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# Principal component and multivariate statistical approach for evaluation of hydrochemical characterization of fluoride-rich groundwater of Shaslar Vagu watershed, Nalgonda District, India

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**Abstract** In order to assess the impact of fluoride-rich groundwater of Shasilair Vagu watershed on groundwater regime, more than hundred groundwater samples for pre- and post-monsoon seasons were collected from bore wells/dug wells and analyzed for major ions. Water quality analysis of major ion chemistry shows elevated concentration of fluoride in groundwater samples. The fluoride concentration ranges from 1.4 to 5.9 mg/l and 1.5 to 5.8 mg/l in pre- and post-monsoons, respectively. The result clearly shows that the seasonal variation of fluoride in groundwater is due to recharge of rain water during monsoon. The water quality data was analyzed by hydrochemical facies (Piper diagram), Gibbs plot, and various plots. Plots of Na versus Cl, Ca versus $SO_4$, and (Na+Cl)-($SO_4$+$HCO_3$) versus (Na+K-Cl) shows positive and negative values, indicating that their source of high concentration are aquifer, evapotranpiration, and other anthropogenic sources. Saturation index of halite and gypsum shows that all groundwater samples were undersaturated and suggests that carbonate minerals influence the concentration. Using multivariate statistical techniques, viz., principal component (factor analysis and cluster analysis), the analysis brought out impact of intensity of excess use of fertilizers and excess withdrawal of groundwater regime. Multivariate statistical techniques are potential tools and provide greater precision for identifying contaminant parameter linkages.

## Introduction

Contamination of the groundwater by domestic, industrial, and agricultural effluent activities is a serious problem faced by developing countries. Industrial wastes water, sewage sludge, and solid waste materials are currently being discharged in the environment; the materials enter subsurface aquifer resulting in the pollution of the irrigation and drinking water.

Fluorine is the most electronegative element in the periodic table, and it occurs in greater abundance than chlorine, copper, and lead. Majority of fluorine found in nature is present in various rocks, soils, waters, plants, slugs, fluxes, and other living organisms. High fluoride in groundwater and surface water have been reported from many parts of the world, particularly in arid and semi-arid areas of India, China, Sri Lanka, Spain, Mexico, and many countries in Africa, Western USA, and South America (Abu Rukah and Alsokhny 2004; Ayoob and Gupta 2006). High concentrations of fluoride in groundwater and surface water also result from evapotranspiration which may trigger calcite precipitation and result in a reduction in the activity of calcium ($Ca^{+2}$) (Jacks et al. 2005). Several studies have noted an increase in dissolved fluoride concentrations with increasing groundwater residence time (Apambire et al. 1997; Edmunds and Smedley 2005; Genxu and Guodong 2001; Nordstrom and Jenne 1977). Granitic rocks contain a relative abundance of fluoride-rich minerals such as micas, apatite, and amphiboles. Fluorite ($CaF_2$) is the principal fluoride mineral, mostly present as an accessory mineral in granites. Dissolution of such minerals can

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constitute a major source of fluoride in groundwater (Ramesham and Rajagopalan 1985; Reddy et al. 2009, 2010; Shaji et al. 2007). Relatively high fluoride concentrations have been found in some deeply circulating groundwater along fault lines (Kim and Jeong 2005; Kundu et al. 2001).

Factor analysis and principal component techniques are for explaining and identifying the local and regional variations in the hydrochemical process and distinguishing the geogenic and anthropogenic pollution. There are three stages in the factor analysis: (a) generation of the correlation matrix for all the variables, (b) extraction of the factors from the correlation matrix based on the correlation coefficients of the variables, and (c) rotation of these factors to maximize and minimize the relation variables.

A few researches were published in referred periodicals on dissimilar applications using principal component analysis, and multivariate statistical approach has been carried out in the different parts of India and other countries: mixing and nonmixing of groundwater (Raghunath et al. 2002), evaluation of spatial and temporal variations in water quality (Singh et al. 2004), water quality evaluation and management (Parinet et al. 2004), groundwater quality in developing urban area, industrial and municipal sewage impact on groundwater quality (Sundaray 2010), groundwater quality in coal mining area (Dhakate et al. 2013), seasonal variation of groundwater quality (Pathak and Limaye 2011), and seawater intrusions and anthropogenic pollution (Nura Umar et al. 2013).

Multivariate statistical analyses, viz., factor, cluster, and principal component analyses, were carried out to investigate the relationship among the major ion elements and factors controlling major ion element distribution in groundwater (Kouping et al. 2006) for a fluoride-rich groundwater samples. The intention underlying the use of multivariate analysis is to achieve great efficiency of data compression from the original data and to gain some information useful in the interpretation of environmental geochemical origin (Ashley and Lloyd 1978; Bengraine and Marhaba 2003; Kuppusamy and Giridhar 2006; Mathew et al. 1978; Martinez Lopez et al. 2008; Raghunath et al. 2002). Multivariate treatment of environmental data is successfully used to interpret relationship among the variables so that the environmental system could be better managed (Grande et al. 1996; Gangopadhyay et al. 2001). Factor and cluster analyses are also used to handle large water quality datasets and identify the dominant mechanisms and factors which control the groundwater chemistry (Kim et al. 2005; Senthilkumar et al. 2008). Factor analysis reveals interrelations among collected samples and variables used in the analysis. Factor and cluster analyses were carried out to understand the mechanism controlling the groundwater pollution due to geogenic or anthropogenic activities and to identify the processes that are responsible for groundwater pollution/contamination.

In the present study, the fluoride-rich groundwater quality characteristics has been evaluated using factor, cluster, and principal component analysis approach with varimax rotation of normalization (Kaiser 1960) using the first three factors, which is applied in the present study. Such analysis was useful in understanding the interrelations among collected samples and variables used in the analysis. Factor and cluster analyses were carried out to understand the mechanism controlling the groundwater pollution.

## Study area

The study area is in semi-arid region of Shasler Vagu watershed situated at Krishna River basin covering the Survey of India Toposheet Nos. 56L/13 and 56 P/1. The area geographically lies between north latitudes from 16° 55′ 00″ to 17° 00′ 00″ and east longitudes from 78° 45′ 00″ to 79° 10′ 00″ and politically placed distribution of Marriguda, Nampally and Gurrampode Mandals, Nalgonda District, Telangana, India (Fig. 1). The drainage pattern of the area is dentritic to subdendritic pattern. Its area is 365 km$^2$, slightly undulating terrain with slight to moderate slopes (2 to 3%), and the annual normal rainfall is 737 mm receiving mainly during south-west and north-east monsoons, which occur during June to September. The average maximum and minimum temperatures are 40 and 28 °C, respectively. The day temperature may occasionally exceed 45 °C during the month of May–June, while during winters, the temperature may drop to about 10 °C.

## Geology and hydrogeology of the study area

Geology of the area comprises of Archaean older metamorphics, Peninsular gneissic complex, and younger intrusive which includes gabbro, dolerite and hornblendite, apatite, pegmatite, quartz and epidote veins, and alluvium (Fig. 1). Older metamorphic rocks include hornblende schists, amphibolites, banded magnetite quartzite, metabasalt, and biotite schist. These rocks occur as enclaves, rafts, linear discontinuous bands, lensoidal, or undigested material within the country rock. Biotite schist rock occurs as lenses, schlieren, and inclusion within the migmatitic gneisses. The exposures of biotite schist are oval shaped trending NNW-SSE in the study area. Low-grade metamorphosed basic igneous rock occurs as enclaves within the porphyritic granite, while banded magnetite quartzite are narrow bands trending NW-SE. Hornblende and amphibolite schist are mainly consists of hornblende and plagioclase as essential mineral, while quartz, sphene, sericite, and magnetite occur as accessory minerals. These rocks occur as elongated in N-S direction with vertical dip. The migmatite rocks are medium to coarse gained in nature and are well

