



Fluoride and nitrate in groundwater: a comprehensive analysis of health risk and potability of groundwater of Jhunjhunu district of Rajasthan, India

**Naresh Tanwer · Meena Deswal ·
Pradeep Khyalia · Jitender Singh Laura ·
Babita Khosla**

Received: 1 November 2022 / Accepted: 21 December 2022 / Published online: 5 January 2023
© The Author(s), under exclusive licence to Springer Nature Switzerland AG 2023

Abstract Groundwater contamination is a major concern in front of the scientific community because it is directly related to human health, especially in arid and semi-arid regions. Therefore, a comprehensive study was engaged to evaluate the water quality, potability, and human health risk assessment due to the consumption of fluoride- and nitrate-contaminated water in Jhunjhunu district of Rajasthan. In order to assess the water quality, samples were collected from 87 locations in the study region, and a total of 16 parameters were analyzed as per the standard methods. The results showed that the value of the number of quality parameters consisting of pH, EC, TDS, fluoride, chloride, nitrate, sulfate, total hardness, calcium, magnesium,

and total alkalinity was higher than the recommended limit of BIS and WHO. The fluoride in 11% and nitrate in 6% of samples were observed to exceed the permissible limit of WHO. The results of risk assessment due to fluoride and nitrate revealed that hazard index values of 71% of groundwater samples for males, 78% of groundwater samples for females, and 75% of groundwater samples for children were greater than 1, indicating the significant health hazard due to consumption of groundwater. The water quality index (WQI) found that 39% of groundwater samples belong to categories that cannot be used for drinking purposes. Principal component analysis (PCA) reduced the large number of variables affecting the overall quality and chemistry of groundwater and determined four major components which account for 69.50% variance in the data. PCA concluded that both geogenic and anthropogenic sources of contamination influenced the groundwater of the study area.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10661-022-10886-z>.

N. Tanwer · M. Deswal · P. Khyalia · J. S. Laura ·
B. Khosla (✉)
Department of Environmental Science, Maharshi
Dayanand University, Rohtak, Haryana, India
e-mail: babitakhosla.env.sc@mdurohtak.ac.in

N. Tanwer
e-mail: nareshntanwer00@gmail.com

M. Deswal
e-mail: meenadeswal02@gmail.com

P. Khyalia
e-mail: pradeep310192@gmail.com

J. S. Laura
e-mail: jslmdu@gmail.com

Keywords Fluoride and nitrate · Groundwater ·
Health risk · PCA · WQI

Introduction

Pure drinking water is the first and foremost need of human civilization. Groundwater and surface water are the two most critical resources of water to suffice the need for drinking, agriculture, and industrial usage (Rashid et al., 2022). To serve the drinking

purpose, groundwater, preferably, is considered to be a significant asset utilized by a huge part of the total populace because of its good quality (Kaur et al., 2019). The drinking and agriculture usage utilize between 60 to 85% of India's groundwater. Its consumption becomes more prominent in arid and semi-arid regions where surface water resources are scarce and have inferior quality (Li & Qian, 2018). It is reported that 65% of global water requirement is fulfilled by groundwater. In India, for their routine use, more than 85% of the rural populace relies on groundwater supplies (Gugulothu et al., 2022, Subba Rao et al., 2019). To feed the exploding population, and growing industrial and agricultural activities, groundwater resources are exploited. Groundwater utilization is much higher than its replenishable rate, especially in Delhi, Rajasthan Haryana, and Punjab (CWC, 2019; Jandu et al., 2021; Tanwer et al., 2022). Consequently, the groundwater quality is deteriorating day by day, progressing toward a drinking water crisis and calling for other environmental challenges (Duvva et al., 2022). Significant factors that influence groundwater quality include recharge sources, geological formations, hydrological context, the mineralogy of the watersheds and aquifers, and water–rock interaction, including rocks dissolution, ion-exchange, redox reaction, and human activities (Iqbal et al., 2021). In the last few decades, some anthropogenic factors like erratic use of fertilizers, agricultural runoff, mismanagement of sewage, spillage of city drains, poultry and dairy waste animal, and humanistic waste significantly polluted the groundwater resources (Rahman et al., 2021). Nitrate and fluoride ions are regarded as the most prevalent impurities and pollutants in drinking water in the majority of rural areas of the world (Subba Rao, 2011; Subba Rao et al., 2013, 2016; Rao et al., 2020, 2021a, b; Ullah et al., 2022). Previous studies revealed that the groundwater of 23 Indian states has fluoride contamination (higher than 1.5 mg/L, permissible limit as per BIS), and 30 states have nitrate contamination (more than 45 mg/L permissible limit as per BIS) (CGWB, 2018). Rajasthan is one that is severely affected by fluoride and nitrate contamination in groundwater. The groundwater of 85% of districts of Rajasthan is reported to have a serious influence of fluoride contamination; on the other hand, reports of nitrate contamination in all districts are also a serious concern (CGWB, 2018).

Fluoride contamination in groundwater is a major issue as around 66 million people in India are suffering from dental and skeleton fluorosis (Kashyap et al., 2020). It is a common and hazardous element found in groundwater as per USEPA (2006), (Sohrabi et al., 2021). Its concentration in drinking water can cause several ill effects such as decaying of the tooth (at a concentration lower than 0.50 mg/L), fluorosis (at a concentration of 1.50–5 mg/L), and bone fluorosis (at a concentration of 5–40 mg/L) (Kimambo et al., 2019). Other associated health effects due to fluoride-contaminated water could be neurological impairments, cancer, arthritis, thyroid, infertility, and hypertension (Kimambo et al., 2019). Approximately 75–90% of fluoride ingested is absorbed as it is transformed to hydrogen fluoride (HF) in an acidic stomach, and absorbed in the intestine (Whitford et al., 1976). After entering the bloodstream, fluoride is easily distributed throughout the body, with around 99% of the body's fluoride load remaining in calcium-rich tissues like bones and teeth (Suthar et al., 2008). Fluoride in groundwater comes from both natural or geogenic and human interventions, with the majority of inputs from geogenic sources (Adimalla et al., 2020). The addition of fertilizers such as phosphate fertilizers can supply fluoride in soil up to the extent of 217–454 mg/kg (Kashyap et al., 2020).

Nitrate is also another well-known pollutant prevalent in groundwater due to both natural and manmade activities (Rao et al., 2022a, b). Human activities such as fertilizer application, improper waste disposal, mismanagement of sewage, agricultural runoff, and landfill leachates are significant contributors to nitrate contamination of groundwater resources. The prolonged consumption of nitrates in drinking water can cause methemoglobinemia (commonly known as blue baby syndrome) in newborn babies and gastric cancer in adults (WHO, 2017). To the high concentration of nitrate in groundwater, pregnant women, children, and infants are at higher risk (Eggers et al., 2018). Other associated diseases with the prolonged ingestion of nitrate-contaminated water are thyroid disorders, teratogenesis, abortions, cancer-causing, and mutagenesis (Wu et al., 2018). Various studies have been conducted in different districts of Rajasthan state to evaluate the groundwater quality, especially in reference to fluoride and nitrate (Ahada & Suthar, 2017; Chaudhary & Satheeshkumar, 2018; Jandu

et al., 2021; Joshi & Seth, 2011; Suthar et al., 2008, 2009). A study conducted by Jandu et al. (2021) in the present study area indicated the significant health effects due to the intake of fluoride and nitrate in groundwater but limited to a very small geographical area. No such detailed study has been conducted to evaluate the potential health effects due to intake of fluoride and nitrate through groundwater in Jhunjhunu district of Rajasthan. The present study will help the concerned to take appropriate measure for safe and pure drinking water. The objectives of this study envisage (1) appraising the groundwater quality in reference to fluoride, nitrate, and other water quality parameters by comparing with BIS and WHO; (2) the critical non-carcinogenic health risk and impacts due to prolonged consumption of fluoride and nitrate-contaminated groundwater; (3) the overall potability of water was evaluated using the water quality index; and (4) the PCA and correlation study estimated the major factors responsible and the possible interaction on these anions and cations in groundwater.

Study region

Jhunjhunu district is situated in Rajasthan State's extreme northeastern region, bordering the state of Haryana, and is situated between latitudes 27° 38' and 28° 31' north and longitudes 75° 02' and 76° 06' east, as depicted in Fig. 1. It covers an area of 5928 km². It is considered to be one of the prosperous regions of Rajasthan. This region primarily has a semi-arid kind of environment. Temperature ranges from 32 to 48 °C in the summer season (March–November), while in winter, it ranges from 1 to 15 °C. The colder time of year is from December to February. The monsoon season extends from June to September. The typical yearly precipitation of the area is 565 mm. The chief crops grown in this region are Bajra, wheat, jawar, maize, oilseeds, and oats (Jandu et al., 2021).

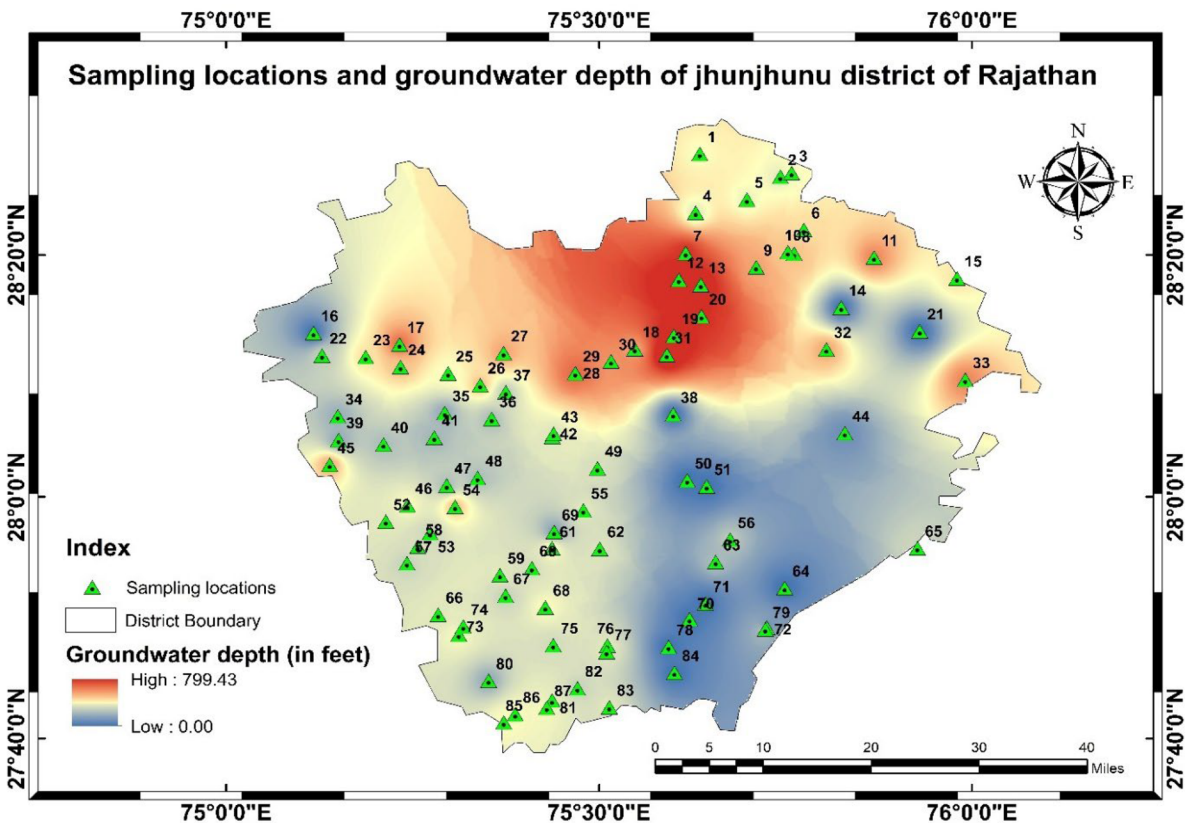
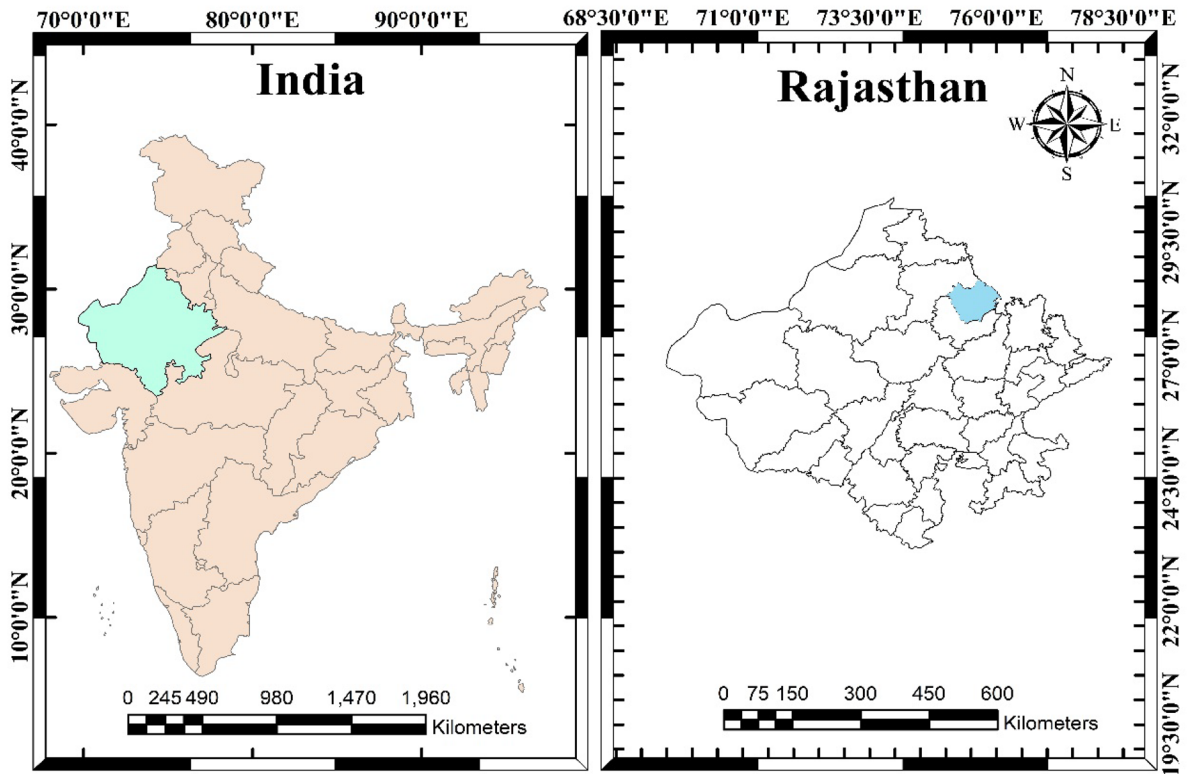
Geomorphology and drainage system

