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Integrated method of groundwater quality evaluation using pollution indices, automatic linear modelling and human health risk model in semi-arid region of India

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ABSTRACT

The aim of our research is to evaluate groundwater quality in the southern part of India using novel integrated methods such as automatic linear modelling (ALM) and human health risk model (HHRM). The water samples were collected based on the industrial and population density in study region. According to the attained results, the Ca–Mg–Cl type of groundwater was found in the higher part of the study region. Nitrate pollution index results revealed that 67.92% and 64.15% of sample locations were contaminated in pre and post monsoon, respectively. The results of HHRM divulged that nitrate contamination levels of all the exposed age groups (in years) of people varied in the order of 1 to 5 > 6 to 12 > above 65 > 30 to 65 > 20 to 29 > 13 to 19. The statistical analysis and ALM revealed that municipal waste disposal and synthetic fertilizers usage are the source of contamination in a north and south east zone of the study region. The present research found that sources of contamination such as anthropogenic activities influenced in northern, north–east, some part of south region and geogenic sources dominated in the southern and south west part of the study region.

Keywords: Groundwater; Nitrate pollution index; Fluoride pollution index; Human health risk model; Automatic linear modeling

1. Introduction

Groundwater is a more critical water source for drinking and agriculture purposes in Asian regional countries, including China, India, Bangladesh and Pakistan [1,2]. In India, due to increase in population growth, rapid growth of industries, urbanization and other man-made development process are the major threats to natural resources in nowadays. The major parts in the southern part of India, people primarily depend on groundwater for their daily needs such as drinking, irrigation and industrial process [3,4]. Roughly more than 58% of the population lives in rural area and their source of income is agriculture. Even though people in urban cities have individual bore-wells for their daily needs such as drinking, bathing, washing, etc., groundwater level depletion and contamination are serious issues that affect the country's economic growth [5]. Therefore, the scientists and researchers are highly involved in identifying and assessing the quality of groundwater, source of contamination, and vulnerable zone in their study region. The study results revealed that the anthropogenic source of contamination highly influences the groundwater quality in a major part of India. This is because the anthropogenic sources are released the high level of nitrate, sulphate and chloride to groundwater [6,7].

Nitrate contamination in groundwater is a major issue in many parts of the world, especially in developing countries like India, Iran, China, Bangladesh etc., The primary source of nitrate contamination in groundwater are natural and anthropogenic origin [8]. In nature source of contamination, the higher concentration of nitrate has been recorded as 10 mg/L and it is accepted for drinking and does not cause

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any serious diseases on human health [9,10]. The anthropogenic activities such as municipal waste dumping yards, household waste disposal, nitrogen fertilizers in agriculture field, industrial effluents, and uncovered septic tank in residential area are the major activities that causes the elevated concentration of nitrate in groundwater [11,12]. The increase in population, urbanization, industrial growth and the living standards of people are highly contributing to ecological degradation and on groundwater quality [13].

In recent years, researchers and scientists are highly involved in groundwater studies and conducted to evaluate the nitrate pollution in groundwater. Haghbin et al. [14] carried out the application of soft computing (SC) model for simulating nitrate concentration in groundwater and found that the SC model helps to simulate and identify the significant factors that control the nitrate contamination of groundwater. The study also stated that, random forest and logistic regression methods are the most accurate for the prediction of nitrate contamination in groundwater. Shukla and Saxena [15] reviewed the sources and leaching of nitrate contamination in groundwater in India and divulged that natural process such as atmospheric fixation and lighting storm, anthropogenic activities such as the application of synthetic fertilizers, and uncovered septic tank effluents are enters the hydrosphere that causes the groundwater contamination. Su et al. [16] assessed the source and human health risk due to fluoride and nitrate contamination of groundwater in loess plateau in China and found that presence of nitrate in soil, synthetic fertilizers and manure and disposal of sewage from the residential area are controlled factors of concentration of nitrate in groundwater. About 96.2% of shallow groundwater samples were causes the non-carcinogenic diseases on children followed by children, teenagers and adults. Yang et al. [17] analysed the land use and fertiliser used data to analyse the nitrate contamination and also statistically approached to evaluate the loading source of nitrogen and spatial-temporal distribution of nitrate in groundwater. The study revealed that nitrogen-based fertilizers used in agriculture field and infiltration of rainwater into aquifers are the primary source of elevated concentration of nitrate in groundwater.

The quantity and quality of water supplied to the community of people will have an important impact on their health [18–20]. The maximum permissible level of nitrate in groundwater is 45 mg/L strongly recommended by the world health organization [21] and Bureau of Indian Standard [22]. The consumption of elevated concentration of nitrate in groundwater react with blood haemoglobin and increases the level of methaemoglobin in blood. The increase in level of methaemoglobin decreases the oxygen-carrying capacity and tissue hypoxia in blood and it is called as methemoglobinemia (Blue baby syndrome). The elevated concentration of nitrate can also cause diabetes, thyroid hypertrophy, hypertension, gastric cancer and birth malformations. Usually, nitrate enter the body in two way such as thermal and oral contact [23,24].

Ramaroson et al. [25] investigated the nitrate contamination in the Madagascar region using a statistical approach and stated that pit latrines, and sewage disposal are factors that influenced the elevated concentration of nitrate in groundwater. The study also revealed that the source of nitrate in groundwater was confirmed by using principal component analysis (PCA). The major ions such as concentration of calcium, magnesium and sodium were dominated by nitrate concentration. Gao et al. [26] focused on health risk assessment associated with nitrate concentration in East China and found the infants and children are highly exposed to nitrate contamination compared to adults (above 18 y).

The higher percentage of the population suffers from various health issues related to water borne diseases, and nitrate is a prominent one among them in the arid and semiarid regions of the study region [27]. The present research aimed to assess the level of nitrate and fluoride contamination [28], evaluate the human health risk due to nitrate contamination with the use of standards recommended by USEPA [29] and statistically analyse the dominating factor on groundwater quality in the study region. The integrated approach of automatic linear modelling, human health risk assessment, correlation, principal component analysis and hierarchical cluster analysis are helpful to identify the high influence factor, water quality parameter in the study region. The results and findings of the present study helps to take remedial measures and action to reduce the source of contamination in the study area.

2. Methods and materials

2.1. Study area and geology formation

Dindigul district is one of the fast-developing districts in the field of industries, education and infrastructure in Tamil Nadu, India. The present study area located at a latitude of 10°25′0″ to 10°45′0″ and longitude of 77°50′0″ to 78°15′0″ in northwest direction of the district. It covers an area of about 1,059.21 km^2 with the population of around 1,23,365 people and agriculture is the major source of income of the people. The geological formations of the study area are crystalline metamorphic group of rock in major part and dark/grey biotite gneiss are identified in the southern part. The identified major minerals such as granite, quartz vein, charnockite, granite gneiss, dark/grey biotite gneiss and etc. The geomorphologic structure of the study area was identified as pediments and buried pediments during the sample collections. The detailed geological formation of the study region shown in Fig. 1. The study boundary population was increased by 28% compared to 2011 census report and it shows that urbanisation of study area. The climatic condition of the study area is driest during the period of February to May and coldest during the month of October to November. The average highest temperature recorded in the year of 2021 was 32.5°C and lowest temperature was 24°C (Fig. 2). The annual recorded rainfall in the study region was 1,480 mm throughout the year of 2021 (https://en.climate-data.org/asia/india/tamil-nadu/dindigul-24012/). The relative humidity of the study area varies from 40% to 85% during the morning and afternoon, respectively.

2.2. Hydrological setting

The pediments and valley fill sediments have been observed during the sample collection and the average range water depth ranges from 35 to 45 m below ground level

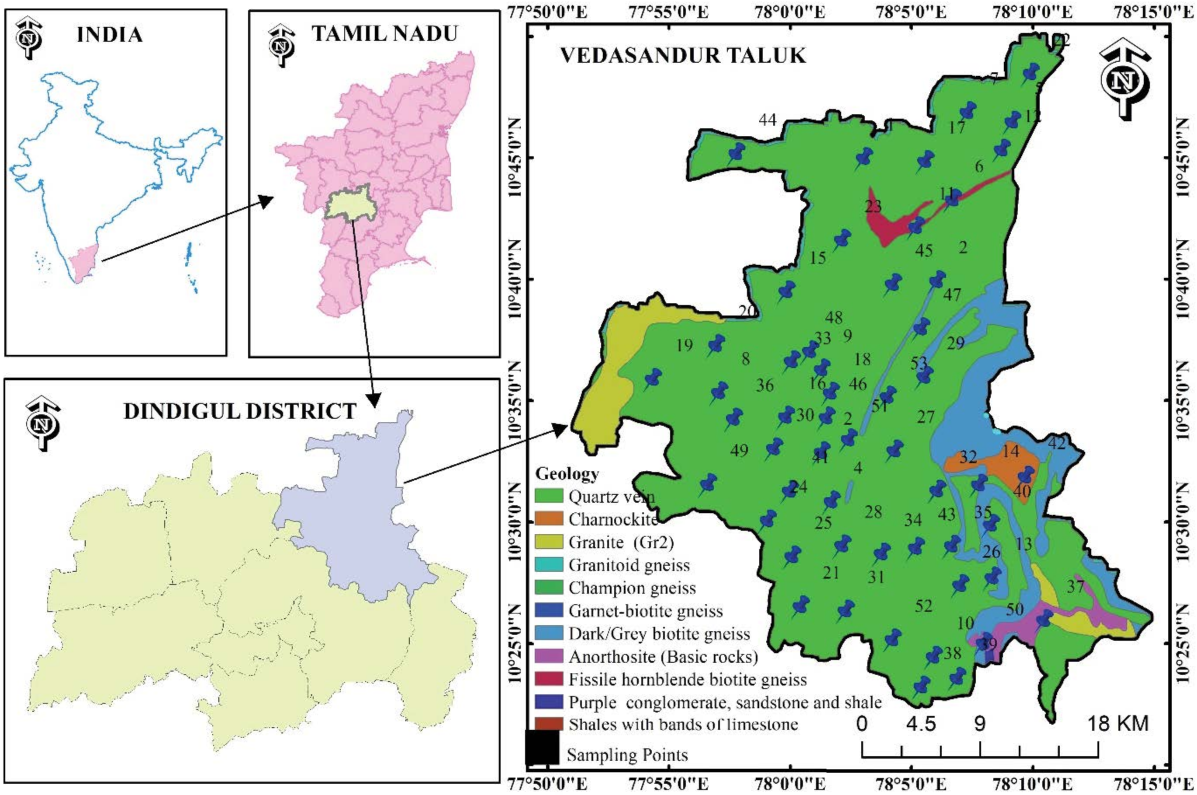

Fig. 1. Sample locations and geological formation of study area.

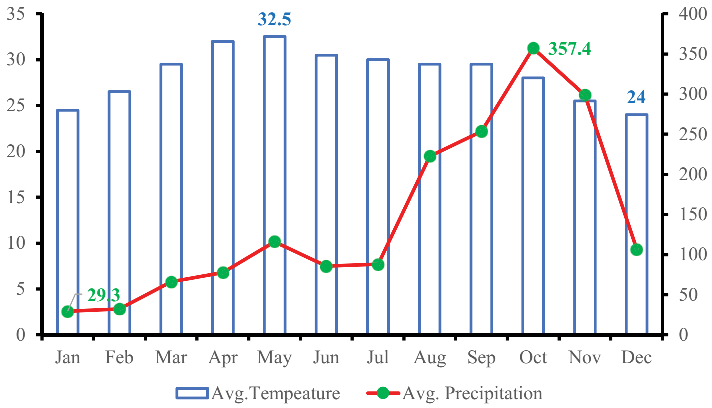

Fig. 2. Average temperature and precipitation in study region.

(bgl) in and around the study region. The observation made during the site investigation; it was noted that extraction of groundwater in deeper well can yield about 200 m^3/d and average continuous pumping of 4–5 h. The groundwater in the study region highly identified in the shallow fractured, under semi-confined and confined aquifers. The depth of weathering varies from different sample locations and the average depth was 25 m bgl. The bore wells are highly used to extract the groundwater for drinking and other domestic purpose. They dug wells are generally used for irrigation purposes and in few sample locations; bore wells are identified for agriculture uses.

