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Hydrochemical characterization and pollution assessment of groundwater in Jammu Siwaliks, India

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Abstract Physico-chemical groundwater (GW) parameters were evaluated to understand the hydrogeochemical processes in the Siwalik plains of Jammu and Kashmir, India. During the 2012–2013 post-monsoon (POM) and pre-monsoon (PRM) seasons, GW samples ($n = 207$) from deep bore wells and shallow open wells were chemically analysed. Cations (Ca^{2+}, Mg^{2+}, Na^+, K^+ and Fe^{2+}) and anions (HCO_3^-, Cl^-, SO_4^{2-} and F^-) showed a wide spatio-temporal variation. Results suggest that weathering and dissolution of carbonates and silicate rocks is the main source of water mineralization. The major hydrochemical facies is characterized by Ca-Mg-HCO_3 and Ca-HCO_3 during the PRM and POM seasons respectively. The presence of sulphate-bearing water in a large number of the samples indicates a significant role of gypsum dissolution and anthropogenic contamination of the GW. Factor analysis (FA) and hierarchical cluster analysis (HCA) revealed that the variability of hydrochemistry is mainly related to rock-water interaction, dissolution of carbonates and other lithological units as well as the influence of anthropogenic activities in the area. Overall, it was found that the GW quality is within the limits of human consumption. The higher concentration of a few chemicals indicates an increasing trend of industrial contamination of the GW. For sustainable development of the portable GW in

Siwaliks, it is necessary to minimize the adverse impacts of the anthropogenic and industrial contamination on the GW resources through best management practices and prevent its further contamination to a level that could make GW unsuitable for human uses.

Keywords Groundwater · Major ions · Weathering · PRM · POM · Factor analysis · HCA

Introduction

Jammu and Kashmir, India, is located in the Himalayas, the Water Tower of Asia and hosts huge reserves of surface and groundwater. Rainfall and snow precipitation, snow- and glacier-melt and discharge from springs are the prime sources of water supply in the region (Romshoo et al. 2015). However, the population expansion and economic development have significantly increased the demand of water for irrigation, drinking water and other domestic and industrial uses (Showqi et al. 2013). Recent climatic changes in the region have impacted the water resources by decreasing glacier extent, altering the precipitation pattern and decreasing the flow of rivers and streams (Kumar et al. 2006; Singh and Kumar 1997; Singh and Bengtsson 2005; Romshoo and Rashid 2014; Dar et al. 2013, Romshoo et al. 2015). Urbanized lifestyles have put extra demands for water consumption (Schot and Van der Wal 1992). All these factors are responsible for the shrinking of the surface water resources and have transformed the water-surplus Jammu Siwalik region into a water-scarce region. The

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Jammu Siwaliks has therefore increasingly become dependent on groundwater resource for meeting the domestic and industrial water demand (Arora 2011; Jasrotia and Kumar 2014). Being situated in the foot slopes of Siwaliks, the region has a good potential of groundwater (GW) and has therefore emerged as an important alternative water resource for meeting the requirement of portable water for various sectors. However, the anthropogenic activities in the form of reckless and unplanned urbanization, lack of solid and liquid waste disposal mechanism and the industrialization in the region have adversely affected the groundwater resources both quantitatively as well as qualitatively (Jasrotia and Singh 2007). The increasing number of bore and tube wells in recent times have augmented the GW withdrawal and this unregulated extraction has exerted pressure on the GW resources with a potential to jeopardize the long-term sustainability of the aquifer. It has been recognized world over that the poor quality of water poses a severe threat to human health, plant growth, economic development and social prosperity (Prasad 1998; Olajire and Imeokparia 2001; Milovanovic 2007; Vasanthavigar et al. 2010; WHO 2014; Khair et al. 2014). It is therefore found necessary to make a hydrochemical assessment of groundwater in Jammu Siwaliks using about 207 data samples belonging to pre-monsoon (PRM) and post-monsoon (POM) seasons. The assessment is based on the use of major ions to understand the geochemical processes and to identify the factors governing the physico-chemical characteristics of the GW. Most of the previous studies in the region have focussed on the general GW aspects based on infrequent and limited number of data (Jasrotia and Singh 2007; Arora 2011; Jasrotia and Kumar 2014; Kanwar and Bhatti 2014).

Study area

Jammu district in the state of Jammu and Kashmir, India is bound by Siwalik Hills in the north and outer plains in the south covering an area of 3092 km^2 (Fig. 1). The topographic gradient of the area is generally low with the average altitude ranging from 315 to 400 m a.s.l. The area experiences subtropical to moist temperate climate with significant variations in temperature from outer plains to hilly areas. The average minimum and maximum temperature in the outer plains ranges from 3 °C in Nov-Feb to the scorching 47 °C during May–June.

Similarly, the minimum and the maximum temperatures in the hilly areas of the region range from 0 °C in Nov-Feb and 35 °C during May–June respectively. The principal process of groundwater recharge in the area is the surface recharge, which in turn is a function of rainfall which has a characteristic spatial and temporal variation over the year. On the basis of the analysis of the rainfall data 1982–2013, it is observed that the region receives highest amount of rain in the months of June–September. The average annual precipitation is 1116 mm dominated by south-western monsoons (Jasrotia and Kumar 2014). The surface water resources are generally dependent on replenishment from the monsoon precipitation but during the non-monsoon periods people largely depend on the groundwater for their domestic, agricultural and industrial water requirements. As per the central groundwater board (CGWB) report, the annual replenishable GW resources of the district are assessed as 85,077 m^3 and the net annual availability for abstraction after accounting for the natural discharge is 75,569 m^3. The annual GW draft for irrigation, industrial and domestic uses is 6636 and 6854 m^3 respectively. The projected annual demand for domestic and industrial uses is up to 2025 is 11,721 m^3 (see, e.g. Arora 2011).

The geological formations of the region include Siwalik rocks and alluvium (Fig. 1). The northern hilly areas lying immediately in the foothill slopes belong to the Kandi Formation comprising of Siwalik rocks of Mio-Pliocene age. The formation comprises of very coarse material from conglomerates, boulders, pebbles, gravels and sandstone, with substantial amount of clay. The southern outer plains belong to Sirowal Formation which is underlain by sediments of Recent to sub-Recent age. This formation comprises of unconsolidated sediments in the form of terraces and coalescent alluvial fans developed by seasonal streams draining Siwaliks. The soil types include ferruginous clay, various types of loam and alluvium deposits.

In the Kandi belt, groundwater generally occurs in unconfined conditions in the weathered portions, cracks, joints and partition plains. Groundwater occurrence is constrained by varied hydrogeology, complex topography and varied geological and tectonic settings. The occurrence of perched water bodies is a common feature in the region. The water level in the Sirowal plains is shallow and occurs as regional bodies under confined and semi-confined conditions, forming the most
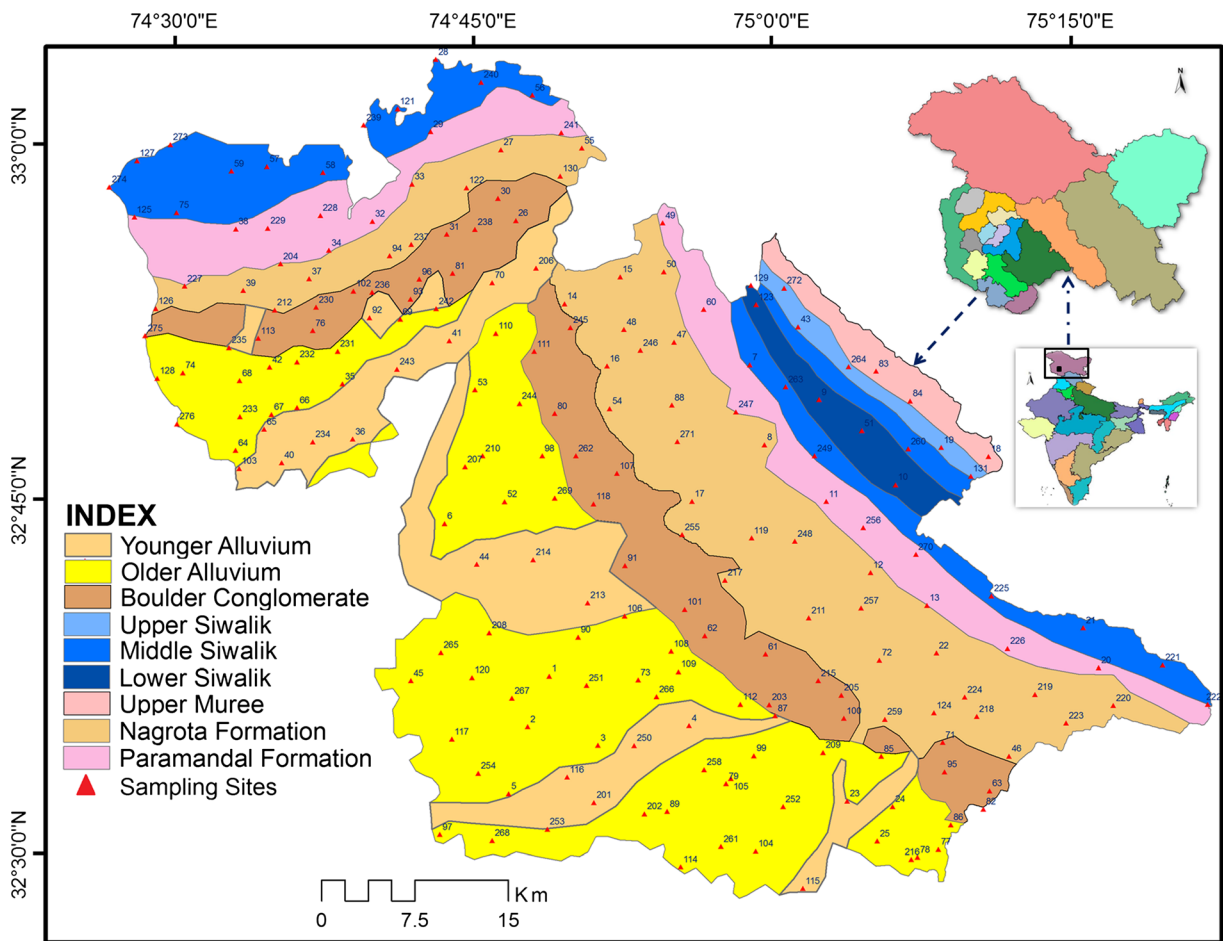
Fig. 1 Geological map of the Jammu district, J&K (modified after Thakur and Rawat 1992), showing the location of the groundwater sampling sites

potential GW reserve. The flow direction of groundwater corresponds roughly to the topographic gradient in varied geologies.

