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ORIGINAL ARTICLE

Application of environmetrics statistical models and water quality index for groundwater quality characterization of alluvial aquifer of Nalagarh Valley, Himachal Pradesh, India

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Abstract Evaluation of groundwater quality to ascertain its utility gain extra concern in the present day life. This study was carried out to reveal the various factors responsible for deterioration of water quality using environmetric techniques (principal component analysis and cluster analysis), water quality index (WQI) and conventional graphical representation such as Piper trillinear diagram in the industrial area of Baddi Barotiwala Nalagarh, Himachal Pradesh, India. The analysis of parameters like pH, EC, TDS, TH and major ions concentrations such as Ca^{2+} Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-} and PO_4^{2-} were carried out to assess the source of pollution in the study area. The parameters like Cl^-, NO_3^- and SO_4^{2-} are within desirable limit as per Bureau of Indian Standards (BIS) for drinking and domestic purposes. pH, TH and Mg^{2+} exceeded the permissible limits at certain sites and about 50 % samples of EC, TDS, Ca^{2+} and Mg^{2+} were above the desirable limits which gives us caution. Piper trillinear diagram classified 93.75 and 90.63 % of groundwater samples for both seasons falls in the fields of Ca^{2+}–Mg^{2+}–HCO_3^- water type indicating temporary hardness. Results of WQI indicate majority of samples falls in poor to unfit range in both seasons. PCA and CA identifies that the groundwater chemistry were influenced by natural as well as minor anthropogenic activities. Thus, the affirmative solution will be proper groundwater development and management practices through artificial recharge to maintain both quality and quantity.

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Introduction

Developing countries are facing immense problems of both quality and quantity of water due to unplanned urbanization and industrialization along with overexploitation and unethical/unscientific disposal of treated or untreated effluent (Simeonov et al. 2003; Brindha et al. 2014). Presently in India, 85 % of the water requirement for domestic use in rural areas, 55 % for irrigation and over 50 % for industrial and urban uses is met from groundwater (Herojeet et al. 2015). The increased dependency on groundwater has made water conservation gain top priority in water management studies. Groundwater resources in the alluvial regions are relatively more prone to contamination due to higher population densities, intensive agriculture and industrial activities in these areas (EPA 1993). Alluvial aquifers constitute a hydrological unit formed by the alluvial deposits and are characterized by a linear and shallow feature which make them highly vulnerable to contamination (Helena et al. 2000; Singh et al. 2006, 2014).

Water quality monitoring data consist of routine measurements of physiochemical variables that could help in understanding the structure and function of particular water body (Sargaonkar and Deshpande 2003; Singh et al. 2008; Murhekar 2012). For easy understanding and effective interpretation, water quality index (WQI) technique is used for demarcating groundwater quality and its suitability for drinking purposes (Tiwari and Mishra 1985; Singh 1992; Rao 1997; Mishra and Patel 2001). Various researchers studied groundwater monitoring with respect to water quality index (Singh et al. 2014; Ramesh and Seetha 2013;

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40

Sustain. Water Resour. Manag. (2016) 2:39–53

Rupal et al. 2012; Kushtagi and Srinivas 2012; Shivasharanappa et al. 2011; Reza and Singh 2010; Ramakrishnaiah et al. 2009). Groundwater chemistry is controlled by various complex factors comprising both natural and anthropogenic influences leading to complex interpretation of data (Sum and Gui 2015). The limitation of WQI can be overcome with the application of multivariate statistical approach (Prasanna et al. 2012; Singh et al. 2014). Multivariate analysis has been considered as a more trustworthy approach for environmental data reduction and revealing common and hidden factors that exist among a set observed variable (Singovszka and Balintova 2012; Okiongbo and Douglas 2015) Recently, several studies reported applications of various multivariate statistical techniques to analyze and interpret water quality data (Sghaier et al. 2011; Lu et al. 2012; Papazova and Simeonova 2012, 2013; Krishnaraj et al. 2013; Bhat et al. 2014; Venkatramanan et al. 2015).

Nalagarh valley belongs to the rapid industrial belt of Baddi, Barotiwala and Nalagarh (BBN) region. The valley has been rated as fastest in industrial growth in the last decade owing to the special packages of incentives granted by the central government (Herojeet et al. 2013b). As per Baddi Barotiwala Nalagarh Development Authority report 2007, around 72 % of industries in Nalagarh are processing without effluent treatment plants (ETPs) which is a major threat to water resources. With the surface water being no longer able to satiate the needs of the valley, groundwater becomes the major freshwater source for various purposes. Thus, groundwater depletion and contamination are major issues in the study area. The present study was carried out to characterize the probable factors controlling the hydrochemistry and discuss the suitability of groundwater for human consumption using environmetric techniques and water quality index.

Study area

The study area represents the southernmost expanse of Solan district which lies between Northern latitudes of 30°52′–31°04′ and Eastern longitudes of 76°40′–76°55′ with an aerial spread of 250 km². The valley is having common border with Haryana towards south–east, i.e. Kalka-Pinjor area and with Punjab towards south–west, i.e. Ropar district (Fig. 1). Rainfall is the major source of recharge to groundwater. Other sources of the groundwater recharge body in the valley are chiefly affected through the influent stream seepage and percolation of surface precipitation and irrigation waters. The valley lacks proper drainage system along with waste disposal facilities where sewage, both treated or untreated, effluent is discharged into drainage system and other aquatic environments. Hence, surface water pollution is a major threat to

groundwater regime, as 50 % of the area is shallow aquifer zone (CGWB 1998).

Geology and hydrogeology

The geology of the area is complex not from the stratigraphical point of view but for its tectonic complexities. Stratigraphically, the Nalagarh valley and its flanks are bounded by the tertiary formations and structurally they are highly disturbed (CGWB 1975). The rock types of the area can be broadly grouped into two tectonic zones striking and trending NW–SE direction. So, the direction of their tectonic zones position from North to South is as follows (Fig. 2):

(a) Belt of lower and middle tertiary occurring along the NE flank of the valley (para-autochthonous).

(b) Belt of upper tertiary confined to the valley and along its SW flank (autochthonous). The contact of these zones is marked by a major fault (Nalagarh thrust).

Tectonically, the area is highly disturbed; the two major thrust trending NE–SW are Nalagarh and Sirsa thrusts. Nalagarh thrust is formed between Kasauli and middle Siwaliks whereas Sirsa thrust separates upper and middle Siwaliks. The major part of the Sirsa river basin is covered by alluvium soil with Holocene and Pre-Holocene deposits. The alluvium soil varies from 10 to 20 m thickness and is mostly of granular form. The upper and middle parts of the river basin are predominated by alternate beds of clay, cobbles, pebbles, gravel and sand. The sediments get finer and finer till it become clay in the downstream part of basin. The stratigraphical sequence of the basin is given in Table 1. The ground water occurs in porous unconsolidated alluvial formation (valley fills) comprising sand, silt, gravel, cobbles and pebbles. The thickness of such deposits is again restricted to 60–100 m below ground level (mbgl). Wells and tube wells are the main ground water abstraction structures. The depth of open dug wells and dug cum bored well in area ranges from 4.00 to 60.00 mbgl wherein depth to water level varies from near ground surface to more than 35 mbgl. Deeper semi-confined aquifers are being developed by tube wells ranging in depth from 65 to 120 mbgl tapping 25–35 m granular zones (CGWB 2007).

