



# Hydrochemical characterization of groundwater quality using chemometric analysis and water quality indices in the foothills of Himalayas

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## Abstract

Groundwater pollution of the watershed is mainly influenced by the multifaceted interactions of natural and anthropogenic process. To analyse the spatial–temporal variation and pollution source identification and apportionment, the dataset was subjected to a globally acknowledged coherent technique using water quality indices and chemometric techniques (principal component analysis (PCA) and cluster analysis). The bulk of the samples tested were below the BIS's permissible levels. Groundwater samples from the pre- and post-monsoon seasons mostly contained the anions  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ , while the primary cations were  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ . Groundwater was alkaline and hard at most of the sites. According to hydro-geochemical facies and relationships, Piper diagrams, and principal component analysis, weathering, dissolution, leaching, ion exchange, and evaporation were the key mechanisms influencing groundwater quality. The hydrochemical facies classified the groundwater samples into the Ca-Mg- $\text{HCO}_3$  type. For all the sampling locations, PIG was determined to be 0.43, 0.52, 0.47, 0.48, 1.00, and 0.70; respectively. The majority of the test locations fell into the low to medium contamination zone, as determined by the groundwater pollution index (PIG) and contamination index. Three principal components, which together account for 93.8% of the total variance, were identified via PCA. The study's findings confirm the value of these statistical techniques in interpreting and understanding large datasets and offering reliable information to reduce the time and expense of programmes for monitoring and evaluating water quality.

**Keywords** Chemometric techniques · Foothills of Himalayas · Region · Industrial toxicity · Irrigation use · Pollution index of groundwater (PIG) · Contamination index ( $C_d$ )

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## 1 Introduction

Groundwater is a significant natural water supply for residential, agricultural, and industrial usage and is utilized as a commodity worldwide (Green, 2016; WWDR, 2015). Water pollution has become a severe ecological concern due to several organic and inorganic pollutants created by commercial, agricultural, and industrial textiles, leather, pharmaceutical, and other industries (Yousefi et al., 2017, 2019a, 2019b, 2021a). Groundwater is divided into different portions world across the globe, with 65 per cent being used for drinking water, 20 per cent for animal feeding and farming, and 15 per cent for industrial and mining uses (Adimalla & Qian, 2020; Saeid et al., 2018; Yousefi et al., 2021b, 2021c). Groundwater is used for household purposes by around 30% of the world's population (Rao et al., 2020; Adimalla & Venkatayogi, 2018). The hydrogeomorphic units of the Gangetic Alluvial Plain and the Himalayan Mountain Belt separate the predominantly mountainous state of Uttarakhand (CGWB, 2021). According to the state's vulnerability and risk assessment, groundwater irrigation to net irrigated land has increased over time (CGWB, 2021). Because of the region's widely varying population density, most residents rely on local water sources (springs) and drilled wells (only in the valleys). Groundwater can be a significant alternative water supply for this region (DTE, 1997). Groundwater is a long-term water source in an area because, if properly developed, it may offer a consistent supply of relatively excellent quality water throughout the year.

Certain physico-chemical properties must be explored in order to assess the influence of pollution, industrialization, and urbanization on groundwater. These are the primary characteristics used to describe the groundwater's fiscal state (Panneerselvam et al., 2020; Matta et al., 2015, 2017, 2020a, 2020b, 2020c). Groundwater characteristics were primarily determined by aquifer resources and geochemical processes beneath the surface, with groundwater mixing with minerals and other materials as it penetrates deeper (Todd & Mays, 2005). Rapid increases in anthropogenic practice impacted groundwater through penetration, filtration, and recharging systems in the last three decades (He et al., 2019; Qin et al., 2013). The effects of geogenic and anthropogenic activities on the aquifer system have recently been researched, and the quality and contamination of groundwater to ensure its long-term development and protection. Kumar et al. (2006) examined at the hydro-geochemical processes that impact groundwater quality in Delhi, India, such as dispersion, mixing, ageing of carbonate minerals ( $\text{CaCO}_3$  concretions), electro dialysis, and surface water interaction. The quality of groundwater is impacted by the natural chemical weathering of sedimentary rocks, limestone, and anthropogenic chemicals, according to Jalali (2009) geochemical characterization of groundwater in Razan, Iran. In the village of Lutfullapur, Nawada region, Ghaziabad, Uttar Pradesh, India, Singh et al. (2012) examined groundwater quality for drinking, household, and irrigation and discovered that the ion exchange mechanism is the major driver of groundwater chemistry variation. Ghalib (2017) conducted a study on the evaluation of groundwater chemistry for drinking and irrigation utilities in East–West province, Central Iraq; groundwater chemistry between locations is due to lithological differences inferences and rock weathering evaporation processes. Nag and Das (2017) examined the groundwater in a portion of the Bankura district of West Bengal, India, using Gibbs and Piper diagrams to assess the groundwater chemistry regulated by lithology. Yulin City, Northwest China, Su et al. (2017) assessed groundwater quality and health risks from contamination due to extensive industrial and agricultural activity in the north margin of the loess plateau. Nishi et al. (2018) used bivariate diagrams to characterize the hydro-geochemistry and groundwater quality in a section of

the Precambrian Terrain in Eastern India, finding that the groundwater chemistry is influenced by both geogenic (carbonate and silicate weathering and dissolution, ion exchange, and evaporation) and anthropogenic sources. Adimalla et al. (2020) assessed the groundwater chemistry and health risk from hard rock terrain in south India using pollution index of groundwater (PIG). According to Patil et al. (2020), based on multivariate statistical and groundwater quality index (WQI) analysis, the main factors responsible for water quality degradation in the Kanavi Halla sub-basin of Belagavi, Karnataka, are weathering of rocks, dissolution, extensive nitrogen fertilizer use, and leaching of industrial and domestic wastewater. Some of the most recent and significant studies on groundwater quality evaluation are Saha et al. (2018), Tirkey et al. (2017), Quino–Lima et al. (2020), Mukherjee et al. (2018), and Chakraborty et al. (2020). The literature listed above demonstrates the influence of geogenic origins linked to soil-rock-water interactions, mineral erosion and deposition and dissolution, ion exchange, and evaporation as the primary controlling processes, as well as the influence of anthropogenic activities like domestic wastewater, agro-chemicals, and irrigation return flows as secondary regulating factors. These fundamental ideas can be useful in determining the quality and pollution of groundwater in the current study region. WQIs (water quality indices) are commonly used statistical approaches for identifying quality classes and determining pollution levels (Abbasi & Abbasi, 2012; Hossain & Patra, 2020; Tripathi & Singhal, 2019). Executives in charge of water quality, lawmakers, environmental managers, and future users of water quality evaluations will find it to be a simple and useful tool. WQIs are commonly used in Asia and Africa (Li et al., 2009; Matta et al., 2018, 2020d, 2022c; Kumar et al., 2021). The World Quality Index (WQI) is based on human health and consumption. Various WQIs have been compared in numerous studies during the last decade (Chaudhary et al., 2016; Zotou et al., 2018; Aouiti et al., 2020; Matta et al., 2018, 2022a). There are several WQIs available, but none that are universally recognized; as a result, this method of integrating multiple WQIs has recently received a lot of interest (Zotou et al., 2020). Two of the most extensively used index models for assessing water quality in various parts of the world are the groundwater contamination index ( $C_d$ ) and the pollution index of groundwater (PIG) (Rao et al., 2012, 2018; Backman et al., 1998, Adimalla et al., 2020). Subba Rao (2012) presented a pollution index of groundwater (PIG) to assess the relative impact of individual chemical parameters on overall groundwater chemical quality and discovered that TDS,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $HCO_3^-$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , and F are considered pollution indicators for groundwater quality assessment.

The PIG and contamination index ( $C_d$ ) quantify the state of water quality and measure concentrations of individual drinking water quality requirements. Because the classification of pollution zones with PIG and  $C_d$  is based on drinking water quality criteria, it may be used to analyse groundwater contamination in any test region. Because groundwater pollution is significant, management techniques such as regular quality monitoring and risk assessment are critical, especially in the Middle and Lower Himalaya. Groundwater accounts for 97 per cent of all accessible freshwater resources and is widely extracted. While plentiful on a global scale, it can only be produced to a certain amount without negatively impacting the ecosystem. It is also very varied worldwide and less renewable when used widely. As a result, this resource must be managed sustainably. The United Nations Sustainable Development Goals (SDGs) clearly account for the crucial role that groundwater serves and will keep playing in sustainable development, maintain ecological and climatic balances, especially in Himalayan Region under SDGs 6 and 13. Recently, during the Pandemic COVID-19 outbreak the first and foremost precaution and prevention was use of clean water and sanitation and as a major source of freshwater, groundwater has played a vital role in all the struggle for survival by the humanity (Matta et al., 2020a,

2020b, 2020c, 2020d, 2022b). The immense water reserve under the Earth's surface, known as groundwater, is a vital resource for humans and ecosystems alike. Groundwater demand is fast rising in tandem with population development, and climate change is putting further strain on water supplies. Despite the relevance of drinking water to the health of the local population in developing nations, and the fact that groundwater is often the major supply of drinking water, a chemical quality evaluation of water should be addressed (Nwankwo et al., 2020). The groundwater monitoring network offers information on which measures may be created and when our water management system's parameters should be changed. Comparison research should light the diverse groundwater elements and their health implications. The study aims to understand the current status of groundwater quality in the respective areas, including pollution sources, and to create a specific dataset for the future studies using chemometric approaches. Further, the study aims to understand nearby regions' ecological conditions while understanding groundwater's suitability for irrigation, and domestic and commercial applicability using certain water quality indices. The study's outcome will contribute as a baseline for future research on industrial complexes in the Himalayan Region, including strengthening of groundwater management standards, resulting in more sustainable decision-making and a decrease in groundwater and environmental pollution problems in the region.