Materials and methods

Groundwater samples were taken from deep and shallow wells based on soil characteristics, lithology and land use/land cover (LULC) pattern of the surrounding areas. The sampled wells are public and private bore wells and the sampling was done using the standard procedures (APHA 1998, USEPA 1989). All the types of wells were chosen (bore wells, hand pumps etc.) for sampling to spatially cover all the GW types in varied geological formations covering every type of anthropogenic and industrial setting. A total of 207 samples were collected, 131 during the POM (2012) and 76 during the

PRM (2013) seasons, and analysed for various physico-chemical parameters. Sampling strategy was designed appropriately to ensure that the samples chosen are representative of the aquifer sampled during both the seasons. However, due to the accessibility constraints, less number of samples were collected during the POM season. pH and conductivity was measured in situ by using a calibrated pH meter and conductivity meter respectively. The cations (Fe^+, Na^+ K^+, Ca^{2+} and Mg^{2+}) and anions (Cl^-, HCO_3^-, NO_3^-, $F^-$and SO_4^{2-}) were determined in the laboratory using standard methods as suggested by APHA 1998.

Modified Z score test, using median absolute deviation (Iglewicz and Hoaglin 1993) and box-whisker plots were used to identify the outliers (>3.5) in the GW data and were removed before doing statistical analysis. Before multivariate analysis, the data was checked for normal distribution using skewness test. The raw data showed

normal distribution for most of the variables. Non-normally distributed variables were transformed to normal data using the log transformation (Davis 2002). The transformed parameters were standardized to ensure that each variable is weighted equally (Bicalho et al. 2012).

For checking normal probability distribution (Gaussian) and to ensure that the range of the values is normally distributed with constant variances, Student's t test was done on the data. Mg^{2+}, Na^+, SO_4^{2-}, Cl^- and Fe were skewed and were log transformed to modify the data sets to meet the required conditions (Sokal and Rohlf 1969). Log-transformed Fe with still high skewness of >1 was discarded from the t test analysis. One-tailed t test was preferred as one of the two sets of data was larger than the other. The test is easier to prove a significant difference as the resulting p value is smaller than calculated in two-tailed test. The test was conducted for a default probability value of $\alpha = 0.05$.

Correlation-based factor analysis (FA) was performed on the hydrochemical data to observe a general variability of chemicals and their possible sources in the GW (Subyani and Al Ahmadi 2010). This method is widely used to group the independent variables into principal components and to find the mechanisms that control and affect their concentration and behaviour (e.g. Farnham et al. 2003; Cloutier et al. 2008a, 2008b; Moral et al. 2008; Moore et al. 2009; Dassi 2011; Belkhiri et al. 2011). Correlation coefficient (Pearson r) and p values were used to evaluate the linear correlation between parameters with p values less than 0.05 giving statistically significant results. The PCA technique helped to identify the interrelations and major sources of various variables. Kaiser criterion was the basis to confer components having eigen values >1. Loadings represent the dominance of individual variables in each component for values greater than 0.7. Each component was characterized by extreme high loadings (positive or negative) and many near-zero loadings fulfilling the objectives of the rotation by maximizing the variance of the principal axes through the varimax normalized rotation (Davis 2002). STATISTICA v.6 (StatSoft Inc. 2004) was used for statistical analysis to group variables and samples according to their correlations.

LULC patterns have a profound effect on the surface and groundwater water quality (Valiela and Bowen 2002). Therefore, LULC mapping of the study area was carried out, using the 2011 Landsat TM satellite imagery, to determine the percentage of land area under different LULC type (Lillesand and Lillesand and Kiefer 1979).

Results and discussions

Spatio-temporal variability of major ions

The statistical results of groundwater chemistry are summarized in Table 1. The groundwater was found generally alkaline in nature with the pH varying from 6.5 to 8.45 and 6.5 to 8.19.during the PRM and POM seasons respectively. The concentration of Ca varied from 10 to 98 and 0 to 86 mg/l with an average of 47 and 39 mg/l during PRM and POM seasons respectively. Similarly, the concentration of Mg^{2+} in the groundwater varied from 6.1 to 75 and 2.4 to 63 mg/l with an average of 24 and 21 mg/l during the PRM and POM seasons respectively. Na^+ (PRM = 2.0–98 mg/l and POM = 1.0–63 mg/l) and K^+ (PRM = 0.2–9 mg/l and POM = 1.0–9 mg/l) followed the same trend with higher concentration observed during the PRM seasons. The concentration of Fe^{2+} ranged between 0.03 and 9.75 mg/l during PRM season and 0.04 and 2 mg/l during the POM season. Cations followed the dominance trend as Ca > Mg > Na > K > Fe. Both Ca^{2+} and Mg^{2+} are derived from the weathering of carbonate-bearing rocks found in the Siwaliks (Ganjoo and Shaker 2007; Sinha et al. 2007; Hossain et al. 2008; Ullah et al. 2009). It is evident from the data (Table 1) that cations and anions show large variability during both the seasons. During the PRM season, 44% samples showed Ca^{2+} dominance, 27% showed Na^+ dominance and 23% showed Mg^{2+} dominance. In the POM season, the trend showed slight decrease in the dominance of Ca^{2+} (43%) and Na^+ (23%) and an increase in the dominance of Mg^{2+} (29%). The high concentration of calcium and sodium cations in the groundwater during the PRM season is generally from the weathering of minerals such as pyroxene, epidote, tourmaline and feldspars found in the Siwalik sediments (Abid et al. 1983) and also from agriculture, domestic wastes and industrial effluents (Jasrotia and Kumar 2014). Similarly, the higher values of magnesium observed during the POM season could be attributed to the agricultural and anthropogenic related activities (Rashid and Romshoo 2012), besides weathering processes (Prasanna et al. 2011). The concentration of Fe^{2+} is slightly higher during PRM than

Table 1 Statistical summary of the physico-chemical parameters of groundwater samples from the study area. The values are in mg/l, except EC which is in μS cm^{-1}. Numerical in brackets show the number of samples analysed in pre-monsoon and post-monsoon season

Parameter	PRM (131)				POM (76)			
	Range	Mean ± SD	CV %	Skewness	Range	Mean ± SD	CV %	Skewness
pH	6.5–8.45	7.45 ± 0.37	5.03	0.0	6.5–8.19	7.36 ± 0.39	5.30	−0.1
EC	58.44–1270	703.78 ± 23	33.53	0.45	58.44–841	581.37 ± 176.9	30.43	−0.61
TDS	37.4–813	450.42 ± 151	33.53	0.45	37.4–542.6	372.08 ± 113.21	30.43	−0.61
Ca^{2+}	10.0–98	47.23 ± 21	44.44	0.9	0.08–86	39.90 ± 14.96	37.48	0.5
Mg^{2+}	6.1–75	24.56 ± 13.28	54.06	1.3	2.4–63	21.90 ± 10.14	46.31	1.0
Na^+	2.0–98	29.94 ± 19.77	66.04	1.3	1.0–63	27.38 ± 11.66	42.59	−0.1
K^+	0.2–9	3.34 ± 2.86	85.62	0.8	1.0–9	3.22 ± 2.72	84.35	0.9
HCO_3^-	36–531	277.74 ± 101	36.28	0.2	60.0–342	223.13 ± 68.57	30.73	−0.5
SO_4^{2-}	5.0–77	23.75 ± 15.71	66.16	1.2	10.0–72	26.25 ± 17.55	66.84	0.6
Cl^-	2.8–92	18.92 ± 17.05	90.12	2.2	6.4–78	11.18 ± 7.97	71.35	1.0
NO_3^-	5.0–81.0	36.60 ± 17.87	48.83	0.2	5.0–60	36.50 ± 14.43	39.54	−0.5
F^-	0.01–0.88	0.28 ± 0.17	59.53	0.5	0.07–0.6	0.33 ± 0.13	40.47	−0.1
Fe^{2+}	0.03–9.75	0.47 ± 1.02	217.92	6.7	0.04–2	0.29 ± 0.53	183.89	3.4
TH	70.1–495	229.96 ± 83.1	36.13	0.66	57.6–358.3	190.32 ± 56.47	29.67	0.11

POM season which may be attributed to the presence of laterites, weathering of marcasite and iron oxide coatings in sediments present in the lithologic formations (Prasanna et al. 2011).

