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Groundwater Quality Assessment Using Hydrochemical Indicators and Statistical Analysis in Semi-Arid Central India

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Abstract

The study evaluates groundwater quality for household consumption and farming purposes, considering natural and human influences on hydrochemistry. Fifteen samples were analysed for their chemical characteristics, irrigation indices, and facies, revealing predominantly slightly alkaline water, ranging from fresh to moderately fresh. Nitrate concentrations ranged between 1.0 and 176 mg/L, with 53.3% of the samples exceeding the threshold of BIS, reflecting significant agricultural and anthropogenic impacts. 46% of the samples were identified as poor, while 20% were identified as unfit for drinking purposes according to the Water Quality Index assessment. Irrigation assessment showed TDS and EC within acceptable limits, with SAR values (0.2-1.8) indicating excellent quality. Based on SAR vs EC plots, 40% of samples fell in C2S1 and 60% in C3S1, requiring careful use in poorly drained soils. PCA and HCA indicated spatial variability driven by natural (rock dissolution, ion exchange) and anthropogenic inputs. Most samples (66.6%) belonged to Mg-HCO_3 facies. Gibbs plots showed rock weathering–evaporation dominance, while geochemical modelling indicated near-equilibrium carbonate minerals. PHREEQC modelling reveals near-equilibrium saturation of carbonate minerals (calcite, aragonite, dolomite), confirming effective buffering of pH and alkalinity, while evaporite minerals remain undersaturated.

Keywords: Groundwater quality, Hydrogeochemistry, Irrigation parameters, Multivariate statistical analysis, Geochemical modelling

1. Introduction

As a major freshwater resource, groundwater is significantly affected by geogenic influences. Population growth, agriculture, and industry contribute to water scarcity and salinity hazards, impacting plant health and causing physiological drought (Siddha and Sahu 2020). In regions with scarce surface water, groundwater plays a key role in irrigation, though its overuse threatens quality. Geochemical processes in aquifers and soils, combined with poor canal and drainage management, intensify this decline. Moreover, rainfall, mineral dissolution, and biological activity affect recharge and contamination, underscoring the need for precise hydrochemical evaluation. (Janardhana Raju et al. 2011). Increasing population, agriculture, and urbanisation in semi-arid regions heighten groundwater reliance, which supplies most irrigation and drinking needs (Adimalla and Qian 2019). Groundwater in India is a major commodity for consumption, residential, and farming needs, with usage exceeding 230 cubic

kilometres annually, necessitating thorough quality assessments for sustainable management (Sharma et al. 2021).

Agricultural productivity in semi-arid zones depends heavily on groundwater quality, which is often compromised by high Sodium Adsorption Ratio (SAR), Per cent Sodium (Na%), and Magnesium Hazard (MH) values, leading to reduced soil fertility and restricted water usability. Rising salinity from overuse, fertilisers, and mineral dissolution, evident in Tunisia, Nigeria, and Central India, stresses the need for hydrochemical monitoring (Ibn Ali et al. 2020; Singhal et al. 2020; Adebayo et al. 2021; Qadir et al. 2021; Dimple et al. 2023). Groundwater suitability for farming is evaluated through hydrochemical indices like SAR, Soluble Sodium Percentage (SSP), Residual Sodium Carbonate (RSC), Kelly's ratio, and Permeability Index (Ghazaryan et al. 2020). Waters with high EC, TDS, and overall hardness (Total Hardness) in specific areas should not be consumed or used for cultivation without being properly treated (Maurya et al. 2023; Rawat et al., 2018). Poor groundwater quality can hinder crop yields, necessitating a comprehensive understanding of irrigation water quality (Fallatah and Khattab 2023). If indices such as Na%, magnesium hazard, and SAR exceed safe limits, targeted water management strategies become necessary (Sunkari et al. 2023). High salt concentrations can harm plant growth, making it critical to track and regulate groundwater quality to avoid unfavourable agricultural consequences (Nwankwoala et al. 2023). Assessing water quality through hydrochemical indices supports management, while monitoring and interventions minimise groundwater impacts on agriculture and health (Saraswat et al. 2023).

Piper and USSL salinity diagrams, as well as other indices and plots, are commonly utilised to evaluate groundwater quality and assess its appropriateness for irrigation. (Diédhiou et al. 2023). Multivariate statistical analysis, encompassing techniques such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), has emerged as an effective approach to decipher complex groundwater chemistry, identify pollution sources, and understand spatial-temporal variations (Zainol et al. 2021; Parisi et al. 2023; Karangoda and Nanayakkara 2023; Zavareh et al. 2023).

Groundwater quality in semi-arid hard-rock and basaltic aquifers exhibits marked spatial variability due to rock–water interactions, recharge conditions, and localised anthropogenic pressures such as agricultural runoff and fertiliser leaching. Studies from semi-arid regions of India report frequent exceedances of drinking and irrigation standards, particularly for salinity, nitrate, and total dissolved solids, highlighting associated health and sustainability concerns (Adimalla and Qian 2019; Deshpande et al., 2023). Such conditions are further exacerbated by the lack of process-level understanding in data-limited basaltic aquifers, which hampers effective drinking water protection and irrigation management strategies.

To interpret such heterogeneity, recent groundwater research increasingly adopts integrated frameworks combining hydrochemical characterisation, multivariate statistical analysis, spatial evaluation, and geochemical modelling, including PHREEQC, to link groundwater chemistry with governing geochemical processes and human influences (Manu et al., 2023; Pötter et al., 2021; Bhatt et al., 2021; Hamma et al., 2024; Benyoussef et al., 2024). Cross-disciplinary approaches have been shown to enhance environmental assessments by linking chemical patterns with governing physical and geochemical processes (Wei et al. 2022).

Similarly, advanced data-driven and optimisation-oriented strategies have been applied to water system analysis to improve interpretive reliability and management relevance (Wang et al. 2024). Collectively, these developments highlight the importance of unified analytical frameworks, particularly for groundwater investigation in data-limited semi-arid aquifers.

In the semi-arid basaltic aquifers of central India, groundwater quality is often compromised by elevated nitrate and poor WQI classes, yet tehsil-scale studies integrating WQI, PCA/HCA, and PHREEQC-based geochemical modelling remain limited, constraining process-based assessment. Unlike many previous studies that apply these tools independently or emphasise classification-based outcomes, the present study explicitly integrates spatial variability, statistical associations, and mineral equilibrium behaviour to derive a coherent, process-oriented interpretation of groundwater quality. This study addresses the gap through an integrated framework linking contamination patterns with hydrogeochemical processes and mineral equilibrium conditions.

The objective of this study is to evaluate groundwater suitability for drinking and agricultural purposes in a semi-arid terrain using an integrated framework that combines physicochemical analysis, irrigation quality indices, multivariate statistical techniques, spatial distribution mapping, and PHREEQC-based geochemical modelling.

2. Methodological Approach

2.1. Geographical Scope

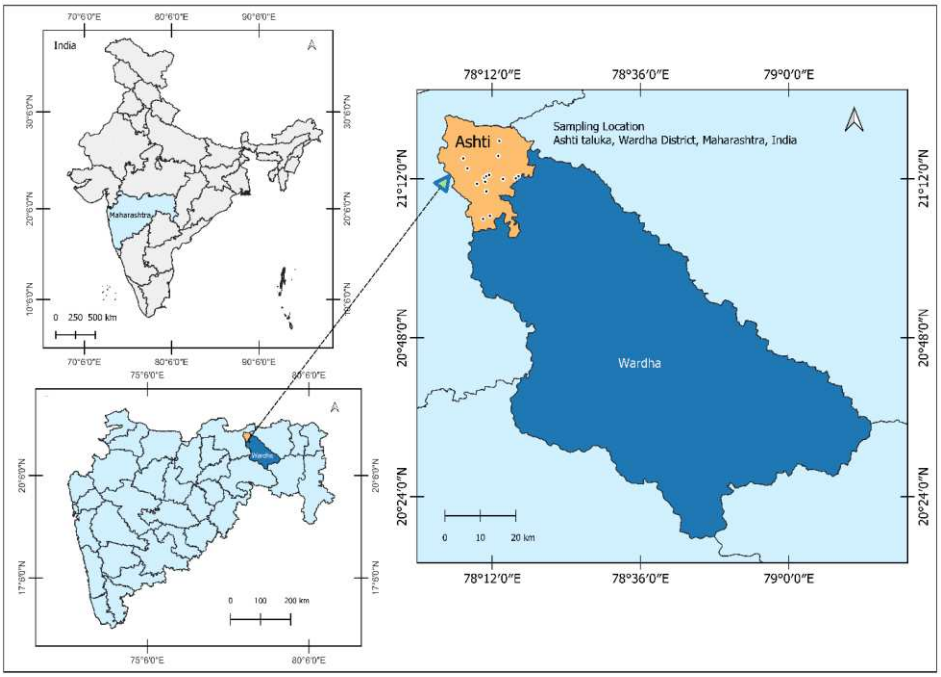


Fig. 1. Study Region Map

The rural Ashti tehsil of Maharashtra (Fig. 1), situated in the central part of India, occupies a specific location at 21° 12' 34.15" N latitude and 78° 11' 41.67" E longitude, and is selected as the study area. This positioning places the village within the scenic landscape of Maharashtra's

north-eastern region. The landscape transitions into a unique setting defined by hilly ridges extending from the Satpura mountain range, accompanied by semi-arid climate conditions.

