

Natural backgrounds and nitrate-fluoride pollution indices for groundwater characterization in a semi-arid area, Rajasthan, India

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Research Article

Keywords: Groundwater quality, nitrate, fluoride, backgrounds, NPI and FPI, semi-arid area, Rajasthan

Posted Date: October 5th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11228121/v1>

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Additional Declarations: The authors declare no competing interests.

Abstract

This study presents an integrated assessment of natural background levels (NBLs) and nitrate-fluoride pollution indices (NPI and FPI) to evaluate groundwater quality in semi-arid region, Rajasthan, Western India. A total of 274 groundwater samples collected during dry-season were analysed for pH, EC, TDS, major ions, TH, TA, nitrate, and fluoride. The hydrochemical characteristics reveal substantial spatial variability governed by the combined influences of geogenic processes and anthropogenic activities. Total dissolved solids (195–6780 mg/L, mean: 968 mg/L) indicate significant salinity enrichment, with 62% of samples exceeding the permissible drinking water limit. Nitrate and fluoride concentrations exceeded the recommended limits in 27% and 15% of samples, respectively, particularly in agricultural and wastewater-affected areas. The derivation NBLs, and threshold values (TVs) have effectively distinguished natural contributions from human-induced contamination. The first threshold values (TV1) for pH, EC, Na^+ , Cl^- , HCO_3^- , TH, TA, NO_3^- , and F^- were 8.2, 480 $\mu\text{S}/\text{cm}$, 49, 35, 135, 72, 135, 16, and 0.26 mg/L, respectively. Several TV2 values (8.5, 620 $\mu\text{S}/\text{cm}$, 715, 610, 561, 250, 360, 55, and 1.56 mg/L, respectively) exceeded drinking water standards, indicating significant water quality deterioration. Nitrate (range: 1–187 mg/L) remains mostly within the natural background range, exceeded the BIS limits at several locations, indicating significant anthropogenic inputs from agricultural practices and urban activities. The NPI (-1.0 to 8.4) has revealed that approximately 68.2% of the samples were affected by nitrate pollution, with distinct hotspots associated with intensive cultivation. Fluoride (0.02–10.0 mg/L) exceeded safe limits ($> \text{TV2}: 1.56 \text{ mg/L}$) in 15% of samples, while the FPI (1.5 to 4.0) indicated that approximately 90.5% samples were moderately to highly polluted by fluoride, enhanced by alkaline condition, HCO_3^- , and high $\text{Na}^+/\text{Ca}^{2+}$ ratios, particularly within the cropland-dominated areas. These findings demonstrate the effectiveness of integrating NBLs, TVs, and pollution indices for identifying contamination sources, assessing groundwater quality, and supporting sustainable groundwater management and risk mitigation strategies in semi-arid regions.

1. Introduction

Groundwater serves as a major freshwater resource, and is significantly vulnerable to pollution from both natural and anthropogenic factors (Nisi et al. 2016; Sharma et al. 2024). Its chemical composition is mainly governed by interactions with geological materials, including minerals dissolution and gas exchange, as well as aquifer residence time (Appelo and Postma 2005; Biddau et al. 2017; Wali et al. 2024). Additionally, groundwater chemistry is influenced by multi factors from precipitation, physicochemical and biological processes within the unsaturated zone, aquifer mineralogy, and water-rock interactions, and mixing dynamics (Edmunds and Shand 2008). Variation of groundwater flow, climatic conditions, rainfall patterns, geological settings, anthropogenic pressures, particularly over-exploitation, which enhance the mobilization of geogenic contaminants and facilitate the infiltration of anthropogenic pollutants into the subsurface (Rajesh et al. 2015; Dermatas 2017; Datta et al. 2021). Globally, freshwater quality is increasingly threatened by anthropogenic activities, a situation further exacerbated by the impacts of climate change on the hydrological cycle (Preziosi et al. 2010; Mondal

and Ahmed 2015; Venkatarao et al. 2019; Neupane et al. 2020). Given that a significant proportion of the global population depends on groundwater for domestic use (Oki and Kanae 2006), its deterioration poses a critical challenge in both developed and developing nations. Consequently, groundwater protection has become a major public health concern, as emphasized by the international agencies and regulatory frameworks (WHO 1992; UN Water 2011). In this context, the European Water Framework Directive provides a comprehensive framework for freshwater protection by establishing baseline conditions and enabling the assessment of groundwater quality status in term of degradation or improvement (Shand et al. 2007; Amulejoye and Olusola 2026).

The natural background level (NBL) (baseline) describes the concentration range of specific chemical constituents in solution that originate purely from natural geological, biological, or atmospheric processes, without any human-induced influences (Edmunds and Shand 2008). However, truly pristine NBLs are increasingly considered unrealistic due to pervasive and long-term human influences on environmental systems (Sellerino et al. 2019; Mikkonen et al. 2018). Groundwater in densely urbanized regions and intensively irrigated regions is particularly susceptible to such influences, mainly through agricultural inputs and wastewater contamination (De Caro et al. 2017; Gao et al. 2020). Moreover, the lack of long-term monitoring data and limited groundwater quality studies complicate the direct estimation of NBLs in the absence of anthropogenic inputs (Gao et al. 2020). In some cases, natural geochemical contributions may exceed anthropogenic inputs, was exemplified by elevated fluoride concentrations originating from rock-water interactions, which pose significant health concerns in several regions of India (Rahman et al. 2013; Govil et al. 2020).

The threshold values (TVs) represent environmental quality standards used to assess groundwater suitability for various purposes (Scheidleder 2012). Their establishment is essential for identifying pollutants and evaluating groundwater bodies at risk of failing to meet the good chemical status criteria of the Water Framework Directive (WFD 2000). Numerous methodologies have been developed to estimate reliable NBLs and TVs (Matschullat et al. 2000; Urresti-Estala et al. 2013; Preziosi et al. 2014; Rothwell and Cooke 2015; Hernandez Crespo and Martín 2015; Rahman et al. 2020, 2021). Among these, the BRIDGE Project has played a significant role since 2005 by proposing standardised approached for the NBL and TV estimation at the European scale, even with limited monitoring datasets (Muller et al. 2006; Preziosi et al. 2010). In this framework, cumulative probability plots are applied, following the establishment of ionic balance thresholds to delineating geochemical populations, and derived the NBLs (Runnells et al. 1998; Rahman et al. 2020, 2021). Parameters such as nitrate, chloride, and sulfate are commonly employed as indicators of anthropogenic contamination, whereas sodium, bicarbonate, and fluoride are used to characterize natural geochemical processes including salinization, water-rock interaction, and evaporative concentration (USGS 2004; Muller et al. 2006; Mullaney et al. 2009; Domagalski and Johnson 2012; Mendizabal et al. 2012; Zhang et al. 2018; Gao et al. 2020; Aragao et al. 2020).

In India, only a limited number of studies have addressed hydrochemical natural background levels (NBLs) or baseline conditions. Notably, preliminary hydrochemical baselines have been delineated using

log-probability distribution techniques in a small channel island of Andhra Pradesh, India (Mondal 2018), a tannery belt of Peninsular India (Mondal 2020), and semi-arid area of Rajasthan (Rahman et al., 2020, 2021). In a broader context, CSIR-NGRI, Hyderabad, has undertaken nationwide geochemical baseline mapping to generate high-quality datasets in a variety of environmental contexts (Govil et al. 2020). This initiative has been involved the analysis of approximately 544 topsoil samples analysed for major oxides and trace elements. Similarly, hydrochemical baseline studies are essential for environmental management, as they help to characterize the natural abundance and spatial distribution of chemical constituents in groundwater, which may subsequently be altered by anthropogenic activities. Furthermore, non-carcinogenic risk assessment provides a comprehensive framework for evaluating potential health impacts across different age groups (i.e, children, teenagers, and adults), considering exposure pathways such as ingestion, dermal contact, and inhalation (Wu et al. 2019, 2020; Rani et al. 2023). Among these, oral ingestion of groundwater is generally recognized as the dominant exposure pathway compared to dermal and inhalation routes (Saxena et al. 2005; Rao et al. 2021; Shah et al. 2023; Singh et al. 2023; Mondal and Tiwari 2026).

Nitrate (NO_3^-) is among the most common anthropogenic contaminants in groundwater worldwide (Wakida et al. 2005). Its primary sources include diffuse (nonpoint) inputs such as intensive fertilizer application and poorly managed sanitation in densely populated regions, as well as point sources including wastewater discharge and irrigation with treated/untreated sewage effluents (McLay et al. 2001). Due to its high solubility, weak adsorption to soil colloids, and limited interaction with positively charged species, nitrate is highly mobile in the subsurface environment. Under oxidizing groundwater conditions, nitrate represents the stable form of nitrogen and migrates with minimal transformation or retardation (Freeze and Cherry 1979). Chronic exposure to elevated nitrate concentrations in drinking water has been associated with adverse health effects, including methemoglobinemia in infants, colorectal cancer, and non-Hodgkin's lymphoma (Ward et al. 1996; Knobeloch et al. 2000; De Roos et al. 2003). Groundwater containing nitrate concentrations above 20 mg/L as NO_3^- is generally considered impacted by anthropogenic activities (human-affected value, HAV) (Spalding and Exner 1993), while the World Health Organization (WHO 2012) recommends a maximum permissible limit of 50 mg/L as BIS limit (2012) as 45 mg/L for the NO_3^- of drinking water. Thus, the Nitrate Pollution Index (NPI) is widely used to quantify the extent of nitrate contamination in groundwater relative to the anthropogenic threshold value of 20 mg/L (Spalding and Exner 1993; Obeidat et al. 2012; Bahrami et al. 2020; Egbueri et al. 2025); however, its application remains limited.

Another fluoride (F^-) contamination in groundwater is an increasing global concern, with numerous cases reported from several countries such as India (Salve et al. 2008, Mondal et al. 2009; Reddy et al. 2010; Tiwari et al. 2020; Rani et al. 2023), USA (WHO 2004), Spain (Hardisson et al. 2001), Argentina (Rosso et al. 2011), and Iran (Mesdaghinia et al. 2011). While trace levels of F^- (< 0.5 mg/L) are essential for dental integrity, concentrations exceeding the BIS (2012) limit of 1.5 mg/L trigger a spectrum of debilitating conditions, including dental and skeletal fluorosis, endocrine disruption, and permanent neurological impairments (Shahroom et al. 2019; Su et al. 2023; Biswas et al. 2025). Globally, over

200 million people remain exposed to unsafe F^- levels, with approximately 11.7 million individuals across 469 Indian districts of 14 states residing in high-risk zones (Kumar and Shah 2004; Bello 2020; Podgorski and Berg 2022; Shaji et al. 2024). This alarming prevalence necessitates the shift from traditional monitoring to sophisticated, process-based diagnostic tools capable of deciphering the complex hydrogeochemical mechanisms occurring F^- concentration in groundwater. But its occurrence is primarily controlled by geological formations, particularly through the weathering of fluoride-bearing minerals (Mondal et al. 2009). Hydrogeological conditions such as Na^+ -rich, Ca^{2+} -poor water is favourable fluoride enrichment via cation exchange processes (Currell et al. 2011). Additionally, alkaline condition (high pH) and elevated HCO_3^- concentrations further enhance the fluoride mobilizations in groundwater system.

