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Groundwater Vulnerability Assessment Using Multivariate Statistical Analysis and GIS in the Foothills of Western Himalayan State, India

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ABSTRACT

The experiment was conducted during July, 2019 to July, 2020 at industrial region of Solan district, Himachal Pradesh, India to study the groundwater quality status. Water quality parameters such as pH, EC, Turbidity, TDS, Ca^{2+}, Cl^-, NO_3^-, BOD, COD, and heavy metals (Fe, Pb, Cr, Cu, Mn) were analyzed and WQI (Water Quality Index) was computed. Thereafter, Arc GIS software was used for the spatial distribution of these parameters to locate the regions with the best drinking water quality within the study area. The results of the study revealed that except for the concentration of BOD and heavy metals such as Fe, Pb, Cr, and Cu, which exceeded the acceptable limits in some places, all of the examined parameters were well below desirable limits as per the Bureau of Indian Standards (BIS) and WHO for drinking and domestic purposes. Furthermore, a correlation matrix and PCA were subsequently formulated and examined using R software and SPSS respectively to determine the most significant parameters contributing to groundwater pollution. The WQI values indicated that only 13.3% of the groundwater sample falls in the good water category, the rest 60% falls in the poor category and 26.7% falls in the very poor category in both seasons. The findings of the present study therefore implied that groundwater of the region was under deteriorating water quality particularly, in the central and north-western region of the watershed and requires proper treatment before consumption as well as protection from the perils of geogenic/anthropogenic contamination.

KEYWORDS: Groundwater, water quality index, GIS, correlation, spatial distribution

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1. INTRODUCTION

Groundwater is vital for human sustenance and global food security, supporting irrigated crops (Aeschbach-Hertig and Gleeson, 2012). It refers to water found underground in soil crevices and rock fractures (Amadi et al., 2011). In regions where surface water is economically unviable, groundwater serves as a critical and secure drinking source. India, with 16% of the global population and 4% of global water resources, accounts for over 30% of the world's irrigated land and leads in groundwater usage, surpassing China and the United States combined (Margat and Van der Gun, 2013). Due to erratic monsoons and limited surface water, India relies heavily on groundwater, meeting 85% of rural domestic needs, 55% of irrigation, and over 50% of industrial and urban demands (Herojeet et al., 2016). Rapid population growth, urbanization, and shifting water use patterns have intensified groundwater abstraction, with 245 billion cubic meters used for irrigation in 2011 alone, constituting 25% of global withdrawals (Anonymous, 2014a; Goldin, 2016). Excessive extraction for agriculture and drinking has caused significant contamination from irrigation runoff, surface pollutants, high evaporation rates, insufficient rainfall, and seawater intrusion, necessitating urgent attention to water quality and management strategies (Ramesh and Elango, 2011) (Wang et al., 2019; Eyankware et al., 2020). Apart from these surface contaminations, regional geology, land use, and geochemical processes also had an impact on groundwater quality (Rajesh et al., 2012; Wagh et al., 2017). Around 30% of urban and 90% of rural households still rely completely on untreated surface or groundwater for their daily needs. As such, it is crucial for groundwater management to have an in-depth understanding of hydrogeochemical characteristics and geogenic and anthropogenic processes that play a significant role in determining the physical and chemical characteristics of groundwater in a particular region (Subramani et al., 2005; Chin, 2006). Due to climate change, groundwater has been exploited more extensively, particularly for agricultural purposes. Therefore, by monitoring and managing the overall quality of water used for crop irrigation, farmers can make informed decisions, optimize resource utilization, protect crop health, and contribute to sustainable agricultural practices in the long run (Bauder et al., 2014). Also, recent years have seen a significant increase in the use of Geographic information system (GIS) and Inverse Distance Weighted (IDW) interpolation methods to assess and monitor groundwater quality, providing to be effective tools for analyzing spatial information about water resources, which has been applied in the present study (Aravindan et al., 2010; Magesh and Elango, 2019; Selvam et al., 2013b; Balamurugan et al., 2020b; Soujanya Kamble et al., 2020).

Nalagarh Valley selected to conduct the present study is the southernmost expanse of Himachal Pradesh and lies in the Baddi, Barotiwala and Nalagarh (BBN) industrial belt. The industrial subsidy package granted to the state in 2003 significantly attracted businesses, leading to unplanned industrial activities and the discharge of treated, partially treated, and untreated effluents, causing surface and groundwater pollution. (Herojeet et al., 2013). A significant drop in groundwater levels, up to 6 meters in some areas, has been observed alongside increasing vulnerability to groundwater pollution. (Dhiman and Kumar, 1998). Therefore, the present study aims to evaluate groundwater quality for drinking purposes using the Water Quality Index (WQI) based on 14 physio-chemical parameters, including pH, electrical conductivity, turbidity, total dissolved solids, calcium, chloride, nitrate, BOD, COD, and heavy metals (Fe, Pb, Cr, Cu, Mn). Previous studies have not fully integrated water quality indices, multivariate statistics, and geostatistical analysis to characterize groundwater in the region, indicating a research gap. This research will definitely aid stakeholders in planning and management, protecting the shallow aquifer for future use.

2. MATERIALS AND METHODS

2.1. *Study area*

The present study was conducted during July, 2019 to July, 2020 in industrial region of Solan district, Himachal Pradesh, India. The Nalagarh valley, having an area of around 230 km^2, is a narrow extension of a larger outermost Himalayan inter-montane valley that extends between the Ghaggar and Beas rivers in a southeast-northwest direction. The study area lies between Northern latitudes of 30°52' to 31°04' and Eastern longitudes of 76°40' to 76°55' which falls in the Survey of India Toposheets no. 53A/12, 53A/16, 53B/9 and 53B/13. The valley is delimited between the Siwalik hills in the northeast (NE) and the Sirsa River in the southwest (SW). Sirsa River is the main river that flows through the central part of the Nalagarh Valley. The entire Nalagarh valley, as well as portions of Kasauli in Solan district of Himachal Pradesh, Ropar in Punjab, and Pinjore in Haryana, are all part of the Sirsa watershed. The entire catchment area of the Sirsa River is approximately 250 km^2. The Nalagarh valley alone covered 230 km^2, with the rest of the areas shared by Solan, Kasauli, Pinjore, and Ropar. Nalagarh, the tehsil headquarters, is located on the north-western edge of the valley.

2.2. *Geology and hydrogeology*

Geologically, the area is complex not because of its stratigraphy, but due to its intricate tectonic structure. From a stratigraphic standpoint, tertiary formations, which have experienced significant structural disruption, surround the Nalagarh Valley and its neighboring areas (Anonymous, 2007). In general, the rocks of this area can be classified into two tectonic zones that strike and trend in opposite directions (i.e. NW-SE direction). Consequently, from

North to South, the tectonic zones are arranged with a belt of lower and middle tertiary rock (para-autochthonous) along the valley's northeastern flank, while the upper tertiary rock belt (autochthonous) is confined within the valley and extends across its southwestern flank. The Nalagarh Thrust, a significant fault, marks the intersection of these zones.

There is a high degree of tectonic disturbance in this region; Nalagarh and Sirsa thrusts are the two major thrusts trending NE-SW. Amid Kasauli and the middle Siwalik range, the Nalagarh thrust forms, whereas upper and middle Siwaliks are separated by the Sirsa thrust. The Sirsa river basin predominantly consists of alluvial soil, characterized by deposits originating from both the Holocene and Pre-Holocene eras, covering significant portion of the region. It is typically granular in texture and measures between 10 and 20 meters in thickness. The majority of the river basin's upper and middle segments are composed primarily of clay, cobbles, pebbles, gravel, and sand. Throughout the basin, in the downstream part, the sediments become finer and finer until they have the consistency of clay. Generally, groundwater is found in porous, unconsolidated alluvial formations (valley fills) consisting of sand, silt, gravel, cobbles, and pebbles (Sharma et al., 2022). These deposits are again restricted to a thickness of 60–100 meters below ground level (mb gl). There are primarily two types of groundwater abstraction structures: wells and tube wells. Also, there are numerous open dug wells and dug cum bored wells in the area, ranging in depth from 4.00 to 60.00 mb gl. The depth to water level, however, can be found anywhere from close to the ground's surface to greater than 35 mb gl. The development of deeper partially enclosed aquifers is being accomplished by drilling tube wells upto 65 to 120 mb gl and tapping into granular zones 25–35 m deep (Anonymous, 2007).