Drainage

The study area lies within the catchment expense of Sirsa River drainage system. Sirsa river is a perennial river which flows south westerly in the area and joins Sutlej 10 km upstream of Ropar. It originates from the SW shoulder of Kasauli Dhar and flows across the valley up to its SW flanks. The master slope of the valley is towards
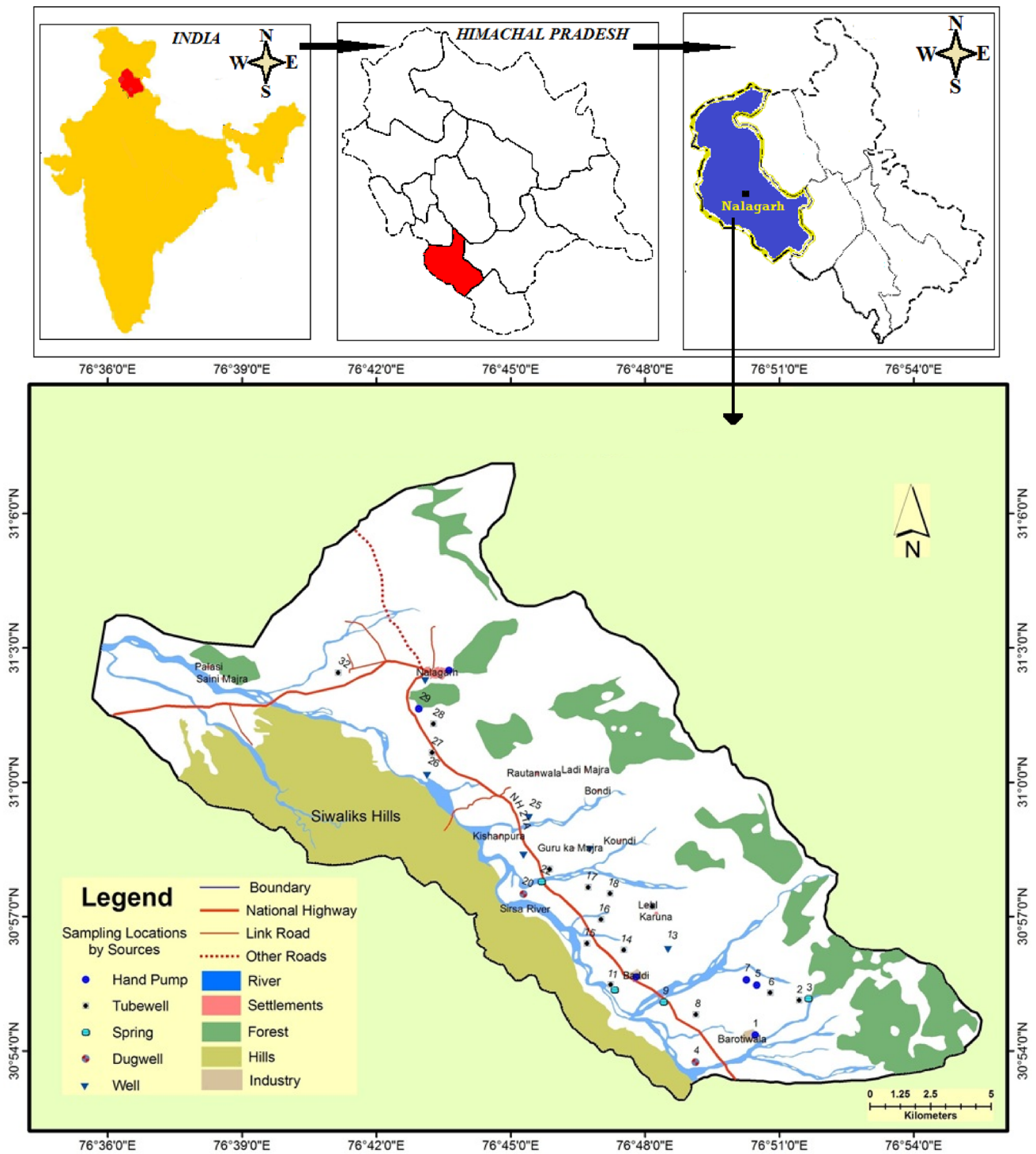
Fig. 1 Location map of the study area with sampling locations

NW direction up to the confluence of Sirsa river along Chikni nadi (small river). The valley is drained by numerous perennial and ephemeral streams emerging from the NE flank passing through industrial belt often loaded with industrial and sewage discharges and transverse flow across the valley, to join Sirsa river (Fig. 3). The important streams among them are Chikni nadi, Phula nadi, Ratta nadi, Balad nadi and Surajpur nadi. All the tributary nadis (small rivers) of Sirsa river flow in NE direction to SW direction and are almost parallel to each other. These streams are fed by numerous secondary streams which form a dendritic type of drainage pattern. The discharge in
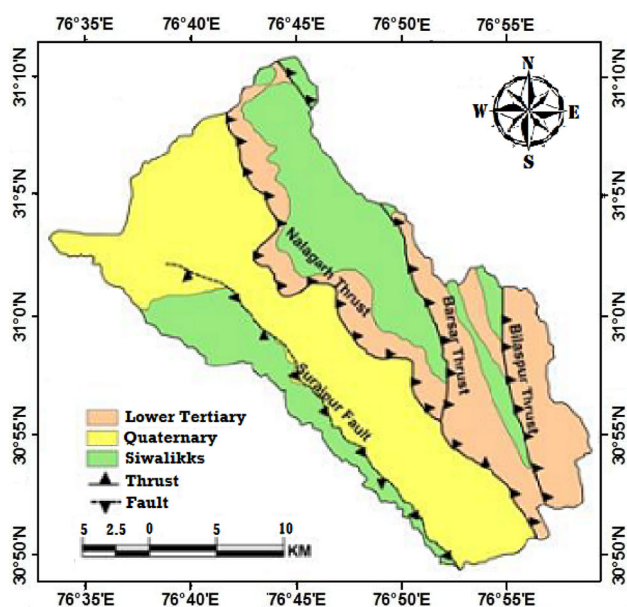
42

Sustain. Water Resour. Manag. (2016) 2:39–53

Fig. 2 Geological map showing thrust and fault of Nalagarh valley

the streams fluctuates in accordance with the climatic conditions. During monsoon, the streams are flooded and carry enormous load of sediments and deposit them in the flood plains of the valley.

Materials and methods

Groundwater samples were collected from 12 Tubewells, 7 Dugwells, 7 Handpumps, 4 Springs and 2 wells on the basis of different industrial unit and land use pattern during May 2012 and October 2012. Good quality, air tight plastic bottles with cover lock was used for sample collection to avoid unpredictable changes in characteristics as per standard procedures. Physical parameters like EC, pH, TDS were measured on the spot at the time of sample collection using portable water and soil analyzes kit. For major cations analysis samples were filtered through were filtered using Whatman filter paper no. 42 of diameter 125 mm and pore size 2.5 μm and preserved by acidifying to pH ∼ 2 with HNO_3 and kept at a temperature of 4 °C until analysis. Chemical analysis of major cations (Na^+, K^+, Ca^{2+},

Mg^{2+}) and anions (SO_4^{2-}, Cl^-, HCO_3^{2-}, CO_3^{2-} and NO_3^{2-}) for the examination of water and wastewater using standard method (APHA 2002) was carried out. The determinations of immediate parameters were made within 2 days after sampling. Ca^{2+}, Mg^{2+}, CO_3^{2-} and HCO_3^- were analyzed by titration. Na^+ and K^+ were measured by flame photometry and NO_3^-, SO_4^{2-} and PO_4^{2-} by UV Spectrophotometer. HCO_3^- and Ca^{2+} were analyzed within 24 h of sampling. Mean value was calculated for each parameters to understand the seasonal variation and standard deviation was used as an indication of the precision of each parameter. Maps were prepared using Mapinfo 6.5 and Piper trillinear diagram were plotted using RockWorks 15. The statistical software Minitab 16, and Microsoft Excel were employed for the calculations and data interpretation.