2.3. Sampling and analysis

The collection of water samples, distribution of groundwater table and frequency of samples were taken into account during the sample collection in the study region. In this regard, sampling locations were gleaned from the urban activities, agricultural practices, industrial zone, density of population and availability of bore and open wells. The climatic condition of the study region is essentially tropical. A total of 53 samples were collected before rainfall (summer monsoon) and after rainfall (winter monsoon) in the year 2016. The samples were collected in cleaned high-density polyethylene (HDPE) bottles capacity of one litre and stored at a temperature of 4°C in the laboratory. Each sample was labelled, latitude and longitude of the location has been recorded. The collected samples were transferred to the laboratory and analysed for physicochemical parameters of groundwater followed the American Public Health Association (APHA 2012) standards procedure. Calcium and magnesium were estimated using ethylenediaminetetraacetic acid (EDTA) solution by titration method. Carbonate and bicarbonate were determined using 0.1 M HCL and 0.1 M NaOH solution by titration method. Chloride and sulphate were determined using UV-VIS spectroscopy (LMSP UV1000B). The concentration of potassium and sodium were estimated using flame photometer (Model S-931). Fluoride concentration was calculated using an ion-selective electrode at 25°C followed by potentiometric analysis method. After completing the sample analysis in laboratory, an ionic balance error method was used to estimate the accuracy (acceptable limit ±10%) and avoid the manual error during the chemical analysis of water sample using the following formula;

$$\text{IBE} = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}} \times 100 \tag{1}$$

2.4. Nitrate and fluoride health risk model

Generally, continuous consumption of contaminated drinking water can lead to a serious health problem (waterborne disease) to human body over two different pathways such as oral (drinking water intake) and dermal (skin contact intake) pathway [30]. The completed evaluation techniques for human health risk were developed by the United States Environmental Protection Agency [24]. In the present research, the health risk evaluation model of oral and dermal pathways of human has been developed for nitrate and fluoride contamination of groundwater (Table S1). The research aimed to assess the health issues in different age group of people such as 1 to 6, 6 to 11, 12 to 19, 20 to 29, and 30 to 65 y and above 65 y. The oral and dermal hazards quotient value for each age group has been calculated using the following formulas:

$$\text{CDI} = \frac{C \times \text{IR} \times \text{ED} \times \text{EF}}{\text{ABW} \times \text{AET}} \tag{2}$$

$$\text{HQ}_{\text{oral}} = \frac{\text{CDI}}{RfD} \tag{3}$$

$$\text{DAD} = \frac{\text{TC} \times C \times \text{ED} \times \text{SSA} \times \text{CF} \times Ki \times \text{EV} \times \text{EF}}{\text{ABW} \times \text{AET}} \tag{4}$$

$$\text{HQ}_{\text{Dermal}} = \frac{\text{DAD}}{RfD} \tag{5}$$

$$\text{HI}_{\text{Total}} = \sum_{i=1}^{n} \left(\text{HQ}_{\text{Oral}} + \text{HQ}_{\text{Dermal}} \right) \tag{6}$$

2.5. Nitrate pollution index

The concentration of nitrate plays a vital role in quality and stable equilibrium of the groundwater. The index value defines the action of nitrate contamination in the groundwater and is named as nitrate pollution index (NPI). The value indicates the impact of man-made and anthropogenic activities on groundwater [31]. The following formula was used to compute the value of NPI is:

$$\text{NPI} = \frac{C_s - T_v}{T_v} \tag{7}$$

where C_s is the nitrate concentration in groundwater samples, T_v is a threshold value of nitrate due to anthropogenic activities (20 mg/L). The classification of groundwater based on NPI value ranges from less 0, 0–1, 1–2, 2–3 and greater than 3 were clean water, light pollution, moderate pollution, significant pollution and very significant pollution, respectively.

2.6. Fluoride pollution index

Fluoride pollution index (FPI) is a significant index value to assess the impact of elevated concentration of fluoride in groundwater. The primarily sources of fluoride in groundwater are ion exchange process, geogenic activities, depth of water, nature of aquifer, inadequate rainfall and increase in temperature [32]. The interaction between the rock and water, weathering of aquifer rocks, evaporite and carbonate dissolution are the major identified natural source of excess fluoride in groundwater [33]. The FPI value helps to identify the contamination level due to high dissolution of fluorite mineral in groundwater. The basic water quality parameters such as pH, calcium, sodium, bicarbonate and fluoride are important to calculate the value of FPI. The weightage has been assigned for each parameter and the average value of all parameter was calculated using the following formula:

$$\text{FPI} = \frac{W_f + W_{\text{HCO3}} + W_{\text{Na/Ca}} + W_{\text{pH}}}{N} \tag{8}$$

where W_f, W_{HCO3}, $W_{\text{Na/Ca}}$, W_{pH} – weight of fluoride, bicarbonate concentration, Na/Ca ratio, pH and N is total number of parameters (Table S2). FPI classification of groundwater were the value ranges from 1 to 2, 2 to 3 and 3 to 4 are low, medium and high pollution, respectively.

2.7. Statistical modelling of groundwater

2.7.1. Correlation

Correlation is a one of the significant statistical analysis methods to express the linear relationship between the two variables. It is a common method to describe the relationship if parameter without the statement of effects and cause of pollution in the study region. In general, four different types of correlation methods are Pearson correlation, Kendal rank, Spearman and point-biserial correlation [34–36]. In the present study Pearson correlation method was adopted to identify the linear relationship of the water quality parameter with significant value ($p < 0.05$). The result of the correlation is expressed in terms of the correlation coefficient (r) value of each parameter.

2.7.2. Principal component analysis

PCA is a one of the most effective methods to analyse the large number of groundwater sample data in the study region. It helps to reduce the dimensionality of large-scale data set of groundwater samples by changing a large data set of parameters into small data set and it contains more information about the larger set of data [37,38]. The four steps were followed to measure the PCA are, first step is standardize the dataset, step two is to calculate the covariance matrix for water quality parameter, third step is to calculate the eigenvalue and eigenvector for covariance matrix of groundwater parameter and final step is to sort the eigenvalues and corresponding eigenvector of each water quality parameters. The result of the PCA indicates that highly influenced and controlled parameters, most relevant parameter responsible for the highest variation in the stable equilibrium of groundwater samples.

2.7.3. Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is another method of analysis to identify the nature of groundwater samples in the study region. It is an investigative tool to design and to divulged the natural grouping within a water quality parameter. The results of the HCA shows that most useful information in tree diagram and it indicates that the similar groups as clusters [39,40]. In the present study, agglomerative method of HCA has been used to observer the data set and groups the cluster of groundwater parameters, groups of clusters are merged and display a tree diagram.

2.7.4. Automatic linear modelling

Automatic linear modelling (ALM) in groundwater quality assessment is the novelty of the present research. ALM described the automatic data preparation steps and built the suitable model for the data set. The model selection techniques are forward selection, backward selection and stepwise selection. The present study used the both forward and backward selection method to increase the accuracy of the prediction value [41,42]. The five steps were followed to calculate the ALM are; first step is preliminary data processing, step two is replacing the missing data values, third step is determining the quality predictor, fourth step is identifying outliers and final step is calculating stepwise model with coefficient (r^2) of determination [43].

2.8. Spatial analysis

GIS is an effective tool to analysis and represent the results of groundwater quality assessment, groundwater flow modelling, impact of disaster, flood, landslides and other related environmental issues (Kumar and Balamurugan [12,45]). In the present research, GIS was used to epitomize the contaminated zone in the study area. However, the study region is flat surface with very small undulation so inverse distance weighted (IDW) techniques were used for spatial analysis of groundwater quality parameters [44,45]. The weight of each cell is a function of inverse distance and assigned to all locations based on the distance between the sample locations. IDW is used to determine the cell value with a linear weighted combination of a data set of sample locations [46].

3. Results and discussion

3.1. Hydrochemical characteristics of groundwater

The descriptive statistical analysis of the groundwater samples was presented in the Table 1 and the compared the values with standards recommended by World Health Organisation [21]. The pH is the important parameter to identify the acidity and alkalinity of the water [47]. pH value varying from 7.10 to 8.7 had an average of 7.98 during summer and 7.10 to 8.8 with a mean of 8.16 during winter season (Fig. S1a). The results show that 7.54% (four sample locations) during the winter season exceed the maximum permissible limit recommended by [21]. Total dissolved solids (TDS) concentration shows that 18.68% and 39.62% of samples exceeded the acceptable limit during summer and winter, respectively. About 1.88% of the sample locations were unsuitable for drinking purpose during the winter season (Fig. S1b). Electrical conductivity (EC) varying from 264 to 3,572 μS/cm had a mean of 1,002.04 and 104 to 3,016 μS/cm with a mean of 664.25 μS/cm during summer and winter, respectively (Fig. S1c and Table S1). The higher concentration of total hardness (TH) recorded was 239 and 348 mg/L during both monsoons. About 7.54% and 11.32% of samples exceeded the acceptable level of TH in the study region (Fig. S1d). A total of 11.32% and 7.54% of samples exceeded the acceptable level of calcium recommended by [21] (Fig. S2a). About 24.52% and 33.96% of the sample in the investigation region exceed the recommended concentration of Mg^{2+} in groundwater. It shows that ion exchange process and inadequate rainfall and evaporation are the major source of contamination in the study zone (Fig. S2b) [48]. The elevated sodium concentration in groundwater recorded as 420 and 302 mg/L during summer and winter seasons. About 16.98% and 18.68% of the samples exceed the maximum permissible level as per [21] (Fig. S2c). The concentration of K^+ ion in groundwater shows that 86.79% and 84.91% of the samples were suitable for drinking purpose (WHO 2017) (Fig. S2d). Cl^- concentration ranged from 108 to 787 mg/L with a mean of 302.85 and 142 to 943 mg/L with a mean of 320.89 mg/L (Fig. S3a). The higher concentration of SO_4^{2-} observed in the study region are 490 and 380 mg/L during summer and winter season (Fig. S3b). The concentration of NO_3^- exceeded the maximum permissible limit in 39.62% and 47.17% of the sample locations in the investigation zone (Fig. S3c). It shows that anthropogenic activities are highly dominating the quality of groundwater. The higher concentration of F^- recorded in both monsoons are 2.63 and 3.78 mg/L in the northern and south west part of the study region (Fig. S3d). It shows that geogenic sources such as weathering and dissolution of fluoride mineral to groundwater

Table 1
Descriptive statistical analysis of groundwater quality parameter during summer and winter

Parameter	Summer			Winter			WHO	
	Min.	Max.	Avg.	Min.	Max.	Avg.	AL	DL
pH	7.10	8.70	7.98	7.10	8.80	8.16	6.5	8.50
TDS	135.00	926.00	376.77	108.00	2,444.00	452.04	500	1,500
EC	264.00	3,572.00	1,002.04	104.00	3,016.00	664.25	–	2,500
TH	108.00	239.00	247.42	63.00	348.00	272.34	100	500
Ca^{2+}	25.00	165.00	48.34	19.00	128.00	46.45	75	200
Mg^{2+}	12.00	74.00	42.50	11.51	85.90	62.06	50	150
Na^{+}	12.00	420.00	116.03	14.00	302.00	98.30	–	200
K^{+}	0.10	16.00	8.57	2.00	57.00	9.42	–	12
Cl^{-}	108.00	787.00	302.85	142.00	943.00	320.89	200	600
SO_4^{2-}	57.00	490.00	143.49	55.00	380.00	137.87	200	400
HCO_3^-	79.35	804.80	270.21	73.24	794.40	264.04	–	–
NO_3^-	12.05	64.00	44.60	16.00	74.00	46.51	–	45
F^-	0.22	2.63	0.79	0.20	2.78	0.83	–	1.50

Min. – Minimum; Max. – Maximum; Avg. – Average; AL – Acceptable limit; DL – Desirable limit

are the major reason for a higher concentration of fluoride in the study region [49,50].

3.2. Piper diagram

Piper trilinear diagram [51] is significant diagram to represent the chemical composition of groundwater. In the present study, the diagram shows that a major part of groundwater samples was fall in the Ca–Mg–Cl type (45.28% and 58.49% of sample location during summer and winter). Also 28.30% and 15.09% of the sample locations are belongs to the Na–Cl type, 22.64% and 24.52% of the sample locations are Ca–Cl type of groundwater in the study area during summer and winter season. The rest of the sample locations (2 samples in summer and 1 in winter) are Ca–Na–HCO_3 type of water in the study region (Fig. 3). The result of Piper diagram reveals that rock water interaction, weathering of parent rock and ion exchange process are highly dominating the nature of groundwater in the study region. The increase in composition of chloride also indicates that anthropogenic activities also influenced the groundwater chemistry in the investigation zone.