2.3. Sampling

The industrial area of Solan district of Himachal Pradesh was selected to carry out the present study during the year 2019–2020 in pre and post monsoon season. To conduct the present study, three locations were selected i.e., Baddi, Barotiwala and Nalagarh, Himachal Pradesh, India. From each of these three locations, five sites were randomly selected covering upstream and downstream areas around the Sirsa River. The groundwater samples were collected in two different seasons (post-monsoon and pre-monsoon) one from each site thus making a total of 15 samples from the study area in one season adhering to the standard procedures of the American Public Health Association (Anonymous, 2017). The collected samples were analysed for various physico-chemical properties. Detailed list of sampling sites along with the area of sample collection, source of sample collection and latitude and longitude of the point of sample collection is presented in Table 1.

The global positioning system (GPS) was used to mark the sampling locations, as illustrated in Figure 1. Samples from the study area were collected from the hand pump (depth: approx. 60 m) and dug wells (depth: 4–30 mb gl). The High-Density Polythene, or HDPE, collecting bottles with a one-liter capacity as per the standard procedure of

Table 1: Detailed list of sampling sites in the study area

Locations	Sites	Area of sample collection	Source	code	Latitude	Longitude
Baddi	Bhud	Residential area	Handpump	Bd_1	30°94.986"N	076°76.815"E
	Bhud	Vicinity of industries	Handpump	Bd_2	30°46.094"N	076°21.344"E
	Kishanpura	Along main NH	Handpump	Bd_3	30°58.631"N	076°45.271"E
	Bhatauli	Residential	Borewell	Bd_4	30°57.299"N	076°49.961"E
	Bhatauli	In vicinity of industries	Borewell	Bd_5	30°57.242"N	076°36.699"E
Barotiwala	Jhadmajri	Industrial	Borewell	Bt_1	30°55.451"N	076°49.641"E
	Balyana	Residential	Handpump	Bt_2	30°55.040"N	076°50.477"E
	Jhadmajri	In vicinity of industries	Borewell	Bt_3	30°55.472"N	076°49.707"E
	Bated	Residential	Handpump	Bt_4	30°54.565"N	076°50.315"E
	Jhohranpur	Village	Borewell	Bt_5	30°54.014"N	076°51.232"E
Nalagarh	Khruni	Along main NH	Borewell	N_1	30°99.525"N	076°74.166"E
	Kheda	In vicinity of industries	Borewell	N_2	31°01.051"N	076°42.877"E
	Thanthewal	Village	Borewell	N_3	31°03.585"N	076°68.83"E
	Ward No. 7	Residential	Handpump	N_4	31°02.891"N	076°43.595"E
	Silnupul	Residential	Borewell	N_5	31°03.841"N	076°45.009"E

Bd: Samples collected from baddi; Bt: Samples collected from Barotiwala; N: Samples collected from Nalagarh

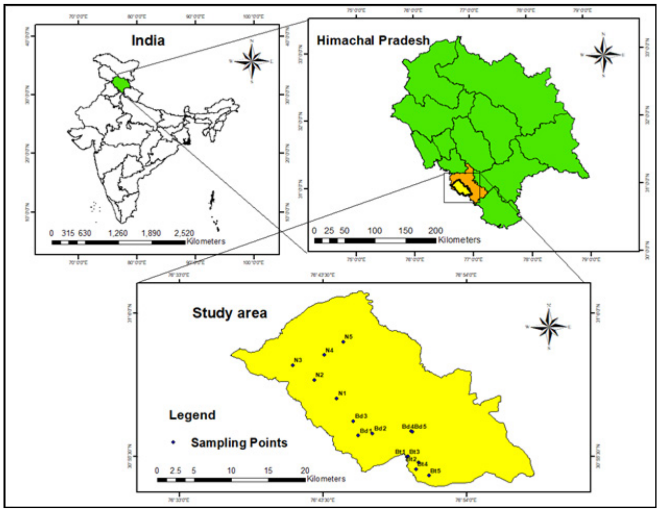


Figure 1: Map of the study area showing sampling locations

(Anonymous, 2012) were used. To prevent any anomalous contamination and successive changes in the properties of groundwater, each was sterilised in an aseptic environment. The inverse distance weighted (IDW) interpolation technique used in the present study for the generation of spatial distribution maps is now-a-days an effective tool for mapping the geographic distribution of groundwater quality parameters Balamurugan et al., 2020b; Kawo and Shankar, 2018; Magesh et al., 2013; Sarfo and Shankar, 2020). The weights were calculated taking into account the nearest specified sites and were applied to various parameters based on distance at each location. Each studied parameter of water quality has been classified into distinct zones on the spatial distribution map in accordance with acceptable/desirable and permissible limits of Anonymous (2012, 2015) and Anonymous (2017) for drinking purposes. A quantitative analysis of the measured groundwater quality parameters and correlation matrix prepared using the R software have been laid down as shown in Tables 2 and Figure 3 (a,b) respectively.

2.4. Collection and preparation of samples

Before taking the sample of groundwater, the water was pumped from the handpump or borewell for 5–7 minutes till the water temperature was stabilized and then the samples were collected. All the samples then after being properly labelled were taken to the laboratory for further analysis of pH, EC, TDS, Turbidity, Ca^{2+}, Cl^-, NO_3^-, BOD, COD, and heavy metals (Fe, Pb, Cr, Cu, Mn). Testing of samples for pH, EC, TDS and BOD was done within 24 hours of sample collection and the remaining samples were stored in the refrigerator at 4°C for performing subsequent analysis.

2.5. Water quality index (WQI)

A water quality index is one of the most efficient methods for disseminating knowledge about the state of any water body. WQI is a mathematical equation used for monitoring and managing water resources, as it simplifies complex water quality data into a single index that is easier to understand and interpret (Stambuk-Giljanovic, 1999). It is described as a classification method which documents the cumulative effect of each selected parameter of water quality on the entire water quality within the region. It is computed with consideration for human consumption by evaluating its

Table 2: Statistical analysis of groundwater quality parameters and its compliance with BIS and WHO standards

Parameter (unit)	Drinking water standards		Statistical analysis of observed value			
	BIS (2012, 2015)	WHO (2017)	Minimum*	Maximum*	Mean	SD (σ)
pH (On scale)	6.5-8.5	7.0-8.0	6.06	7.62	6.95	0.353
EC (dS m^{-1})	0.75-3	-	0.005	0.015	0.01	0.003
Turbidity (NTU)	-	1.00-5.00	1.44	4.04	2.77	0.687
TDS (mg l^{-1})	500-2000	-	193	763	458.20	163.948
Ca^{2+} (mg l^{-1})	75-200	100-300	115	184	151.13	17.795
Cl^- (mg l^{-1})	250-1000	250	15	48	28.87	8.169
NO_3^- (mg l^{-1})	45	50	1.3	22	8.95	5.331
BOD (mg l^{-1})	-	5	3.18	6.02	4.61	0.866
COD (mg l^{-1})	250	-	113	152	131.33	10.182
Fe(mg l^{-1})	1	0.3	0.18	1.11	0.54	0.304
Pb (mg l^{-1})	0.01	-	0.04	0.2	0.09	0.049
Cr (mg l^{-1})	0.05	-	0.01	0.26	0.13	0.076
Cu (mg l^{-1})	0.05-1.5	-	0.01	0.21	0.11	0.058
Mn (mg l^{-1})	0.1-0.3	-	0.02	0.16	0.08	0.039

suitability for drinking purposes.