To address these controlling factors, the fluoride pollution index (FPI) has been developed to evaluate and classify fluoride related hazards by incorporating key parameters such as pH, HCO_3^- and Na^+/Ca^{2+} ratio (Sajil Kumar 2017). This FPI has been successfully applied in several countries, including Ethiopia (Haji et al. 2021), Pakistan (Rehman et al. 2022), Algeria (Maha et al. 2024), Mexico (Morales-Arredondo et al. 2023), and India (Sajil Kumar 2017; Mahanta and Goswami 2024). A comprehensive assessment of groundwater quality in a semi-arid of Jaipur district, Rajasthan, western India, was initially conducted using the arithmetic weighted water quality index (AWWQI), entropy weighted water quality index (EWWQI), and total carcinogenic hazard index (TCHI). The study revealed that groundwater quality is adversely affected by both geogenic and anthropogenic contaminants, resulting in substantial non-carcinogenic and carcinogenic health risks to the local population, with children identified as the most vulnerable group (Mondal and Tiwari, 2026). However, to date, no study has comprehensively integrated nitrate and fluoride indices with their respective their backgrounds in conjunction with LULC patterns for a combined assessment. Thus, the main objectives of this study are two folds: 1) to estimate NBLs and TVs of hydrochemical constituents, including nitrate and fluoride in groundwater of a semi-arid area in Rajasthan, and 2) to delineate polluted zones using nitrate and fluoride pollution indices (NPI and FPI) for drinking water assessment.

2. Material and methods

2.1 Background of the study area

The study area of Jaipur district is located in the eastern-central part of Rajasthan, spans $\sim 11,061 \text{ km}^2$ between longitudes: $74^\circ 54' 36''\text{E}$ to $76^\circ 15' 36''$ and latitudes: $26^\circ 26' 31.2''$ to $26^\circ 27' 36''\text{N}$, as shown in Fig. 1. Administratively, it consists of 15 blocks, with Pawta and Jalsu added in 2014. The district lies at the elevations of 270–788 m, amsl, with undulating terrain and the Aravalli hills dominating in the north and central parts. The climate is arid to semi-arid, with average annual rainfall of $\sim 576 \text{ mm}$ (1971–2014). The area frequently experiences droughts (i.e., 1984 to 1989, and 1999 to 2002), through occasional floods also occurs, such as in 1981 (CGWB 2013, 2023). Average annual temperatures between 2000 and 2022 ranged from 12.55°C to 36.23°C , coupled with high evapotranspiration ($\sim$

average 1,745 mm annually). Geologically, the district is complex, with the oldest Bhilwara Super Group (gneisses and schists) overlain by younger Alwar and Ajabgarh rocks of the Delhi Super Group (quartzites, schists, conglomerates, and dolomitic limestone). Younger intrusive such as granite and amphibolite are also present. Extensive Quaternary alluvial ($\sim 129 \text{ km}^2$) covers large parts, particularly in the north and east, where thickness exceeds 100 m. In contrast, the southern and southwestern regions exhibit thinner alluvial deposits. The land use and land cover (LULC) shows $\sim 63\%$ of the district is cropland, $\sim 17\%$ forest (mainly in the north-eastern part), and $\sim 14\%$ built-up urban land centred around Jaipur city. Water bodies occupy only 78 km^2 , and barren lands cover $\sim 59 \text{ km}^2$. According to the CGWB (2013, 2023), approximately $8,989 \text{ km}^2$ of the study area is covered by alluvial soil, while $2,071 \text{ km}^2$ is covered by grey and brown soils. Groundwater occurs in both unconsolidated Quaternary formations and consolidated rocks of Bhilwara and Delhi Super Groups (CGWB 2013). Productive aquifers are formed by older alluvium, weathered and fractured schists of Bhilwara Super Group. Shallow unconfined aquifers and deeper semi-confined aquifers support the irrigation and drinking needs. However, groundwater resources are severely stressed. The Dynamic Groundwater Resource Assessment classifies the district as over-exploited (CGWB 2013), with a gross annual groundwater draft exceeding 1475,000 Ham, largely for irrigation (107,004.97 Ham), followed by domestic (38,927.03 Ham) use. This excessive abstraction risks aquifer depletion and contamination in the district.

2.2 Analytical hydrochemical data

A total of 274 analytical hydrochemical data collected from wells during the dry season in May 2021 were retrieved from Department of Ground Water, Rajasthan (<https://water.rajasthan.gov.in/wr/#/home/dptHome>). In situ measurements of electrical conductivity (EC) and pH meters were performed at the time of sampling using calibrated portable meters. Concentrations of major ions (Na^+ and K^+) were determined by flame photometer, while nitrate (NO_3^-) and fluoride (F^-) were analysed via UV-visible spectrophotometer techniques. The remaining major ions along with total hardness (TH) were quantified using standard volumetric procedures in accordance of APHA (1985) methodologies at the Regional Chemical Laboratory, Department of Ground Water, Jaipur, Rajasthan.

2.3 Charge balance error

The cations-anions charge balance method was used to evaluate the accuracy and reliability of analysed groundwater chemical data. Based on electroneutrality, total cation and anions concentrations should be nearly equal; deviations indicate analytical uncertainty or unmeasured species. The charge balance error (CBE) (Mandel and Shiftan 1980), was calculated after converting the ion concentrations from mg/L (milligram per liter) to meq/L (milliequivalent per liter), using the following equation of Cherry and Freeze (1979) and Hem (1985).

$$\text{Charge balance error} = \left\{ \frac{(\sum \text{cation} - \sum \text{anion})}{(\sum \text{cation} + \sum \text{anion})} \right\} * 100 \quad (1)$$

A CBE within $\pm 5\%$ indicates good analytical quality (Hounslow 2018), while $\pm 10\%$ is generally acceptable for groundwater studies (Katz et al. 1998). If it exceeds 10, the measurement fails the validation test. In this work, all analytical data of 274 groundwater samples had shown the CBE values between 0.00-9.29% and confirmed the data reliability.

2.4 Background level and threshold value

After validation and reliability checks, major ions including nitrate and fluoride concentrations were analysed to establish natural background levels (NBLs) of groundwater using cumulative probability plots, and thresholds (TVs) were determined following the BRIDGE methodology (Muller et al. 2006).

2.5 Natural background level (NBL) derivation

Groundwater chemistry represents an integrated outcome of both natural and anthropogenic processes acting within groundwater and their surroundings. Each dissolved constituent in groundwater processes a characteristic natural background level (NBL), which reflects only natural geochemical processes. However, in recent decades, groundwater chemistry has undergone progressive deterioration due to increasing anthropogenic inputs. Consequently, distinguishing between natural elevated concentrations and those influenced by human activities remains a major challenge.

Determining the NBLs under real hydrogeological conditions is complex because each chemical species may incorporate signals from multiple origins (Chen et al. 2022). Several approaches have been developed to derive NBLs (Mondal 2020; Rahman et al. 2020, 2021), among which cumulative probability distribution methods, originally applied in geochemical mineral exploration (Sinclair 1974, 1991), are widely recognized for hydrochemical studies (Runnells et al. 1998).

The cumulative probability method is a straightforward statistical tool for defining the NBLs of both single and multiple chemical parameters (Panno et al. 2006). It has a key advantage in that it can include data affected by anthropogenic influence while still allowing separation of natural populations. This is achieved by identifying inflection points in the cumulative probability curve plotted against the logarithm of concentration. The first inflection point, corresponding to lower concentrations, generally represents the NBL (Rahman et al. 2020). When mixed population exists, the curve reveals distant bends with multiple inflection points, indicating concentrations from different sources (Panno et al. 2006).

The extensive discussion of the methodology, its application and limitations are available in the works of Sinclair (1991), Runnells et al. (1998), and Panno et al. (2006), Mondal (2020), and Rahman et al. (2020). Overall cumulative probability distribution has proven highly effective in discriminating natural from anthropogenic signatures within complex groundwater datasets, making it one of the most reliable tools for establishing hydrochemical NBLs, which had been utilized in our study.

2.5.1 Threshold value (TV) derivation

According to the BRIDGE methodology, the threshold value (TV) of a pollutant is calculated based on its estimated natural background level (NBL). However, its practical important mainly depends on the relevant Standard Reference Value (SRV) set for drinking water quality. In some cases, the TV may be equal to or even more significant than the NBL, depending on the specific SRV application to the receptor (such as humans). In this study, the Indian Drinking Water Standards (BIS 2012) were used as the SRV for calculating the TV, following the recommendations of the drinking water directive ((8/83/EC). The TV was calculated using prescribed equations and guidelines.

$$TV = \frac{SRV+NBL}{2}, \text{ If } NBL < SRV \quad (2)$$

$$TV = NBL, \text{ If } NBL > SRV \quad (3)$$

2.6 Nitrate pollution index (NPI)

The Nitrate Pollution Index (NPI), proposed by Spalding and Exner (1993), is used to assess nitrate contamination in groundwater. It is computed based on the measured nitrate concentration (C_s) and the human-affected value (HAV), set at 20 mg/L (Spalding and Exner 1993; Obeidat et al. 2012). The HAV represents the threshold concentration (decided through the estimated background levels) mainly related to anthropogenic activities.

$$NPI = \frac{C_s - HAV}{HAV}$$

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Based on the calculated NPI values, groundwater samples were classified into different categories: clean or unpolluted (< 0.0), light pollution ($0.0-1.0$), moderate pollution ($1.1-2.0$), significant pollution ($2.1-3.0$), and very significant pollution (> 3.0) in the study area.

2.7 Fluoride pollution index (FPI)

The chemical analysis results were used to calculate the Fluoride Pollution Index (FPI). Firstly, the weights were assigned to each parameter based on their concentration levels. These weights reflect the relative importance of fluoride (F^-), bicarbonate (HCO_3^-), sodium to calcium ratio (Na^+/Ca^{2+}), and pH in controlling fluoride contamination. Using the assigned weights, the FPI was calculated following the method proposed by Sajil Kumar (2017).

$$FPI = \frac{W_F + W_{HCO_3} + W_{Na/Ca} + W_{pH}}{N}$$

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where, W_F , W_{HCO_3} , $W_{Na/Ca}$, and W_{pH} represent the weights given to fluoride, bicarbonate, Na^+/Ca^{2+} ratio, and pH, respectively, and N represents the total number of selected parameters. Based on the calculated

FPI values, groundwater samples were classified into three categories: low pollution (1.0–2.0), medium pollution (2.1–3.0), and high pollution (3.1–4.0) in the study area.