Water quality index (WQI) computation

Water quality index is one of the most effective tools to communicate information on the quality of any water body. WQI is a mathematical equation used to transform large number of water quality data into a single number (Stambuk-Giljanovic 1999). Water quality index (WQI) is defined as a technique of rating that provides the composite influence of individual water quality parameter on the overall quality of water. It is calculated from the view point of human consumption. Water quality status and its suitability for drinking purpose can be assessed by determining its quality index. For computing WQI, Bureau of Indian standards (BIS 1991) has considered water standard of each chemical parameter in mg/l. The index developed by Tiwari and Mishra (1985) was used. In the present study ten water quality parameters, namely, pH, EC, TDS, TH, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, NO_3^- and SO_4^{2-} were considered for computing WQI.

The calculation involves the following steps:

The first step involved computing the relative weight (wi) of each parameter using Eq. (1). The unit weight (wi) for various water quality parameters is assumed to be inversely proportional to the recommended standards for the corresponding parameter.

Table 1 Geological sequence of the Nalagarh valley

| Rocks	Lithology	Age
Holocene deposits	Modern alluvium and river sediments	Recent
Pre-Holocene deposits	River terrace	Upper Pleistocene
Upper Siwaliks	Boulder conglomerates, sand rocks and clays	Lower Pleistocene
Middle Siwaliks	Sandstones, clays and conglomerates	Pleistocene
Lower Siwaliks	Grey sandstones and purple clays	Upper Miocene
Kasauli series	Purple, grey sandstones and purple clays and shales	Lower Miocene

Sustain. Water Resour. Manag. (2016) 2:39–53

43
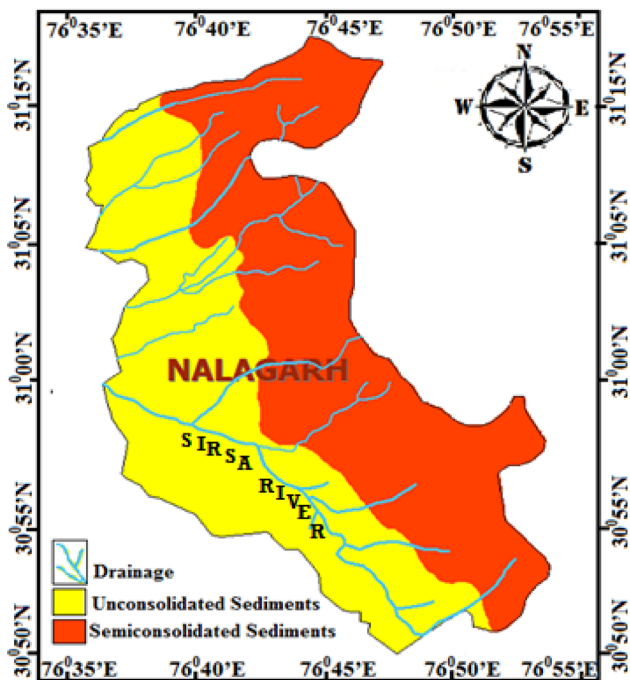
Fig. 3 Drainage map of the study area

$$\text{wi (unit weight)} \propto 1/S_n \Rightarrow \text{wi} = K/S_n \qquad (1)$$

where K (constant) $= \dfrac{1}{1/V_{s_1} + 1/V_{s_2} + 1/V_{s_3} + \cdots + 1/V_{s_n}}$ and $S_n =$ standard permissible value. The calculated unit weight of each parameters based on the Indian drinking water standards (IS: 10500, 1991) are also given in Table 2.

In the second step, water quality rating (qi) was computed for each parameter using Eq. (2).

$$\text{qi} = 100 \times \frac{(V_a - V_i)}{(V_s - V_i)} \qquad (2)$$

Table 2 Unit weightage of parameters based on the BIS (IS: 10500, 1991)

Parameters	Highest permitted values of water (Si)	Unit weightage (Wi)
pH	8.5	0.56422
EC	750	0.00639
TDS	300	0.01598
TH	300	0.01598
Ca^{2+}	75	0.06394
Mg^{2+}	30	0.15986
Cl^-	250	0.01918
HCO_3^-	200	0.02397
SO_4^{2-}	200	0.02397
NO_3^-	45	0.10657

where $V_a =$ actual value present in the water sample, $V_i =$ ideal value (0 for all parameters except pH which is 7.0), and $V_s =$ standard value.

Third, the summation of these sub-indices in the overall index. The water quality index (WQI) is then calculated as follows using Eq. (3).

$$\text{Water quality index (WQI)} = \sum_{i-1}^{n}(Q_i W_i) / \sum_{i-1}^{n} W_i \qquad (3)$$

where Q_i is the sub-index of ith parameter, W_i is the unit weightage for ith parameter and n is the number of parameters considered.

According to this, water quality index is classified into five different water quality status with maximum permissible value is 100 and above this value is unfit for human consumption.

Multivariate statistical analysis

Multivariate statistical techniques have been applied by many researchers to characterize and evaluate freshwater, marine water and sediment quality (Lin et al. 2003; Reghunath et al. 2002; Shrestha and Kazama 2007). Environmetrics, also called multivariate statistical methodologies, such as principal component analysis/PCA and cluster analysis/CA were employed with the objective to group the sampling site according to water quality characteristics and identify the probable factors influencing the water chemistry.

Principal component analysis

Principal component analysis (PCA) is one of the best multivariate statistical techniques for extracting linear relationships among a set of variables (Simeonov et al. 2003). PCA is most widely used as an analytical technique whereby a complex dataset containing variables is transformed to a smaller set of new variables, which maximize the variance of the original dataset. PCA provides information on the significant parameters with minimum loss of original information (Singh et al. 2004). This is achieved by transforming to a new set of variables which are uncorrelated, and which are ordered so that the first few retain most of the variation present in all the original variables. Therefore standardization (z scale) was made on each chemical parameter prior to statistical analysis (Simeonov et al. 2004), to eliminate biasness by any parameter of different units with high concentration and renders the data dimensionless. The principal components are generated in a sequentially ordered manner with decreasing contributions to the variance, i.e. the first principal component (PC1) explains most of the variations

44

Sustain. Water Resour. Manag. (2016) 2:39–53

present in the original data, and successive principal components account for decreasing proportions of the variance (Pires et al. 2009; Vieira et al. 2012). Principal components corresponding to absolute loading values "strong", "moderate" and "weak", corresponding to absolute loading values of >0.75, 0.75–0.50 and 0.50–0.30, respectively (Liu et al. 2003).

