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An investigation of water quality index and health risks of fluoride and nitrate in the arid groundwater (India)

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Abstract

Groundwater in arid regions such as Northwestern Rajasthan of India is under increasing pressure due to climatic extremes, excessive extraction, and contamination from both geogenic and anthropogenic sources. This study assesses the seasonal dynamics of groundwater quality in Bikaner, focusing on fluoride and nitrate contamination and their implications for drinking suitability and public health. Twenty samples were collected from tube wells during the monsoon (2019) and pre-monsoon (2020) periods and analysed for a suite of physicochemical parameters following standard protocols. Water usability was gauged using several parameters including pH, electrical conductivity, total hardness, total dissolved solids, and ions such as calcium, magnesium, potassium, sodium, bicarbonate, carbonate, chloride, fluoride, nitrate and sulphate, while overall quality was synthesized using the Water Quality Index (WQI). Spatial patterns of contamination were visualized through geostatistical mapping, and hydrochemical facies were interpreted via Piper diagrams. Results revealed that over 65% of pre-monsoon samples surpassed WQI thresholds for safe use, signalling deteriorating groundwater quality. Elevated concentrations of fluoride (up to 5 mg/L) and nitrate (up to 320 mg/L) were commonly detected, with several areas falling into unsuitable categories for drinking. A health risk assessment using the Hazard Index framework found that all demographic groups especially infants were exposed to non-carcinogenic risk, with HI values reaching beyond 12 in critical zones. These findings underscore the urgent need for localized groundwater management strategies in the arid regions where seasonal fluctuations and geogenic factors are intensifying fluoride and nitrate contamination. The spatial clustering of high-risk zones especially in central and southeastern areas suggests persistent vulnerability requiring targeted mitigation. Prioritizing seasonal monitoring, fluoride and nitrate treatment technologies, and community-level interventions to mitigate health hazards and secure water resilience in ecologically fragile region of northwestern Rajasthan.

Keywords: Groundwater, water quality index (WQI), nitrate, fluoride, health risks, arid zone

Introduction

Arid and semi-arid zones constitute approximately 30–40% of Earth's land surface, spanning all continents, with dominance in Australia, Asia (especially the Middle East), and Africa (including North Africa and the Sahel). These regions are defined by low annual precipitation with less than 25 cm/year rainfall in arid zones and 25–50 cm/year in semi-arid zones (Bouchaou et al. 2024). Around 2.5 billion people inhabit these environments, facing chronic water scarcity and climatic extremities (Bouchaou et al. 2024). India's arid zone accounts for 15.8% of its land area, with approximately 61% located in Rajasthan, primarily in the Thar Desert (196,150 km^2 area). The region experiences erratic rainfall, high evaporation, extreme heat, and frequent droughts, making it ecologically fragile (Kalsi 2007). Hence, groundwater sources are vital for daily use. However, escalating demand, over-extraction, and localized pollution sources have led to alarming declines in both

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quantity and quality of groundwater resources in the desertic environments. Recent studies across semi-arid India have underscored seasonal influences on groundwater chemistry and found that groundwater in several locations contains harmful substances that exceed safety standards, such as fluoride, nitrate and metals (Duvva et al. 2022; Gugulothu et al. 2022a; Bojago et al. 2023; Kumar & Yadav 2025; Sane et al. 2025). Gugulothu et al. (2022a) assessed health risks from nitrate and fluoride exposure in rural groundwater of Telangana. Similarly, Duvva et al. (2022) assessed toxicity of nitrate and fluoride in groundwater in Medchal (South India). Kom et al. (2023) found geochemical sources and health risk from high fluoride in hard rock aquifers in South India. The levels of fluoride and nitrate was found up to 6.5 mg/L and 118.8 mg/L respectively with 30% samples unfit for drinking in the groundwater of Gokak, Karnataka (Sane et al. 2025). The annual groundwater quality report of central groundwater board (CGWB 2024a) concerned for nitrate, fluoride, arsenic and uranium contaminants in groundwater. Rajasthan ranks among the worst-affected states, with over 49% of groundwater samples exceeding the safe nitrate limit of 45 mg/L. Nitrate pollution is largely due to agricultural runoff, especially from nitrogen-based fertilizers. Livestock waste and poor waste management also contribute to nitrate leaching. High nitrate levels pose serious health risks, including methemoglobinemia (blue baby syndrome) in infants. Fluoride contamination is also widespread and severe in Rajasthan as some districts reached fluoride level as high as 31 mg/L which is far above the permissible limit of 1.5 mg/L. Fluoride contamination is concentrated in confined aquifers especially in rural and arid zones. Its long-term exposure can lead to skeletal and dental fluorosis, affecting vulnerable populations. The threat of uranium is also there as Rajasthan accounts for 42% of India's uranium-contaminated groundwater samples, with some exceeding 100 µg/L, more than three times the safe limit (30 µg/L). The contamination is linked to deep aquifer exploitation and possibly geogenic sources. Overextraction of groundwater appears to worsen uranium levels, exposing communities to risks of kidney damage and cancer. The main cause is Rajasthan's arid climate and erratic rainfall which limit natural recharge. Urban expansion and paved surfaces further reduce infiltration. Excessive pumping for irrigation and domestic use has led to declining water tables which in turn exposes deeper, contaminated layers (Lohia 2025).

Groundwater samples from Shekhawati region (Jhunjhunu, Sikar, and Churu districts) of Rajasthan revealed elevated levels of fluoride, nitrate, and total dissolved solids (TDS), often exceeding national and international safety standards (Singhal et al. 2020). The study compared pre-monsoon and post-monsoon data and found that contaminant concentrations tend to spike during the dry season likely due to reduced dilution and increased extraction. High fluoride levels were linked to dental and skeletal fluorosis, while excessive nitrate posed risks of methemoglobinemia, especially in infants and pregnant women. The region's dependence on groundwater for drinking and agriculture has led to declining water tables exposing deeper aquifers with higher mineral content and contamination. Contaminants were traced to both natural geological formations and human activities, such as fertilizer use, poor sanitation, and unregulated borewell drilling. The findings underscore an urgent need for regular monitoring, community awareness and remedial strategies like rainwater harvesting and fluoride removal technologies. Henceforth, it is the main consideration of groundwater safety, gaps in managing the resource, and the urgent need for reliable solutions in these dry parts of India (Ahamad et al. 2023). Implementation of seasonal monitoring and remediation methods need to be done. The localized assessments that integrate water suitability, hydro-chemical facies, and health risk evaluation remain limited. Moreover, the unique combination of high salinity, declining water tables, and population pressure in Bikaner underscores the need for region-specific investigations.

This study aims to assess groundwater quality and its drinking suitability in the Bikaner region of Rajasthan. It evaluates seasonal variations in physicochemical parameters, interprets hydrogeochemical facies through Piper diagrams, and quantifies health risks associated with fluoride and nitrate ingestion using the Hazard Index approach. By integrating geospatial analysis with health risk assessments, the study seeks to inform sustainable groundwater management strategies in vulnerable arid zones.

Materials and methods

Study area and sampling

The study was conducted in the arid region of Bikaner district, Rajasthan, India, part of the Thar Desert ecosystem, characterized by low annual rainfall and high evapotranspiration.