3. Results

3.1 General groundwater chemistry

In general hydrochemistry, the analytical data indicated that Total dissolved solids (TDS) ranged from 195 to 6780 mg/L, with an average of 968 mg/L (in Table 1), exceeding the permissible limit, indicating increased the salinity in the study area. About 45% of the samples was within the permissible TDS range (500–1500 mg/L). While approximately 8% groundwater samples exceeded the limit greater than 2000 mg/L, making them unfit for drinking. The EC is another parameter that reflected the concentration of dissolved ions in water directly related to the TDS. It ranged from 320 to 11,300 $\mu\text{S}/\text{cm}$, with a mean of 1664 $\mu\text{S}/\text{cm}$. This wide range of EC had suggested significant variability in water quality across the study area. The pH ranged from 7.60 to 9.10, with an average of 8.40, suggesting on average slight alkaline water. The permissible pH range for drinking water according to BIS (2012) is typically between 6.5 and 8.5. As a result, the observed pH values slightly exceeded the BIS limit, which may affect water drinking and agriculture uses.

The Na^+ concentrations ranged from 24 to 2200 mg/L, with an average of 296 mg/L (in Table 1). Elevated sodium levels indicated the strength of salinity in the groundwater, especially in areas with excessive irrigation or improper wastewater disposal. Potassium levels ranged from 2 to 98 mg/L, with an average of 6 mg/L. Potassium was typically less problematic in drinking water. Both Ca^{2+} and Mg^{2+} were essential for water hardness, which affected both human health and the scaling of pipes and machinery. The concentrations of Ca^{2+} ranged from 2 to 124 mg/L, with a mean of 18 mg/L, and Mg^{2+} concentrations ranged from 2 to 275 mg/L, with a mean of 34 mg/L. While the concentrations of both ions were within acceptable limits for drinking water (75–200 mg/L for the Ca^{2+} , and 30–100 mg/L for Mg^{2+}), they could contribute to water hardness, which was undesirable for domestic use in the study area.

The chloride levels ranged from 14 to 3084 mg/L, with an average of 298 mg/L. It was a key indicator of salinity in groundwater, and its' concentration above the BIS limit of 250–1000 mg/L (~ 6% samples) had suggested the presence of saline water, often from either natural sources or anthropogenic contamination mainly in the southern part of the study area. While the SO_4^{2-} concentrations were observed with a mean of 59 mg/L. Although mean sulfate levels were lower compared to chloride, high concentrations (> 200 mg/L) in 10% samples were caused a bitter taste in water in the south-western part and may pose health risks if consumed in excess. But the HCO_3^- concentrations ranged from 37 to 1318 mg/L, with a mean of 336 mg/L. These levels indicated moderate alkalinity, which was typically expected in groundwater.

Nitrate (NO_3^-) levels varied from 1 to 187 mg/L, exceeding the BIS (2012) permissible limit of 45 mg/L in 27% samples, mainly contaminated from anthropogenic sources. Fluoride (F^-) concentrations ranged from 0.02 to 10.00 mg/L, with a mean of 0.96 mg/L. About 15% samples exceeded the BIS permissible limit of 1.5 mg/L, particularly in the southern part, posing potential health risks. Based on the combined NO_3^- and F^- , approximately 44% of the area had groundwater quality classified as poor to unfit for drinking due to the elevated levels of either NO_3^- or F^- . The primary contaminants identified were nitrate and fluoride, both of which contribute to non-carcinogenic health risks. Nitrate contamination was mostly anthropogenic in origin, whereas fluoride concentrations in some regions exceed safe limits and posed significant health concerns.

Total hardness (TH) is the concentration of dissolved Ca^{2+} and Mg^{2+} in groundwater. It ranged from 30 to 1350 mg/L, with mean value of 184 mg/L. Whereas total alkalinity (TA) varied from 30 to 1480 mg/L with an average 235 mg/L. More than 25% and 63% of the sampled groundwaters were exceeded the permissible limits for drinking water use.

Table 1

Statistics of major ions including nitrate and fluoride concentrations of groundwater samples at Jaipur district, Rajasthan, India in dry season

Parameters	Units	Minimum	Maximum	Mean	Std. Deviation	Standards (BIS 2012) (mg/L)
EC	$\mu\text{S/cm}$	320	11300	1664	1622	750–3000
TDS	mg/L	195	6780	968	957	500–2000
pH	---	7.60	9.10	8.40	0.30	8.50
Na^+	mg/L	24	2200	296	307	200
K^+	mg/L	2	98	6	8	12
Ca^{2+}	mg/L	2	124	18	15	75–200
Mg^{2+}	mg/L	2	275	34	34	30–100
Cl^-	mg/L	14	3084	298	447	250–1000
SO_4^{2-}	mg/L	ND	720	59	89	200–400
CO_3^-	mg/L	ND	240	31	42	---
HCO_3^-	mg/L	37	1318	336	206	300–600
NO_3^-	mg/L	1	187	38	36	45
F^-	mg/L	0.02	10.00	0.96	1.44	1.50
TH	mg/L	30	1350	184	157	200–600
TA	mg/L	30	1480	329	235	200–600

ND: Not detected.

3.2 LULC based hydrochemistry

The spatial distribution of hydrochemical parameters across major LULC classes such as forest, built-up area, crop land, and waterbodies had shown pronounced hydrochemical heterogeneity governed by coupled geogenic and anthropogenic processes. Electrical conductivity (EC) had shown a progressive increased from forest areas (average: 1275 $\mu\text{S/cm}$) to built-up areas ($\sim 1281 \mu\text{S/cm}$) and crop lands ($\sim 1835 \mu\text{S/cm}$), with exceptionally high averages in waterbodies ($\sim 7750 \mu\text{S/cm}$) and peak values up to 11,300 $\mu\text{S/cm}$ (in Fig. 2a). This trend had reflected enhancing ionic loads and salinity build-up under intensified land use activities. The elevated EC in crop land and waterbodies had indicated evaporate

concentration under semi-arid climatic conditions, irrigation return flow, and accumulation of dissolved salts from agricultural and wastewater infiltration.

Total hardness (TH) had shown elevated concentrations, particularly in crop land (maximum: 1350 mg/L) (in Fig. 2b), indicating substantial contributions from Ca^{2+} and Mg^{2+} derived from carbonate dissolution and silicate weathering. However, the extreme hardness had observed in agricultural areas had suggested additional enrichment through soil-water interaction, fertilizer amendments, and prolonged irrigation practices. Waterbodies also displayed relatively high hardness, likely linked to evaporative concentration and stagnation effects.

Sodium (Na^+) concentrations were significantly elevated in crop land (maximum: 2200 mg/L) and waterbodies (1833 mg/L) (in Fig. 2c), suggesting active cation exchange processes and salinization derived by irrigation return flows. Under alkaline and semi-arid hydroclimatic settings, sodium enrichment was further amplified by evaporative mechanism and weathering of feldspathic minerals. High Na^+ levels might also contribute to sodicity hazards affecting soil permeability.

Magnesium (Mg^{2+}) had shown enhanced concentrations in cropland (maximum: 275 mg/L), reinforcing the dominance of carbonate and silicate weathering (in Fig. 2d), compounded by agricultural intensification. Bicarbonate (HCO_3^-) had remained the dominant anion across the all LULC classes, with maxima exceeding 1318 mg/L in built-up areas (in Fig. 2f). This had indicated strong carbonate weathering, and prolonged groundwater-rock interaction within the aquifer system.

Chloride (Cl^-) concentrations had revealed extremely high maxima in crop land (3049 mg/L) and waterbodies (2084 mg/L) (in Fig. 2e), serving as a conservative tracer of anthropogenic influence. Such elevated chloride levels had indicated contamination from agricultural runoff, domestic sewage, and possible wastewater discharge, thereby signifying progressive salinity hazards in intensively utilized land parcels.

Nitrate (NO_3^-) concentrations were markedly elevated in built-up, crop land and waterbody water samples (maximum: 187 mg/L) (in Fig. 2g), significantly exceeding permissible drinking water limits. The spatial association of nitrate with the urban and agricultural land uses had confirmed its predominantly anthropogenic origin, including fertilizer leaching, septic tank effluents, and improper waste disposal. In contrast, forest areas had shown relatively lower nitrate levels, highlighting minimal anthropogenic disturbance.

Fluoride (F^-) concentrations were substantially elevated in the crop land (maximum: 10.00 mg/L), and built-up zones (7.04 mg/L), far exceeding the recommended limit of 1.5 mg/L (in Fig. 2h). Unlike nitrate, fluoride enrichment was primarily geogenic, linked to dissolution of fluoride-bearing minerals in granitic lithology. Alkaline pH, high bicarbonate concentration, and extended residence time further had enhanced fluoride mobilization in the study area.

The hydrochemical constituents clearly indicated that the crop land and waterbody were most vulnerable to salinization, sodicity, and nutrient contamination, followed by built-up areas, whereas the forest zones had maintained comparatively better hydrochemical integrity.

3.3 Spatial hotspots of groundwater quality

The spatial distribution of major cations (Na^+ and Ca^{2+}) and anions (Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- , and F^-) along with total dissolved solids (TDS) in the groundwater of Jaipur district was comparatively elevated (in Figs. 3, 4). The results had indicated pronounced spatial heterogeneity, with relatively higher ionic concentrations predominantly concentrated in the southern part of the district. The TDS levels had revealed a distinct southward increasing trend, exceeding 2000 mg/L over large areas and reached up to 5000 mg/L in localized pockets such as Chakshu, Mozamabad and Paghi (in Fig. 3a). This elevated salinity corresponds spatially with higher concentrations of Na^+ and Cl^- (in Figs. 3b, d), suggesting intensified mineral dissolution and evaporative concentration processed in these regions. Among the anions, Cl^- had shown the elevated concentrations in the southern and southwestern parts, coinciding with high TDS zones, and indicated possible contributions from anthropogenic sources and evaporite dissolutions. The SO_4^{2-} distribution (in Fig. 3e) had revealed localized enrichment in parts of Renwal, Phulera and Dudu, reflecting heterogenous lithological control and localized geochemical processes. The HCO_3^- concentrations (in Fig. 3f) were comparatively widespread but had shown moderate to high values in central and southern parts, implying dominant carbonate weathering reaction influencing groundwater chemistry. A similar spatial trend was observed for NO_3^- concentration, particularly in Mozamabad and Paghi, where the NO_3^- levels (in Fig. 4a) ranged between 136 to 225 mg/L, significantly above the permissible limit set by the BIS (2012) for drinking water. In addition NO_3^- hotspots were observed in Sanganer, Jaipur and Amer tehsils, suggesting strong anthropogenic inputs, likely from agricultural return flow, sewage infiltration, and urban activities. Fluoride (F^-) concentration (in Fig. 4b) were found to be markedly high along the peripheral zones in the extreme southern boundary of the district. The concurrent occurrence of high TDS, Na^+ , Cl^- , NO_3^- and F^- concentrations had suggested that these contaminants were major contributors of the elevated salinity and overall groundwater pollution in the region. The southern region of Jaipur district had emerged as the most affected zone in terms of groundwater quality degradation. To better visualize the contamination pattern, contours of NO_3^- and F^- levels were used to illustrate in Fig. 4. The diagrams clearly showed that drastic rise in TDS concentrations, particularly in the southern region, well correlated strongly with the elevated NO_3^- and F^- concentrations in groundwater.