2.2. Sample Acquisition and Analysis Techniques

Groundwater sampling was carried out during the pre-monsoon season (March 2023), a hydrologically critical period characterised by maximum groundwater stress and elevated solute concentrations due to limited recharge. A total of 15 groundwater samples were collected from open dug wells, selected through purposive sampling to ensure adequate spatial coverage across the tehsil and representation of dominant hydrogeological settings, land-use conditions, and groundwater abstraction zones. During sampling, observed water levels ranged from 10m to 20m below ground level (mbgl), indicating abstraction from shallow to moderately deep groundwater systems typical of Deccan Trap hard-rock aquifers, primarily within the weathered basalt zone. The selected sources, therefore, represent the commonly exploited shallow groundwater regime used for drinking and irrigation in the region.

In-situ measurements of pH, electrical conductivity (EC), total dissolved solids (TDS), and temperature were recorded at each sampling location using calibrated portable meters. Groundwater samples were collected for physicochemical parameters following APHA standard methods outlined in (R. Baird et al., 2017). High-grade polyethene bottles with a capacity of 1 litre were used for collection and stored at 4 °C; for lab analysis, these were transported.

2.3. Sample Acquisition, Analysis Techniques and Quality Control

Groundwater analysis involved measuring pH and electrical conductivity with a Mettler Toledo FEP 30 instrument and TDS by gravimetric filtration. Titrimetric determination of alkalinity, different hardness types, and chloride. The ionic composition was determined through standard calculations, whereas a flame photometer was used to analyse Na^+ and K^+, and nitrate, sulphate and phosphate were quantified by UV–Visible spectrophotometric analysis. Analytical quality control (QC) procedures were followed in the field, and laboratory blanks were analysed to identify potential contamination during sampling and analysis. All field and laboratory instruments were calibrated before analysis to ensure analytical accuracy and reproducibility. The pH meter was calibrated using a three-point calibration with standard buffer solutions of pH 4.0, 7.0, and 10.01. Electrical conductivity (EC) measurements were calibrated using a 1413 µS/cm standard solution. Sodium (Na^+) and potassium (K^+) concentrations were determined using a flame photometer calibrated with three-point calibration curves prepared from standard solutions. Nitrate (NO_3^-), sulphate, and phosphate analyses by UV–Visible spectrophotometry were performed using a five-point calibration curve. Appropriate sample dilutions were performed for nitrate, where concentrations exceeded the linear calibration range. These calibration procedures ensured reliable and consistent analytical performance throughout the study.

Ionic charge balance errors (CBE) were calculated for all samples, and results within ±5% were considered acceptable for hydrogeochemical interpretation. This ensured the reliability of major ion data used for statistical and geochemical modelling.

2.4. Water Quality Index and Irrigation Indices

The Weighted Arithmetic Water Quality Index (WAWQI) was calculated using parameter-specific quality ratings and unit weights based on the drinking-water standards prescribed by BIS. Calculations derive weighted sub-indices, averaged to classify water from excellent to unfit for consumption.

$$WQI = \sum QiWi / \sum Wi$$

In the WQI method, unit weights (*Wi*) are derived from standards (*Si*) using a proportionality constant (*K*). Quality ratings (*Qi*) compare observed values with ideal conditions, and the weighted average classifies water from excellent to unfit (Tanwer et al., 2023; Zotou et al., 2020).

Standard irrigation quality indices, including SAR, SSP, RSC, Kelly's ratio, permeability index, and related parameters, were computed to assess agricultural suitability.

2.5. Hydrogeochemical Analysis Methods

Geospatial spread of nitrate levels and the Quality of Groundwater Index were created in QGIS using inverse distance weighting (IDW) interpolation, which helped identify zones of contamination and water quality variability.

Recent studies demonstrate that GIS-based interpolation techniques such as inverse distance weighting (IDW) effectively visualise spatial variability in groundwater quality under limited data conditions. Applications from agricultural regions of Punjab, Pakistan show that IDW reliably delineates contaminant trends using the parameters of groundwater quality datasets (Tayyab et al. 2024). Similar evaluations confirm that deterministic methods, including IDW, can fill spatial data gaps and produce interpretable groundwater maps (Susatio et al., 2024; Ahamad et al., 2018), supporting their use in QGIS-based hydrogeochemical assessments. Spatial analytical approaches are widely used in geoscience to enhance the understanding of subsurface variability. (Xu, 2024) highlighted the value of integrating imaging and numerical modelling for spatial interpretation of geological heterogeneity. Accordingly, IDW interpolation in QGIS, supported by OriginPro, R, and Grapher, was used to map and interpret groundwater quality patterns.

Given the limited number of sampling points, it is adequate for the process-oriented hydrogeochemical interpretation adopted in this study. Sampling locations were selected to ensure spatial representation of the basaltic aquifer system across the tehsil. IDW interpolation was applied solely for exploratory visualisation of relative spatial trends in nitrate and WQI, rather than for predictive mapping, which is suitable for datasets with limited sampling density. Such exploratory applications have been reported to yield eloquent insights even with moderate sample sizes when variable numbers are limited (Ahamad et al. 2018). Multivariate techniques, including Pearson correlation, PCA, and HCA, were employed to identify dominant

geochemical associations and controlling processes rather than to develop statistically generalizable models.

The study employed Pearson correlation and PCA to analyse thirteen groundwater parameters, thereby identifying correlations and major governing factors. Visualisation was performed through Origin Pro 2022. In addition, HCA was carried out on normalised data in R software (v4.5.1), employing Euclidean distance metrics and Ward's hierarchical linkage method. The clustering outcomes were visualised through dendrograms and heatmaps to illustrate sample groupings. Geochemical characteristics were further interpreted using Chaddha and Gibbs plots generated in MS Excel to understand hydrochemical facies and controlling processes. Piper diagrams created in Origin Pro 2022 illustrated water type and ion distributions. The USSL diagram, generated in Grapher, was employed to assess salinity levels and risk of sodium. In addition, Wilcox plots prepared in MS Excel compared the sodium hazard against salinity, providing a broader understanding of water quality status.

PHREEQC modelling is inherently sample-specific, with each groundwater sample treated as an independent geochemical system; thus, robust calculations of aqueous speciation and mineral saturation indices do not require large datasets. Geochemical modelling was conducted using USGS PHREEQC (version 3.8.6-17100) with the default thermodynamic database *phreeqc.dat*. Measured pH, electrical conductivity, and major ion concentrations (pH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, NO_3^{-}, SO_4^{2-}, PO_4^{3-}, and F^{-}**)** were used as inputs, with charge balance errors maintained within acceptable limits. Simulations were performed at 25 °C under equilibrium conditions to calculate ionic strength, aqueous speciation, and saturation indices of relevant mineral phases. Model outputs were visualised using saturation and scatter plots to interpret groundwater mineral interactions.

3. Outcomes and Interpretation

3.1. Evaluating Hydrochemical Characteristics for Agricultural and Potable Applications

The evaluation of groundwater quality includes analysing various physicochemical parameters to identify its chemical properties and assess its potential effects on soil, crops, and human health.