## 2 Material and methods

### 2.1 Hydrogeology of the sampling area

Dehradun District is the State capital of Uttarakhand and is located in the Lower Himalayan Region of Northern India, with latitudes and longitudes of 30.3165° N, 78.0322° E. The average elevation of the Dehradun District is around 447 m above sea level, and the total area of the sampling location is 196.48 Km<sup>2</sup>. Conferring to the national census of 2011, the overall population of Dehradun District is 803,983. This region may be categorized into four geomorphological components: alluvium, structural and denudational hills, piedmont fan deposits, and residual hills. The area's climatic condition is subtropical and varies from cold to tropical depending upon the elevation of the location. The average yearly rainfall is around 2073.3 mm, and the constant relative humidity ranges from 14.9% to 67.6%. The identification was made for groundwater sampling sites based on the effective use of groundwater impact (expected), majorly near agricultural and industrial areas. The groundwater of these sampling locations used is for ingestion, domestic, and irrigation purposes.

The Dehradun region receives drinking water from significant sources, surface water, and groundwater. According to hydrogeological conditions, the Dehradun is distributed in 3 hydrological components. Himalayan mountain belt, Siwalik zone, and Doon gravels. In the Himalayan mountain belt unit, groundwater separates local bodies from confined and unconfined conditions. This unit's major rock types are present: quartzite, shale, slate, phyllite, limestone, sandstone, and dolomite of Jaunsar. In the Siwalik zone, groundwater is found under confined and unconfined conditions, and this unit's water level is comparatively deep. The part of the intermountain valley in the Dehradun District is sustained through alluvial fan deposits. These alluvial fan deposits are known as Doon gravels, primarily consisting of sandstone, phyllite, and quartzite rocks. The groundwater depth in the southernmost part of Dehradun District is close to the hill and characterized by a water

table > 15 mg/l (metres below ground level). The intermediate part range is between 10 and 15 mg/l.

## 2.2 Sample collection and water quality analysis

In the years 2019 and 2020, a total of 72 water samples were collected from various groundwater sources (hand pumps, submersible pumps, and deep tube wells) during both pre-monsoon (36 samples) and post-monsoon (36 samples) from six sampling locations in the Dehradun District (Fig. 1). For hydrochemical analysis, the acquired water samples were placed in one-litre pre-acid-washed polypropylene containers. Samples were maintained in an ice bucket at 4 °C until transferred to the laboratory and refrigerated to avoid contamination and the effects of temperature and light. After increasing the amount to 50 ml by adding deionized water, the final volume was filtered with a Whatman No. 42 filter paper (APHA, 2017; USEPA, 1999). A portable multi-analyser from HACH (HQ40D) Multi Meter from Germany was used to test pH and total dissolved solid (TDS). Total alkalinity, total hardness, and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are estimated by titration method with 0.1 N hydrochloric acid and ethylene diamine tetraacetic acid (acidic acid EDTA) (Trivedy et al., 1987). Nitrate ( $\text{NO}_3^-$ ) and sulphate ( $\text{SO}_4^{2-}$ ) contents in groundwater samples were determined by UV spectrophotometric band screening and turbidimetric procedures, respectively (APHA, 2017; Trivedy et al., 1987). The content of  $\text{Na}^+$  and  $\text{K}^+$  in groundwater samples was analysed by a flame photometer (1382, ESICO).

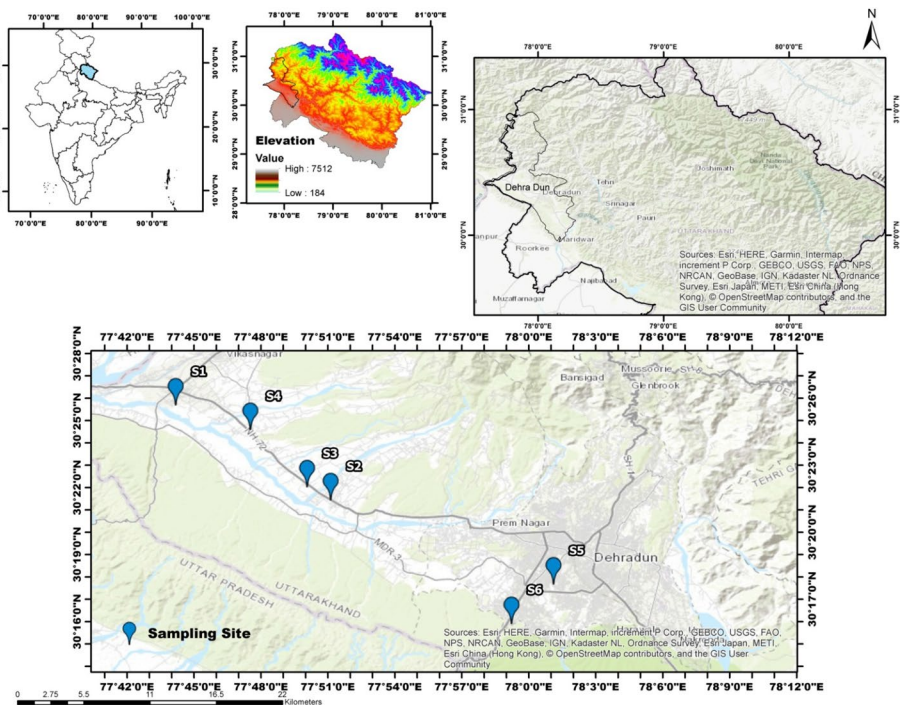


Fig. 1 Geographical map of groundwater sampling sites in Dehradun region, Uttarakhand (India)

## 2.3 Quality assurance and quality control (QA/QC)

The equipment used for all analyses was pre-calibrated using standard solutions or as indicated by their company guidelines to preserve accuracy and precision in observations. Before each in situ assessment, all electrodes were thoroughly cleaned with deionized water. The probes were conditioned in the sample before each usage to ensure the best stabilization time. Freshly produced buffer solutions of two units were used to calibrate the washed and dried pH probe. Standard operating protocols for each instrument and chemical analysis were followed throughout the research period with sufficient safety. All chemical analyses were performed using “A” grade quality glassware and chemicals from Borocile, Merck, and Fisher Scientific in the USA for reliable results.

## 2.4 Assessment of groundwater suitability for irrigation

Groundwater is known to contain a high concentration of dissolved ions (cations and anions), which can harm the physical and chemical conditions of both plant life and soils, such as lowering osmotic pressure, which reduces water flow or transmission through various branches to leaves, and weakening of soil structure and texture, which may lead to reduced permeability (Nagaraju et al., 2014). Sodium adsorption ratio (SAR), which indicates sodium hazard determined to various harvests and reveals the intensity of cation exchange reflexes in water existing in soil, is a common property whose indices provide the foundation for determining the appropriateness of groundwater for irrigation (Salifu et al., 2017). Salinity and alkalinity hazard (SAH), which is measured by electrical conductivity (EC) and the US salinity Laboratory diagram (USSL), soluble sodium percentage (SSP), which reflects the maximum sodium percentage, reduces soil permeability for irrigation (Purushothman et al., 2012; Wilcox, 1955). It is a most important index for monitoring water quality for irrigation purposes, with calcium, sodium, magnesium, and potassium concentrations included in the SSP calculation and magnesium hazard (MH), which reveals how much magnesium is present in the water. Anionic mismatch in soil caused by an overabundance of magnesium compared to calcium in groundwater might reduce crop production (Kumar et al., 2007). The MH was examined using an equation (Palliwal, 1972). The calcium and magnesium concentrations utilized in this computation are expressed in milliequivalents per litre (meq/L). Table 1 shows the relationships used to estimate the indices mentioned above.

## 2.5 Water quality indices

### 2.5.1 Contamination index ( $C_d$ )

The applicability of the contamination index is used to assess the water quality by calculating the contamination level and calculated individually for every water sample. The maximum permissible concentration (MAC) is calculated as the number of individual components' contamination factors exceeding the upper permissible value. As a result, the  $C_d$  sums up the cumulative effects of many water quality parameters that

**Table 1** Water quality indices and irrigational water quality parameters

Index	Equation	Index value		Number of samples		Water condition	
		Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon
Sodium adsorption ratio (Wilcox, 1955)	$SAR = \frac{Na^+}{\sqrt{Ca^{2+} + Mg^{2+}}} \times 100$	SAR < 10	36	36	36	Excellent	Excellent
		10 < SAR < 18	–	–	–	Good	Good
Salinity and alkalinity hazard (Wilcox, 1955)	Total salt concentration	18 < SAR < 26	–	–	–	Doubtful	Doubtful
		SAR > 26	–	–	–	Unsuitable	Unsuitable
		EC < 250	–	–	–	Excellent	Excellent
		250 < EC < 750	36	36	36	Good	Good
		750 < EC < 2250	–	–	–	Permissible	Permissible
Soluble sodium percentage (Wilcox, 1955)	$SSP = \frac{Na^{++} + K^+}{Ca^{2+} + Mg^{2+} + Na^{++} + K^+} \times 100$	EC > 2250	–	–	–	Unsuitable	Unsuitable
		< 20	–	–	–	Excellent	Excellent
		20–40	27	27	33	Good	Good
		40–60	9	9	3	Permissible	Permissible
		60–80	–	–	–	Doubtful	Doubtful
Magnesium hazard (Bhardwaj & Singh, 2011)	$MH = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100$	> 80	–	–	–	Unsuitable	Unsuitable
		MH < 50%	–	–	–	Suitable	Suitable
Gibbs Ratio I (For Anion)	$Cl^- / (Cl^- + HCO_3)$	MH > 50%	36	36	36	Harmful and Unsuitable	Harmful and Unsuitable
Gibbs Ratio II (For Cation)		–	–	–	–	–	–
		–	–	–	–	–	–
		–	–	–	–	–	–

are considered detrimental to household water. The Contaminatiex ( $C_d$ ) for each of the influential parameters is expressed as the following equation:

$$C_d = \sum_{i=0}^n C_{fi} \quad (1)$$

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1 \quad (2)$$

The rating scale of  $C_d$  is proposed as  $C_d < 1$  (low contamination),  $C_d = 1-3$  (medium contamination),  $C_d > 3$  (high contamination) (Backman et al., 1998).