3.3. Nitrate pollution index

In the present study, a total of 21 and 25 samples exceeded the maximum permissible limit of NO_3^- concentration in the study region (Fig. 4). NPI classification of groundwater in the study region are 3.77% of sample are clean in both season, 28.30% and 32.08% of samples are light pollution, 58.49% and 50.94% of samples were moderate pollution, 9.43% and 13.21% of samples were significant pollution due to excess concentration nitrate in groundwater during summer and winter, respectively (Table 2). The spatial analysis revealed that 2.02 km^2 of area were clean during both monsoon, 86.46 and 79.11 km^2 of area were light pollution, 960.46 and 954.62 km^2 of area were moderate pollution, 8.18 and 22.33 km^2 of area were

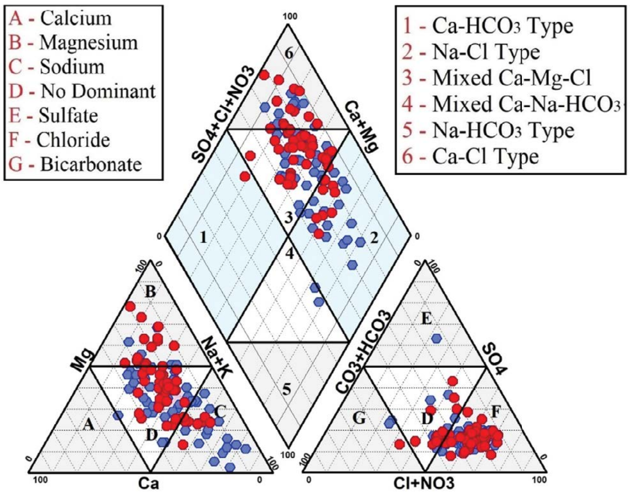

Fig. 3. Piper trilinear diagram of groundwater during summer and winter.

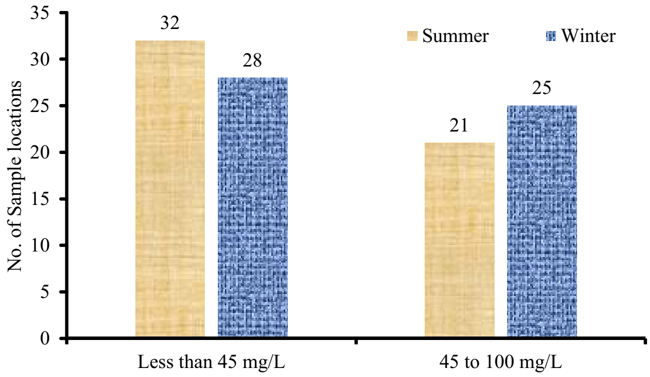

Fig. 4. Group of groundwater sample based on NO_3^- concentration.

significant pollution during summer and winter, respectively (Fig. 5a and b). The results indicates that northern part, southeast zone and few locations in southern region are clean and light pollution. The NPI value of groundwater revealed that anthropogenic activities such as usage of synthetic manure for agriculture purpose, modern agricultural trends, disposal municipal waste in open land, leachates from the dumping yards are the primary source of nitrate in the entire investigation zone [15,52,53].

3.4. Fluoride pollution index

The elevated fluoride concentration in groundwater causes serious health issues such as teeth diseases, Skelton and bone problem on human body [54]. The FPI classification revealed that 84.9% and 67.93% of the samples were low and medium pollution during summer and winter, respectively (Table 3). The spatial analysis results show that 91.41 and 68.54 km^2 of area were low pollution, 932.68 and 984.54 km^2 of area were medium pollution and 33.04 and 4.05 km^2 of area were high pollution during summer and winter in the study area (Fig. 6). It also revealed that northern and southeast zone are highly contaminated during summer period. The results indicates that dissolution of fluoride bearing mineral such as granite biotite and grey biotite gneiss are the major source of excess fluoride in groundwater and that identified in some part of the study region [16].

3.5. Human health risk model

The novelty of the present study is to evaluate the non-carcinogenic risk impact on different age groups of people such as 1 to 5 y, 6 to 12 y, 13 to 19 y, 20 to 29 y, 30 to 65 y and above 65 y. The human health risk model (HHRM) comprised the main exposure of two pathway are dermal

Table 2
NPI classification of groundwater samples

NPI value	Contamination type	Summer		Winter	
		No. of samples	% of samples	No. of samples	% of samples
<0	Clean	2	3.77	2	3.77
0 to 1	Light pollution	15	28.30	17	32.08
1 to 2	Moderate pollution	31	58.49	27	50.94
2 to 3	Significant pollution	5	9.43	7	13.21
>3	Very significant pollution	0	0.00	0	0.00

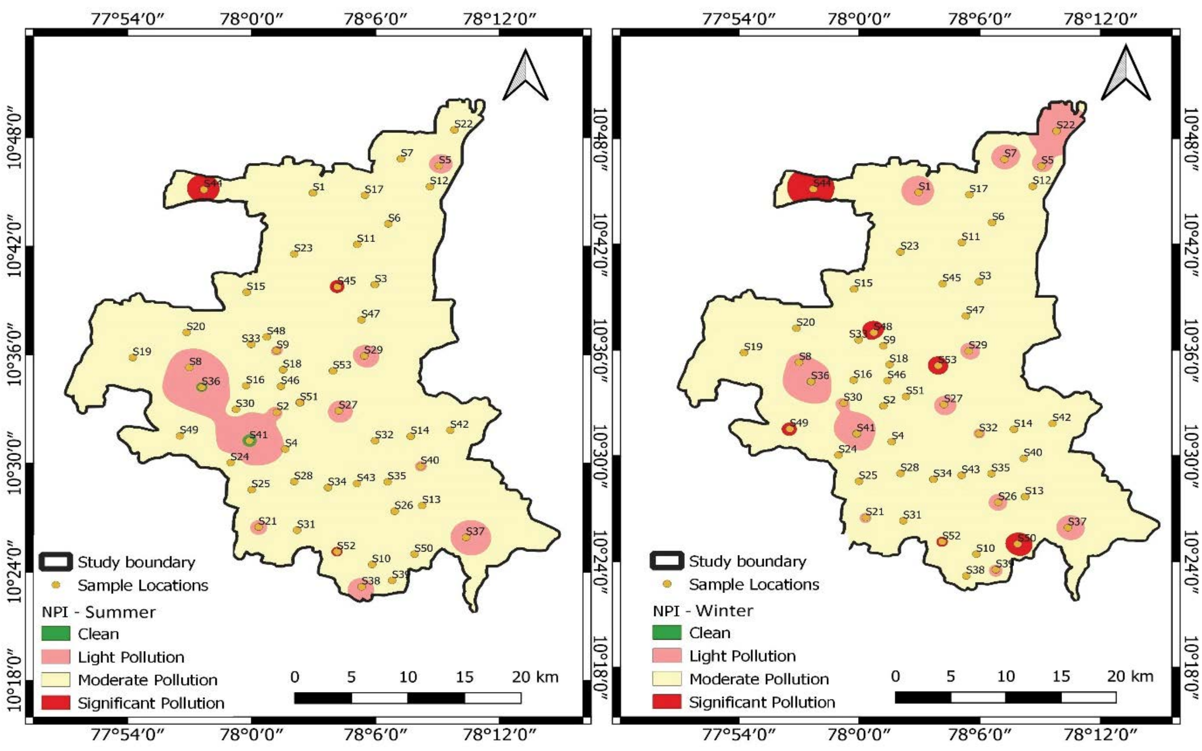

Fig. 5. Spatial analysis of nitrate pollution index of groundwater sample in study region during (a) summer and (b) winter.

Table 3
Classification of groundwater based on FPI value

FPI range	Water class	Summer		Winter	
		No of samples	% of samples	No of samples	% of samples
1 to 2	Low pollution	9	16.98	10	18.87
2 to 3	Medium pollution	36	67.92	26	49.06
3 to 4	High pollution	8	15.09	17	32.08

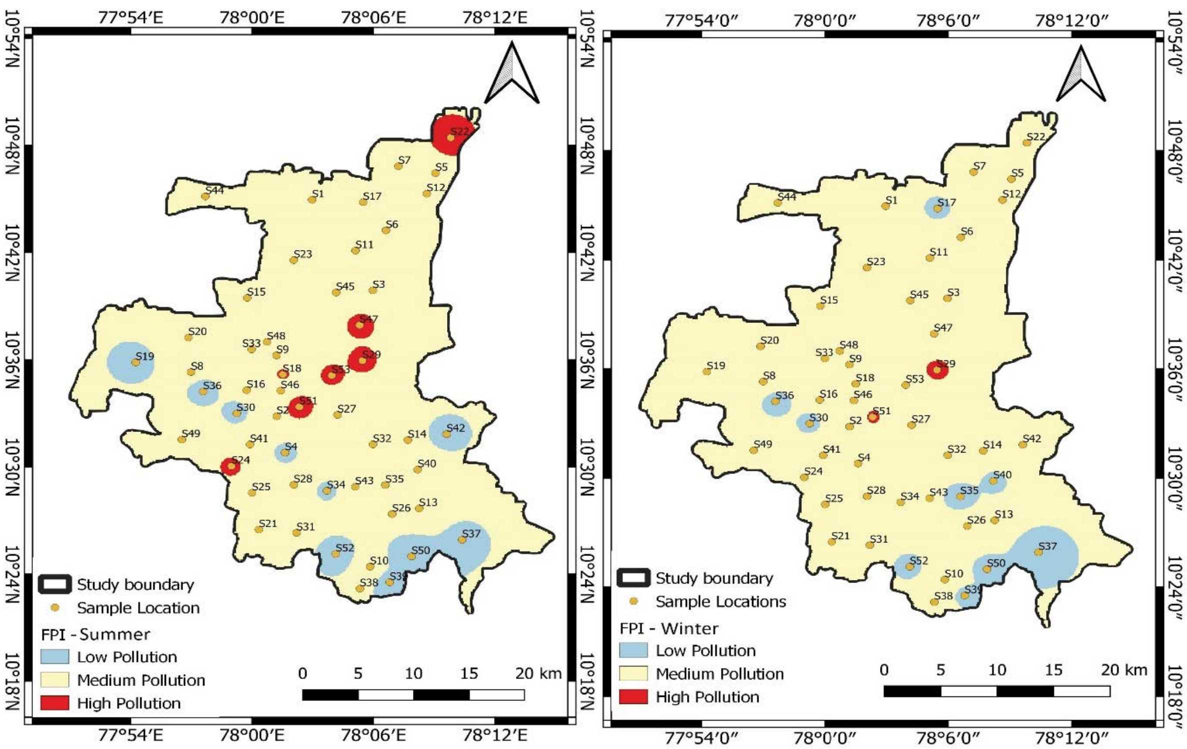

Fig. 6. Spatial analysis of fluoride pollution index of groundwater sample in study region during (a) summer and (b) winter.