For the computation of WQI, the drinking standards as proposed by Anonymous (2017) and Anonymous (2012) have been taken into account. Using this approach, the weighting of different water quality parameters was assumed to be inversely correlated to the recommended standards for every parameter in question. The computation method consisted of three stages. The initial step of the analysis involved assigning weights to each one of the selected fourteen parameters (pH, EC, Turbidity, TDS, Ca^{2+}, Cl^-, NO_3^-, BOD, COD, Fe, Pb, Cr, Cu, Mn) based upon their noted influence on the primary human health (Table 3).

Considering the importance of parameters such as BOD, COD, and nitrate in determining water quality, a maximum weight of 3 has been assigned to them (Dwivedi and Pathak, 2007; Abrahao et al., 2007). As pH, TDS, calcium, and chloride do not play a significant role in evaluating the quality of water, they were given a minimum weight of 1 (Ram et al., 2021).

In the second stage, to calculate the relative weight (Wi) for every parameter, Eq. (1) is used. Accordingly, the relative weights (Wi) of the various water quality parameters are inversely related to the recommended standards for these parameters.

$W_i=K/S_n$ ....(1)

where Wi is the unit weight for the ith parameter, Sn is the standard value for ith parameters, K is the proportional constant. In the following equation, K is assumed to be '1' and is determined using the following formula.

$K=1/\sum(1/S_n)$ ....(2)

In the third stage, a quality rating scale (qi) is computed for each one of the parameters using Eq. (3):

$q_i=C_i/S_i\times100$ ....(3)

where qi is the quality ranking, Ci is the concentration of each chemical parameter in every water sample in milligrams per liter and Si represents the WHO standard for each of the analyzed chemical parameters in milligrams per liter (Table 2).

For estimating the WQI, the SI (Sub-index) is first calculated for each chemical parameter using Eq. (3), and the WQI was thereafter determined using Eq. (4):

$SI_i=W_i\times q_i$ ....(4)

where SIi is the sub-index of ith parameter, qi is the rating based on the concentration of ith parameter and n is the number of parameters.

The sum of the sub-index value of each groundwater sample was then used to determine the overall water quality index (WQI) as follows (Sadat-Noori et al., 2014; Ramakrishnaiah et al., 2009):

$WQI=\sum SI_i$ ....(5)

The calculated WQI values are typically categorized into five classes (Table 4): excellent, good, poor, very poor, and unfit for human consumption (Sahu and Sikdar, 2008). Many authors have provided detailed descriptions of the calculation procedure for WQI (Asadi et al., 2007; Dwivedi and Pathak, 2007; Saeedi et al., 2010; Pradhan et al., 2001; Yidana and Yidana, 2010).

Table 3: Weightage (w_i), relative weightage (W_{ir}), and unit weightage (W_i) of each groundwater quality parameter

Parameter	BIS Standard	Weightage (w_i)	Relative weight (W_{ir})	Wi (k/Sn)
pH	8.5	1	0.037	0.000929
EC	3	2	0.074	0.000003
Turbidity	1	2	0.074	0.007894
TDS	2000	1	0.037	0.000004
Ca^{2+}	200	1	0.037	0.000040
Cl^-	1000	1	0.037	0.000008
NO_3^-	45	3	0.111	0.000175
BOD	5	3	0.111	0.001579
COD	250	3	0.111	0.000032
Fe	1	2	0.074	0.007894
Pb	0.01	2	0.074	0.789368
Cr	0.05	2	0.074	0.157874
Cu	1.5	2	0.074	0.005262
Mn	0.3	2	0.074	0.026312
		wi=27	∑Wir=1.000000	Wi=1.00

Table 4: Groundwater quality classification based on WQI (Sahu and Sikdar, 2008)

WQI Range	Type of water
>50	Excellent water
50-100	Good water
100-200	Poor water
200-300	Very poor water
>300	Water unsuitable for drinking purpose

2.6. *Principal component analysis*

PCA, a vital multivariate statistical method, is utilized to reduce data dimensions while emphasizing its inherent structure to capture the maximum data variability (Watkins, 2021). In the present study, the varimax rotation technique was employed to understand the correlation between pollution sources and key indicators. To achieve this, the original dataset was normalized to address differences in units, resulting in an entirely distinct set of independent pseudo-variables termed principal components (PCs). Utilizing PCA improves the accuracy and cost-effectiveness of estimating water quality by significantly reducing the labor, expenses, and time required to evaluate various variables. It eliminates redundant or highly correlated variables from the dataset. The principal components (PCs) are organized sequentially, with each successive PC contributing less to the total variability. Essentially, the first PC explains the largest portion of variance, while subsequent PCs capture smaller proportions of variance.

3. RESULTS AND DISCUSSION

3.1. *Groundwater quality parameters*

The summary statistics of the data for each of the 10 physico-chemical parameters considered for the groundwater samples and their corresponding permissible limits have been shown in Table 2. The groundwater quality maps for the current study with the selected parameters stated above are displayed in Figure 2–15.

The different parameters that were taken into account for the study, along with any seasonal fluctuations are being discussed in the paragraphs that follow. As a reference for the present study, the Bureau of Indian Standards (Anonymous 2012, 2015) and World Health Organization (Anonymous, 2017) drinking water standards have been used.

3.1.1. *pH*

Based on the results of the current study, the pH ranged between 6.06 (minimum) to 7.62 (maximum), thus falling within the permissible limit (6.5–8.5). For human consumption, the pH values of water must range from 6.5 to 8.5 (Anonymous, 1995). Considering its close affinity to other chemical components of water, it represents a crucial parameter for assessing the purity and toxicity of any groundwater system. The values of pH were found to be higher in the pre-monsoon season as compared to the post-monsoon season (Table S1, S2). Herojeet et al. (2016), also reported a reduction in groundwater pH during post-monsoon season. According to previous studies higher pH levels in the pre-monsoon season could be ascribed to decreased volume of water by evaporation and lower values in the winter due to decreased evaporation as a result of shorter daylight duration. The results of the study indicated slight alkalinity of water resources falling well within the prescribed limit of 6.5–8.5 as per Anonymous (2012) and Anonymous (2017) guidelines for drinking water quality. According to the distribution map (Figure 2), the south-eastern stretch of the study area illustrated higher values of pH (>7.5) at locations Bd_2, Bd_4, Bd_5 and Bt_2, which might have been attributed to the presence of a huge industrial setting in the adjacent areas of these locations.

3.1.2. *Electrical conductivity (EC)*

It was found that the electrical conductivity of the sample in the present study varied between 0.005 and 0.015 dS m^{-1}. This indicated that all the values were well within the permissible range. It is desirable to have EC below 0.75 dSm^{-1} for drinking purposes. As shown in Figure 3 , the value of EC gradually increased (>0.0095 dS m^{-1}) towards the northern part with a small scattered patch in the SW region of the study area. This could be explained by the region's saline geology and the fact that these places are close to densely populated areas which raises the possibility that sewage has mixed with the groundwater. However, the pre-monsoon season attained high EC values as compared to the post-monsoon season (Table S1, S2). In general, pre-monsoon season had higher conductivity than post-monsoon season owing to the dilution of the aquifer system caused by rainwater infiltration, thereby lowering conductivity during post-monsoon season (Kamaldeep et al., 2011). The research findings of Prasad and Minhas (2007) and Rajput et al. (2008), which noted a similar decline in the EC values during the post-monsoon season, provide additional support for the findings of the current analysis.