The study was conducted in the arid region of Bikaner district, situated in Rajasthan state of India. Bikaner is part of the Thar Desert ecosystem and exhibits a unique geological profile shaped by both ancient marine transgressions and desertification processes. The city and its surroundings are predominantly covered by quaternary aeolian deposits, consisting of fine to medium sand that forms shifting dunes and flat sandy plains. These sediments are largely unconsolidated and represent recent geological activity driven by wind erosion and deposition. Beneath the surface sands, the region reveals a complex stratigraphy such as (i) Pleistocene formations (Bap Boulder Beds) containing pebbles, cobbles, and boulders of granite, quartzite, rhyolite, and dolomite, indicating fluvial and colluvial processes; (ii) Tertiary layers (especially near Kolayat and Nokha) include clay, limestone, and sandstone, suggesting earlier lacustrine and shallow marine environments; (iii) Vindhyan Supergroup rocks which are encountered in deeper boreholes and consist of sandstone-clay-limestone sequences (part of the Trans-Aravalli Vindhyan basin). The sandy terrain and underlying formations influence groundwater occurrence. Aquifers are typically found in interbedded layers of sandstone and clay, with variable water quality depending on depth and lithology (CGWB, 2013). Bikaner is characterized by low annual rainfall and high evapotranspiration. Monsoon rainfall (June–September) is significantly higher, especially in July and August, with a combined total of 6.99 mm in the year 2019. Pre-monsoon rainfall (March–May) is minimal, totalling around 1.55 mm across three months in the year 2020. Twenty groundwater samples were systematically collected from tube wells distributed across urban and peri-urban zones (Figure 1). Sampling occurred over two distinct seasons: monsoon (2019) and pre-monsoon (2020). To ensure data reliability, samples

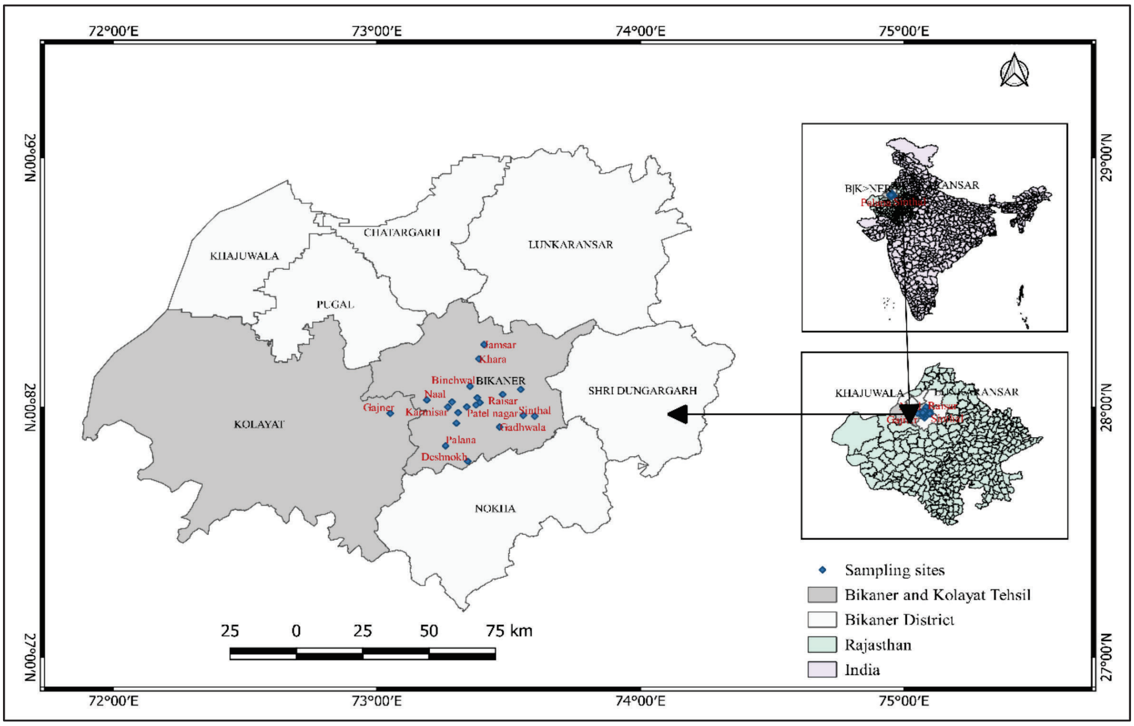


Figure 1. Sampling locations in the map of Bikaner City.

Table 1. Chemometric analytical methods.

Chemometric parameter	Analytical method
pH	Electrometric method via digital pH meter (Model Orion 5-Star, Thermo Scientific Ltd.)
Electrical Conductivity (EC), Total dissolved solids (TDS)	Electro-conductivity meter (Model 308, Systronics Ltd.)
Total Hardness (TH), calcium (Ca^{2+}) and magnesium (Mg^{2+})	EDTA titration method
Sodium (Na^{+}) and potassium (K^{+})	Flame photometric method
Chloride (Cl^{-})	Mohr's argentometric method
Fluoride (F^{-})	SPADNS [sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate dye] spectrophotometric method
Nitrate (NO_3^{-})	UV spectrophotometric method
Bicarbonate (HCO_3^{2-}) and carbonate (CO_3^{2-})	Titrimetric method
Sulphate (SO_4^{2-})	Turbidimetric method

were preserved using analytical-grade nitric acid immediately post-collection and stored in pre-cleaned polyethylene bottles.

Analytical procedures

Standard methods of analysis were used to assess the physicochemical parameters like pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), calcium (Ca^{2+}), potassium(K^{+}), magnesium (Mg^{2+}), sodium (Na^{+}), chloride (Cl^{-}), fluoride (F^{-}), bicarbonate (HCO_3^{-}), nitrate (NO_3^{-}), carbonate (CO_3^{2-}), and sulphate (SO_4^{2-}) (APHA 2017). These chemometric parameters were determined by using analytical methods mentioned in Table 1.

Geospatial and hydro-chemical analysis

Spatial visualization of water quality parameters was conducted using the Inverse Distance Weighting (IDW) interpolation technique in QGIS v3.38.3 (Grenoble release). For hydro-chemical facies classification, Piper diagrams were generated using Grapher v10.0.583 (free license 21.1.299), facilitating the interpretation of ion dominance and water types.

Water Quality Index (WQI) computation

Groundwater quality was quantified using the weighted arithmetic index method as proposed by Horton (1965). The water quality is categorized into five classes (Ramakrishnaiah et al. 2009) such as excellent (0–49), good (50–100), poor (101–200), very poor (201–300) and unsuitable (>300) as represented in Table 2. It was calculated by the given equations:

$$\mathrm{WQI} = \sum \mathrm{Wi}.\sum \mathrm{qi}$$

$$\mathrm{Wi} = \frac{\mathrm{K}}{\mathrm{Si}} \quad \text{and} \quad \mathrm{qi} = \frac{\mathrm{Ci}}{\mathrm{Si}} X100$$

Where, Wi = unit weight of the parameter, qi = quality sub-index of the parameter, K = proportionality constant (0.00028 for the present study), Si = standard value (BIS standard) of the parameter, and Ci = concentration of the parameter.