**Fig. 1** Key map of the study area showing geology, major and minor lineaments
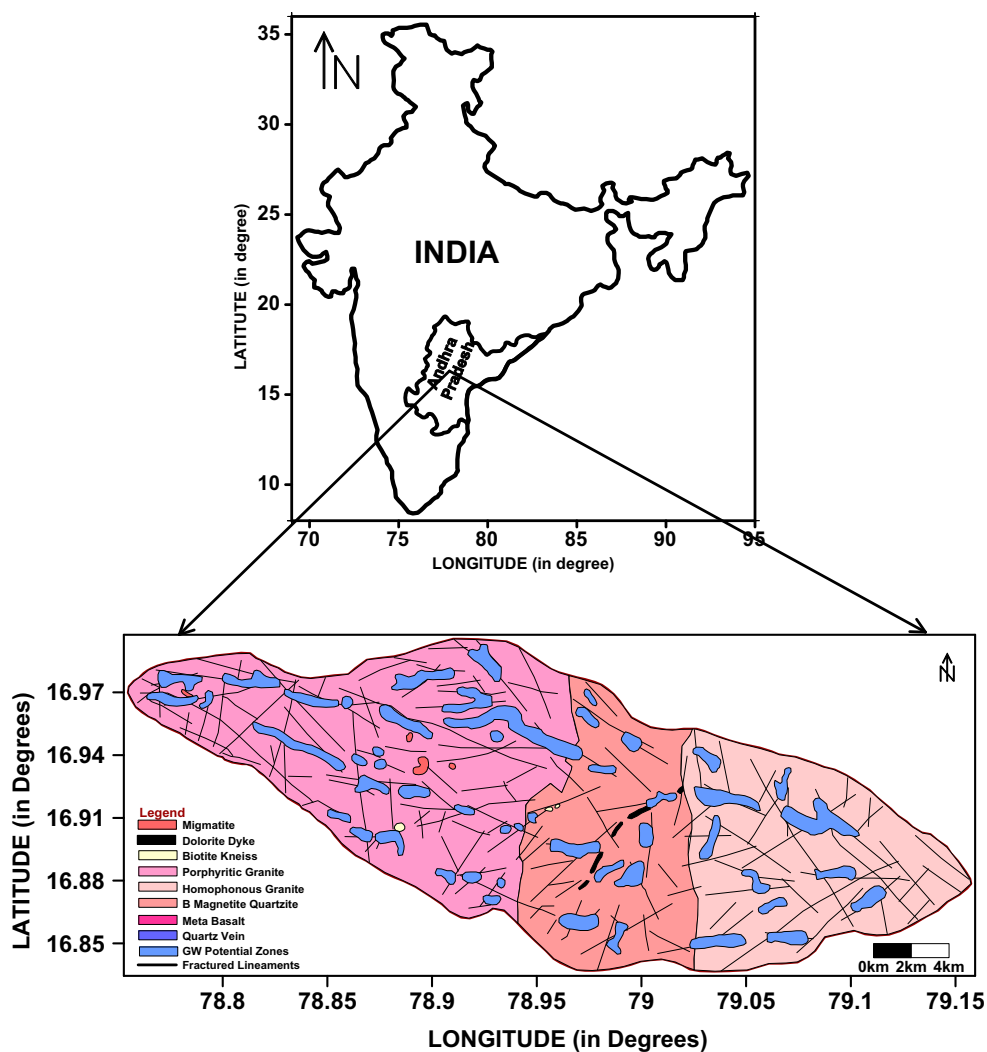


exposed, while biotite gneisses are generally banded in nature and occur as sheets and inselbers in low topographic areas. Alluvium occurs along the stream channels and commonly consists of silts, sand, and gravel. The stratigraphic succession based on the field observations is given in Table 1.

The groundwater in the area is being tapped by shallow dug well and deep bore well. The depth of shallow dug well ranges from 5 to 20 m below ground level, whereas deep bore depth ranges from 30 to 50 m below ground level. Groundwater exists under unconfined conditions in the weathered zone as well as under semi-unconfined conditions to confined conditions in the fractured zone. The yield of shallow dug well ranges from 50 to 70 $m^3$/day and sustains pumping for 2–4 h per day and requires 12–48 h for recuperation, whereas deep bore well yield ranges from 30 to 100 $m^3$/day. The bore well tapping groundwater from deep fractures yield more water. The weathered zone in the study area ranges from 5 to 13 m, while fracture zone ranges from 13 to 40 m. The depth of water level varies from 3.8 to 14 m below ground level, shallow water level was observed along the valley portion, and deeper water level was observed on elevated part of

the area. In general, the groundwater movement is from high to low topography. The groundwater prospects are more along the valleys and low-lying areas and less along high topographic areas. Recharge areas are identified at topographical high places, basin boundaries, and at steep slope areas, where groundwater levels is high and observed in western, north-western, and

**Table 1** Geostratigaphic succession of the study area

| Age | | Rock types |
| --- | --- | --- |
| Archaean | Intrusive rocks | Acidic: pegmatites/quarze veins/-epidote veins/aplite/pink granite |
| | | Basic: gabbro/dolerites/hornblende |
| | Peninsular gneissic complex rocks | Granite gneisses (quartze-feldspar-biotite gneiss/quartze-feldspar-hornblende gneiss/-migmatites) |
| | Older metamorphic rocks | Amphibolites schist, banded magnetite quartzite, chlorite-actinolite schist/biotite schist |

southern parts of study area. Discharge areas are located in topographic low areas, and the water level is found close to surface located along valley floors.

## Materials and methods

Total 107 groundwater samples were collected from bore wells during pre- and post-monsoons seasons following the standard methods (Brown et al. 1983; APHA 1995). The locations of the samples are shown in Fig. 2. The samples, from the deep wells in which pumps were already installed, were collected after half an hour of pumping, and the screen interval of the well represents the average sample depth. The samples were collected in 1000-ml cleaned 1–1 polyethylene bottles, and field filtration was carried out through filter papers to remove suspended solids. Each sample was then carefully sealed, labeled, and taken to laboratory at the Department of Geology, Osmania University, Hyderabad, for analyses. The standard analytical procedures were followed for analysis of physicochemical parameter and major cation and anion concentrations (i.e., pH, EC, TDS, TH, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $CO_3^{2-}$, $HCO_3^-$, $SO_4^{2-}$, $Cl^-$, and $F^-$). The accuracy of the analysis for major ions was cross-checked from the ionic balance such that the ion charge balance was within ±5% (Mandel and Shiftan 1980; Danielsson et al. 1999) for all the samples. Ions were converted from milligram per liter to milliequivalent per liter. The results of concentrations were interpreted with Piper, Gibbs, and Wilcox diagrams for predictable type of water and different irrigation indices like salinity, sodicity, and bicarbonate. The chlorinity and magnesium index hazards were also predicted by calculated methods (Szaboles and Darab 1964).

## Results and discussions

### Groundwater quality

In the study area, pH values vary from 7.3 to 8.5 and 6.7 to 8.5 for pre- and post-monsoon seasons, respectively, showing slightly acidic to mild alkaline in nature. Overall, all the

samples show pH value within the permissible limit of 6.5–8.5 (BIS 1998). Electrical conductivity (EC) concentration varies from 97.4 to 2403.7 μS/cm and 419.8 to 2585.0 μS/cm during pre- and post-monsoons, respectively. TDS concentration varies from 327 to 1528 and 299 mg/l to 1674 mg/l during pre- and post-monsoons, respectively. $Ca^{2+}$ concentration varies from 14 to 150.70 mg/l and 16 to 308.6 mg/l in pre- and post-monsoons, respectively. $Mg^{2+}$ concentrations in the groundwater samples are 1.2–146 and 4.8–114 mg/l in pre- and post-monsoons, respectively. $Na^+$ concentrations vary from 9 to 183 mg/l and 20.7–210 mg/l in pre- and post- monsoons, respectively. $K^+$ varies from 1 to 116 mg/l and 1 to 95 mg/l in pre- and post-monsoons, respectively. Total hardness (as $CaCO_3$) concentrations vary from 115.5 to 976.7 mg/l and 115 to 900 mg/l in the pre- and post-monsoons, respectively. $HCO_3$ concentrations vary from 38.4 to 543 mg/l and 145 to 702 mg/l in pre- and post-monsoons seasons, respectively. $SO_4$ concentrations vary from 10 to 220 mg/l and 19 to 254 mg/l in pre- and post-monsoons, respectively. The concentrations of $Cl^-$ vary from 7 to 404 mg/l and 12 to 561 mg/l in pre- and post-monsoons, whereas $F^-$ concentrations vary from 1.4 to 5.9 mg/l and 1.5 to 5.8 mg/l in pre- and post-monsoons, respectively. The statistical summary like minimum, maximum, mean, and standard deviation of groundwater samples for pre- and post-monsoon seasons is given in Table 2.

The sample no. 86 shows the $Ca^{2+}$ concentration more than permissible limit in pre- and post-monsoon seasons; all remaining samples are within permissible limits of 200 mg/l. $Mg^{2+}$ is present in all natural waters and most common element in the Earth's crust. The common sources are mafic minerals (i.e., amphiboles, olivine, and pyroxenes), dolomite, chlorite, magnesite, and clay minerals. It is also an important contributor to water hardness. $Mg^{2+}$ concentrations at sample no. 103 and at sample nos. 41 and 51 during pre- and post-monsoon are crossing the permissible limits while the remaining samples are within permissible limits. $Na^+$ is a common ion in minerals, commonly found in soils and minerals such as feldspars (Albite), halite (NaCl), clay, and industrial wastes. In these forms, they readily dissolve in water. It is released



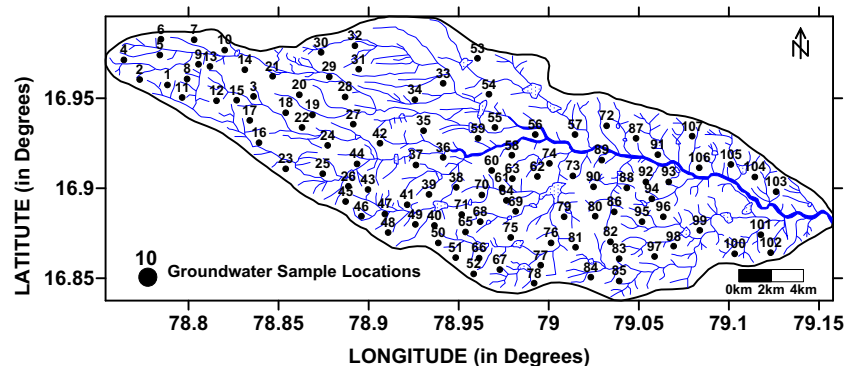**Fig. 2** Map showing the sample location in study area