3.1.3. *Turbidity*

The turbidity values of the collected samples ranged between 1.44–4.04 NTU. BIS has specified 1 NTU as the acceptable limit and 5 NTU as the permissible limit when an alternate source of drinking water is unavailable. It was observed that all samples contained levels within the permissible range during the course of the present study. The spatial distribution pattern of turbidity indicated that the SW region of the study area, particularly the locations Bd_1, and Bd_2 and Bd_3 had higher concentrations (>3.2 NTU) as compared to the other regions (Figure 4). Higher

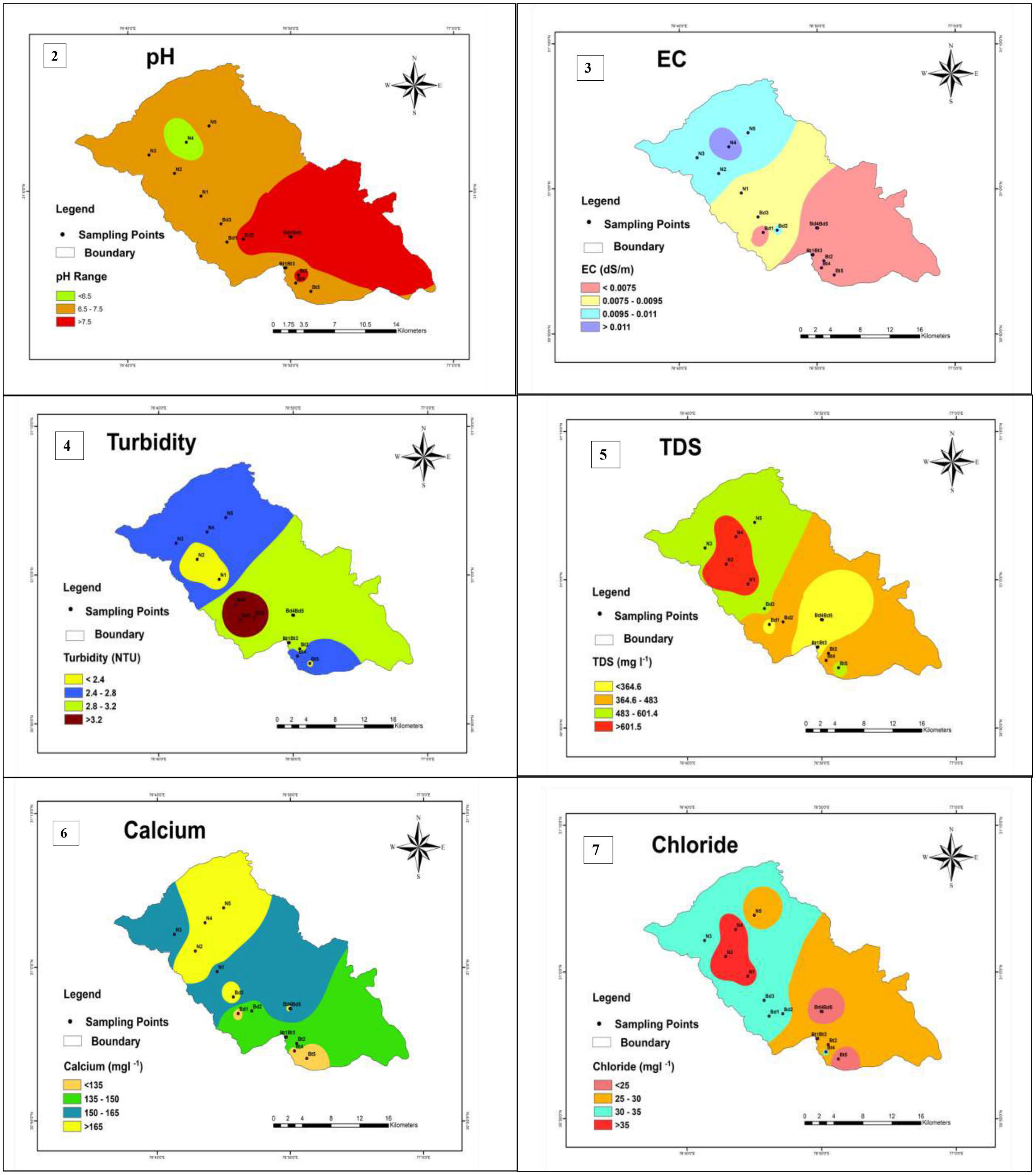


Figure 2-7: Spatial distribution map pH, EC, turbidity, TDS, calcium, chloride

turbidity values at these locations during the post-monsoon season (Table S2) might be associated with the unscientific disposal of sewage, industrial effluents, domestic wastewater, and other waste materials directly into surface water sources, which eventually percolates into the groundwater after leaching. The degree of turbidity in drinking water is significant for both aesthetic and operational reasons in treatment plants, where high levels of turbidity serve to protect harmful microorganisms from the effects of disinfectants and make water filtration more challenging