3.4 Background-threshold hydrochemistry

The hydrochemical dataset showed substantial spatial variability in groundwater quality, reflecting both natural background geochemical signatures and progressive mineralization trends. The first threshold value (TV1) represented the baseline or natural background conditions, whereas the second and third

(TV2 and TV2) indicated progressively elevated concentration levels relative to the drinking water standards prescribed by the BIS (2012) (in Table 2, Fig. 5). These standards were adopted as the reference criteria because the study area is located in India and the assessment was intended to evaluate groundwater quality in the context of Indian drinking water requirements.

The electrical conductivity (EC) ranged from 320 to 11,300 $\mu\text{S}/\text{cm}$, and its first TV (480 $\mu\text{S}/\text{cm}$) lied well within the desirable BIS limit (750–3000 $\mu\text{S}/\text{cm}$). It had indicated fresh groundwater conditions at baseline levels (in Table 2). However, the second TV (620 $\mu\text{S}/\text{cm}$) had approached the desirable limit, but the third TV (3500 $\mu\text{S}/\text{cm}$) had exceeded the permissible range (in Fig. 5a), showing significant salinity build-up in affected south-wester zones of the study area. Similarly, TDS varied from 195 to 6780 mg/L. The first TV (261 mg/L) and second TV (365 mg/L) indicated low to moderate mineralization, whereas the third TV (1911 mg/L) approached the upper permissible limit (2000 mg/L), which had suggested advanced dissolution processes in certain areas.

The pH (7.6–9.1) indicated mildly to moderately alkaline conditions. The first TV (8.2) had shown near-neutral to slightly alkaline background water, while the second TV (8.5) obtained the upper recommended limit, and had indicated increasing alkalinity.

Among cations, sodium (24–2200 mg/L) was showing marked enrichment. The first TV (49 mg/L) represented background levels within the permissible limit (200 mg/L), but the second TV (715 mg/L) significantly exceeded the standard (in Fig. 5c), and indicated salinization and possible ion-exchange processes. Potassium (2–98 mg/L) remained low at the first TV (7.5 mg/L), but the second TV (20 mg/L) exceeded the BIS limit (12 mg/L), and suggested localized anthropogenic inputs. Calcium (2–124 mg/L) and magnesium (2–275 mg/L) had represented increasing trends from first TVs (8 and 10 mg/L, respectively) to second TVs (21 and 55 mg/L), with Mg^{2+} exceeding its permissible limit (30–100 mg/L) in higher concentration zones.

Chloride (14–3084 mg/L) was encountered significant variability; the first TV (35 mg/L) indicated fresh conditions, whereas the second TV (610 mg/L) exceeded the desirable limit (250 mg/L), confirming high salinity hotspots (in Figs. 3d, 5f). Sulphate had shown a first TV of 25 mg/L, well within safe limits, though maximum values surpassed the permissible range (200–400 mg/L). Bicarbonate (37–1318 mg/L) increased from a first TV of 135 mg/L to a second TV of 561 mg/L (in Fig. 5h), and were reflecting intensified carbonate weathering.

Nitrate (1–187 mg/L) remained low at background levels (first TV: 16 mg/L) but exceeded the BIS limit (45 mg/L) at the second TV (55 mg/L), had represented anthropogenic contamination. Fluoride (0.02–10.0 mg/L) similarly had raised from a safe first TV (0.26 mg/L) to slightly above the permissible limit at the second TV (1.56 mg/L) (in Fig. 5j), and it had indicated for geogenic mobilization.

Total hardness (30–1350 mg/L) and total alkalinity (30–1480 mg/L) increased progressively from background levels (72 and 135 mg/L, respectively) to the elevated third TVs (550 and 700 mg/L, respectively) (in Figs. 5k, l). It was confirmed cumulative mineralization. Overall, the transition from first

to higher threshold values had clearly indicated progressive groundwater quality deterioration driven by both geogenic and anthropogenic processes in the study area.

Table 2
Estimated background and threshold values of hydrochemical constituents of groundwater at Jaipur district, Rajasthan, India in dry season

Sl. No.	Parameter	Range	Standards (BIS, 2012)	First TV	Second TV	Third TV
1	EC	320-11300	750–3000	480	620	3500
2	TDS	195–6780	500–2000	261	365	1911
3	pH	7.6–9.1	8.5	8.2	8.5	---
4	Na ⁺	24-2200	200	49	715	---
5	K ⁺	2–98	12	7.5	20	---
6	Ca ⁺⁺	2-124	75–200	8	21	---
7	Mg ⁺⁺	2-275	30–100	10	55	---
8	Cl ⁻	14-3084	250–1000	35	610	---
9	SO ₄ ⁻⁻	ND-720	200–400	25	---	---
10	HCO ₃ ⁻	37-1318	300–600	135	561	---
11	NO ₃ ⁻	1-187	45	16	55	---
12	F ⁻	0.02-10.00	1.50	0.26	1.56	---
13	TH	30-1350	200–600	72	250	550
14	TA	30-1480	200–600	135	360	700

3.5 Natural backgrounds of hydrochemistry

The spatial distribution of natural background level (NBL) of TDS in groundwater across the study area had shown systematic gradients (in Fig. 3a). Lower concentrations (≤ 200 –210 mg/L) were predominated in the north-central part, particularly around Chomu and Shahpura blocks, indicating fresher groundwater influenced by recent recharge or limited evaporation. Moderate TDS (210–230 mg/L) was observed in the central and southern western areas in the Renwal, Phulera, Jaipur, Sanganer, and Phagi blocks. Higher TDS values (> 240 –250 mg/L) were concentrated in the south-eastern and southern fringes in the Bassi, Chaksu, and Kotkhawat blocks, which had likely shown stronger mineralization, evapotranspiration effects, and geogenic solute inputs. The spatial distribution of Na⁺ NBLs revealed notable variability (in Fig. 3b), with higher concentrations (> 40 mg/L) concentrated in the

northern and central parts around Amer and Chomu. These values were gradually decreased towards the southern and western parts (Phagi, Dudu, and Bassi), where it had dropped below 30–35 mg/L. This distribution indicated a localized accumulation controlled by lithological composition, anthropogenic recharge, and groundwater flow dynamics. The NBL map of Ca^{2+} had shown a clear spatial gradient, ranging from approximately 4 to 8 mg/L (in Fig. 3c). Higher concentrations (7–8 mg/L) were concentrated in the western and central tehsils, and indicated a strong lithological control from carbonate-rich formations. Moderate (5–6 mg/L) was dominated in the northern and eastern tehsils such as Kotputli, Shahpura, and Jamwa Ramgarh, indicated more limited mineral dissolution.

The chloride (Cl^-) NBLs distribution varied between 14–35 mg/L (in Fig. 3d). Higher concentrations (~ 35 mg/L) were observed in localized zones near Amer and the eastern region such as Jamwa Ramgarh, while lower values (25–30 mg/L) were dominated the surrounding areas. The spatial distribution of SO_4^{2-} in the NBLs had shown a concentration range of approximately 5 to 25 mg/L, with the majority of the area falling within the lower range of 5–10 mg/L. Localized pockets of relatively higher concentrations (10–25 mg/L) were observed around Amer, Jaipur, and Shahpura blocks (in Fig. 3e), indicating mild spatial variability. The elevated NBLs of HCO_3^- (120–135 mg/L) were observed in the central and western parts (in Jaipur, Mozamabad, and Dudu blocks), while relatively lower concentrations (90–100 mg/L) occurred in the north-eastern areas, including Kotputli, and Viratnagar blocks (in Fig. 3f). This pattern had suggested that the bicarbonate was largely controlled by carbonate weathering and groundwater-rock interaction processes with localized variability.

The spatial distribution of NO_3^- NBL had shown considerable heterogeneity, with concentrations ranging approximately from 1 to 16 mg/L across the study area. Lower concentration (1–6 mg/L) were widespread, particularly in the north-eastern and south-eastern regions (in Fig. 4a), and it had indicated relatively minimal anthropogenic influence. In contrast, localized pockets of higher concentrations (10–16 mg/L) around Jaipur, Phulera, and parts of the central-western region were observed, and suggested inputs from agricultural and urban activities. The distribution of F^- NBLs had shown generally low, ranging from 0.02 to 0.26 mg/L across the study area (in Fig. 4b). Most regions had shown around 0.08–0.16 mg/L, indicating a generally low background level. Slightly elevated concentrations (0.16–0.26) were observed in localized zones around Phulera, Mozamabad, and parts of Jaipur, indicated minor geogenic enrichment.

3.6 Nitrate concentration and NPI

Nitrate concentration (range: 1–187 mg/L, in Fig. 4a) remained low at background levels (first TV: 16 mg/L) in the study area but exceeded the BIS limit (45 mg/L) at the second TV (55 mg/L, in Fig. 5i), had indicated anthropogenic contamination. With the help of Eq. (4) and $\text{HAV} = 20$ mg/L (Spalding and Exner 1993; Obeidat et al. 2012), the NPIs were estimated at all well sites, and varied from -1.0 to 8.4 , with an average of 0.9 . As shown in Fig. 6, the nitrate concentrations were categorized into three classes: low (< 20.0 mg/L), medium (20.1–45.0 mg/L), and high (> 45.0 mg/L). The high class exceeds the BIS (2012) drinking water standards. It was indicated that in the forest areas, about 50% of the samples contained $<$

20.0 mg/L of nitrate concentration, and had shown relatively low anthropogenic influences (Mondal and Tiwari, 2026), whereas 33% and 17% had fallen within 20.1–45.0 mg/L and > 45.0 mg/L, respectively (Fig. 6b). In built-up areas, its distribution was widely, with 33% of samples < 20.0 mg/L, 36% between 20.1–45.0 mg/L, and 31% exceeding 45.0 mg/L. It was suggested the influence of urban wastewater, septic systems and other anthropogenic sources. In the cropland areas, a considerable proportion of samples had been fallen in the 20.1–45.0 mg/L range (43%), followed 32% < 20.0 mg/L and 26% > 45.0 mg/L, indicating the impact of agricultural activities such as fertilizer application and irrigation return flows. For the waterbody, thorough the number of samples was limited, 50% fallen within 20.1–45.0 mg/L and 50% exceeded 45.0 mg/L. It had implied that potential nitrate inputs from surrounding land uses.

The based on the estimated NPI values (range: -1.0 to 8.4), five water classes were identified: Clean (unpolluted), Light pollution, Moderate pollution, Significant pollution, and Very significant pollution, corresponding to the NPI values of < 0.0, 0.0–1.0, 1.1–2.0, 2.1–3.0, and > 3.0, respectively, as presented in Table 3. The results had indicated that 31.8% (n = 87) of the samples had fallen under the clean (unpolluted) category, and had shown relatively good water quality. The largest proportional, 37.6% (n = 103), corresponded to lightly polluted groundwater, and suggested the onset of anthropogenic influence. Moderate pollution was observed in 13.1% (n = 36) of the samples, and indicated increasing contamination levels. The significant pollution had assessed for 6.9% (n = 19), and highlighted areas of concern that may require management intervention. Notably, about 10.6% (n = 29) of the samples had fallen into very significant pollution category, which represented severely impacted groundwater.