Non-carcinogenic health risk assessment

Non-carcinogenic risks from nitrate and fluoride exposure were evaluated using Hazard Quotient (HQ) and Hazard Index (HI), following U.S. EPA guidelines (USEPA 2004). Parameters were differentiated by population groups such as infants, children, older adults, and pregnant women, enabling vulnerability-specific assessments. Hazard quotient (HQ) is the ratio of the chronic daily intake to the reference dose of the contaminant in mg/kg/day (R_fD).

$$\text{Hazard Quotient (HQ)} = \frac{\mathrm{CDI}}{\mathrm{RfD}}$$

$$\mathrm{CDI\ (mg/kg/day)} = \frac{\mathrm{C} * \mathrm{IR} * \mathrm{EF} * \mathrm{ED}}{\mathrm{BW} * \mathrm{AT}}$$

Where, C is contaminant concentration in groundwater (mg/L), IR is average daily water ingestion rate (1.104 L/day for infant, 1.258 L/day for children, 3.229 L/day for old adult and 2.0935 L/day for pregnant women), EF is exposure frequency (365 days/year), ED is exposure duration (0.5 years for infant, 11 years for children, 78 years for old adult and 45 years for pregnant women), BW is body weight (7.4 kg for infant, 31.8 kg for children, 80 kg for old adult and 73 kg for pregnant women), and AT is the average lifetime of human exposure (ATSDR 2023; Roy et al. 2023).

The sum of hazard quotient in groundwater is called hazard index (HI).

$$\text{Hazard Index (HI)} = \sum_{i=1}^{n} \mathrm{HQ}$$

Groundwater is considered safe for drinking when the value of HI is less than 1. Whereas, an HI value more than 1 indicates potential non-carcinogenic health risks.

Statistical analysis

Descriptive statistical parameters such as mean, mode, median, standard deviation, variance, skewness, kurtosis) and Pearson's correlation matrices were computed using Microsoft Excel 2013, supporting the

Table 2. Water quality index (WQI) classification (Ramakrishnaiah et al. 2009).

Water quality index (WQI)	Class	Application
0–49	Excellent	Drinking, irrigation, and industrial
50–100	Good	Drinking, irrigation, and industrial
101–200	Poor	Irrigation and Industrial
201–300	Very poor	Irrigation
> 300	Not suitable for drinking	Require treatment before use

interpretation of seasonal hydrogeochemical dynamics and inter-parameter relationships.

Results and discussion

Chemometric parameters

Table 3 displays descriptive statistics of groundwater parameters of monsoon season. pH levels ranged from 7.2 to 8.2, with a mean of 7.8, indicating slightly alkaline water. Low kurtosis (-1) and slight negative skewness (-0.3) suggest a relatively uniform distribution. TDS and EC values were notably high, averaging 1925 mg/L and 2887 µS/cm respectively, reflecting elevated salinity and mineral content. Strong positive skewness (2) and high kurtosis point to outlier concentrations of EC and TDS. Total Hardness (TH) varied widely (160–1350 mg/L) with a mean of 480 mg/L, indicating hard water and its distribution showed elevated kurtosis (3). Na^+ and K^+ concentrations showed moderate variability, with average of 516 mg/L and 17 mg/L of Na^+ and K^+ respectively. Their skewness and kurtosis near zero suggest normal distribution. Ca^{2+} and Mg^{2+} exhibited pronounced variability and peaked distributions (kurtosis 9 and 3 respectively), especially for calcium with a mean of 86 mg/L. Cl^-, F^-, SO_4^{2-}, and NO_3^- showed elevated values, particularly Cl^- (mean 757 mg/L) and SO_4^{2-} (mean 234 mg/L). High kurtosis and skewness suggest episodic pollution or geogenic spikes. CO_3^{2-} and HCO_3^- values were moderate with relatively symmetric distributions.

The descriptive statistics of chemometric groundwater parameters of pre-monsoon season are shown in Table 4. pH ranged from 6.8 to 8.4, averaging 7.5. Slight positive skewness (0.4) and near-zero kurtosis indicate stable acidity levels. TDS and EC values remained high, averaging 1855.8 mg/L and 2783.9 µS/cm respectively and kurtosis (8.4) and skewness (2.5) indicate peaked, right-tailed distributions. TH showed reduced mean (436.8 mg/L), though still indicating hard water. Distribution of TH was heavily peaked and right-skewed (kurtosis 11.2). Sodium and potassium levels averaged 450.7 mg/L and 8.6 mg/L, respectively. Sodium displayed a slightly platykurtic and left-skewed distribution. Ca^{2+} and Mg^{2+}levels were slightly elevated compared to monsoon, with Ca^{2+} showing strong kurtosis (9.6) and skewness (2.8). Cl^- and NO_3^- concentrations were lower than monsoon season but still showed skewed distributions with moderate variability. F^- averaged 1.4 mg/L, remaining within health relevant thresholds but still elevated from natural baseline. HCO_3^- and CO_3^{2-} levels showed consistent trends across seasons with low skewness and platykurtic profiles. SO_4^{2-} and NO_3^- retained moderate variability and leptokurtic profiles, with slight seasonal increases.

The comparative assessment of groundwater quality across monsoon and pre-monsoon seasons revealed distinct hydro-chemical variations indicative of seasonal influences and geogenic processes. A slight reduction in mean pH values from 7.8 to 7.5 suggested a transition toward near-neutral conditions preceding monsoon recharge. Electrical conductivity and TDS remained consistently elevated, though marginally

Table 3. Descriptive statistics of physicochemical groundwater parameters of monsoon season.

Parameter	Minimum	Maximum	Mean	Median	Mode	Standard Deviation	Sample Variance	Kurtosis	Skewness
pH	7.2	8.2	7.8	7.8	7.9	0.3	0.1	-1	-0.3
TDS (mg/L)	750	5200	1925	1740	1850	1171	1370279	2	2
EC (µS/cm)	1130	7800	2887	2610	2780	1752	3069127	2	2
TH (mg/L)	160	1350	480	400	380	321	102931	3	2
Na^+ (mg/L)	95	870	516	568	750	202	40815	0	0
K^+ (mg/L)	6	35	17	15	12	9	74	1	1
Ca^{+2} (mg/L)	24	490	86	46	42	113	12865	9	3
Mg^{+2} (mg/L)	17	210	63	44	34	53	2774	3	2
Cl^- (mg/L)	225	2200	757	648	750	483	233684	3	2
F^- (mg/L)	0	5	1	1	1	1	1	6	2
HCO_3^- (mg/L)	64	340	179	162	180	74	5422	0	1
CO_3^{-2} (mg/L)	22	75	45	44	56	15	237	-1	0
SO_4^{-2} (mg/L)	27	1265	234	155	220	273	74528	11	3
NO_3^- (mg/L)	15	320	102	68	65	83	6852	2	2

Table 4. Descriptive statistics of physicochemical groundwater parameters of pre-monsoon season.

