enough that a seasonal recharge event does not alter the overall chemistry.

4.6. Gibbs plots

This diagram plots the ratio of major ions against total dissolved solids (TDS) which shows the dominant mechanism controlling the water chemistry in the study area is rock-water interaction. It is a bivariate plot used to determine the primary mechanisms that control the hydrochemistry of water. The two main plots are:

- Total Dissolved Solids (TDS) vs. Cation Ratio: $[\text{Na}++\text{K}+]/[\text{Na}++\text{K}++\text{Ca}^{2+}]$
- Total Dissolved Solids (TDS) vs. Anion Ratio: $[\text{Cl}-]/[\text{Cl}-+\text{HCO}_3-]$

Almost all the data points are clustered in the central-bottom portion of the plot in . The cation ratio is low, but the TDS is moderate to high. Similarly, the points are in the central-bottom area. The anion ratio is low, but the TDS is moderate to high.

The clustering of data points in the central part of both plots (pre-and post monsoon season) indicates that the water chemistry is predominantly controlled by rock-water interaction. The water is not dominated by rainfall (as seen by the moderate to high TDS) and is not at a stage of extreme evaporation (as the TDS is not excessively high, and the ion ratios are not close to 1). This suggests that the water has had sufficient residence time to dissolve minerals from the surrounding rock formations.

5. Conclusion

Based on the interpretations drawn from hydrochemical diagrams presented in previous section, a comprehensive and consistent understanding of the groundwater system in the study area is give below.

5.1. Water Type and Dominant Ions

The Piper and Durov diagrams consistently show the water samples clustering in the calcium-magnesium bicarbonate (Ca-Mg-HCO₃) field. This indicates that calcium, magnesium, and bicarbonate ions are the most abundant major ions in the water. The Schoeller diagrams reinforce this, with the lines for Ca^{2+} and HCO_3^- consistently plotting at the highest concentrations. The Chadha diagrams further support this by placing all samples in the quadrant characteristic of waters dominated by alkaline earths and weak acidic anions, which is a key signature of the Ca-Mg-HCO₃ facies.

5.2. Controlling Hydrochemical Process

The Gibbs diagrams provide direct evidence of the process controlling the water's chemistry. All data points fall within the "Rock Dominance" field, clearly ruling out precipitation or evaporation as the primary drivers. This suggests that the water's composition is a result of interaction with the surrounding geological formations. The Gaillardet diagrams provide a more specific confirmation, as the data points plot in the carbonate weathering zone. This precisely links the high concentrations of calcium and bicarbonate ions to the dissolution of carbonate minerals like calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) from the aquifer.

5.3. Seasonal Stability

A key finding across all diagrams is the remarkable lack of seasonal variation between the pre-monsoon and post-monsoon periods. The data points occupy the exact same fields in the Piper, Durov, Gibbs, Chadha, and Gaillardet diagrams. The Contour Piper diagrams beautifully illustrate this by showing the highest density of samples in the same zone for both seasons. The parallel lines in the Schoeller diagrams also indicate that the relative proportions of ions

remain unchanged. This suggests that the groundwater system is very stable, with a strong geogenic signature that is not significantly altered by the addition of rainwater during the monsoon. The aquifer likely has a high buffering capacity, or the residence time of the water is long enough to mask short-term seasonal inputs.

The systematic interpretation of all diagrams reveals a cohesive story of the groundwater hydrochemistry in the study area. The water is a calcium-magnesium bicarbonate type, with its chemistry being fundamentally controlled by rock-water interaction, specifically the weathering of carbonate rocks. This geogenic control is so dominant that it masks any potential changes from monsoon recharge, leading to a highly stable hydrochemical signature throughout the year. The interpretations are mutually consistent and provide a robust understanding of the system's hydrogeochemical dynamics.

Compliance with ethical standards

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Disclosure of conflict of interest

None of the authors have no conflict of interest.

Contribution of Authors:

- Author 1: Fieldwork, Data collection, Chemical Analysis and preparation of manuscript.
- Author 2,3: Fieldwork, Data collection, Laboratory treatment of samples and Chemical Analysis.
- Author 4: Coding support for clustering and visualizations

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