HCO_3^- showed variation from 36 to 531 and 60 to 342 mg/l, Cl^- ranged from 2.8 to 92 and 6.4 to 78 mg/l, NO_3^- from 5.0 to 81 and 5.0 to 60 mg/l, SO_4^{2-} from 5.0 to 77 and 10.0 to 72 mg/l and the concentration of F^- varied between 0.01 and 0.88 mg/l and 0.07 and 0.6 mg/l during the PRM and POM seasons respectively. The TDS values varied from 37.4 to 813 and 37.4 to 542.6 mg/l, EC from 58.44 to 1270 and 58.44 to 841 μS cm^{-1} and TH from 70.1 to 495 and 57.6 to 358.3 mg/l during the PRM and POM seasons respectively. The anions were found with concentrations in the following order: $HCO_3^- > Cl^- > NO_3^- > SO_4^{2-} > F^-$. 77% of the samples showed bicarbonate character during the PRM season. This also indicates the weathering of carbonate minerals such as calcium and magnesium found in the litho units such as sandstones, mudstones and carbonate-bearing paleosols which significantly contribute to the total hardness of the water. The increased concentration of sulphates during the POM season indicates the impact of anthropogenic factors such as domestic sewage and agricultural activity (Langmuir 1971; Jasrotia and Kumar 2014). Similarly, the observed increase in the concentration of NO_3^- in

POM is due to leaching from plant nutrients and nitrate fertilizers, industrial effluents and septic tanks after recharge occurs due to the monsoon rains (Freeze and Cherry 1979; Spalding et al. 1993; Peterson et al. 2001; Kingsbury and Shelton 2002, Rashid and Romshoo 2012). It is pertinent to mention here that higher values of Cl^- were observed in few of the wells located within the immediate vicinity of the industrial and residential areas (Fig. 2). On the basis of land use and land cover mapping of the study area, built up and industrial areas constitute 6.17 and 0.13% of the total land area respectively. The agricultural area covers about 47% of the district. Therefore, the higher concentration of NO_3^- and Cl^- could be attributed to excessive use of fertilizer in the agriculture fields and the leaching of the untreated wastes from the industrial and residential areas respectively. Besides, the coarse alluvial deposits of the area increase the chance of direct recharge into the alluvial aquifers from the surface during the rainy seasons.

Fluoride showed slight decrease during the POM season which might be due to the dilution effect. Leaching of the fluoride rich minerals, long irrigation periods and long residence time of groundwater are the most likely factors responsible for the presence of fluoride in the groundwater (Sharma et al. 2013). Agriculture-affected parameters, viz. nitrates, sulphates
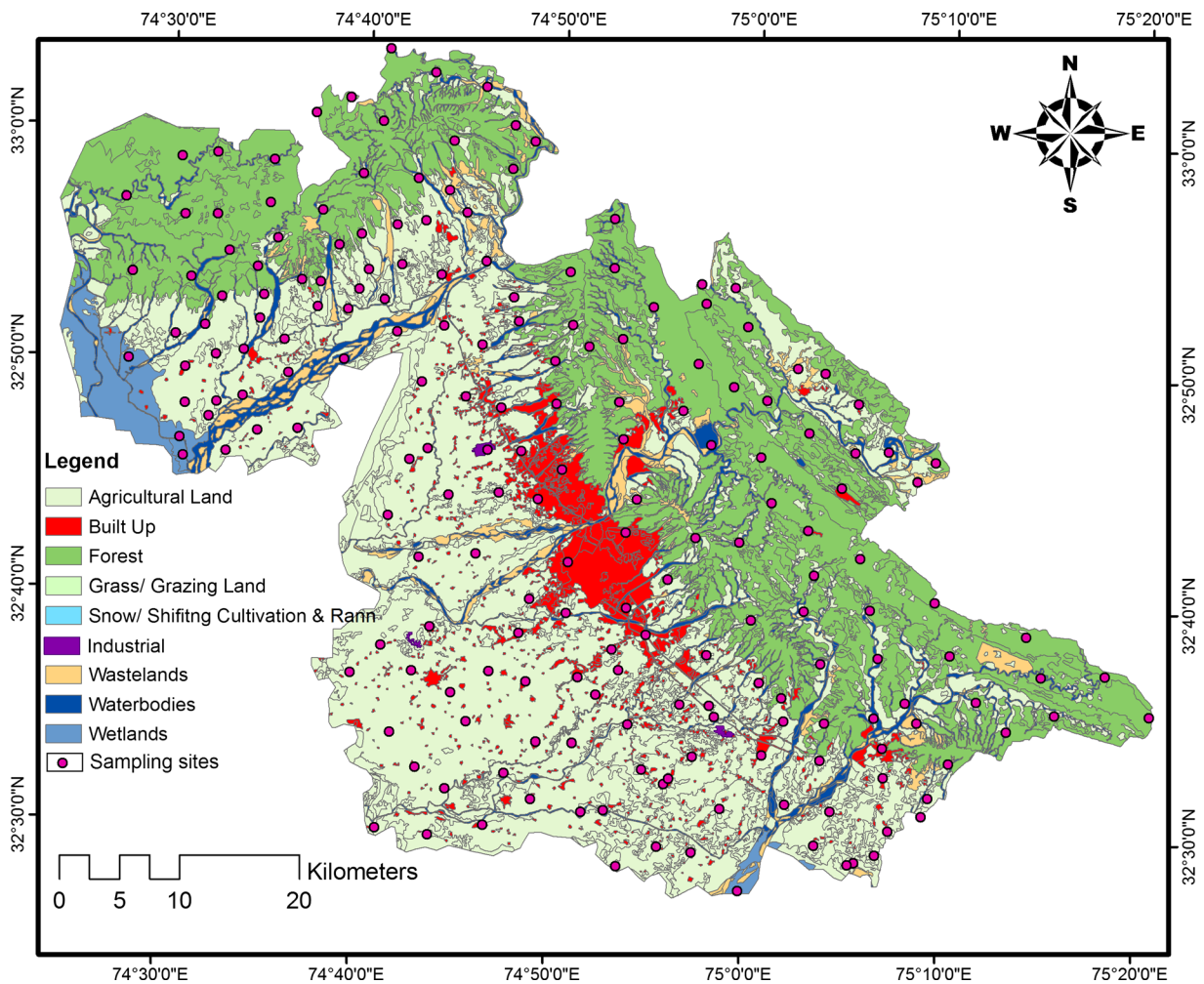
Fig. 2 Land use land cover map of the study area

and potassium derived from fertilizers, liquid sprays and manures, causes their enrichment in the groundwater (Tizro and Voudouris 2008). The slight decrease of TDS, Ca, Na, bicarbonate and total hardness during the POM season is due to the mixing of fresh recharging rainwater that dilutes the more mineralized stored water (Dar et al. 2014).

Water types observed during the PRM and POM seasons and the percentage of wells falling under a particular type are summarized in Table 2. An increase of Mg^{2+}-bearing water types is observed in the POM samples reflecting the release of more Mg from carbonate weathering. A shift toward the SO_4^{2-}-rich water types reflects weathering of sulphate minerals. This type of behaviour in the groundwater chemistry could be attributed to the de-dolomitization process during which Mg^{2+} and SO_4^{2-} increase and Ca remains in saturation

state (Saunders and Toran 1994). Additionally, SO_4^{2-} can also be added from agriculture or other anthropogenic sources. Na-bearing water types are generally found pervasive during the PRM which could be due to the weathering of Na-bearing rocks like silicates.

The Hill Piper plot (Piper 1953) shows that most of the water samples collected during both the seasons fall in Ca-Mg-HCO_3 type (Fig. 3). The large spread of samples indicates the presence of the Ca-Mg-Na-SO_4 ion combinations. During the POM season, majority of the samples fall in the Ca-HCO_3 type with minor representations from the mixed HCO_3-Cl-SO_4 type. Overall, four hydrochemical facies can be recognized in the order of Ca-HCO_3 > Ca-Mg-HCO_3 > Ca-Mg-Na-SO_4 > HCO_3-Cl-SO_4 type. In the diamond field of the diagram, 95 and 99% of the samples fall in the HCO_3-Ca-Mg field during the PRM and POM seasons

Table 2 Showing major water types and percentage of the wells falling under a particular water type in the study area during PRM and POM

Water type	Pre-monsoon % samples	Post-monsoon % samples
Ca-Mg-HCO3	27	18
Mg-Ca-HCO3	13	6
Mg-Ca-Na-HCO3	9	24
Ca-HCO3	7	6
Mg-Na-Ca-HCO3	7	–
Ca-Mg-Na-HCO3	6	18
Ca-Na-HCO3	5	4
Na-Ca-Mg-HCO3	5	–
Ca-Na-Mg-HCO3	4	3
Na-Ca-HCO3	4	–
Mg-HCO3	2	–
Na-Mg-Ca-HCO3	2	3
Na-Mg-Ca-HCO3-Cl	2	–
Na-Mg-HCO3-Cl	2	–

respectively. This indicates dominant weathering of carbonate rock formations composed of limestone and dolomite or influx from the active recharge zones with short residence time (Nadiri et al. 2013). However, during the PRM season, 5% of samples fall in the mixed zone of diamond field where neither anions nor cations are dominant (Todd and Mays 2005). This demonstrates that the groundwater is together affected by weathering

of other rocks and anthropogenic activities. A negligible number of samples in the mixed field during the POM season showed the dilution effect due to the monsoon recharge.