**Table 2**  Summary statistics of hydrochemical concentrations in Shasler Vagu Watershed, Nalgonda District, Southern India

| Hydrochemical parameters | Pre-monsoon | | | | | Post-monsoon | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Min | Max | Mean | SD | CV | Min | Max | Mean | SD | CV |
| pH | 7.30 | 8.50 | 7.97 | 0.25 | 3140 | 6.70 | 8.50 | 7.46 | 0.36 | 2063 |
| EC | 97.40 | 2403.70 | 864.48 | 299.68 | 288 | 419.80 | 2585.30 | 1024.03 | 370.76 | 276 |
| TDS | 327.10 | 1528.10 | 657.76 | 188.15 | 350 | 299.80 | 1674.10 | 715.92 | 237.53 | 301 |
| TH | 115.50 | 976.70 | 232.62 | 106.39 | 219 | 115.00 | 900.00 | 315.06 | 139.34 | 226 |
| $Ca^{2+}$ | 14.30 | 150.70 | 48.07 | 24.00 | 200 | 16.00 | 308.60 | 61.29 | 36.86 | 166 |
| $Mg^{2+}$ | 1.20 | 145.90 | 27.27 | 20.74 | 131 | 4.80 | 114.20 | 39.03 | 22.21 | 176 |
| $Na^+$ | 9.00 | 183.00 | 84.80 | 33.13 | 256 | 20.70 | 210.00 | 80.94 | 44.27 | 183 |
| $K^+$ | 1.00 | 116.00 | 20.06 | 25.53 | 79 | 1.00 | 95.00 | 15.94 | 16.63 | 96 |
| $HCO_3^-$ | 38.40 | 542.90 | 337.78 | 90.77 | 372 | 145.00 | 701.50 | 322.60 | 104.73 | 308 |
| $CO_3^-$ | 0.00 | 30.00 | 8.80 | 8.30 | 106 | 0.00 | 9.00 | 1.67 | 2.32 | 72 |
| $Cl^-$ | 7.00 | 404.10 | 75.57 | 53.14 | 142 | 12.40 | 561.00 | 115.25 | 92.23 | 125 |
| $SO_4^{2-}$ | 9.50 | 220.10 | 36.46 | 27.89 | 131 | 19.10 | 254.30 | 67.26 | 45.85 | 147 |
| $F^-$ | 1.40 | 5.90 | 3.05 | 0.95 | 322 | 1.50 | 5.80 | 2.98 | 0.89 | 335 |
| Anhydrite | −2.93 | −1.28 | −2.27 | 0.32 | – | −3.43 | −1.51 | −2.59 | 0.30 | – |
| Dolomite | −1.63 | 3.01 | 0.17 | 0.82 | – | −1.18 | 2.33 | 1.07 | 0.70 | – |
| Gypsum | −2.70 | −1.05 | −2.04 | 0.32 | – | −3.19 | 2.45 | −2.31 | 0.55 | – |
| Halite | −7.87 | 6.91 | −6.65 | 1.40 | – | −7.91 | −6.01 | −6.88 | 0.40 | – |

The values are in mg/l except pH and EC in μS/cm

*SD* standard deviation, *CV* coefficient of variance

slowly upon dissolution of rocks. The $K^+$ is released commonly by weathering of feldspar minerals (orthoclase and microcline), feldspathoids, micas, and clay. Potassium is gradually released from rocks. Many of these rocks are relatively soluble, and potassium concentrations in groundwater increase with time. Potassium being an important fertilizer, there are no health-based drinking water standards for potassium, neither has a secondary drinking standard. Total hardness (TH) is governed by the presence of cations such as calcium and magnesium and anions such as carbonate, bicarbonate, chloride, and sulfate in water. Sample nos. 69 and 103 for pre-monsoon and sample nos. 41, 51, 86, 98, and 99 are crossing the permissible limits during post-monsoon season. Majority of the samples fall within the permissible limits of 600 mg/l (BIS 1998). The sources of $HCO_3$ are limestones and dolomites.

The source of bicarbonate is attributed to the dissociation of the carbonic acid. Oxidation of organic matter by microbes generates $CO_2$ which then combine with water to form carbonic acid. The high carbonate indicated that intense chemical weathering has taken place in the drainage basin due to microbial activity. The sources of $SO_4^{2-}$ are oxidation of sulfide ores, gypsum, and anhydrides. It occurs in water as the inorganic sulfate salts as well as dissolved gas ($H_2S$) sulfate. High concentration of sulfates indicated pollution from application of fertilizers to agricultural lands. In the study area, sulfate concentrations varied from 10 to 220 mg/l and 19 to 254 mg/l in pre- and post-monsoons, respectively, within permissible limits of 400 mg/l (BIS 1998). The $Cl^-$ is present in all natural waters, and the sources are igneous and sedimentary rocks (evaporates), usually in relatively small amount of

**Table 3**  Ranges for fluoride, classification, and associated risk for human health

| Range of F (mg/l) | Classification | Pre-monsoon | | Post-monsoon | | Associated risk |
|---|---|---|---|---|---|---|
| | | No. of samples | % of samples | No. of samples | % of samples | |
| ≤1.5 | Safe areas | 2 | 1.87 | 2 | 1.87 | WHO permissible limits |
| 1.5–3.0 | Low-risk areas | 55 | 51.4 | 56 | 52.33 | Dental fluorosis |
| 3.0–5.0 | High-risk areas | 48 | 44.86 | 47 | 43.92 | Dental fluorosis and mild skeletal fluorosis |
| 5.0–10 | Very-high-risk area | 2 | 1.87 | 2 | 1.87 | Severe mild skeletal fluorosis |
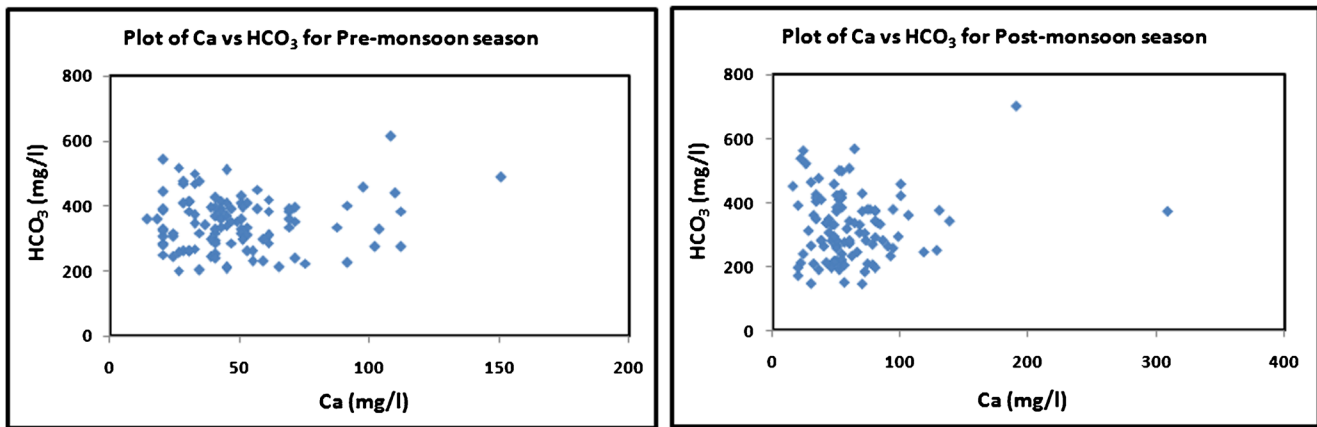
**Fig. 3** Scatter plot of Ca vs HCO₃ for pre- and post-monsoon seasons

weathering and subsequent release of ions from the underlying rocks and human sources (Freeze and Cherry 1979). High concentration of chloride content imparts a salty taste to water. About all samples fall within the permissible limits of 250 mg/l (BIS 1998). The most common source of $F^-$ is apatite, and the natural concentration of fluoride commonly varied from 0.01 to 10.00 mg/l (Freeze and Cherry 1979). Fluoride in excessive concentration may cause dental defects, affect bone structure, and causes acute fluorosis. It is notable that all samples are crossing the permissible limits of 1.5 mg/l (BIS 1998). Therefore, the groundwater is not suitable for the drinking purposes. The ranges of fluoride concentration with numbers of samples/percentage of samples with its impact on human health are categorized in Table 3. The natural and anthropogenic origin of nitrate in the study area was due to leaching of organic substances from weathered soil and excessive use of nitrate fertilizers in agricultural field.

**Hydrogeochemical evaluation**

Concentration of different major elements and their interrelationship were studied to understand and illustrate the hydrochemical processes that were involved in aquifer domain during the evolution of different groundwater facies.