The hills of the Aravalli range, which run in a north-easterly direction, are what define the mountainous area in the district's south-eastern corner. The tallest mountain, which is 1051 m high, is located south which borders Sikar district. Khetri and Udaipurwati

tehsils contain the majority of the hills. With the exception of a few acacia and cactus, hills are nearly devoid of vegetation. The overall height above mean sea level ranges from 300 to 450 m. The northern portion of the district is occupied by the desertic plain, which is typically at an altitude of around 300 m and is covered in sand dunes. The terrain generally slopes from south to north. The region has desertic soil having an inland draining pattern. It is mostly a part of the Sekhawati basin, and the northwest portion is outside the basin and has inland drainage. Mostly, the Kantli River drains the region. Singhana River drains the region in the district's southeast, and Budhi Nala drains a small portion of the district's southwest (CGWB, 2008). The Dohana River drains the south and east hill ranges in the Khetri region. All of the rivers/nalas are transient and only flow in response to monsoon-related high precipitation.

Hydrogeological structure and stratigraphy

The hydrogeological groundwater holding structure and formation are unconsolidated quaternary alluvium in the present study area. The primary water-bearing formation in the district is quaternary alluvium, which occupies 4663 km² (or 78.70% of the district), and hard rocks from the Delhi Super Group 11, including the post-Delhi intrusive of lower-Proterozoic era, which make up accessory aquifers on 1265 km² (or 21.30% of the district) (CGWB, 2021). The primary and potentially available aquifer in the region is alluvium, which is made up of sand, silt, clay, kankar, and gravel. Alluvial sediment deposition increases from the district's southern (< 60 m) to northern and northern-eastern portions (> 100 m). The south-eastern portion of the district, which includes parts of the Khetri and Buhana blocks, is covered by quartzite, schist, phyllite, gneisses, and limestone of the Delhi Super Group, as well as granites, amphibolites, and pegmatites of post-Delhi intrusives (CGWB, 2008). These rocks also make up the ancillary aquifer. Further, deep buried structures such as fractures, joints, contacts, and other hard formation are present where groundwater occurs under unconfined to semi-confined conditions. Groundwater is the main hotspot for the water system here. Soils of Jhunjhunu area are sandy to loamy sand, non-calcareous, structureless, free, and very well-drained (CGWB, 2008). The



◀**Fig. 1** Map showing the location of the study area and sampling points

majority of soil type is desertic (which covers 45% area) sand dunes (which cover 36% area), and some parts have red desertic, lithosols, and older alluvium types. Around here, the significant wellspring of water is groundwater and extracted through handpump, tube well, and open or bore well for drinking and agrarian purposes (CGWB, 2008).

Materials and methods

Sampling

A total of 87 samples are collected from the district to cover most of the part of the area in December, 2021, as shown in Fig. 1. Pre-treated polyethylene bottles (soaked with 10% HNO₃ acid overnight and rinsed with distilled water multiple times to remove the impurities clinging to the interior wall of the bottle) were used for the collection of groundwater samples. The sampling source (hand pump, tube well, municipality submersible) was allowed to run for 2–3 min to discard the water that is in the pipe to get the homogeneous and fresh sample from the source. Sample bottles were rinsed with source water to be collected to remove any traces of acid or distilled water to reduce the chances of error.

Physiochemical analysis of water quality parameters

A total of 16 water quality parameters were determined to evaluate the quality and potability of groundwater. Seven in situ water quality parameters

to minimize the change in water properties. The total hardness (TH) and total alkalinity (TA) were determined by titrating with standard solution of EDTA and H₂SO₄. Calcium hardness was estimated by titrating with standard EDTA, and magnesium hardness was calculated by subtracting calcium hardness from total hardness. Carbonate and bicarbonate were computed through alkalinity relationships. The chloride was determined by the argentometric method (BIS, 2012). The fluoride, sulfate, nitrate, and phosphate were estimated by photo-spectrometry (UV-visible spectrophotometer, Labman) using the SPADNS dye method, turbidity method, UV spectrophotometric method, and stannous chloride method, respectively, as per the standard protocol of APHA (2017).

Estimation of health risks due to fluoride and nitrate

The fluoride and nitrate contamination are generally higher in groundwater compared to surface water (Shirke et al., 2020), and exposure due to contaminated water can be through two pathways, i.e., ingestion and dermal contact. The dermal route of exposure is considered negligible in respect to the oral route of exposure (Jandu et al., 2021). The human health risk was estimated for three groups of populations, i.e., male, female, and children, for both fluoride and nitrate. Fluoride and nitrate are considered non-carcinogenic for human health. This method of non-carcinogenic human health risk assessment is widely used for the estimation of risk due to the consumption of contaminated water (Adimalla, 2019; Ali et al., 2019; Rao et al., 2020; Satyanarayana et al., 2017). The chronic daily intake dose (CDID) was calculated as per Eq. (1) given below.

Chronic Daily Intake Dose (mg/kg/day)

$$= \frac{\text{Concentration of Fluoride or Nitrate } (C_f) \text{ or } (C_n) \times \text{Daily water Intake (DWI)} \times \text{Average Lifetime (AL)} \times \text{Exposure Frequency(EF)}}{\text{Mean Body Weight (MBW)} \times \text{Mean Age Exposure Duration(MAED)}} \tag{1}$$

(pH, EC, TDS, salinity, DO, ORP, and temperature) were determined in the field itself using portable water sensors (Water Analyser, 371, Systronic, India). The portable water quality sensors were calibrated with known standards All other lab parameters were analyzed within 72 h of sample collection

The parameters used in the above equation are as per the latest recommendation of USEPA (2017), and some parameters are adjusted as per regional statistical data of the studied area. The details of different parameters used in the health risk assessment are described in Table 1.

Table 1 Parameters values used for the estimation of CDID for fluoride and nitrate

S. No.	Parametric symbol	Parameter description	Units	Values	Source references
1	C_f	Concentration of fluoride in groundwater	mg/L		Observed in this study
2	C_n	Concentration of nitrate in groundwater	mg/L		Observed in this study
3	DWI	Daily water intake	L/day	Adult, 2.5 Children, 1.5	WHO (2017), USEPA (2014), Wagh et al. (2019)
4	AL	Average life time	Years	Male, 65.5 Female, 70.2 Children, 12	NITI Aayog (2020)
5	EF	Exposure frequency	Days/year	365	USEPA (2014)
6	MBW	Mean body weight	Kg	Male, 60 Female, 55 Children, 35	Nair and Augustine (2018) NIN-ICMR (2011)
7	MAED	Mean age exposure duration	Days	Male, 23,908 Female, 25,623 Children, 4380	

Hazard quotient

The hazard quotient was calculated as the ratio of chronic daily intake dose and reference dose (RD) of chronic oral exposure. The reference doses for fluoride and nitrate are 0.04 mg/kg/day and 1.6 mg/kg/day (USEPA, 2020). It was calculated by Eq. (2)

$$\text{Hazard quotient} = \frac{\text{Chronic Daily Intake Dose (mg/kg/day)}}{\text{Reference dose(mg/kg/day)}} \tag{2}$$

Hazard index

The hazard index was estimated by adding the hazard quotient due to the non-carcinogenic risk associated with the consumption of fluoride and nitrate in drinking water. It was computed using Eq. (3) as

$$HI = HQ_f + HQ_n \tag{3}$$

where HQ_f is the hazard quotient due to fluoride and HQ_n is due to nitrate present in water. The value of the hazard index greater than one is indicating significant non-carcinogenic health hazard due to consumption of contaminated water. Its value below one indicates that no significant health hazard is associated with the consumption of water (USEPA, 2014).

Water quality index (WQI)

Water quality index is a mathematical technique to determine the acceptability of groundwater for drinking purpose by considering the effect of individual parameters (Subba Rao et al., 2019). The quality of water is decided on the basis of calculated WQI as shown in Table 2. It was calculated by the weighted arithmetic index method using Eq. (4) (Brown et al., 1970)

$$WQI = \frac{\sum W_n \times Q_n}{\sum W_n} \tag{4}$$

where W_n is the unit weight of n^{th} parameter considered in calculating the water quality index (Table 3)

Table 2 Water quality index, their respective grade, and possible usage

Water quality index	Water grade	Possible usage
0–25	Excellent	Drinking, irrigation, and industrial
26–50	Good	Drinking, irrigation, and industrial
51–75	Poor	Irrigation and industrial
76–10	Very poor	Irrigation
< 100	Not suitable for drinking	Require treatment before use

and Q_n is the quality rating of n^{th} parameter taken to calculate the WQI. Unit weight (W_n) is calculated by Eq. (5):

$$W_n = \frac{k}{S_n} \tag{5}$$

where k is the constant proportionality and S_n is the permissible limit for a particular water quality parameter given by the standard agency and calculated as per Eq. (6):

$$\text{Percentage of ion balance error} = \frac{\sum \text{cations (meq/L)} - \sum \text{anions (meq/L)}}{\sum \text{cations (meq/L)} + \sum \text{anions (meq/L)}} \times 100 \tag{8}$$

$$k = \frac{1}{\sum 1/S_n} \tag{6}$$

Quality rating (Q_n) was calculated using Eq. (7):

$$Q_n = \frac{(P_n - C_i)}{(S_n - C_i)} \times 100 \tag{7}$$

where P_n is the actual value of the water parameter and C_i is the ideal concentration of the parameter and is considered as 0 (zero) except for pH and DO which are taken as 7 (neutral) and 14.6 mg/L, respectively.