Except Fe^{2+}, the values of K^+, Na^+ and Cl^-, (Fig. 4) show high coefficient of variation during both the seasons followed by SO_4^{2-} and NO_3^- as these ions are mostly associated with the anthropogenic sources. This indicates that the GW in the region is affected by human contamination like domestic and industrial waste, sewage, fertilizers etc. High variability of F^-, Fe^{2+}, Ca^{2+} and Mg^{2+} indicates the influence of the industries which are widely operating in some areas in the region. Weathering of marcasite, presence of laterites and iron oxide coating in the litho units as well as iron released from the industries might be the reasons for their increased concentration.

The output results of Student's t test are given in Table 3 for various parameters. The null hypotheses, that the means of the parameters before and after recharge (PRM and POM samples) being same, was tested. The value of T Stat > t critical rejects the null hypothesis (i.e. mean of parameter in PRM minus mean of parameter in POM = 0) which means that a statistically significant change has occurred in the data set of two seasons. Since the data was unpaired, single-tailed results were more emphasized.

It is clear from Table 3 that significant changes have occurred from PRM to POM samples in case of Ca^{2+}, HCO_3^-, Cl^-, and F^-. These ions in GW generally reflect
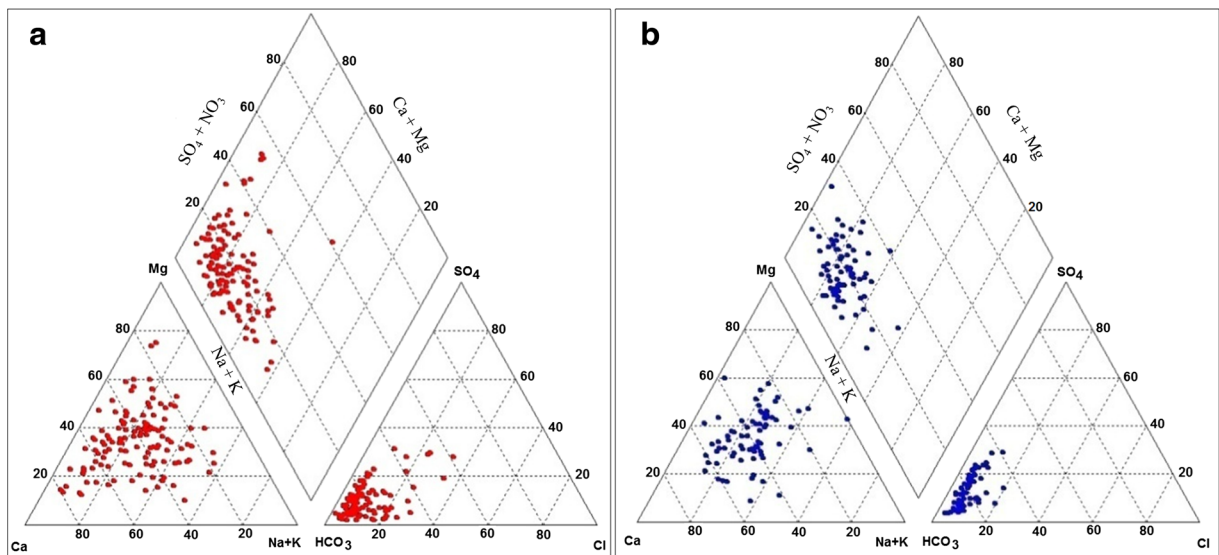

Fig. 3 Piper Trilinear diagram (**a** pre-monsoon and **b** post-monsoon) showing hydrogeochemical facies for groundwater of the study area
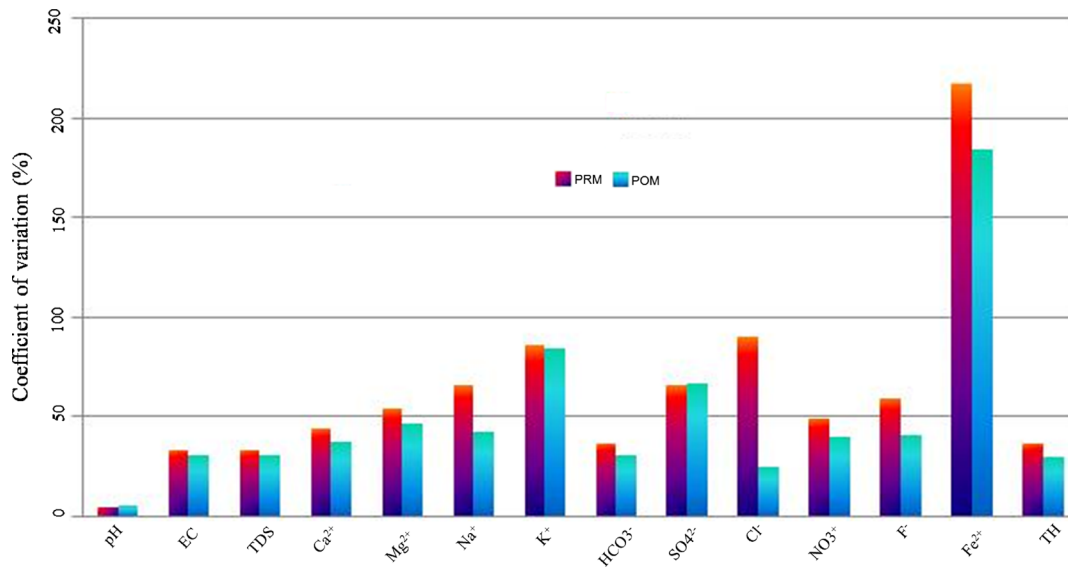
Fig. 4 Coefficient of variation of major ions during PRM and POM seasons

the combined sources of mineral weathering as well as the nature of anthropogenic contamination thus reflecting that the GW in the area has also significant human-related contamination. The null hypothesis is also rejected as is observed by the results of p value i.e. $P(T \leq t)$ is less than the selected $\alpha = 0.05$ level (rejecting null hypothesis).

Hydrochemical evolution of the groundwater

The source of Ca^{2+} and Mg^{2+} in the groundwater is generally the dissolution of calcite and dolomite minerals present in the Siwalik rocks. The general equilibrium equation used to infer the processes of this mineral dissolution and water–rock interaction is described as follows:

$$CaCO_3 + H_2O + CO_2 : Ca^{2+} + 2HCO_3^- \qquad (1)$$
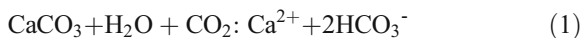
As per Eq. 1, equivalent moles of Ca^{2+} and HCO_3^- should fall along 1:1 equiline which is not observed in

this study (Fig. 5). This disequilibrium reveals that the ions like Mg^{2+} is also involved in the process (e.g. Wu et al. 2009; Dar et al. 2014). Thus, a possible chemical reaction that controls the carbonate groundwater chemistry is described as follows:

$$CaMg(CO_3)^2 + 2H_2O + 2CO_2 : Ca^{2+} + Mg^{2+} + 4HCO_3^- \qquad (2)$$
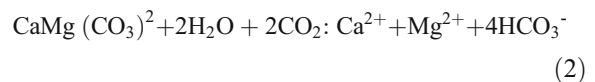
The scatter plots of Ca + Mg vs HCO$_3$ + SO$_4$ shows that 54% of the samples lie close to the 1:1 line during the PRM season and 28% during the POM season which indicates that $Ca^{2+} + Mg^{2+}$ equilibrates the $HCO_3^- + SO_4^{2-}$ concentration. This indicates the role of SO_4^{2-} in the groundwater hydrochemistry in the region which is released from both the anthropogenic activities and carbonate rocks.

The plot of Na^+ and Cl^- (Fig. 5a) is an indication of the rock weathering as the dominant source of these ions are silicate rocks (Jasrotia and Kumar 2014). However, a

Table 3 Summary statistics of t test for observations, 127 (PRM) and 27 (POM) assuming unequal variances. *Df* degree of freedom