Cluster analysis

Cluster analysis (hierarchical clustering), on the other hand, is a useful method of objectively organizing a large dataset into groups on the basis of a given set of characteristics. The primary objective of CA is to identify relatively homogenous groups or clusters of sampling sites based on their similarities/dissimilarities (Wai et al. 2010). The grouping of similar objects occurs first and eventually, as the similarity decreases, all subgroups are merged into a single cluster. In this study, cluster variable (CA) was performed on the standardized dataset by means of the ward's method using squared Euclidean distance as a measure of similarity to obtain dendrogram. The dendrogram provides a visual summary of the clustering processes, presenting a picture of the groups and their proximity, with a dramatic reduction in dimensionality of the original data. The seasonal variability of groundwater quality was determined from CA using the linkage distance, reported as D_{link}/D_{max}, which represents the quotient between the linkage distances for a particular case divided by the maximal linkage distance. The quotient is then multiplied by 100 as a way to standardize the linkage distance represented on the y-axis (Wunderlin et al. 2001; Simeonov et al. 2003; Singh et al. 2004, 2005).

Results and discussion

The physiochemical composition of groundwater samples are presented in Table 3 and also show the critical parameters exceeding the BIS (1991) desirable and permissible limits. The ionic dominance pattern is in the order of $Mg^{2+}>Ca^{2+}>Na^+>K^+$ among cations and $HCO_3^->SO_4^{2-}>NO_3^->PO_4^{2-}$ among anions during pre-monsoon and post-monsoon, respectively. During the period of investigation, mean value of all parameters, except EC, TDS, Na$^+$ and K$^+$, respectively, were more pronounced in post-monsoon than pre-monsoon. The pH values in the study area were well within the prescribed limits for both seasons except for 1 sample above permissible limit in both the seasons. EC accounted for 68.75 and 50 % above desirable limit with mean values 908.59 and 807.59 µS/cm during the period of investigation. TDS values above desirable limit were more in pre-monsoon

(68.75 %) as compare to post-monsoon (46.875 %) which may be attributed to over extraction of groundwater and declining of water table during pre-monsoon. TH 3.125 and 9.375 % samples were found exceeding permissible limits for pre-monsoon and post-monsoon, respectively. The higher degree of hardness in the study area can definitely be attributed to higher soluble concentration of Ca^{2+}, Mg^{2+} and HCO_3^- ions in aquifers system. The calcium concentrations above desirable limit were more prominent during post-monsoon (53.375 %) than pre-monsoon (40.625 %). Magnesium accounted for 3.125 and 15.625 % samples were found to be unsafe for both seasons and also majority of samples were above desirable limits which required attention and regular monitoring. Dissolved magnesium exceeds calcium in water once calcium precipitates after reaching super saturation and accounts for higher magnesium concentrations than calcium (Hem 1991). The higher concentrations of Mg^{2+} in the study area are due to combination of weathering of minerals magnesite, sandstone, dolomite and also from various industrial effluents, as these locations are very close to a cluster of several industries (Herojeet et al. 2013a). Mean value of HCO_3^- was more significant during post-monsoon due to dissolution of carbonate rocks, weathering of feldspar by carbonic acids and oxidation of NO_3^- and SO_4^{2-} with organic matter as compared to pre-monsoon (Awadh and Ahmed 2013). The parameters like Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{2-} were well within desirable limits. At least one or more parameters such as EC, TDS, TH, Ca^{2+} and Mg^{2+} accounted for water samples above desirable limits of more than 50 % of 32 samples examined which gives us caution for deterioration of water quality in near future and being unfit for drinking and other purposes.

Hydrochemical diagram

Hydrochemical diagram aims at facilitating interpretation of evolutionary trends, particularly in conjunction with distribution maps and hydrochemical sections of water regime. The graphical representations of facies are useful in identifying chemical processes and detecting the effects of mixing water within the different lithological frameworks (Todd 1980). Various workers namely Collins (1923), Piper (1944, 1953), Black (1960), Walton (1970) and Chadha (1999) proposed the concept of graphical methods of representation of chemical analysis of water.

Piper trillinear diagram

Piper (1944) diagrams were employed for hydrochemical characterization of groundwater. On the basis of Piper diagram (Fig. 4; Table 4) of groundwater during pre-monsoon

Sustain. Water Resour. Manag. (2016) 2:39–53

45

Table 3 Seasonal variation in physiochemical of groundwater

Parameters	Prescribed limit IS: 10500, 1991		Pre-monsoon				Post-monsoon			
	PL	DL	Range	Mean	Above desirable limit	Above permissible limit	Range	Mean	Above desirable limit	Above permissible limit
pH	–	6.5–8.5	7.17 8.7	7.57	NIL	1	7.03 8.07	7.19	NIL	1
EC	2000 µS/cm	750 µS/cm	500 µS/cm 1513 µS/cm	908.59 µS/cm	22	NIL	440 µS/cm 1348 µS/cm	807.59 µS/cm	16	NIL
TDS	2000 mg/l	500 mg/l	324 mg/l 992 mg/l	588.78 mg/l	21	NIL	284 mg/l 875 mg/l	522.41 mg/l	15	NIL
TH	600 mg/l	300 mg/l	206 mg/l 622 mg/l	306.38 mg/l	13	1	186 mg/l 772 mg/l	380.56 mg/l	13	2
Ca^{2+}	200 mg/l	75 mg/l	35.32 mg/l 157.28 mg/l	74.01 mg/l	13	NIL	27.55 mg/l 139.59 mg/l	79.8 mg/l	17	NIL
Mg^{2+}	100 mg/l	30 mg/l	20.64 mg/l 137.2 mg/l	56.7 mg/l	29	1	31.72 mg/l 172.82 mg/l	73.38 mg/l	27	5
Na^{+}	200 mg/l		12 mg/l 99.9 mg/l	35.02 mg/l	NIL		9.1 mg/l 62.5 mg/l	29.45 mg/l	NIL	
K^{+}	12 mg/l		0.9 mg/l 8.8 mg/l	2.44 mg/l	NIL		0.4 mg/l 10.1 mg/l	2.06 mg/l	NIL	
HCO_3^{-}	600 mg/l	200 mg/l	60 mg/l 196 mg/l	118.93 mg/l	NIL	NIL	62 mg/l 204 mg/l	129.56 mg/l	1	NIL
Cl^{-}	1000 mg/l	250 mg/l	2.98 mg/l 38.77 mg/l	14.6 mg/l	NIL	NIL	3.98 mg/l 39.76 mg/l	15.48 mg/l	NIL	NIL
NO_3^{-}	–	45 mg/l	0.49 mg/l 6.27 mg/l	3.08 mg/l	NIL	NIL	0 mg/l 18.92 mg/l	3.91 mg/l	NIL	NIL
SO_4^{2-}	400 mg/l	200 mg/l	9.98 mg/l 27.01 mg/l	12.74 mg/l	NIL	NIL	9.69 mg/l 26.48 mg/l	13.28 mg/l	NIL	NIL
PO_4^{2-}	–	–	0.01 mg/l 0.95 mg/l	0.18 mg/l	–	–	0.01 mg/l 0.05 mg/l	0.03 mg/l	–	–

PL permissible limit, *DL* desirable limit

46

Sustain. Water Resour. Manag. (2016) 2:39–53

and post-monsoon, all groundwater samples belong to alkaline earth elements ($Ca^{2+}+Mg^{2+}$) and exceed the alkali elements ($Na^{+}+K^{+}$) where Mg^{2+} is leading cation in the study area. Also weak acids ($CO_3^{2-}+HCO_3^{-}$) exceed the strong acids (SO_4^{2-} and Cl^{-}) during both the seasons indicating HCO_3^{-} is the principal anion in groundwater.