Table 4
Total hazards question value for nitrate concentration of groundwater in study region

Age group	Summer			Winter		
	Min.	Max.	Avg.	Min.	Max.	Avg.
1 to 5	8.30E-01	4.41E+00	3.07E+00	1.10E+00	5.09E+00	3.20E+00
6 to 12	3.41E-01	1.81E+00	1.26E+00	4.52E-01	2.09E+00	1.32E+00
13 to 19	2.54E-01	1.35E+00	9.40E-01	3.37E-01	1.56E+00	9.81E-01
20 to 29	2.62E-01	1.39E+00	9.70E-01	3.48E-01	1.61E+00	1.01E+00
30 to 65	2.82E-01	1.50E+00	1.04E+00	3.75E-01	1.73E+00	1.09E+00
Above 65	2.58E-01	1.37E+00	9.56E-01	3.43E-01	1.59E+00	9.97E-01

and oral consumption of groundwater in the study area. The HQtotal of nitrate contamination results shows that 98.11% and 100% of the sample locations were fall under the risk category for 1 to 5 age group of people, 88.68% and 90.57% of the sample locations were exceed the safer limit for 6 to 12 y age group of people, 37.74% and 43.40% of the sample locations were risk for 13 to 19 y age group of people, 39.62% and 47.17% of the sample locations were risk for 20 to 29 y age group of people, 50.94% and 54.72% of the sample locations were not safe for 30 to 65 y age group of people, 39.62% and 45.28% of the sample locations were risk for above 65 y age group of people during summer and winter, respectively (Table 4). The results imply that groundwater sample were more contaminated during winter than summer monsoon season. The spatial analysis of the HHRM results revealed that roughly 4.5% of the sample locations were more contaminated in winter compared with the summer season in the study region (Table 5). The non-carcinogenic risk assessment of nitrate contamination level of all the exposed age groups of peoples varied in the order of 1 to 5 y > 6 to 12 y > above 65 y > 30 to 65 y > 20 to 29 y > 13 to 19 y. This indicates that below 12 y and above 65 y peoples in the investigation zone are highly potentially exposed to non-carcinogenic risk than another group of people. It also shows that lower body weight and less immunity level of people were easily affect at greater level of health risk issues due to nitrate contamination (Adimalla et al. [2]). The HQtotal of fluoride contamination divulged that 67.92% and 69.81% of the sample locations were risk for 1–5 y of age group during summer and winter. The rest of the age group values shows that 4 sample locations were contaminated during both seasons (Table S3). The order of people affected due to fluoride contamination is the same like the nitrate contamination and lower immunity power people were easily exposed to non-carcinogenic health issues. The results of HHRM for nitrate and fluoride imply that the reason for non-carcinogenic health risk on human body is excess nitrate concentration in the study area [55–57].

3.6. Statistical analysis

3.6.1. Correlation

The correlation coefficient of each parameter in both seasons were calculated for 13 water quality parameters (Tables S4 and S5). The correlation results of summer implying that EC has positively correlated with Ca^{2+} (r = 0.65), Na^{+} (r = 0.51) and SO_4^{2-} (r = 0.83). TH has strong positive correlation with Mg^{2+} (r = 0.81), Cl^{-} (r = 0.52) and

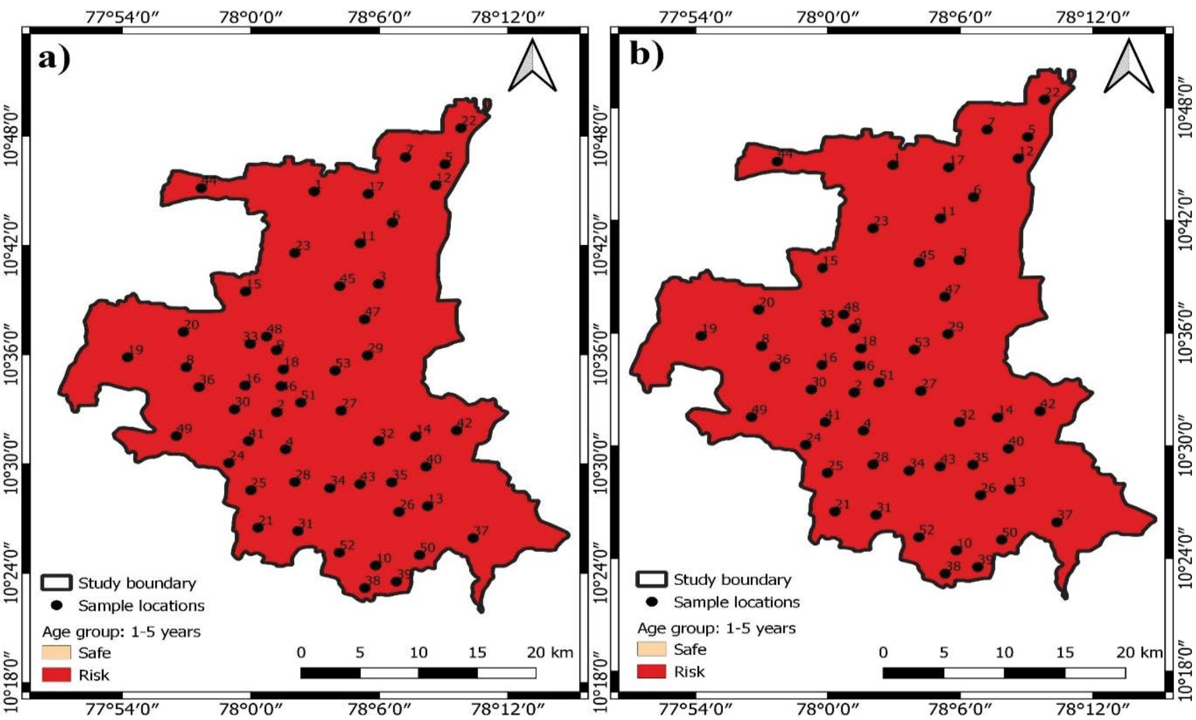

Fig. 7. Spatial analysis of nitrate human health risk model for an age group of 1 to 5 y during (a) summer and (b) winter.

Table 5
Spatial analysis of HHRM for nitrate contamination in study area

Age group (in years)	Summer (area in km²)		Winter (area in km²)		Cite
	Safe	Risk	Safe	Risk	
1 to 5	0.31	1056.83	0	1057.14	Fig. 7a and b
6 to 12	22.74	1034.40	14.02	1043.12	Fig. 8a and b
13 to 19	868.62	188.52	650.61	406.53	Fig. 9a and b
20 to 29	711.05	346.10	500.60	556.54	Fig. 10a and b
30 to 65	279.44	777.70	178.02	879.12	Fig. 11a and b
Above 65	802.25	254.89	574.35	482.79	Fig. 12a and b

HCO_3^- (r = 0.53). This reveals that the chemical composition of groundwater is highly influenced by the process of ion exchange and weathering of parent rocks [58]. Ca^{2+} has positively correlation with Na^+ (r = 0.66) and SO_4^{2-} (r = 0.79). It proved that chemical composition of Ca^{2+}–SO_4^{2-} type of water in the study. Na has positive correlation with SO_4^{2-} (r = 0.56) and HCO_3^- (r = 0.51). It reveals that salinity and influence of waste disposal into open land and leachates from the dumping yards are the factor primarily controlled the quality of groundwater in the study region (Zhang et al. 2018). The correlation analysis of winter shows that EC has positive correlation with TH (r = 0.51) and SO_4^{2-} (r = 0.56), TH has positively correlation with Cl^- (r = 0.52) and negatively correlate with F^- (r = –0.05). It shows that weathering of rocks and ion exchange process are dominating the quality of water. SO_4^{2-} has positively correlation with Ca^{2+} (r = 0.68), Mg^{2+} (r = 0.60), K^+ (r = 0.53) and Cl^- (r = 0.54). It indicates that anthropogenic influence such as waste disposal from household, small scale industries disposal, uncovered usages of septic tank, usage of nitrogen and phosphate-rich synthetic fertilizers such as diammonium phosphate and monoammonium phosphate [59,60].

3.6.2. Principal component analysis

The principal component analysis of groundwater parameter of both seasons was presented in table. The eigenvalue (greater than 1) was computed as 4.269 to 1.192 during summer and 4.260 to 1.490 winter, respectively (Fig. S4). PCA1 is in control of 32.83% of the variance with high loading factors for EC, TH, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-} and HCO_3^-. The high loading factor PC2, PC3 and PC4 components has 16.97%, 10.45% and 9.16% of variance, respectively (Table 6). The results shows that TH, Mg^{2+}, NO_3^-, F^- ion are high loading factors and represents that anthropogenic contamination during the summer period. The variance of each component (4 component) shows that 32.77%, 14.86%, 12.05% and 11.46% during the winter period, respectively (Table 6). The results of winter divulged that EC, TH, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-} and HCO_3^- has high loading factors in the first component (PCA1). Nitrate has high loading factor in PCA4 and indicates that man-made source of groundwater in the study region (Fig. S5). The results of PCA analysis implies that natural source of contamination such as weathering of parent rocks, dissolution of minerals such as calcium, magnesium, sodium, bicarbonate from the aquifers and ion exchange process (Kumar et al.). The high loading factor for nitrate and sulphate indicates that anthropogenic activities such as usage of fertilizers, disposal of waste and open discharge of wastewater from the household are the primary factor influenced the chemical composition of groundwater [61–63].

3.6.3. Hierarchical cluster analysis

HCA were performed for groundwater samples in the study region and the cluster results represented in dendrogram diagram (Fig. 13). It implies that classification of chemical composition of groundwater were five separate cluster namely group I to V (Table 7). Cluster 1 comprise of 56.6% and 52.83% cluster II comprise of 7.5% and 9.43%, cluster III comprise of 9.43% and 20.75%, cluster IV comprise of 9.43% and 9.43%, cluster V comprise of 16.98% and 7.5% of sample locations during summer and winter

Table 6
Factor loading of variable using varimax rotation

Parameter	Summer				Winter			
	Component				Component			
	1	2	3	4	1	2	3	4
pH	–0.101	**0.526**	0.34	–0.166	–0.238	**0.796**	0.074	0.329
TDS	0.356	0.334	0.458	0.469	–0.112	0.178	–0.152	**0.778**
EC	**0.827**	–0.299	0.121	0.115	**0.637**	0.411	–0.442	0.127
TH	**0.652**	**0.503**	–0.267	–0.329	**0.704**	–0.275	0.004	–0.030
Ca^{2+}	**0.618**	–0.643	–0.108	0.001	**0.661**	–0.391	0.019	–0.012
Mg^{2+}	**0.521**	**0.528**	–0.415	–0.314	**0.773**	–0.033	0.321	–0.041
Na^+	**0.825**	–0.12	0.205	0.094	**0.617**	0.274	–0.346	0.318
K^+	0.266	0.269	–0.431	0.317	**0.526**	0.418	–0.270	–0.336
Cl^-	**0.627**	0.22	–0.323	0.071	**0.658**	–0.239	0.178	0.225
SO_4^{2-}	**0.73**	–0.589	–0.013	–0.012	**0.886**	–0.088	–0.156	–0.022
HCO_3^-	**0.747**	0.212	0.235	–0.068	**0.609**	0.388	**0.535**	0.003
NO_3^-	–0.012	0.33	–0.228	**0.771**	0.015	–0.408	0.396	**0.679**
F^-	0.366	0.384	**0.569**	–0.103	0.085	0.486	**0.740**	–0.178
% of variance	32.835	16.972	10.451	9.167	32.770	14.864	12.051	11.460
Cumulative %	32.835	49.807	60.258	69.424	32.770	47.634	59.684	71.145

Extraction method: principal component analysis
Rotation method: varimax with Kaiser normalization
Kaiser–Meyer–Olkin measure of sampling adequacy: 0.702 and 0.64 during summer and winter

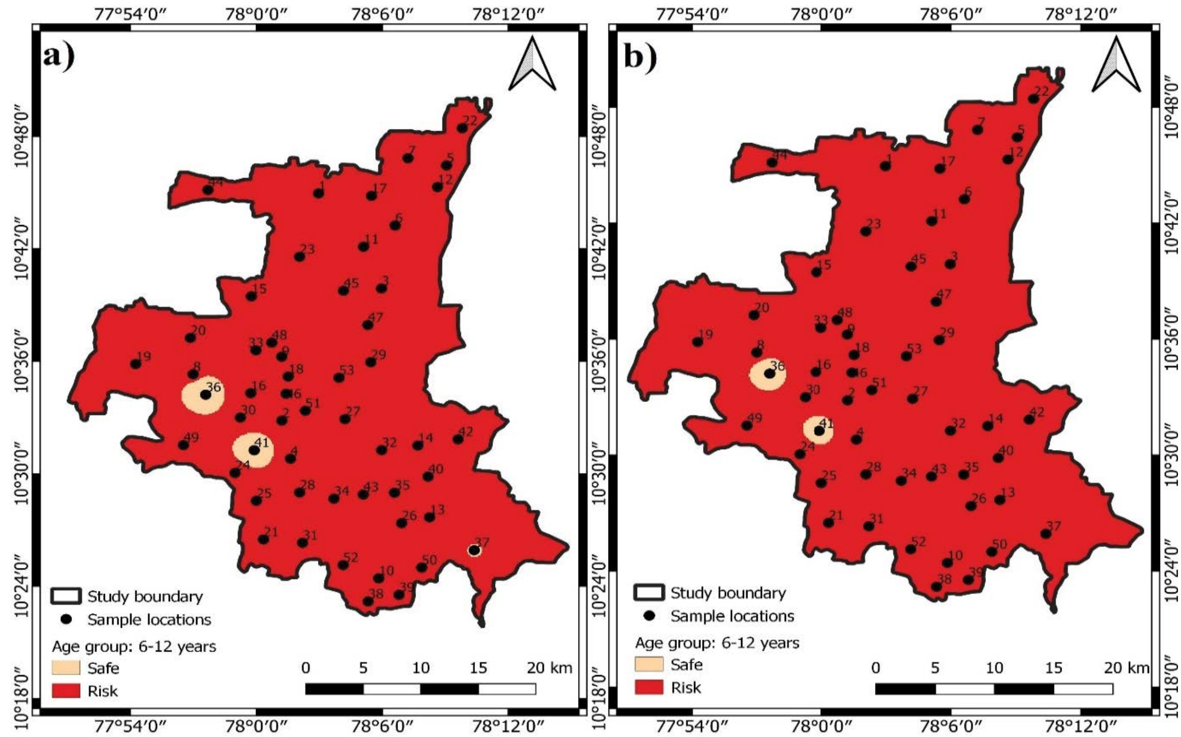

Fig. 8. Spatial analysis of nitrate human health risk model for an age group of 6 to 12 y during (a) summer and (b) winter.