Parameter	Minimum	Maximum	Mean	Median	Mode	Standard Deviation	Sample Variance	Kurtosis	Skewness
pH	6.8	8.4	7.5	7.5	7.2	0.4	0.2	-0.2	0.4
TDS (mg/L)	950.0	4840.0	1855.8	1710.0	1150.0	837.0	700525.4	8.4	2.5
EC (µS/cm)	1425.0	7260.0	2783.9	2565.0	1725.0	1255.5	1576279.1	8.4	2.5
TH (mg/L)	218.0	1170.0	436.8	410.0	430.0	194.7	37892.7	11.2	3.0
Na^{+} (mg/L)	120.0	794.0	450.7	456.0	NA	198.0	39191.4	-1.0	-0.2
K^{+} (mg/L)	2.0	18.0	8.6	8.0	10.0	4.3	18.8	-0.2	0.5
Ca^{+2} (mg/L)	38.0	360.0	102.1	82.0	78.0	70.7	4995.5	9.6	2.8
Mg^{+2} (mg/L)	24.0	86.0	54.6	53.0	44.0	17.3	297.8	-0.6	0.1
Cl^{-} (mg/L)	110.0	956.0	549.3	590.0	110.0	271.7	73818.2	-1.2	-0.2
F^{-} (mg/L)	0.3	3.3	1.4	1.3	1.3	0.7	0.5	1.9	0.9
HCO_3^{-} (mg/L)	102.0	332.0	181.5	169.0	138.0	64.5	4159.1	0.1	0.9
CO_3^{-2} (mg/L)	22.0	94.0	54.0	55.0	42.0	18.4	339.9	-0.2	0.2
SO_4^{-2} (mg/L)	70.0	494.0	262.7	272.0	284.0	111.2	12361.5	0.3	0.3
NO_3^{-} (mg/L)	26.0	156.0	61.1	56.5	41.0	36.4	1328.4	2.4	1.6

lower in the pre-monsoon season, implying sustained mineral enrichment with moderate seasonal dilution (Raut et al., 2025). Total hardness also decreased slightly, yet remained within the hard water classification. Noteworthy reductions were observed in sodium (Na^+), potassium (K^+), chloride (Cl^-), and nitrate (NO_3^-) concentrations, likely driven by rainfall dilution and reduced agricultural leachates (Bisht et al., 2024). Conversely, calcium (Ca^{2+}), fluoride (F^-), sulphate (SO_4^{2-}), and carbonate (CO_3^{2-}) levels rose during the pre-monsoon season, possibly attributable to evaporative concentration and geogenic mobilization (Ram et al. 2022; Ali et al., 2023). The stability in bicarbonate (HCO_3^-) levels across seasons reinforced the buffering role of carbonate equilibria (Gugulothu et al., 2022b). Statistical indicators such as kurtosis and skewness further highlighted non-normal distributions and the presence of episodic pollution, reinforcing the need for seasonal groundwater monitoring to support sustainable resource management in semi-arid regions.

Table 5 represents health effect of fluoride with different concentration levels in the groundwater. Most samples fall within the 0.5–1.5 mg/L range, indicating beneficial fluoride levels (Adimalla et al., 2019a; Roy et al. 2025). However, an increase in samples with potential dental fluorosis is noted in pre-monsoon season.

Nitrate Pollution Index (NPI) of groundwater is shown in Table 6. Although extremely high nitrate levels (>3 mg/L) remain prevalent, there is a slight reduction in very significantly polluted samples in pre-monsoon season, with moderate and significant categories increasing (Panneerselvam et al. 2020; Subba Rao et al., 2020; Karunanidhi et al. 2024).

Correlation matrix

The correlation analysis of groundwater parameters during the monsoon (Table 7) and pre-monsoon (Table 8) seasons uncovered distinct hydrogeochemical dynamics shaped by seasonal recharge and anthropogenic pressures. In the monsoon season, strong positive correlations among EC, TDS, TH, Ca^{2+}, Mg^{2+}, and SO_4^{2-} ($r > 0.80$) suggest mineral dissolution and enhanced ionic mobility due to rain-induced recharge. Fluoride (F^-) also

Table 5. Fluoride concentrations in groundwater samples (Adimalla et al., 2019b; Roy et al. 2025).

Fluoride concentration (mg/L)	Effects on human health	Number of groundwater samples	
		Monsoon (2019)	Pre-monsoon (2020)
< 0.5	Favourable for dental caries	2 (10%)	2 (10%)
0.5–1.5	Helps in good dental health	10 (50%)	10 (50%)
1.5–4.0	Dental fluorosis in children	7 (35%)	8 (40%)
4.0–10.0	Dental and skeletal fluorosis	1 (5%)	-
> 10.0	Immobilizing skeletal fluorosis	-	-

Table 6. Nitrate Pollution Index (NPI) in groundwater samples (Panneerselvam et al. 2020).

Nitrate concentration (mg/L)	Category	Number of groundwater samples	
		Monsoon 2019	Pre-monsoon 2020
< 0	Unpolluted or clean	-	-
0–1	Slightly polluted	1 (5%)	1 (5%)
1–2	Moderately polluted	-	1 (5%)
2–3	Significantly polluted	2 (10%)	5 (25%)
> 3	Very significantly polluted	17 (85%)	13 (65%)

showed significant associations with Ca^{2+} and SO_4^{2-} (r ≈ 0.72–0.84), indicating geogenic origins linked to fluorite-bearing lithologies, consistent with findings from Fatehpur, Sikar district, where elevated fluoride and sulphate levels were attributed to weathering processes and rock-water interactions (Barwar et al. 2018).

In contrast, the pre-monsoon season exhibited weaker correlations and more fragmented relationships, reflecting evaporative concentration and localized contamination. While EC, TH, and SO_4^{2-} retained moderate positive associations (r ≈ 0.56–0.66), the inter-parameter connectivity was less cohesive. The linkage between calcium and hardness persisted (r = 0.80), affirming its role in overall water chemistry. However, NO_3^- and HCO_3^- showed negative or weak associations with most variables, highlighting independent contamination pathways, possibly linked to agricultural activity or shallow recharge. Notably, the inverse relationship between CO_3^{2-} and K^+ (r = –0.50) suggests divergent geochemical behaviour under dry conditions, a pattern similarly observed in Tonk district, where seasonal shifts in EC and TDS were linked to evaporation and silicate weathering (Bairwa et al. 2024). These findings align with broader regional assessments by the Central Ground Water Board (CGWB 2024b), which identified fluoride and nitrate as persistent contaminants in Rajasthan's aquifers, with seasonal variation driven by agricultural runoff and aquifer lithology. The observed seasonal contrast underscores the importance of temporal monitoring and multivariate analysis in semi-arid regions like Bikaner, where groundwater serves as a critical resource amid climatic variability and increasing anthropogenic stress. Incorporating such insights into groundwater management frameworks can aid in identifying contamination hotspots and guiding sustainable water use strategies.