High sodium content among cations in the groundwater of two seasons (Table 2) could be due to weathering of silicate rocks such as granite and gneisses, which was further enhanced by evapotranspiration processes as proven in the scatter plot of $Ca^{++}$ versus $HCO_3^-$; $Na^+$ versus $Cl^-$ and $Ca^{++}$ versus $SO_4^-$ for pre- and post-monsoon seasons, respectively (Figs. 3, 4, and 5). Where most of the samples were plotted in a horizontal line parallel to x-axis reflecting evapotranspiration process played crucial role in increasing the concentration of all the species in the water. The plot of Ca versus HCO₃ and $Ca^{++}$ versus $SO_4^-$ (Figs. 3 and 5) revealed that the dissolution of dolomite was one of the prime processes involved in enrichment of $Ca^{++}$ (Pophare and Dewalkar 2007; Stallard and Edmond 1983; May and Loucks 1995). Similarly, plot of Ca versus SO₄ for pre- and post-monsoons (Fig. 5) does not show strong correlation; this indicate that the Ca and SO₄ are independent and derived from different source materials. The plot of (Na+Cl)-(SO₄+HCO₃) versus (Na+K-Cl) for pre-monsoon season shows that the sum of (Na+Cl)-(SO₄+HCO₃) are negative, indicating the different source for their high concentration, while the sum of (Na+K-Cl) for pre-monsoon shows that most of them are positive, indicating that the source are from aquifer material. Similarly for post-monsoon, the sum of (Na+Cl)-(SO₄+HCO₃) are again negative, indicating the different
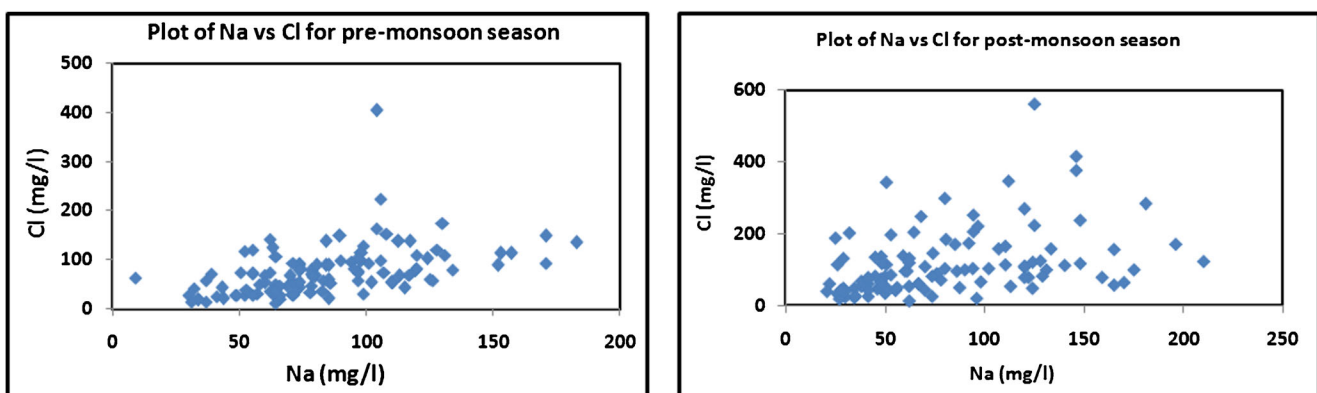


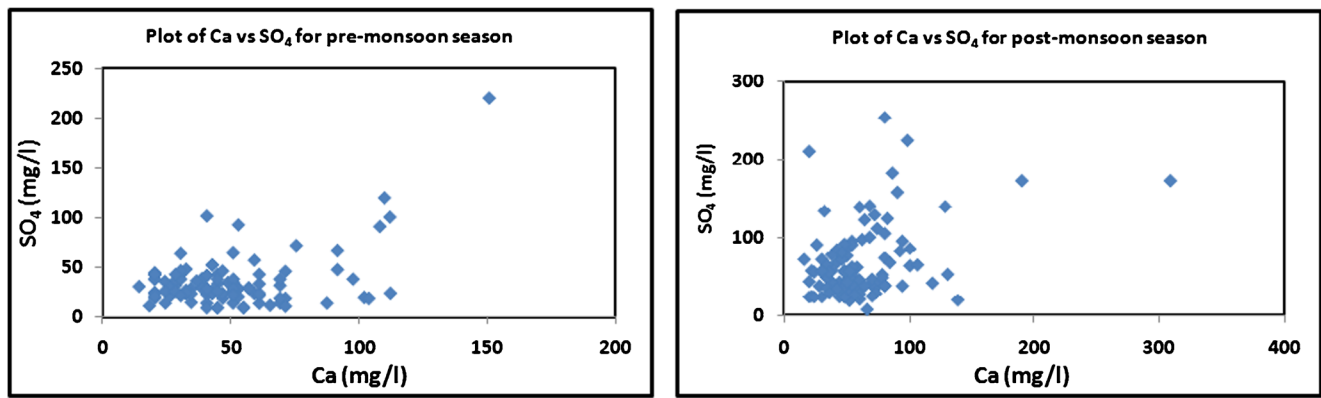**Fig. 4** Scatter plot of Na vs Cl for pre- and post-monsoon seasons

**Fig. 5** Scatter plot of Ca vs SO₄ for pre- and post-monsoon seasons

source for their high concentration, while the sum of (Na+K-Cl) for post-monsoon shows that half of values are negative and positive, indicating that half of the sample concentrations are derived from aquifer material, while for half of the samples, the sources are different. The plot of (Na+Cl)-(SO₄+HCO₃) versus (Na+K-Cl) for pre- and post-monsoon seasons are shown in Fig. 6. The correlation matrixes between different elements for pre- and post-monsoon seasons are given in Tables 4 and 5. The matrixes do not show any strong correlation among each other.

**Piper trilinear diagram**

The hydrogeochemistry of groundwater can be understood by plotting the major cations and anions on the Piper trilinear diagram (Piper 1944). This diagram reveals similarities and differences among groundwater samples because those with similar qualities will tend to plot together as groups (Todd 2001). This diagram is very useful in bringing out chemical relationships among groundwater in more definitive terms (Fig. 7a, b). The geochemical evolution can be understood from the Piper plots, which has been divided into six

subcategories, viz., type I calcium-magnesium-bicarbonate, type II calcium-chloride, type III calcium-sodium-bicarbonate, type IV calcium-sodium-chloride, type V calcium-magnesium-chloride, and type VI sodium-bicarbonate (Table 6). Majority of the samples show the water type of Ca+Mg type indicating 60 and 74% in pre- and post-monsoon seasons, while 40 and 26% shows the Ca-Cl type water during pre- and post-monsoon seasons, and 90 and 33% shows Ca-Na-Cl type water during pre- and post-monsoon seasons, respectively (Table 6).

*Gibbs diagram*

For the groundwater chemistry and the relationship of the chemical components of water to their respective aquifers such as chemistry of the rock types, chemistry of precipitated water, and rate of evaporation, Gibbs (1970) has suggested a diagram in which ratio of dominant anions and cations are plotted against the value of TDS. Gibbs diagrams, representing the ratio 1 for cations $[(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})]$ and ratio 2 for anions $[Cl^-/(Cl^- + HCO_3^-)]$ as a function of TDS and are widely employed to assess the functional
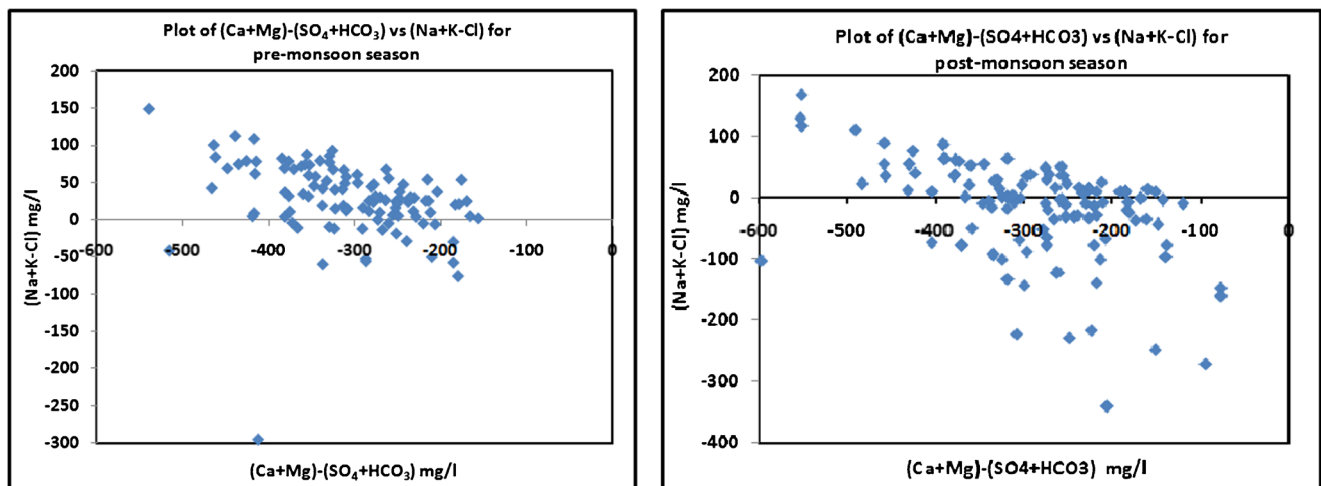


**Fig. 6** Scatter plot of (Ca+Mg)-(SO₄+HCO₃) vs (Na+K-Cl) for pre- and post-monsoon seasons

**Table 4** Correlation matrix for pre-monsoon season

| | pH | TDS | Na | K | Ca | Mg | Cl | SO$_4$ | F | HCO$_3$ | CO$_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | | | | | | | | | | |
| TDS | −0.03 | 1 | | | | | | | | | |
| Na | 0.07 | 0.65 | 1 | | | | | | | | |
| K | −0.09 | 0.49 | 0.27 | 1 | | | | | | | |
| Ca | −0.22 | 0.36 | −0.11 | 0.03 | 1 | | | | | | |
| Mg | 0.09 | 0.62 | 0.12 | 0.06 | 0.01 | 1 | | | | | |
| Cl | −0.06 | 0.82 | 0.44 | 0.28 | 0.52 | 0.58 | 1 | | | | |
| SO$_4$ | −0.09 | 0.66 | 0.21 | 0.15 | 0.45 | 0.60 | 0.69 | 1 | | | |
| F | 0.01 | −0.19 | −0.24 | −0.14 | 0.09 | −0.13 | −0.07 | −0.10 | 1 | | |
| HCO$_3$ | −0.01 | 0.85 | 0.62 | 0.44 | 0.09 | 0.53 | 0.47 | 0.34 | −0.25 | 1 | |
| CO$_3$ | 0.45 | −0.03 | 0.07 | 0.07 | −0.16 | 0.00 | −0.10 | −0.17 | −0.04 | −0.07 | 1 |

sources of dissolved chemical constituents, such as precipitation dominance, rock dominance, and evaporation dominance (Gibbs 1970). The chemical data of groundwater samples are plotted in the Gibbs diagram (Fig. 8a, b). Majority of the samples fall in the evaporative dominance. Evaporation increases the salinity by increasing Na$^+$ and Cl$^−$ in relation to increase of TDS. The anthropogenic activities (agricultural fertilizers and irrigation return flows) also influence the evaporation by increasing Na$^+$ and Cl$^−$ and thus TDS. Few samples were represented by rock dominance and precipitation dominance (Fig. 8a, b).