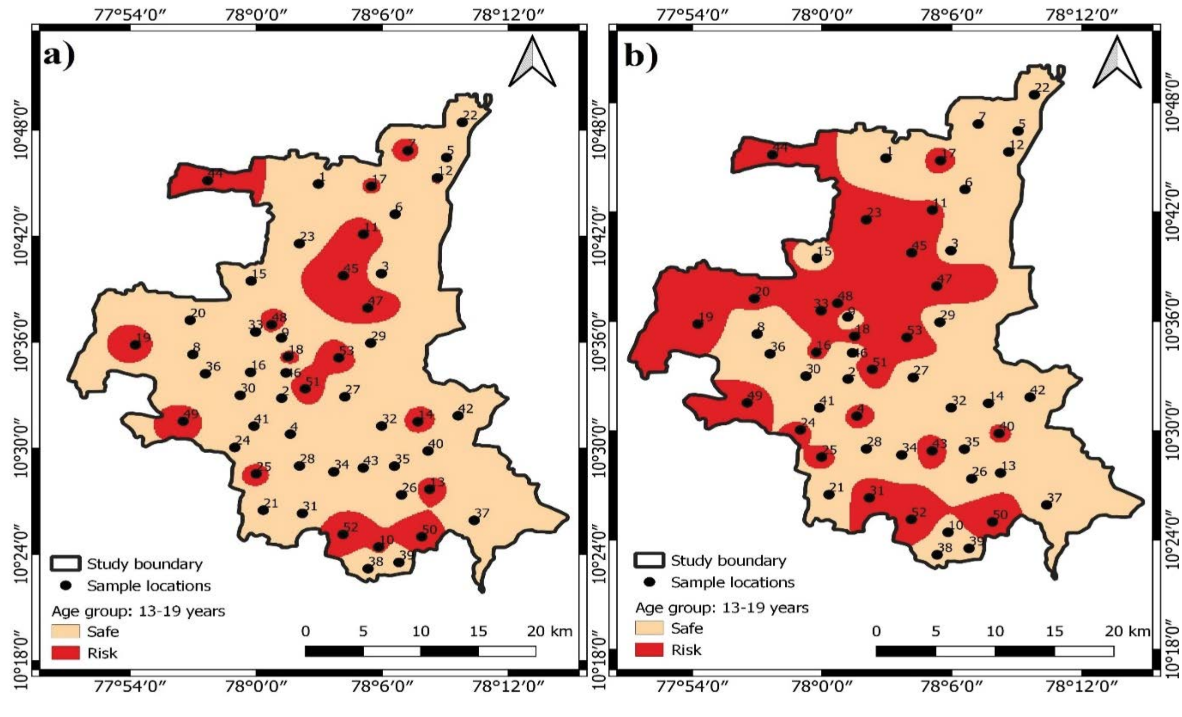

Fig. 9. Spatial analysis of nitrate human health risk model for an age group of 13 to 19 y during (a) summer and (b) winter.

season. The results divulged that a higher percentage of the samples were the same chemical composition with unique geological properties (Quartz vein and Champion gneiss groups). HCA of groundwater parameters were computed and presented in Table S6 and Fig. S6. The parameter classification was pH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, NO_3^{-} and F^{-} were the cluster I, TDS, TH, HCO_3^{-} and Cl^{-} were the cluster II and EC in cluster III during both monsoon seasons. It indicating

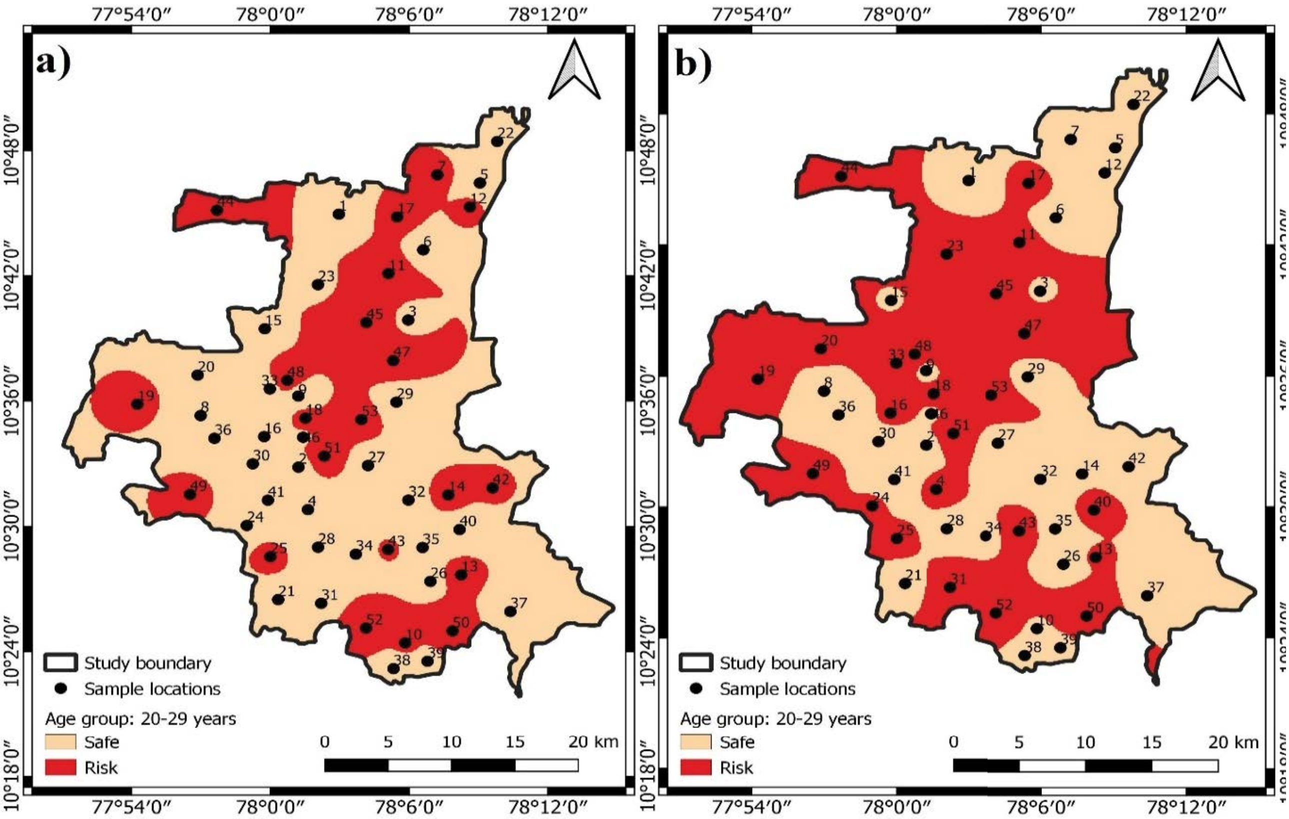

Fig. 10. Spatial analysis of nitrate human health risk model for an age group of 20 to 29 y during (a) summer and (b) winter.

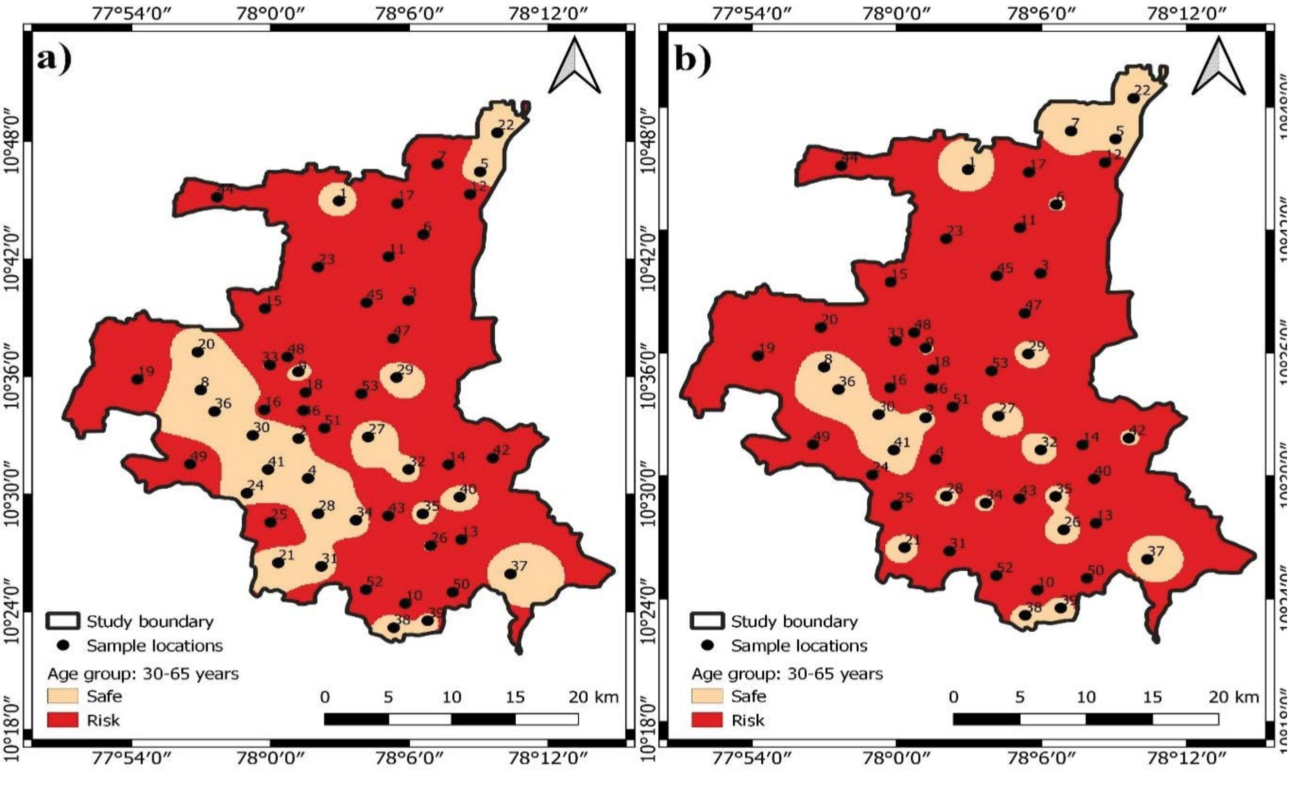

Fig. 11. Spatial analysis of nitrate human health risk model for an age group of 30 to 65 y during (a) summer and (b) winter.