Table 3 Water quality parameter, relative weight index, and permissible limits (Brown et al., 1970)

S. No.	Parameters	$W_n = K/S_n$	$1/S_n$	Permissible limits (WHO, 2017)
1	pH	0.142	0.118	8.5
2	TDS (mg/L)	0.001	0.001	1000
3	EC (μS/cm)	0.001	0.001	1500
4	F ⁻ (mg/L)	0.802	0.667	1.5
5	Cl ⁻ (mg/L)	0.005	0.004	250
6	NO ₃ ⁻ (mg/L)	0.024	0.020	50
7	SO ₄ ²⁻ (mg/L)	0.005	0.004	250
8	Total hardness (mg/L)	0.002	0.002	500
9	Total Alkalinity (mg/L)	0.002	0.002	500
10	Ca ²⁺ (mg/L)	0.004	0.003	300
11	Mg ²⁺ (mg/L)	0.012	0.010	100

Quality control and assurance

All the chemicals were used of analytical grade, and double distilled water was used throughout all analytical measurements. The analysis of water quality was ensured through procedural blank measurements, careful standardization, and spiked and triplicate measurements. The ion balance error percentage was estimated to ensure the accuracy of ions analysis. The ion balance error percent was estimated using Eq. (8):

The concentration of ions was converted from mg/L to meq/L by Eq. (9):

$$\text{Cations or anions (meq/L)} = \frac{\text{Ion concentration} \left(\frac{\text{mg}}{\text{L}} \right) * \text{Valency}}{\text{molecular weight}} \tag{9}$$

The percentage of ions balance error estimated for each sample was below 10% percent, which reflects the accuracy and reliability of analytical data (Rao et al., 2020). The reproducibility of analytical data was below 5%.

Statistical analysis

Descriptive statistical analysis of water quality data was performed using Microsoft Excel professional plus 2019, and principal component analysis (PCA) was performed using Origin 2019 software. The correlational analysis aids to determine the dependence and independence of water quality parameters. The significance of the Pearson correlation coefficient between the two parameters was determined with a 0.05 and 0.01 alpha level and a 95% and 99% confidence interval, respectively, and it was estimated using Origin 2019. PCA is a common method for reducing data complexity and helps to infer major factors influencing the water quality. In this study, the sources of pollutants were revealed using PCA, and result revealed different combinations of the ions in form of PCs, which inferred origins and sources of the geochemical processes as well as the poor quality of the groundwater.

Results and discussion

Groundwater quality analysis

As the area comes under the arid and semi-arid region of India, the surface water resources are less, and groundwater is primarily used for drinking purposes by the residents of the area. Comprehensive sampling was employed to assess the groundwater quality of Jhunjhunu district of Rajasthan. In the present study, 87 groundwater samples were collected, and the samples were clear, odor-free, and potable. The collected samples are analyzed for 16 water quality parameters, and the summary of all parameters is shown in Table 4. The pH was found to vary from 6.6 to 9.1 with a mean and median value of 8.2 and 8.3, respectively. The pH decides the acidic and basic nature of water which depends on equilibrium of CO_2 - CO_3^{2-} - HCO_3^- (Hem, 1991; Subba Rao, 2018). The pH value in 76% of samples was within the prescribed limit, and 34% of samples were observed to have pH in the alkaline range, greater than recommend limit of BIS and WHO. The recommended pH range for drinking water should be 6.5–8.5 (BIS, 2012). The similar pH range was also reported in northern Rajasthan (Ahada & Suthar, 2017). TDS value was observed in the range between 170 and 4205 mg/L with an average value of 908 mg/L. TDS value in 75% of samples was higher than the desirable limit of 500 mg/L as per BIS. In 2% of samples, TDS was observed to be exceeded the permissible limit of 2000 mg/L, prescribed by BIS. In 34% of samples, TDS was higher than the recommended limit of WHO. As per the Freeze and Cherry (1979) classification shown in Table 5, 57 samples are placed under the category of fresh water, while the rest of the 30 samples are of brackish type (Freeze & Cherry, 1979). A material's ability to carry an electric current is measured by its electrical conductivity (EC), and a greater EC implies that the groundwater is more enriched in salts. The electrical conductivity in groundwater samples was observed to be varying from 265 to 6570 $\mu\text{S}/\text{cm}$ with a mean value of 1422 $\mu\text{S}/\text{cm}$. EC value less than 1500 $\mu\text{S}/\text{cm}$ indicates low enrichment of salts, classified as type I. If the EC value lies between 1500 and 3000 $\mu\text{S}/\text{cm}$, it indicates the moderate enrichment of salts, classified as type II. If the EC value is greater than 3000 $\mu\text{S}/\text{cm}$, it indicates the high enrichment of salts, classified as type III (Subba Rao et al., 2012). EC value in 40% of samples was higher than the recommended limit of 1500 $\mu\text{S}/\text{cm}$

as per BIS and WHO, while others were within the standard limit. Thirty eight percent of samples had moderate enrichment of salts, while 2% of samples had high enrichment of salts from source rocks. This is because moderate and high salts enriched water samples belong to topographic lows (northern region) and follow the underground stream flow (Subba Rao et al., 2012). The EC also depends upon the dissolved salts and comes from the leaching and dissolution of localized aquifer material (Hem, 1991). ORP (oxidation–reduction potential) is an important parameter to know the nature and quality of water. ORP was found to vary from 15 to 197 mV. It indicates the prevailing oxic (oxidizing) nature of water, which is considered to be good. The salinity value was observed to range between 125 and 3088 mg/L with a mean value of 667 mg/L. The fluoride level in 79% of samples was within the permissible limit of BIS. The desirable limit of fluoride in groundwater is 1.0 mg/L as per BIS, while the permissible limit is 1.5 mg/L as per BIS and WHO (BIS, 2012; WHO, 2017). 1 mg/L fluoride in water is required microbial protection and delays tooth decay, while its concentration greater than 1.5 mg/L can cause skeletal and dental fluorosis. The cases of such problems as dental fluorosis, yellowing of teeth, pain in legs and shoulders, bone twisting, and deformities are enhanced by the high concentration of fluoride in groundwater (Kothari et al., 2021). In our study, 11% of samples were observed to have fluoride levels higher than the permissible limit of BIS and WHO. The fluoride in groundwater samples of Doodi (2.58 mg/L), Ladunda (3.16 mg/L), Dulaniya (3.06 mg/L), Pilod (2.59 mg/L), Surajgarh (3.30 mg/L), Kasani (2.46 mg/L), Bakatwarpara (3.43 mg/L), Ojtu (3.13 mg/L), Brijlalpura (1.58 mg/L), and Birol (1.93 mg/L) was higher than threshold limit of 1.5 mg/L as per BIS and WHO recommendation. Both natural (geogenic) and anthropogenic sources contribute to fluoride in groundwater. The minerals such as apatite, biotite, hornblende, and clay are the natural contributor, while agricultural fertilizers especially phosphatic are the anthropogenic contributor of fluoride in groundwater in basic environment (Subba Rao, 2018). Previous investigation in northern Rajasthan conducted by Suthar et al. (2008) overserved that 90% of the samples were having the fluoride content higher than recommended limit of BIS. The distribution of fluoride in Jhunjhunu is shown in Fig. 2. North and northeastern parts are majorly influenced by fluoride contamination in groundwater as

Table 4 The minimum, maximum, mean, and median along with no. of samples above the desirable and permissible limit of BIS and WHO

S. No.	Parameters	Minimum	Maximum	Mean	Median	BIS (2012)		BIS (2012)		WHO (2017)	
						Desirable limit	Permissible limit	No. of samples above desirable limit (percentage)	No. of samples above permissible limit of WHO (2017) (%)	Desirable limit	Permissible limit
1	pH	6.55	9.18	8.24	8.30	6.5–8.5	6.5–8.5	30 (34%)	30 (34%)	6.5–8.5	30 (34%)
2	TDS (mg/L)	170	4205	908	858	500	2000	65(75%)	2 (2%)	600–1000	33(38%)
3	EC (µS/cm)	265	6570	1422	1342	1500	1500	35(40%)	35(40%)	-	-
4	ORP (mV)	15	197	96	96	-	-	-	-	-	-
5	Salinity (mg/L)	125	3088	667	631	-	-	-	-	-	-
6	DO (mg/L)	0.00	9.10	1.14	0.00	-	-	-	-	-	-
7	Fluoride (mg/L)	0.14	3.43	0.81	0.60	1	1.5	18(21%)	10(11%)	1.5	10(11%)
8	Chloride (mg/L)	4.30	986.40	157.61	130.40	250	1000	15(17%)	NS	200	24(28%)
9	Nitrate (mg/L)	2.90	115.00	25.75	23.00	45	45	7(8%)	7(8%)	50	5(6%)
10	Sulfate (mg/L)	1.90	449.20	75.23	53.16	200	400	7(8%)	1(1%)	250	5(6%)
11	Phosphate (mg/L)	BDL	BDL	-	-	-	-	-	-	-	-
12	TH (mg/L)	37	928	214	175	200	600	35(40%)	2(2%)	100	75(86%)
13	Ca ²⁺ (mg/L)	9.60	277.60	53.97	46.20	75	200	15(17%)	1(1%)	75	15(17%)
14	Mg ²⁺ (mg/L)	2.76	110.40	18.93	15.27	30	100	13(15%)	1(1%)	50	6(7%)
15	TA (mg/L)	100	1000	397	300	200	600	71(81%)	16 (18%)	-	-
16	Bicarbonate(mg/L)	100	1000	397	300	-	-	-	-	-	-

Table 5 Water type is based on TDS (Freeze & Cherry, 1979)

Water type	TDS range (mg/L)	No. of samples
Fresh	Less than 1000	57 (66%)
Brackish	1000–10,000	30 (34%)
Saline	10,000–100,000	-
Brine	Higher than 10,0000	-

shown in Fig. 2. Except in 17% of samples, the chloride was lower than the desirable limit of 250 mg/L as per BIS recommendation. No sample of chloride was higher than the permissible limit of BIS. The permissible limit of chloride in drinking water as per WHO is 200 mg/L (WHO, 2017). Twenty eight percent of samples were having the chloride content higher than the standard limit of WHO. Along with geological composition, chloride concentration in groundwater

is influenced by anthropogenic activities consisting of improper management of septic tanks, sewage disposal, and animal waste, which causes the mixing of sewage in the groundwater table (Rao et al., 2021b). However, it also depends upon the soil porosity and rock permeability of the area (Kothari et al., 2021).

The nitrate in groundwater samples of Jhunjhunu district was observed to be varying from 2.90 to 115.00 mg/L with a mean value of 25.75 mg/L. Groundwater with NO_3^- concentrations lesser than 45 mg/L poses no health risk. Between 45 and 100 mg/L, the health risk is high, and beyond 100 mg/L, health risk is extremely significant (Rao et al., 2020). The desirable/acceptable limit of nitrate in drinking water is 45 mg/L with no relaxation (BIS, 2012). Eight percent of the samples were having nitrate levels higher than the standard limit as per BIS, while 5% of samples exceeded the recommended limit as per WHO.