## 2.5.2 Pollution index of groundwater (PIG)

In 2012, Subba Rao firstly proposed the pollution index of groundwater. PIG is a realistic technique for assessing the water quality by computing the PIG value involving 5 steps in this process. The first step is to measure the relative weight ( $R_w$ ) for every water quality parameter. The relative weight scale range varies from (1) to (5), depending on human well-being. The highest value of (5) was TDS,  $SO_4^{2-}$ ,  $NO_3^-$ ; (4) to pH,  $Cl^-$ ; (3) to  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $HCO_3^-$  and (2) to turbidity and  $Na^+$ ; (1) to  $K^+$  (Table 2). The lowest number of (1) in the relative weight refers to the least essential feature, while the most significant value of (5) in the relative weight shows the most important role in human health. The weight parameter (WP) is calculated for each chemical parameter in the second phase to determine its proportional contribution to overall groundwater quality. The formula to calculate the WP:

$$WP = \frac{RW}{\sum RW} \quad (3)$$

The third step is to calculate the concentration status (SC), which is calculated using the following equation:

**Table 2** Weighing scale for drinking water quality standard with respect to water quality parameters

Water quality Parameters	Units	Drinking water quality standard (Ds)	Relative weight (Rw)	Weight parameter (Wp)
pH		7	4	0.108108
TDS	mg/l	500	5	0.135135
Turbidity	mg/l	1	2	0.054054
Ca <sup>2+</sup>	mg/l	75	3	0.081081
Mg <sup>2+</sup>	mg/l	30	3	0.081081
Na <sup>+</sup>	mg/l	200	2	0.054054
K <sup>+</sup>	mg/l	10	1	0.027027
HCO <sub>3</sub> <sup>-</sup>	mg/l	300	3	0.081081
Cl <sup>-</sup>	mg/l	250	4	0.108108
SO <sub>4</sub>	mg/l	150	5	0.135135
NO <sub>3</sub>	mg/l	45	5	0.135135
Sum			37	1.00



$$SC = \frac{C_i^n}{DWQS_i^n} \quad (4)$$

where C is the concentration of chemical parameter “n” and DWQS is the “nth” parameter of the drinking water quality standard. The overall groundwater quality (OW) is determined in the fourth step by multiplying the WP with the SC, as stated in Eq. (5)

$$OW = WP \times SC \quad (5)$$

Eventually, *PIG* is estimated by using the following equation:

$$PIG = \sum_i^n OW \quad (6)$$

Furthermore, Subba Rao (2012) categorized the pollution index of groundwater for five classes based on *PIG* values as Insignificant pollution ( $PIG < 1.0$ ), Low pollution ( $1.0 < PIG < 1.5$ ), Moderate pollution ( $1.5 < PIG < 2.0$ ), High pollution ( $2.0 < PIG < 2.5$ ), Very high pollution ( $PIG > 2.5$ ).

## 2.6 Chemometric techniques

The study deals with chemometric tools such as PCA and CA to establish inter-variable relationships using IBM SPSS Statistics 26 software.

### 2.6.1 Principal component analysis (PCA) and cluster analysis (CA)

By defining and standardizing the major responsible water quality indicators, PCA reduces the dimensionality of the initially observed dataset. Because the scales of measurements and magnitudes of water quality variables differed, the data had to be standardized to fit the normal distribution of all parameters (Maji & Chaudhary, 2019; Mishra, 2010). PCA makes the process of estimating water quality more realistic and cost-effective by dramatically reducing the work, cost, and time necessary for a large number of variables. PCA can get information about a specific variable with the least damage to the entire dataset (Singh, 2004). PCA eliminated variables that were duplicated or highly linked (Sharma et al., 2015). The Kaiser–Meyer–Olkin (KMO) and Bartlett’s tests were used to determine whether the dataset was suitable for PCA. Community values  $> 0.5$  were used to investigate variable selection for PCA. The varimax rotation approach was utilized to identify the relationship between data sources and critical factors (Noori et al., 2010). The data are obtained by converting the original dataset into a normalized version due to unit variation, which produces a new set of uncorrelated pseudo-variables known as principal components (PCs). PCs were identified by producing screen plots with eigen values larger than 1 (Kaiser normalizing approach).

Cluster analysis is a convenient technique of impartially assembling a massive dataset into clusters based on their similar properties. The main aim of clustering is to classify comparatively similar monitoring stations based on their similar water quality characteristics (Zhaoa et al., 2012). The hierarchical method of clustering was used for CA and based on Ward’s linkage method by the standardized dataset. The classification was performed using the square Euclidean distance measure, which is relatively similar to producing a dendrogram. Clusters in dendrograms represent high external heterogeneity (between

clusters) and internal consistency (within clusters) (Kazi et al., 2009; Shrestha & Kazama, 2007).

### 3 Result and discussion

#### 3.1 The temporal disparity of physico-chemical properties of groundwater

The physico-chemical properties of groundwater samples collected in pre-monsoon and post-monsoon seasons during the years 2019–2020 are shown in Table 3. During the study period, pH values ranged from 7.12 to 8.12, indicating slightly alkaline water in both seasons. Water samples with pH values of 6.5 to 8.4 should be used for irrigation (Souza et al., 2020; Hosseinifard et al., 2015; Müller & Cornel, 2017). These groundwater samples are within safe ranges of WHO (2011) and BIS (2012). EC levels remained more significant than the allowed limit of 250 microS/cm during each season (WHO, 2017). All samples had mean EC (S/cm) values more critical than the permitted limits, i.e. 478.25 (in pre-monsoon) and 602.11 (in post-monsoon). TDS in mg/L was found to be less than the allowed limits of WHO (2017) and BIS (2012), with average values of 384.21 (pre-monsoon) and 392.38 (post-monsoon). There was a modest rise in EC and TDS in the post-monsoon season compared to the pre-monsoon season. Geochemical processes like ion exchange, mineralization, sediment/soil dissolution, and precipitation can all produce significant fluctuations in EC and TDS levels (Ehya & Marbouti, 2016). This variance in the research region has been attributed to the leaching, dissolving, or mixing of salts caused by geochemical or anthropogenic activity (Rao et al., 2018, 2020; Sharma et al., 2017). During the summer, the water in the interspaces of the soil evaporates, accumulating salts in the upper layer of the soil, which are then leached back out during the monsoon period, resulting in high EC and TDS levels (Singh et al., 2013). Total hardness levels in drinking water ranged from 293.69 mg/L to 297.69 mg/L, higher than the recommended 200 mg/L limit. (BIS, 2012). Total hardness in groundwater can be classified as soft (0–75), mild (75–150), hard (150–300), or very hard (>300), according to Singh et al. (2020). Pre-monsoon alkalinity levels ranged from 188.57 mg/L (pre-monsoon) to 191.39 mg/L (post-monsoon). Alkalinity is another critical metric for assessing water quality; alkalinities comprise essential components such as carbonates and bicarbonates (Panghal et al., 2020).