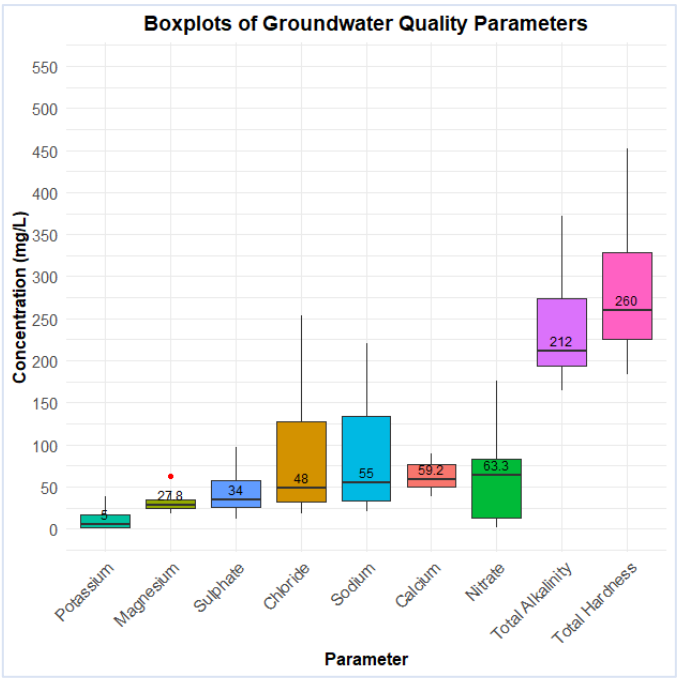


Fig. 2. Box plots showing the distribution of major physicochemical parameters in groundwater samples (n = 15). The plots depict the median, interquartile range, whiskers, and outliers, enabling comparison of the concentration ranges and variability of the measured parameters.

The boxplots (Fig. 2), standardised on a 0–550 mg/L scale, illustrate the concentrations of various groundwater ions across 15 samples. Total hardness (~260 mg/L) and total alkalinity (~212 mg/L) exhibit the highest levels, while potassium (~5 mg/L) shows the lowest, followed by magnesium (~27.8 mg/L), sulphate (~34 mg/L), chloride (~48 mg/L), sodium (~55 mg/L), calcium (~59.2 mg/L), and nitrate (~63.3 mg/L). Magnesium presents an outlier, and potassium and magnesium show minimal variation. Nitrate, sodium, and chloride display greater spread and skewness, suggesting localised or regional influences. The patterns indicate a carbonate-controlled system where alkalinity and hardness dominate. Permanent hardness is implied when hardness exceeds alkalinity. Monitoring salt, chloride, and nitrate is crucial for detecting changes in water composition.

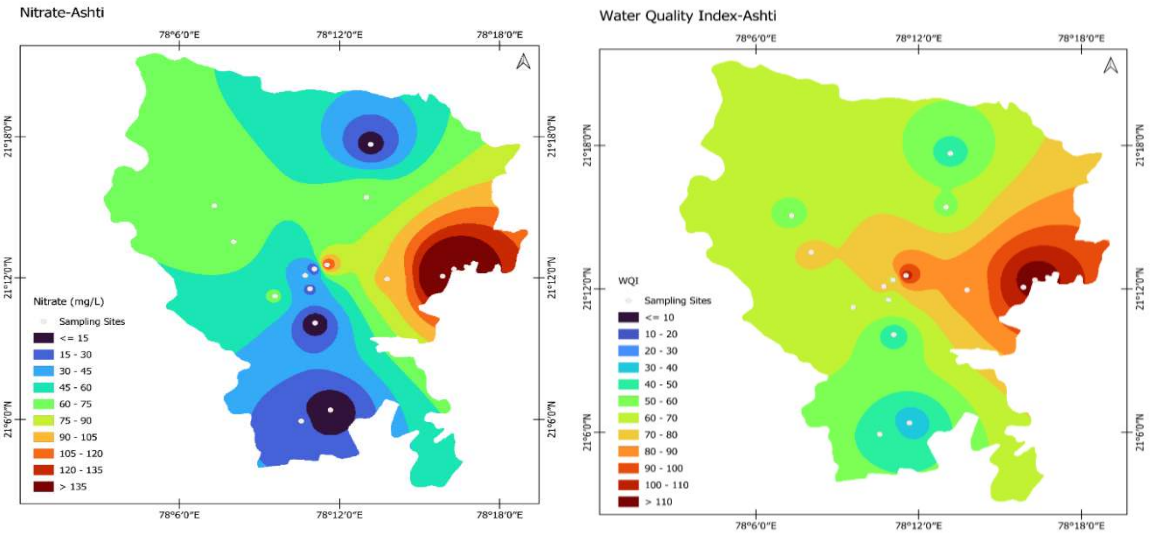


Fig. 3. Spatial mapping of Nitrate concentrations and the WQI across the study region.

Through inverse distance weighting (IDW) interpolation in QGIS, the Nitrate and WQI in the spread of the study region were assessed (Fig. 3). Nitrate concentrations ranged from 1.0 to 176 mg/L, with a mean value of 63.8 mg/L. Based on the BIS permissible limit of 45 mg/L, 46.7% of the samples complied with the guideline. In contrast, 53.3% exceeded it, including three locations with concentrations above 100 mg/L, indicating localised nitrate enrichment likely linked to agricultural and anthropogenic inputs. WQI results revealed that 26.7% of samples were classified as good quality, approximately 46% as poor, 6.7% as very poor, and 20% as unfit for drinking, reflecting overall degradation of groundwater quality.

Given the limited number of sampling locations (n=15), IDW was applied primarily for exploratory visualisation of spatial trends rather than precise prediction. Given the limited dataset, the method may produce overly smooth patterns, and prediction uncertainty can be substantial. Leave-one-out cross-validation (LOOCV) was conducted to evaluate interpolation reliability, yielding an RMSE of 39.89 mg/L for nitrate and 17.67 for WQI. The results indicate that the IDW maps reflect general spatial patterns, although predictions at individual locations remain uncertain. IDW was chosen for its simplicity and transparency with small datasets. Increasing the number of sampling points in future studies could enhance the accuracy and reliability of spatial interpolations.

Insights into Nitrate Variability Across Multiple Locations

The nitrate concentrations obtained in this study were compared with reported values across India and other countries (Table 1). In India, the observed range in Valsad, Gujarat (1.70–60.89 mg/L; Jodhani et al., 2025) was similar to Mathura, Uttar Pradesh (0.76–35.5 mg/L; Islam et al., 2025) and South 24 Parganas, West Bengal (0–41 mg/L; Pal et al., 2024). Higher levels occurred in East and West Godavari, Andhra Pradesh (0–537 mg/L; Dasari et al., 2025) and Palani, Tamil Nadu (5–73 mg/L; Panneerselvam et al., 2023). Globally, concentrations were lower in Hennaya, Algeria (12.79–49.08 mg/L; Laoufi et al., 2025) and Qom, Iran (7.69–90.3 mg/L; Mahboobi et al., 2023), but below maximums in Lethbridge, Canada (<0.1–1350 mg/L; Kyte et al., 2023), Songnen, China (0.02–497 mg/L; Zhai et al., 2017), and Liaohe, China (0–247.9 mg/L; Teng et al., 2019). Moderate ranges were also seen in Tehran-Karaj, Iran (6–150 mg/L), West Nile Delta, Egypt (0–202 mg/L), and Mexico (0.05–133 mg/L).

Elevated nitrate concentrations in several groundwater samples raise concerns regarding drinking water safety and sustainable agricultural practices. Recent advances in analytical techniques for drinking water monitoring reflect increasing global concern about contaminants and associated health risks (Tong 2022), underscoring the significance of nitrate exceedances identified in the present groundwater assessment. Excessive nitrate intake is associated with health risks such as methemoglobinemia, while groundwater enrichment is commonly linked to fertiliser application, irrigation return flows, and other anthropogenic inputs. Recent studies using nitrate isotopes and hydrochemical modelling have improved the identification of contamination hotspots and quantified source contributions in agricultural regions, with advanced analytical approaches effectively distinguishing nitrate sources and anthropogenic influences (He et al., 2025; Gao et al., 2020; Li et al., 2021; Wei et al., 2024; Karunanidhi et al., 2024). Although this study did not include isotopic analysis, previous

research shows that isotope-based approaches can effectively distinguish nitrate sources and support targeted mitigation strategies in agricultural landscapes.