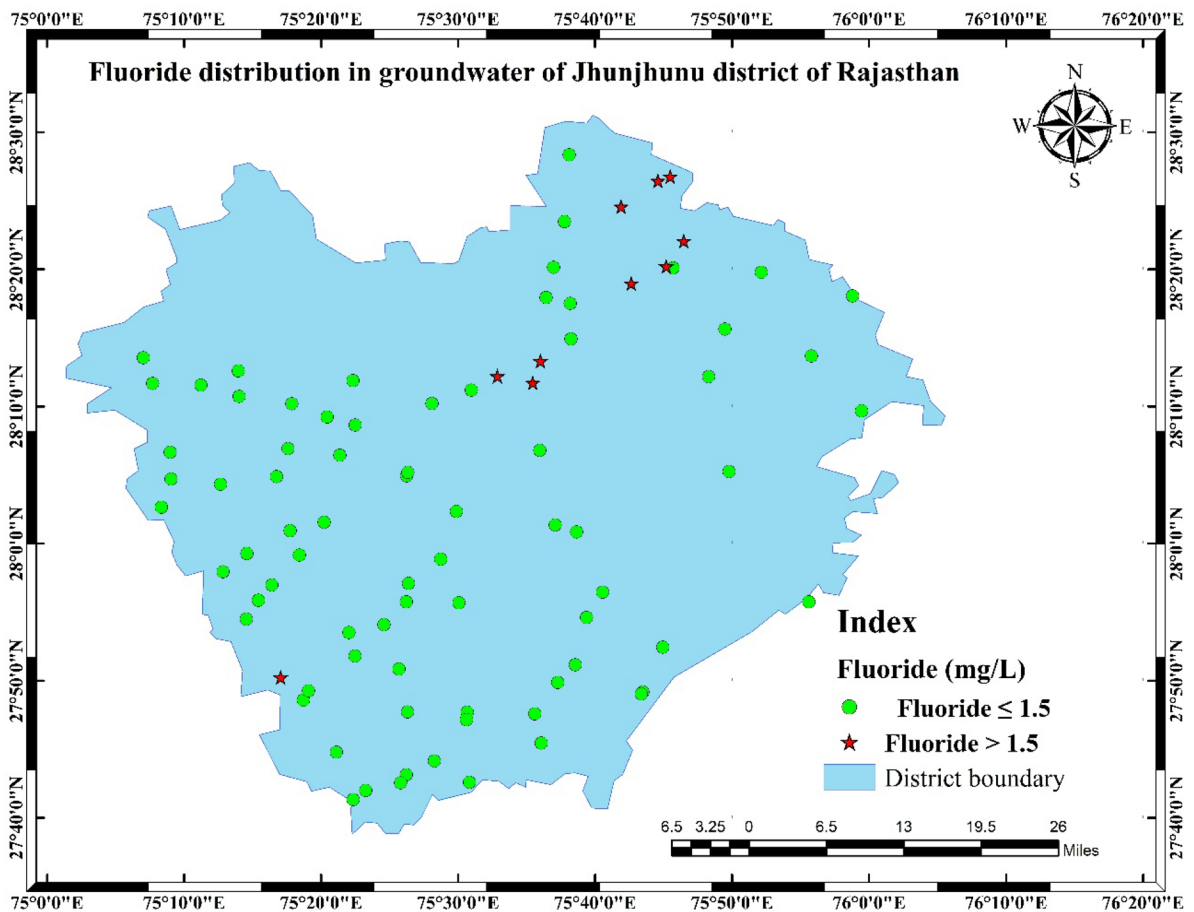


Fig. 2 Spatial distribution map of fluoride distribution of Jhunjhunu district of Rajasthan

The nitrate in groundwater samples of Bangothari (115 mg/L), Doodi (71 mg/L), Jeeni (52 mg/L), Kasani (49 mg/L), Chirawa (56 mg/L), Brijlalpura (46 mg/L), and Raipur (85 mg/L) was higher than threshold limit of 45 mg/L as per BIS recommendation. Similar to Cl^- , nitrate has also non-lithological source (Hem, 1991). In water, it does not get above 10 mg/L under natural circumstances (Rao et al., 2021b). Therefore, the increasing NO_3^- content above this threshold is a sign of human-caused pollution (Wu & Sun, 2016). The possible source of nitrate contamination includes sewage waste, septic tank leaks, agricultural fertilizer, and animal waste on the aquifer system resulting in NO_3^- contamination of groundwater (Ullah et al., 2022).

The observed results of nitrate congrued with previous investigations of the study area (Jandu et al., 2021). The high content of nitrate is associated with various diseases like methemoglobinemia, thyroid disorders,

teratogenesis, abortions, cancer-causing, and mutagenesis (Wu et al., 2018). Similar to fluoride, the North and northeastern region is primarily influenced by nitrate contamination in groundwater as shown in Fig. 3.

The sulfate in 7% of samples was higher than the desirable limit of 200 mg/L as per BIS, while in 1 sample, it exceeded the permissible of 400 mg/L, prescribed by BIS. The high sulfate content can produce a bad taste in the water. Besides anthropogenic inputs such as soil amendment using gypsum and sulfate fertilizers; sulfates from minerals of aquifer dissolve in groundwater (Subba Rao, 2018). The phosphate content in all collected water samples was below the detection limit. The total hardness (TH) was observed to be varying from 37 to 928 mg/L with a mean value of 214 mg/L. Forty two percent of groundwater samples were observed as a very hard category. Only 2% of samples were observed

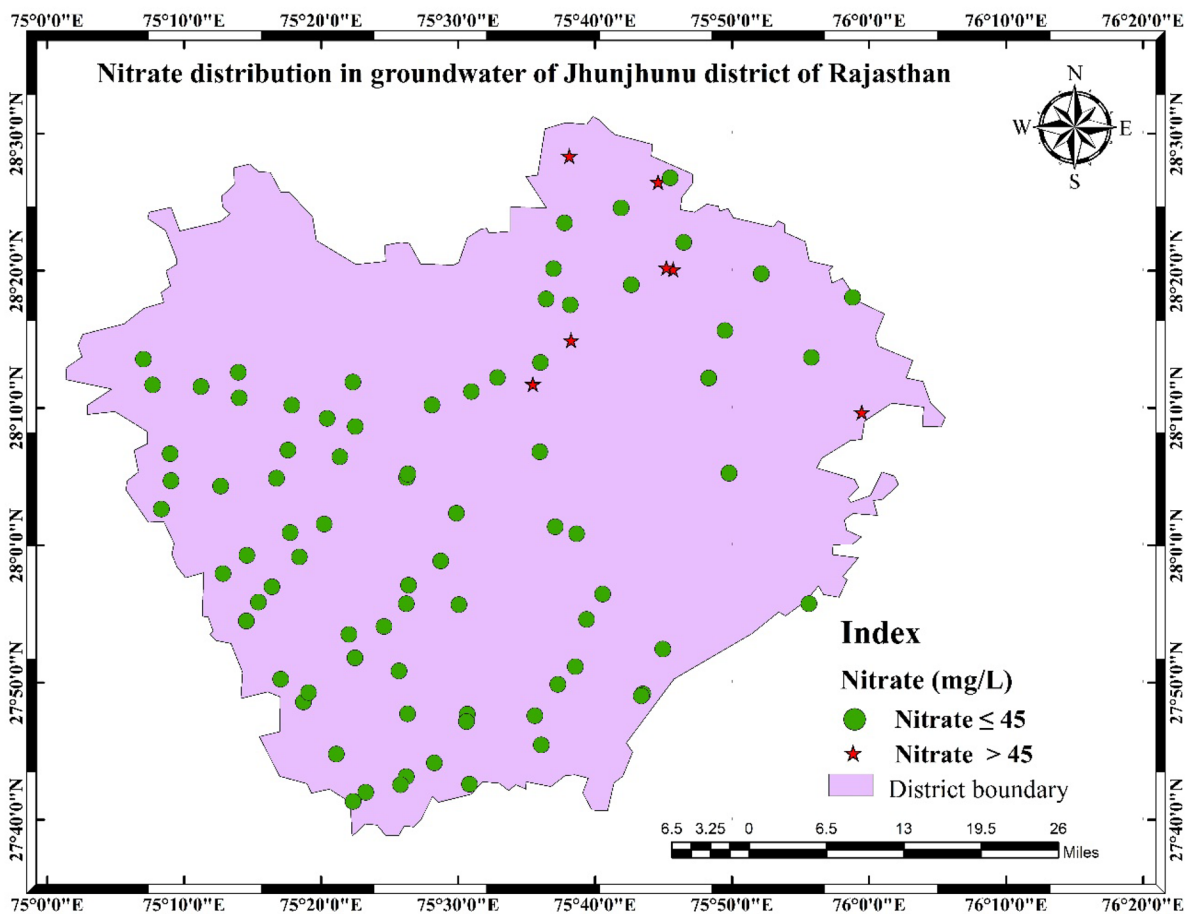


Fig. 3 Spatial distribution map of nitrate distribution of Jhunjhunu district of Rajasthan

to lie in the soft category. A detailed description of the hardness categories of all samples is shown in Table 6.

The acceptable and permissible limits of hardness in drinking water samples are 200 mg/L and 600 mg/L, respectively (BIS, 2012). In 35% of groundwater samples, the hardness value was above the desirable limit, while in 2% of samples, it was higher than the permissible limit. The total hardness value only in 14% of samples was below the permissible limit, and the rest of 86% of the samples were above the standard limit of 100 mg/L as per WHO. The hardness in groundwater comes from the dissolution of major cations such as calcium and magnesium which is attributed to the geology of the area. The primary source of TH in groundwater is the weathering and dissolving of calcium- and magnesium-bearing rocks (Ahada & Suthar, 2017). The calcium content was observed in between the range of 9.60–277.60 mg/L with an average of 53.97 mg/L. The acceptable and permissible limit for calcium is 75 mg/L and 200 mg/L, respectively (BIS, 2012). Only 1% of the samples was having calcium content higher than the permissible limit, but 17% of samples crossed the desired limit of calcium as per BIS and WHO. The magnesium content in 15% of samples had exceeded the desirable limit of BIS, but only in 1% of samples, it was crossed the permissible limit. The total alkalinity in 81% of samples was greater than the desirable limit of 200 mg/L, but in 18% of samples, it passed the permissible limit of 600 mg/L as per the BIS. As the samples were devoid of hydroxyl and carbonate alkalinity, therefore, total alkalinity was due to bicarbonate which was observed to vary from 100 to 1000 mg/L with a mean value of 397 mg/L. The soil atmosphere has higher partial pressure of CO₂ as the consequence of decomposing organic materials and root respiration. The soil CO₂ enters into the groundwater system and reacts with water to create HCO₃⁻. Higher HCO₃⁻ in water suggests that mineral dissolution is more prevalent (Stumm & Morgan, 1981).

Table 6 Groundwater type based on hardness

Hardness range	Water type	Samples (percentage)
0–60	Soft	2 (2%)
61–120	Moderately	16 (19%)
121–180	Hard	27 (31%)
> 180	Very hard	42 (48%)

Box and whisker plot

The box plots are an easy way to diagrammatically represent the statistical parameters and the data distribution. The box plots are drawn for TDS, EC, salinity, total alkalinity, ORP, chloride, sulfate, total hardness, calcium, magnesium, fluoride, and nitrates as shown in Fig. 4.

The lower line, middle line, and upper line of the box represent the 25th percentile (first quartile), 50th percentile (median), and 75th percentile (third quartile). The lower whisker of the plot was calculated by subtracting 1.5 times of IQR (interquartile range) from the first quartile of data, while the upper whisker was calculated by adding the 1.5 times of IQR (interquartile range) in the third quartile of data. The lower dot represents the lower outlier values of data; on the other hand, upper dot represents the higher side outlier values of data. In all box plots, the square sign represents the mean value of data. Debarring ORP, the mean value of TDS, EC, salinity, chloride, sulfate, total hardness, calcium, magnesium, total alkalinity, bicarbonate, fluoride, and nitrate is greater than the median value. This shows that data in the case of the aforementioned parameters are positively skewed. The long whiskers represent the greater variation observed in analytical data.