#### 3.2 The Spatial disparity of physico-chemical properties of groundwater

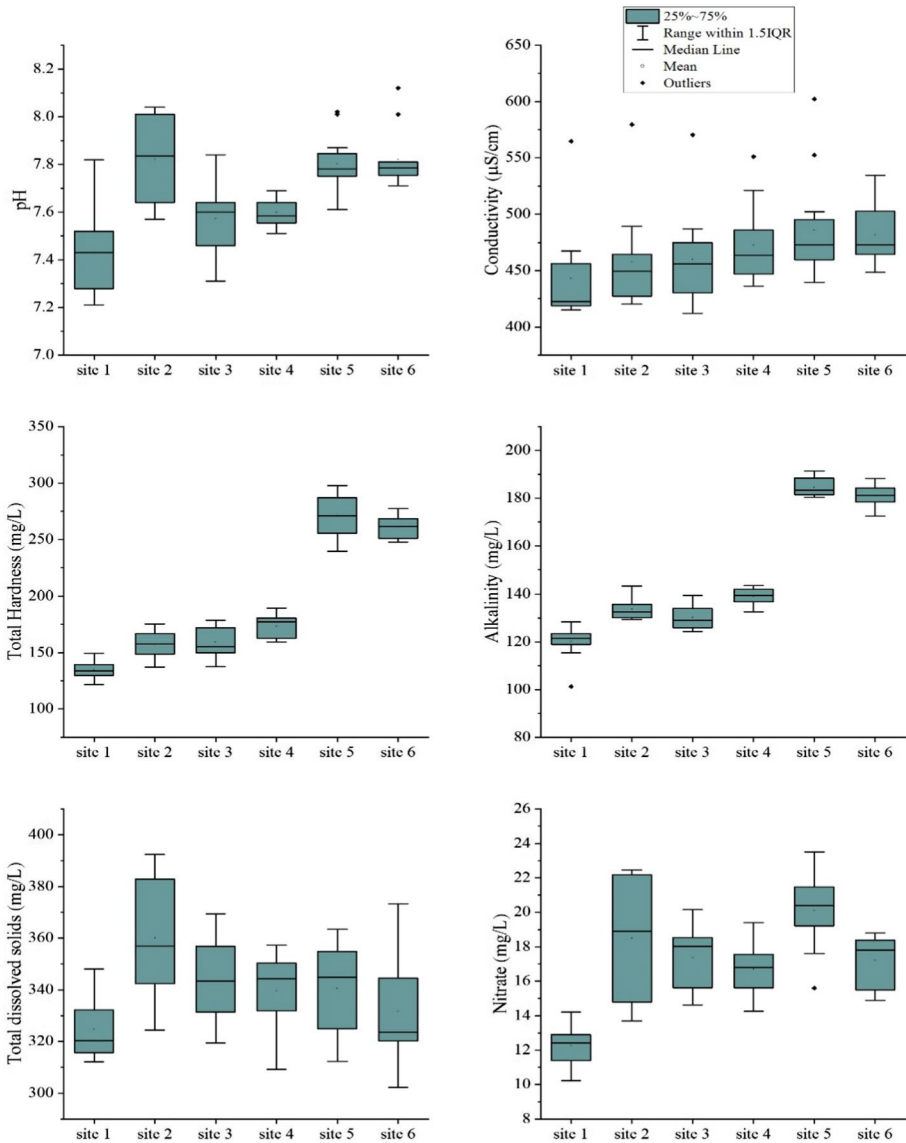
Improper storage or disposal of composite waste, which includes wastewater discharged from business complexes and domestics and detergents, oils, medications, paints, pesticides, and disinfectants, can result in severe groundwater contamination (Anwar, 2003; Kass et al., 2005). According to a UN report, 2 million tonnes of sewage, industrial, and agricultural waste are dumped into the world's water (UNWWAP, 2003). Table 4 shows the mean range of physico-chemical parameters in the groundwater for each sampling sites. Spatial variation in the total groundwater samples was examined independently based on physico-chemical contents by box plots (Fig. 2a, b). The box plot is a powerful statistical tool that displays the data distribution's median, range, and shape. Since the distributions of water quality parameters are usually skewed to the right, it is preferable to consider the median as the indicator of central tendency. The box's centred horizontal line, the 25th and 75th percentiles (quartiles), the top and bottom of the box, and the ends of the

**Table 3** Temporal descriptive statistics of different physico-chemical parameters in Groundwater samples

Season	Pre-monsoon season					Post-monsoon season					BIS Standard		
	Min	Max	Mean±SD	No. of sample > than desirable limit	No. of sample > than permissible limit	Min	Max	Mean±SD	No. of sample > than desirable limit	No. of sample > than permissible limit	Max desirable limit	Max permissible limit	
pH	7.12	8.12	7.71±0.04	-	-	7.23	8.01	7.67±0.23	-	-	6.5-8.5	-	
Conductivity	412.34	478.25	446.68±19.89	<b>36</b>	36	414.28	602.11	486.78±47.87	<b>36</b>	<b>36</b>	-	-	
TDS	298.34	384.21	335.27±19.44	-	-	312.31	392.38	344.14±21.82	-	-	500	2000	
Turbidity (NTU)	0.24	1.11	0.90±0.09	<b>4</b>	-	0.90	1.44	1.06±0.14	<b>7</b>	-	1	5	
TH	121.57	297.69	192.36±56.12	<b>12</b>	-	128.32	293.69	193.01±54.37	<b>12</b>	-	200	600	
Alkalinity (mg/L)	101.19	188.57	147.96±4.00	-	-	115.32	191.39	151.71±28.10	-	-	200	600	
Bicarbonates	115.49	178.57	146.98±18.88	<b>36</b>	-	117.18	175.28	149.16±14.35	<b>36</b>	-	30	500	
Nitrates	11.4	23.51	16.91±3.19	-	-	10.23	22.45	17.12±3.15	-	-	45	-	
SO <sub>4</sub>													
(mg/L)	12.7	24.19	17.25±3.10	-	-	12.4	23.58	17.84±3.21	-	-	200	400	
Cl (mg/L)	13.2	22.5	17.92±2.73	-	-	14.56	23.48	19.05±2.61	-	-	250	1000	
K (mg/L)	11.41	21.17	15.73±2.50	-	-	12.35	23.21	16.95±2.73	-	-	-	-	
Na (mg/L)	11.4	23.51	16.91±3.19	-	-	10.23	22.45	17.12±3.15	-	-	-	200	
Ca	40.56	129.35	81.42±25.35	<b>19</b>	-	64.11	129.42	88.78±20.49	<b>24</b>	-	75	200	
Mg	15.41	59.88	36.74±11.64	<b>21</b>	-	28.56	58.14	41.69±7.81	<b>29</b>	-	30	100	

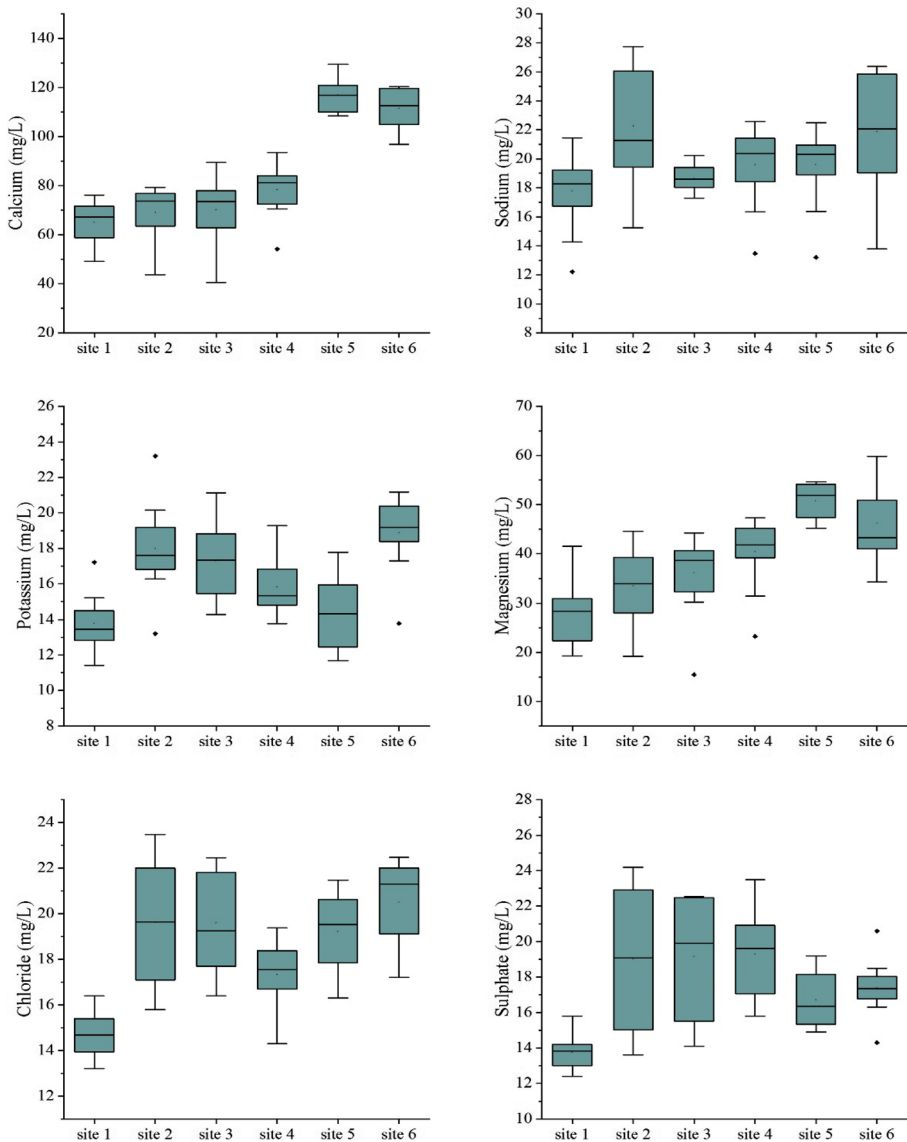
**Table 4** Spatial descriptive statistics of different physico-chemical parameters in groundwater samples