Table 1. Reported Ranges of Nitrate Concentrations in Groundwater from India and Other Countries

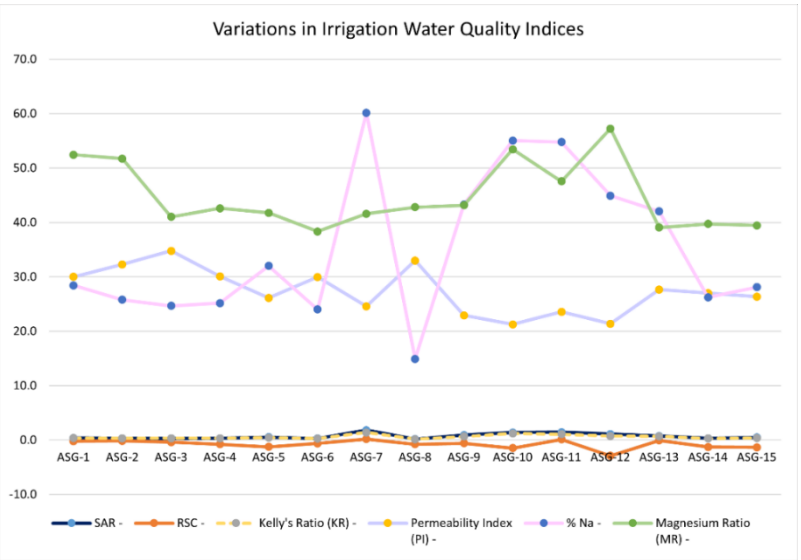
Locations	Sampling Years	Range of Nitrate		Reference
Locations in India		**Min**	**Max**	
Valsad, Gujarat	2020–2021	1.70	60.89	(Jodhani et al. 2025)
South 24 Parganas Sundarbans, West Bengal	-	0	41	(Pal et al. 2024)
Mathura, Uttar Pradesh	2024	0.76	35.5	(Islam et al. 2025)
East and West Godavari districts, Andhra Pradesh	-	0	537	(Dasari et al., 2025)
Palani, Dindigul, Tamil Nadu	-	5	73	(Panneerselvam et al. 2023)
Locations in other Countries				
West Nile Delta, Egypt	-	0	202	(Salem et al. 2025)
Tehran-Karaj, Iran	2007–2018	6	150	(Alizadeh et al. 2024)
Hennaya, Tlemcen, Algeria	2023–2024	12.79	49.08	(Laoufi et al. 2025)
Lethbridge, Alberta	2016–2017	<0.1	1350	(Kyte et al., 2023)
Mexico, North America	2012-2020	0.05	133	(Mahlknecht et al. 2023)
Songnen, Northeast China.	2014	0.02	497	(Zhai et al. 2017)
Liaohe, Liaoning, China	2011	0	247.9	(Teng et al. 2019)
Qom city aquifer in Iran	2019	7.69	90.3	(Mahboobi et al. 2023)

3.2. Evaluation of Irrigation Suitability

Suitability of groundwater was assessed through critical parameters such as TDS, EC, SAR, %Na, Kelly's Ratio (KR), MR, RSC, and Permeability Index (PI) for irrigation. By categorising water samples by these indices, it is possible to ensure soil and crop health while guiding their effective agricultural use. The descriptive statistics of the calculated irrigation water quality indices are presented in Table 2, while their variations are illustrated in Fig. 4.

277 **Table 2.** Analytical Results of Groundwater Physicochemical Properties

	SAR	%Na (%)	KR	MR (%)	RSC (meq/L)	PI (%)
Minimum	0.2	15	0.2	38	-2.9	21
Maximum	1.8	60	1.4	57	0.2	35
Average	0.7	35	0.6	45	-0.8	27
Std. Deviation	1	14	0.4	6	0.8	4
Std. Error	0.1	3.5	0.1	1.6	0.2	1.1



278 **Fig. 4.** Variations in irrigation water quality indices.

279 The classification criteria adopted for these irrigation water quality indices, along with the
280 corresponding categories and the number of groundwater samples falling within each category,
281 are presented in Table 3.
282

283 **Table 3**. Irrigation Suitability Rankings for Groundwater Samples (Sharma et al. 2021; Gautam et al. 2023)

	Scale	Category	No. of Samples
Total Dissolved Solids (TDS) (mg/L)	<1000	Fresh	12
	1000–10,000	Brackish	3
	10,000–100,000	Saline	ND
	>100,000	Brine	ND
Salinity Hazard (EC; μS/cm)	C1: <250	Excellent	ND
	C2: 250–750	Good	6
	C3: 750–2250	Permissible	9
	C4: 2250–5000	Unsuitable	ND
Sodium Adsorption Ratio	<10	Excellent	15
	10–18	Good	ND
	18–26	Doubtful	ND
	>26	Unsuitable	ND
Soluble Sodium Percentage (%Na) (%)	<20	Excellent	1
	20–40	Good	8
	40–60	Permissible	5
	60–80	Doubtful	1
	>80	Unsuitable	ND
Kelly's Ratio	<1	Suitable	13
	>1	Unsuitable	2
Magnesium Ratio (MR) (%)	>50%	Suitable	7
	<50%	Unsuitable	8
Residual Sodium Carbonate (mEq/L)	<1.25	Suitable	15
	1.25–2.5	Marginally Suitable	ND
	>2.5	Unsuitable	ND
Permeability Index (%)	Class 1 (Excellent)	>75%	ND
	Class 2 (Good)	25%- 75%	11
	Class 3 (Unfit)	< 25%	4

284 *ND: Not Detected*

285 **(The table contains information on several metrics, including TDS, EC, SAR, SSP, KR, MR, RSC, and PI. These*
286 *factors are critical for deciding the appropriateness of water for farming.)*

3.2.1. Salinity Hazard

Irrigation water salinity is measured by Electrical Conductivity (EC). Water can be categorised into four types: C1, C2, C3, and C4. Water classified as C1 or C2 is generally suitable for irrigation, with C1 representing "Excellent" quality and C2 indicating "Good" quality, which may necessitate moderate leaching practices. In contrast, C3 and C4 classes present severe issues, with C3 being "Doubtful" and potentially needing special management practices, and C4 being "Unsuitable" for irrigation. EC and TDS indicate salinity levels that can hinder water uptake, causing osmotic stress and negatively affecting soil and plant growth. In this study, most samples fell within the 750 to 2250 s/cm range for acceptable irrigation, with EC values ranging from 520 to 1823 s/cm. TDS levels varied from 312 to 1094 mg/L, with 12 samples classified as fresh and 3 as brackish (Table 3), indicating that salinity is not a major constraint to irrigation in the region.

3.2.2. Sodium Adsorption Ratio

Elevated SAR levels can lead to soil dispersion and decreased permeability, which negatively affect crop growth and soil health.

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+}+Mg^{2+})/2}} \qquad \text{(Sudhakaran et al. 2020)} \qquad (1)$$

SAR measures the proportion of sodium to calcium and magnesium cations, which influences the structure of soil and permeability. High sodium levels can disrupt soil, reduce water infiltration, and impede plant growth. Fortunately, all samples in this study had favourable SAR values ranging from 0.2 to 1.8, categorised as "excellent" (<10) (Table 3). This indicates minimal risk of sodium-related soil issues under standard irrigation practices.

3.2.3. Soluble Sodium Percentage (%Na)

Sodium harms water quality by damaging soil and reducing plant growth. Elevated sodium classifies water as saline (chloride/sulphate dominant) or alkaline (carbonate/bicarbonate dominant).

$$\text{SSP} = \frac{(Na^+ + K^+)\times 100}{Ca^{2+}+Mg^{2+}+Na^+ + K^+} \qquad \text{(Karakuş and Yıldız 2020)} \qquad (2)$$

The SSP quantifies the proportion of sodium relative to the total cation concentration, such as sodium, calcium and magnesium in irrigation water. While SSP is not the most comprehensive indicator for irrigation suitability, it provides a general perspective on potential sodium hazards. In this study, SSP values ranged from 15% to 60%. Eight samples were categorized as "good" (20-40% SSP), while five samples were classified as "permissible" (40-60% SSP). One sample fell under the "doubtful" category (60-80% SSP) (Table 3). While the majority of samples had acceptable SSP levels, a few samples suggest the potential for long-term sodium accumulation issues, warranting monitoring and management practices in those areas.

3.2.4. Kelly's Ratio

The KR value determines groundwater suitability for irrigation. A KR value surpassing 1 signifies groundwater unsuitability for irrigation.

$$KR = \frac{Na^+}{Ca^{2+} + Mg^{2+}} \quad \text{(Yıldız and Karakuş 2020)} \tag{3}$$

In this study, KR readings varied from 0.2 to 1.4. Only two samples surpassed the required KR limit (Table 3), indicating the possibility of sodium accumulation and its adverse impact on soil aggregation.

3.2.5. Magnesium Ratio

The Magnesium Ratio (MR), determined according to the Szabolcs and Darab equation. An MR above 50% indicates high magnesium levels that can raise soil alkalinity, impair soil quality, and lower crop yield. Practically, water with an MR less than 50% is deemed unfit for irrigation because of its potential negative impacts upon the soil's pH and infiltration capacity.

$$MR = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100 \quad \text{(Aydin et al. 2021)} \tag{4}$$

A magnesium ratio greater than 50% indicates an elevated level of magnesium, which can increase the alkaline status of the soil and negatively impact soil quality, resulting in lower crop output. Water samples exhibiting a Magnesium Ratio below 50% are generally regarded as unsuitable for irrigation because they may adversely affect soil pH levels and reduce its infiltration capacity. Magnesium Ratio (MR) ranged from 38% to 57%. Eight samples fell below the desirable level of <50% MR (Table 3). suggesting a possible imbalance between sodium and magnesium that could affect soil stability.