## Saturation index

Saturation indexes are used to evaluate the degree of equilibrium between water and minerals. Changes in saturation state are useful to distinguish different stages of hydrochemical evolution and help in identifying which geochemical reaction is important in controlling water chemistry (Drever 1997; Langmuir 1997; Coetsiers and Walraevens 2006). The saturation index of a mineral is obtained from the following equation (Garrels and Mackenzie 1967):

$$SI = \log\left(\,^{IAP}/_{Kt}\right)\text{————}\tag{1}$$

where IAP is the ion activity product of the dissociated chemical species in solution, and $Kt$ is the equilibrium solubility product for the chemical involved at the sample temperature.

A saturation index (SI) less than 0 indicates that the groundwater is undersaturated with respect to that particular mineral. An SI greater than 0 specifies that the groundwater is supersaturated with respect to the particular mineral phase and therefore incapable of dissolving more of the mineral. Such an index value reflects groundwater discharging from an aquifer containing ample amount of the mineral with sufficient resident time to reach equilibrium. Nonetheless, supersaturation can also be produced by other factors that include incongruent dissolution, common ion effect, evaporation, rapid increase in temperature, and CO$_2$ exsolution (Appelo and Postma 1996;

**Table 5** Correlation matrix for post-monsoon season

| | pH | TDS | Na | K | Ca | Mg | Cl | SO$_4$ | F | HCO$_3$ | CO$_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | | | | | | | | | | |
| TDS | −0.03 | 1 | | | | | | | | | |
| Na | 0.15 | 0.69 | 1 | | | | | | | | |
| K | −0.09 | 0.44 | 0.23 | 1 | | | | | | | |
| Ca | −0.27 | 0.56 | 0.00 | 0.29 | 1 | | | | | | |
| Mg | 0.00 | 0.58 | 0.17 | 0.06 | 0.16 | 1 | | | | | |
| Cl | −0.16 | 0.77 | 0.37 | 0.35 | 0.66 | 0.62 | 1 | | | | |
| SO$_4$ | −0.23 | 0.52 | 0.29 | 0.23 | 0.36 | 0.40 | 0.43 | 1 | | | |
| F | −0.06 | −0.27 | −0.32 | −0.13 | −0.04 | −0.12 | −0.20 | −0.13 | 1 | | |
| HCO$_3$ | 0.22 | 0.66 | 0.63 | 0.23 | 0.11 | 0.27 | 0.13 | 0.02 | −0.18 | 1 | |
| CO$_3$ | 0.05 | −0.00 | −0.05 | −0.07 | 0.03 | 0.07 | 0.00 | −0.04 | −0.04 | 0.00 | 1 |

**Fig. 7** Piper trilinear plot of the samples for **a** pre- and **b** post-monsoon seasons



a



b
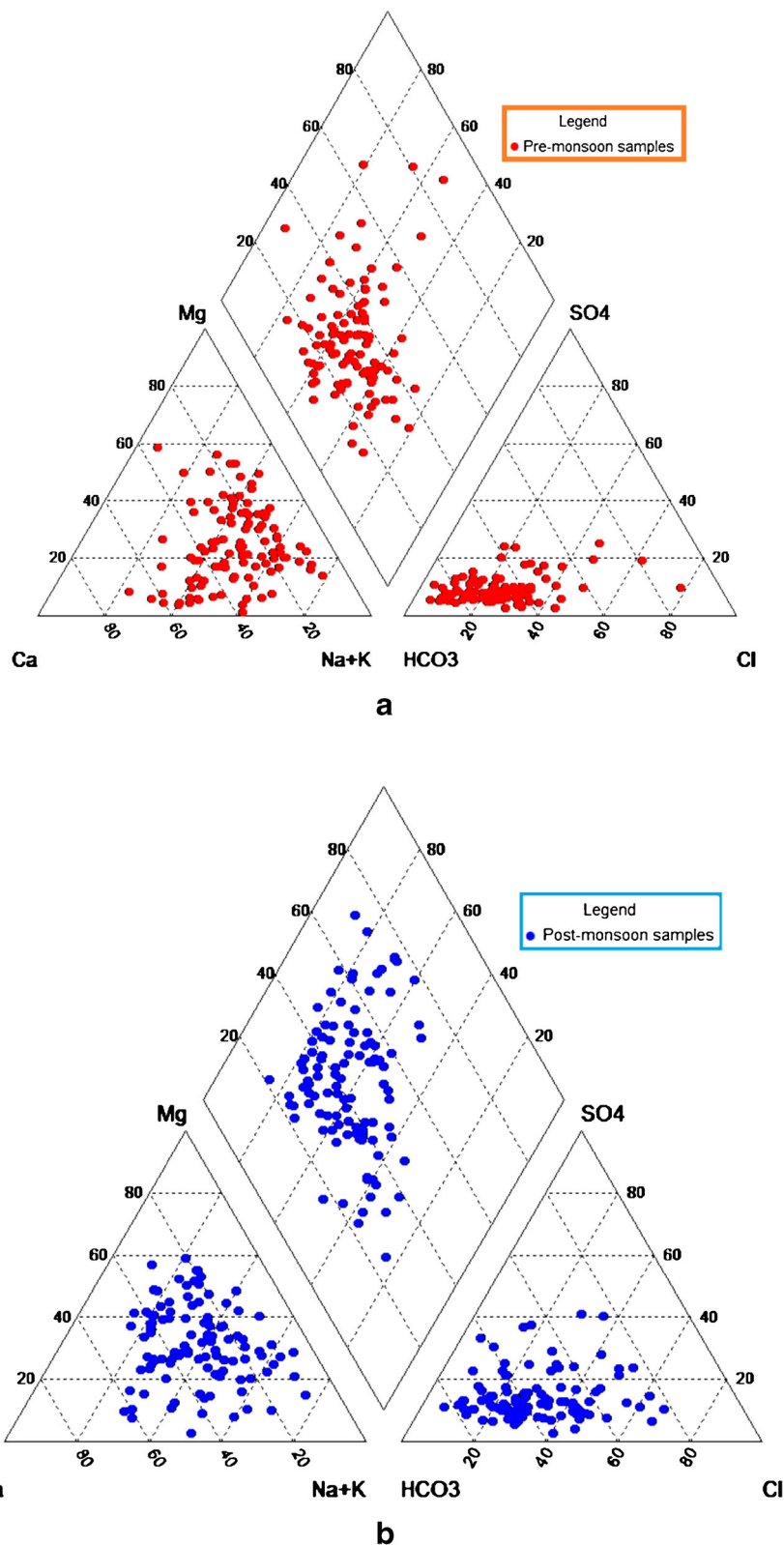
Langmuir 1997). The plots of SI for halite and gypsum against TDS for all the investigated water for pre- and post-monsoon seasons are shown in Fig. 9a, b. Nearly all water samples were undersaturated with respect to halite and gypsum, suggesting that these carbonate mineral phases may have influenced the chemical composition of the study area.

**Table 6** Characteristics of Piper trilinear diagram

| Subdivision of the diamond | Classes | Samples fallen in dissimilar seasons | | | |
|---|---|---|---|---|---|
| | | Pre-monsoon | | Post-monsoon | |
| | | % | No. of samples and range | % | No. of samples and range |
| 1 | Alkaline earth ($Ca^{2+}+Mg^{2+}$) exceed alkalies ($Na^{+}+K^{+}$) | 60 | 65 | 74 | 80 |
| 2 | Alkalies exceeds alkaline earths | 40 | 43 | 26 | 28 |
| 3 | Weak acids ($CO_3+HCO_3$ exceed strong acids ($SO_4+Cl$) | 10 | 11 | 67 | 72 |
| 4 | Strong acids exceeds weak acids | 90 | 97 | 33 | 36 |
| 5 | Magnesium bicarbonates | 53 | 57 | 44 | 48 |
| 6 | Calcium-chloride type | 2 | 2 | 5 | 5 |
| 7 | Sodium-chloride type | 3 | 3 | 4 | 4 |
| 8 | Sodium-bicarbonate type | 2 | 2 | 1 | 1 |
| 9 | Mixed type (no. cation-anion exceed 50%) | 40 | 44 | 46 | 50 |
| | Total | 100 | 108 | 100 | 108 |

## Principal component analyses

The hydrochemical data was subjected to multivariate analytical techniques such as factor and cluster analyses. The principal component approach was undertaken by extracting eigenvalues and eigenvectors of the correlation matrix. Values for elements below the detection limit (DL) were substituted with DL/2 prior to statistical analyses. When the values below the DL are small, replacing them with a constant (i.e., DL/2) is generally suggested (Farnham et al. 1998; Stetzenbach Claus et al. 1999). The comparative statistical parameters of major cations for pre- and post-monsoon groundwater samples in terms of minimum, maximum, mean, standard deviation, and skewness are presented in Table 7. From basic statistical data, values for all elements presented in pre-monsoon are considered to decrease in post-monsoon. The standard skewness should be in the range between 2 and −2; otherwise, it is considered as extreme (Reimann et al. 2008). For both seasons, the skewness presented in Table 7 is positive value for right-skewed data for major ions and is considered to be extreme.