Parameters	Site 1 (Mean $\pm$ SD)	Site 2 (Mean $\pm$ SD)	Site 3 (Mean $\pm$ SD)	Site 4 (Mean $\pm$ SD)	Site 5 (Mean $\pm$ SD)	Site 6 (Mean $\pm$ SD)
pH	7.43 $\pm$ 0.18	7.82 $\pm$ 0.17	7.57 $\pm$ 0.13	7.59 $\pm$ 0.05	7.80 $\pm$ 0.11	7.82 $\pm$ 0.12
Conductivity	442.99 $\pm$ 42.46	457.63 $\pm$ 43.71	459.77 $\pm$ 42.50	472.51 $\pm$ 34.50	485.92 $\pm$ 47.42	481.58 $\pm$ 28.05
TDS	324.68 $\pm$ 12.74	360.18 $\pm$ 22.90	343.27 $\pm$ 15.48	339.62 $\pm$ 15.38	340.54 $\pm$ 17.00	331.60 $\pm$ 18.80
Turbidity	0.86 $\pm$ 0.10	0.93 $\pm$ 0.12	0.95 $\pm$ 0.08	0.88 $\pm$ 0.32	1.10 $\pm$ 0.17	1.09 $\pm$ 0.07
TH	134.74 $\pm$ 7.68	157.08 $\pm$ 12.36	159.18 $\pm$ 13.32	173.27 $\pm$ 10.32	271.13 $\pm$ 19.01	260.8 $\pm$ 10.59
Alkalinity	120.23 $\pm$ 6.96	133.64 $\pm$ 4.27	130.17 $\pm$ 5.19	138.90 $\pm$ 3.51	184.62 $\pm$ 3.79	181.01 $\pm$ 4.79
Bicarbonates	115.24 $\pm$ 7.06	126.52 $\pm$ 3.49	123.96 $\pm$ 11.09	137.78 $\pm$ 7.48	313.73 $\pm$ 33.16	155.03 $\pm$ 4.17
Nitrates	12.25 $\pm$ 1.19	18.49 $\pm$ 3.60	17.38 $\pm$ 1.86	16.68 $\pm$ 1.43	20.09 $\pm$ 2.08	17.20 $\pm$ 1.47
Sulphate	13.73 $\pm$ 0.91	19.02 $\pm$ 4.01	19.16 $\pm$ 3.48	19.27 $\pm$ 2.33	16.70 $\pm$ 1.54	17.39 $\pm$ 1.48
Chloride	14.67 $\pm$ 0.97	19.61 $\pm$ 2.86	19.6 $\pm$ 2.16	17.32 $\pm$ 1.43	19.22 $\pm$ 1.76	20.50 $\pm$ 1.85
Potassium	13.78 $\pm$ 1.51	17.97 $\pm$ 2.43	17.27 $\pm$ 2.01	15.82 $\pm$ 1.81	14.31 $\pm$ 1.98	18.88 $\pm$ 1.95
Sodium	17.77 $\pm$ 2.65	22.26 $\pm$ 3.93	18.65 $\pm$ 0.91	19.58 $\pm$ 2.62	19.58 $\pm$ 2.60	21.88 $\pm$ 4.10
Calcium	64.94 $\pm$ 9.00	68.98 $\pm$ 11.33	70.03 $\pm$ 12.61	78.41 $\pm$ 10.17	116.84 $\pm$ 7.55	111.42 $\pm$ 7.93
Magnesium	28.34 $\pm$ 7.04	33.45 $\pm$ 7.60	36.12 $\pm$ 7.87	40.45 $\pm$ 6.95	50.76 $\pm$ 3.56	46.18 $\pm$ 7.75



**Fig. 2** a Box plots show the range of physico-chemical parameters (pH, conductivity, total hardness, alkalinity, TDS, nitrates) at different sampling locations b (calcium, sodium, potassium, magnesium, chloride, and sulphate)

whiskers stand in for the 10th and 90th percentiles of the data, respectively. The 95% confidence interval of the median is indicated by the gap in the box. When there is no overlap between the notches of the boxes, the medians may be drastically different. Box plots are used to depict an entire dataset because of their visual qualities (mean, median, interquartile range and presence-absence of outliers, etc.). In all of the sampling locations, the pH ranged from  $7.43 \pm 0.18$  to  $7.82 \pm 0.17$ , according to Table 4. In most cases, pH indicates



**Fig. 2** (continued)

how the water's assets react with the alkaline and acidic substances in the water (Ahmad et al., 2019). The pH values of all sampling sites varied with roughly identical mean values, as shown in Fig. 2a. The study region's groundwater system has a little pH change due to climatic conditions and the persistent character of the groundwater system. In the sampling sites, the highest concentrations of TDS and EC were reported at  $324.68 \pm 12.74$  to  $360.18 \pm 22.90$  and  $442.99 \pm 42.46$  to  $485.92 \pm 47.42$ , respectively. Conductivity and TDS are essential factors in assessing the long-term viability of a water supply (Acharya, 2008; Doza et al., 2020). Some alkaline minerals, such as calcium, magnesium, and uneven

bicarbonates, contribute to the hardness of water (Bharadwaj & Singh, 2011). The highest alkalinity value was observed at site 5 ( $184.62 \text{ mg/L} \pm 3.79$ ), while the lowest was reported at site 1 ( $120.23 \text{ mg/L} \pm 6.96$ ). The maximum and lowest total hardness concentrations in all sample locations ranged from  $134.74 \text{ mg/L} \pm 7.68$  to  $271.13 \text{ mg/L} \pm 19.01$ . The box plots of TDS, EC, conductivity, alkalinity, and TH revealed that site 1 has a low mean value followed by site 2, site 3, site 4, site 5, and site 6. The value of these parameters' 25th and 75th percentiles was also lower for site 1 compared to other sampling sites. Total hardness was the most critical factor in critical box plots, with calcium and magnesium being the primary ions at sample sites 5 and 6. During several sample sites in 2015, Umamageswari et al., (2019) showed a similar trend of box plots for groundwater assessment. Groundwater is contaminated with dangerous metals and ions due to weathering of rocks and minerals, industrial effluents and wastes, and sewage runoff (Sharma & Bhattacharya, 2017; Vetrimurugan et al., 2017).

### 3.3 Temporal and spatial variability of anion and cation in groundwater samples

Table 3 depicts the temporal change in cation and anion concentrations in groundwater. In this study, the predominant anions and cations discovered in the pre- and post-monsoon seasons were  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$  and  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ , respectively. Bicarbonates and calcium were the most prevalent anion and cation in the groundwater samples. In both pre- and post-monsoon seasons,  $\text{HCO}_3^-$  levels range from  $146.98 \pm 18.88 \text{ mg/L}$  to  $149.16 \pm 14.35 \text{ mg/L}$  with  $\text{Cl}^-$  levels ranging from  $17.92 \text{ mg/L}$  to  $19.05 \text{ mg/L}$ ,  $\text{SO}_4^{2-}$  ranges from  $17.25 \text{ mg/L}$  to  $17.84 \text{ mg/L}$ , and  $\text{NO}_3^-$  varies from  $16.91 \text{ mg/L}$  to  $17.12 \text{ mg/L}$  in groundwater samples. According to spatial variation (Table 4), the highest and lowest concentration of all anions such as  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  was found in between  $115.24 \text{ mg/L} \pm 7.06$  to  $313.73 \text{ mg/L} \pm 33.16$ ,  $14.67 \text{ mg/L} \pm 0.97$  to  $20.50 \text{ mg/L} \pm 1.85$ ,  $13.73 \text{ mg/L} \pm 0.91$  to  $19.16 \text{ mg/L} \pm 3.48$  and  $12.25 \text{ mg/L} \pm 1.19$  to  $20.09 \text{ mg/L} \pm 1.85$  in all the studied sampling sites. According to Kumar et al., 2009; Singh et al., 2013; Dev & Bali, 2018; Humbarde et al., 2014, the amount of carbonates and bicarbonates in groundwater may be responsible for the weathering process of carbonate, the dissolution of carbonic acid owing to chemical weathering. After the monsoon season, this weathering process causes the calcium and magnesium levels to rise (Sharma & Chhipa, 2016; Sharma et al., 2019).

The main mineral dissolution character can be seen in groundwater with more bicarbonates and carbonates (Ghalib, 2017). Chlorides are the second most common anion in this study's groundwater. All natural sources of chlorides in groundwater include rock water interaction, treated wastewater, human-made sources, fertilizers such as gypsum fertilizers (Vengosh et al., 2002), municipal landfills, industrial and sewage effluents, and leachate (Srinivasamoorthy et al., 2014; Vengosh et al., 2002). The sulphate concentration was within acceptable limits in all the groundwater samples analysed. When sulphate and chloride concentrations in the human body surpass the water cap, it can cause gastrointestinal discomfort, hypertension, dehydration, asthma, and osteoporosis (Ghalib, 2017). One of the main causes of excessive chloride concentrations has been leaching salts with rainwater (Purushothaman et al., 2012; Pathak et al., 2014).  $\text{NO}_3^-$  levels in groundwater samples were below the BIS permitted limits ( $45 \text{ mg/l}$ ) (BIS, 2012). Normally, the highest concentrations of nitrates in groundwater come from human-made sources such as agricultural activities (overuse of fertilizers), septic tank outflow, and improper dumping of

animal waste and residential waste (Agarwal et al., 2019; Mallick et al., 2018; Perez Vilarreal et al., 2019).