Correlation analysis

Correlation analysis is done to know the possible correlation between the water quality parameters as shown in Table 7. Pearson correlation coefficient estimates the negative and positive correlation between the parameters. Twelve parameters (pH, TDS, EC, ORP, salinity, DO, fluoride, chloride, nitrate, sulfate, TH, and TA) were taken into consideration to calculate the correlation coefficient. However, the correlation between the 2 parameters is just not relied on the value of Pearson's correlation coefficient but also on the level of significance of the analysis as done by the *t*-test. Two-tailed *t*-test was applied and a *p* value was calculated. The coefficient bearing *p* value less than 0.05 (95% level of significance) is considered significant, marked by a single asterisk, while the *p* value for.

the correlation coefficient is less than 0.01 (99% level of significance), considered highly significant as shown in Table 7. EC, TDS, and salinity are linearly

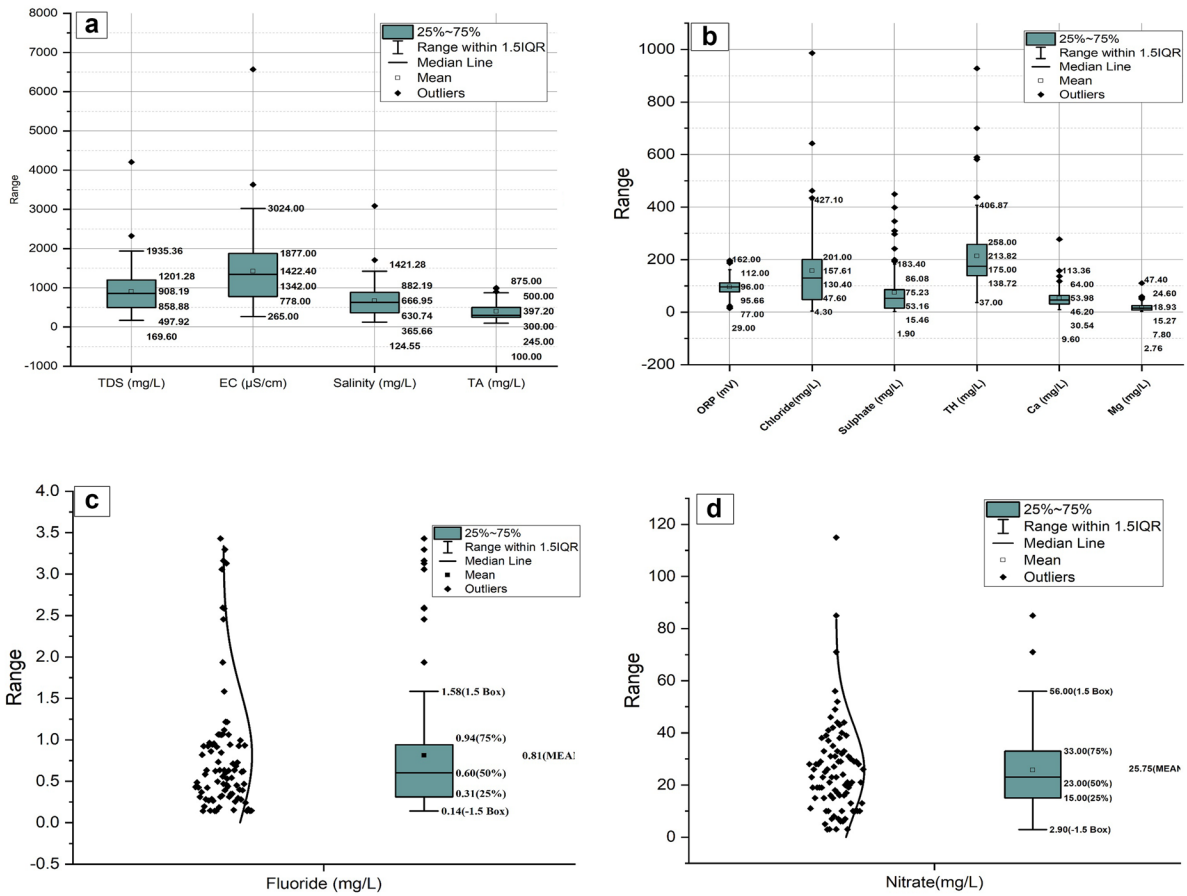


Fig. 4 a Box and whisker plot of TDS, EC, salinity and total alkalinity. b Box and whisker plot of ORP, chloride, sulfate, total hardness, calcium, and magnesium. c Box and whisker plot of fluoride. d Box and whisker plot of nitrate

correlated, and the *p* values' state correlation coefficient is significant because the estimation of parameters is interdependent. TDS was found to be correlated with chloride ($r=0.484^{**}$), nitrate ($r=0.473^{**}$), sulfate ($r=0.403^{**}$), total hardness($r=0.395^{**}$), and total alkalinity (0.674^{**}). The correlation of TDS with these parameters is highly significant (marked with double asterisks showing the *p* value is less than 0.01) indicating the leaching of anions and cations from rocks into groundwater due to the long-term flow of water in the groundwater zone. Fluoride showed a weak negative correlation with pH, while a weak positive correlation with total hardness and total alkalinity, but no one was observed to have a significant correlation. Total alkalinity (TA) was found with a positive significant correlation with total hardness ($r=0.426^{**}$) and nitrate ($r=0.486^{**}$). If the

correlation between two parameters is less than 0.500 and statistically significant, then parameters are said to be weakly correlated, and this correlation is not by chance (Bhardwaj et al., 2020; Taylor, 1990). A similar trend of correlation in the water quality parameters was reported in the study groundwater of Rajasthan by Joshi and Seth (2011) and Singh and Mukherjee (2014).

Health risk analysis due to fluoride and nitrate

As fluoride and nitrate in the studied area were higher than the permissible limits of BIS and WHO, therefore, the health risk assessment had been done, and the estimated chronic daily intake dose (CDID) for males, females, and children is detailed in Table 1 (supplementary information). The CDID estimates

Table 7 Pearson's correlation matrix of water quality parameters

	pH	TDS (mg/L)	EC (μ S/cm)	ORP (mV)	Salinity (mg/L)	DO (mg/L)	Fluoride (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Sulphate (mg/L)	TH (mg/L)	TA (mg/L)
pH	1.000											
TDS (mg/L)	-0.239*	1.000										
EC (μ S/cm)	-0.238*	1.000**	1.000									
ORP (mV)	-0.357**	-0.002	-0.001	1.000								
Salinity (mg/L)	-0.239*	1.000**	1.000**	-0.002	1.000							
DO (mg/L)	-0.241*	-0.170	-0.172	0.206	-0.170	1.000						
Fluoride (mg/L)	-0.006	-0.030	-0.029	-0.042	-0.030	-0.196	1.000					
Chloride (mg/L)	0.271*	0.484**	0.485**	-0.240*	0.484**	-0.341**	0.113	1.000				
Nitrate (mg/L)	-0.147	0.473**	0.476**	-0.201	0.473**	-0.257*	0.173	0.128	1.000			
Sulphate (mg/L)	0.038	0.403**	0.401**	-0.055	0.403**	-0.255*	-0.103	0.442**	0.018	1.000		
TH (mg/L)	-0.289**	0.395**	0.394**	0.314**	0.395**	-0.227*	0.052	0.063	0.162	0.121	1.000	
TA (mg/L)	-0.259*	0.674**	0.672**	-0.152	0.674**	-0.135	0.171	0.357**	0.486**	0.161	0.426**	1.000

* p value < 0.05; ** p value < 0.01

the fluoride or nitrate taken by males, females, and children as per specific parameters prescribed for different gender and age criteria of residents of the region. The hazard quotients (HQ) determine the non-carcinogenic risk associated to consume water containing fluoride and nitrate. A value of HQ (separately for fluoride and nitrate) greater than 1 indicates a significant health hazard due to the consumption of fluoride and nitrate-contaminated water. Hazard index (HI) was calculated by the addition of HQ values from fluoride and nitrate. HI greater than one indicates significant hazards due to the consumption of fluoride and nitrate-contaminated water as per USEPA (2014). The HI value for males, females, and children was estimated to range from 0.30–4.54, 0.33–4.95, and 0.31–4.67 respectively. The representation of the HI value for groundwater samples is greater than one is indicated by red stars, while less than one is indicated by the green stars for males, females, and children as shown in Fig. 5. The HI values of 71% of groundwater samples for males, 78% groundwater samples for females, and 75% groundwater samples for children were greater than 1, indicating significant health hazards due to consumption of groundwater. HI value was most significant for

females because of the highest average lifetime and exposure duration among the three. The order of hazard index in decreasing order was as female > children > male. A similar order of hazard index was observed in another study conducted on a small region of the study area (Jandu et al., 2021).

Water quality index (WQI)

The water quality index was computed to consider the contribution of all parameters toward overall water quality and potability. The water quality index was observed to be varying from 13 to 196. The different WQI categories and the number of samples with their cumulative percentage are shown in Fig. 6. The different range of observed WQI in the study area is represented by colors shown in Fig. 7. It was found that 28% and 47% of samples were observed to lie in the excellent and good categories, respectively, which can be used for drinking, irrigation, and industrial usage. Twenty eight percent of groundwater samples were observed in the poor category of WQI and cannot be utilized for drinking purposes but are suitable for industrial and irrigational purposes. Jandu et al. (2021) in their study of some villages in the

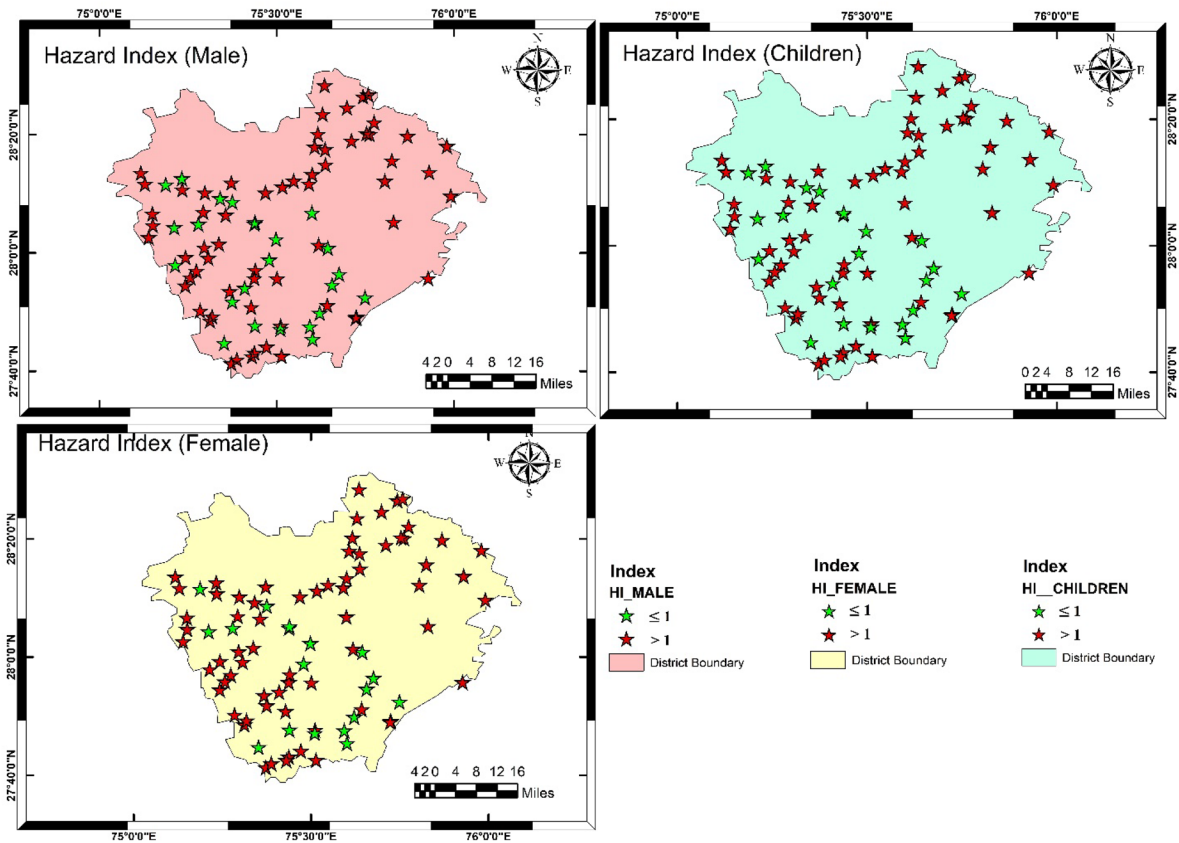


Fig. 5 HI presentation for males, females, and children due to fluoride and nitrate-contaminated groundwater

district concluded that 32.14% of groundwater samples belong to categories of water quality which is not suitable for drinking purposes.