### Factor analyses

The principal component solution obtained eigenvalues and percent (%) of the variance is given in Table 7. The output of the final rotated loading matrix obtained from the present data indicates that in the pre-monsoon season, the obtained results of the three-factor analysis explain 70.75% of the total variance: factor analysis I (FA/PC-I) contributes 44.69%, factor analysis II (FA/PC-II) 15.11%, and factor analysis III (FA/PC-III) 10.95%, with 13 chemical variables. The number of sampling locations and the statistics for all the major ions are

shown in Fig. 2 and Table 1. Each factor analysis can be used to interpret as a specific hydrochemical process through an examination of the loadings. In the post-monsoon season, the obtained results of the three-factor analysis explain 66.59% of the total variance: FA/PC-I contributes 42.60%, FA/PC-II 14.71%, and FA/PC-III 9.28%, with 13 chemical variables.

FA/PCA was applied to the varimax normalized data to compare the compositional patterns between the analyzed water samples and to identify the factors that influence each one. The factor loading are classified (Liu et al. 2008) as strong, moderate, and weak corresponding to absolute loading values of 0.75, 0.75–0.50, and 0.50–0.30, respectively. The plots between different factors for pre- and post-monsoon seasons are shown in Fig. 10a–c, respectively.

Scatter plot of the FA loadings between FA-I and FA-II, FA-I and FA-III, and FA-II and FA-III are illustrated in Fig. 11a–c for pre- and post-monsoon seasons. This figure can be read for the variation from possible to negative loadings of each FA and also the scatter between the FA the difference pairs. The Scree plot was used to identify the number of PCs to be retained in order to comprehend the underlying data structure in the present study; the Scree plot (Fig. 12) for pre- and post-monsoon seasons showed a pronounced change of slope after the sixth eigenvalue.

Projections of the original variables on the subspace of the PCs are called loadings and coincide with the correlation coefficients between PCs and variables. Rotation of the axis defined by PCA produced a new set of factors, each one involving primarily a subset of the original variables with as little overlap as possible, so that the original variable are divided into groups somewhat independent of each other. Thus, factor analysis of the present dataset of Sasilar Vagu watershed
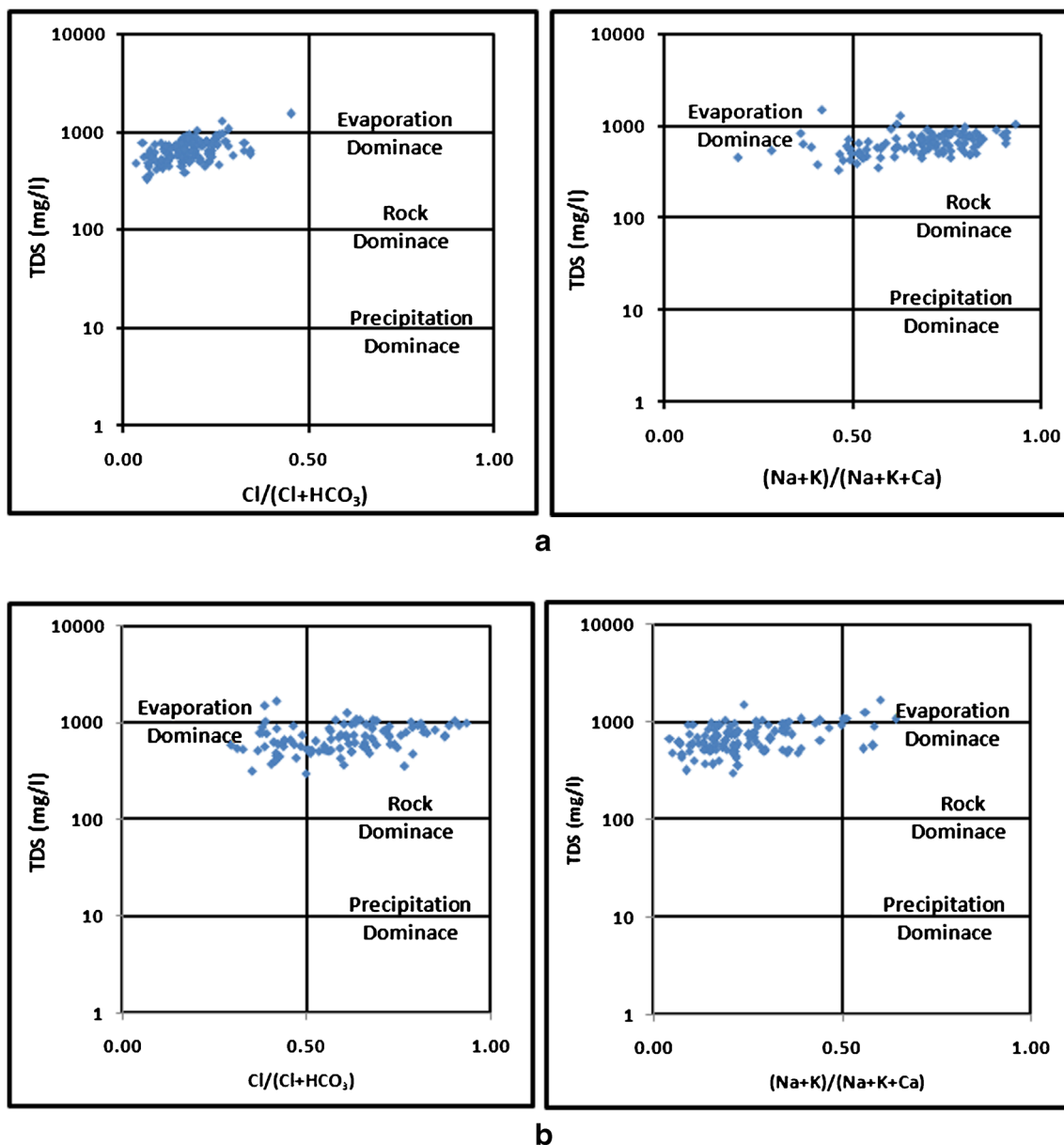
**a**



**b**

**Fig. 8  a**, **b** Gibb's plot of the samples for pre- and post-monsoon seasons

further reduced the contribution of less significant variables obtained from PCA.

*Factor analyses and principal component analyses*

FA/PCA-I dominated by strong positive variable are TDS, TH, Mg, Cl⁻, and SO⁴ (which is greater than 0.75); moderately positive variables are TDS and $Ca^{2+}$, and the remaining variables are weak except $CO_3$ and also fluoride and pH indicating positive results. This factor is derived mainly from dissolution of carbonate precipitates along with ion exchange process in groundwater, and Mg, Cl⁻, and SO⁴ are controlled by geogenic processes and anthropogenic inputs. EC values are controlled by Cl⁻ and SO⁴. PC 1 has high loadings of both

monsoons (>0.50) for EC, TDS, Na, TH, Ca, Mg, Cl⁻, and $SO_4$ accounting for 44.69% of the variance in the hydrochemistry in the area. EC, TDS, Na, TH, Ca, Mg, Cl⁻, and $SO_4$ show positive loadings under PC 1 and are derived from industrial, domestic, and agricultural wastes in the study area. PC 2, which accounts for 15.11% of the total variance, contains high loadings for EC, TDS, Na, K, and $HCO_3$, representing the contribution of agricultural activities and weathering of K-feldspar from underlying geology; a process accompanied by rise in pH shows negative loadings. PC 3, which accounts for 10.95% of the total variance in the hydrochemistry, shows positive loadings for TDS, Na, TH, Ca, K⁺, Cl⁻, $SO_4$, and F⁻ (0.06), representing the weathering of minerals of Na and K in the study area (Liu et al. 2008).
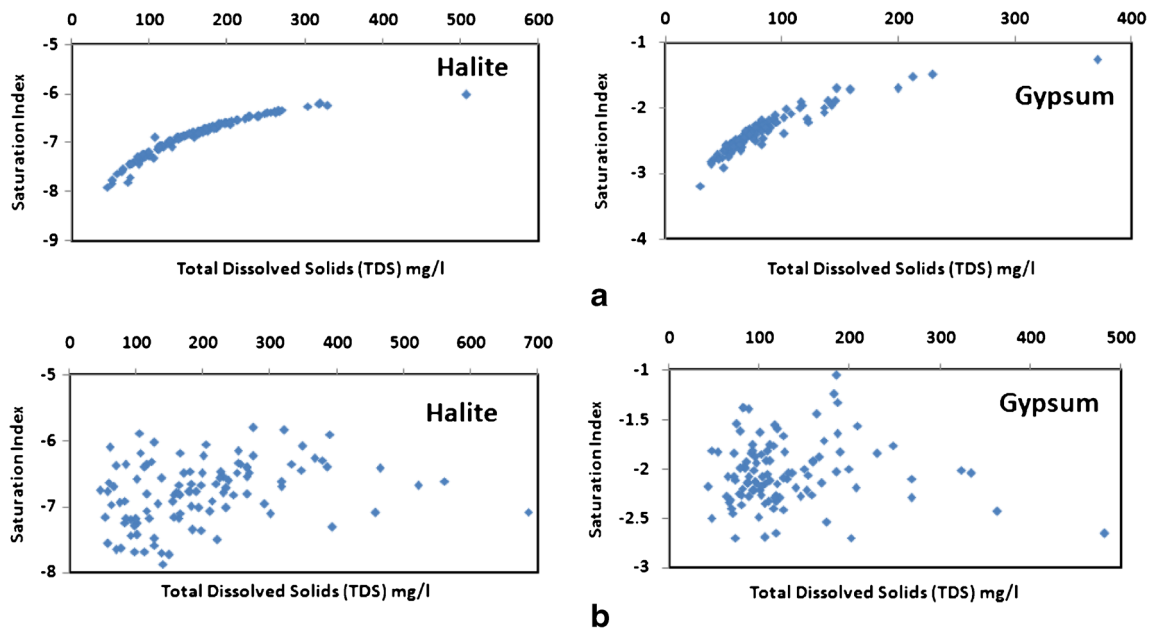
**Fig. 9** Plots of saturation indexes with respect to halite and gypsum against total dissolved solids (TDS) for **a** pre-monsoon and **b** post-monsoon seasons

*Cluster analysis*

Cluster analysis comprises a series of multivariate methods that are used to find true groups of data. In clustering, the objects are grouped such that similar objects fall into the same class (Danielsson et al. 1999). Hierarchical cluster analysis is the most widely applied techniques in the earth sciences. Hierarchical clustering joins the most similar observations, and then successively the next most similar observations.