The cation triangle shows that Mg^{2+} (87.5 %) is dominating ion in both the seasons. However, 9.25 % samples are in Ca^{2+} type for pre-monsoon and the remaining 3.13 and 12.5 % samples fall in no dominant cation zone in both the seasons. The anion triangle exhibits that HCO_3^{-} (93.75 and 90.63 % samples) is the dominant ion and (6.25 and 9.37 % samples) falls in no dominant zone during pre-monsoon and post-monsoon. This indicates that Na^{+}, K^{+} and Cl^{-}, SO_4^{2-} ions have insignificant dominance in both seasons. Majority of groundwater samples (93.75 and 90.63 %) fall in the field of Ca^{2+}–Mg^{2+}–HCO_3^{-} water types indicating temporary hardness; the groundwater of the study area is of Mg^{2+}–HCO_3^{-} facies having secondary salinity exceeds 50 % indicating inverse or reverse ion exchange, leaching process of dolomites, limestones and gypsum responsible for controlling groundwater chemistry (Davis and Dewiest 1966; Tay 2012). The remaining samples (6.25 and 9.37 %) are Ca^{2+}–Mg^{2+}–Cl^{-}–SO_4^{2-} water types which exhibit mixed Ca^{2+}–Mg^{2+}–Cl^{-} facies where groundwater cannot be classified as either cation or anion dominant hydrochemical facies for both pre-monsoon and post-monsoon seasons (Todd and Mays 2005).

Water quality index

Water quality index computation shows variation in the quality status related to the suitability for human consumption during pre-monsoon and post-monsoon seasons is given in Table 5. A perusal of Table 5 reveals that 93.76 and 81.25 % samples in pre-monsoon and post-monsoon seasons, respectively, fall in poor to unfit class whereas the percentages of sample falling in good class in pre-monsoon and post-monsoon seasons were 6.25 and 18.75 %, respectively. The decline in poor to unfit class and rise in good class in post-monsoon season as compared to pre-monsoon season may be attributed to the dilution due to recharge of aquifer in post-monsoon season. The groundwater samples falling in poor to unfit class in both the seasons may be due to high water table, lesser soil filter media, valley fill aquifer formation and lack of proper drainage system. The calculated WQI for individual samples is represented in Table 6 and Fig. 5 shows the variation of WQI in the study area which indicates fluctuation in water class that require proper attention and regular monitoring.

Environmentric model

Principal component analysis (PCA)

PCA was applied on the analyzed dataset to draw the latent factors influencing the hydrochemistry. An eigenvalue gives a measure of the significance of the factor and factors
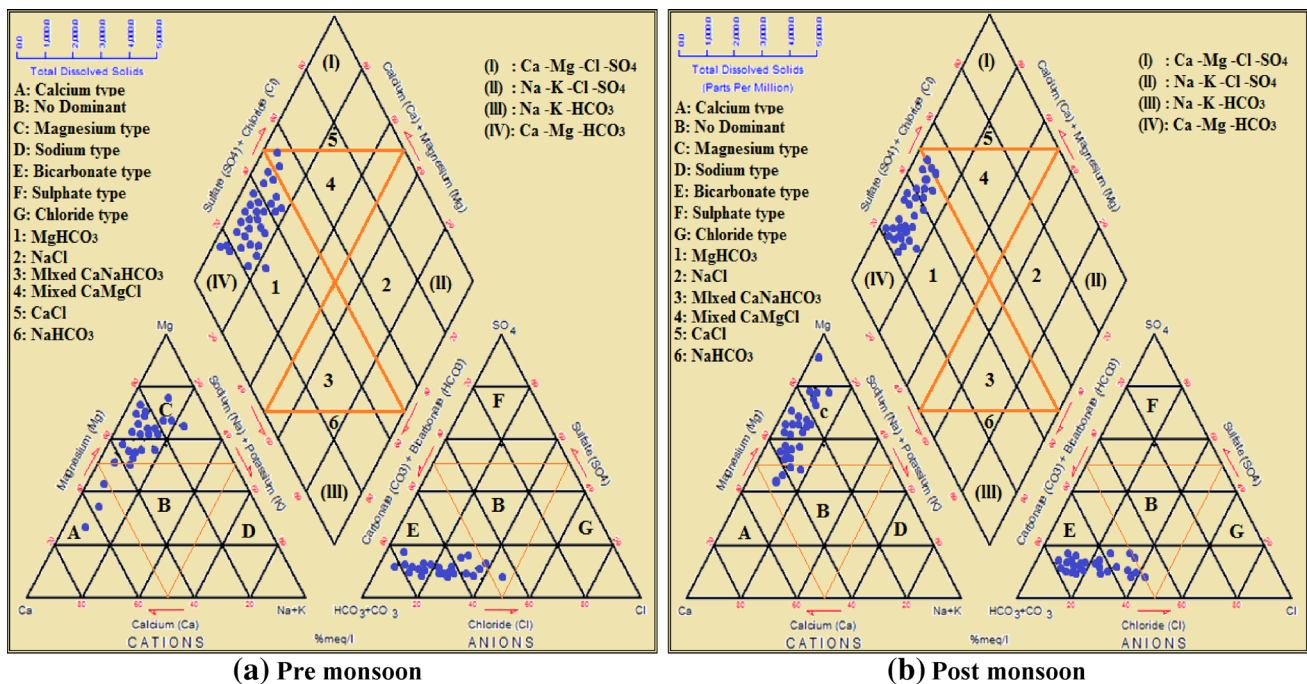

Fig. 4 Piper classification diagram illustrating the chemical composition of groundwater

Table 4 Groundwater samples characterization based on Piper diagram

Class	Groundwater types corresponding subdivisions of facies	Samples in the different category			
		Pre-monsoon		Post-monsoon	
		No. of samples	Percentage	No. of samples	Percentage
I	Ca^{2+}–Mg^{2+}–Cl^-–SO_4^{2-}	2	6.25	3	9.37
II	Na^+–K^+–Cl^-–SO_4^{2-}	NIL	NIL	NIL	NIL
III	Na^+–K^+–HCO_3^-	NIL	NIL	NIL	NIL
IV	Ca^{2+}–Mg^{2+}–HCO_3^-	30	93.75	29	90.63
1	HCO_3^-–CO_3^{2-} and Ca^{2+}–Mg^{2+} (temporary hardness); magnesium bicarbonate type (carbonate hardness exceeds 50 %)	30	93.75	29	90.63
2	Cl^-–SO_4^{2-} and Na^+–K^+ (saline); sodium chloride type (non-carbonate alkali exceeds 50 %)	NIL	NIL	NIL	NIL
3	Mixing zone (Ca^{2+}–Na^+–HCO_3^-); base ion exchange processes	NIL	NIL	NIL	NIL
4	Mixing zone (Ca^{2+}–Mg^{2+}–Cl^-); reverse ion exchange processes	2	6.25	3	9.37
5	Cl^-–SO_4^{2-} and Ca^{2+}–Mg^{2+} (permanent hardness); calcium chloride type (non-carbonate hardness exceeds 50 %)	NIL	NIL	NIL	NIL
6	HCO_3^-–CO_3^{2-} and Na^+–K^+ (alkali carbonate); sodium bicarbonate type (carbonate alkali exceeds 50 %)	NIL	NIL	NIL	NIL

