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Appraisal of groundwater quality in a crystalline aquifer: a chemometric approach

P. D. Sreedevi¹ · P. D. Srekanth² · S. Ahmed¹ · D. V. Reddy¹

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Abstract

The purpose of this study is to assess the groundwater quality and identify the processes that control the groundwater chemistry in a crystalline aquifer. A total of 72 groundwater samples were collected during pre- and post-monsoon seasons in the year 2014 in a semi-arid region of Gooty Mandal, Anantapur district, Andhra Pradesh, India. The study utilized chemometric analysis like basic statistics, Pearson's correlation coefficient (r), principal component analysis (PCA), Gibbs ratio, and index of base exchange to understand the mechanism of controlling the groundwater chemistry in the study area. The results reveal that groundwater in the study area is neutral to slightly alkaline in nature. The order of dominance of cations is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ while for anions, it is $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{F}^-$ in both seasons. Based on the Piper classification, most of the groundwater samples are identified as of sodium bicarbonate ($\text{Na}^+ - \text{HCO}_3^-$) type. According to the results of the principal component analysis (PCA), three factors and two factors were identified pre and post monsoon, respectively. The present study indicates that the groundwater chemistry is mostly controlled by geogenic processes (weathering, dissolution, and ion exchange) and some extent of anthropogenic activities.

Keywords Groundwater · Crystalline aquifer · Hydrogeochemistry · Chemometric analysis · Semi-arid region

Introduction

Groundwater is a vital natural resource, particularly for drinking and irrigation, uses where there are no surface water resources available. The world's totaled groundwater withdrawal is around 1000 km³ per year, of which about 67% is utilized for irrigation, 22% is for household purposes, and 11% is for the industry (IGRAC 2010; Wada et al. 2010). Two thirds of this is abstracted in Asia, where India, China, Pakistan, Iran, and Bangladesh are the significant consumers (Jac van der 2012). In India, the accessibility of surface water is higher than that of groundwater. However, due to the decentralized availability of groundwater, it is easily accessible and forms the most significant share of India's irrigation and drinking water supply. Eighty-nine percent

of groundwater extracted is utilized in the irrigation sector, making it as the peak group of users in the country, followed by domestic use of which is 9%. Industrial use of groundwater is only 2%. Fifty percent of urban water requirements and 85% of rural household water requirements are also achieved by groundwater (Suhag 2016). In India, groundwater is being used as raw water for 85% of public water supply (WHO 1998). The World Bank estimated that 21% of communicable diseases in India are water related (DeNormandie and Sunitha 2002), and India loses about 360 billion rupees per year due to water-related diseases (Shanmuganandan 1999).

The quality of groundwater is controlled by natural (geogenic) processes as well as anthropogenic activities (Caschetto et al. 2014; Nagaraju et al. 2016; Nigro et al. 2017). Groundwater always contains little amount of soluble salts dissolved in it (Barbieri et al. 2005). The type and nature of these salts depend upon the sources for recharge of the groundwater and the strata through which it flows (Andre et al. 2005). The abundant amount of soluble salts may lead to many health problems in the population and may also be harmful to many crops (Appelo and Postma 1993; Khodapanah et al. 2009). Appraisal of groundwater quality is necessary for human health as well as crop growth or in avoiding crop failures (Sappa et al. 2014).

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The quality of groundwater is essential for a specified usage, and hence, it needs to be critically evaluated. Numerous techniques (graphical and advanced statistical) are available for interpretation of groundwater quality. However, proper methods should be applied, because of the complexities of the regional hydrological conditions and hydrochemical processes that are involved in aquifers which are difficult to identify and document (Liu et al. 2003). The interpretation of data in graphical methods is limited to two dimensions, for example, the Hill diagram (Hill 1940), Langelier and Ludwig diagram (Langelier and Ludwig 1942), Durov triangular diagram (Durov 1949), Stiff diagram (Stiff 1951), and Schoeller diagram (Scholler 1964). Hence, to add another dimension, advanced techniques like multivariate statistical analysis were used. These methods gave a representative and reliable estimation of the quality of groundwater, and this will clarify the correlation among a large number of variables concerning a small number of factors without losing much information (Nagaraju et al. 2016). Nationally and internationally, many researchers have focused on identification of influencing factors for groundwater quality variation using chemometric analysis (Srinivasa Rao et al. 2008; Sappa et al. 2014; Liu et al. 2003; Nagaraju et al. 2016; Kamtchueng et al. 2016; Tay et al. 2017; Aksever and Buyuksahin 2017; Sudheer Kumar et al. 2017; Barzegar et al. 2017; Bhuiyan et al. 2016; Bencer et al. 2016; Ahada et al. 2017; Isa et al. 2017; Hamzah et al. 2017). In this light, a study was carried out in Gooty Mandal by analyzing the hydrogeochemical parameters to understand the quality of groundwater for various purposes and also to identify the processes that control the groundwater using chemometric analysis.

Study area

Groundwater is the primary source for drinking and irrigation purposes in Gooty Mandal, due to lack of surface water resources. The study area lies in the northern part of the Anantapur district of Andhra Pradesh, South India, and falls in the Survey of India (SOI) Toposheet no. 57 E/12 and 16 having longitude 77° 31' 05" to 77° 46' 01" E and latitude 15° 01' 44" to 15° 13' 59" N. The total geographical area is 295 km² (Fig. 1).