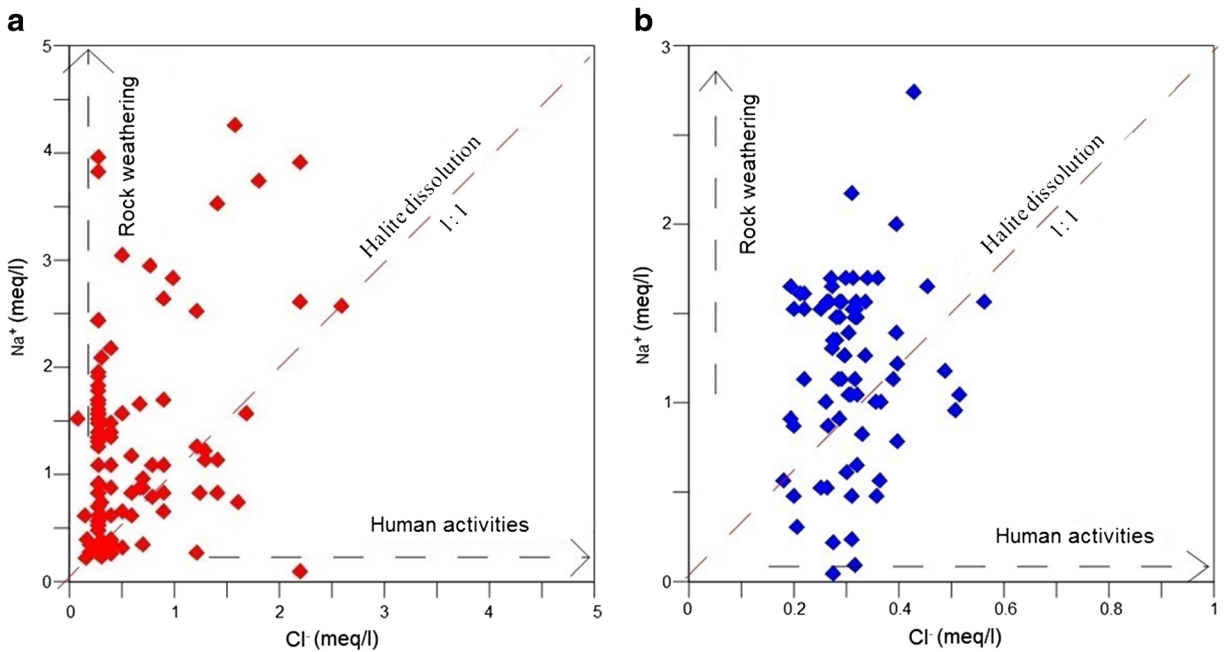|	ph	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	HCO$_3^-$	SO$_4^{2-}$	Cl$^-$	NO$_3^-$	F$^-$
Df	142	187	147	152	154	190	137	174	174	178
t Stat	1.587	2.858	1.241	0.180	0.285	4.531	−0.678	5.038	0.072	−2.022
P(T ≤ t)	0.057	0.002	0.108	0.429	0.388	0.00001	0.249	0.000001	0.471	0.022
t critical	1.656	1.653	1.655	1.655	1.655	1.653	1.656	1.654	1.654	1.653

Fig. 5 Plot showing the effect of rock weathering and anthropogenic effect on the subsurface water (**a** pre-monsoon and **b** post-monsoon)

clear human effect is also discernible from the distribution of the ions. During the post-monsoon season, it is observed that the dilution has shifted the samples to lower ratio (Fig. 5b).

The Gibbs diagram (Na^+/Na^++Ca^{2+}) and ($Cl^-/Cl^- + HCO_3^-$) vs. log TDS also showed the role of water–rock interaction (Fig. 6). Similarly, from the LL-diagram (Langelier and Ludwig 1941), it is observed that

broader scatter and samples fall in the silicate dissolution (III) field with a few samples lying in the gypsum/anhydrite (I) and carbonate dissolution (II) fields. This indicates the silicate source of Na^+, K^+ and Cl^- and carbonate and gypsum/ anhydrite source of Ca^{2+}, Mg^{2+} and HCO_3^- ions (Fig. 7). Almost 99% of the groundwater samples were found to be of bicarbonate alkali type in
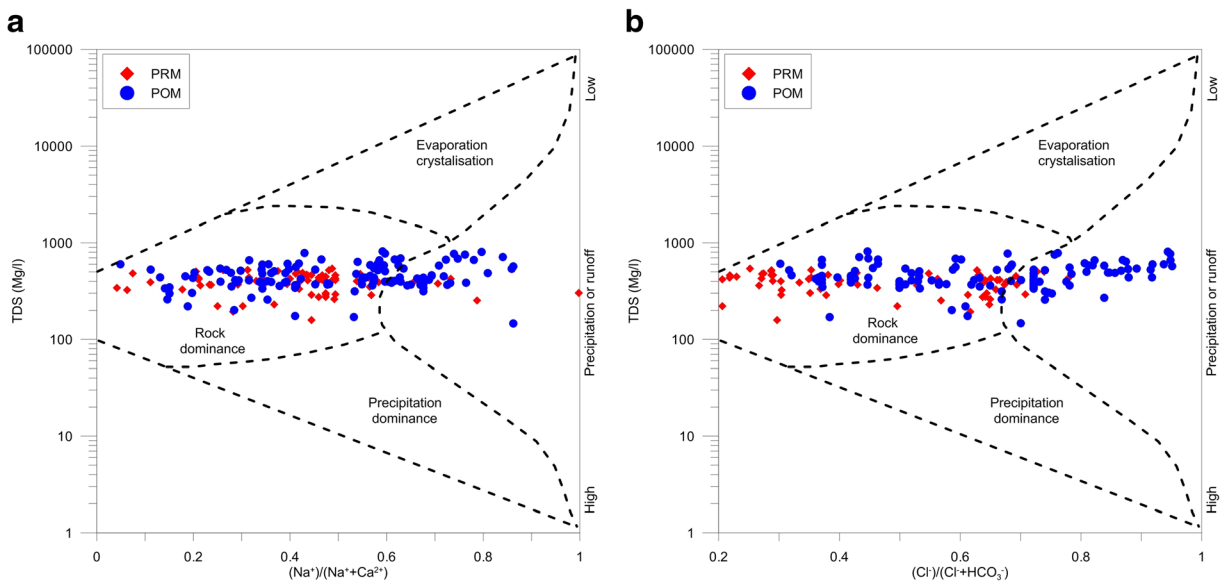

Fig. 6 Gibbs plot showing the mechanism that controls the geochemical characteristics of groundwater (**a** cations, **b** anions)
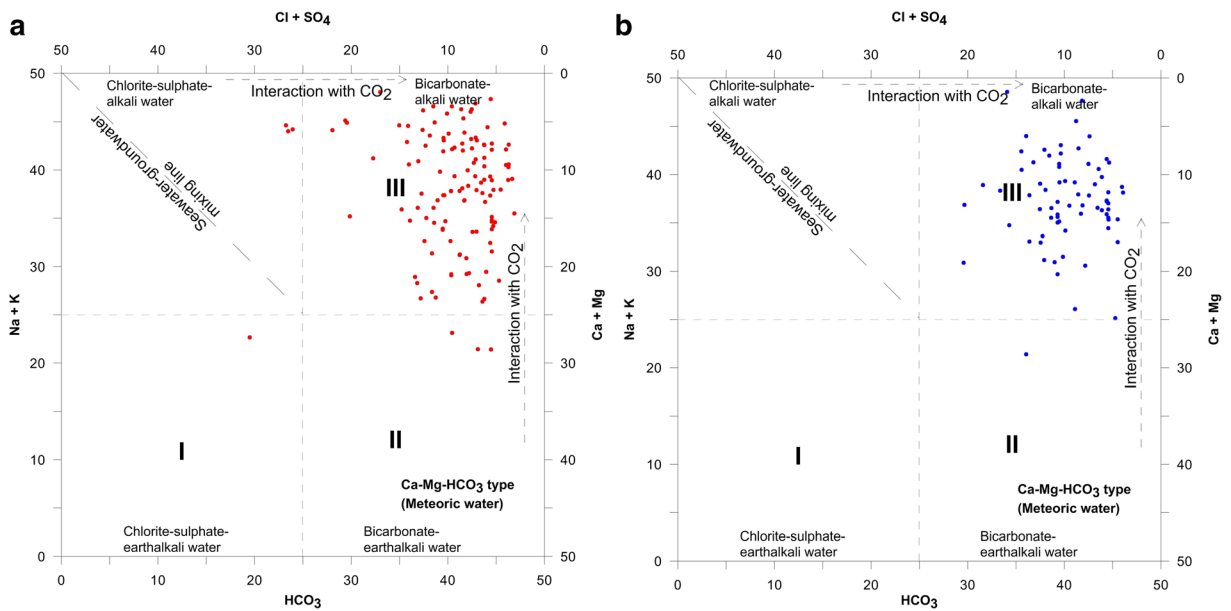
Fig. 7 LL-diagram showing hydrogeochemical evolution of groundwater during **a** PRM and **b** POM seasons

character. The above discussion clearly indicates the significant role of weathering and anthropogenic activities in controlling the chemistry of groundwater in the area.

Factor analysis

Multivariate statistical analysis was employed to reduce the number of parameters and variables into similar groups based on factor analysis (e.g. Steinhorst and Williams 1985; Cloutier et al. 2008a, 2008b). The hierarchical cluster analysis (HCA) and the principal components analysis (PCA) methods give a better understanding of the physico-chemical properties operating in the system in space and time (Helsel and Hirsch 1992; Davis 2002; Liu et al. 2003; Love et al. 2004; Hussain et al. 2008; Subyani and Al Ahmadi 2010; Amadi et al. 2013). Before carrying out the analyses, four groundwater samples with incomplete data and the additive parameters like, EC and TDS were removed and descriptive statistics was computed (Table 1). Normal distribution of the samples was checked which showed that two of the parameters were having non-normal behaviour which were then log transformed. All the parameters were then standardized to make each variable equally weighted. New standardized values of parameters for each sample (i.e. $Z_i = (X_i-mean)/standard deviation$, Davis 2002) gave a new data set with units of standard deviation and this data set was analysed as

described in Schot and Van der Wal (1992); Guler et al. (2002); Cloutier et al. (2008a, 2008b).

Factor analysis helped to compute the variances and co-variances of different variables and the varimax rotation distinguished variables with high factor loadings. A total of four factors with Eigen values >1 were identified in the PRM samples and five in the POM samples (Table 4) that best explained the dominant mechanisms controlling the groundwater composition in the area.