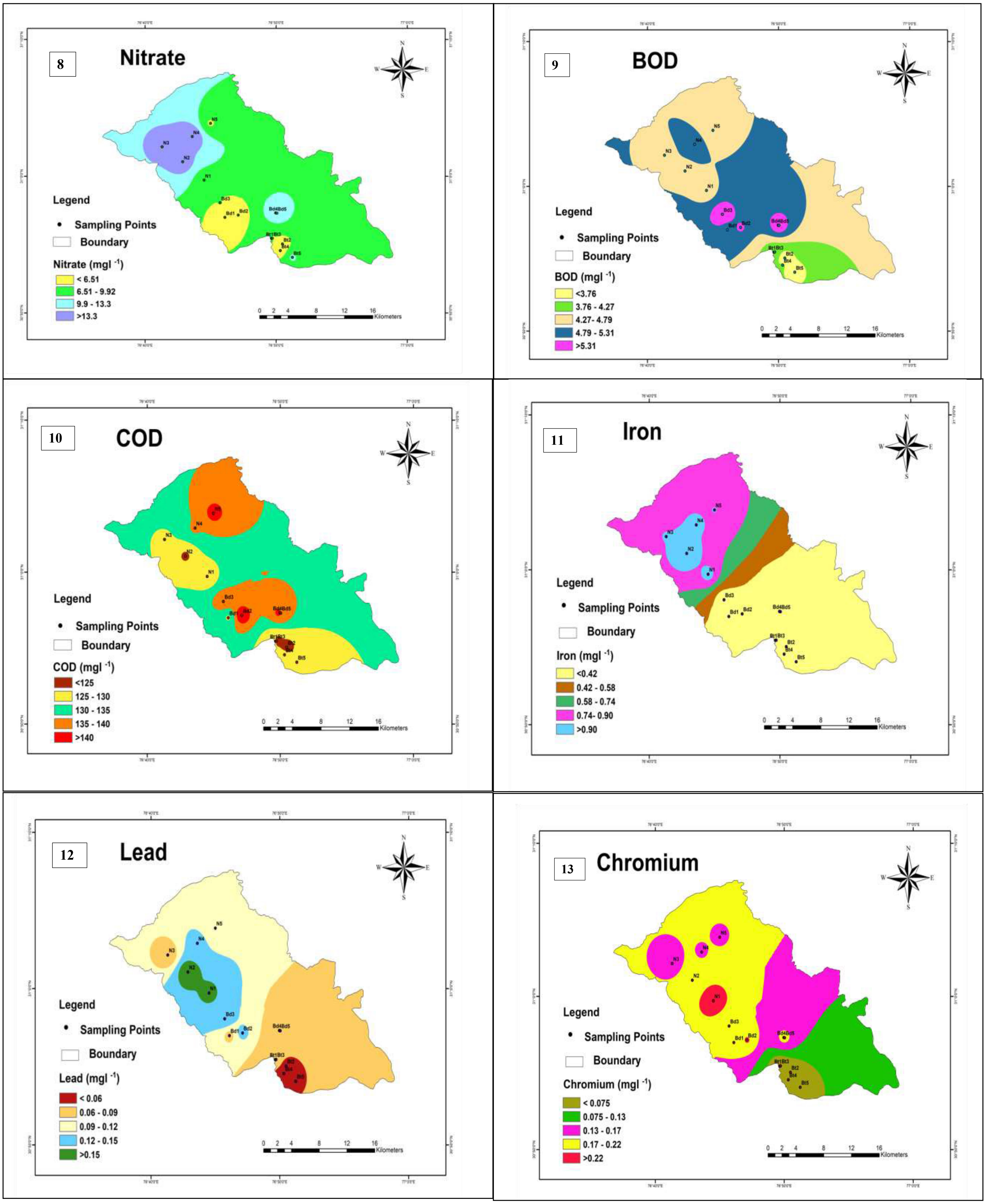


Figure 8-13: Spatial distribution map of nitrate, BOD, COD, iron, lead, chromium

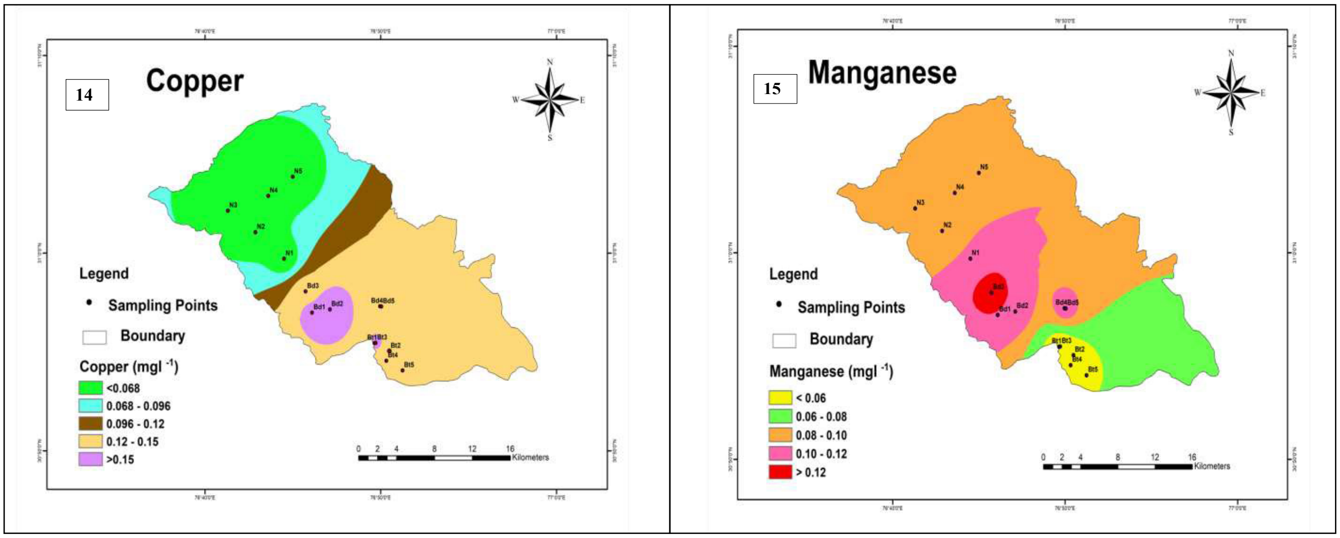


Figure 14-15: Spatial distribution map of copper and manganese

Table S1: Groundwater quality parameters during pre-monsoon

Locations	pH	EC	Turbidity	TDS	Ca^{2+}	Cl^-	NO_3^-	BOD	COD	Fe	Pb	Cr	Cu	Mn	WQI
Bd_1	6.86	0.008	2.84	351	136	30	1.3	5.53	125	0.37	0.06	0.22	0.13	0.14	129.22
Bd_2	7.36	0.011	2.98	468	152	24	3.4	5.84	145	0.35	0.1	0.25	0.14	0.15	167.24
Bd_3	6.92	0.009	3.02	553	173	29	5.8	5.93	137	0.42	0.12	0.23	0.1	0.16	180.76
Bd_4	7.62	0.008	2.61	295	167	15	7.5	5.76	143	0.31	0.07	0.21	0.14	0.12	136.13
Bd_5	7.52	0.007	2.54	312	164	21	11.3	6.02	131	0.38	0.03	0.2	0.12	0.13	106.14
Bt_1	6.93	0.007	2.43	342	153	18	4.6	4.28	124	0.36	0.04	0.07	0.13	0.07	85.66
Bt_2	7.28	0.008	2.56	484	149	21	3.2	3.18	116	0.32	0.03	0.06	0.16	0.04	74.07
Bt_3	7.08	0.009	2.31	348	138	30	5.4	4.16	113	0.41	0.08	0.05	0.14	0.06	110.87
Bt_4	7.24	0.008	1.82	492	141	25	4.2	3.95	122	0.43	0.02	0.04	0.12	0.05	61.18
Bt_5	7.16	0.006	1.94	594	132	16	6.3	3.62	123	0.46	0.03	0.09	0.13	0.08	77.66
N_1	6.82	0.009	1.52	720	169	35	7.2	4.98	121	1.01	0.12	0.23	0.05	0.12	170.53
N_2	6.98	0.01	1.44	756	184	37	9.3	5.26	120	1.02	0.16	0.2	0.07	0.08	195.80
N_3	6.94	0.012	2.01	604	157	27	10.8	5.12	124	0.93	0.07	0.17	0.05	0.06	127.12
N_4	6.28	0.015	2.04	763	172	34	12.5	5.43	130	0.89	0.11	0.18	0.08	0.07	160.21
N_5	7.18	0.013	1.98	547	179	20	5.2	4.83	139	0.88	0.08	0.16	0.06	0.05	131.27

and expensive (Singh and Hussain, 2016). The presence of suspended materials, such as sand, silt, clay, industrial waste, and sewage, causes turbidity in water (Ibrahim et al., 2019).

3.1.4. Total dissolved solids (TDS)

In the current study area, TDS varied from 193 to 763 mg l^{-1} indicating that TDS values were well within the permissible limit of 2000 mg l^{-1} as per Anonymous, 2012 and water can be used for domestic purposes. The TDS content of groundwater may rise at places, when there is a lack of chemical equilibrium between water and deposited salts and is directly related to EC (Durfor and Beckor, 1964). The increase in the TDS value with an increase in the value of EC was also visible from the distribution map (Figure 5) as higher values were mainly concentrated towards the northern region of the study area in both cases. Taking into account the seasonal variation, there was a decrease in the values of TDS during the post-monsoon season (Table S2). The present trend was confirmed by the findings of Verma et al. (2020) who stated that the decrease in TDS values during the post-monsoon season may be due to the dilution and leaching of salts in the rainy season. By classifying

Table S2: Groundwater quality parameters during post-monsoon

Locations	pH	EC	Turbidity	TDS	Ca^{2+}	Cl^-	NO_3^-	BOD	COD	Fe	Pb	Cr	Cu	Mn	WQI
Bd_1	6.61	0.005	3.56	296	125	34	4.9	4.78	132	0.2	0.09	0.12	0.18	0.1	139.08
Bd_2	7.14	0.009	3.98	357	143	38	6.2	4.86	148	0.18	0.15	0.16	0.21	0.09	194.16
Bd_3	6.86	0.008	4.04	496	168	36	7.3	5.52	140	0.24	0.17	0.11	0.17	0.12	204.97
Bd_4	7.45	0.007	3.72	193	163	20	11.9	4.92	152	0.21	0.12	0.12	0.15	0.08	165.65
Bd_5	7.32	0.006	3.54	245	150	26	19.3	5.68	136	0.25	0.06	0.13	0.16	0.1	124.86
Bt_1	6.42	0.005	3.18	217	141	22	9.3	3.78	138	0.43	0.07	0.02	0.15	0.03	105.65
Bt_2	6.98	0.005	3.26	367	132	28	6.6	3.29	122	0.4	0.06	0.02	0.08	0.05	96.68
Bt_3	6.81	0.007	3.31	238	126	34	7	3.82	119	0.36	0.1	0.03	0.19	0.02	128.38
Bt_4	6.91	0.007	3.26	363	125	37	6	3.62	135	0.33	0.04	0.01	0.18	0.02	80.67
Bt_5	6.95	0.005	2.82	471	115	21	14.5	3.43	128	0.38	0.08	0.02	0.16	0.03	110.35
N_1	6.59	0.007	2.71	615	152	38	9.2	3.96	129	0.9	0.19	0.26	0.03	0.08	231.66
N_2	6.86	0.011	2.65	684	163	42	22	4.09	126	1.11	0.2	0.15	0.02	0.09	227.87
N_3	6.62	0.011	3.25	514	141	32	17.9	4.27	134	0.89	0.05	0.13	0.02	0.1	115.85
N_4	6.06	0.012	3.04	627	159	48	21	4.68	142	0.96	0.15	0.14	0.03	0.13	193.47
N_5	6.89	0.007	2.86	434	165	28	7.3	3.82	146	0.93	0.1	0.15	0.01	0.12	150.98

groundwater based on its TDS values and associated hydrochemical properties, it's possible to make informed decisions about its suitability for different uses (Anonymous, 2012; Kaplay and Patode, 2004).