The spatial distribution of the NPI is illustrated in Fig. 7a. Very significant pollution of nitrate concentration in groundwater was predominantly observed as localized patches in the southern parts, particularly within the Phagi, Phulera, Mozamabad, Jaipur, Dudu, and Sangner blocks. In addition, it was also occurred in Koturli block in the extreme northern part. The based on LULC analysis, it had showed that the cropland (n = 16) and built-up areas (n = 10) were primarily associated with zones of the very significant nitrate pollution. It had suggested that agricultural fertilizers application and an untreated or partially treated domestic wastewater were the major sources of nitrate concentration. In contrast, the clean (unpolluted) nitrate water were mainly found in the Renwal, Jamwa Ramgarh, and Shahpura blocks, predominantly within the forest (n:12), built up (n:32) and cropland(n = 43) areas.

Table 3

Nitrate pollution index (NPI) and fluoride pollution index (FPI) range, class, number and percentage of groundwater samples in Jaipur district, Rajasthan, India

Categorization of the samples according to the NPI				
NPI range	NPI class	Type of groundwater as per NPI interpretation	Number of samples	% of samples
< 0.0	1	Clean (unpolluted)	87	31.8
0.0–1.0	2	Light pollution	103	37.6
1.1–2.0	3	Moderate pollution	36	13.1
2.1–3.0	4	Significant pollution	19	6.9
> 3.0	5	Very significant pollution	29	10.6
Categorization of the samples according to the FPI				
FPI range	FPI class	Type of groundwater as per FPI interpretation	Number of samples	% of samples
1.0–2.0	1	Low	26	9.5
2.1–3.0	2	Moderate	153	55.8
3.1–4.0	3	High	95	34.7

3.7 Fluoride concentration and the FPI

Four hydrochemical parameters (i.e., F^- , HCO_3^- , Na^+/Ca^{2+} , and pH) were selected to estimate the fluoride pollution index (FPI) using the Eq. (5). The groundwater quality parameters used in the calculation and their weights are presented in Table 4. Fluoride concentration ranged from 0.02–10.00 mg/L, in Fig. 4b), with background levels remaining low (first TV: 0.26 mg/L), but exceeding the BIS limit of 1.50 mg/L at the second TV (1.56 mg/L, in Fig. 5j). More than 15% ($n = 41$) samples were encountered the fluoride value (> 1.5 mg/L), which were rendering unsuitable for the drinking purposes. Bicarbonate concentrations varied 37–1318 mg/L, with two TVs (First: 135 mg/L and second: 561 mg/L) identified. The Na^+/Ca^{2+} ratio ranged from 0.6 to 235.2, with an average of 24.3, showing the dominance of Na^+ concentration in groundwater chemistry. The evaluated Na^+ concentrations in the study area were largely controlled by two prominent processes such as silicate weathering and untreated effluents enriched in NaCl. Enrichment from both sources causes the dominance of Na^+ over Na^+ in the groundwater. All the samples in the study area were in alkaline in nature, with pH values ranging from 7.6–9.1. The FPI for all groundwater samples was calculated by incorporating the assigned weights (Sajill Kumar 2017), as mentioned in Table 4.

Based on the estimated FPI values (range: 1.5 to 4.0, average: 2.9), groundwater was classified into three categories: low (1.0–2.0), moderate (2.1–3.0), and high (3.1–4.0), as presented in Table 3. The results had indicated that 9.5% (n = 26) of the samples had fallen under the low category, observed mainly in the built-up areas, and had shown relatively good water quality. The largest proportional, 55.8% (n = 153), corresponded to moderate category, and indicated increasing contamination levels. The high pollution was found in 34.7% (n = 95) samples, which represented severely impacted groundwater in term of fluoride contamination, mainly associated with the cropland areas. These highly contaminated areas were distributed across the Dudu, Phagi, Chaksu, and Kotputli blocks in the southern part (in Fig. 7b), with additional occurred in the western part, including the Phulera, Renwal, and Chomu blocks. Although a slight variation from the fluoride concentration and the estimated FPI was observed in some samples, these were classified under the high category due to the factors of other triggering factors governing fluoride dissolution in semi-arid environment. The elevated HCO_3^- concentrations and higher $\text{Na}^+/\text{Ca}^{2+}$ ratios were likely enhanced the dissolution of fluoride-bearing mineral present in the aquifer system. The low FPI category was observed in the northern part, with a few localized patches also present in the southern part of the study area.

Table 4
Weight assigned to water quality parameters involved in calculating Fluoride Pollution Index (FPI) (Sajil Kumar 2017)

Parameter	Concentration (in mg/L)	Weight	Parameter	Concentration ratio and pH value	Weight
Fluoride (F^-)	< 0.6	1	Sodium/Calcium ($\text{Na}^+/\text{Ca}^{2+}$)	< 1.0	1
	0.61–1.2	2		1.1–2.0	2
	1.21–1.5	3		2.1–3.0	3
	> 1.5	4		> 3.0	4
Bicarbonate (HCO_3^-)	< 100.0	1	pH	< 7.0	1
	100.1–200	2		7.1–8.0	2
	200.1–300	3		8.1–9.0	3
	> 300	4		> 9.0	4

4. Discussion

The present study had shown that groundwater quality in the semi-arid region of Rajasthan was controlled by a complex interplay of geogenic processes and anthropogenic pressures, as drawn by the wide variability in hydrochemical parameters and pollution indices. The TDS values ranging from 195 to 6780 mg/L (mean: 968 mg/L, in Table 1) had indicated pronounced salinity enrichment with nearly 62% of samples exceeding the drinking water limits, prescribed the BIS (2012). Such elevated salinity was

typical of semi-arid hydrogeological settings, where limited recharge and high evaporation rates enhanced solute concentration and mineral dissolution (Appelo and Postma 2005; Gao et al. 2020; Mondal and Tiwari 2026). The EC (range: 320 – 11,300 $\mu\text{S}/\text{cm}$; mean: 1664 $\mu\text{S}/\text{cm}$) further corroborated the accumulation of dissolved ions, particularly in the southern and southwestern parts of the study area, where the TDS frequently exceeded 2000 mg/L, and also reached up to 5000 mg/L in some localized zones (in Fig. 3a). Correlation analysis revealed strong positive relationships among TDS- Na^+ ($r = 0.976$), TDS- Cl^- ($r = 0.954$), and Na^+ - Cl^- ($r = 0.913$), indicating that sodium and chloride were major contributors to groundwater salinity, while the moderate Mg^{2+} - Cl^- correlation ($r = 0.624$) suggested additional mineral weathering and anthropogenic influences (Mondal and Tiwari 2026). In addition, the bivariate plots had shown the elevated TDS, Na^+ , Cl^- , and Mg^{2+} concentrations, particularly in the southern and southwestern parts of the study area, indicating the combined influence of geogenic processes, agricultural return flows, and evaporative concentration.

The deviation of natural background levels (NBLs) had provided a quantity basis to distinguish natural hydrochemical signatures from anthropogenic pollution. The first TVs (e.g., NO_3^- : 16 mg/L, F^- : 0.26 mg/L, Na^+ : 49 mg/L) had represented baseline conditions controlled primarily by lithology and water-rock interaction. It was supported by the Gibbs plot, which had indicated that most groundwater samples fallen within the rock dominance field, with many occurring in the evaporation-precipitation zones (Mondal and Tiwari 2026). It was also suggested that groundwater chemistry was predominantly governed by rock-water interactions, with evaporation exerting a secondary influence under the semi-arid climatic conditions of the study area. Whereas the second TVs (NO_3^- : 55 mg/L, F^- : 1.56 mg/L, Na^+ : 715 mg/L, in Fig. 5) had shown anthropogenic enrichment exceeding permissible limits. The earlier study had also shown that the first three factors of principal component analysis accounted for 75.50% of the total variance. Factor 1 (39.46%), dominated by EC, TDS, Na^+ and Cl^- , reflected the combined influence of salinity related geogenic processes and anthropogenic inputs, while Factor 2 (29.30%), characterized by pH, HCO_3^- , CO_3^{2-} and TA, indicated predominantly geogenic controls through mineral dissolution and rock-water interactions. Factor 3 (6.73%), mainly associated with Ca^{2+} , represented a minor geogenic contribution to groundwater chemistry (Mondal and Tiwari 2026). The marked increase between these thresholds had indicated progressive mineralization and contamination, consistent with approaches recommended under the Water Framework Directive and the BRIDGE methodology (Muller et al. 2006; Shand et al. 2007). For instance, chloride had increased from a background of 35 mg/L to 610 mg/L, while bicarbonate had increased from 135 mg/L to 561 mg/L, highlighted both the salinization and intensified carbonate weathering. The spatial distribution NBLs in groundwater had shown systematic hydrochemical gradients (Figs. 4, 5). Low TDS and ion concentrations in recharge dominated in north-central areas, moderate levels in the central-western regions, and elevated values in the southern and southern eastern zones were reflecting enhanced mineralization, evapotranspiration, lithological control, and localized anthropogenic influences. While Nitrate had revealed heterogeneous enrichment from agricultural and sources, and fluoride remained generally low with minor geogenic contribution.

Nitrate contamination had emerged as a major anthropogenic concern in the study area. The concentration ranged from 1 to 187 mg/L, with 27% samples exceeding the permissible limits of 45 mg/L. Spatially, nitrate hotspots (> 100 mg/L) were concentrated in agricultural and urbanized areas such as Mozamabad, Phagi, and Sanganer blocks (in Fig. 4a), indicating strong inputs from fertilizer leaching, irrigation return flows, and wastewater infiltration. The nitrate pollution index (NPI) varying from - 1.0 to 8.4 (mean: 0.9), had revealed that approximately 68.2% of the samples had fallen under the polluted categories, including 37.6% lightly polluted, as shown in Fig. 7a. About 13.1% moderately polluted, and 17.5% significantly to very significantly polluted. This distribution had confirmed the pervasive influence of anthropogenic nitrogen loadings. The mobility of nitrate under oxidizing conditions and its weak adsorption to soil matrices facilitated rapid transport into groundwater (Freeze and Cherry 1979; Wakida et al. 2005). Moreover, nitrate concentrations exceeding 20 mg/L (human-affected value) had clearly indicated the anthropogenic inputs (Spalding and Exner 1993).