The levels of similarity at which observations are merged are used to construct a dendrogram. Some measures of similarity must be computed between every pair of objects. In this study, a standardized m-space Euclidian distance (Davis 1986). Cluster analysis groups variables into clusters on the basis of similarities (or dissimilarities) such that each cluster represents a specific process in a system (Yidana et al. 2008). For cluster analysis, single linkage method was used. In this method, the distance between the clusters was determined by

**Table 7** Summary statistic of the factor loadings

| Parameters | Pre-monsoon | | | Post-monsoon | | |
|---|---|---|---|---|---|---|
| | Factor 1 | Factor 2 | Factor 3 | Factor 1 | Factor 2 | Factor 3 |
| pH | 0.02 | −0.05 | −0.85 | −0.34 | 0.45 | −0.46 |
| EC | 0.81 | 0.58 | 0.00 | 0.83 | 0.54 | 0.05 |
| TDS | 0.74 | 0.66 | 0.04 | 0.75 | 0.64 | 0.10 |
| TH | 0.98 | −0.01 | 0.04 | 0.96 | 0.08 | −0.13 |
| $Ca^{2+}$ | 0.60 | −0.22 | 0.43 | 0.78 | −0.10 | 0.21 |
| $Mg^{2+}$ | 0.78 | 0.15 | −0.26 | 0.69 | 0.22 | −0.41 |
| $Na^+$ | 0.13 | 0.82 | −0.11 | 0.15 | 0.87 | 0.15 |
| $K^+$ | 0.07 | 0.66 | 0.14 | 0.29 | 0.30 | 0.56 |
| $HCO_3^-$ | 0.46 | 0.75 | −0.01 | 0.13 | 0.82 | −0.06 |
| $CO_3^-$ | −0.07 | 0.04 | −0.76 | 0.10 | −0.05 | −0.62 |
| $Cl^-$ | 0.84 | 0.31 | 0.11 | 0.88 | 0.20 | 0.04 |
| $SO_4^-$ | 0.82 | 0.10 | 0.14 | 0.62 | 0.09 | 0.23 |
| $F^-$ | 0.02 | −0.46 | 0.06 | −0.08 | −0.44 | −0.06 |
| Eigenvalue | 5.81 | 1.96 | 1.42 | 5.54 | 1.91 | 1.21 |
| Cumulative | 5.81 | 7.77 | 9.20 | 42.60 | 14.71 | 9.28 |
| % Variance | 44.69 | 15.11 | 10.95 | 5.54 | 7.45 | 8.66 |
| Cumulative % | 44.69 | 59.80 | 70.75 | 42.60 | 57.31 | 66.59 |
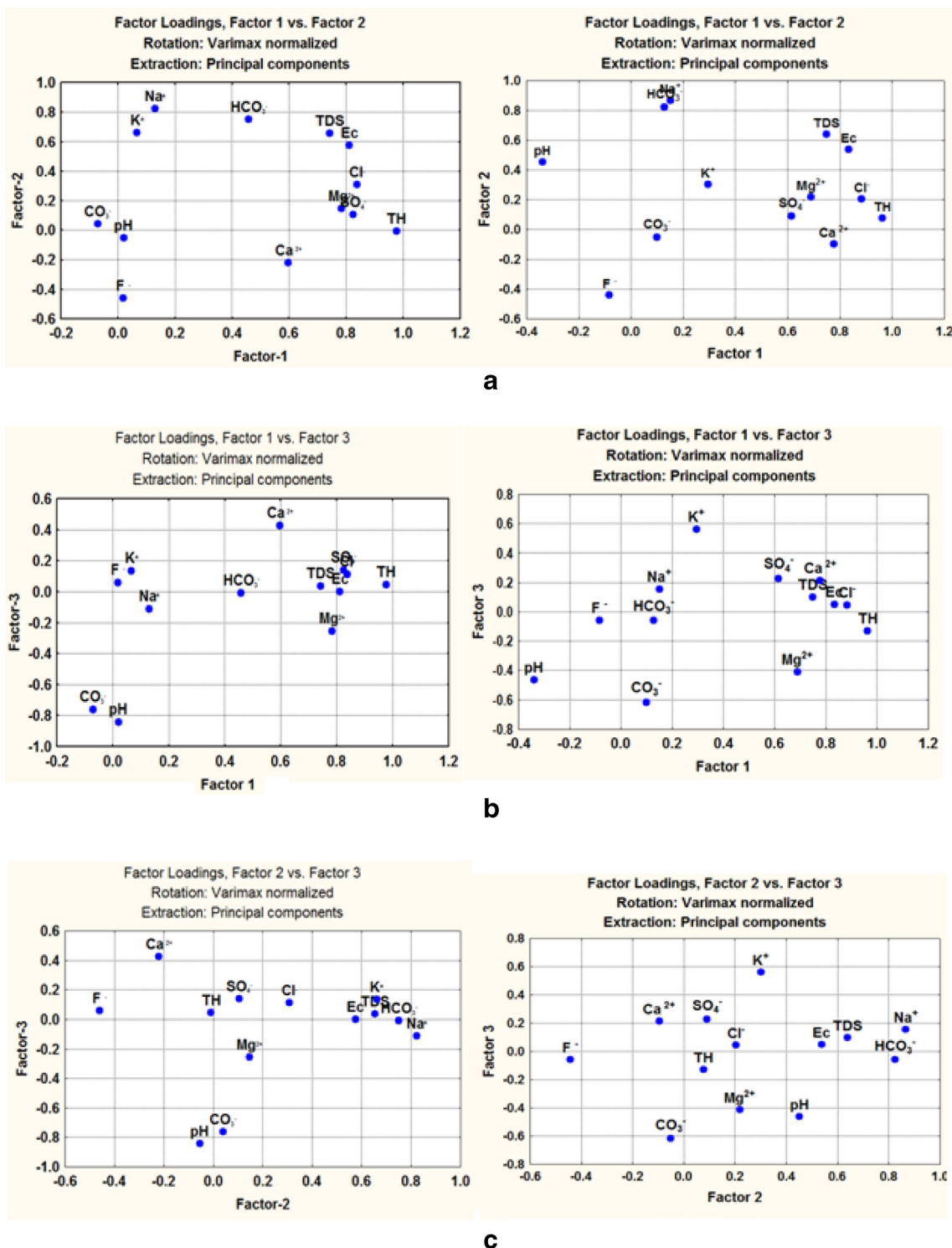
Fig. 10 a–c Factor loadings using rotation varimax normalized extraction with principal components for pre- and post-monsoon seasons

the distance of the two closest objects (nearest neighbor) in the different cluster.