3.2.6. Residual Sodium Carbonate

RSC below 1.25 meq/L is safe for irrigation; 1.25–2.5 meq/L requires caution, while above 2.5 meq/L is unsuitable due to soil structure damage from carbonate precipitation.

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad \text{(Sutradhar and Mondal 2021)} \tag{5}$$

Residual Sodium Carbonate (RSC) represents the potential for carbonate mineral precipitation, which can reduce soil permeability. In this investigation, Residual Sodium Carbonate values varied between -2.9 to 0.2, all of which were below the crucial level of 1.25. This means that precipitation poses a low risk to water infiltration.

3.2.7. Permeability Index

Excess sodium in irrigation water reduces soil permeability, worsened by carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions precipitating calcium and magnesium as $CaCO_3$ and $MgCO_3$. This removes essential cations, increasing soil sodium, disrupting structure, and

hindering water flow. The Permeability Index (PI), calculated using Doneen's (1964) formula, evaluates these effects on soil permeability, guiding irrigation suitability assessment.

$$PI = \frac{Na^{+}+\sqrt{HCO_3^{-}}}{Ca^{2+}+Mg^{2+}+Na^{+}} \times 100 \quad \text{(Şahin Kiy and Arslan 2021)} \qquad (6)$$

The Permeability Index (PI) classifies irrigation water based on its impact on soil permeability. Class 1 (Excellent) water with >75% PI indicates maximum permeability, making it most suitable for irrigation. Class 2 (Good), characterised by a Permeability Index (PI) ranging from 25% to 75%, reflects moderate permeability and is generally considered suitable for irrigation, with 11 samples classified in this group. Conversely, Class 3 (Unfit), defined by a PI below 25%, indicates poor permeability and is unsuitable for irrigation, encompassing 4 samples (Table 3).

3.3. Hydrochemical Evaluation and Multivariate Interpretation

3.3.1. Correlation matrix of groundwater samples

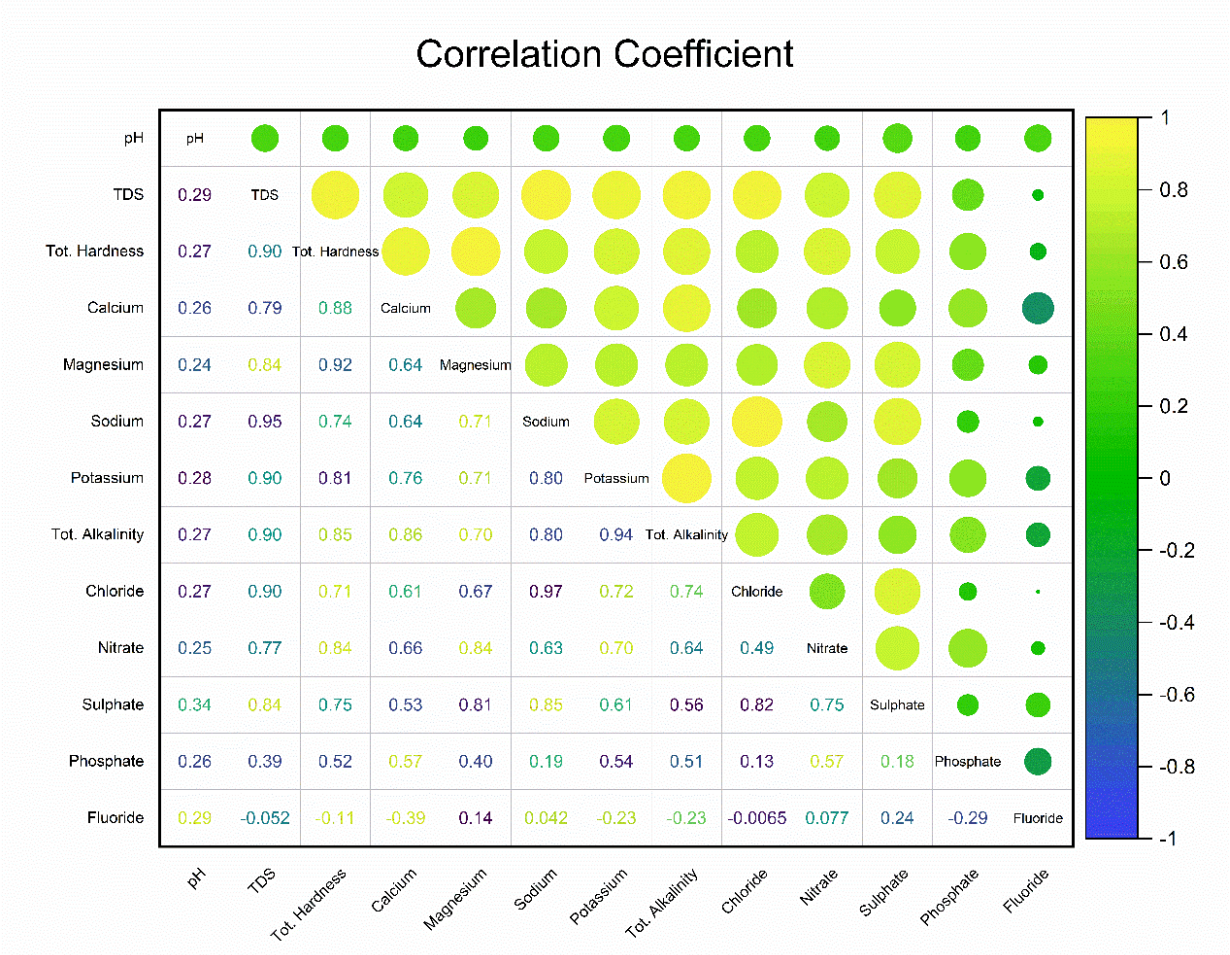
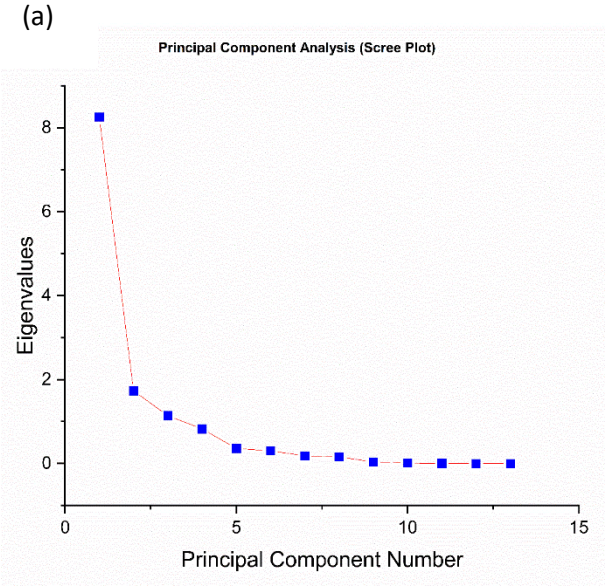


Fig. 5. Pearson correlation matrix (correlogram) showing the relationships among groundwater physicochemical parameters. The lower triangle displays Pearson correlation coefficients (r), whereas the upper triangle represents the strength and direction of correlations using coloured circles.

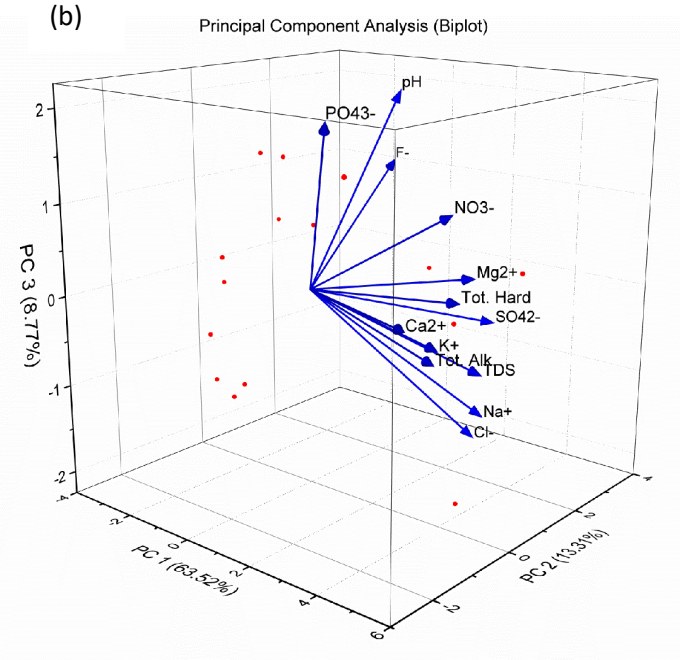
The Pearson correlation matrix (Fig. 5) was used to examine the relationships among groundwater physicochemical parameters. Major findings indicate that total dissolved solids (TDS) share strong positive associations with water quality variables, including hardness, calcium, magnesium, sodium, potassium, alkalinity, and chloride, suggesting these ions originate from similar geochemical sources. Water hardness notably aligns with calcium and magnesium concentrations. Sulphate and nitrate both show good alignment with TDS, and sodium also demonstrates considerable linkage, while nitrate has a moderate connection with TDS. In contrast, fluoride and phosphate display weak or negative correlations (e.g., fluoride-TDS r = -0.05; phosphate-potassium r = 0.39), suggesting different hydrogeochemical behaviours. This matrix clarifies which ions are tightly coupled and which vary independently in groundwater.