In contrast, fluoride contamination was predominantly geogenic, although modulated by hydrochemical conditions and land use practices. Fluoride concentrations ranged from 0.02 to 10.00mg/L (in Table 1), with 15% of the samples exceeding the permissible limits of 1.5 mg/L. Elevated fluoride levels (> 2.50 mg/L) and up to 10.00 mg/L were primarily found in the southern and western parts of the study area, particularly in Dudu, Chaksu, and Phulera blocks (in Fig. 4b). The fluoride pollution index (FPI) ranging from 1.5 to 4.0 (mean: 2.9) had indicated that about 90.5% of the samples had fallen under moderate (55.8%) to high (34.7%) pollution categories, signifying widespread fluoride enrichment (in Fig. 7b). This was attributed to the dissolution of fluoride-bearing minerals in aquifers, enhanced by alkaline pH (7.6–9.1), high bicarbonate concentrations (up to 1318 mg/L), and elevated $\text{Na}^+/\text{Ca}^{2+}$ ratios (0.6-235.2, mean: 24.3). These conditions had promoted ion exchange, and reduced the Ca^{2+} activity, thereby increasing fluoride solubility in these areas (Pickering et al. 1988; Currell et al. 2011; Chakraborti et al. 2013).

The land use and land cover (LULC) analysis had further revealed the role of anthropogenic activities in groundwater quality deterioration. Cropland areas had shown the highest EC (~ 1835 $\mu\text{S}/\text{cm}$), Na^+ (up to 2200 mg/L), and NO_3^- (up to 187 mg/L) had indicated the influence of fertilizer application and irrigation return flows. Waterbodies had shown extreme salinity (average EC: 7750 $\mu\text{S}/\text{cm}$), reflecting evaporative concentration and stagnation. Built up areas were characterized by the elevated nitrate and chloride levels, suggested the contamination from domestic sewage and septic systems in the study area. In contrast, forest areas had maintained relatively low nitrate (< 20 mg/L in approbatory 50% samples), and lower salinity, which had represented near the background condition with minimal anthropogenic disturbance.

The co-occurrence of nitrate and fluoride contamination significantly had affected drinking water suitability. Approximately 44% of the study area had fallen under poor to unfit categories due to the elevated NO_3^- and /or F^- concentrations. While nitrate poses risks such as methemoglobinemia and potential carcinogenic affects (Ward et al. 1996; De Roos et al. 2003), excessive fluoride intake leads to dental and skeletal fluorosis, a major public health issues in India (Chakraborti et al. 2013). The

simultaneous presence of both contaminants worsened non-carcinogenic health risks, particularly in rural populations depend on untreated groundwater. Mondal and Tiwari (2026) similarly identified the highest health-risk zones were using Total Chronic Hazard Index (TCHI), concentrated mainly in the southern and south and south-western parts of the study area, particularly Phulera, Dudu, Mozamabad, Phagi, Chaksu, Sanganer, and Amer blocks, with isolated hotspots in Viratnagar, Kotputli, and Jamwa Ramgarh. Children were the most vulnerable, with 67.2% of the area exceeding the safe TCHI threshold, followed by females and males, indicating widespread non-carcinogenic health risks associated with groundwater contamination.

The integration of NBLs, TVs, NPI, and FPI had provided a comprehensive framework for groundwater quality assessment in semi-arid areas in Rajasthan. The quantitative thresholds (i.e., NO_3^- : 16 and 55 mg/L, F^- : 0.26 and 1.56 mg/L), and pollution indices had delineated contamination gradients, and also identified critical hotspots. Such an approach had not only improved the understanding of hydrochemical processes but also supported the suitable mitigation strategies, including controlled fertilizers use, wastewater management, and artificial recharge. Importantly, the findings will contribute to sustainable groundwater management, and aligned with the global goals such as the Clean Water and Sanitation (SDG-6), emphasizing the local need for integrated monitoring and policy interventions in vulnerable semi-arid regions.

5. Conclusions

This study has provided an integrated assessment of groundwater quality in semi-arid region of Rajasthan using natural background levels (NBLs), threshold values (TVs), and nitrate-fluoride pollution indices (NPI and FPI). Major findings are revealed that significant spatial heterogeneity in groundwater chemistry are governed by both geogenic and anthropogenic influences under the conditions of limited recharge and high evaporation. Groundwater is predominately alkaline and saline, with 62% of the samples exceeding permissible TDS limits and have indicated the mineralization driven by carbonate weathering, silicate dissolution, and evaporation condition, further intensified by irrigation return flows and wastewater inputs.

The derived NBLs and TVs have effectively distinguished natural baseline conditions from human-induced contamination. Nitrate levels are exceeded the permissible limits in 27% of the samples, primarily due to agricultural and urban activities, with 68.2% of the sample classified as polluted based on the NPI. In contrast, fluoride contamination is mainly geogenic, through hydrochemical conditions such as high bicarbonate, elevated $\text{Na}^+/\text{Ca}^{2+}$ ratios, and alkaline pH have significantly enhanced its mobilization. Approximately 15% of the samples are exceeded safe fluoride limits, while the FPI have indicated widespread moderate to high concentration (~ 90.5%).

The land use and land cover has shown cropland and built up areas as major contamination hotspots, whereas the forest regions are largely influenced natural background conditions. The combined occurrence of nitrate and fluoride has extracted approximately 44% of the groundwater samples

unsuitable for drinking in the study area. The applied integrated framework provides a robust approach for groundwater quality assessment, and supports sustainable water resource management in alignment with the United Nations Sustainable Development Goals (SDGs).

Declarations

Acknowledgments

The analytical hydrochemical data are retrieved from Department of Ground Water, Rajasthan. Professors, scientists, technical staffs and research scholars of CSIR-NGRI, Hyderabad and NIT, Srinagar, Uttarakhand have helped directly and indirectly during the course of this research. The Director of CSIR-NGRI, Hyderabad has kindly accorded the approval for the publication of this work (Ref. No.: NGRI/Lib/2026/Pub-46). The authors are thankful to them.

Authorship contribution

N.C. M.: Conceptualized and designed the research, interpreted the analytical hydrochemical data, prepared the figures, and drafted as well as critically revised the manuscript. **K.K.T.:** Retrieved and curated the analytical hydrochemical data from the Department of Ground Water, Rajasthan, and approved finally to be submitted. **M.J.N.:** Supervised the research work.

Ethical Approval: Not applicable to this manuscript.

Consent to Participate: Not applicable.

Consent for Publication: All authors agree to this submission.

Availability of data and materials: Not applicable.

Funding. *The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.*

Declarations Conflict of interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

Data availability. Data was used for the research described in the article.

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Figures

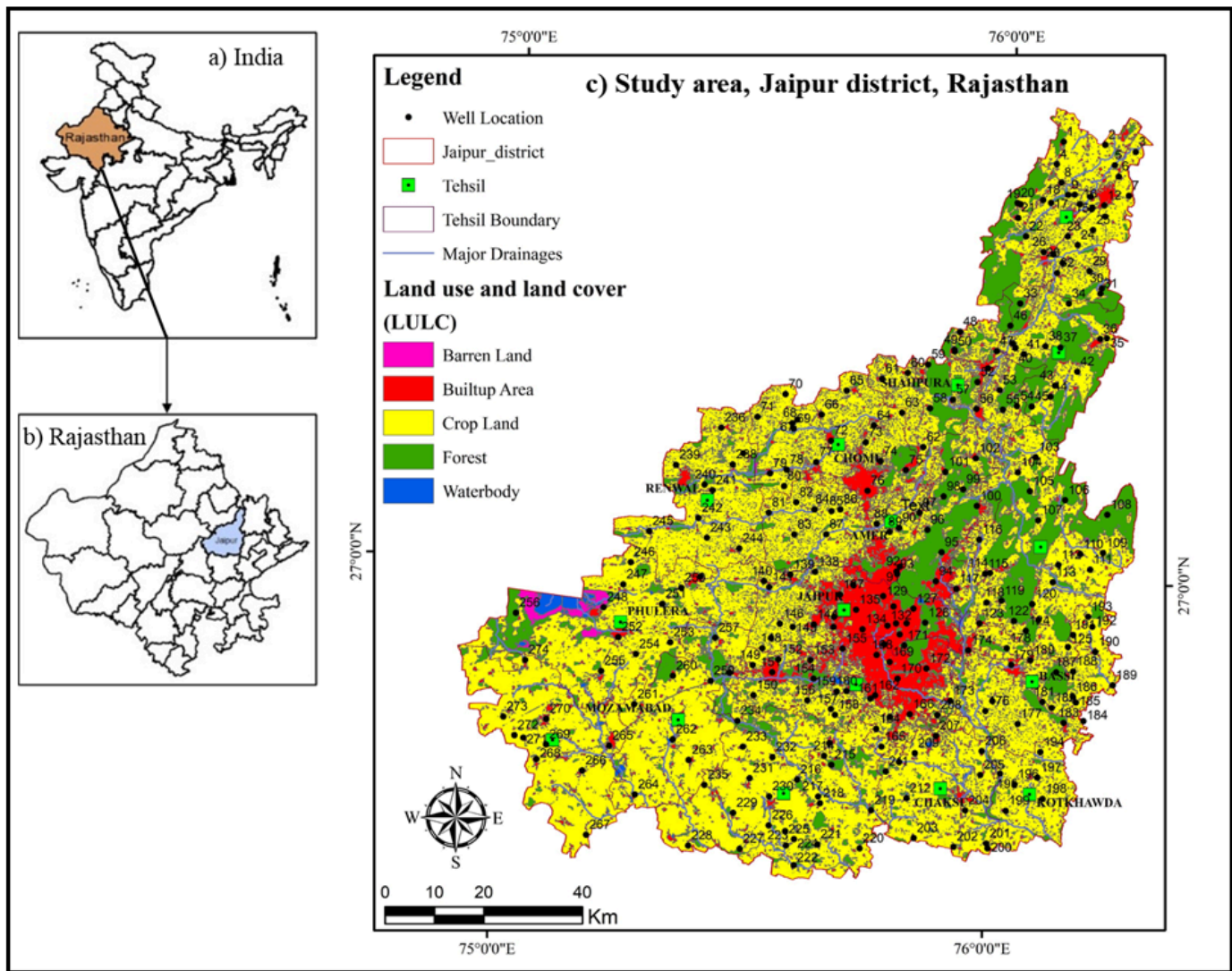


Figure 1

Location and LULC map of Jaipur district, Rajasthan, Western India depicting tehsils, major drainages, and groundwater sampling points