During the PRM season, four factors expressed 60.7% of the total variance sum and during the POM seasons, four factors account for only 57.9% of total variance sum. From the results (Table 5), it is obvious that weathering and anthropogenic sources are the major reasons for the presence of chemical ions in the groundwater of Jammu Siwaliks.

During the PRM season, factor 1 accounts for 20.6% of total data variance (TDV) with positive factor loadings of Mg^{2+} and SO_4^{2-} indicating water mineralization or the degree of rock weathering of carbonates and plagioclase-bearing rocks. Factor 2 with 19.5% of TDV describes the effect of Ca^{2+} ions. Factor 3 with 10.6% of TDV elucidates the effect of weathering and human effects and the factor 4 with 10% of TDV describes the industrial and domestic influence on the groundwater chemistry. Design of factors was observed and studied by plotting F1-F2, F1-F3 and F1-F4 combinations to decipher the general behaviour of the variables (Figs. 8 and 9). From these plots, it is evident that

Table 4 Principal component loadings with the explained variance for different factors with Varimax normalized rotation for PRM data. Only four factors define the total variance of 64%. Italic values: loadings >0.4

Parameter	PRM samples ($n = 127$)				POM samples ($n = 72$)			
	F1	F2	F3	F4	F1	F2	F3	F4
pH	0.17	*0.62*	−0.23	0.19	−0.23	−0.14	−0.05	*0.77*
Ca^{2+}	−0.06	*0.75*	0.07	0.01	0.33	*0.54*	0.13	0.29
Mg^{2+}	*0.76*	0.20	0.19	−0.01	*−0.52*	*0.49*	0.09	−0.03
Na^+	0.02	−0.15	*0.84*	0.03	*−0.63*	0.31	−0.27	0.15
K^+	−0.05	0.09	−0.01	*0.89*	0.11	−0.10	*0.74*	0.02
HCO_3^{2-}	0.24	0.27	*0.72*	−0.03	0.11	*0.51*	*0.51*	0.21
SO_4^{2-}	*0.80*	−0.07	0.05	−0.06	0.31	*0.42*	0.39	−0.17
Cl^-	0.14	*0.64*	*0.50*	0.10	0.08	*0.68*	*−0.42*	0.09
NO_3^-	0.40	*−0.41*	0.04	0.36	*−0.66*	−0.21	*0.48*	0.00
F^-	0.47	−0.39	0.09	0.25	*−0.75*	0.08	0.14	−0.04
Fe^{2+}	−0.12	*0.48*	−0.26	*−0.44*	0.23	−0.27	0.05	*0.65*
Eigen Values	2.26	2.14	1.17	1.10	2.00	1.68	1.49	1.21
Variability (%)	20.58	19.48	10.61	10.00	18.17	15.26	13.52	10.98
Cumulative %	20.58	40.06	50.68	60.68	18.17	33.42	46.94	57.92

Mg and SO_4^{2-} are closely associated with each other and also with HCO_3^- at large distance which link these ions with carbonate weathering (mostly dolomite or de-dolomitization process). During the POM season, factor 1 accounts for 18.2% of the total data variance and is characterized by negative loadings of ions which is mainly related to the anthropogenic contamination. Factor 2 (15.3% of TDV) has high loadings of ions related to the carbonate and gypsum rocks and thus indicates

carbonate weathering with other sources of Cl^-. Factor 3 with 13.5% of TDV is mainly related to the domestic waste. Parameters in the factor 4 are of industrial origin (Table 5). These groupings of the ions are also seen in the factorial plots as shown in Fig. 9.

Thus, during the PRM season, the rock–water interaction, mineral dissolution and anthropogenic contamination are the major processes and factors determining the groundwater chemistry in the area. During the POM

Table 5 Major loadings of parameters on each factor and the possible reasons of chemicals

| Factor	Parameters	Probable reasons
Pre-monsoon (PRM)		
F1	Mg, SO4,	Dolomite and gypsum dissolution
F2	pH, Cl, NO3, Ca, Fe	Anthropogenic sources
		Weathering of carbonates or Ca/Fe-bearing rocks
F3	Na, HCO3, Cl,	Weathering and anthropogenic contamination
F4	K, Fe	Industrial and domestic waste
Post-monsoon (POM)		
F1	Mg, Na, NO3, F	Mostly due to anthropogenic contamination as all have negative loadings
F2	Ca, Mg, HCO3, SO4, Cl,	Carbonate and gypsum dissolution
F3	K, HCO3, Cl, NO3	Domestic waste
F4	pH, Fe	Industrial source
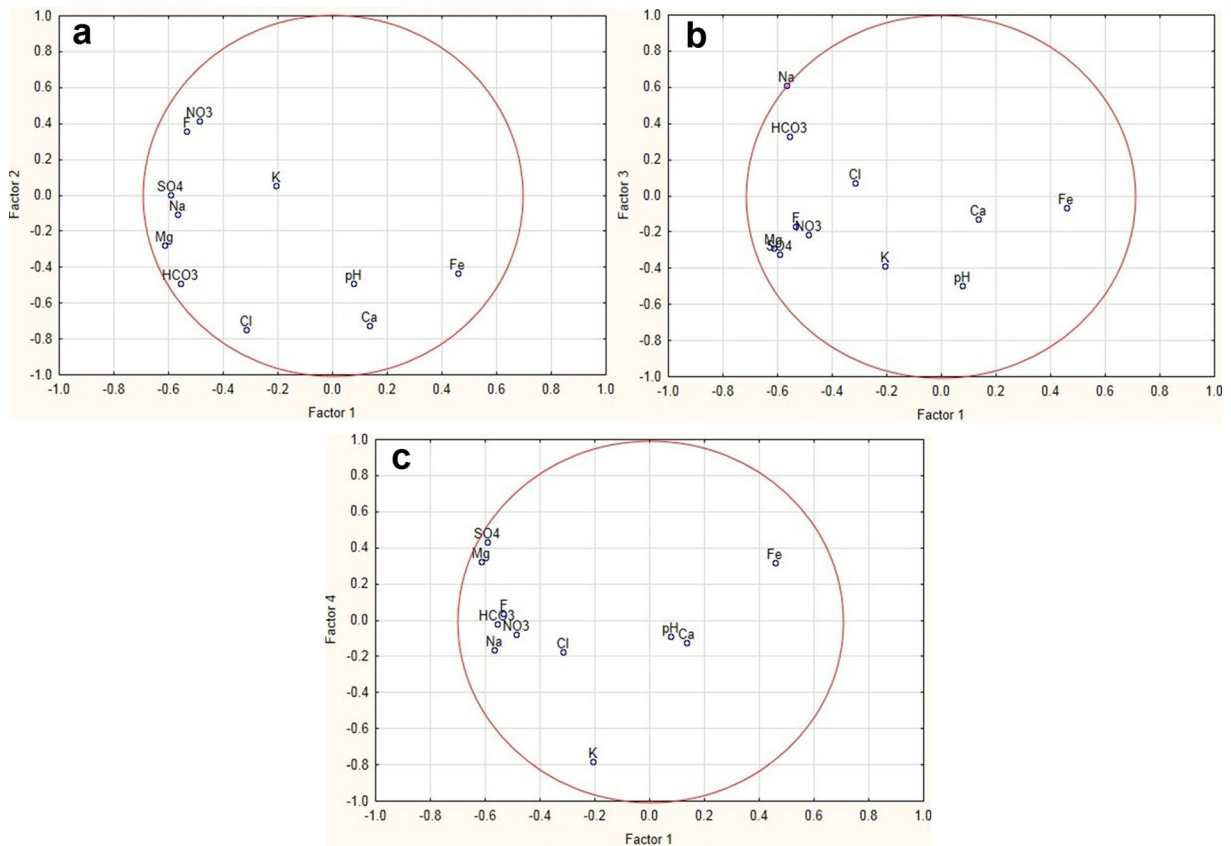
Fig. 8 **a** Plot of factor 1 versus factor 2. **b** Factor 1 versus factor 3. **c** Factor 1 versus factor 4 of PRM

season, major contribution is from the anthropogenic sources particularly agriculture as large area in the region is cultivated during summer season followed by the weathering of rocks. The high concentration of Fe^{2+} and its grouping with K^+ and pH during both the seasons (Fig. 9) indicates that the anthropogenic and industrial effluents are releasing chemicals into the groundwater. The shift of parameters from one factor to other during the PRM and POM seasons may be due to the changing ion exchange processes.

The factor analysis showed interesting observations: (1) that there is the lack of better correlation among most of the variables (Table 6) and (2) that there is a grouping of the variables. Ca^{2+}, Mg^{2+} and HCO_3^- are associated together in a single group, particularly in groundwater exposed to limestone (dolomite) as reported in recent studies (e.g. Wayland et al. 2003; Fitzpatrick et al. 2007; Dar et al. 2014). Dissolution of limestone might be enhanced through the introduction of agricultural chemicals by changing the ion strength and pH of the water (e.g. Long et al. 2012). Either of these

mechanisms could account for the observed decoupling of Ca^{2+} and Mg^{2+} in the groundwater. The large distance of Mg^{2+} from the ions of carbonate system in the POM factorial plots also indicates the de-dolomitization process. Though insignificant but the correlation of F^- and Na^+ may indicate that F^- is geogenic as well as anthropogenic in nature as it is equally correlated with NO_3^-. Similarly, the relation between HCO_3^- and Na^+ is due to simultaneous weathering of silicates and carbonates. Although the results suggest dominant role of lithology, but until there is a better understanding of the occurrence and distribution of geology within the study area, the exact description of the weathering reactions remain unresolved.