3.1.5. Calcium

The calcium levels varied from 115 to 184 mgl^{-1} in the current study. Additionally, the spatial distribution map of Ca^{2+} suggested that the concentrations varied within acceptable limits across the area of study (Figure 6). Calcium is often present in groundwater in the form of dissolved calcium carbonate ($CaCO_3$), which is a common mineral in the Earth's crust. The solubility of calcium carbonate is affected mainly by temperature, pressure, and the presence of other ions in the water (Chaurasia et al., 2021). Also, the concentration of carbon dioxide in the air above the groundwater, along with its partial pressure, can influence the solubility of calcium carbonate. Looking into the seasonal variation of Ca^{2+} values, the pre-monsoon season attained high Ca^{2+} values as compared to the post-monsoon season (Table S1, S2). A study conducted by Khan et al, 2015 also reported a drop in Ca^{2+} values during the post-monsoon season. In groundwater, Ca^{2+} is primarily associated with the electrostatic exchange of mineral deposits from local bedrock. Furthermore, this could also be attributed to the presence of $CaCO_3$ and $CaSO_4$ minerals in the soil as a result of the evaporation of soil water, which includes gypsum $CaSO_4.2H_2O$, anhydrite $CaSO_4$, calcite $CaCO_3$, and dolomite $Ca.Mg(CO_3)_2$ (Ram et al., 2021). As a result of their higher concentration, consumption of such water can cause abdominal discomfort and encrustation (Catroll, 1962).

3.1.6. Chloride

The content of chloride ion in groundwater of the sampled area ranged from 15 to 48 mg l^{-1} which was significantly less than the desired limit (250 mg l^{-1}). However, post-monsoon values of analysed groundwater samples were considerably higher than pre-monsoon levels (Table S1, S2). Similar increase in chloride concentration during post-monsoon was observed by Yashoda et al. (2014) pertaining to the seepage of inorganic fertilizers, landfill leachates, septic tank effluents, animal feeds, industrial effluents, irrigation drainage, run-off from road de-icing salts into the groundwater after the monsoons. Figure 7 also clearly depicted that a higher concentration of chloride (>35 mg l^{-1}) was observed in the NW part of the research area primarily at locations N_1, N_2 and N_4. Chlorides play a crucial role in identifying groundwater contamination (Purandara et al., 2003; Sameer et al., 2011). Excessive chloride content gives water a saline flavor that can have laxative effects on individuals who aren't accustomed to drinking it (Pius et al., 2012).

3.1.7. Nitrate (NO_3^-)

In the examined area, nitrate concentration ranged from 1.3 to 22 mg l^{-1} indicating all of the samples were significantly below the permitted level. Seasonally, nitrate concentration during the post-monsoon season was higher as compared to the pre-monsoon season (Table S1, S2). The spatiotemporal map of nitrate (Figure 8) depicted higher concentration (>13.3 mg l^{-1}) within collected groundwater samples at locations N_2, N_3, and N_4, which might be due to abandoned sewer tanks, an inadequate sewage system, untreated discharges from industries and agriculture fields that can indeed contribute to contamination of phreatic aquifers (Hei et al., 2020; Kumar et al., 2023). Nitrate is a highly soluble and mobile form of nitrogen that can easily leach into groundwater systems during rains (Galloway et al., 2004; Rivett et al.,2008). Nitrate concentrations in natural water are often quite low (less than 10 mg l^{-1} NO_3^-), but due to human activities such as excessive fertilizer use in agriculture[49], industrial and domestic effluents, and emissions from combustion engines, nitrate concentrations often exceed the levels that are considered normal.

3.1.8. BOD (Biological oxygen demand)

A chemical process called biological oxygen demand (BOD) measures how quickly biological organisms in a body of water utilize oxygen for the breakdown of organic materials. The sources of BOD in water are indeed readily biodegradable organic carbon, orthophosphate, and ammonia, which are commonly found in or produced as metabolic by-products of plant and animal wastes, as well as human activities (Sawyer et al., 2003). All the samples were well within the prescribed desirable limit of 5 mg l^{-1} as given by Anonymous, (2017) except few samples collected from Baddi (Bd_2, Bd_3, Bd_4, Bd_5) and Nalagarh (N_4) (Figure 9 during the pre-monsoon season (Table S1) which might be pertinent to the high load of organic pollutants from industrial and sewage wastes, low stream flow and high temperature causing reduction of DO followed by increased BOD (Anshu et al., 2011). Also in a study conducted by Herojeet et al. (2017), higher BOD concentrations were observed during pre-monsoon season.

3.1.9. COD (Chemical oxygen demand)

COD measurement identifies the amount of toxicity by highlighting the strength of physiologically resistant organic toxins in contaminated water. The acceptable COD level is 250 mg l^{-1} and in the area under research, it varied from 113 to 152 mg l^{-1} thereby indicating light pollution levels in the analysed samples. The seasonal variation of COD depicted higher concentrations during the post-monsoon season relative to the pre-monsoon (Table S1, S2). However, the spatial distribution map of COD (Figure 10) indicated increasing concentration (>140 mg l^{-1}) at some sampling sites in Baddi (Bd_2, Bd_4) and Nalagarh (N_5).

3.1.10. Iron (Fe^{2+})

The concentration of iron in the current study ranged between 0.18 and 1.11 mgl^{-1}, which exceeding the permissible limit of 1.0 mgl^{-1} (Anonymous, 2015). Few samples from Nalagarh (N_1 and N_2) exceeded the permissible limit of 1 mg l as presented in table S1, S2 and Figure 11, thus making groundwater unfit for drinking purposes that pertain to the discharge of untreated industrial wastewater and extensive application of fertilizer in farmlands (kamaldeep et al., 2011). In many aquifers, iron is often found in the reduced Fe^{2+} state, which is soluble in groundwater. In this reduced form, iron typically does not pose significant health risks. However, in the presence of atmospheric oxygen or with the assistance of certain bacteria associated with iron, Fe^{2+} is oxidized to Fe^{3+}, which then forms insoluble hydroxides in the groundwater. Consequently, iron concentrations in groundwater are typically higher than those in surface waters (Ram et al., 2021). The reddish-brown coloration and the formation of precipitates leading to the staining of plumbing fixtures near the tap and hand pumps, laundry, and even a metallic taste in the water indicates the presence of a higher concentration of iron in the water (Ansari and Hemke, 2013).

3.1.11. Lead (Pb)

The Pb concentration in groundwater samples was in the range of 0.04–0.20 mg $^{-1}$ thereby depicting that all the samples have crossed the BIS and WHO prescribed desirable limit of 0.01 mg l^{-1}. The maximum concentration of lead was found in the NW region of the study area predominantly at two locations (N_1 and N_2) in Nalagarh (Figure 12). Rout et al. (2017) who evaluated the concentrations of heavy metals in groundwater in urban and semi-urban areas of the Nalagarh tehsil also found lead concentration exceeding the permissible limits.. Thus, due to excessive lead concentrations, water is unfit for human consumption. Lead (Pb), a naturally occurring element is commonly found in rocks and mineral deposits in various degrees of solubility. As a result of the leaching of such rocks and minerals, elevated concentrations of lead (Pb) can be found in groundwater (Mallongi et al., 2022). Moreover, mining and industrial activities can also contribute to the release of lead into the environment.