The study area represents semi-arid conditions marked by hot summer and mild winter. The temperature varies from 36 to 43 °C during summer and 15 to 25 °C during winter. The annual average rainfall is only 564 mm (44-year data, from 1971 to 2014) with significant yearly variations. The drainage pattern is dendritic to sub-dendritic at higher elevations and parallels to sub-parallel at lower elevations. There are no perennial streams in the study area, and the ephemeral ones flow only during the rainfall events. Most of the study area is covered by red soil and certain patches with black soil.

Geologically, the area is covered by the Peninsular Gneissic Complex (PGC) of Achaean age, mainly composed of crystalline rocks such as granites and gneisses with many basic and acidic intrusions (Fig. 1). The gneisses contain hornblende–biotite gneisses, hornblende gneisses, and biotite gneisses (GSI 1995, 2004). Groundwater occurs under unconfined conditions mainly in the weathered and fracture zones and semi-confined conditions under deeper fractures. The depth to groundwater levels varies from 5 to 35 m below ground level (bgl) in different seasons.

Materials and methods

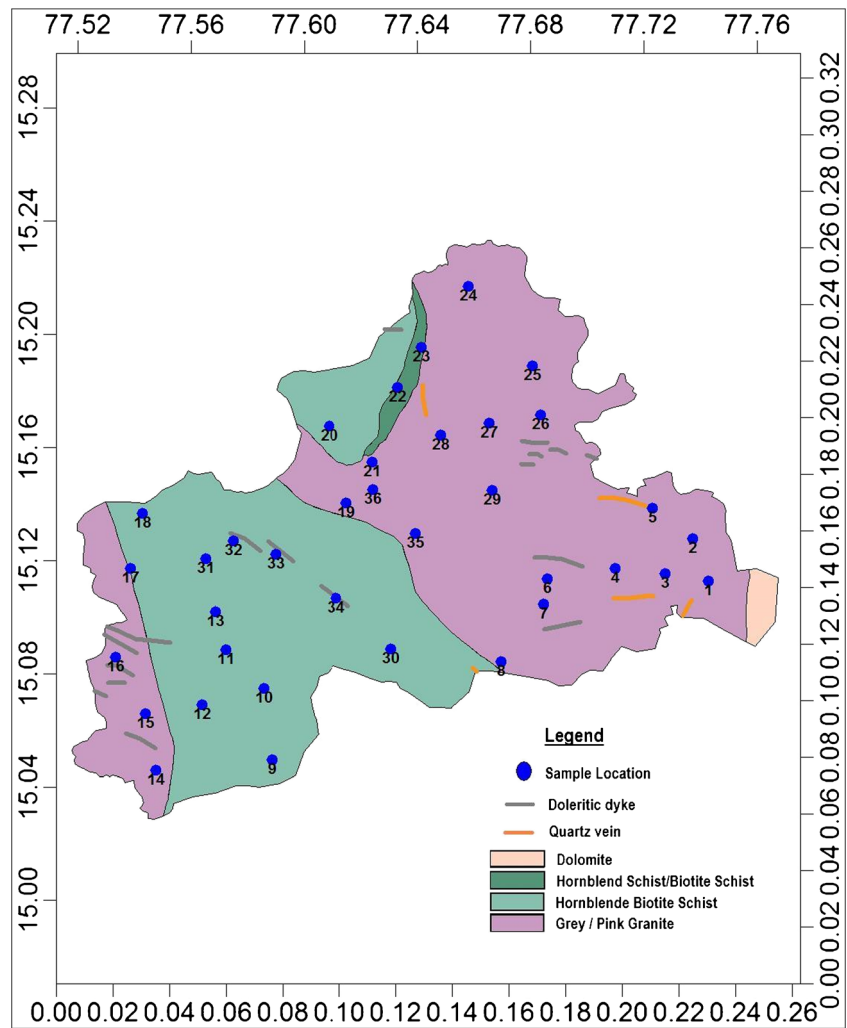
A total of 72 groundwater samples have been collected from 36 bore wells within the depth range of 3 to < 40 m during pre- (May 2014) and post- (December 2014) monsoon seasons. Sampled well locations were recorded using the global positioning system (GPS). The selected well's waters are used for domestic as well as drinking and irrigation purposes without any treatment. Some of these wells are fitted with hand pumps, and the rest are with submersible pumps.

The samples were collected and analyzed using standard procedures (AWWA 1971). The hydrogen-ion concentration (pH), electrical conductivity (EC), and total dissolved solids (TDS) were measured with their respective probes. Carbonates (CO₃²⁻) and bicarbonates (HCO₃⁻) were measured by titration method. Major anions like chloride, fluoride, nitrate, and sulfate (Cl⁻, F⁻, NO₃⁻, and SO₄²⁻) and cations like calcium, magnesium, sodium, and potassium (Ca²⁺, Mg²⁺, Na⁺, and K⁺) were analyzed using Dionex ion chromatograph. The analytical accuracy of the measurements of cations and anions was verified using Ionic Balance Error (IBM) from ion expressed in milliequivalents per liter (Domenico and Schwartz 1998; Al-Shujairi 2016). The value of IBM was observed to be within a limit of ± 10%.

Data analysis

In the first-stage fundamental statistical analysis, Pearson's correlation matrix and principal component analysis (PCA) were performed using the XLSTAT (statistical software package for Microsoft Excel) to understand the hydrochemical processes in groundwater. Pearson's correlation matrix analysis gives the magnitude of the degree of relationship between two related variables. The relationship between two variables is the correlation coefficient (*r*), which is the percentage of variance in the dependent variable, explained by the independent variable. The value of "*r*" is always between + 1 and - 1. The results of the correlation analysis are presented in

Fig. 1 Location map



the subsequent interpretation and shown in Table 1 (Guildford 1973).