3.3.2. Principal Component Analysis

(a)



(b)



(c)

Eigenvalues of the Correlation Matrix

	Eigenvalue	Percentage of Varianc	Cumulative
1	8.25772	63.52%	63.52%
2	1.7303	13.31%	76.83%
3	1.14041	8.77%	85.60%
4	0.82381	6.34%	91.94%
5	0.35849	2.76%	94.70%
6	0.30176	2.32%	97.02%
7	0.18144	1.40%	98.41%
8	0.15694	1.21%	99.62%
9	0.03584	0.28%	99.90%
10	0.01284	0.10%	100.00%
11	3.23E-4	0.00%	100.00%
12	1.26E-4	0.00%	100.00%
13	0	0.00%	100.00%

(d)

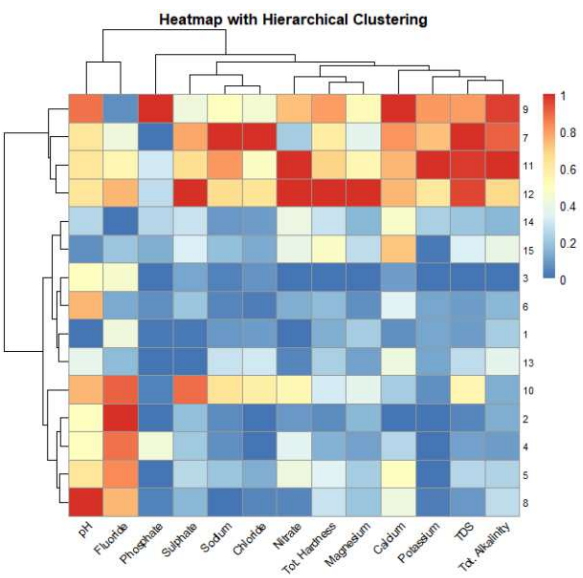


Fig. 6. PCA of groundwater chemistry: **(a)** Scree plot showing eigenvalue distribution, **(b)** 3D biplot illustrating the loading of physicochemical parameters on the first three principal components, **(c)** Eigenvalues of components, **(d)** HCA heatmap for samples

3.3.3. Exploratory Multivariate Statistical Analysis

Principal Component Analysis (PCA) was employed as an exploratory approach to examine the relationships among groundwater quality variables, given the limited sample size (n = 15). Three principal components collectively account for 85.6% of the total variance (Fig. 6a), and interpretation is confined to the dominant loading patterns. PC1, explaining 63.5% of the variance, is characterised by strong contributions from total hardness, TDS, major cations, alkalinity, and chloride, reflecting overall mineralisation and salinity processes. PC2 (13.3%) is primarily associated with sulphate and phosphate, whereas PC3 (8.8%) represents localized variations in pH, fluoride, and nitrate. The PCA biplot (Fig. 6b) is interpreted qualitatively to illustrate general associations among variables rather than distinct hydrochemical facies.

Hierarchical Cluster Analysis (HCA) was applied to normalised data to explore similarities among groundwater samples and to complement PCA results. The dendrogram with heatmap (Fig. 6d) broadly groups fifteen samples into two clusters, indicating general differences in ionic composition. Given the dataset of 15 samples, clustering results are interpreted cautiously and are not used to infer distinct contamination sources or spatial boundaries. Samples within one cluster exhibit relatively elevated fluoride, phosphate, and alkalinity, whereas others show lower concentrations of hardness-related parameters. Overall, HCA serves as a supportive exploratory tool consistent with PCA-derived trends.

3.3.4. Hydrochemical Facies and Process Interpretation

Graphical hydrogeochemical tools were employed to support facies classification and to provide a conceptual overview of the dominant processes controlling groundwater chemistry. The Chadha diagram (Fig. 7A) was employed as a supplementary hydrochemical classification tool to broadly identify dominant water types. Most groundwater samples plot within the Ca-Mg-HCO_3 field, indicating the general dominance of carbonate weathering processes in the basaltic aquifer system. A limited number of samples fall within the Na-Cl and Na-HCO_3 fields, suggesting secondary influences such as ion exchange, evaporation, or localised anthropogenic inputs.

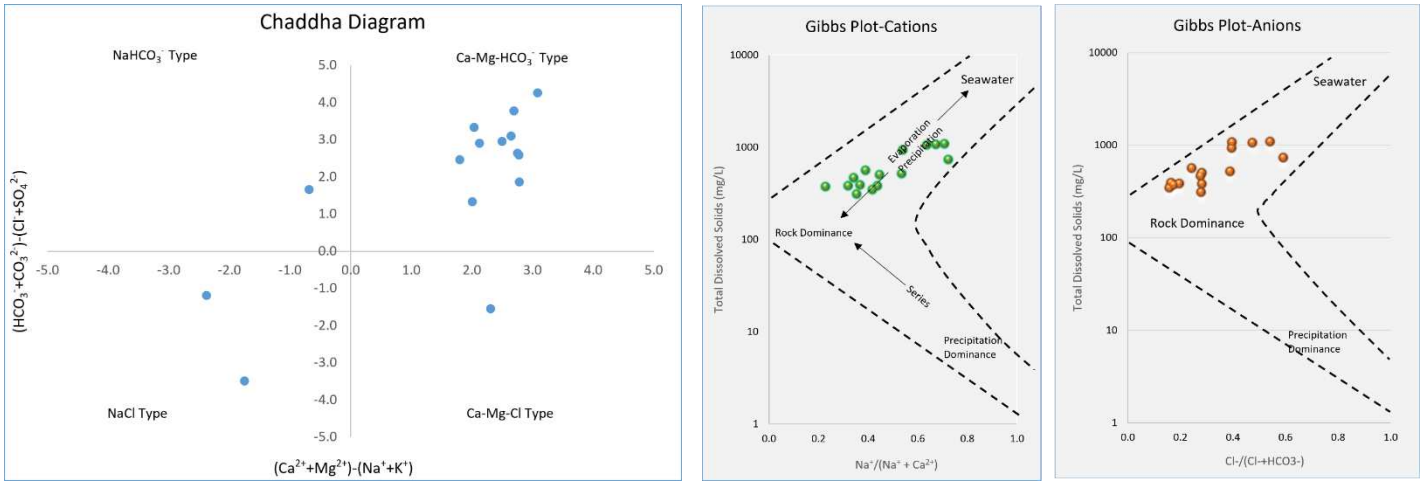
Gibbs plots (Fig. 7B) were used to provide a conceptual overview of the dominant mechanisms controlling groundwater chemistry. Most samples plot within the rock-water interaction and evaporation dominance fields based on $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ ratios. These trends broadly suggest that mineral weathering processes, coupled with evaporative concentration under semi-arid climatic conditions, exert a primary control on groundwater chemistry. Gibbs plots are used selectively to support process-level insights from ionic, multivariate, and geochemical analyses. Considering the sample size, the graphical and multivariate analyses are intended to provide process-based and conceptual insights rather than statistically generalizable relationships.