A small fraction, i.e., only two samples were observed to be lying in the very poor WQI category and can be used for irrigational usage only. 9% of samples of Jhunjhunu district were observed to have WQI higher than 100, indicating the worst quality of water which cannot be used for any purpose at all. The groundwater of these locations demands some kind of treatment before use. Except for one sample, all these samples, having WQI greater than 100, belong to the northern part of the district. This part of the district was found to have maximum fluoride and nitrate contamination in groundwater.

Principle component analysis

Principle component analysis (PCA) is a multivariate statistical analysis tool that reduces a large number

of variables into a few principle components (PCs) which account for the most of variance in the data (Krishan et al., 2022; Panghal et al., 2021). A huge dataset’s variation and compositional patterns can be explained using this method, which also yields conclusions that are reasonable, impartial, trustworthy, and scientific. As a result, a multivariate dataset is summarized while reducing initial information loss, streamlining the data structure, and creating new, uncorrelated variables known as principle components from the original variables (Ahada & Suthar, 2017). PCA was used to discover potential factors influencing groundwater chemistry and, as a result, which variables share a common source of origination in groundwater. The varimax rotation was employed on principal components (PCs), and Kaiser’s criterion was considered to select PCs having eigenvalues greater than one (Rao et al., 2020). The PCs with eigenvalue, factor loading, % variance or eigenvalue %, and cumulative % variance are shown in Table 8.

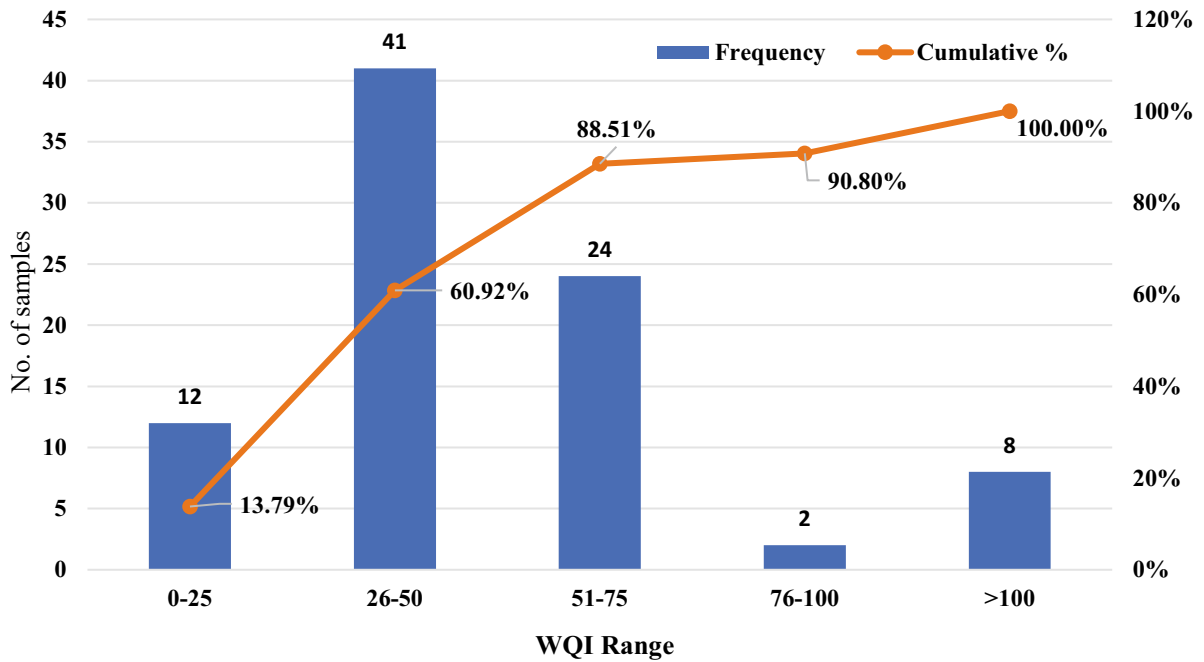


Fig. 6 Histogram showing WQI range and samples lying in respective categories

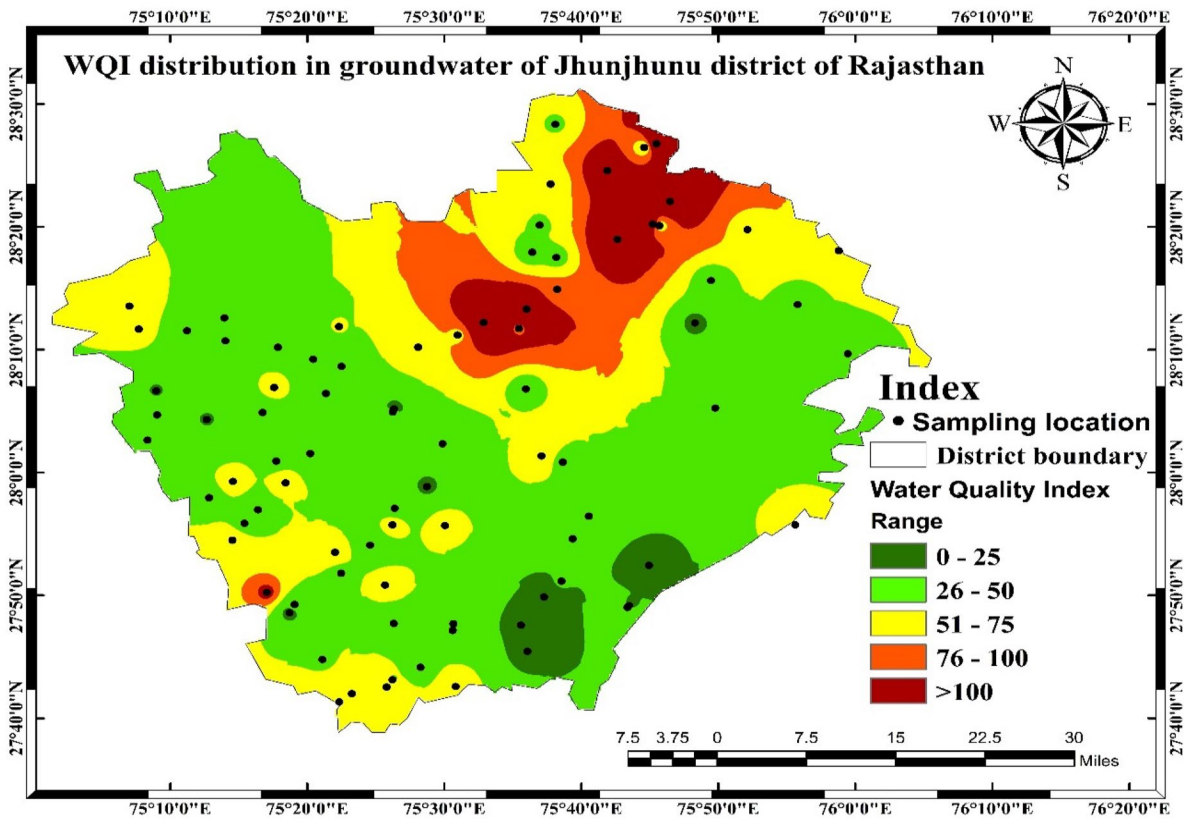


Fig. 7 Map showing different WQI categories of water samples observed in the Jhunjhunu district

Table 8 Four PCs with eigenvalues, % variance, cumulative % variance

Parameters	PC 1	PC 2	PC 3	PC 4
pH	-0.30	-0.54	0.51	0.03
TDS (mg/L)	0.91	-0.16	-0.19	0.22
EC (µS/cm)	0.91	-0.16	-0.19	0.22
ORP (mV)	0.00	0.70	-0.06	0.31
Salinity (mg/L)	0.91	-0.16	-0.19	0.22
DO (mg/L)	-0.29	0.26	-0.70	0.16
Fluoride (mg/L)	0.10	-0.06	0.22	-0.66
Chloride(mg/L)	0.50	-0.56	0.30	0.20
Nitrate(mg/L)	0.54	-0.20	-0.18	-0.43
Sulfate (mg/L)	0.38	-0.30	0.26	0.57
Phosphate (mg/L)	0.00	0.00	0.00	0.00
TH (mg/L)	0.64	0.63	0.38	-0.02
Ca ²⁺ (mg/L)	0.51	0.61	0.37	0.06
Mg ²⁺ (mg/L)	0.61	0.46	0.28	-0.11
TA (mg/L)	0.84	-0.08	-0.18	-0.30
Bicarbonate (mg/L)	0.84	-0.08	-0.18	-0.31
Eigenvalue	5.78	2.37	1.53	1.45
% Variances or eigenvalue%	36.13	14.79	9.53	9.05
Cumulative % variances	36.13	51.91	60.45	69.50

Bold value - factor loadings ≥0.5

The first four PCs (PC 1, PC 2, PC 3, and PC 4) were selected which accounts for a 69.51% variation in the data. The four PCs comprising PC 1, PC 2, PC 3, and PC 4 having an eigenvalue greater than one were chosen. PC 1 having an eigenvalue of 5.78 accounts for 36.13% variance. PC 2 having an eigenvalue of 2.37 accounts for 14.79% variance. PC 3 having an eigenvalue of 1.53 accounts for 9.53% variance. PC 4 having an eigenvalue of 1.45 accounts for 9.05% variance. The scree plot is showing all PCs and their respective eigenvalue% (Fig. 8). Principle component 1 shows several positive factors loading greater than 0.5 (bold in Table 8) which were contributed by TDS (0.91), EC (0.91), salinity (0.91), chloride (0.50), nitrate (0.54), TH (0.64), calcium (0.51), magnesium (0.61), TA (0.84), and bicarbonate (0.84). PC 1 had the highest loading factor for most of the parameters. By demonstrating a significant contribution of strong positive loadings (greater than 0.5) for all parameters, PC 1 revealed that both geogenic and anthropogenic sources influenced the groundwater quality in the research area (Ullah et al., 2021). TDS, EC calcium, magnesium, and bicarbonate may be high due to erosion, dissolution, and leaching as a result