Table 5 Water quality index classification

Sl. no.	WQI	Status	Pre-monsoon		Post-monsoon	
			No. of samples	Percentage	No. of samples	Percentage
1.	0–25	Excellent	NIL	NIL	NIL	NIL
2.	26–50	Good	2	6.25	6	18.75
3.	51–75	Poor	22	68.75	11	34.38
4.	76–100	Very poor	7	21.87	13	40.63
5.	>100	Unfit	1	3.13	2	6.25

with eigenvalues >1.0 are considered significant (Shrestha and Kazama 2007). In this study, PCA was performed on the standardized dataset among the variables and the PC scores extracted by the scree plot method as shown in Fig. 6a, b and obtained four PCs which explained 80.1 and 75.7 % of the total variance for pre-monsoon and post-monsoon, respectively, through varimax rotation.

Principal components (PCs) corresponding to absolute loading values of >0.75 (marked bold in the table) and additionally second level of interpretation (bold plus italics) are taken into consideration as statistically significant in the interpretation by PCA. The calculated component loadings, cumulative percentage, percentages of variance and communality explained by each factor are listed in Table 7.

During pre-monsoon, PC1 explained 28.0 % of the total variance was strong positive correlation with TH, Mg^{2+} and SO_4^{2-} and moderately with EC, TDS and Na^+ reflects lithogenic factor. This condition can be associated with silicate weathering in addition to dolomite, limestone and pyrite dissolution (Okiongbo and Douglas 2015). The

high-positive loading of Mg^{2+} and SO_4^{2-} with TH indicates permanent hardness. Sulphate ions are associated with higher concentration of Mg^{2+} and Na^+ acts as a laxative and may cause gastric disorders (Montgomery 1985; Herojeet et al. 2015). PC2 (25.9 % of total variance) has strong positive loading with EC, TDS, Cl^-, moderate positive loading NO_3^- and inversely proportional with pH could be conditionally named as anthropogenic factors. The positive loading of Cl^- and NO_3^- may be due to industrial and domestic wastes and agricultural runoff (Dinkaa et al. 2015; Ghosh et al 2010). The applications of fertilizer such as anhydrous ammonium chloride have main elemental components of N and Cl. The negative loading of pH is associated with organic matter oxidation related to anthropogenic activities (Krishnaraj et al. 2011). PC3 was strongly negative weighted on Ca^{2+} and moderate positive score on Na^+, K^+ and HCO_3^- accounts for 16.1 % of the total variance related to natural factor. For instance, a strong negative loading of Ca^{2+} reflects the cation exchange reactions leading to adsorption of Ca^{2+} on clay minerals and simultaneous

48

Sustain. Water Resour. Manag. (2016) 2:39–53

Table 6 Calculation of WQI for individual water samples

Sample no.	Pre-monsoon WQI		Post-monsoon WQI		Sample no.	Pre-monsoon WQI		Post-monsoon WQI	
	Values	Class	Values	Class		Values	Class	Values	Class
1	66.06	Poor	63.93	Poor	17	54.42	Poor	62.14	Poor
2	63.82	Poor	71.15	Poor	18	59.13	Poor	86.45	Very poor
3	96.05	Very poor	84.28	Very poor	19	84.06	Very poor	48.63	Good
4	69.06	Very poor	75.09	Very poor	20	54.3	Poor	63.31	Poor
5	75.6	Very poor	47.44	Good	21	64.22	Poor	41.24	Poor
6	79.1	Very poor	43.87	Good	22	56.78	Poor	43.06	Good
7	59.71	Poor	63.08	Poor	23	62.6	Poor	55.73	Poor
8	94.94	Very poor	58.14	Poor	24	63.81	Poor	99.96	Very poor
9	47.72	Good	41.18	Good	25	60.38	Poor	75.49	Very poor
10	56.63	Poor	109.01	Unfit	26	59.51	Poor	57.17	Poor
11	55.21	Poor	79.31	Very poor	27	57.13	Poor	81.54	Very poor
12	58.73	Poor	98.07	Very poor	28	68.44	Poor	75.51	Very poor
13	54.08	Poor	74.99	Very poor	29	75.2	Very poor	57.01	Poor
14	46.16	Good	83.4	Very poor	30	74.6	Poor	84.43	Very poor
15	72.15	Poor	88.04	Very poor	31	101.67	Unfit	121.84	Unfit
16	59.01	Poor	61.29	Poor	32	62.79	Poor	36.14	Good
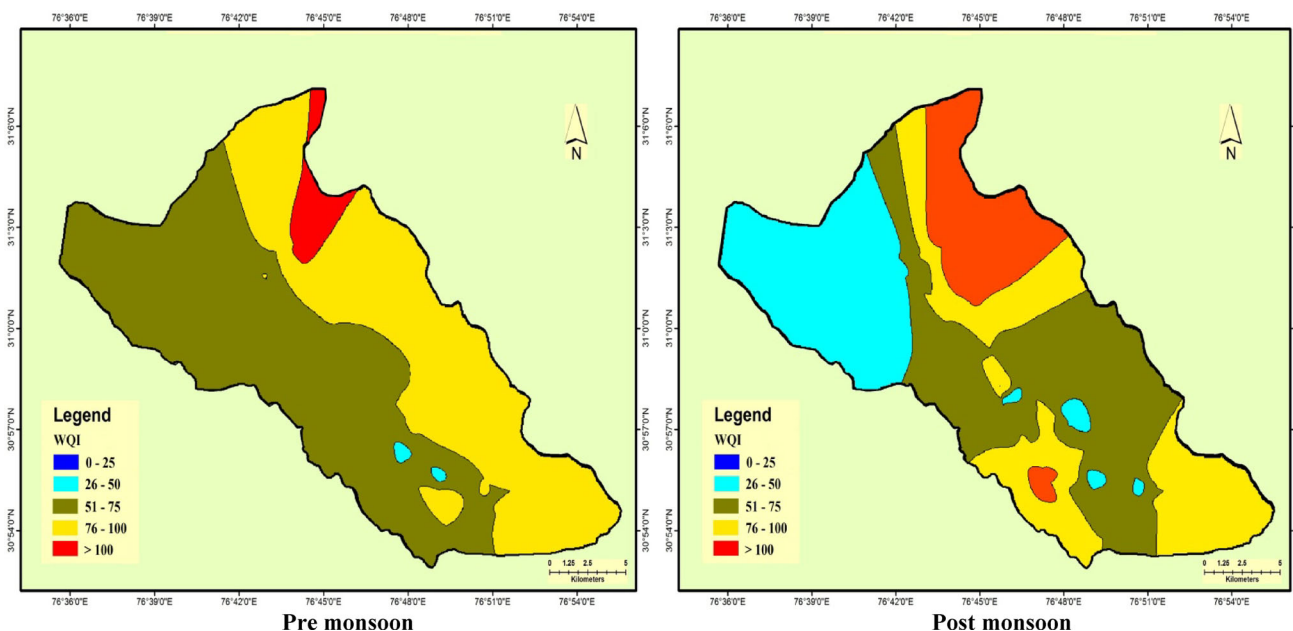
Fig. 5 Variation of WQI in groundwater

releasing of Na^+ and K^+ ions. The strong loading of HCO_3^- ions with alkali earth metals supports the view of natural weathering sources (Srivastava and Ramanathan 2008). Additional 10.1 % of the total variance explained PC4 having strong negatively weighted on PO_4^{2-} and weak negative loading with NO_3^-. This may be attributed to anthropogenic activities such as irrigated agricultural activities and domestic wastes.