Hierarchical cluster analysis

The hierarchical cluster analysis (HCA) was used to investigate the variation in the hydrochemical data (e.g. Batayneh and Zumlot 2012) using Wards linkage-rule (Ward 1963) and Euclidean distance method
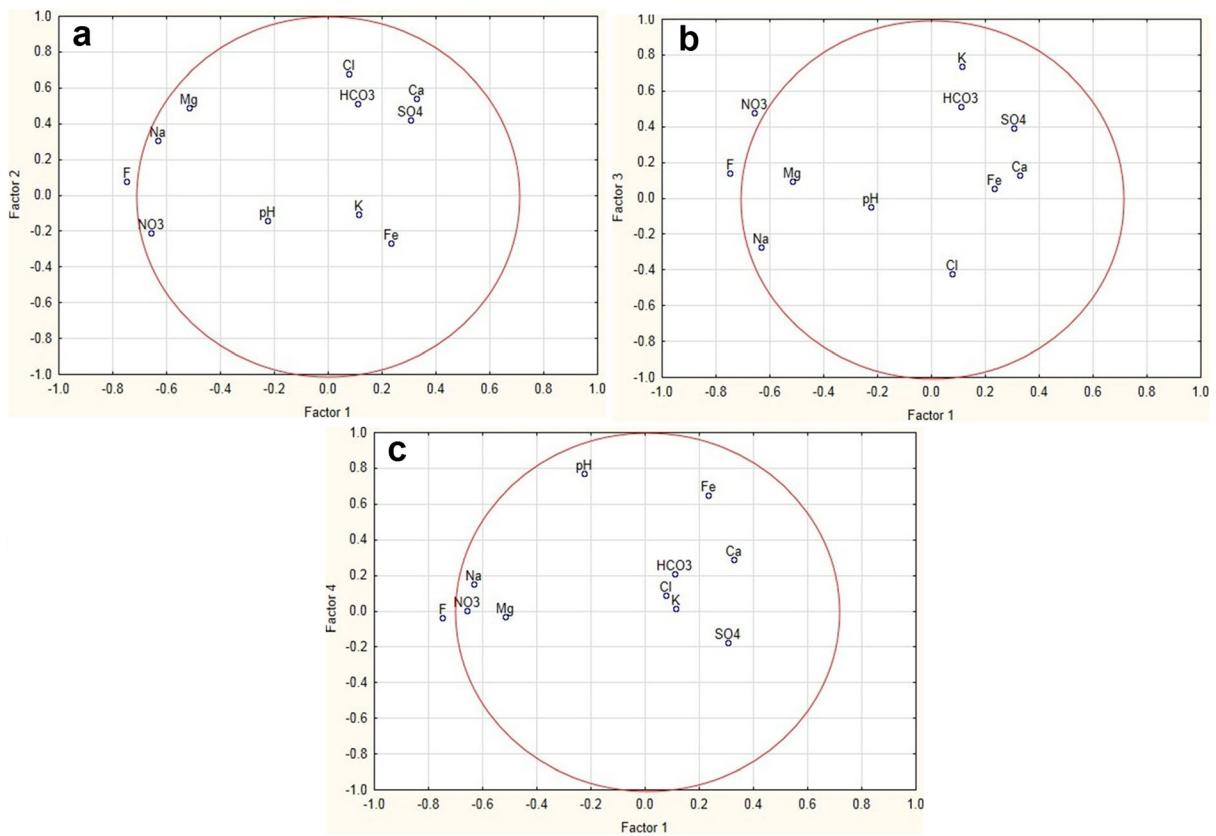
Fig. 9 **a** Plot of factor I versus factor II. **b** Factor I versus factor III. **c** Factor I versus factor IV of POM

(StatSoft Inc. 2004). The results of HCA of the PRM and POM water samples are reported in the form of dendrograms (Fig. 10). Samples were grouped according to their similarity with each other in terms of the observed chemistry. On the basis of the connecting distances, six clusters are geochemically distinct up to a Phenon line of 15 (Fig. 10). The reason for the increased linkage distance in the PRM dendrogram is that more mineralisation causes the samples to spread out and indicates variability of water chemistry. Broadly, two main clusters of variables were observed on the dendrogram during both the seasons (not plotted); HCO^{3-}, Ca^{2+}, Cl^-, Mg^{2+} corresponds to the influence of weathering and rock–water interactions and Fe^{2+}, F^-, pH and K^+ cluster corresponding to the contribution from anthropogenic degradation.

From HCA analysis, the groups with more anthropogenic contamination (higher concentration of anthropogenic related pollutants; Na+, K+, Cl-, NO3-, and SO_4^{2-}) include groups 1, 2 and 4 in PRM and groups 1, 2 and 5 in POM season. The three groups of

PRM had total 67 samples, out of which 35% are located in the Alluvium Formation, 32% in the Nagrota Formation and 23% in the Siwalik Formation. Similarly, in POM out of the total 33 samples of the three groups, 52, 33 and 22% lie in these three rock formations respectively. In GW studies, the relevant anthropogenic related components generally include

Table 6 Pearson correlation coefficient between various pairs of parameters of PRM season. We used Guildford's thumb rule with values >0.3 corresponding to low to very high correlation because no major correlation was observed in the data. Italic values in brackets are for POM samples

	Cl^-	HCO_3^-	Na^+	Mg^{2+}	Ca^{2+}	SO_4^{2-}	NO_3^-
EC	0.55	0.91	0.5	0.48	0.33	–	–
	–	*(0.93)*	–	–	*(0.42)*	*(0.42)*	–
HCO_3^-	–	–	0.42	–	–		
SO_4^{2-}	–	–	–	0.41	–		
F^-	–	–	*(0.37)*	–	–	–	*(0.4)*

Fig. 10 Tree diagram showing
major clusters at a linkage
distance of 15 during PRM for
127 and for POM samples at a
linkage distance of 10 for 72
samples. Ward's method and
Euclidean distances were used in
analysis. *N* is the number of
samples in each group.
Associated table shows the mean
values of major ions for each
group
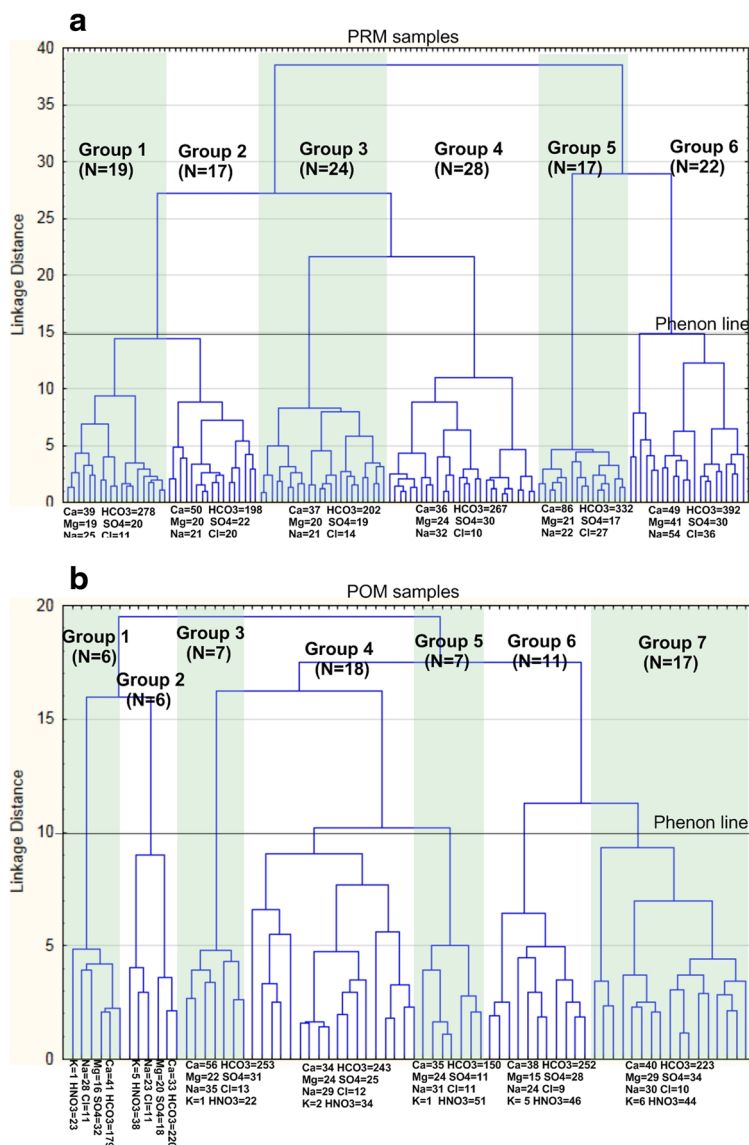
NO$_3^-$, SO$_4^{2-}$, Na$^+$, Cl$^-$, and K$^+$ and their ion ratios are used to evaluate the nature of anthropogenic pollutions. Since these ions are also liberated from other sources, like weathering of minerals, their normalized ratios with respect to HCO$_3^-$ negate these weathering effects and highlight the intensity of human-related contamination. To validate the results of HCA further, the molar ratios of SO$_4^{2-}$/HCO$_3^-$ vs. C^{1-}/HCO$_3^-$ and Na$^+$/HCO$_3^-$ vs. K$^+$/HCO3$^-$ were plotted (Fig. 11). Samples of groundwater from natural conditions (little anthropogenic/industrial effects) should plot more toward the lower molar ratios (e.g. Lang et al. 2006). However, the plots of the GW samples, with PRM (red