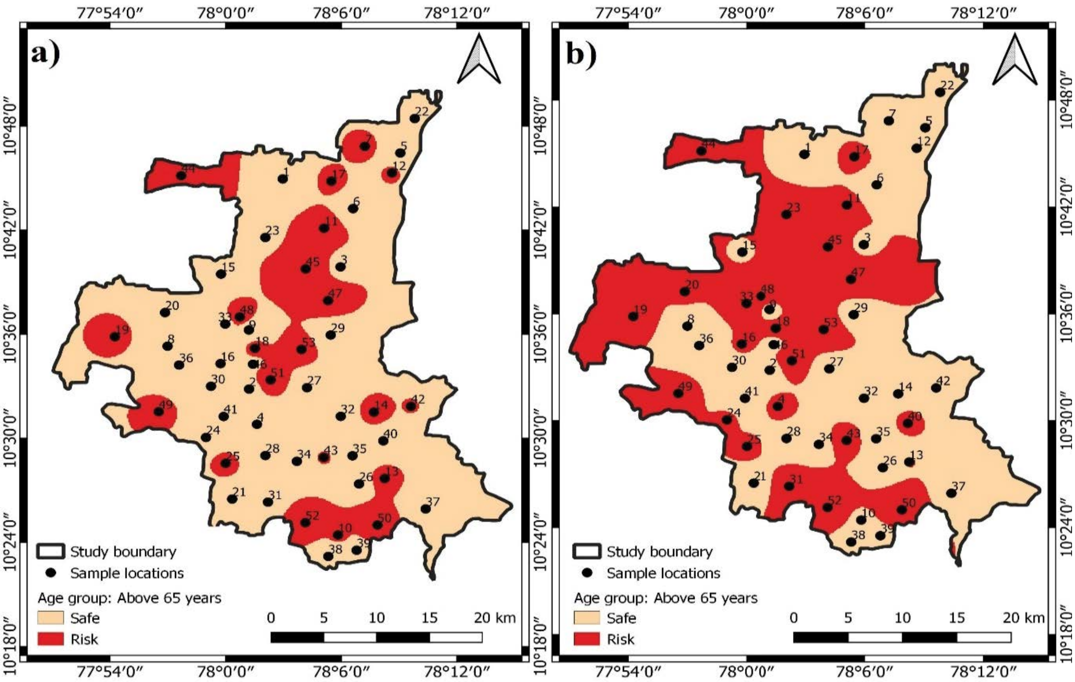

Fig. 12. Spatial analysis of nitrate human health risk model for an age group of above 65 y during (a) summer and (b) winter.

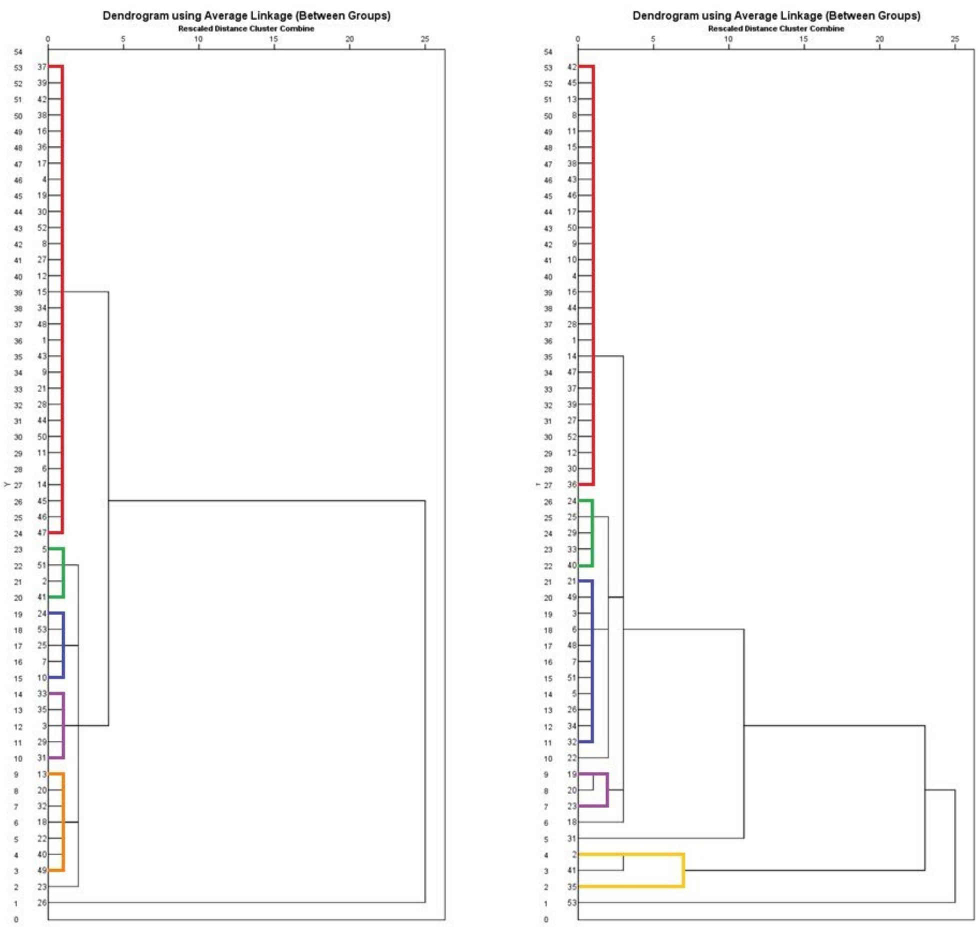

Fig. 13. Dendrogram of groundwater sample locations in study area during both monsoon.

Table 7
Sample location classification based on HCA during both seasons

Group	Summer		Winter	
	No. of samples	% of samples	No. of samples	% of samples
I	30	56.60	28	52.83
II	4	7.5	5	9.43
III	5	9.43	11	20.75
IV	5	9.43	5	9.43
V	9	16.98	4	7.5

that anthropogenic activities are highly dominated the quality of groundwater and geogenic activities such as weathering, rock water interaction, ion exchange process and dissolution of mineral in parent rock are also affect the groundwater quality [64,65].

3.6.4. Automatic linear modelling of water quality index

The novelty of the present study is to assess the quality of groundwater based on the automatic linear modelling method (ALM) and also ALM of water quality index were performed for both monsoon season in the study area. A total of 12 water quality parameters were used to predict the water quality index using ALM method. The accuracy of the model shows that 100% during the both monsoon season (Fig. S7). The significance value (p) of less than 0.05 has been maintained to evaluate the importance of each parameter on water quality index (WQI) of groundwater samples. The detailed importance of each parameter during each monsoon is tabulated in Table 8. It shows that high and low influenced parameter as HCO_3^- (k = 0.261) and lower EC (k = 0) during the summer season. TDS (k = 0.278), TH

Table 8
Importance of each parameter on groundwater quality during summer and winter

Parameters	k	%	k	%
pH	0.0000	0.00	0.005	0.50
TDS	**0.1950**	**19.50**	**0.278**	**27.80**
EC	0.0000	0.00	0.002	0.20
TH	0.0220	2.20	**0.167**	**16.70**
Ca^{2+}	0.0040	0.40	0.001	0.10
Mg^{2+}	**0.1570**	**15.70**	0.008	0.80
Na^+	0.0060	0.60	0.001	0.10
K^+	0.0070	0.70	0.016	1.60
Cl^-	**0.1560**	**15.60**	0.073	7.30
SO_4^{2-}	0.0280	2.80	0.073	7.30
HCO_3^-	**0.2610**	**26.10**	**0.251**	**25.10**
NO_3^-	0.0840	8.40	0.059	5.90
F^-	0.0800	8.00	0.066	6.60
Cumulative importance	1.00	100.00	1.00	100.00

Bold values are high influenced parameter on water quality

(k = 0.167) and HCO_3^- (k = 0.251) are high influenced parameter and Na^+ (k = 0.001) and Ca^{2+} (k = 0.001) are low influenced parameter during the winter season (Fig. 14). The results of the ALM of WQI divulged those anthropogenic activities such as waste disposal, leachate from the municipal yards, uncovered septic tank and usage of excess quantity of synthetic fertilizers are the major threats to groundwater quality in the investigation zone.

3.6.5. Source of nitrate and fluoride in study area

The present research found that excess concentration of nitrate and fluoride plays a vital role in groundwater

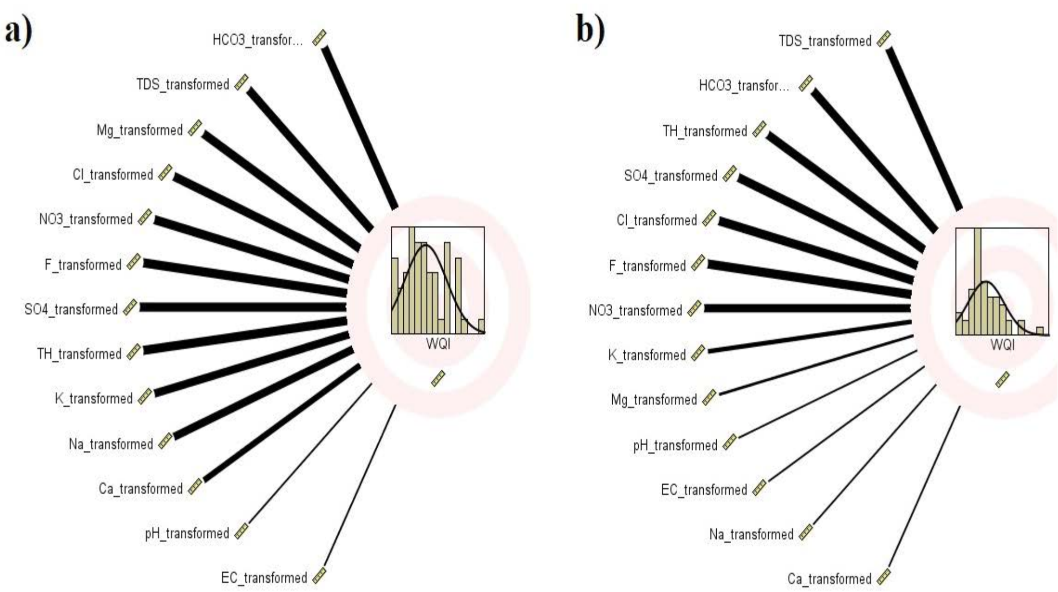

Fig. 14. Effects of each parameter on WQI prediction during (a) summer and (b) winter.

quality in the study region. The source of nitrate contamination has been observed during the preliminary survey and sample collection in the investigation area. The high agriculture activities were found throughout the study region, and it was high in the eastern part of the study region. In some place, municipal waste is disposed in the open land, and also waste dumping yards are also found in the southern part of the study region. The south east part of the study region was rich in urban activities such as schools, government buildings, and residential areas. The untreated waste disposal from the municipal and residential zone was dumped into specific location are found in the study region (Fig. S8). It was concluded that these are the major source of nitrate and sulphate in groundwater [66,67]. The excess fluoride concentration was found in the south west and western zone of the study region and the locations were covered by garnet biotite gneiss and dark biotite gneiss mineral rock (rich in fluorite mineral). The dissolution of mineral is high during the rainy season and it reach the water table in winter period. The results also evident that a higher percentage of samples were affected due to excess concentration of fluoride during the winter season [16].

4. Recommendations

In order to reduce the anthropogenic activities in the study region, the research outcomes recommended that to reduce the usage of high synthetic fertilizers, pesticides in the agriculture field, follow traditional agricultural activities to achieve the high yield of crops, construct the covered septic tank to avoid the infiltration of wastewater, training program for disposal of waste generated from the household and commercial zone, periodic investigation of underground pipelines are the greater remedial measure to avoid the groundwater contamination in the study region.

5. Conclusions

The detailed assessment of groundwater quality for human health risk and factor affecting suitability for domestic purpose has been carried. The study concluded that, hydro geochemistry revealed that simultaneous geogenic and anthropogenic activities are play a vital role in the chemical composition of groundwater.

- The piper classification of groundwater in both seasons revealed that Ca–Mg–Cl type of water in higher percentage of study region. NPI value divulged that 67.92% and 64.15% of water samples were highly contaminated due to excess nitrate concentration in groundwater. FPI result indicates that 965.68 and 988.59 km^2 of area were fall under the medium to high pollution level in the study region.
- HHRM results concluded that below 12 y and above 65 y peoples in the investigation zone are highly potentially exposed to non-carcinogenic risk than another group of people.
- The PCA and HCA analysis results imply that natural sources of contamination such as weathering of parent rocks, dissolution of minerals such as calcium, magnesium, sodium, bicarbonate from the aquifers, and ion exchange process.
- The ALM analysis of WQI revealed those anthropogenic activities such as waste disposal, leachate from the municipal yards, uncovered septic tank and usage of excess quantity of synthetic fertilizers are the major threats to groundwater quality in the investigation zone.