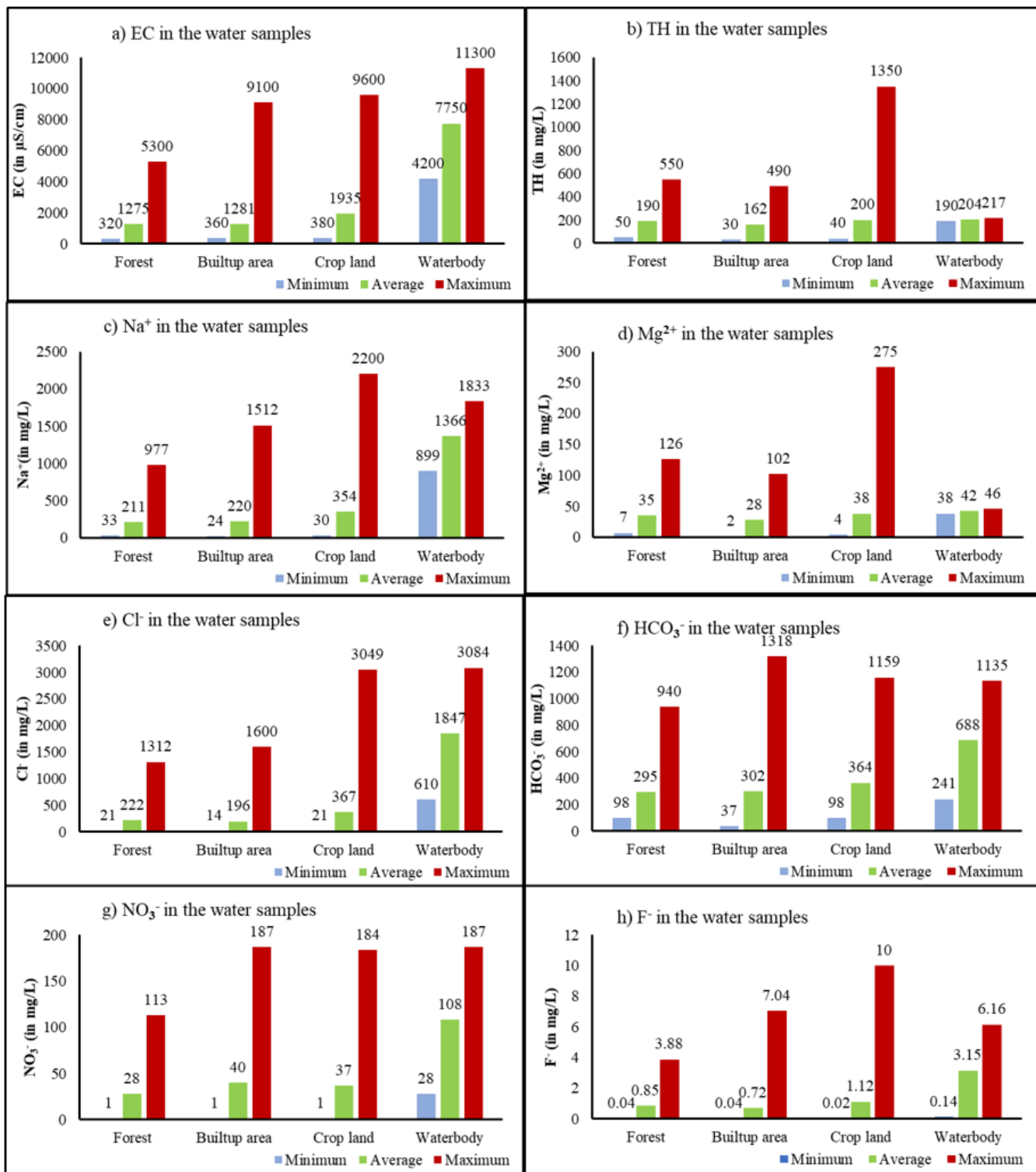


Figure 2

Statistics based on the LULC of a) EC, b) TH, c) Na^+ , d) Mg^{2+} , e) Cl^- , f) HCO_3^- , g) NO_3^- , and h) F^- concentrations in Jaipur district, Rajasthan, western India

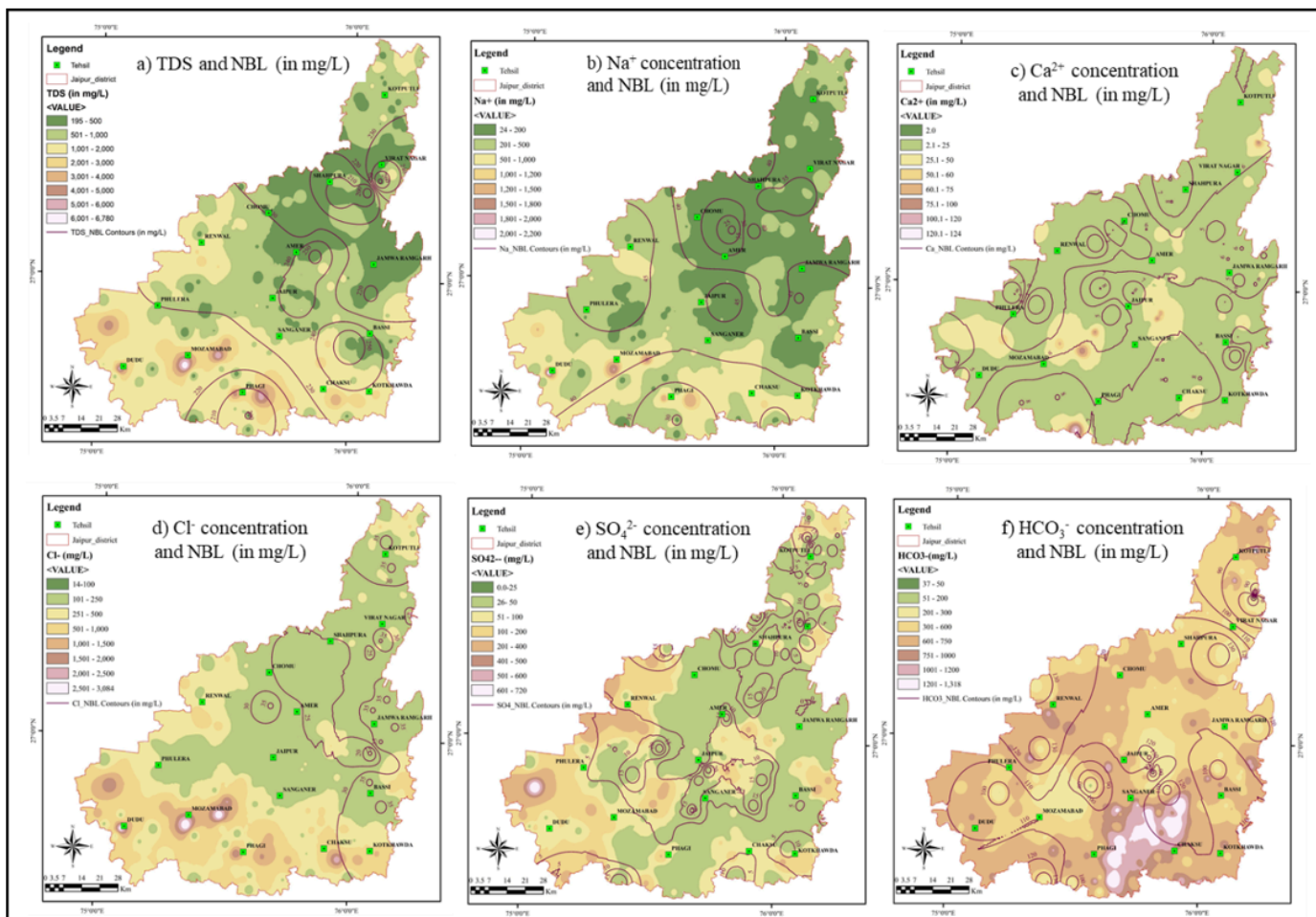


Figure 3

Spatial distribution of a) TDS, b) Na⁺, c) Ca²⁺, d) Cl⁻, e) SO₄²⁻, and f) HCO₃⁻ concentrations, and their NBLs in groundwater of Jaipur District, Rajasthan, Western India

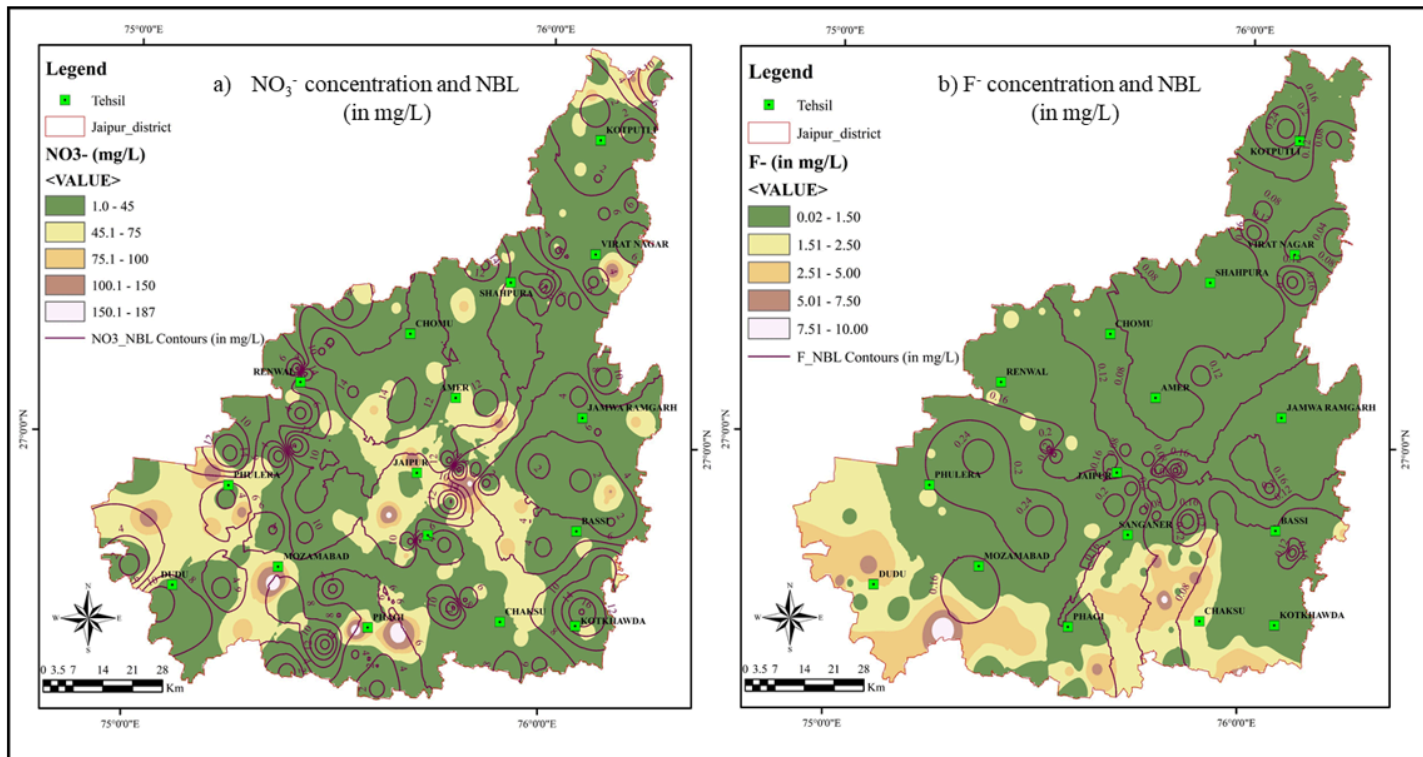


Figure 4

Spatial distribution of a) NO₃⁻, and b) F⁻ concentrations, and their NBLs in groundwater samples of Jaipur District, Rajasthan, Western India