PCA is a technique to reduce original data variables into a smaller set of factors for interpretation of data (Davis 2002; Nagaraju et al. 2016). The eigenvalues were calculated which quantify the contribution of a factor to the total variance, and their percentages were computed. When the eigenvalue is greater than 1, it indicates that the contribution of a factor is significant. The first few significant factors were noted, and these factors contain the considerable variance in order. The

Table 1 Rule of thumb for interpreting the size of a correlation coefficient

| Size of correlation | Interpretation |
|---------------------|--------------------------------------|
| ±0.0 to 0.29 | Negligible or little correlation (N) |
| ±0.3 to 0.49 | Weak or low correlation (W) |
| ±0.5 to 0.69 | Moderate correlation (M) |
| ±0.7 to 0.89 | Strong or high correlation (S) |
| ±0.9 to 1.00 | Perfect or very high correlation (P) |

varimax rotation technique was used for calculating the factor loadings. These weights are classified into three categories: if the values are closer to “− 1,” it is classified as a negative contribution; “0” represents no contribution; and “+ 1” indicates a positive contribution (Briz Kishore and Murali 1992; Ayla 2015; Nagaraju et al. 2016).

In the second stage, Gibbs ratio I (GRI) and Gibbs ratio II (GRII) were calculated to understand the relationship between chemical constituents of groundwater from their respective aquifer lithology (Gibbs 1970). Indexes of base exchange, i.e., chloroalkaline index I (CAI) and chloroalkaline index II (CAII), were calculated to understand the ion exchange between groundwater and its host environment during travel or residence. The following formulas are used for calculating GRI, GRII, CAI, and CAII (Scholler 1965, 1967).

$$GRI \text{ (for anion)} = \frac{Cl}{Cl + HCO_3} \quad (1)$$

$$GRII \text{ (for cation)} = \frac{Na + K}{Na + K + Ca} \quad (2)$$

$$\text{CAI} = \frac{(\text{Cl} - (\text{Na} + \text{K}))}{\text{Cl}} \quad (3)$$

$$\text{CAII} = \frac{(\text{Cl} - \text{Na} + \text{K})}{(\text{SO}_4 + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3)} \quad (4)$$

where ions are considered in milliequivalents per liter.

Results and discussion

The results of the hydrochemical data for pre- and post-monsoon seasons are summarized, and the minimum, maximum, and mean values (mg/L and meq/L) and the statistical parameters are given in Tables 2 and 3, respectively. In the present study, groundwater quality has been assessed based on the Bureau of Indian Standards for drinking (BIS 2012) and the Food and Agricultural Organization (FAO 1985) guidelines for irrigation purposes (Tables 2 and 3; Figs. 2 and 3). The orders of dominance of the major ions in pre- and post-monsoon seasons are respectively $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{F}^-$ (Fig. 4).

Temporal variation of hydrochemical parameters

Water samples collected during pre-monsoon indicate that pH is ranging between 6.96 and 8.24 with a mean of 7.52, while in the post-monsoon samples it varies from 6.90 to 7.94 with a mean of 7.48. It indicates that the nature of groundwater is neutral to slightly alkaline. The EC ranged from 715 to 5490 $\mu\text{S}/\text{cm}$ with a mean of 2260 and 730 to 5560 $\mu\text{S}/\text{cm}$ with a mean of 1904 $\mu\text{S}/\text{cm}$ for pre- and post-monsoon, respectively. TDS of the groundwater varies from 381 to 2970 mg/L with a mean of 1213 mg/L during the pre-monsoon and 389 to 3010 with a mean of 1020 mg/L during the post-monsoon. The EC and TDS values are slightly higher in the post-monsoon; it could be due to the migration of ions from soils into groundwater by monsoon recharge waters (Subba Rao et al. 2012). The slightly alkaline nature of water with high EC and high TDS in groundwater can be attributed to the high reactivity of soil and anthropogenic contamination in the study area.

The Na^+ concentration ranges from 70 to 1075 mg/L with an average concentration of 322 mg/L in pre-monsoon and 86 to 1118 mg/L with an average of 305 mg/L in post-monsoon. The concentration of K^+ ranges from 0.4 to 93 mg/L and from 0 to 125 mg/L with an average of 12 and 9 mg/L during pre- and post-monsoon, respectively. The high concentration of Na^+ in drinking water may cause to change its taste (WHO 1998), and for irrigation, it may cause

foliage and foliar burning if sufficient amounts of Na^+ accumulate in leaf tissue.

The concentration of Ca^{2+} ranges from 24 to 463 mg/L and from 22 to 456 mg/L with a mean of 128 and 112 mg/L during both seasons. The Mg^{2+} concentration in groundwater ranges from 13 to 227 mg/L and from 16 to 227 mg/L with an average value of 71 and of 62 mg/L during pre- and post-monsoon. If consumed in high concentration, Ca^{2+} and Mg^{2+} in water for drinking may cause kidney stones and joint pains (WHO 2009). The high content of Ca^{2+} is most desirable for irrigation water (FAO 1985). The concentration of Ca^{2+} and Mg^{2+} decreases relative to Na^+ , and the sodium adsorption ratio (SAR) value will be higher. This process may cause an alkalizing effect and increase the pH.