This research highlights that source of contamination were anthropogenic activities influenced in northern, north–east, some part of south region and geogenic sources dominated in southern and southwest part of the study region. Therefore, the findings and recommendations of the present research are more helpful in implementing the remedial measure by the municipal water supply board, water management authority and non-governmental agency.

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Supplementary information

Table S1
Standard value for oral and dermal pathway of different age group people

Parameters	1–5 y	6–12 y	13–19 y	20–29 y	30–65 y	>65 y
	Ingestion pathway					
Ingestion rate (IR in L/d)	1	1.32	1.82	2.34	2.94	2.73
Exposure frequency (EF in d/y)	365	365	365	365	365	365
Exposure duration (ED in y)	6	6	6	30	30	30
Average body weight (BW in kg)	9.1	29.3	54.2	67.6	78.8	80
Average exposure time (AT in d)	2,190	2,190	2,190	10,950	10,950	10,950
	Dermal pathway					
Skin surface area (SSA in cm^2)	4,500	10,500	15,700	19,550	19,800	19,400
Contact time (CT in h/event)	0.54	0.54	0.54	0.71	0.71	0.71
Exposure frequency (EF in d/y)	350	350	350	350	350	350
Exposure duration (ED in y)	6	6	6	30	30	30
Conversion factor (CF in L/cm^3)	0.001	0.001	0.001	0.001	0.001	0.001
Average body weight (BW in kg)	9.1	29.3	54.2	67.6	78.8	80
Average exposure time (AT in d)	2,190	2,190	2,190	10,950	10,950	10,950
Dermal adsorption factor (K_i in cm/h)	0.001	0.001	0.001	0.001	0.001	0.001

Table S2
Weightage of each water quality parameters

Parameter	Concentration (mg/L)	Weight
F^-	Less than 0.6	1
	0.6–1.2	2
	1.2–1.5	3
	Greater than 1.5	4
HCO_3^-	Less than 100	1
	100–200	2
	200–300	3
	Greater than 300	4
Na^+/Ca^{2+}	Less than 1	1
	1–2	2
	2–3	3
	Greater than 3	4
pH	Less than 6.5	1
	6.5–7.5	2
	7.5–8.5	3
	Greater than 8.5	4

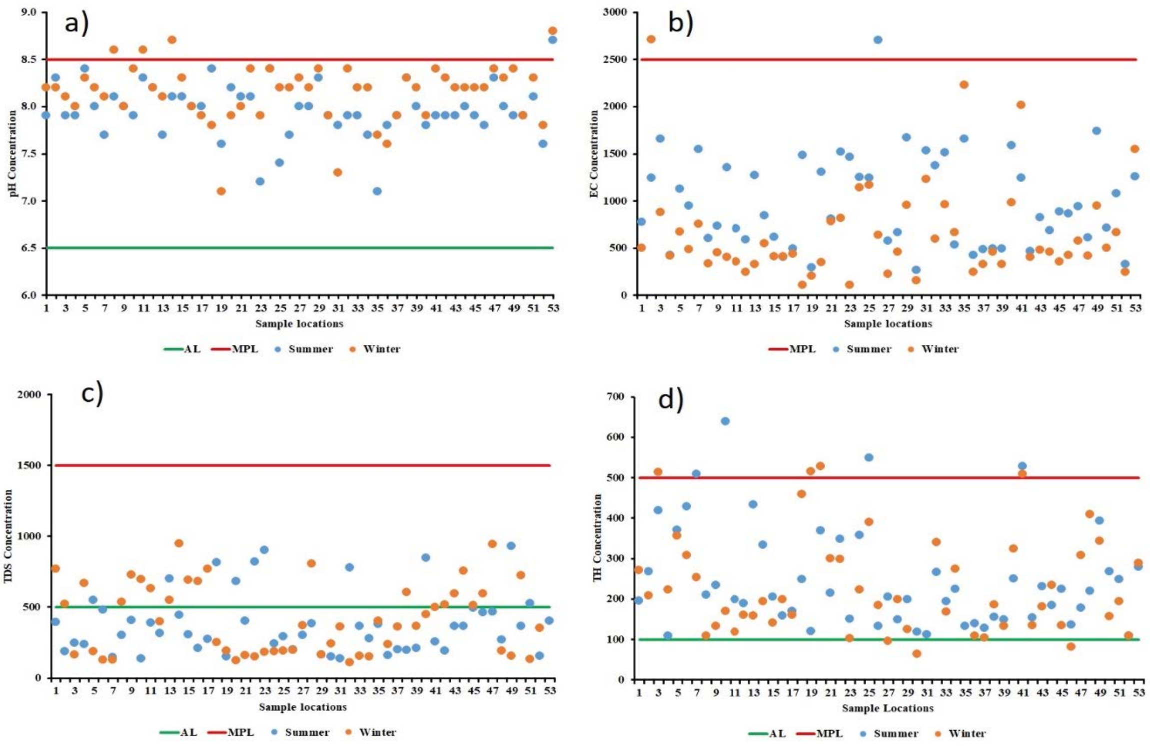

Fig. S1. Variation in concentration of groundwater parameters (a) pH, (b) EC in μS/cm, (c) TDS in mg/L and (d) TH in mg/L.

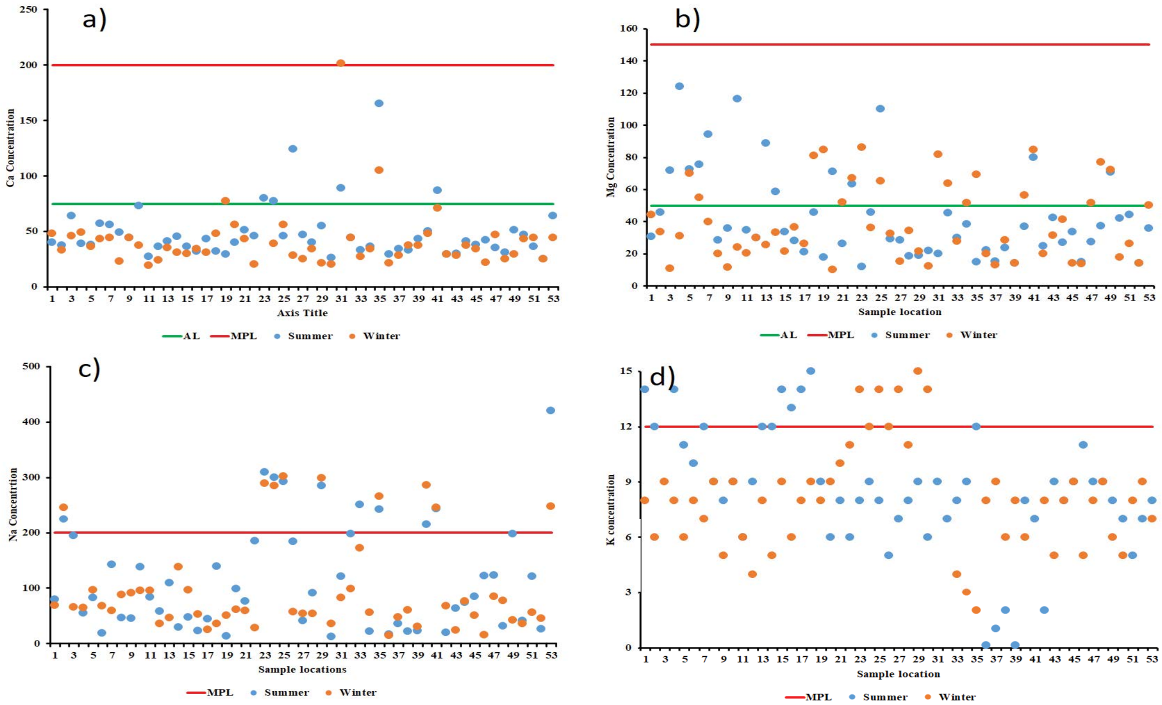

Fig. S2. Variation in concentration (mg/L)of groundwater parameters (a) Ca, (b) Mg, (c) Na and (d) K.

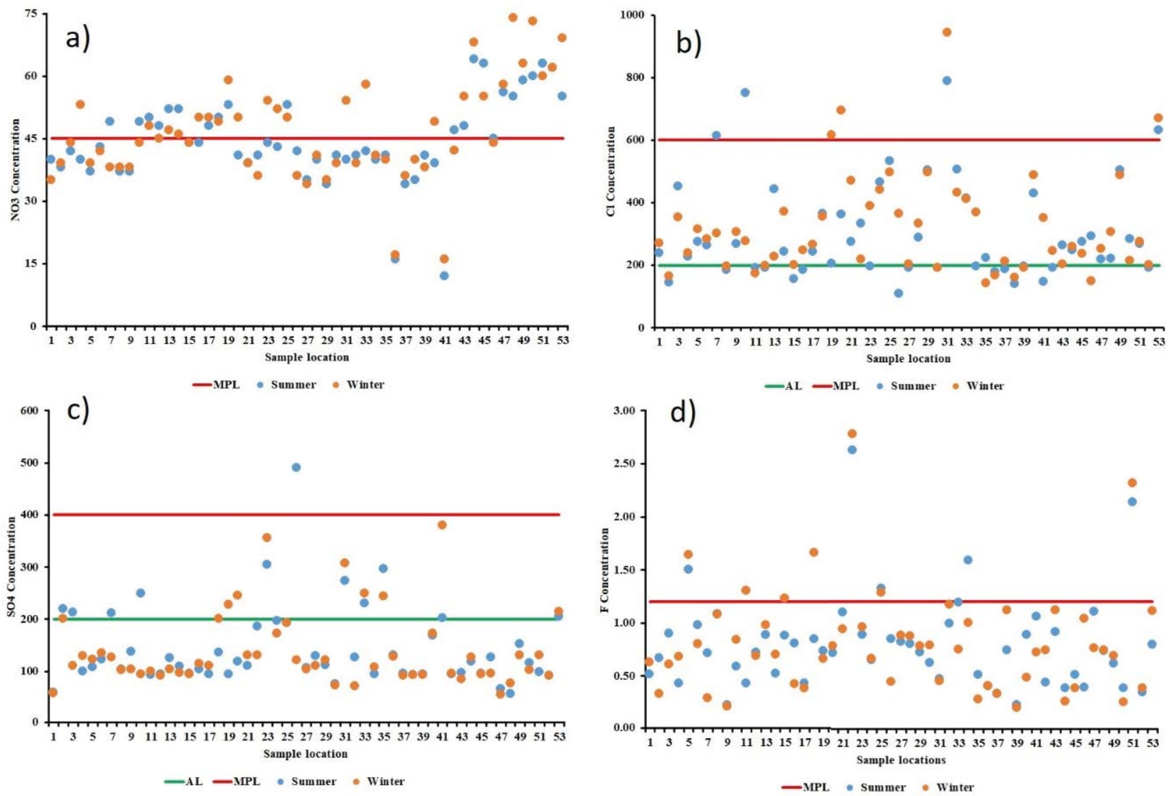

Fig. S3. Variation in concentration (mg/L) of groundwater parameters (a) NO_3^-, (b) Cl^-, (c) SO_4^{2-} and (d) Cl^-.