3.1.12. Chromium (Cr)

Chromium content in the sampled area varied from 0.01 to 0.26 mg l^{-1}. As per the data represented in Tables S1 and S2, a large variation in pre- and post-monsoon concentrations of copper was observed. It is primarily the industrial sources that contribute to the enrichment of chromium in this region. As indicated by the pattern of Cr accumulation in groundwater (Figure 13), the southern portion of the study area had a no-risk status, while the northern portion was deemed unsafe in terms of chromium contamination (concentration greater than 0.13 mg l^{-1}). The leaching of chromium from topsoil and rocks is indeed one of the most significant natural sources of chromium entry into water bodies. In addition to natural sources, anthropogenic activities contribute significantly to the presence of chromium in water bodies including leather dyeing wastes, petroleum and ore refinement wastes, electroplating wastes, and pulp industry wastes. These industries release chromium-containing waste materials into the environment, including liquid and solid forms, which can ultimately reach subsurface water (Kanagaraj and Elango, 2019). Waste solids from chromate-processing plants can contaminate groundwater when disposed of improperly in landfills, where chromium may remain for several years. Also, there is a significant impact of tanning industries on the presence of chromium in the groundwater. There have been several studies regarding the effects of leather tanning industries on the quality of groundwater in India (Hutton and Shafahi, 2019; Kanagaraj and Elango, 2019; Nur-E-Alam et al., 2020; SajilKumar and James, 2019). A large amount of Cr consumption can result in problems associated with the gastrointestinal, hematological, respiratory, hepatic, renal, as well as the cardiovascular system (Mukherjee and Singh, 2021).

3.1.13. Copper (Cu)

It is evident from the data represented in Tables S1 and S2 that a number of the samples in the study area were above the minimum desirable limit of Cu^{2+} (0.05 mg l^{-1}) as per BIS (2012) except a few samples in Nalagarh (Figure 14), which was likely attributed to domestic sewage and leachate from extensive farmed area (Wu et al., 2008). However, all the samples were well within the permissible limit of 1.5 mg l^{-1} as given by Anonymous, 2012. Copper constitutes a crucial dietary nutrient, but its overexposure can cause anemia, damage to the kidneys and liver, and irritability to the stomach and intestines (Chaurasia et al., 2021). The element occurs naturally in rocks, soils, plants, animals and groundwater at very low concentrations. Several activities such as quarrying and mining operations, agricultural practices, manufacturing processes, and the release of municipal or industrial waste all have the potential to enhance the concentration of copper in the groundwater.

3.1.13. Manganese (Mn)

In groundwater, manganese occurs naturally, especially in anaerobic environments. The release of manganese into groundwater is influenced by several factors, including the pH of the water, redox conditions (presence or absence of oxygen), mineral composition, and the overall geochemical characteristics of the aquifer. The chemistry of rainfall, aquifer geology, groundwater conveyance pathways, the geochemical surroundings, and residence times are some of the variables that can dramatically change the concentration of Mn in groundwater over a broad array of spatial and temporal scales (Ram et al., 2021). This was visible from a quite large difference in the pre and post-monsoon manganese concentrations (Table S1, S2). As evident from the findings of the current study, manganese concentrations were within the permissible limit of 0.3 mgl^{-1} with values ranging between 0.005 and 0.221 mgl^{-1}.

3.2. Statistical analysis

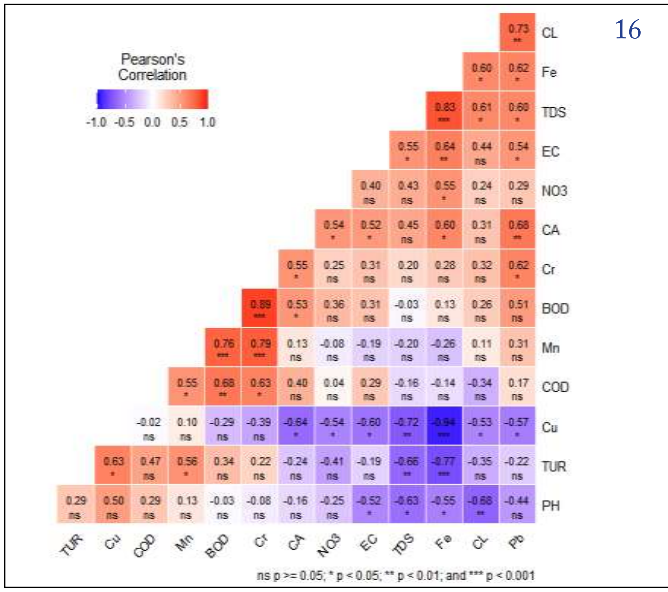
The inter-element relationship during pre-monsoon and post-monsoon was evaluated using the Pearson correlation matrix of different groundwater quality parameters (Figure 3 a,b).

During pre-monsoon season high positive correlation at $p<0.001$ was found between Cr-BOD (0.89), Fe-TDS (0.83), Cr-Mn (0.79) and BOD-Mn (0.76), demonstrating a considerable impact on the overall assessment of the groundwater quality in comparison to any other major components. However, during post-monsoon season only Fe was found to be significantly correlated with TDS (0.78) at $p<0.001$. Taking into account the correlation at $p<0.01$, Pb-Cl (0.73), BOD-Fe (0.68) and Pb-Ca (0.68) were found to be significantly correlated during pre-monsoon as compared to correlation during post-monsoon between Turbidity with Cu and BOD, EC with Cl^-, Mn with Cr and BOD, TDS with EC and Cl^- and Cr with Mn and Pb (Figure 16,17).

A high negative correlation of Fe with Turbidity (-0.77) and Cu (-0.94) was found at $p<0.001$ during both pre-monsoon and post-monsoon (Figure 16, 17). This finding was similar to the previous report by Nayak et al. (2023). Further, at $p<0.01$, TDS was found to be negatively correlated with Turbidity (-0.66) and Cu (-0.72) during pre-monsoon season. However, pH was found to be weakly correlated with EC (-0.052), TDS (-0.63) and Iron (-0.55) at $p<0.05$ during pre-monsoon season implying that as water becomes more acidic, more ions and salts get dissolved from the soil minerals into it (Amfo-otu et al., 2014; Mahato et al., 2018).

3.3. Principal component analysis

Principal Component Analysis (PCA) was conducted individually for groundwater parameters in both pre-and post-monsoon seasons. This was done to discern and elucidate the prevailing geochemical processes and sources of pollution influencing the characteristics of groundwater in the study area (Table 5). During pre-monsoon, three distinct factors were identified, collectively accounting for 78.87% of the total variance. Component I represent 42.95% of the total variance with loadings of EC, TDS, Ca^{2+}, Cl^-, NO_3^-, BOD, Fe, Pb and Cr. This suggests a prominent presence of ions, influenced by a combination of natural and anthropogenic activities in the study area. Component II was represented by Turbidity, BOD, COD, Cr and Mn with a total variance of 26.84%. This represents wastewater discharge, agricultural runoff, or effluents from industrial activities, all of which can introduce elevated levels of organic matter and heavy metals



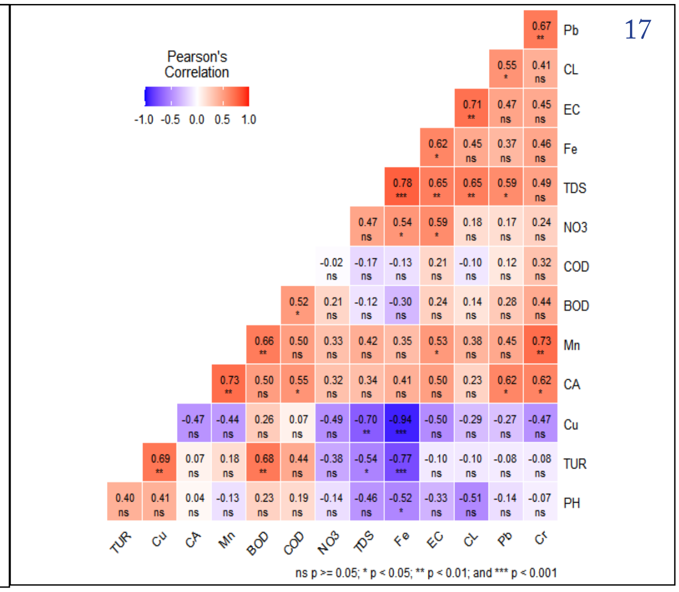


Figure 16; 17: Correlation matrix among different groundwater quality parameters in pre-monsoon and post-monsoon season; PH: pH; EC: Electrical conductivity; TUR: Turbidity; TDS: Total dissolved salts; CA: Calcium; CL: Chloride; NO_3: Nitrate; BOD: Biological oxygen demand; COD: Chemical oxygen demand; Fe: Iron; Pb: Lead; Cr: Chromium; Cu: Copper; Mn: Manganese; ns: non-significant