The concentration of CO_3^{2-} varies from 0 to 160 mg/L and from 0 to 80 mg/L with an average value of 13 and 18 mg/L during pre- and post-monsoon, respectively. The concentration of HCO_3^- ranges from 220 to 1160 mg/L and from 230 to 1120 mg/L with an average value of 536 and 496 mg/L during pre- and post-monsoon, respectively. High concentrations of HCO_3^- and CO_3^{2-} in irrigation water may increase the SAR index. When HCO_3^- and CO_3^{2-} ions combined with Ca^{2+} or Mg^{2+} , they will precipitate as calcium carbonate (CaCO_3) or magnesium carbonate (MgCO_3). This solution may develop the drying conditions in soils (FAO 1985).

Cl^- and SO_4^{2-} are considered important inorganic constituents of water, which may deteriorate the quality of drinking water at greater extents. The concentration of Cl^- ranges from 18 to 1091 mg/L and from 17 to 1322 mg/L with a mean of 323 and 276 mg/L. The mean of the Cl^- concentration is low in post-monsoon; it could be due to groundwater recharge during the monsoon season. The concentration of SO_4^{2-} ranges from 8 to 473 mg/L and from 7 to 543 mg/L with a mean of 128 and 114 mg/L during pre- and post-monsoon, respectively. SO_4^{2-} plays a vital role in the total hardness of water. The high concentration of Cl^- may develop injury symptoms on crop, such as leaf burn or drying of leaf tissue (Ayers and Westcot 1985).

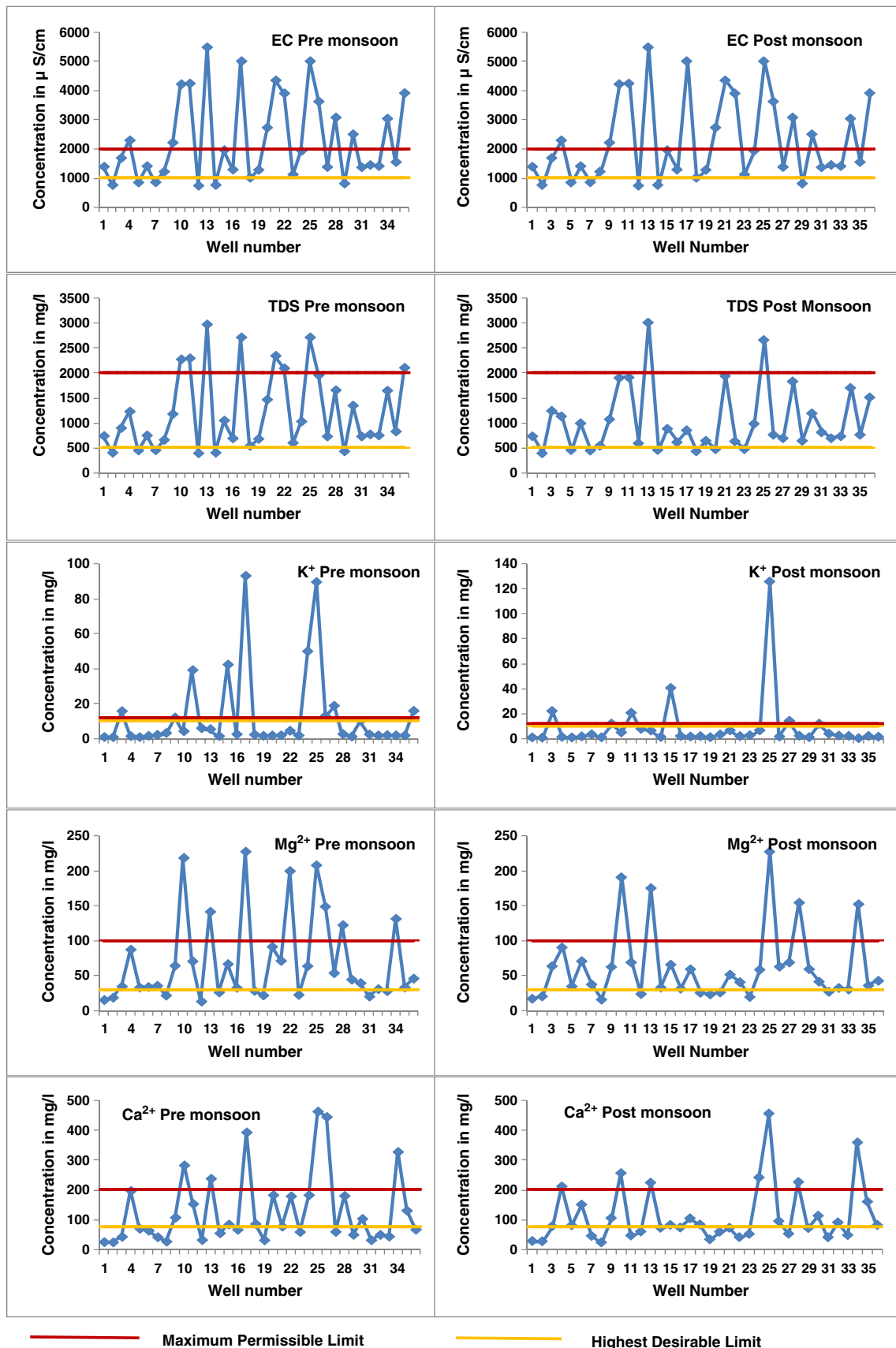
The concentration of NO_3^- ranges from 3 to 1114 mg/L and from 3 to 1242 mg/L with a mean of 238 and 201 mg/L. The highest concentration of NO_3^- in groundwater is due to anthropogenic activities like leaching of organic and inorganic fertilizers from agricultural land by infiltration of rain and irrigation waters, animal waste, and seepage from the sewers (Hem 1985). Nitrogen is a nutrient; it helps to stimulate crop growth. The excessive quantities of nitrogen may cause over-stimulation of growth or delayed maturity (FAO 1985). NO_3^- in drinking water is associated with some health issues such as blue baby syndrome in children and gastrointestinal problems, etc., in human beings (Deshmukh 2012).