Magnesium and calcium are significant cations that are engaged in a number of enzymatic systems and are crucial for many biological functions, including the prevention of cancer. Calcium and magnesium for cardiovascular illnesses have been shown several times in academic literature regarding drinking water (Rubenowitz et al., 1999; Nerbrand et al., 2003; Kousa et al., 2006; Maksimovi et al., 2010). In this study, the major cations found are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  in all the water samples. The highest and lowest levels of all the cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  varied from  $64.94 \text{ mg/L} \pm 9.00$  to  $116.84 \text{ mg/L} \pm 7.55$ ,  $28.34 \text{ mg/L} \pm 7.04$  to  $50.76 \text{ mg/L} \pm 3.56$ ,  $13.78 \text{ mg/L} \pm 1.51$  to  $18.88 \text{ mg/L} \pm 1.95$  and  $17.77 \text{ mg/L} \pm 2.65$  to  $22.26 \text{ mg/L} \pm 3.93$  in all the sampling sites. Calcium levels in freshwater are typically less than 15 mg/litre, 30–100 mg/litre in waters near carbonate rocks, and 400 mg/litre in ocean waters (Bruvo et al., 2008). Calcium at its highest concentration causes serious health concerns such as kidney stones and cardiovascular disease (WHO, 2017). The principal source of  $\text{Ca}^{2+}$  in groundwater is the dissolution of carbonate from sedimentary rocks and minerals such as limestone, dolomite, and calcite. Some harsh agricultural operations can play a key role in developing calcium and magnesium weathering processes of silicate minerals and the hydrolysis processes of  $\text{CaCO}_3$  and  $\text{Ca-Mg}(\text{CO}_3)_2$ , both of which are magnesium-rich minerals (Alsuhaime et al., 2019). The sodium and potassium levels are both within safe ranges. In humans, high sodium levels ( $>200 \text{ mg/L}$ ) cause major health concerns, such as kidney and neurological system abnormalities, as well as hypertension (WHO, 2017). High sulphate ion levels during the post-monsoon may result from a variety of human activities, including leaching, the decomposition of organic materials in the soil, overuse of fertilizers. In their respective studies, Ganiyu et al. (2018) and Hejaz et al. (2020) discovered comparable findings. The highest potassium content in groundwater is caused by the solubility of potassium behaviour rocks, which are frequently present in a variety of rocks. Chemical emissions from businesses and excessive fertilizer use are the primary causes of potassium in groundwater (Mallick et al., 2018).

### 3.4 Interpretation of Water quality indices

The geographical variability in a quality class of groundwater system was analysed using two well-known WQIs, namely PIG and  $C_d$ . The PIG is a useful tool for determining the quality of water. Several researchers have used it substantially (Rao et al., 2018; Subba Rao & Chaudhary, 2019). Table 5 depicts the classification of the groundwater pollution index from six test locations. The indices were calculated using several sample locations' mean dataset of evaluated water quality metrics. For six sampling locations, PIG was determined to be 0.43, 0.52, 0.47, 0.48, 1.00, and 0.70, respectively. According to the rating scale of that index, the groundwater quality at sampling site 5 falls into the low pollution zone. In the low pollution zone, the pH (1.25), TDS (0.108), calcium (0.170), magnesium (0.200), and bicarbonates (0.110) indicate levels of  $O_w$  greater than 0.1, which are considered more than natural contributions to groundwater quality. However, the water quality at test locations 1, 2, 3, 4, and 6 is insignificantly polluted. As a result, they clearly show that anthropogenic sources, rather than geogenic origins, impact the groundwater system. To demonstrate the role of geogenic and anthropogenic causes as suppliers of dissolved salts in the aquifer system, the difference in  $O_w$  values between the insignificant pollution zone and the low pollution zone must be investigated. Table 5 shows that the values of  $O_w$  in



**Table 5** Calculated parameters of water quality indices and irrigation water quality

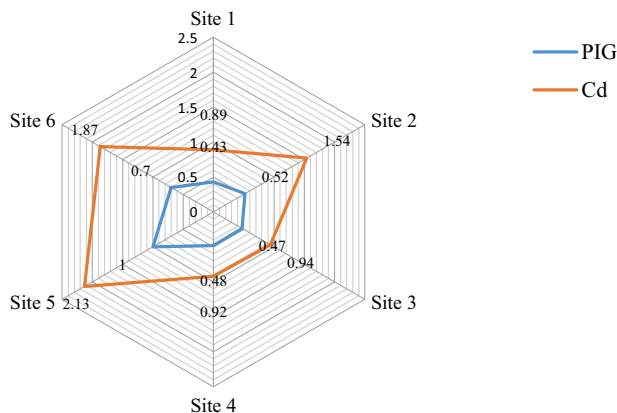
Parameter	Site 1 (Ow values)	Site 2 (Ow values)	Site 3 (Ow values)	Site 4 (Ow values)	Site 5 (Ow values)	Site 6 (Ow values)
pH	0.177	0.123	0.116	0.117	0.125	0.121
TDS	0.081	0.097	0.091	0.088	0.108	0.092
Turbidity	0.084	0.050	0.051	0.047	0.075	0.058
Calcium	0.084	0.079	0.058	0.052	0.170	0.131
Magnesium	0.051	0.055	0.039	0.043	0.200	0.113
Sodium	0.002	0.004	0.002	0.003	0.012	0.008
Potassium	0.024	0.031	0.037	0.041	0.059	0.049
Bicarbonates	0.031	0.034	0.033	0.037	0.110	0.051
Chloride	0.006	0.012	0.014	0.007	0.032	0.008
Sulphate	0.010	0.012	0.011	0.016	0.050	0.015
Nitrate	0.011	0.025	0.019	0.030	0.055	0.050
PIG value	<b>0.43</b>	<b>0.52</b>	<b>0.47</b>	<b>0.48</b>	<b>1.00</b>	<b>0.70</b>
PIG class	Insignificant pollution zone	Insignificant pollution zone	Insignificant pollution zone	Insignificant pollution zone	Low pollution zone	Insignificant pollution zone
Cd value	<b>0.89</b>	<b>1.0</b>	<b>0.94</b>	<b>0.92</b>	<b>2.13</b>	<b>1.87</b>
Cd class	Low contamination	Medium contamination	Low contamination	Low contamination	Medium contamination	Medium contamination

the situations of turbidity, sodium, potassium, chloride, sulphate, and nitrate do not differ significantly between the low pollution zone and the unimportant zone. The radar chart is a useful graphical representation of multivariate data in the form of a two-dimensional chart with several quantitative variables depicted on the axis beginning at the same point. The use of radar charts to highlight the performance parameters of any ongoing programme is control quality improvement (Kassir et al., 2015; Walkenbach, 2003). Figure 3 depicts the spatial variance in PIG and  $C_d$  levels for each sampling location. The groundwater contamination index ( $C_d$ ) is also useful for assessing groundwater quality (Backman et al., 1998). In all sampling locations, the  $C_d$  value ranges from 0.89 to 1.0, 0.94 to 0.92, and 2.13 to 1.87. According to the index's rating scale, groundwater quality at sample sites 2, 5, and 6 is in the medium pollution zone. In contrast, groundwater at sampling sites 1, 3, and 4 is low in contamination.

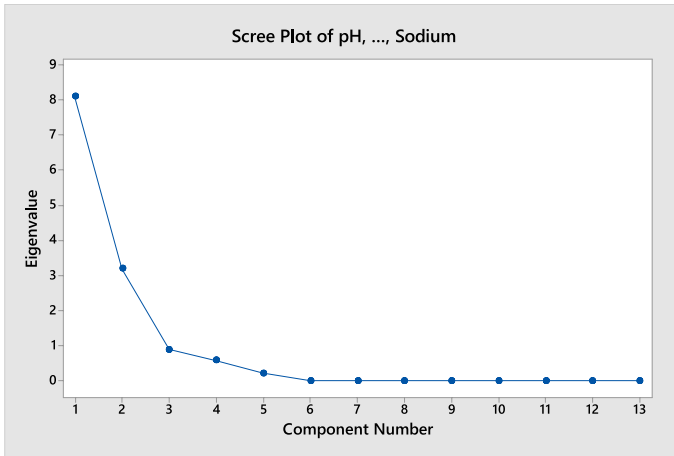
### 3.5 Statistical analysis of water quality parameters

Principal component analysis (PCA), a chemometric approach, is used by many researchers in hydro-geochemical studies (Ahmad et al., 2020; Matta et al., 2020a, 2020b, 2020c, 2020d). This method displays the greatest amount of alternatives for the fewest components (PCs). To recognize the parameter structure, the screen plot is utilized to decide how many major components should be preserved. A screen plot (Fig. 4) depicted the variability of the original mean dataset, revealing that the top three components account for 93.8 per cent of the total variance. As a result, the details of the water quality at each of the six sampling locations may be calculated using only three variables. To categorize sampling sites, we used several principal components. Table 6 shows the factor weights values of observed factors related to each principal component. Based on their factor loading values (0.30–0.50, 0.50–0.75, and > 0.75, respectively), the PCs are classed as weak, moderate, and strong (Liun et al., 2003). It was determined that the PC1 was connected with a positive weight with pH (0.318), conductivity (0.324), TH (0.313), alkalinity (0.316), bicarbonates (0.340), calcium (0.301), magnesium (0.317), and nitrates (0.301) with 62.33 per

Radar chart of Pollution Index of Groundwater (PIG) & Contamination Index ( $C_d$ )



**Fig. 3** Radar chart is conducted to reveal the range for each specification value of pollution index of groundwater (PIG) and contamination index ( $C_d$ ) for each sampling sites



**Fig. 4** Principle component analysis (PCA) screen plot of the eigen values of analysed parameters

**Table 6** Loading values of physico-chemical parameters on significant principal components for groundwater samples

Parameters	Principal components		
	PC1	PC2	PC3
pH	0.318	-0.141	0.143
TDS	0.103	-0.468	-0.354
Conductivity	0.324	0.147	-0.147
TH	0.313	0.249	0.080
Alkalinity	0.316	0.235	0.104
Bicarbonates	0.340	0.137	-0.059
Sulphate	0.147	-0.416	-0.331
Potassium	0.158	-0.376	0.520
Calcium	0.301	0.286	0.077
Magnesium	0.317	0.206	-0.183
Nitrates	0.301	-0.156	-0.422
Chloride	0.296	-0.237	0.081
Sodium	0.231	-0.291	0.456
Eigen value	<b>8.10</b>	<b>3.19</b>	<b>0.90</b>
% of variance	<b>62.33</b>	<b>24.6</b>	<b>6.9</b>
Cumulative %	<b>62.33</b>	<b>86.9</b>	<b>93.8</b>

cent variation. With a 24.6 per cent variance, the variables pH (-0.141), TDS (-0.468), sulphate (-0.416), and potassium (-0.376) showed a negative factor weight in the synthesis of PC2. TDS (-0.354), sulphate (-0.331) and nitrates (-0.422) had negative weight in PC3, but potassium (0.520) and sodium (0.456) had positive weight with 6.9% variance. This revealed a mixed source of contamination from natural and anthropogenic activities, such as soil erosion or weathering, air deposition, biofertilizers, and runoff from ore producers, among others (Matta et al., 2022a). The higher ion loadings in the post-monsoon period compared to the pre-monsoon period indicate that ions are being leached from the