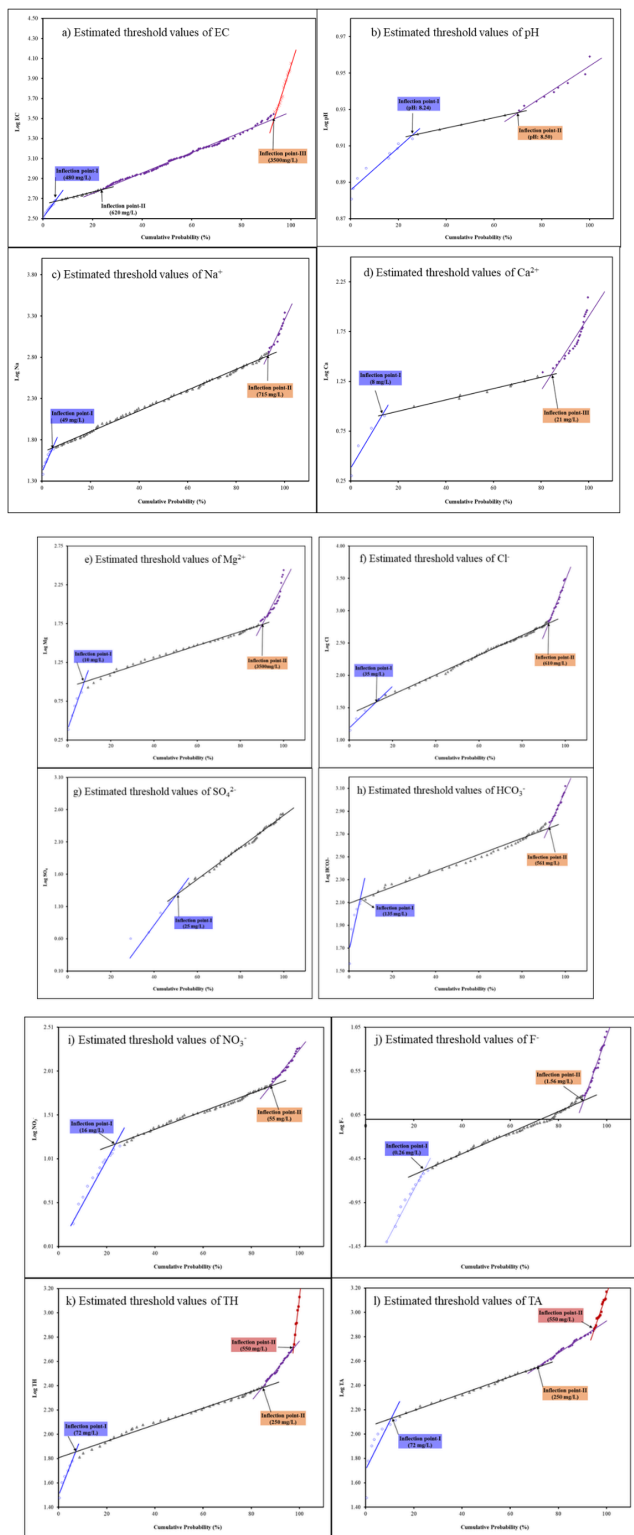


Figure 5

Showing the cumulative plots and estimated threshold values of a) EC, b) pH, c) Na⁺, and d) Ca²⁺ in groundwater of Jaipur District, Rajasthan, Western India

Showing the cumulative plots and the estimated threshold values of e) Mg²⁺, f) Cl⁻, g) SO₄²⁻, and h) HCO₃⁻ concentrations in groundwater of Jaipur District, Rajasthan, Western India

Showing the cumulative plots and estimated threshold values of i) NO₃⁻, j) F⁻, k) TH, and l) TA concentrations in groundwater of Jaipur District, Rajasthan, Western India

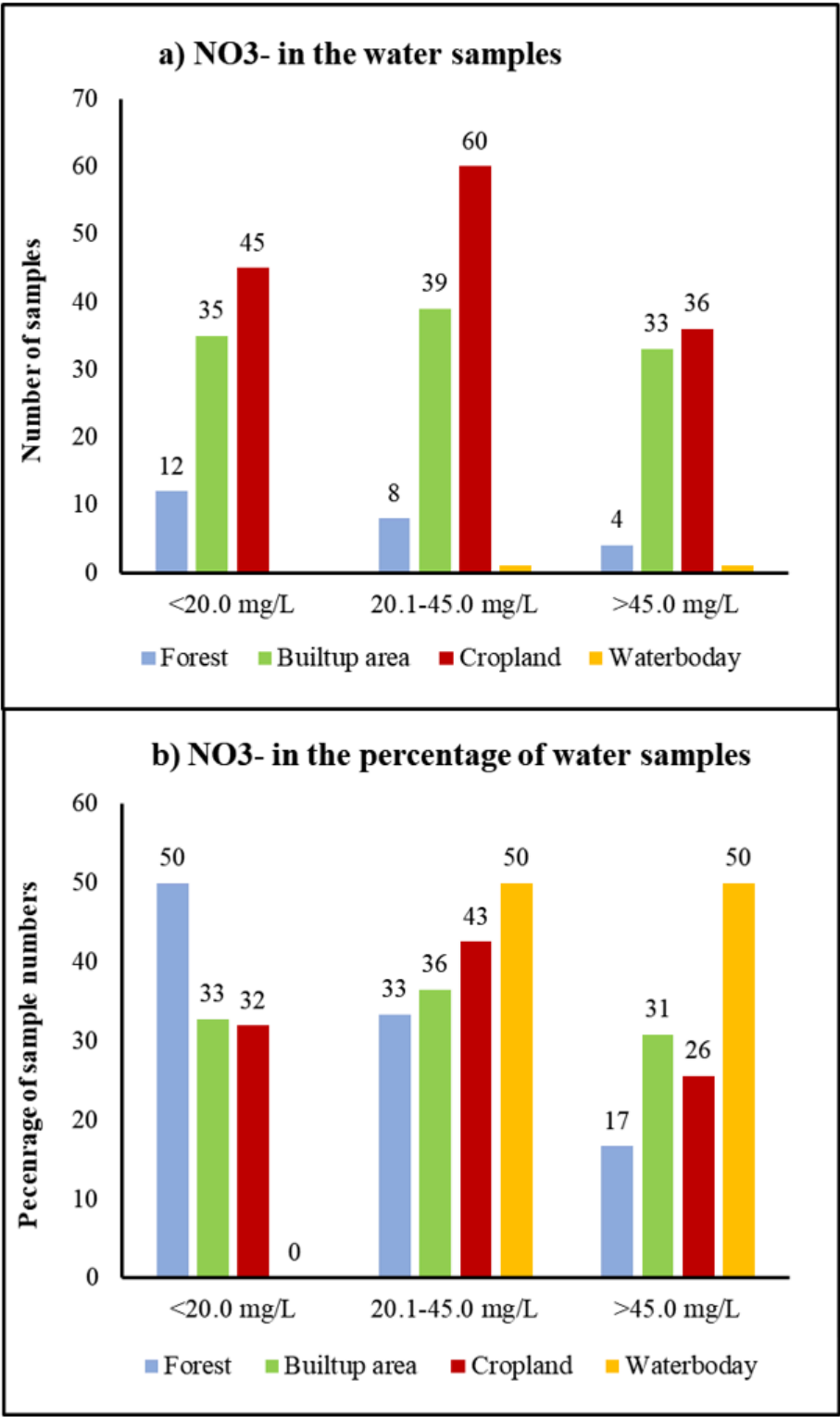


Figure 6

Showing a) frequency distribution of the nitrate concentration (in mg/L), and b) percentage of the collected samples of Jaipur District, Rajasthan, Western India

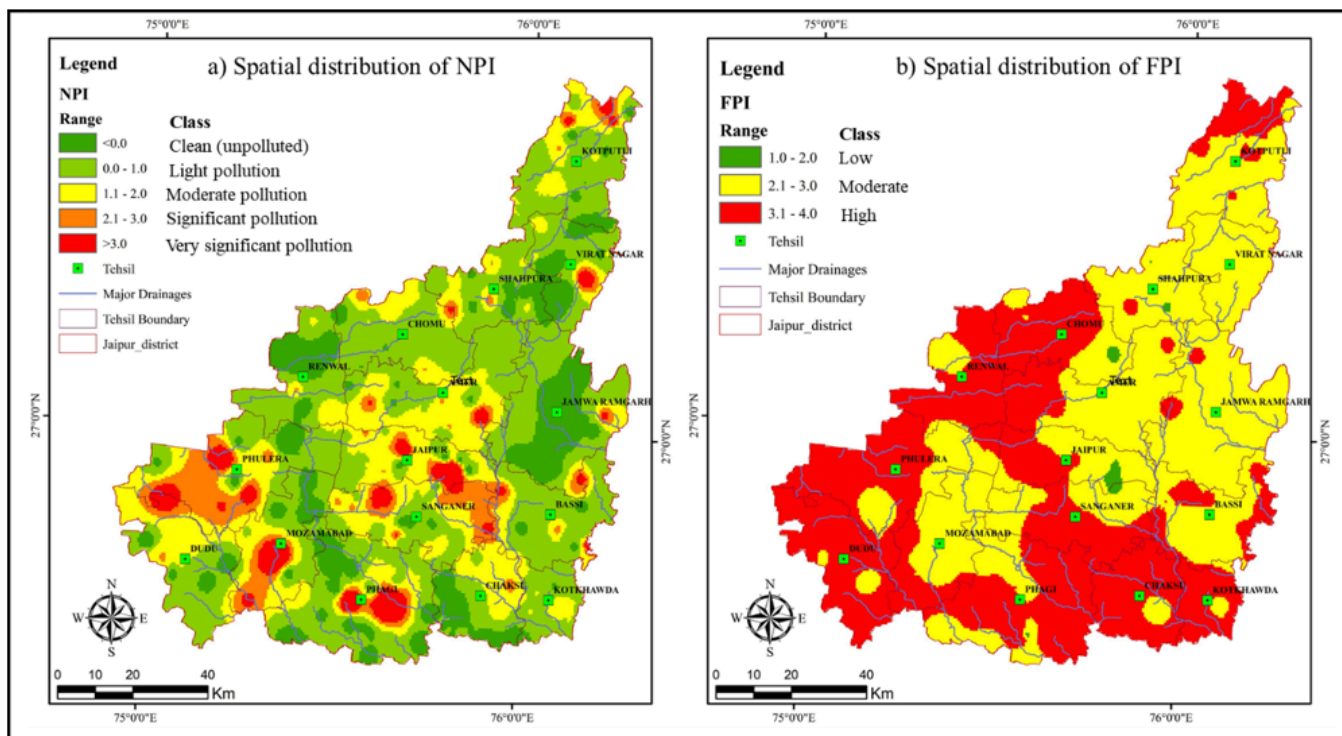


Figure 7

Spatial distribution of a) NPI, and b) FPI in groundwater of Jaipur District, Rajasthan, Western India