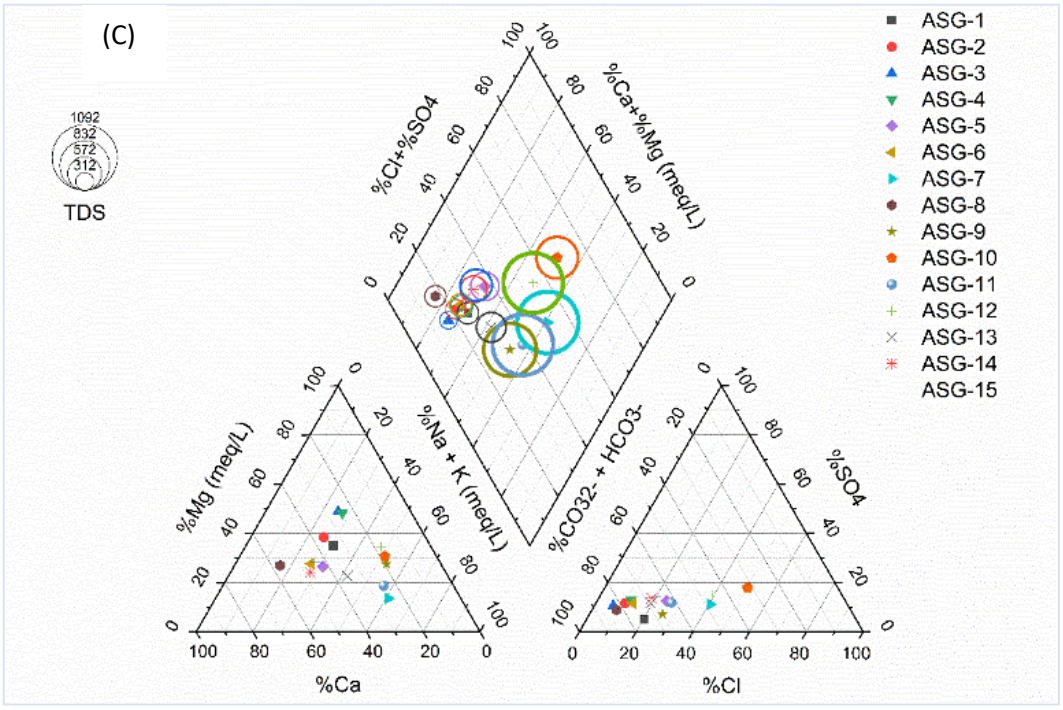
3.3.5. **Hydrochemical Facies Characterization**

The chemistry of groundwater samples was analysed using a Piper diagram (Fig. 7C) generated in Origin 2022 (Arthur M. Piper 1944). This trilinear plot shows the relative proportions of key cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (HCO_3^{-}, SO_4^{2-}, Cl^{-}) as per cent milliequivalents. 66.66 of % samples are grouped in the central diamond's Mg-HCO_3 facies, indicating dominance of magnesium and bicarbonate from carbonate-rich geology. A smaller subset plots in the Na-Cl field, i.e. 13.3 %, reflecting saline or anthropogenic influence. The remaining 20% samples display mixed facies, suggesting varied geochemical environments. The Piper diagram effectively visualises similarities and differences in groundwater ionic composition (Goswami et al. 2022).

The hydrochemical characteristics observed in the present study are consistent with groundwater evolution patterns reported from semi-arid and hard-rock aquifer systems in India and comparable global settings. The hydrochemical facies identified from the Piper and Chadha diagrams (Fig. 7A and Fig. 7C), together with the geochemical processes inferred from the Gibbs diagrams (Fig. 7B), indicate that groundwater chemistry is primarily controlled by carbonate and silicate weathering, ion exchange, and prolonged rock–water interaction. Similar Ca-Mg-HCO_3 facies have been reported from aquifers of Himalayan foothill and tropical river basins in India, where mineral dissolution governs major ion chemistry (Nayak et al. 2023; Anjali et al. 2025). Comparable hydrochemical facies distributions have also been documented in semi-arid groundwater systems outside India, reinforcing the broader applicability of these geochemical controls (Al-Dulaimi and Al-Shammaa 2023). The consistency of Mg-HCO_3 facies across these regional and global studies suggests that the hydrochemical regime identified in the present study reflects well-established groundwater evolution processes rather than a localised anomaly. The dominance of Mg–HCO_3 facies indicates that groundwater chemistry is primarily controlled by water-rock interactions and subsurface geological conditions. Recent coupled modelling studies demonstrate that rock heterogeneity and fluid-rock interactions strongly regulate hydrological processes in geological formations (Liu et al. 2025), supporting the role of natural controls in facies evolution.

(A) (B)





451 **Fig. 7.** Graphical hydrogeochemical interpretation of groundwater using **(A)** Chadha, **(B)**
452 Gibbs, and **(C)** Piper diagrams for hydrochemical facies classification and identification of
453 the dominant geochemical processes.

(A) (B)

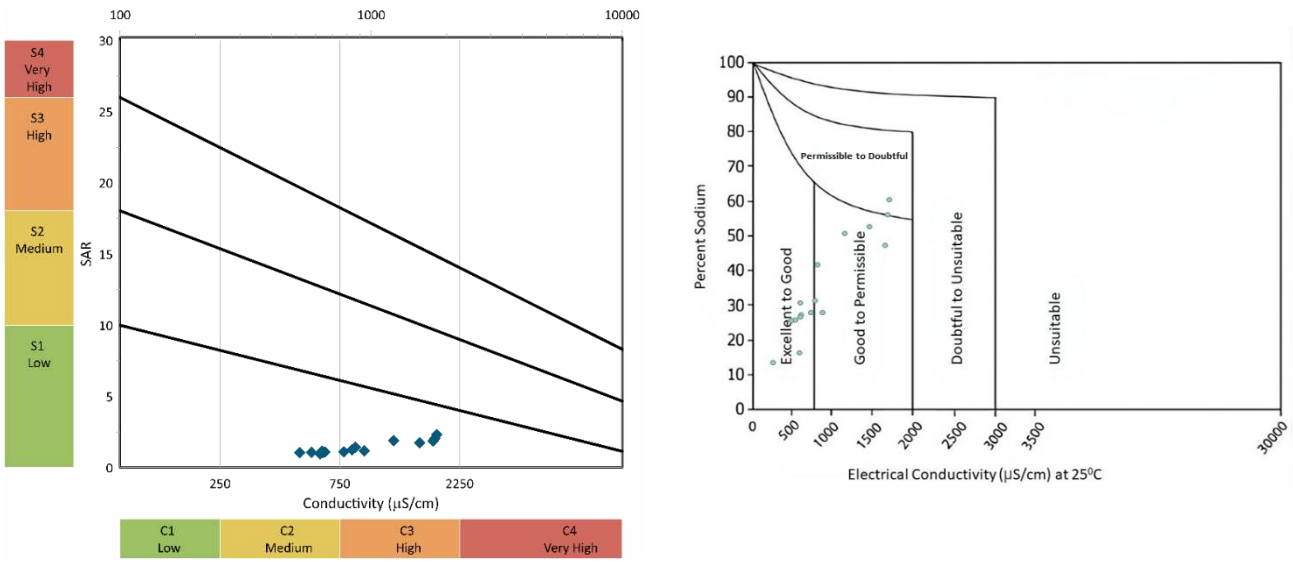


Fig. 8. (A) USSL Diagram (The graph shows the calculated quantities of SAR and EC for groundwater samples). **(B)** Wilcox Diagram (Sodium Percentage vs. Electrical Conductivity Plot depicts a plot of Na% versus EC, used to classify water quality for agricultural suitability into five categories, from Excellent to Unsuitable.)

3.4. Representation of Irrigation Water Quality

3.4.1. USSL Diagram

The SAR and EC plot helps to identify the class of irrigation water. This plot is created using Grapher™ software. Salinity indicates the total dissolved salt concentration, while sodium hazard reflects the proportion of sodium relative to calcium and magnesium in the water. Both parameters have the potential to deteriorate soil quality and negatively impact crop growth. From the plot (Fig. 8A), analysis reveals that 40% of the water specimens fit into class C2S1, characterised by moderate salinity with a small sodium hazard, generally suitable for cultivation with moderate leaching. However, the remaining 60% fall under the C3S1 category, which denotes elevated salinity levels but minimal sodium hazard. In well-drained soils, such water can be used for irrigation, provided salinity is managed through appropriate practices. Yet, for poorly drained soils, using C3S1 water is not advisable due to the risk of increased soil salinisation. It's essential to consider factors like crop salt tolerance and conduct long-term soil salinity monitoring.

The majority of samples fall within the C3S1 class, indicating high salinity but low sodium hazard, such that groundwater can be sustainably used for irrigation under controlled management practices. The low sodium risk reduces the likelihood of soil dispersion; however, elevated salinity necessitates appropriate leaching fractions, the selection of salt-tolerant crops, and periodic monitoring of soil salinity to prevent long-term degradation, alike adaptive and preventive irrigation strategies have been recommended in recent studies addressing sustainable agricultural water management under saline conditions (Lu et al. 2025; Meng et al.