Groundwater quality index

Figure 2 illustrates groundwater quality index across multiple locations in and around Bikaner region,

Table 7. Correlation matrix of groundwater samples of monsoon season.

	pH	TDS	EC	TH	Na^+	K^+	Ca^{+2}	Mg^{+2}	Cl^-	F^-	NO_3^-	HCO_3^-	CO_3^{-2}	SO_4^{-2}
pH	1.00													
TDS	0.13	1.00												
EC	0.13	1.00	1.00											
TH	0.02	**0.91**	**0.91**	1.00										
Na^+	-0.11	**0.59**	**0.59**	**0.61**	1.00									
K^+	-0.47	0.10	0.10	0.20	-0.02	1.00								
Ca^{+2}	-0.01	**0.85**	**0.85**	**0.91**	**0.57**	0.21	1.00							
Mg^{+2}	-0.11	**0.85**	**0.84**	**0.88**	**0.64**	0.43	**0.90**	1.00						
Cl^-	-0.01	**0.85**	**0.85**	**0.81**	0.43	0.22	**0.62**	**0.68**	1.00					
F^-	0.31	**0.73**	**0.73**	**0.65**	0.39	0.02	**0.72**	**0.63**	0.39	1.00				
NO_3^-	0.09	0.03	0.03	-0.11	-0.23	-0.18	-0.14	-0.14	-0.06	0.07	1.00			
HCO_3^-	-0.12	0.13	0.13	0.14	0.20	0.22	0.02	0.18	0.19	-0.06	-0.05	1.00		
CO_3^{-2}	-0.08	0.10	0.10	0.13	-0.02	-0.02	0.08	0.03	0.04	0.26	0.05	0.47	1.00	
SO_4^{-2}	0.08	**0.84**	**0.84**	**0.80**	0.49	-0.03	**0.90**	**0.75**	**0.53**	**0.84**	0.09	0.04	0.26	1.00

Table 8. Correlation matrix of groundwater samples of pre-monsoon season.

	pH	TDS	EC	TH	Na^+	K^+	Ca^{+2}	Mg^{+2}	Cl^-	F^-	NO_3^-	HCO_3^-	CO_3^{-2}	SO_4^{-2}
pH	1.00													
TDS	0.20	1.00												
EC	0.20	1.00	1.00											
TH	0.34	0.31	0.31	1.00										
Na^+	-0.21	0.37	0.37	0.47	1.00									
K^+	0.09	0.34	0.34	0.33	**0.63**	1.00								
Ca^{+2}	0.21	0.41	0.41	**0.80**	0.41	0.27	1.00							
Mg^{+2}	0.16	0.22	0.22	0.33	0.33	0.20	**0.72**	1.00						
Cl^-	0.05	**0.50**	**0.50**	0.22	0.48	0.28	0.37	0.40	1.00					
F^-	0.15	0.31	0.31	0.43	0.21	0.26	0.37	0.03	0.28	1.00				
NO_3^-	0.00	-0.23	-0.23	0.12	0.23	0.15	-0.09	-0.05	-0.39	-0.10	1.00			
HCO_3^-	0.00	0.03	0.03	0.16	0.03	-0.21	0.01	0.13	-0.06	-0.42	0.33	1.00		
CO_3^{-2}	0.05	-0.15	-0.15	-0.03	-0.11	-0.50	0.09	0.43	0.01	-0.42	0.13	**0.58**	1.00	
SO_4^{-2}	0.07	**0.63**	**0.63**	**0.56**	**0.66**	0.33	**0.64**	0.48	**0.76**	0.37	-0.11	0.09	0.01	1.00

with varying levels of water suitability in monsoon and pre-monsoon seasons. In monsoon season, locations such as Ridmalsar, Ghardwala, Napasar, Antodaynagar and Karmisar fall under good quality indicating safe and potable groundwater with minimal contamination. Poor to very poor quality of water was shown by Naurangdesar, Sagar, Sinthal, Udasar, Naal, Deshnokh, Palana, Udayramsar, Gangasahar, Patel nagar, and Bichwal which indicates higher contamination levels and water may need treatment before use. Groundwater of Raisar, Gajner, Khara and Jamsar was unsuitable for use because of high levels of pollutants or geogenic contaminants and water is unsuitable without treatment. Central and southeastern zones of the study area show declining water quality trends. Areas marked in red may correspond to high fluoride, nitrate, or salinity concerns, aligned with prior groundwater contamination patterns.

In pre-monsoon season, areas like Napasar, Deshnok, Palana and Karmisar retain good water quality, likely due to deeper aquifers or limited human impact. Most sites exhibit poor to unsuitable WQI, possibly linked to geogenic contaminants such as fluoride and nitrate. High-risk zones (WQI > 300) such as Sagar, Ridmalsar, Ghardwala, Sinthal, Udasar, Naal, Gajner, Udairamsar, Gangasahar, Patel nagar, Khara, Jamsar, and Bichwal may require urgent remediation. Groundwater samples of both monsoon and pre-monsoon seasons did not meet the criteria classified under the 'excellent' category of water quality index, indicating limitations in potable suitability across temporal scales.

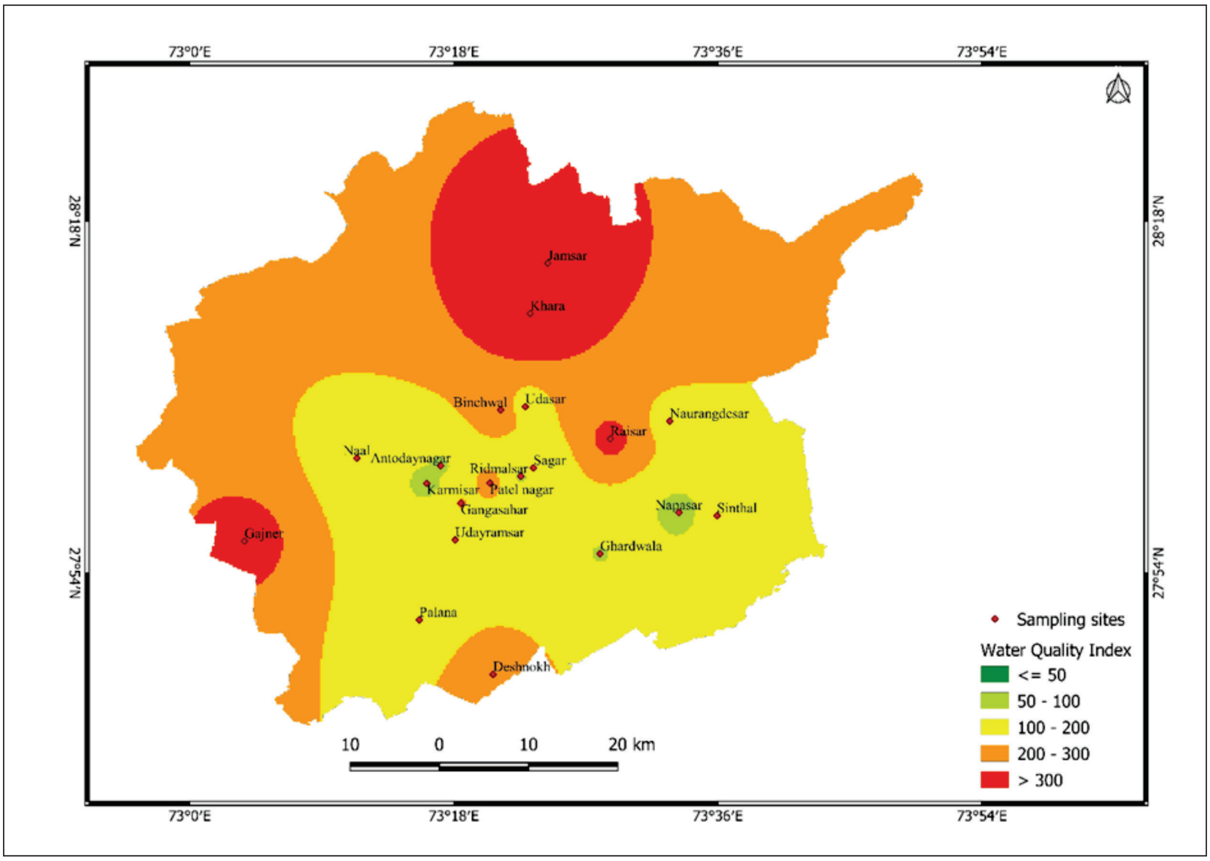
WQI values show a concerning decline in groundwater quality by pre-monsoon, with the percentage of samples categorized as unsuitable increasing from 20% to 65% as shown in Table 9.