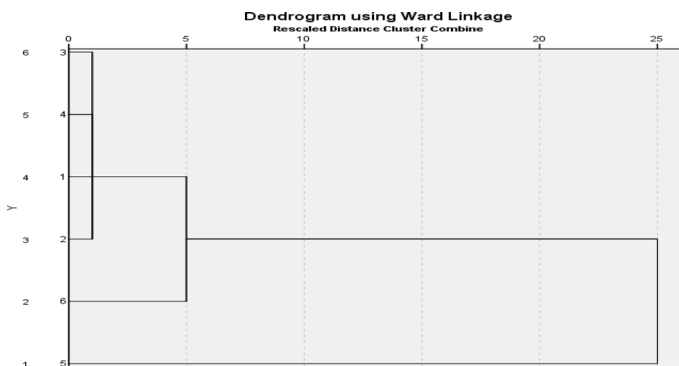
source material through weathering, dissolution, ion exchange, leaching, and evaporation as the dominant factors, as well as the influence of human interferences as secondary factors, resulting in variation in groundwater quality (Table 3). Furthermore, the PCA supports the conclusions of geochemical correlations and groundwater chemical characteristics, both of which impact groundwater quality.

A dendrogram (Fig. 5) depicts the cluster analysis of multiple sample locations using Ward's methods; cluster 1 has four sampling sites, namely sites 1, 2, 3, and 4. Cluster analysis demonstrates that sampling sites 5 and 6 are completely separate from the other sampling locations. The clustering of water samples may be influenced by the similarity of the aquifer and groundwater flow. It is a well-known fact that leaching and excessive use of fertilizers also affect groundwater quality. As a result, the clustering of water samples may be affected by linked agricultural practices and human-made activities.

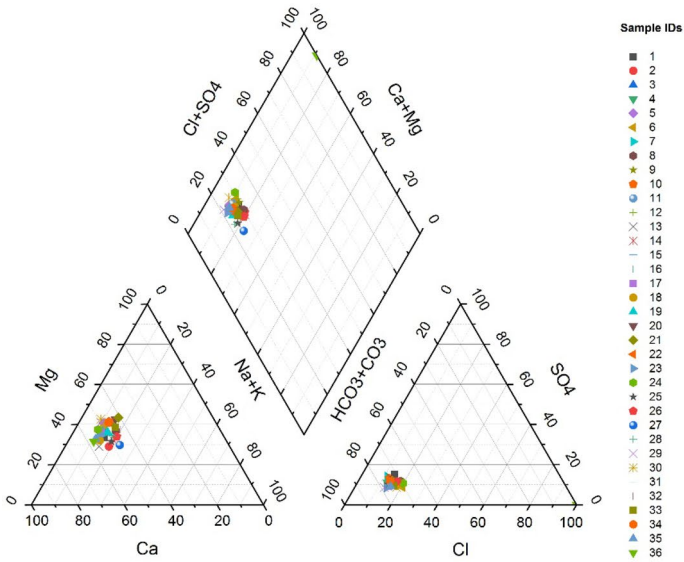
### 3.6 Groundwater suitability for irrigation purposes and hydrogeochemical facies

The sodium adsorption ratio (SAR), soluble sodium percentage (SSP), salinity, alkalinity hazard (SAH), and magnesium hazard are the major factors that determine whether groundwater is suitable for irrigation (MH). An overabundance of soluble cations and anions can reduce the quantity of water available to plants and induce toxicity in sensitive plants and crops. In many circumstances, the USSL salinity diagram and the Wilcox diagram are used to determine groundwater suitability for irrigation. Table 1 shows the percentages for all of the irrigation water quality parameters, which have been grouped into numerous categories. Uttarakhand has discovered groundwater suitable for agriculture and drinking in the Doon valley in the outer Himalayas (Dudeja et al., 2011).

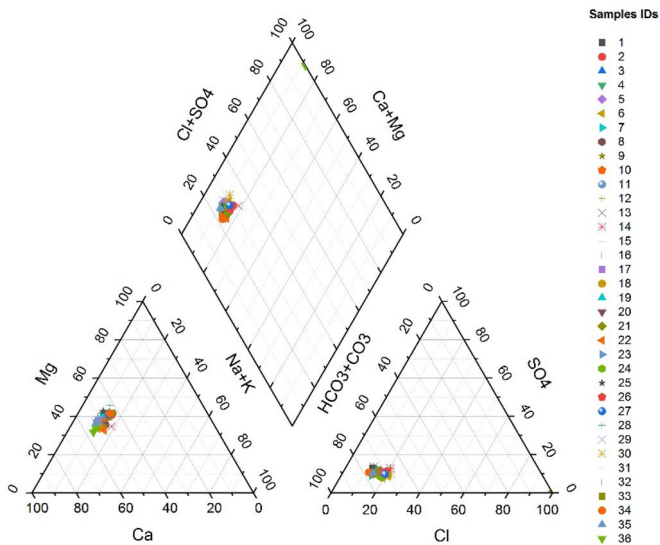
Using the Piper diagram for graphical analysis, we study the origin, structure, and chemical bonding between dissolved anions and cations in the groundwater hydro-geochemical facies of the sampling location (Alsuhaime et al., 2019; Othman, 2005; Piper, 1944). Groundwater's hydrochemical characteristics are greatly influenced by lithology, regional water flow patterns, and resident time (Domenico, 1972). Water is classified into three varieties based on its chemical composition: bicarbonate, sulphate, and chloride (Alsuhaime et al., 2019). In (Fig. 6a, b), a Piper diagram is used to show the schematic scattering of all anions and cations in groundwater during the pre-monsoon and post-monsoon



**Fig. 5** Dendrogram shows the hierarchical clusters of different sampling locations. **a** Piper diagram for pre-monsoon groundwater samples **b** Piper diagram for post-monsoon groundwater samples



(a) Piper diagram for Pre-monsoon groundwater samples



(b) Piper diagram for Post-monsoon groundwater samples

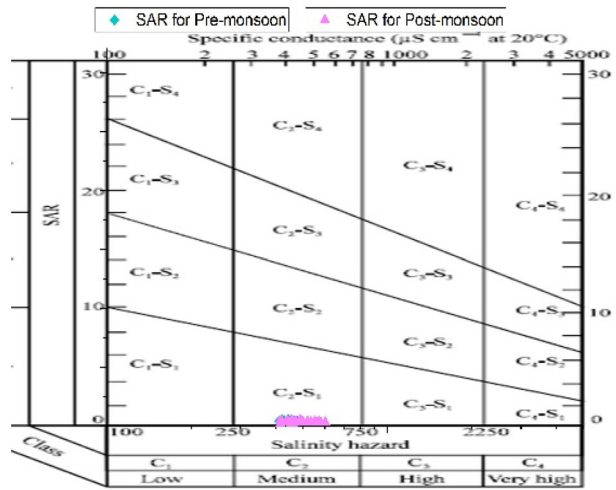
Fig. 6 Geochemical representation of all groundwater samples collected during the a pre-monsoon and b post-monsoon seasons using Piper diagram

seasons. The Piper diagram shows all of the estimated hydrochemical data in two triangular and upper diamond-shaped fields. The Piper diagram can observe the clustering of similar groundwater sample groups. The resulting diamond-shaped field revealed that all of the samples were tributaries of the Ca–Mg–HCO<sub>3</sub> type. As a consequence, there was no discernible change in geochemical facies in water samples over both seasons, and Kaur et al. (2017) found the same thing. Ca<sup>2+</sup> levels were found to be high due to pesticide dissolution during the monsoon (Singh et al., 2013). Because of the presence of dolomite, the primary source of Mg<sup>2+</sup> ions has been identified. The presence of bicarbonates and calcium in groundwater samples could be due to the natural dissolution of carbonate minerals (Modibo et al., 2019; Srinivasamoorthy et al., 2014).

Groundwater becomes salty as a result of the high salt content, reducing its availability for irrigation. Even though excessive salt content in groundwater produces saline soil formation and lowers crop plant salt intake capacity, salinity and alkalinity hazard (SAH) is a critical factor for groundwater quality for irrigation (Singh et al., 2020). Electrical conductivity (EC) values are often utilized to estimate the salinity threat. Wilcox (1955) categorized groundwater according to its salinity and alkalinity hazard (SAH) to measure its suitability for irrigation. He split the groundwater samples into five categories. Following the examination, it was revealed that all of the groundwater samples were in good condition during both the pre-monsoon and post-monsoon seasons. SAR is an important criterion for determining if groundwater is suitable for irrigation. Due to soil structure disruption, higher sodium content in groundwater has the detrimental effect of restricting soil permeability and seed water absorption (Nagaraju et al., 2014; Sharma et al., 2017). SAR values in the research area were less than 10 in both seasons, indicating that the water samples collected in both seasons were of excellent quality. Table 1 shows that the groundwater in the study region was acceptable for irrigation in both pre-monsoon and post-monsoon seasons. It has been claimed that sodium affects soil permeability by interacting with the ions present in the soil (Ca<sup>2+</sup> and Mg<sup>2+</sup>) (Selvakumar et al., 2014). The clay particles absorbed the Na<sup>+</sup> ion, which disrupted the soil structure (Singh et al., 2015).