Table 2 Statistical parameters of pre-monsoon season groundwater samples

| Constituents | Units | Minimum | Maximum | Mean | Standard deviation | BIS—IS 10500 (2012) | | FAO (1985) | Usual range in irrigation water | Samples were exceeding max. permissible limit of drinking standards (%) | Samples were exceeding max. permissible limit of irrigation standards (%) |
|-------------------------------|-------|---------|---------|---------|--------------------|-------------------------|---------------------------|------------|---------------------------------|---|---|
| | | | | | | Highest desirable limit | Maximum permissible limit | | | | |
| pH | | 6.96 | 8.24 | 7.52 | 0.31 | 6.5–8.5 | No relaxation | 6.0–8.5 | 0 | 0 | 0 |
| EC | µS/cm | 715 | 5490 | 2259.69 | 1429.66 | 1000 | 2000 | 0–3000 | 42 | 42 | 31 |
| TDS | mg/L | 381 | 2970 | 1213.28 | 774.14 | 500 | 2000 | 0–2000 | 22 | 22 | 22 |
| Na ⁺ | mg/L | 70 | 1075 | 322.13 | 267.60 | – | – | – | – | – | – |
| K ⁺ | mg/L | 0 | 93 | 12.35 | 22.87 | 10 | 12 | – | 25 | 25 | – |
| Mg ²⁺ | mg/L | 13 | 227 | 70.74 | 62.43 | 30 | 100 | – | 22 | 22 | – |
| Ca ²⁺ | mg/L | 24 | 463 | 128.57 | 120.48 | 75 | 200 | – | 17 | 17 | – |
| Cl ⁻ | mg/L | 18 | 1091 | 323.20 | 329.29 | 250 | 1000 | – | 8 | 8 | – |
| SO ₄ ²⁻ | mg/L | 8 | 473 | 128.19 | 127.22 | 200 | 400 | – | 6 | 6 | – |
| HCO ₃ ⁻ | mg/L | 220 | 1160 | 536.11 | 257.57 | – | – | – | – | – | – |
| CO ₃ ²⁻ | mg/L | 0 | 160 | 13.33 | 39.13 | – | – | – | – | – | – |
| NO ₃ ⁻ | mg/L | 3 | 1114 | 238.45 | 234.25 | 45 | No relaxation | – | 67 | 67 | – |
| F ⁻ | mg/L | 0.8 | 3.8 | 2.09 | 0.72 | 1 | 1.5 | – | 78 | 78 | – |
| Na ⁺ | meq/L | 3.06 | 46.78 | 14.01 | 11.64 | – | – | 0–40 | – | – | 8 |
| K ⁺ | meq/L | 0.01 | 2.38 | 0.32 | 0.58 | – | – | 0–2 | – | – | 6 |
| Mg ²⁺ | meq/L | 1.09 | 18.69 | 5.82 | 5.14 | – | – | 0–5 | – | – | 42 |
| Ca ²⁺ | meq/L | 1.18 | 23.11 | 6.42 | 6.01 | – | – | 0–20 | – | – | 6 |
| Cl ⁻ | meq/L | 0.50 | 30.77 | 9.12 | 9.29 | – | – | 0–30 | – | – | 6 |
| SO ₄ ²⁻ | meq/L | 0.16 | 9.84 | 2.67 | 2.65 | – | – | 0–20 | – | – | 0 |
| HCO ₃ ⁻ | meq/L | 3.61 | 19.01 | 8.79 | 4.22 | – | – | 0–10 | – | – | 25 |
| CO ₃ ²⁻ | meq/L | 0.00 | 5.33 | 0.44 | 1.30 | – | – | 0–0.1 | – | – | 11 |
| NO ₃ ⁻ | meq/L | 0.05 | 17.96 | 3.85 | 3.78 | – | – | 0–10 | – | – | 6 |
| Gibbs ratio I | meq/L | 0.08 | 0.81 | 0.40 | 0.22 | – | – | – | – | – | – |
| Gibbs ratio II | meq/L | 0.32 | 0.92 | 0.68 | 0.18 | – | – | – | – | – | – |
| C.A.I.—I | meq/L | -10.68 | 0.48 | -2.15 | 2.60 | – | – | – | – | – | – |
| C.A.I.—II | meq/L | -0.35 | 29.79 | 8.27 | 9.20 | – | – | – | – | – | – |