In this study, the hierarchical cluster analysis (HCA) was applied to the raw data for 103 different sample locations using Statistica-7 software to analyze the water quality data. A classification scheme using the Euclidean distance for similarity measures (Guler et al. 2002) from dendrogram of 11 indexes based on the cluster analysis is depicted in Fig. 13 for pre- and post-monsoon seasons. On the basis of dendrogram of 11 indexes can be grouped into three main clusters pre- and post-monsoon data. First cluster group shows close association between pH and F. This group is associated with group second to a
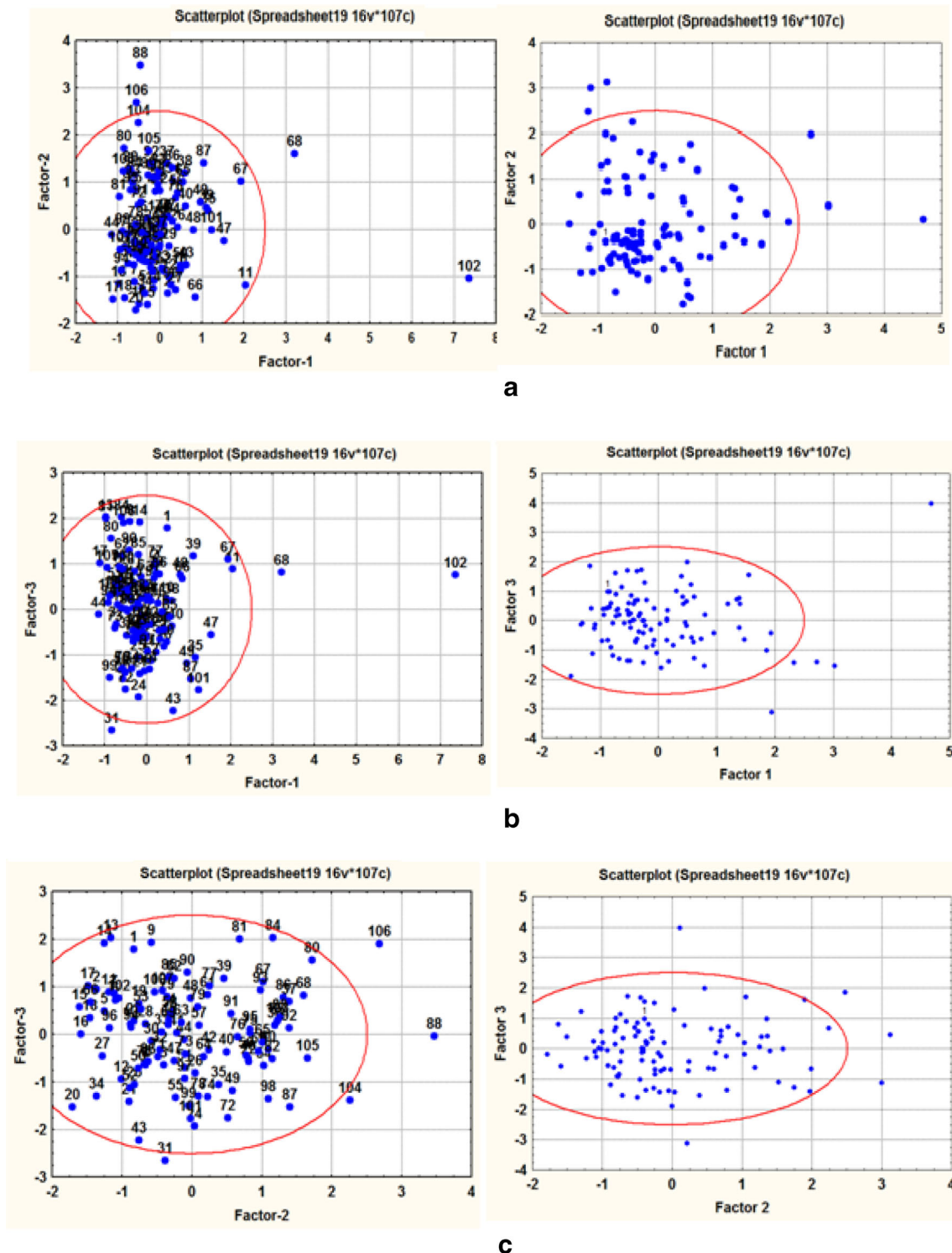
Fig. 11  a–c Scatter plots of between factor loadings 1, 2, and 3 for pre- and post-monsoon seasons

lesser degree having total alkalinity and total hardness indexes. The third group shows close association between chloride and sodium. This finding corroborates the result of correlation and cluster analysis. The enrichment of Na and Cl ions in groundwater is due to the interaction of water with rocks and secondly association of TDS with higher concentration of Na

and Cl ions. This indicates anthropogenic activities such as discharge of sewage and agricultural runoff, which support the contamination of groundwater. Yidana et al. (2008) observed similar results for surface water. The concentration of total alkalinity in the groundwater is nothing but the result of reaction of soil $CO_2$ that originates from $HCO_3$.
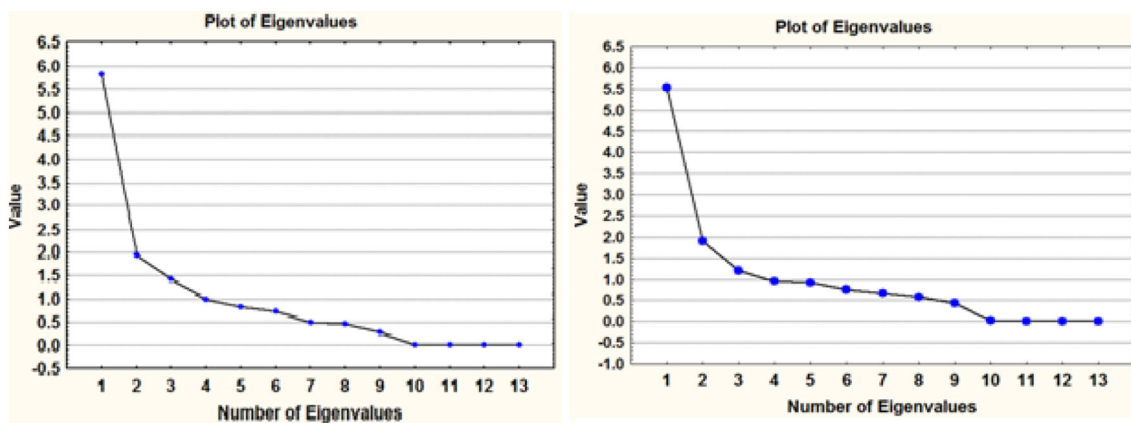
Fig. 12 Scree plots of eigenvalues for pre- and post-monsoon seasons showed a pronounced change of slope after the sixth eigenvalue

The negative loading of pH suggests that decrease of $CO_2$ and $HCO_3$ values during the outgassing of $CO_2$ decreases there is sharp rise in pH value which shifts the water towards alkaline side and concentration of $HCO_3$ increases. Minerals of bedrock are subjected to weathering and subsequently affected by leaching, which contribute dissolved salts to groundwater, resulting in an increase in TDS and EC.

## Conclusions

High level of fluoride concentration was observed in groundwater sample in the study area, indicating the unsuitability of most water samples for potable purposes. The concentration of fluoride ranges from 1.40 to 5.90 mg/l and 1.50 to 5.80 mg/l in pre- and post-monsoon seasons. Various plots like Ca versus $HCO_3$, Na versus Cl, Ca versus $SO_4$, and (Na+ Cl)-(SO4+HCO3) versus (Na+K-Cl) show positive and negative values, indicating their source of high concentration in aquifer, evapotranpiration, and other anthropogenic sources. Saturation index of halite and gypsum shows that all groundwater samples were undersaturated and suggests that carbonate minerals influence the concentration. The high concentration of fluoride in study area is due to geogenic origin. Concentrations of other major ions, viz., chloride, magnesium, potassium, and bicarbonate, also show elevated concentrations than permissible limits. Majority of the samples show the Ca+Mg, Ca-Cl, and Ca-Na-Cl type water during pre- and post-monsoon seasons, respectively. The study supported by the factor analysis and cluster analysis reveal that predominant agriculture and geogenic effect in the groundwater samples and the contaminants in the pre-monsoon are more compared
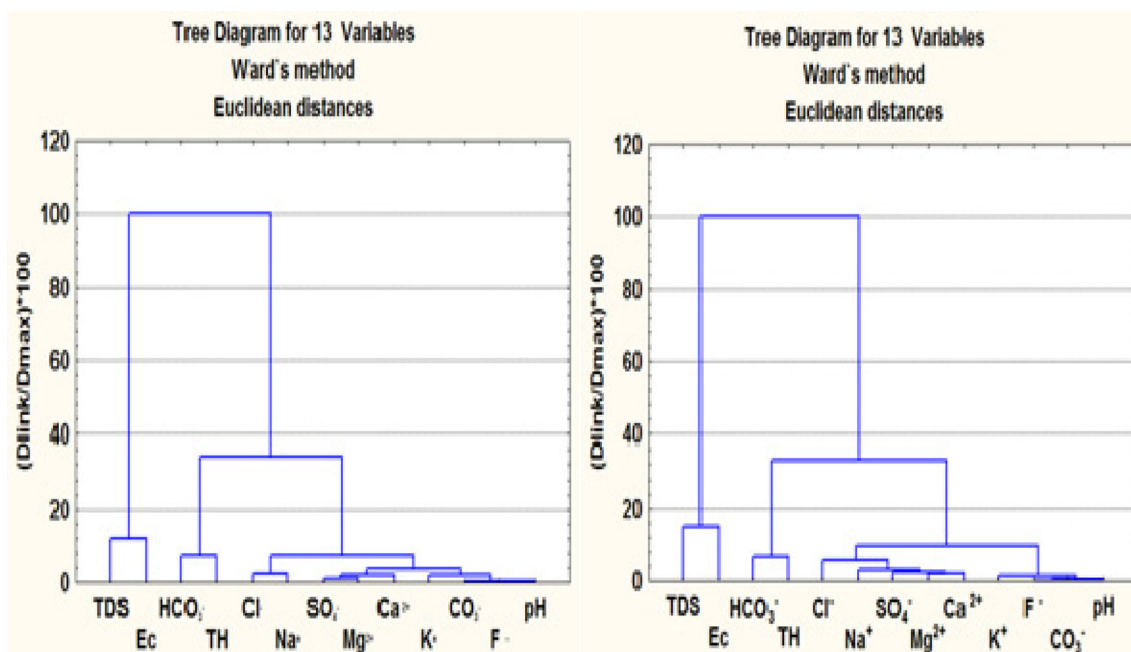


Fig. 13 Dendrogram showing the clustering of chemical parameters for pre and post-monsoon seasons

to post-monsoon due to the monsoonal effects. Multivariate statistical analyses, viz., factor and cluster analyses, explain that intensive use of agriculture fertilizers activities and water-rock interaction are the factors that influence the groundwater quality of Shaslar Vagu study area. Multivariate statistical techniques are potential tools and provide greater precision for identifying contaminant parameter linkages. Such studies can be applied to other watersheds in the region for understanding the water chemistry and the predominant factors which controls the groundwater quality.

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