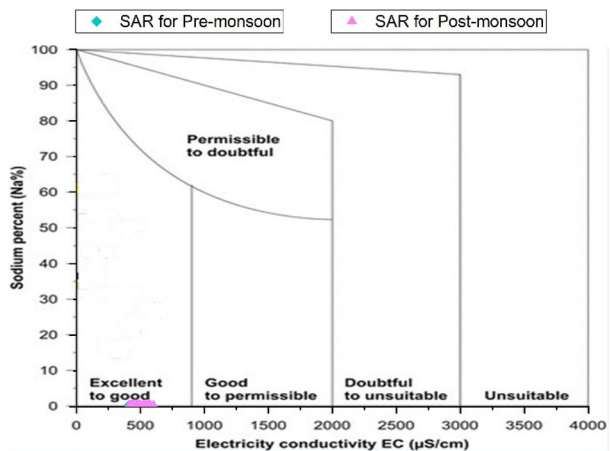
As a result, classifying water based on the soluble sodium percentage (SSP) is crucial when determining its suitability for irrigation. Wilcox (1955) divided the water samples into five categories based on their sodium content to assess their irrigation feasibility (Table 1). After analysing the samples, it was discovered that during the pre-monsoon period, 27 groundwater samples were in the good class and 9 samples were in the permissible class, while during the post-monsoon period, 33 groundwater samples were in the good class and 3 samples were in the permissible classes. Based on the Magnesium Hazard (MH) value, groundwater was divided into two categories: appropriate (<50%) and (>50%) unsuitable (Khodapanah et al., 2009). Mg<sup>2+</sup> and Ca<sup>2+</sup> are generally found in equilibrium concentrations with each other. However, when the Mg<sup>2+</sup> level of water is higher, the soil becomes alkaline, which has a negative impact on crop yield (Kumar et al., 2017; Nagaraju et al., 2014). After further investigation, it was discovered that MH values exceeded 50% in both seasons. As a result, both seasons' water samples fell into the unfit category (Table 1). According to a previous study, the large levels of Mg<sup>2+</sup> ion at sample locations were attributed to high dolomite minerals dissolution (Singh et al., 2020). The USSL (United States Salinity Laboratory diagram) is used to evaluate irrigation groundwater efficiency (USSL, 1954; Bhandari & Joshi, 2013). Groundwater was categorized into C1, C2, C3, and C4 kinds based on salinity danger (EC) and S1, S2, S3, and S4 types based on sodium hazard (SAR) on the basis of this diagram (Lokhande & Mujawar, 2016). Groundwater samples' electrical conductivity and SAR values are presented in Fig. 7, and in both seasons, all groundwater samples are classed as medium salinity and low sodium

**Fig. 7** USSL Salinity diagram showing classification of groundwater in pre-monsoon and post-monsoon seasons for irrigation purposes



(C2-S1). Salt concentrations that are too high have negative impacts on plant growth and development, such as nutritional imbalances and osmotic effects. The percentage of soluble sodium in the soil is also a significant metric for determining groundwater content for irrigation in terms of soil permeability (Nagarju et al., 2014). Excess sodium facilitates the interaction of sodium with chloride and carbonates in the soil, resulting in alkalinity and salinity. Water quality is determined by the concentration and composition of soluble salts in it (Zaman et al., 2018). Wilcox (1955) provided a graphic to evaluate the viability of water for irrigation by classifying it into different types based on EC and Na % readings (Singh et al., 2020). The five categories for the samples were excellent to good, good to permissible, permissible to doubtful, doubtful to unsuitable, and inappropriate. This graph plots the electrical conductivity (EC) versus the fraction of soluble sodium. According to this diagram, all of the water samples fell into the excellent to good group (Fig. 8). Table 1 shows the results, which show that the groundwater in the research area was suitable for irrigation throughout both seasons, as reported in a previous study (Singh et al., 2020). The

**Fig. 8** Wilcox diagram shows the water quality in relation to electrical conductivity (EC) and sodium per cent (Na%) for pre-monsoon and post-monsoon seasons

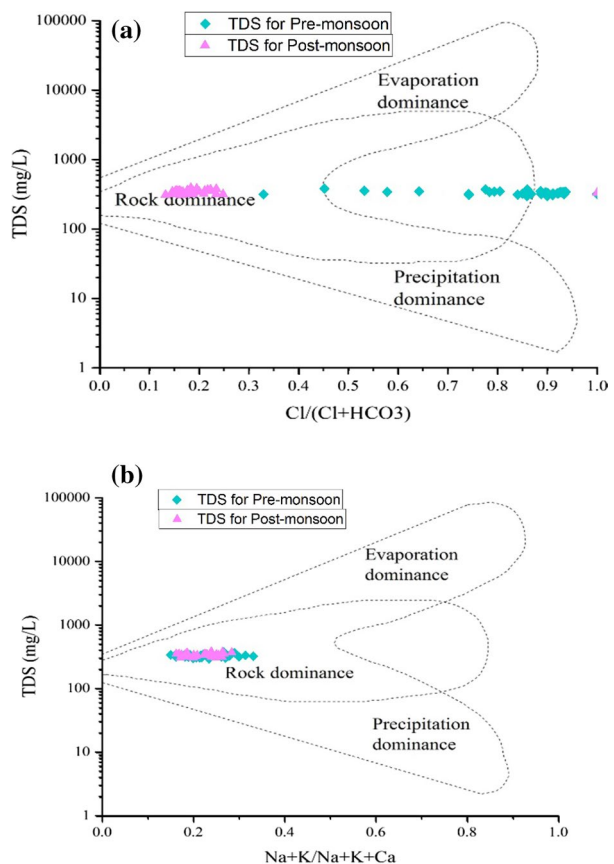


ion chemistry process in groundwater samples is interpreted using Gibbs diagrams (Gibbs, 1977). Precipitation dominance, evaporation dominance, and rock dominance are depicted in the Gibbs diagram. The Gibbs formula is shown in Table 1. The graph of the ratio of cations  $[(Na + K)/(Na + K + Ca)]$  and anions  $[Cl/(Cl + HCO_3)]$  against TDS is known as a Gibbs plot. The Gibbs plot indicates that the research region's whole sample is made up of rock dominance (Figs. 9a, b). The rock–water interface is the fundamental mechanism that affects groundwater chemistry in alluvial plains (Alam, 2013; Raju et al., 2011).

## 4 Conclusions

The necessity and need for groundwater quality assessment in Uttarakhand's lower Himalayan region, as well as chemical alignment and suitability for irrigation of groundwater supplies, are defined in this paper. At some sampling sites, the quality of groundwater was found to be hard in character. The majority of the samples were below the BIS's allowed and permitted levels. In the pre-monsoon and post-monsoon seasons, the order of major cations was  $Ca^{2+} > Mg^{2+} > Na^+ > K^+$  and the order of major anions was  $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ . In all seasons, the hydro-geochemical facies and piper plots confirmed that the majority of the analysed groundwater samples fell into the Ca-Mg- $HCO_3$

**Fig. 9** Gibbs diagram for **a** anion and **b** cation against total dissolved solids (TDS) in groundwater samples for pre-monsoon and post-monsoon seasons





type. A similar method using two widely utilized WQIs (PIG and  $C_d$ ) performed well in expanding on water quality variance across space. According to the groundwater pollution index and contamination index, the bulk of the test locations fell into the low to medium contamination zone. The box plot modelling depicted the variability in each parameter of the respective location. The PCA analysis elucidates the link between essential factors by reducing the number of PCs and their contribution to variance. It also aids in the identification of pollutant sources. The first 3 principal components account for 93.8% of the total variance. According to the values depicted on the USSL graph, all groundwater samples belonged to the C2-S1 (medium salinity, low sodium) group in the pre- and post-monsoon seasons. All of the groundwater samples from both seasons are excellent to good, as shown by the Wilcox graph. Based on irrigational compatibility indicators including SAR, SAH, and SSP, several groundwater samples were confirmed to be in the “good to permitted” category during the pre- and post-monsoon seasons. Magnesium hazard claims that all groundwater testing were inappropriate and hazardous in both seasons. The results of the study highlighted the importance of ongoing analysis to identify changes in groundwater conditions brought on by important industrial units in the area, including indices to classify based on consumption, irrigation, as well as assessing contamination limits. This study examines groundwater quality using integrated statistical approaches, and the results provide critical information for groundwater conservation, management, and pollution control measures. Due to the research area’s proximity to the Indian Himalayan Region and the role that groundwater evaluation plays in the region’s ecological circumstances, this study also contributes to sustainability in terms of SDG 13 (Climate Action), in specifically. In order to establish uniform laws and regulations, the results of this study further highlight the need for extensive, long-term regional-scale investigations to clarify the state of pollution and source attribution. Additionally, the results will help policymakers and conservationists avert harmful effects, secure and conserve groundwater while reducing pollution sources and improving conservation awareness among conservationists and the general public employing techniques of scientific communication.

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## Declarations

**Ethical approval and consent to participate** Inapplicable.

**Consent for publication** No consent was required for publishing.

**Conflict of interest** Inapplicable.

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