Table 3 Statistical parameters of post-monsoon season groundwater samples

| Constituents | Units | Minimum | Maximum | Mean | Standard deviation | BIS—IS 10500 (2012) | | FAO (1985) | | Samples were exceeding max. permissible limit of drinking standards (%) | Samples were exceeding max. permissible limit of irrigation standards (%) |
|-------------------------------|-------|---------|---------|---------|--------------------|-------------------------|---------------------------|---------------------------------|--------------|---|---|
| | | | | | | Highest desirable limit | Maximum permissible limit | Usual range in irrigation water | Post-monsoon | | |
| pH | | 6.9 | 7.94 | 7.48 | 0.25 | 6.5–8.5 | No relaxation | 6.0–8.5 | 0 | 0 | 0 |
| EC | µS/cm | 730 | 5560 | 1904.47 | 1191.79 | 1000 | 2000 | 0–3000 | 69 | 19 | 19 |
| TDS | mg/L | 389 | 3010 | 1020.08 | 643.10 | 500 | 2000 | 0–2000 | 6 | 6 | 6 |
| Na ⁺ | mg/L | 86 | 1119 | 304.81 | 243.08 | – | – | – | – | – | – |
| K ⁺ | mg/L | 0 | 125 | 8.61 | 21.55 | 10 | 12 | – | 14 | – | – |
| Mg ²⁺ | mg/L | 16 | 227 | 62.31 | 52.37 | 30 | 100 | – | 14 | – | – |
| Ca ²⁺ | mg/L | 23 | 456 | 111.77 | 97.62 | 75 | 200 | – | 19 | – | – |
| Cl ⁻ | mg/L | 17 | 1322 | 276.39 | 298.31 | 250 | 1000 | – | 3 | – | – |
| SO ₄ ²⁻ | mg/L | 7 | 544 | 114.38 | 129.65 | 200 | 400 | – | 6 | – | – |
| HCO ₃ ⁻ | mg/L | 230 | 1120 | 496.44 | 208.80 | – | – | – | – | – | – |
| CO ₃ ²⁻ | mg/L | 0 | 80 | 17.78 | 24.27 | – | – | – | – | – | – |
| NO ₃ ⁻ | mg/L | 3 | 1242 | 200.87 | 245.01 | 45 | No relaxation | – | 61 | – | – |
| F ⁻ | mg/L | 0.9 | 4.1 | 2.35 | 0.72 | 1 | 1.5 | – | 83 | – | – |
| Na ⁺ | meq/L | 3.75 | 48.66 | 13.26 | 10.57 | – | – | 0–40 | – | 6 | 6 |
| K ⁺ | meq/L | 0.00 | 3.20 | 0.22 | 0.55 | – | – | 0–2 | – | 3 | 3 |
| Mg ²⁺ | meq/L | 1.31 | 18.71 | 5.13 | 4.31 | – | – | 0–5 | – | 36 | 36 |
| Ca ²⁺ | meq/L | 1.13 | 22.77 | 5.58 | 4.87 | – | – | 0–20 | – | 3 | 3 |
| Cl ⁻ | meq/L | 0.48 | 37.29 | 7.80 | 8.42 | – | – | 0–30 | – | 3 | 3 |
| SO ₄ ²⁻ | meq/L | 0.15 | 11.32 | 2.38 | 2.70 | – | – | 0–20 | – | 3 | 3 |
| HCO ₃ ⁻ | meq/L | 3.77 | 18.36 | 8.14 | 3.42 | – | – | 0–10 | – | 17 | 17 |
| CO ₃ ²⁻ | meq/L | 0.00 | 2.67 | 0.59 | 0.81 | – | – | 0–0.1 | – | 44 | 44 |
| NO ₃ ⁻ | meq/L | 0.06 | 20.03 | 3.24 | 3.95 | – | – | 0–10 | – | 8 | 8 |
| Gibbs ratio I | meq/L | 0.09 | 0.78 | 0.39 | 0.19 | – | – | – | – | – | – |
| Gibbs ratio II | meq/L | 0.32 | 0.94 | 0.69 | 0.17 | – | – | – | – | – | – |
| C.A.I.—I | meq/L | -11.98 | 0.48 | -2.03 | 2.47 | – | – | – | – | – | – |
| C.A.I.—II | meq/L | -0.32 | 35.91 | 6.91 | 8.33 | – | – | – | – | – | – |



— Maximum Permissible Limit — Highest Desirable Limit

Fig. 2 Physicochemical ion concentration for drinking water standards in pre- and post-monsoon seasons (BIS 2012)