Scree plot

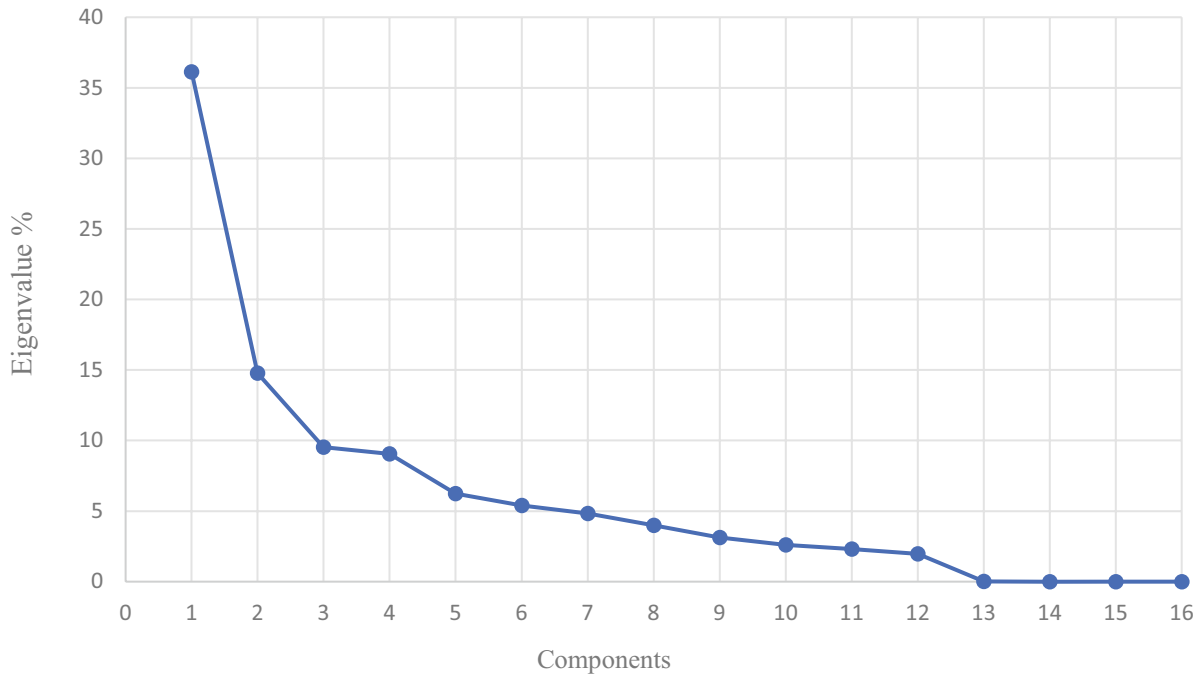


Fig. 8 Scree plot of PCA shows all PC with % variance or eigenvalue%

of water–rock interaction, inferencing PC 1 contributor had geogenic origin (Rao et al., 2020; Ullah et al., 2021). while salinity, chloride, and nitrate sourced from domestic waste and agricultural additives imply anthropogenic influence (Gugulothu et al., 2022; Rashid et al., 2022). Ahada and Suthar (2017) in their study of groundwater analysis in North Rajasthan concluded that both geogenic and anthropogenic factors influenced the groundwater quality. In PC 2, the factor loading was greater than 0.5 which was contributed by ORP (0.70), TH (0.63), and calcium (0.61). This may be due to water and calcium-bearing rock interaction, which implies geogenic origin (Ullah et al., 2021). PC 3 having only one parameter, namely, pH (0.51), implies the alkaline nature of water (Rao et al., 2020). Similarly, PC 4 has only one parameter, i.e., sulfate having a factor loading of 0.57 indicating the dissolution of minerals like gypsum applied for soil amendment (Gugulothu et al., 2022).

Conclusion

A detailed investigation of the Jhunjhunu district was implemented to assess the health risk assessment due to the consumption of fluoride and nitrate, and potability was evaluated by the water quality index. Sixteen parameters of groundwater were analyzed as per the standard methods of APHA (2017) collected from 87 locations in the study region, and results found that the value of the number of qualities parameters consisting of pH, EC, TDS, fluoride, chloride, nitrate, sulfate, total hardness, calcium, magnesium, and total alkalinity was observed higher than the recommended limit of BIS (2012) and WHO (2017). The fluoride in 10 and nitrate in 5 samples was observed to exceed the permissible limit of WHO. A correlation study found various parameters strongly correlated at a 99% level of confidence. TDS was observed to be correlated with chloride ($r=0.484^{**}$), nitrate ($r=0.473^{**}$), sulfate ($r=0.403^{**}$), total hardness ($r=0.395^{**}$), and total alkalinity ($r=0.674^{**}$) at 0.01 level of significance. Total alkalinity (TA) was found with a positive significant correlation with total hardness ($r=0.426^{**}$) and nitrate ($r=0.486^{**}$). Hazard assessment indicated the chronic daily intake dose, HQ, and HI for males, females, and children is a

significant subject to non-carcinogenic health risk associated with the drinking of fluoride- and nitrate-contaminated water. HI value of 71% of groundwater samples for males, 78% of groundwater samples for females, and 75% of groundwater samples for children was greater than 1 indicating the significant health hazard due to the consumption of groundwater. The water quality index observed that only 63% of groundwater samples can be used for drinking purposes, while the rest of the samples need treatment to make them potable. PCA revealed that the four PCs account for 69.50% of the variance in data. It reduced the 16 water quality parameters in the four major components affecting the chemistry of groundwater. The first component had the majority of water parameters with a loading factor higher than 0.05, which influence 36% variability in data with an eigenvalue of 5.78. It inferred that both geogenic and anthropogenic factors significantly contribute to groundwater contamination.

Acknowledgements The authors would like to acknowledge members of TSC-4, NRFCC, BRNS; HPD, HS&E Group, BARC, and NUP, for their continuous support in the execution of the project. The authors are also thankful to Maharshi Dayanand University, Rohtak, for providing all the facilities required to carry out this project. Authors acknowledge the technical help for ArcGIS by Abhishek Kumar and Pankaj Yadav, Research Scholars, Department of Geography, Maharshi Dayanand University, Rohtak, Haryana.

Author contribution Naresh Tanwer has done experimental, analyzed data, and wrote initially draft of manuscript. Meena Deswal helped in experimental and analysis of data. Pradeep Khyalia helped in experimental and analysis of data. Jitender Singh Laura conceptualized the work and critical reviewing of manuscript. Babita Khosla conceptualized the work, drafting, and critical reviewing of manuscript. All authors have read, understood, and have complied the work done in the paper.

Funding This study was funded by Board Research in Nuclear Sciences, Department of Atomic Energy under National Uranium Project with sanction no. 36(4)/14/18/2017-BRNS dated 04–12-2017.

Data availability All data generated or analyzed during this study are included in this manuscript and supplementary file.

Declarations

Conflict of interest The authors declare no competing interests.

References

Adimalla, N. (2019). Human and ecological risk assessment : An international spatial distribution, exposure, and potential health risk assessment from nitrate in drinking water from semi-arid region of South India assessment from nitrate in drinking water from semi-arid. *Human and Ecological Risk Assessment* 1–25. <https://doi.org/10.1080/10807039.2018.1508329>

Adimalla, N., Marsetty, S. K., & Xu, P. (2020). Assessing groundwater quality and health risks of fluoride pollution in the Shasler Vagu (SV) watershed of Nalgonda. *India. Human and Ecological Risk Assessment*, 26(6), 1569–1588. <https://doi.org/10.1080/10807039.2019.1594154>

Ahada, C. P., & Suthar, S. (2017). Hydrochemistry of groundwater in North Rajasthan, India: Chemical and multivariate analysis. *Environmental Earth Sciences*, 76(5), 1–16.

Ali, S., Fakhri, Y., Golbini, M., Thakur, S. K., Alinejad, A., Parseh, I., Shekhar, S., & Bhattacharya, P. (2019). Concentration of fluoride in groundwater of India: A systematic review, meta- analysis and risk assessment. *Groundwater for Sustainable Development*. <https://doi.org/10.1016/j.gsd.2019.100224>

APHA. (2017). Standard methods for the examination of water and wastewater (23rd ed.). American Public Health Association/American Water Works Association/ Water Environment Federation.

Bhardwaj, S., Shukla, D. P., & Halder, A. (2020). Spatial distribution of uranium and chemo-radiological assessment in Hamirpur district, Himachal Pradesh, India. *Journal of Radioanalytical and Nuclear Chemistry*, 324(2), 467–480.

BIS. (2012). Bureau of Indian standards specification for drinking water IS: 10500: 91. Bureau of Indian standards.

Brown R. M., McClellan N. I., Deininger R. A, and Tozer R. G. (1970). A waterquality index—do we dare? *Water Sew Works*, 117, 339–343.

Chaudhary, V., & Satheshkumar, S. (2018). Assessment of groundwater quality for drinking and irrigation purposes in arid areas of Rajasthan. *India. Applied Water Science*, 8(8), 1–17.

CGWB. (2008). Groundwater brochure, Jhunjhunu district, Western region Jaipur, Central Ground Water Board, Ministry of Water Resources, Government of India.

CGWB. (2018). Groundwater quality in shallow aquifers in India. Central Ground Water Board, Ministry of Water Resources RD and GR, Government of India

CGWB. (2021). Central Ground Water Board, Department of Water Resources, River Development & Ganga Rejuvenation, Ministry of Jal Shakti, Western Region, Jaipur, Government of India. November 2021, Ground Water Year Book 2020 – 2021. Retrieved October 28, 2022, from <http://cgwb.gov.in/Regions/WR/Reports/GW%20Year%20Book%202020-21-Rajasthan.pdf>

CWC. (2019). Water and related statistics. Central Water Commission, Department of Water Resources, RD and GR, Ministry of Jal Shakti, Government of India, New Delhi, India.

Duvva, L. K., Panga, K. K., Dhakate, R., & Himabindu, V. (2022). Health risk assessment of nitrate and fluoride toxicity in groundwater contamination in the semi-arid area of Medchal. *South India. Applied Water Science*, 12(1), 1–21. <https://doi.org/10.1007/s13201-021-01557-4>

Eggers, M. J., Doyle, J. T., Lefthand, M. J., Young, S. L., Moore-Nall, A. L., Kindness, L., et al. (2018). Community engaged cumulative risk assessment of exposure to inorganic well water contaminants, crows reservation, Montana. *International Journal of Environmental Research and Public Health*, 15(1). <https://doi.org/10.3390/ijerph15010076>

Freeze, R. A., & Cherry, J. A. (1979). Groundwater. Prentice-Hall.

Gugulothu, S., Subba Rao, N., Das, R., Duvva, L. K., & Dhakate, R. (2022). Judging the sources of inferior groundwater quality and health risk problems through intake of groundwater nitrate and fluoride from a rural part of Telangana. *India. Environmental Science and Pollution Research*, 29(32), 49070–49091. <https://doi.org/10.1007/s11356-022-18967-9>

Hem, J. D. (1991). *Study and interpretation of the chemical characteristics of natural water: USGS professional paper book 2254*. Scientific Publishers.

Iqbal, J., Su, C., Rashid, A., Yang, N., Baloch, M. Y. J., Talpur, S. A., et al. (2021). Hydrogeochemical assessment of groundwater and suitability analysis for domestic and agricultural utility in southern Punjab. *Pakistan. Water (switzerland)*, 13(24), 2–3. <https://doi.org/10.3390/w13243589>

Jandu, A., Malik, A., & Dhull, S. B. (2021). Fluoride and nitrate in groundwater of rural habitations of semiarid region of northern Rajasthan, India: A hydrogeochemical, multivariate statistical, and human health risk assessment perspective. *Environmental Geochemistry and Health*, 43(10), 3997–4026. <https://doi.org/10.1007/s10653-021-00882-6>

Joshi, A., & Seth, G. (2011). Hydrochemical profile for assessing the groundwater quality of Sambhar lake city and its adjoining area. *Environmental Monitoring and Assessment*, 174(1), 547–554.