Table S3
Total hazards question value for fluoride concentration of groundwater in study region

Age group	Summer			Winter		
	Min.	Max.	Avg.	Min.	Max.	Avg.
1 to 5	4.09E-01	4.82E+00	1.46E+00	3.67E-01	6.94E+00	1.52E+00
6 to 12	1.68E-01	1.98E+00	5.98E-01	1.51E-01	2.85E+00	6.26E-01
13 to 19	1.25E-01	1.48E+00	4.46E-01	1.12E-01	2.12E+00	4.66E-01
20 to 29	1.29E-01	1.52E+00	4.61E-01	1.16E-01	2.19E+00	4.81E-01
30 to 65	1.39E-01	1.64E+00	4.96E-01	1.25E-01	2.36E+00	5.18E-01
Above 65	1.27E-01	1.50E+00	4.54E-01	1.14E-01	2.16E+00	4.74E-01

Table S4
Correlation analysis of groundwater quality parameters during summer in study area

Parameter	pH	TDS	EC	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	F^-
pH	1.00												
TDS	0.07	1.00											
EC	–0.10	0.30	1.00										
TH	0.09	0.18	0.33	1.00									
Ca^{2+}	–0.37	–0.01	0.65	0.13	1.00								
Mg^{2+}	0.03	0.13	0.23	0.81	0.04	1.00							
Na^+	–0.18	0.06	0.51	0.33	0.66	0.18	1.00						
K^+	0.01	0.11	0.12	0.21	0.11	0.31	0.18	1.00					
Cl^-	0.03	0.13	0.40	0.52	0.21	0.42	0.19	0.19	1.00				
SO_4^{2-}	–0.32	0.02	0.83	0.19	0.79	0.12	0.56	0.02	0.29	1.00			
HCO_3^-	0.04	0.33	0.42	0.53	0.27	0.34	0.51	0.16	0.39	0.36	1.00		
NO_3^-	0.00	0.20	–0.03	0.02	–0.19	0.04	–0.26	0.19	0.18	–0.15	–0.04	1.00	
F^-	0.19	0.36	0.25	0.30	–0.03	0.24	0.10	0.02	0.05	0.08	0.40	–0.02	1.00

Table S5
Correlation analysis of groundwater quality parameters during winter in study area

Parameter	pH	TDS	EC	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	F^-
pH	1.00												
TDS	0.29	1.00											
EC	0.14	0.11	1.00										
TH	–0.37	–0.12	0.51	1.00									
Ca^{2+}	–0.38	–0.10	0.10	0.40	1.00								
Mg^{2+}	–0.23	–0.16	0.06	0.29	0.92	1.00							
Na^+	0.33	0.09	–0.02	0.11	–0.02	–0.06	1.00						
K^+	0.05	–0.10	0.47	0.14	0.20	0.12	–0.09	1.00					
Cl^-	–0.22	–0.01	0.20	0.48	0.39	0.21	0.20	0.20	1.00				
SO_4^{2-}	–0.32	–0.09	0.56	0.52	0.68	0.60	–0.14	0.53	0.54	1.00			
HCO_3^-	0.16	–0.05	0.29	0.32	0.23	0.17	–0.04	0.35	0.42	0.42	1.00		
NO_3^-	–0.06	0.25	–0.19	0.06	0.12	0.10	0.04	–0.38	0.25	–0.01	0.04	1.00	
F^-	0.29	–0.12	–0.06	–0.05	–0.07	0.03	–0.05	0.05	–0.03	–0.02	0.53	–0.05	1.00

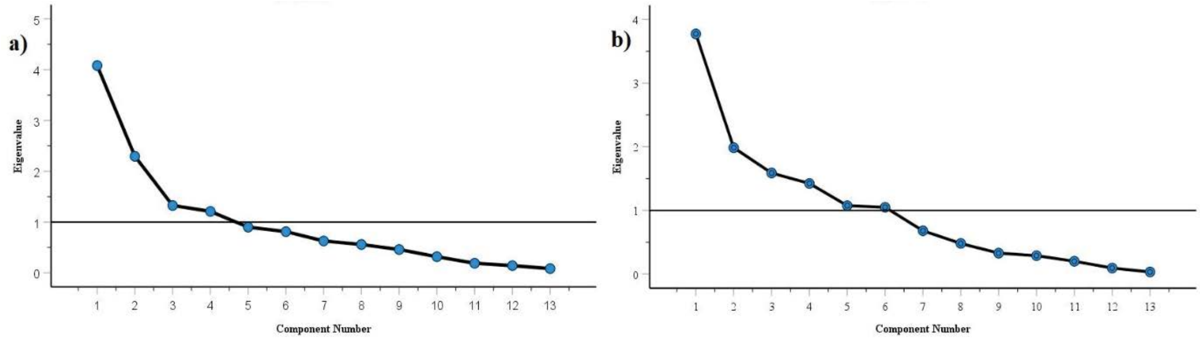

Fig. S4. Eigenvalue of PCA variable for groundwater sample during both monsoon seasons.

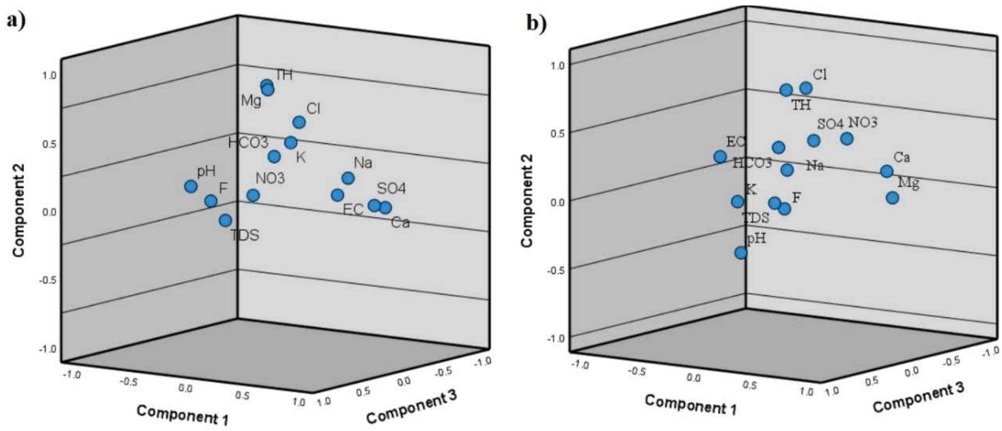

Fig. S5. PCA of groundwater in study area during summer and winter season.

Table S6
HCA cluster group of groundwater quality parameters during both monsoon

Group	Summer	Winter
I	pH, K^+, F^-, Ca^{2+}, Na^+, NO_3^-, Mg^{2+} and SO_4^{2-}	pH, K^+, F^-, Ca^{2+}, Na^+, NO_3^-, Mg^{2+} and SO_4^{2-}
II	TH, HCO_3^-, Cl^- and TDS	TH, HCO_3^- and Cl^-
III	EC	TDS and EC

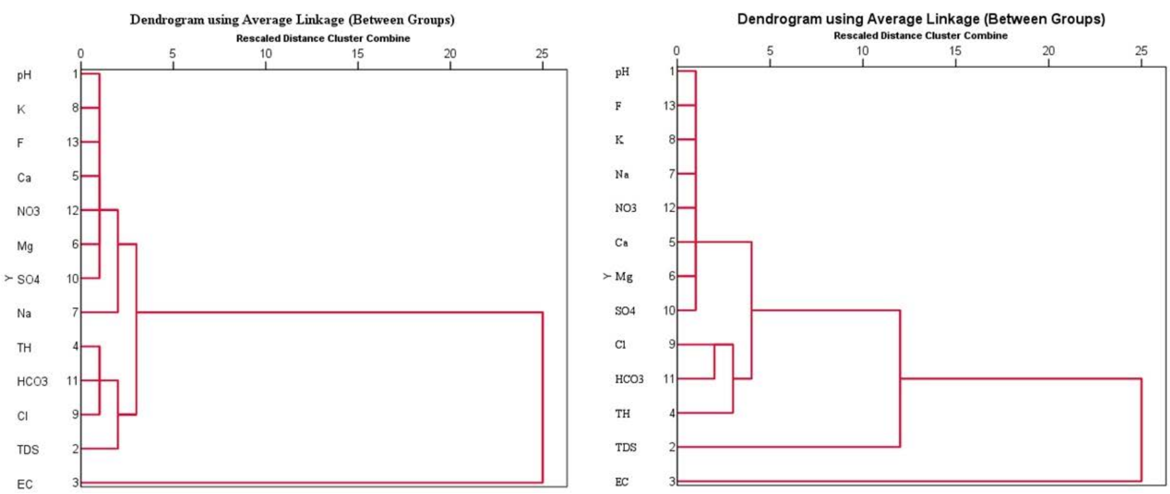

Fig. S6. Dendrogram of groundwater parameter in study area during both monsoon.

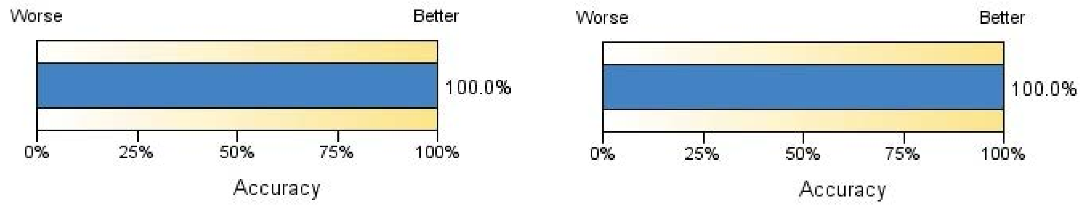

Fig. S7. Accuracy of the ALM for both season.

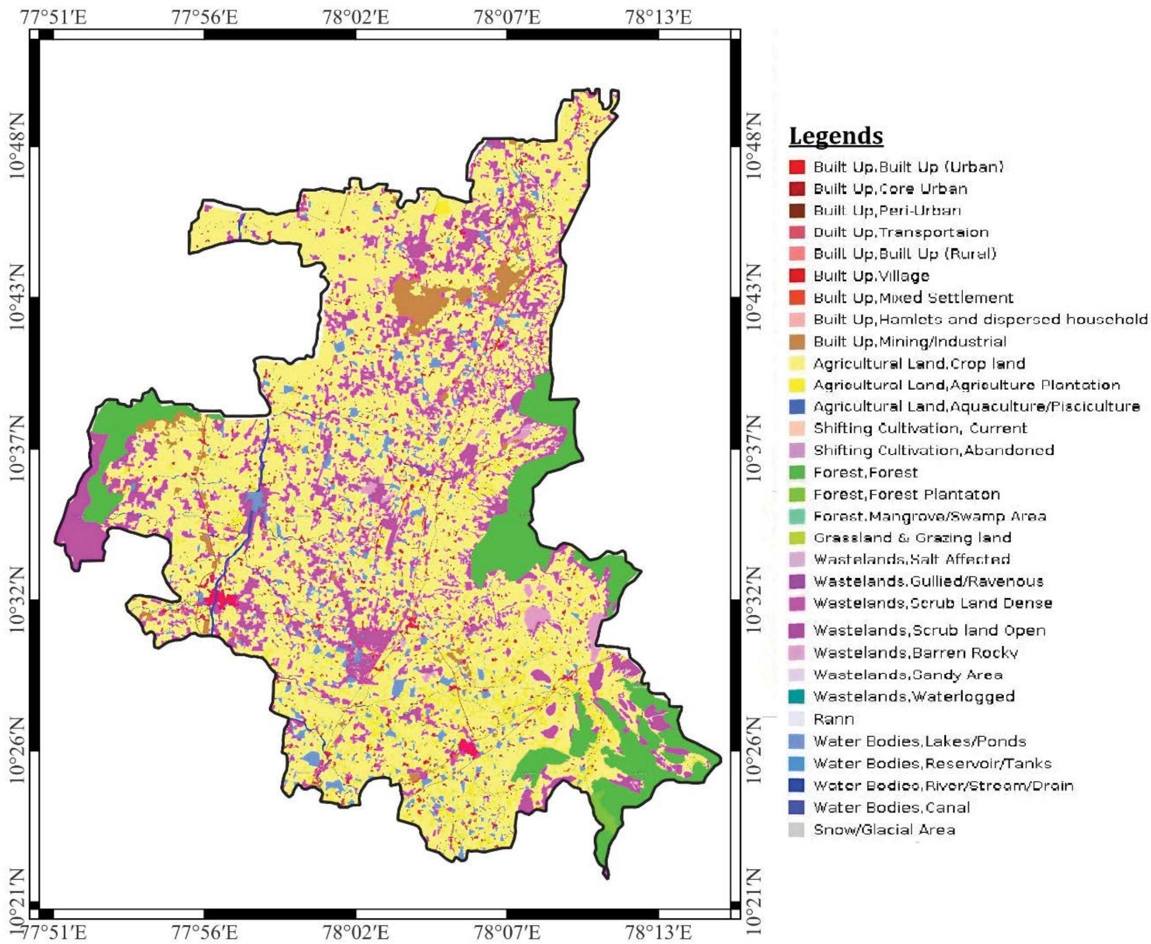

Fig. S8. Land use and land cover details of the study region (*Source*: Bhuvan, Indian Geo-platform of ISRO).