Hydro-chemical characterization of groundwater

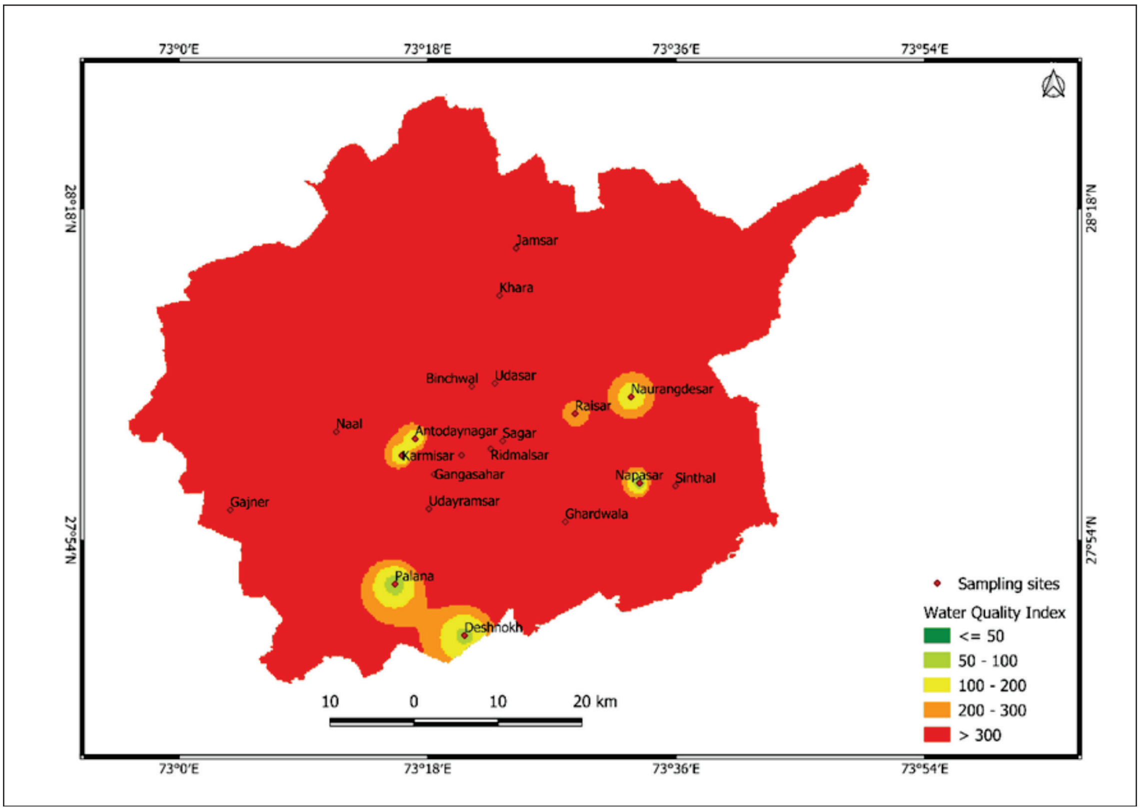
Piper diagram of groundwater of pre-monsoon and monsoon seasons of the years 2019 and 2020 are

Table 9. Water Quality Index (WQI) in groundwater samples.

Water quality index values	Category	Number of groundwater samples	
		Monsoon 2019	Pre-monsoon 2020
< 50	Excellent	-	-
50–100	Good	5 (25%)	4 (20%)
100–200	Poor	7 (35%)	2 (10%)
200–300	Very poor	4 (20%)	1 (5%)
> 300	Unsuitable	4 (20%)	13 (65%)



(a) Monsoon season



(b) Pre-monsoon season

Figure 2. Groundwater quality index in (a) monsoon and (b) pre-monsoon seasons.

depicted in Figure 3 and Figure 4 individually. In the monsoon season, the cation composition remains similar, with calcium and magnesium being the dominant ions. There is a slight increase in the presence of sodium and potassium due to dilution and mixing effects from the monsoon rains. Bicarbonate and chloride are still the main anions. The concentrations of sulfate and carbonate remain relatively stable. The central diagram shows a slight shift in the water type with a minor increase in sodium and potassium contributions. However, it remains primarily calcium-magnesium-bicarbonate-chloride. Throughout both pre-monsoon and monsoon periods, the groundwater is predominantly composed of calcium, magnesium, bicarbonate, and chloride ions. The monsoon period introduces slight changes in the groundwater composition, with a minor increase in sodium and potassium ions due to the dilution effect of rainfall. The water quality remains relatively stable between the pre-monsoon and monsoon periods, with minor variations in ion concentrations. The consistent water type indicates that the groundwater composition is not significantly impacted by seasonal changes. Overall, W-1, W-2, W-10, W-16, W-17, W-18, and W-19 samples cluster close to the Ca^{2+}-Mg^{2+} corner, indicating dominance by calcium and magnesium ions, typical of groundwater in contact with carbonate rocks and calcium-magnesium type water. W-4, W-5, W-6, and W-7 samples are shifted slightly toward the Na^{+}+K^{+} corner, showing a minor influence of sodium and potassium ions indicating mixed water type with a slight sodium-potassium enrichment. W-1, W-2, W-10, W-14, W-16, and W-17 samples cluster strongly toward the HCO_3^{-}+CO_3^{2-} corner, indicating bicarbonate dominance and bicarbonate-type water. This suggests recharge from areas with carbonate minerals. Mixed anion type (bicarbonate-sulfate or bicarbonate-chloride is observed in samples W-4, W-5, W-6, W-7, W-18, and W-19 as these samples are slightly closer to the Cl^{-} and SO_4^{2-} edges, suggesting contributions from sulfate or chloride, possibly due to minor evaporation, industrial inputs, or gypsum dissolution. W-1, W-2, W-10, W-14, W-16, and W-17 samples dominate the lower-left region of the central diamond, which confirms a calcium-bicarbonate (Ca-HCO_3) water type. This is typical of recently recharged groundwater in carbonate aquifers. Samples W-4, W-5, W-6, W-7, W-18, and W-19 fall closer to the central or right-hand regions of the diamond, indicating Mixed Ca-Mg-SO_4 or Ca-Mg-Cl water. This suggests some mixing with water influenced by evaporation, gypsum dissolution, or anthropogenic sources.

In the pre-monsoon season, the groundwater samples show a dominance of calcium and magnesium ions. Sodium and potassium ions are present but in lower concentrations compared to calcium and magnesium. The anions in the groundwater are primarily bicarbonate and chloride. However, sulfate and carbonate ions are present in smaller amounts. The central diamond-shaped diagram indicates that the overall water type is mainly calcium-magnesium-bicarbonate-chloride, suggesting that these ions are the dominant constituents in the groundwater during the pre-monsoon period.