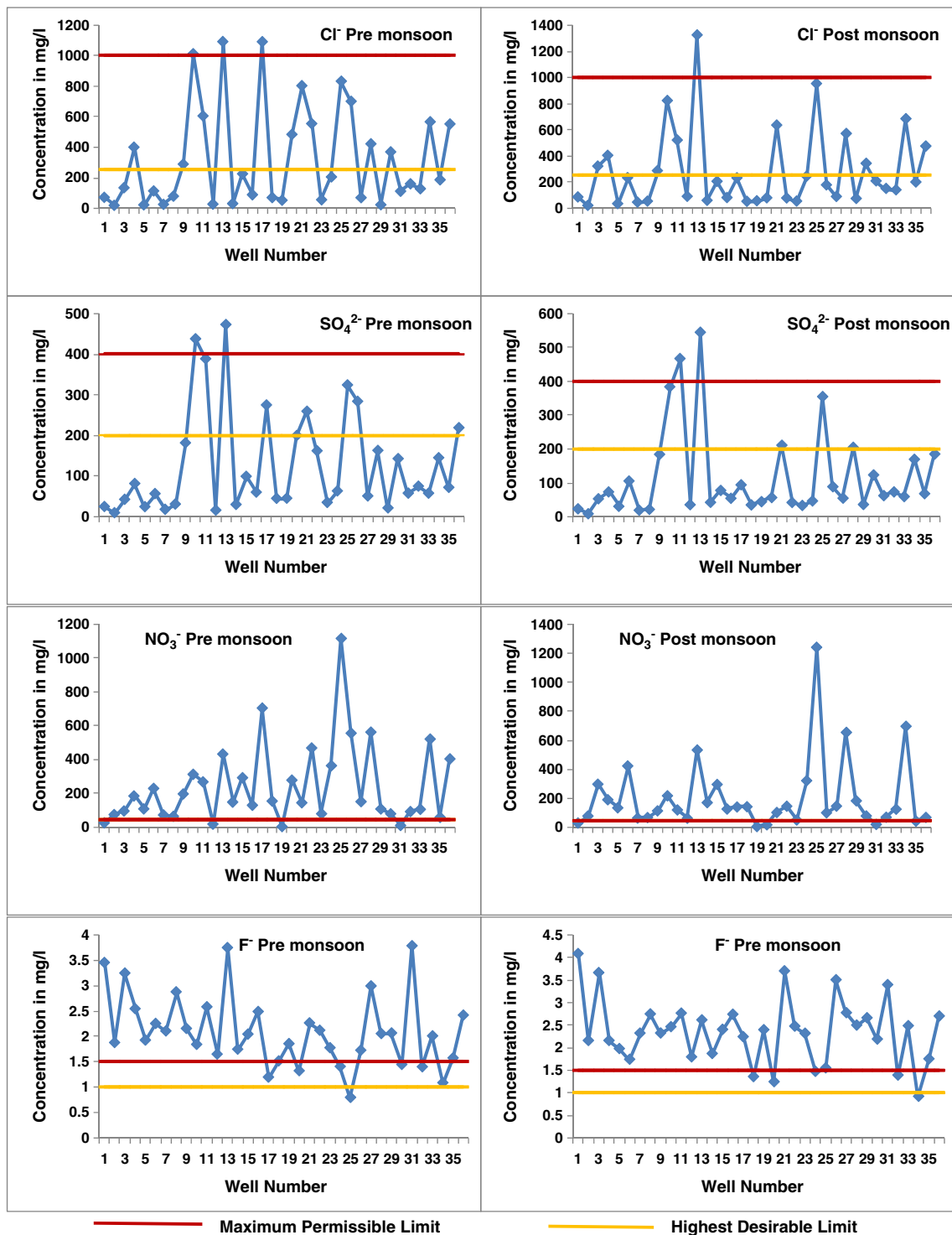


Fig. 2 (continued)

The concentration of F⁻ in groundwater ranges from 0.8 to 3.8 mg/L and from 0.9 to 4.1 mg/L with a mean of 2.1 and 2.3 mg/L in both seasons. An F⁻ concentration less than 0.5 mg/L results in dental caries, 0.5 to 1.5 mg/L promotes dental health, and > 1.5 mg/L creates dental and

skeletal problems in human health. Hence, it is essential to maintaining the F⁻ concentration between 0.5 and 1.5 mg/L in drinking water (WHO 2011). The NO₃⁻ and F⁻ values are slightly higher in the post-monsoon; it could be due to the migration of ions from soils and