Also, the PCA of data obtained for post-monsoon extracted four PCs which accounted 75.7 % of the total variance. PC 1 explained 34.3 % of the total variance with strong positive loading on Ca^{2+}, Cl^- and moderate positive loading with Na^+ and SO_4^{2-} is associated with various hydro geochemical processes resulting in high TDS (mineralized water). It indicates natural weathering of more soluble minerals like calcite, feldspar and chloride and
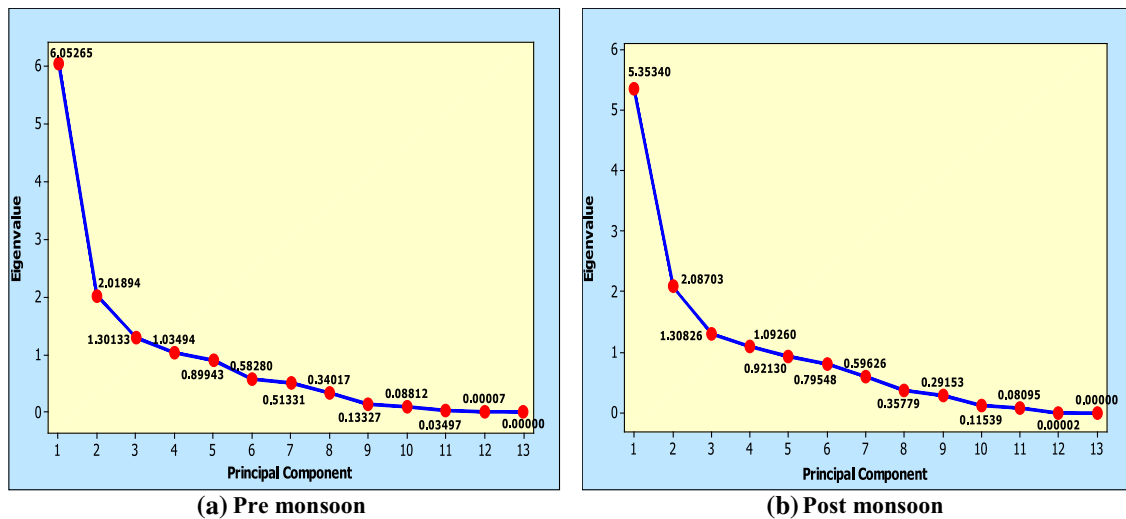
Fig. 6 Scree plot extracting principal component

Table 7 Varimax rotated component matrix of analysed groundwater samples

Variables	Component (pre-monsoon)					Component (Post-monsoon)				
	PC1	PC2	PC3	PC4	Communality	PC1	PC2	PC3	PC4	Communality
pH	−0.308	**−0.582**	−0.041	−0.093	0.444	−0.264	0.268	0.024	*0.553*	0.448
EC	*0.519*	**0.794**	0.211	−0.028	0.946	**0.933**	−0.157	0.222	−0.125	0.960
TDS	**0.523**	**0.793**	0.207	−0.027	0.945	**0.933**	−0.158	0.223	−0.124	0.960
TH	**0.913**	0.296	0.001	−0.004	0.922	0.235	**−0.949**	−0.053	0.022	0.960
Ca^{2+}	−0.069	0.371	**−0.754**	−0.269	0.784	**0.794**	0.031	−0.021	0.111	0.644
Mg^{2+}	**0.915**	0.171	0.240	0.081	0.930	0.079	**−0.986**	−0.051	−0.000	0.981
Na^+	*0.572*	0.234	*0.625*	−0.328	0.880	*0.696*	−0.222	0.463	−0.155	0.772
K^+	0.104	0.115	*0.652*	0.085	0.456	0.071	0.009	*0.683*	−0.104	0.482
HCO_3^-	0.356	0.442	*0.572*	−0.357	0.777	0.454	0.026	*0.732*	−0.194	0.780
Cl^-	0.315	**0.844**	−0.191	0.104	0.860	**0.892**	−0.098	−0.110	−0.014	0.818
NO_3^-	−0.354	*0.660*	0.092	−0.304	0.663	0.115	−0.209	−0.066	**0.845**	0.776
SO_4^{2-}	**0.798**	0.307	0.417	−0.101	0.916	*0.676*	−0.348	0.281	−0.059	0.661
PO_4^{2-}	0.008	−0.063	−0.137	**−0.929**	0.885	−0.016	0.080	*0.747*	0.189	0.601
Eigen value	6.0526	2.0189	1.3013	1.0349		5.3534	2.087	1.3083	1.0926	
Cumulative % of variance	28.0	53.9	70.0	80.1		34.3	51.4	66.6	75.7	
% of variance	28.0	25.9	16.1	10.1		34.3	17.1	15.2	9.0	

various ion exchange processes in the groundwater system. PC 2 explained 17.1 % of the total variance shows strong negative loading of TH and Mg^{2+}, and may be attributed to natural factor contributing from the weathering of magnesium bearing minerals. PC 3 (10.1 % of the total variance) was explained by moderate positive score with PO_4^{2-}, HCO_3^- and K^+. PC 4 was responsible for 9.0 % of the total variance have strong positive loading with NO_3^- and moderate loading with pH. Both PC3 and PC4 may be attributed to anthropogenic activities. It indicates the

leaching of agricultural runoff (NPK fertilizer) and seepage of wastewater due to lack of proper sewerage system.

Cluster analysis (CA)

CA is used to detect the similarity group between 32 sampling points for pre-monsoon and post-monsoon. CA rendered a dendrogram in Fig. 7a, b, grouping all the sampling points into four cluster significance at (D_{link}/D_{max}) × 100 < 90 for pre-monsoon and ($D_{link}/$
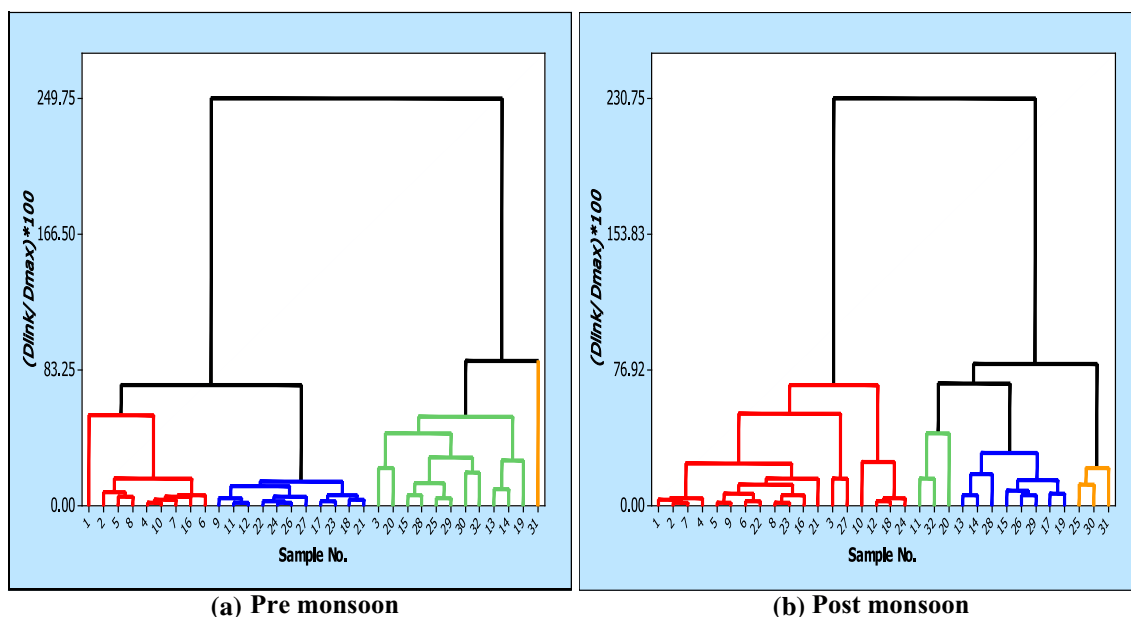
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Sustain. Water Resour. Manag. (2016) 2:39–53