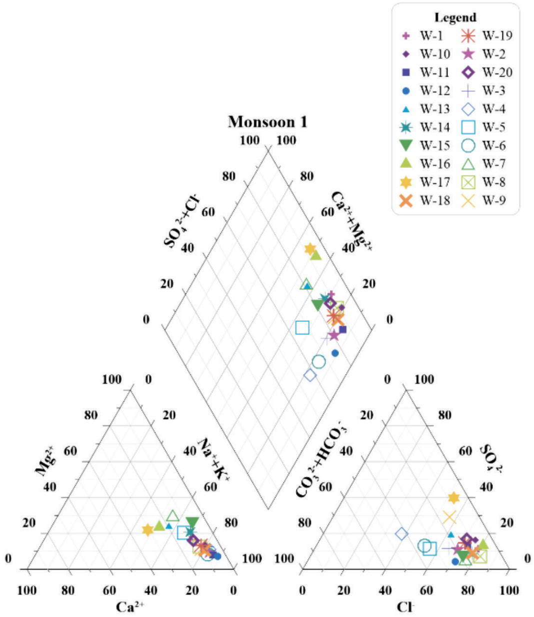


Figure 3. Piper diagram of groundwater of monsoon season.

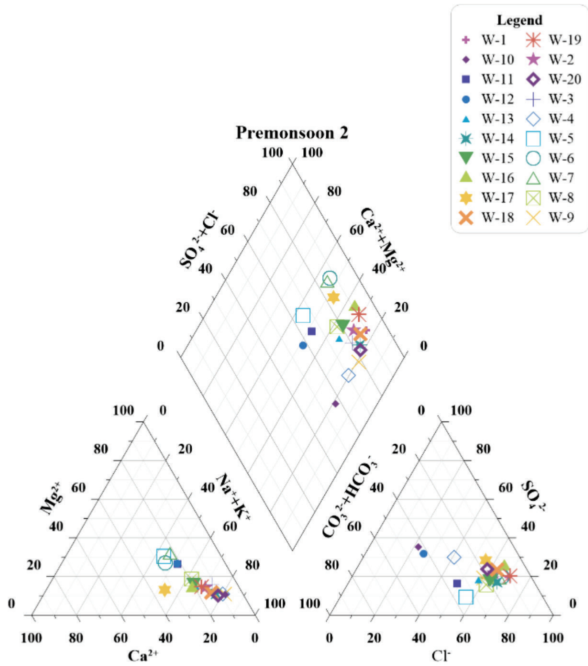


Figure 4. Piper diagram of groundwater of pre-monsoon season.

Assessment of health risks of fluoride and nitrate

The non-carcinogenic risk evaluation based on Hazard Index (HI) values during the monsoon season

Table 10. Hazard quotient and hazard index of groundwater samples in monsoon season.

Sample	Hazard quotient (HQ) Nitrate				Fluoride				Hazard Index (HI) Nitrate + Fluoride			
	Infant	Children	old adult	pregnant women	Infant	Children	old adult	pregnant women	Infant	Children	old adult	pregnant women
GW1	6.53	1.73	1.77	1.76	2.49	0.66	0.67	0.67	9.01	2.39	2.44	2.43
GW2	1.40	0.37	0.38	0.38	2.98	0.79	0.81	0.80	4.38	1.16	1.19	1.18
GW3	12.31	3.26	3.33	3.32	1.24	0.33	0.34	0.34	13.55	3.59	3.67	3.65
GW4	2.80	0.74	0.76	0.75	2.98	0.79	0.81	0.80	5.78	1.53	1.56	1.56
GW5	4.48	1.19	1.21	1.21	2.98	0.79	0.81	0.80	7.46	1.98	2.02	2.01
GW6	29.84	7.91	8.07	8.04	1.99	0.53	0.54	0.54	31.83	8.44	8.61	8.58
GW7	8.86	2.35	2.40	2.39	3.73	0.99	1.01	1.01	12.59	3.34	3.41	3.39
GW8	4.20	1.11	1.14	1.13	2.98	0.79	0.81	0.80	7.18	1.90	1.94	1.93
GW9	25.18	6.68	6.81	6.78	4.97	1.32	1.35	1.34	30.15	7.99	8.16	8.12
GW10	20.98	5.56	5.68	5.65	5.47	1.45	1.48	1.47	26.45	7.01	7.16	7.13
GW11	6.06	1.61	1.64	1.63	0.99	0.26	0.27	0.27	7.06	1.87	1.91	1.90
GW12	3.92	1.04	1.06	1.06	1.24	0.33	0.34	0.34	5.16	1.37	1.40	1.39
GW13	6.06	1.61	1.64	1.63	0.99	0.26	0.27	0.27	7.06	1.87	1.91	1.90
GW14	8.86	2.35	2.40	2.39	2.49	0.66	0.67	0.67	11.34	3.01	3.07	3.06
GW15	13.05	3.46	3.53	3.52	3.73	0.99	1.01	1.01	16.78	4.45	4.54	4.52
GW16	5.04	1.34	1.36	1.36	3.98	1.05	1.08	1.07	9.01	2.39	2.44	2.43
GW17	7.93	2.10	2.14	2.14	11.19	2.97	3.03	3.02	19.11	5.07	5.17	5.15
GW18	6.06	1.61	1.64	1.63	3.48	0.92	0.94	0.94	9.54	2.53	2.58	2.57
GW19	2.80	0.74	0.76	0.75	6.22	1.65	1.68	1.68	9.01	2.39	2.44	2.43
GW20	13.05	3.46	3.53	3.52	3.98	1.05	1.08	1.07	17.03	4.52	4.61	4.59
Mean	9.47	2.51	2.56	2.55	3.51	0.93	0.95	0.94	12.97	3.44	3.51	3.50
Minimum	1.40	0.37	0.38	0.38	0.99	0.26	0.27	0.27	4.38	1.16	1.19	1.18
Maximum	29.84	7.91	8.07	8.04	11.19	2.97	3.03	3.02	31.83	8.44	8.61	8.58

Table 11. Hazard quotient and hazard index of groundwater samples in pre-monsoon season.