2025). Therefore, while the groundwater remains conditionally suitable for irrigation, proactive soil-water management is essential in the semi-arid agricultural setting.

The hydrochemical characteristics and irrigation suitability observed in this study are consistent with other semi-arid and hard-rock aquifers in India. In the Kundalika River Basin, Maharashtra, most groundwater was Ca-HCO_3 facies with C2-S1, C3-S1, and C3-S2 categories (Deshpande et al. 2023), aligning with the Mg-HCO_3 facies and C3-S1 dominance here. Similarly, (Sivakumar et al. 2023) reported high-salinity, low-sodium hazard water in Kovilpatti Taluk, Tamil Nadu, and (Sharma et al. 2021) documented Ca-Mg-Cl dominated, rock-controlled groundwater in Dera Bassi, Punjab. These comparisons confirm that the hydrochemical facies, ion associations, and irrigation suitability trends in this study are robust and representative of Indian semi-arid aquifers.

3.4.2. Wilcox Diagram

According to the Sodium Percentage versus EC plot (Fig. 8B), 40% of samples fall in the highest irrigation suitability category, suggesting these sources can be used for a wide range of crops with minimal restrictions. Around 33.3% are considered suitable but may pose some limitations depending on soil and crop characteristics. Approximately 13.3% require more careful management and are best suited for salt-tolerant crops. The remainder are positioned between high and moderate suitability classes.

3.5. Geochemical Modelling

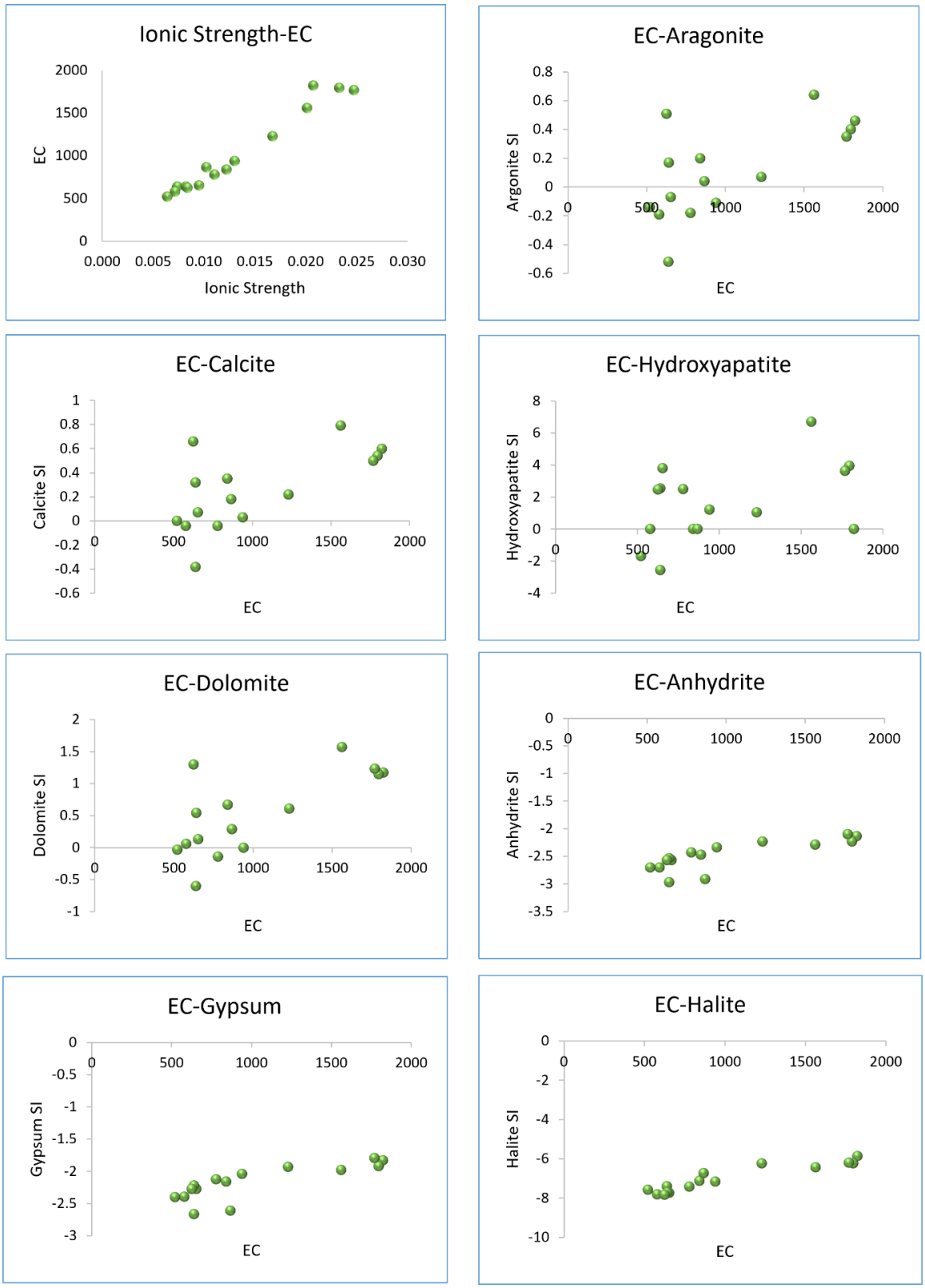


Fig. 9. Scatter Plots of Mineral Saturation Indices Versus Electrical Conductivity and Ionic Strength in Groundwater Samples

PHREEQC-based geochemical modelling of the groundwater dataset provides insights into mineral saturation states, their relationships with electrical conductivity (EC), and ionic strength, reflecting the prevailing geochemical processes within the aquifer (Hussainzadeh & Samani, 2022). Scatter plots (Fig. 9) demonstrate that EC and ionic strength are positively correlated, highlighting the role of mineralisation in governing solubility and precipitation kinetics. Saturation indices (SI) of carbonate minerals such as calcite and aragonite hover near equilibrium (SI $\approx$ 0), indicating active carbonate dissolution and precipitation under quasi-equilibrium conditions. Hydroxyapatite exhibits variable SI, spanning sub- to supersaturation, likely reflecting episodic phosphate mineralisation influenced by localised chemical or anthropogenic factors. Dolomite shows slight supersaturation in selected samples with increasing EC, suggesting potential precipitation or secondary mineral transformation. Evaporite minerals, including anhydrite, gypsum, and halite, remain consistently undersaturated (negative SI), indicating insufficient ion activity for salt formation.

Recent system-level studies highlight the importance of interpreting environmental data through integrated, process-based frameworks rather than isolated indicators (Di et al. 2025). In line with this, the present study combines hydrochemical indices, multivariate statistics, spatial analysis, and geochemical modelling to derive a coherent understanding of groundwater quality evolution in a semi-arid basaltic aquifer.

4. Conclusion

Groundwater in the semi-arid basaltic aquifer is slightly alkaline but locally unsuitable for drinking due to elevated hardness, salinity, and nitrate, with more than half of the samples exceeding permissible nitrate limits because of sustained agricultural pressure. Although groundwater remains conditionally suitable for irrigation, the dominance of C3S1-class water highlights the need for proactive salinity management to protect long-term soil health. By integrating water quality indices, multivariate statistics, hydrochemical facies analysis, and PHREEQC-based modelling, this study provides a process-oriented framework linking spatial variability, geochemical processes, and anthropogenic influences at the tehsil scale.

From a management perspective, the findings support adaptive irrigation strategies in semi-arid, groundwater-dependent systems, including controlled leaching to manage root zone salinity, crop salt-tolerance selection, and periodic soil salinity monitoring to prevent long-term degradation of water and soil resources. In light of climate-driven alterations in groundwater recharge, salinity, and quality associated with changes in the hydrological cycle, sustainable groundwater management must incorporate climate-resilient strategies, identified in recent reviews of climate impacts on groundwater (Dao et al., 2024; Swain et al., 2022)

This study's integrated use of hydrochemical indices, spatial mapping, multivariate statistics, hydrochemical facies analysis, and PHREEQC-based geochemical modelling within a unified framework is a significant strength. This multi-method convergence allows for cross-validation of WQI and irrigation assessments, decreases interpretational ambiguity, and improves process-level knowledge of groundwater quality evolution in data-scarce basaltic aquifers with anthropogenic input.

While the limited sample size restricts statistical generalisation, the qualitative interpretations remain robust for process understanding. Future studies incorporating seasonal monitoring and higher sampling density would further strengthen sustainable groundwater management in data-limited hard-rock aquifers.

Ethical responsibilities declarations

All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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This is not applicable.

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This is not applicable.

Consent to Publish

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