Fig. 7 Hierarchical dendogram of sampling locations of groundwater

Table 8 Average values for the water quality parameters for each cluster

Cluster	Pre-monsoon				Post-monsoon			
	Cluster 1 (1, 2, 5, 8, 4, 10, 7, 16, 6)	Cluster 2 (9, 11, 12, 22, 24, 26, 27, 17, 23, 18, 21)	Cluster 3 (3, 20, 15, 28, 25, 29, 30, 32, 13, 14, 19)	Cluster 4 (31)	Cluster 1 (1, 2, 7, 4, 5, 9, 6, 22, 8, 23, 16, 21, 3, 27, 10, 12, 18, 24)	Cluster 2 (11, 32, 20)	Cluster 3 (13, 14, 28, 15, 26, 29, 17, 19)	Cluster 4 (25, 30, 31)
Parameter								
pH	7.98	7.38	7.46	7.3	7.46	7.36	7.38	7.29
EC	584.89	842.0	1185.46	1513	613	941	1008.37	1306.33
TDS	378.44	545.09	767.91	992	396.5	609.33	651.63	846.33
TH	233.11	302.91	341.09	622	358.67	312	379.25	584
Ca^{2+}	75.79	71.72	76.15	59.71	63.84	70.81	110.32	103.16
Mg^{2+}	38.40	56.42	64.65	137.2	71.93	58.85	65.62	117.32
Na^+	21.04	27.2	49.81	84	22.14	42.37	31.73	54.33
K^+	1.97	2.0	3.03	5.2	1.22	8.53	1.27	2.77
HCO_3^-	96.67	109.45	143.46	152	114.22	187.33	130.75	160.67
Cl^-	6.41	12.83	21.96	26.84	9.05	14.25	25.59	28.17
NO_3^-	2.19	3.16	3.96	0.59	4.05	1.22	5.02	2.83
SO_4^{2-}	10.73	12.34	14.89	27.01	11.30	14.32	13.49	23.56
PO_4^{2-}	0.18	0.12	0.21	0.14	0.02	0.04	0.03	0.023

D_{max}) × 100 < 80 for post-monsoon. The clustering procedure generated four groups in a very convincing way, as the sampling locations at each groups have similar characteristic features.

However, three clusters (C1, C2, C3) for pre-monsoon and four clusters (C1, C2, C3, C4) for post-monsoon were characterized by mixed features where sampling locations were included randomly in each cluster without any specific trends. The pattern formed by each clusters cannot be sought for explanation only considering certain special

parameters. Therefore, the specific tracers for each pattern representing individual clusters can be clarified by calculating the average values of each chemical parameter belonging to individual clusters. The results are presented in Table 8.

During pre-monsoon, Cluster 1 was characterized by highest levels of pH and higher tracer of Ca^{2+} and Cluster 2 has no specific tracers which depict natural water quality influenced by rock water interaction. Cluster 3 has highest tracers on Ca^{2+}, NO_3^-, PO_4^{2-} and higher value of K^+

which can be marked by anthropogenic activities contributing from agricultural and domestic sources. Cluster 4 was characterized by single sampling location having highest level of EC, TDS, TH, Mg^{2+}, Na^+, K^+, HCO_3^- and Cl^- may be concluded mixed factor (natural and anthropogenic sources) influencing the hydrochemistry.

The dataset obtained in post-monsoon also statistically displayed four clusters. Cluster 1 was detected as the biggest group of sampling sites where the average values for all the water quality parameters are less than the other remaining clusters except pH reflects natural quality water. Cluster 2 was characterized by highest tracers of K^+, HCO_3^- and PO_4^{2-}. Cluster 3 confirmed the highest levels of Ca^{2+}, Cl^- and NO_3^- and higher level of PO_4^- indicates anthropogenic activities. The sampling location group in Cluster 2 and 3 was almost similar with Cluster 3 of pre-monsoon. Finally, Cluster 4 formed a pattern of highest level of EC, TDS, TH, Mg^{2+}, Na^+, Cl^- and SO_4^{2-} and lowest pH reflects natural and anthropogenic sources controlling the groundwater chemistry. High concentrations of Cl^- and SO_4^{2-} have negligible concentration of HCO_3^- resulting low pH in groundwater (Hounslow 1995).

However, it was observed that some sampling locations for both seasons clustered under different group indicate different sources of pollution from point or nonpoint sources localized from the surrounding area or microsite effect of constituent bearing rock minerals. The findings obtained from PCA and CA indicate water chemistry were strongly controlled by natural factors like weathering of minerals, ion exchange and rocks water interaction and anthropogenic factors mainly agricultural, domestic and industrial wastes. Even though there are some differences between the CA and PCA results, a good agreement between the two statistical techniques is evident in all the datasets analyzed.

Conclusion

The present study highlighted the usefulness of multivariate statistical techniques, WQI and conventional graphical representations for interpreting or understanding the factors controlling water chemistry, geochemical and hydrochemical evolution of groundwater system. The overall water samples are suitable for drinking and domestic purposes, except for some selected sites where parameters like pH, TH and Mg^{2+} were above the permissible limit of BIS. The Piper plot classified 93.75 and 90.83 % of samples for both seasons under Ca^{2+}–Mg^{2+}–HCO_3^- water types indicating temporary hardness and remaining 6.25 and 9.37 % under Ca^{2+}–Mg^{2+}–Cl^-–SO_4^{2-} mixed type of water. The plot also highlighted the influence of inverse or reverse ion exchange and dominance of alkaline earth metals over the alkalis and weak acidic anions over strong acidic anions in the study area. The WQI shows groundwater samples falling in poor to unfit class in both seasons due to high water table, valley fill aquifer formation, lesser soil filter media and lack of proper drainage system and there is also rise in good class in post-monsoon which may be attributed to recharge of aquifer during monsoon period. PCA and CA identify the groundwater chemistry was strongly controlled by natural factors namely rock water interaction, ion exchange and leaching of parent materials with minor anthropogenic factors like agricultural runoff and seepage of industrial and domestic wastes. An integrated institutional system for groundwater conservation and recharging measures will be affirmative solution for sustainable water resources management.

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52

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