Sample	Hazard quotient (HQ)								Hazard Index (HI)			
	Nitrate				Fluoride				Nitrate + Fluoride			
	Infant	Children	old adult	pregnant women	Infant	Children	old adult	pregnant women	Infant	Children	old adult	pregnant women
GW1	2.98	0.79	0.81	0.80	3.23	0.86	0.87	0.87	6.22	1.65	1.68	1.68
GW2	2.80	0.74	0.76	0.75	3.23	0.86	0.87	0.87	6.03	1.60	1.63	1.62
GW3	13.80	3.66	3.73	3.72	3.73	0.99	1.01	1.01	17.53	4.65	4.74	4.72
GW4	14.55	3.86	3.94	3.92	3.23	0.86	0.87	0.87	17.78	4.71	4.81	4.79
GW5	3.82	1.01	1.03	1.03	0.75	0.20	0.20	0.20	4.57	1.21	1.24	1.23
GW6	2.42	0.64	0.66	0.65	4.97	1.32	1.35	1.34	7.40	1.96	2.00	1.99
GW7	3.17	0.84	0.86	0.85	2.98	0.79	0.81	0.80	6.15	1.63	1.66	1.66
GW8	5.31	1.41	1.44	1.43	2.74	0.73	0.74	0.74	8.05	2.13	2.18	2.17
GW9	8.76	2.32	2.37	2.36	2.98	0.79	0.81	0.80	11.75	3.12	3.18	3.17
GW10	7.65	2.03	2.07	2.06	0.75	0.20	0.20	0.20	8.39	2.23	2.27	2.26
GW11	5.97	1.58	1.61	1.61	2.24	0.59	0.61	0.60	8.21	2.18	2.22	2.21
GW12	5.41	1.43	1.46	1.46	2.49	0.66	0.67	0.67	7.89	2.09	2.14	2.13
GW13	6.06	1.61	1.64	1.63	2.98	0.79	0.81	0.80	9.04	2.40	2.45	2.44
GW14	2.61	0.69	0.71	0.70	2.49	0.66	0.67	0.67	5.10	1.35	1.38	1.37
GW15	5.22	1.38	1.41	1.41	3.98	1.05	1.08	1.07	9.20	2.44	2.49	2.48
GW16	3.17	0.84	0.86	0.85	4.48	1.19	1.21	1.21	7.65	2.03	2.07	2.06
GW17	7.09	1.88	1.92	1.91	6.22	1.65	1.68	1.68	13.30	3.53	3.60	3.58
GW18	5.59	1.48	1.51	1.51	4.97	1.32	1.35	1.34	10.57	2.80	2.86	2.85
GW19	3.82	1.01	1.03	1.03	4.48	1.19	1.21	1.21	8.30	2.20	2.25	2.24
GW20	3.73	0.99	1.01	1.01	8.21	2.18	2.22	2.21	11.94	3.16	3.23	3.22
Mean	5.70	1.51	1.54	1.54	3.56	0.94	0.96	0.96	9.25	2.45	2.50	2.49
Minimum	2.42	0.64	0.66	0.65	0.75	0.20	0.20	0.20	4.57	1.21	1.24	1.23
Maximum	14.55	3.86	3.94	3.92	8.21	2.18	2.22	2.21	17.78	4.71	4.81	4.79

(Table 10) reveals significant health concerns associated with nitrate and fluoride exposure in groundwater. Across all demographic groups-infants, children, older adults, and pregnant women-mean HI values notably exceeded the safety threshold of 1, indicating potential adverse health effects from combined contaminant ingestion. Infants presented the highest susceptibility, with a mean HI of 12.97 and a maximum reaching 31.83 (sample GW6), signifying critical exposure levels. Children, older adults, and pregnant women recorded mean HI values of 3.44, 3.51, and 3.50 respectively, reinforcing elevated health risks across sensitive populations. Several groundwater samples, including GW6, GW9, GW10, and GW20, consistently exhibited HI values above 7 for all groups, highlighting them as high-priority zones for intervention.

The health risk assessment using Hazard Index (HI) values for nitrate and fluoride ingestion during the pre-monsoon season (Table 11) indicates widespread non-carcinogenic risks across all population groups. Infants remain the most vulnerable, recording a mean HI of 9.25 and a maximum of 17.78 (sample GW4), significantly surpassing the acceptable threshold (HI < 1). Children, older adults, and pregnant women also demonstrated elevated mean HI values of 2.45, 2.50, and 2.49 respectively, signaling consistent exposure concerns. Notably, samples GW3, GW4, GW17, GW18, and GW20 exhibited HI values exceeding 10 for infants and greater than 3 for other groups, emphasizing critical groundwater zones requiring immediate attention. These high-index samples point to cumulative effects from both nitrate and fluoride, with nitrate contributing dominantly to overall HI. The consistently elevated HI levels underscore a pressing need for groundwater remediation strategies, particularly in regions with frequent use by sensitive subpopulations. Monitoring and public health interventions are essential to mitigate long-term health consequences associated with chronic exposure to these contaminants.

The elevated Hazard Index (HI) values observed in both monsoon and pre-monsoon seasons across all demographic groups in the study align with broader regional and national concerns regarding groundwater contamination. In particular, the high HI values for infants (mean HI: 12.97 in monsoon; 9.25 in pre-monsoon) underscore their heightened vulnerability to nitrate and fluoride exposure. Shankar et al. (2025) found that over 76% of groundwater samples in Bellandur (Karnataka) exceeded the HI threshold for infants, indicating significant non-carcinogenic risks due to nitrate contamination, an observation that strongly parallels our results for sensitive populations. Similarly, Duvva et al. (2022) assessed groundwater in Medchal District and reported that 88% of samples exceeded the permissible nitrate limit of 45 mg/L, with HI values above 1 for both adults and children. Further, Reddy et al. (2022) evaluated groundwater in Nellore urban area and found that fluoride levels remained within safe limits but nitrate concentrations frequently exceeded WHO guidelines. Their hazard index analysis revealed that 100% of children and 95% of women were at risk, reinforcing the disproportionate impact on sensitive populations. Adimalla and Li (2018) found that 26% of samples exceeded the permissible nitrate limit (45 mg/L) and 20.59% exceeded the fluoride limit (1.5 mg/L) in the groundwater of Telangana. Total hazard index (THI) for children was ranged from 0.39 to 5.5. These values highlighted that the highest health risks were faced by the children followed by women and men due to their lower body weight and higher water intake per unit body mass which is consistent with our findings where children and infants showed elevated HI values well above the safe threshold. Their study also attributed contamination to both geogenic sources (e.g., weathering of fluoride-bearing minerals) and anthropogenic activities, such as agricultural runoff and improper waste disposal. These findings reinforce the urgency of groundwater in semi-arid regions is increasingly vulnerable to fluoride and nitrate contamination, and health risks are disproportionately borne by infants and children, necessitating targeted mitigation and policy interventions. Collectively, these studies corroborate the urgency of addressing groundwater contamination through targeted interventions, especially in arid regions like Rajasthan where aquifer vulnerability is compounded by climatic and land-use pressures.

Conclusions

This study presents compelling evidence of groundwater deterioration in Bikaner's arid zone, with high salinity, nitrate, and fluoride concentrations severely limiting its suitability for drinking purpose. Over two-thirds of samples exhibit unsuitability for use without treatment, emphasizing the urgency for robust water quality management. The seasonal comparison reveals that pre-monsoon conditions exacerbate contamination risks through evaporative concentration and reduced aquifer recharge. The seasonal contrast of chemometric correlation analysis suggests that monsoonal recharge enhances ionic connectivity and mineral mobilization, while pre-monsoon conditions fragment hydro-chemical relationships due to evaporative concentration and localized inputs. These findings emphasize the importance of temporal monitoring to detect emerging contamination trends and inform sustainable groundwater management.

Elevated hazard index values across all age groups, especially infants. Incorporating spatial analysis and hydro-chemical profiling allowed for a nuanced understanding of contamination hotspots, which reinforce the need for immediate intervention ranging from fluoride mitigation technologies to stricter control of agrochemical practices. Seasonal monitoring, public education, and groundwater recharge initiatives (e.g., rainwater harvesting) are vital for safeguarding rural communities in Rajasthan. The study contributes to the broader discourse on groundwater sustainability in arid environments and underscores the imperative of harmonizing environmental stewardship with human health protection.

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