Table 5: Factor loadings of various physicochemical groundwater parameters during pre- and post-monsoon seasons

Sl. No.	Pre-monsoon				Post-monsoon			
	Parameters	Principal component matrix			Principal component matrix			
		Component I	Component II	Component III	Parameters	Component I	Component II	Component III
1.	pH	-0.630	0.298	0.477	pH	-0.447	0.438	-0.402
2.	EC	0.716	0.030	0.159	EC	0.805	0.108	0.209
3.	Turbidity	-0.531	0.683	-0.247	Turbidity	-0.409	0.808	0.302
4.	TDS	0.820	-0.335	-0.031	TDS	0.852	-0.295	0.147
5.	Ca^{2+}	0.734	0.305	0.400	Ca^{2+}	0.668	0.528	-0.313
6.	Cl^-	0.739	-0.115	-0.589	Cl^-	0.670	-0.024	0.683
7.	NO_3^-	0.567	-0.050	0.183	NO_3^-	0.575	-0.098	-0.226
8.	BOD	0.426	0.852	-0.017	BOD	0.170	0.892	0.106
9.	COD	0.060	0.827	0.412	COD	0.124	0.734	-0.278
10.	Fe	0.912	-0.299	0.165	Fe	0.847	-0.454	-0.216
11.	Pb	0.816	0.263	-0.227	Pb	0.677	0.255	0.237
12.	Cr	0.526	0.794	-0.072	Cr	0.726	0.380	-0.087
13.	Cu	-0.884	0.124	-0.211	Cu	-0.789	0.370	0.391
14.	Mn	0.035	0.874	-0.345	Mn	0.690	0.571	-0.085
Eigen value		6.013	3.757	1.272	Eigen value	5.812	3.447	1.293
% of variance		42.949	26.837	9.086	% of variance	41.517	24.619	9.233
Cumulative %		42.949	69.786	78.872	Cumulative %	41.517	66.136	75.369

Values in bold indicate high loadings greater than 0.4

into the groundwater. In some instances, the infiltration of surface water contaminated with organic waste into the groundwater may also be a pertinent factor. However, during the post-monsoon season, three factors described 75.37% of the total variance. Component I accounted for 41.52% of the variance with loadings of EC, TDS, Ca^{2+}, Cl^{-}, NO_3^{-}, Pb, Cr and Mn. This component illustrates both the natural geogenic influence of rock weathering, characterized by mineral dissolution in groundwater, and the anthropogenic pollution resulting from agricultural activities. Component II explained 24.61% of the total variance with positive loadings for pH, Ca^{2+}, BOD, COD and Mn. Through the findings of PCA, it can therefore be concluded that major polluting sources of groundwater in the region are untreated effluents from industrial and urban areas and the leaching of precipitates from excessive use of fertilizers in agriculture.

The higher cumulative PCA loading values observed in the pre-monsoon season in comparison to the post-monsoon season in groundwater were likely due to lower groundwater levels during the pre-monsoon period, resulting from prolonged dry spells and limited recharge from rainfall. As a result, there was an increased build-up of various solutes and ions in the groundwater, resulting in higher variability and subsequently higher PCA loading values. The reduced dilution effect in the absence of significant rainfall leads to a more pronounced influence of the existing geological and anthropogenic sources of contamination.

3.4. Water quality index

A comprehensive water quality index (WQI) map outlined four different quality classes—excellent, good, poor, and extremely poor-across sampled locations, specifically for drinking purposes (Table 6; Figure 18). A significant portion of the study area, as evident from the WQI map indicated poor groundwater quality (60%) while good (26.7%) and very poor (13.3%) were predominate in isolated pockets in SE and NW part respectively (Figure 4). This means that nearly 73.3% of the samples were in a poor state and were therefore unsuitable for consumption. As can be observed from the WQI map, the quality of groundwater in the Barotiwala region fell within a good category in terms of potability for human consumption as a smaller number of industries exists in this area in the remaining portion of the research area. The quality of the groundwater varied gradually from extremely poor in the northwestern region

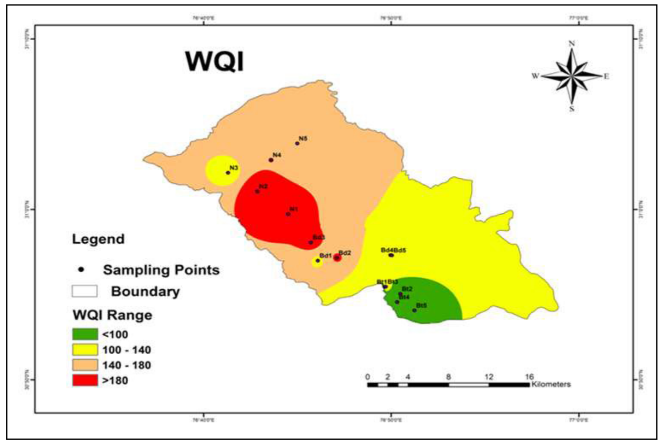


Figure 18: Water quality index map of the study area

Table 6: Water quality index values for analyzed groundwater samples in the study area

Sl. No.	Sites	Area of sample collection	Source	code	Final WQI	Class
1.	Bhud	Residential	Handpump	Bd_1	134.15	Poor
2.	Bhud	In the vicinity of industries	Handpump	Bd_2	180.70	Poor
3.	Kishanpura	Along main NH	Handpump	Bd_3	192.86	Poor
4.	Bhatauli	Residential	Borewell	Bd_4	150.89	Poor
5.	Bhatauli	In the vicinity of industries	Borewell	Bd_5	115.50	Poor
6.	Jhadmajri	Industrial	Borewell	Bt_1	95.66	Good
7.	Balyana	Residential	Handpump	Bt_2	85.37	Good
8.	Jhadmajri	In the vicinity of industries	Borewell	Bt_3	119.63	Poor
9.	Bated	Residential	Handpump	Bt_4	70.92	Good
10.	Jhohranpur	Village	Borewell	Bt_5	94.00	Good
11.	Khruni	Along main NH	Borewell	N_1	201.10	Very poor
12.	Kheda	In the vicinity of industries	Borewell	N_2	211.83	Very poor
13.	Thanthewal	Village	Borewell	N_3	121.48	Poor
14.	Ward No. 7	Residential	Handpump	N_4	176.84	Poor
15.	Silnupul	Residential	Borewell	N_5	141.13	Poor

(Nalagarh) to good in the south-eastern region (Barotiwala), where almost all the estimated values of WQI fell within the potable drinking water category. It was primarily attributed to the variations in a hydraulic gradient and the movement of groundwater towards the northwest region. Additionally, the shallow groundwater levels (<10 m) were mostly to be held accountable for this decline in water quality from the southeast to the northwest region.

4. CONCLUSION

The water quality rating showed that 60% of samples fell into the 'poor' category for drinking. The WQI map indicated higher contamination vulnerability in the northern region than the south. Concentrations of BOD and heavy metals (Fe, Pb, Cr) exceeded permissible limits in some areas. PCA analysis highlighted the area's high vulnerability to pollution due to recent industrialization, emphasizing the need for a close water quality monitoring network.

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