Kashyap, C. A., Ghosh, A., Singh, S., Ali, S., Singh, H. K., Chandrasekhar, T., & Chandrasekharam, D. (2020). Distribution, genesis and geochemical modeling of fluoride in the water of tribal area of Bijapur district, Chhattisgarh, central India. *Groundwater for Sustainable Development*, 11(April), 100403. <https://doi.org/10.1016/j.gsd.2020.100403>

Kaur, L., Rishi, M. S., Sharma, S., Sharma, B., Lata, R., & Singh, G. (2019). Hydrogeochemical characterization of groundwater in alluvial plains of river Yamuna in northern India: An insight of controlling processes. *Journal of King Saud University - Science*, 31(4), 1245–1253. <https://doi.org/10.1016/j.jksus.2019.01.005>

Kimambo, V., Bhattacharya, P., Mtalo, F., Mtamba, J., & Ahmad, A. (2019). Fluoride occurrence in groundwater systems at global scale and status of defluoridation – State of the art. *Groundwater for Sustainable Development*, 9, 100223. <https://doi.org/10.1016/j.gsd.2019.100223>

Kothari, V., Viji, S., Sharma, S. K., & Gupta, N. (2021). Correlation of various water quality parameters and water quality index of districts of Uttarakhand. *Environmental and Sustainability Indicators*, 9(December 2020), 100093. <https://doi.org/10.1016/j.indic.2020.100093>

Krishan, G., Bhagwat, A., Sejwal, P., Yadav, B. K., Kansal, M. L., Bradley, A., et al. (2022). Assessment of groundwater salinity using principal component analysis (PCA): A case study from Mewat (Nuh), Haryana. *India. Environmental Monitoring and Assessment*. <https://doi.org/10.1007/s10661-022-10555-1>

- Li, P., & Qian, H. (2018). Water resources research to support a sustainable China. *International Journal of Water Resources Development*, 34(3), 327–336. <https://doi.org/10.1080/07900627.2018.1452723>
- Nair P. K. M., & Augustine, L. F. (2018). Country-specific nutrient requirements & recommended dietary allowances for Indian: Current status & future directions, (November), 522–530. <https://doi.org/10.4103/ijmr.IJMR>
- NITI Aayog. (2020). Government of India. Retrieved October 13, 2022, from <https://niti.gov.in/content/life-expectancy>
- NIN-ICMR. (2011). Dietary guidelines for Indians -A manual. National Institute of Nutrition - Indian Council of Medical Research.
- Panghal, V., Singh, A., Kumar, R., Kumari, G., Kumar, P., & Kumar, S. (2021). Soil heavy metals contamination and ecological risk assessment in Rohtak urban area, Haryana (India). *Environmental Earth Sciences*, 80(21), 1–20. <https://doi.org/10.1007/s12665-021-10028-7>
- Rahman, A., Mondal, N. C., & Tiwari, K. K. (2021). Anthropogenic nitrate in groundwater and its health risks in the view of background concentration in a semi arid area of Rajasthan, India. *Scientific Reports*, 11(1), 1–13. <https://doi.org/10.1038/s41598-021-88600-1>
- Rao, N. S., Dinakar, A., & Kumari, B. K. (2021a). Appraisal of vulnerable zones of non-cancer-causing health risks associated with exposure of nitrate and fluoride in groundwater from a rural part of India. *Environmental Research*, 202(June), 111674. <https://doi.org/10.1016/j.envres.2021.111674>
- Rao, N. S., Dinakar, A., Sravanthi, M., & Kumari, B. K. (2021b). Geochemical characteristics and quality of groundwater evaluation for drinking, irrigation, and industrial purposes from a part of hard rock aquifer of South India. *Environmental Science and Pollution Research*, 28(24), 31941–31961. <https://doi.org/10.1007/s11356-021-12404-z>
- Rao, N. S., Das, R., & Gugulothu, S. (2022a). Understanding the factors contributing to groundwater salinity in the coastal region of Andhra Pradesh. *India. Journal of Contaminant Hydrology*, 250, 104053. <https://doi.org/10.1016/j.jconhyd.2022.104053>
- Rao, N. S., Dinakar, A., & Sun, L. (2022b). Estimation of groundwater pollution levels and specific ionic sources in the groundwater, using a comprehensive approach of geochemical ratios, pollution index of groundwater, unmix model and land use/land cover—A case study. *Journal of Contaminant Hydrology*, 248, 103990. <https://doi.org/10.1016/j.jconhyd.2022.103990>
- Rao, N. S., Ravindra, B., & Wu, J. (2020). Human and ecological risk assessment : An international geochemical and health risk evaluation of fluoride rich groundwater in Sattenapalle Region, Guntur district, Andhra Pradesh, India. *Human and Ecological Risk Assessment: An International Journal*, 1–33. <https://doi.org/10.1080/10807039.2020.1741338>
- Rashid, A., Ayub, M., Khan, S., Ullah, Z., Ali, L., Gao, X., et al. (2022). Hydrogeochemical assessment of carcinogenic and non-carcinogenic health risks of potentially toxic elements in aquifers of the Hindukush ranges, Pakistan: Insights from groundwater pollution indexing, GIS-based, and multivariate statistical approaches. *Environmental Science and Pollution Research*, (0123456789). <https://doi.org/10.1007/s11356-022-21172-3>
- Satyanarayana, E., Dhakate, R., Kumar, D. L., Ravindara, P., & Muralidhara, M. (2017). Hydrochemical characteristics of groundwater quality with special reference to fluoride concentration in parts of Mulugu-Venkatapur Mandals, Warangal district, Telangana. *Journal of Geological Society of India*, 89, 247–258. <https://doi.org/10.1007/s12594-017-0597-8>
- Shirke, K. D., Kadam, A., & Pawar, N. J. (2020). Human and ecological risk assessment : An international health risk assessment and prevalence of fluoride in groundwater around the geological diversity of Ambadongar South Gujarat, India. *Human and Ecological Risk Assessment: An International Journal*, 1–20. <https://doi.org/10.1080/10807039.2020.1858270>
- Singh, C. K., & Mukherjee, S. (2014). Aqueous geochemistry of fluoride enriched groundwater in arid part of Western India. *Environmental Science and Pollution Research*, 22(4), 2668–2678.
- Sohrabi, N., Kalantari, N., Amiri, V., Saha, N., Berndtsson, R., Bhattacharya, P., & Ahmad, A. (2021). A probabilistic-deterministic analysis of human health risk related to the exposure to potentially toxic elements in groundwater of Urmia coastal aquifer (NW of Iran) with a special focus on arsenic speciation and temporal variation. *Stochastic Environmental Research and Risk Assessment*, 35(7), 1509–1528. <https://doi.org/10.1007/s00477-020-01934-6>
- Stumm, W., & Morgan, J. J. (1981). Aquatic chemistry: Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. A Wiley-Interscience-Publication.
- Subba Rao, N. (2011). High-fluoride groundwater. *Environmental Monitoring and Assessment*, 176(1–4), 637–645. <https://doi.org/10.1007/s10661-010-1609-y>
- Subba Rao, N. (2018). Groundwater quality from a part of Prakasam District, Andhra Pradesh. *India. Applied Water Science*, 8(1), 1–18. <https://doi.org/10.1007/s13201-018-0665-2>
- Subba Rao, N., Dinakar, A., Surya Rao, P., Rao, P. N., Madhnure, P., Prasad, K. M., & Sudarshan, G. (2016). Geochemical processes controlling fluoride-bearing groundwater in the granitic aquifer of a semi-arid region. *Journal of the Geological Society of India*, 88(3), 350–356. <https://doi.org/10.1007/s12594-016-0497-3>
- Subba Rao, N., Srihari, C., Deepthi Spandana, B., Sravanthi, M., Kamalesh, T., & Abraham Jayadeep, V. (2019). Comprehensive understanding of groundwater quality and hydrogeochemistry for the sustainable development of suburban area of Visakhapatnam, Andhra Pradesh. *India. Human and Ecological Risk Assessment*, 25(1–2), 52–80. <https://doi.org/10.1080/10807039.2019.1571403>
- Subba Rao, N., Subrahmanyam, A., & Babu Rao, G. (2013). Fluoride-bearing groundwater in Gummanampadu sub-basin, Guntur district, Andhra Pradesh. *India. Environmental Earth Sciences*, 70(2), 575–586.
- Subba Rao, N., Surya Rao, P., Venktram Reddy, G., Nagamani, M., Vidyasagar, G., & Satyanarayana, N. L. V. V. (2012). Chemical characteristics of groundwater and assessment of groundwater quality in Varaha River Basin, Visakhapatnam District, Andhra Pradesh. *India. Environmental Monitoring and Assessment*, 184(8), 5189–5214. <https://doi.org/10.1007/s10661-011-2333-y>
- Suthar, S., Bishnoi, P., Singh, S., Mutiyar, P. K., Nema, A. K., & Patil, N. S. (2009). Nitrate contamination in groundwater

- of some rural areas of Rajasthan. *India. Journal of Hazardous Materials*, 171(1–3), 189–199.
- Suthar, S., Garg, V. K., Jangir, S., Kaur, S., Goswami, N., & Singh, S. (2008). Fluoride contamination in drinking water in rural habitations of Northern Rajasthan. *India. Environmental Monitoring and Assessment*, 145(1), 1–6.
- Tanwer, N., Khayalia, P., Deswal, M., Laura, J. S., & Khosla, B. (2022). Spatial distribution of uranium in groundwater and its health risk assessment in Haryana, India. *Rasayan Journal of Chemistry*, 15, 343–349. <https://doi.org/10.31788/RJC.2022.1516608>
- Taylor, R. (1990). Interpretation of the correlation coefficient: A basic review. *Journal of Diagnostic Medical Sonography*, 6(1), 35–39.
- Ullah, Z., Talib, M. A., Rashid, A., Ghani, J., Shahab, A., Irfan, M., et al. (2021b). Hydrogeochemical investigation of elevated arsenic based on entropy modeling, in the aquifers of district sanghar, sindh, Pakistan. *Water (Switzerland)*, 13(23). <https://doi.org/10.3390/w13233477>
- Ullah, Z., Xu, Y., Zeng, X. C., Rashid, A., Ali, A., Iqbal, J., et al. (2022a). Non-carcinogenic health risk evaluation of elevated fluoride in groundwater and its suitability assessment for drinking purposes based on water quality index. *International Journal of Environmental Research and Public Health*, 19(15). <https://doi.org/10.3390/ijerph19159071>
- USEPA. (2006). USEPA region III Risk-based concentration table: Technical background information. United States Environmental protection Agency.
- USEPA. (2014). Human health evaluation manual, supplemental guidance: Update of standard default exposure factors-OSWER Directive 9200.1–120, p. 6. United States Environmental Protection Agency, Washington, DC, USA.
- USEPA. (2017). Regional screening levels (RSLs)–Generic tables; Retrieved May 10, 2022, from <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables>
- USEPA. (2020). Regional screening levels (RSLs)–Generic tables; Retrieved May 10, 2022, from <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables>
- Wagh, V. M., Panaskar, D. B., Mukate, S. V., & Nashik, R. B. (2019). Human and ecological risk assessment : An international nitrate associated health risks from groundwater of Kadava River Basin Nashik, Maharashtra, India. *Human and Ecological Risk Assessment: An International Journal*, 1–19. <https://doi.org/10.1080/10807039.2018.1528861>
- Whitford, G. M., Pashley, D. H., & Stringer, G. I. (1976). Fluoride renal clearance: A pH-dependent event. *American Journal of Physiology-Legacy Content*, 230(2), 527–532.
- WHO. (2017). *Guidelines for drinking water quality: Fourth edition incorporating the first addendum*. World Health Organization.
- Wu, J., & Sun, Z. (2016). Evaluation of shallow groundwater contamination and associated human health risk in an alluvial plain impacted by agricultural and industrial activities, mid-west China. *Exposure and Health*, 8(3), 311–329.
- Wu, J., Yin, Y., & Wang, J. (2018). Hydrogen-based membrane biofilm reactors for nitrate removal from water and wastewater. *International Journal of Hydrogen Energy*, 43(1), 1–15. <https://doi.org/10.1016/j.ijhydene.2017.10.178>

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.