symbol) and POM (blue symbol), spread few samples further away from majority of the sample cluster suggesting the effects of anthropogenic contamination. By observing the spatial relationship of these deviated water samples on the geological map, it is found that during PRM, 46% of these samples lie in Alluvium Formation, 20% in the Nagrota Formation and 20% in the Siwalik sediments. Similarly, out of the samples which spread more in POM season, 33% lie in Alluvium and Nagrota Formation each and 16% in the Siwalik rocks. Thus, HCA and Fig. 11 indicate that the groundwater in these formations are more contaminated than rest of the area and has anthropogenic
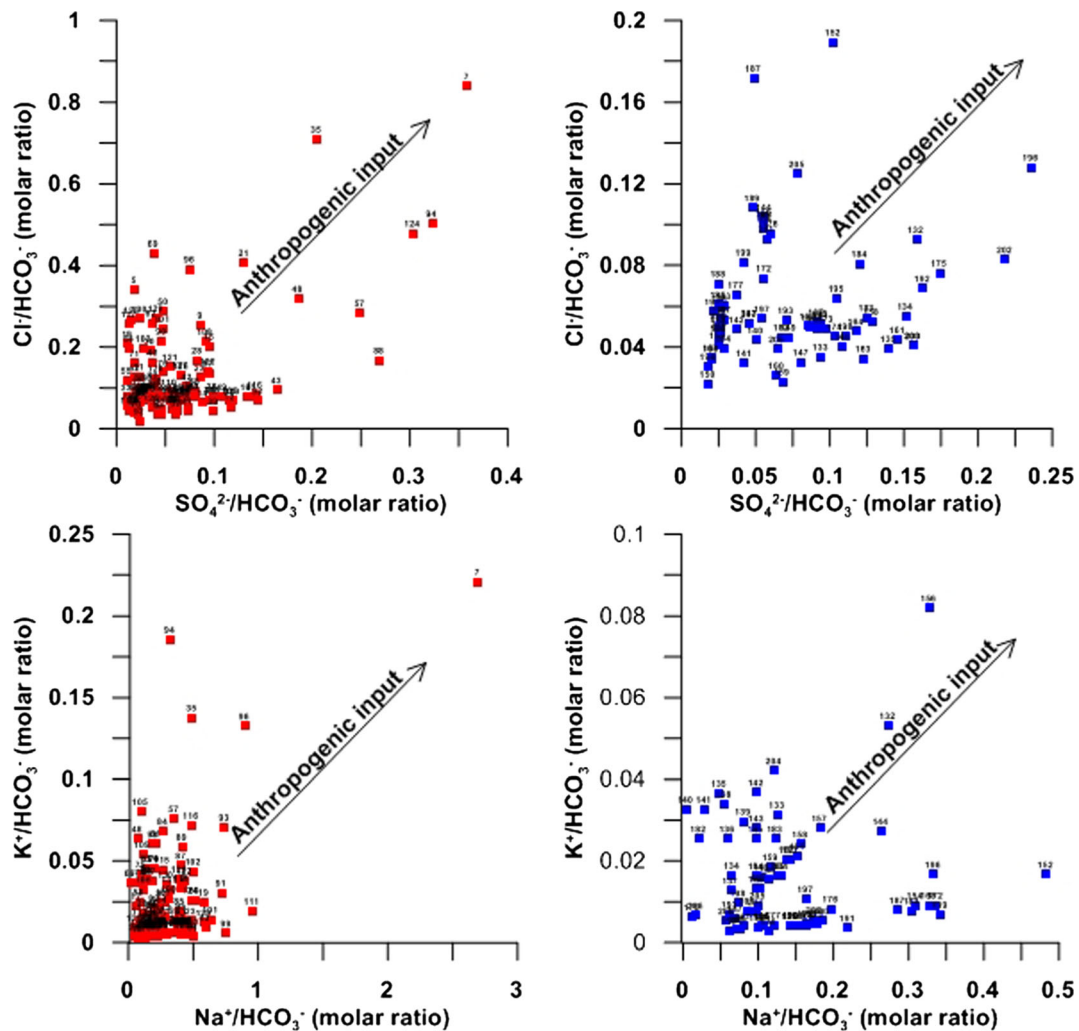
Fig. 11 Plot of HCO_3^- normalized SO_4^{2-} vs. Cl^- values and HCO_3^- normalized Na^+ vs. K^+ (molar ratios) of groundwater of the study area

pollution from source like municipal sewage, industrial effluents and agriculture cultivation which are even more effectual in the Alluvium aquifers. The land use map shows that the industrial units, build-up land, and grazing pastures spread more in this formation which release various water polluting chemicals in the region. Keeping the growing urbanization, industrialisation, and changing land use scenario in Jammu region in view, it is obvious that the groundwater of Alluvium aquifers is further liable to deterioration. Thus, a comprehensive monitoring strategy is required in the more contaminated areas so as to provide best management practices such as managed aquifer recharge, rainwater harvesting and proper well design alongside the developmental progress of the region to prevent further groundwater

pollution to a level that could be unsuitable for drinking and other purposes in future. Further, comprehensive analysis using tracer and isotope studies is required for more detailed monitoring of mechanisms affecting the groundwater chemistry.

Quality of groundwater for drinking purposes

The chemical assessment of the GW, as described in the proceeding sections, gives a clear picture about the usability of GW in Jammu Siwaliks for different purposes (Suresh et al. 1991; SubbaRao 1997; Naik and Purohit 2001; Edmunds et al. 2002; Rao 2006; Avvannavar and Shrihari 2008; Vasanthavigar et al. 2010; Molina-Navarro et al. 2014). The physico-chemical parameters analysed during the pre-

Table 7 Comparison of POM (2012) and PRM (2013) groundwater quality of the Jammu district with the BIS and WHO drinking water standards. EC is in μS cm^{-1}; other values are in mg/l except pH

Parameters	BIS		WHO	Analysed range		Samples exceeding allowable limit (%)	
	Desirable limit	Permissible limit	Max. allowable conc.	PRM	POM	PRM	POM
pH	6.5–8.5	No relaxation	8.5	6.5–8.45	6.5–8.19	0	0
Ec	–		1500	58.44–1270.3	58.44–847.8	0	0
TDS	500	2000	1000	37.4–813.01	37.4–542.6	0	0
Ca^+	75	200	100	10.0–98	0.08–86	0	0
Mg^+	30	–	50	6.1–75	2.4–63	6	1
Na^+	–	–	200	2.0–98	1.0–63	0	0
K^+	10	–	10	0.2–9	1.0–9	0	0
HCO_3^-	300	–	350	36–531	60.0–342	33	0
SO_4^{2-}	200	400	400	5.0–77	10.0–72	0	0
Cl^-	250	1000	250	2.8–92	6.4–78	0	0
NO^{3-}	45	100	50	5.0–81.0	5.0–60	16	4
F^-	1	1.5	1.5	0.01–0.88	0.07–0.6	0	0
Fe^{2+}	1	1.5	1.5	0.03–9.75	0.04–2	11	6
TH	300	600	500	70.1–495	57.6–358.3	0	0

monsoon and post-monsoon seasons generally reflect the portability of water (Table 7) when compared with the standard values (WHO 1996 and BIS 1991). However, the higher concentration of certain ions above the maximum allowable limits like Mg^{2+}, HCO_3^-, NO_3^- and Fe^{2+} may indicate the rising trend of the groundwater contamination from various sources. NO_3^- concentration exceeds the prescribed limits in 5–12% of the samples and reflects the contamination from the anthropogenic sources. HCO_3^- concentration in 25% of wells exceeds the allowable limits and concentration of iron exceeds in 7–8% of wells.

Since the groundwater quality in the region is still within the prescribed quality limits and is suitable for all the purposes, no major treatment is required except some minor chlorination process. However, the spatial and seasonal variability of water quality among samples and chemical parameters provided an overview of the areas which are more prone to further water quality deterioration. Furthermore, a significant change is observed in anthropogenic source related parameters. Thus, the area requires proper groundwater management policies in order to prevent its further contamination to a level that could make water unsuitable for human uses.

Conclusions

The hydrochemical data of the groundwater (GW) was analysed during the PRM and POM seasons to understand the origin and geochemical evolution of physico-chemical parameters in the Jammu Siwaliks. The significant variation during the PRM and POM seasons reveals that the chemical composition of GW is strongly influenced by weathering and leaching of rock minerals. Groundwater generally falls in Ca-Mg-HCO3, Ca-HCO3 and mixed Ca-Mg-Na and HCO3-Cl-SO4 types. Multivariate statistical analysis (FA and HCA) reveals that the weathering of carbonate-bearing rocks and other rock-water interactions are dominantly controlling groundwater chemistry. Anthropogenic activities, like agriculture and sewage, are emerging as the contaminating sources as is evident from the elevated concentration of Mg, nitrate and iron that exceed the maximum allowable limits in few of the samples. Effluents from industrial areas, septic tanks, automobile emissions, fertilizers and manures show profound seasonal and spatial effects on the chemical composition of the groundwater in the area. The area requires proper groundwater management policies in order to prevent its further contamination to a level that could make water unsuitable for human uses. Further comprehensive analysis using tracer and isotope

studies is required for more detailed monitoring of various mechanisms affecting the groundwater chemistry in the area.

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