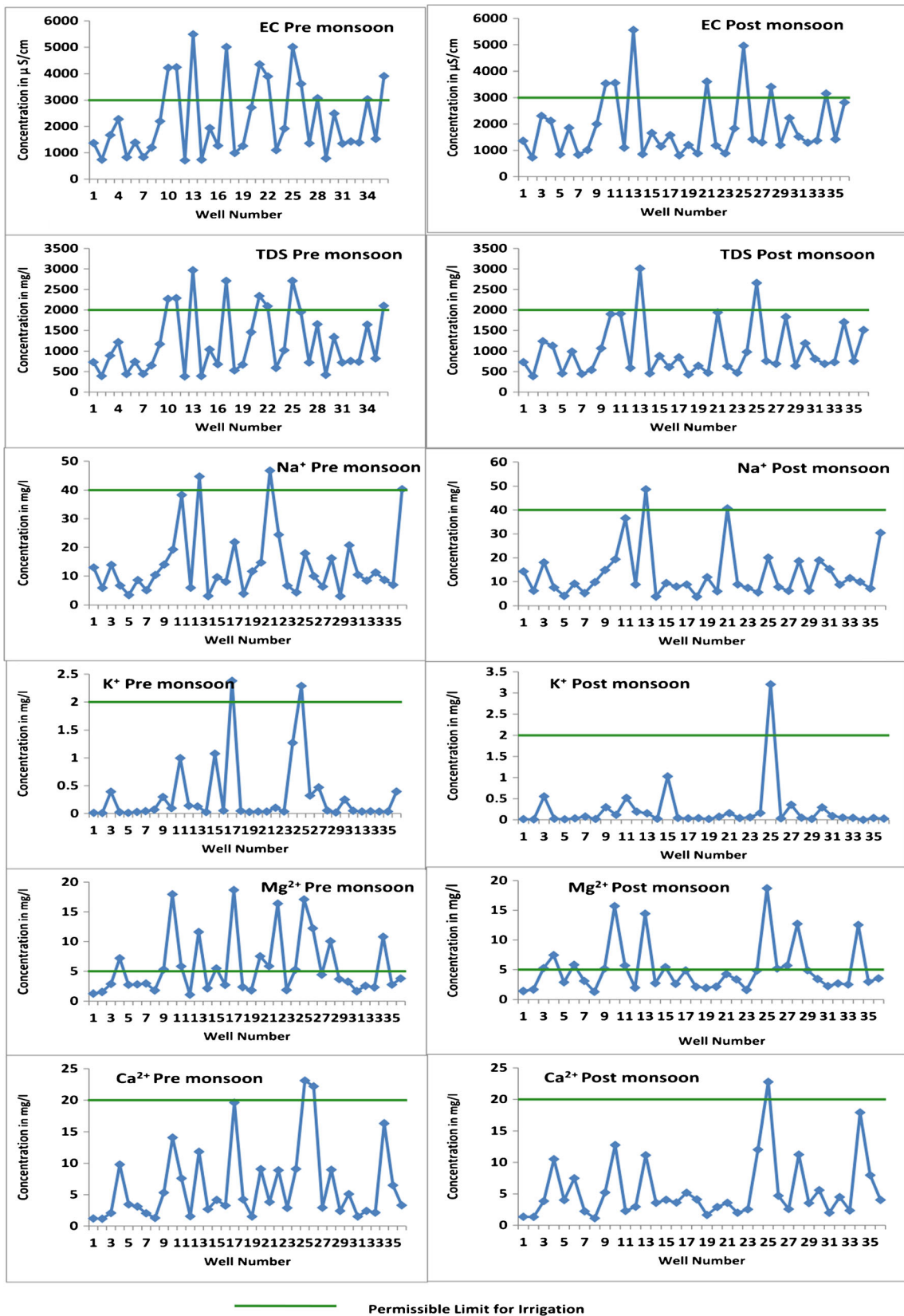
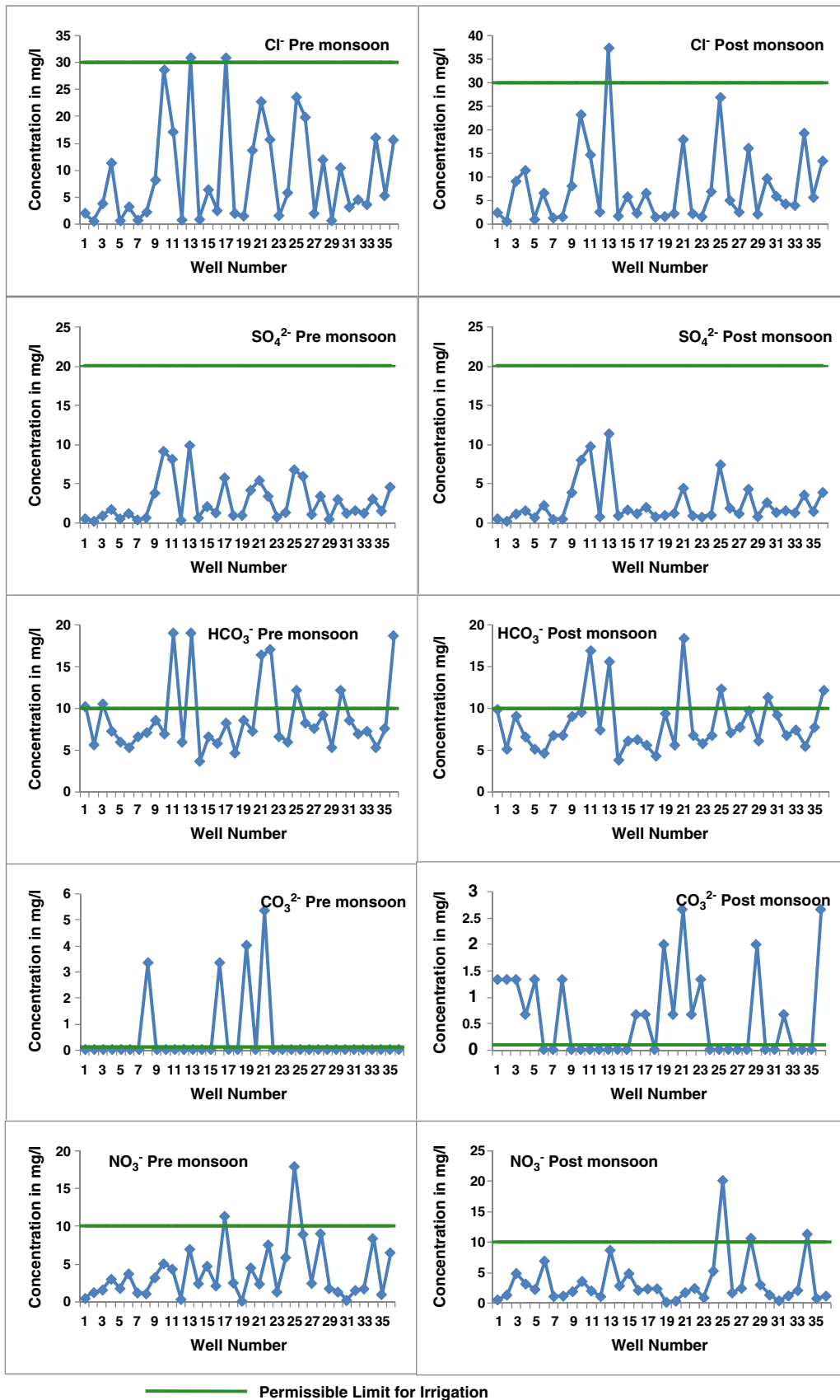


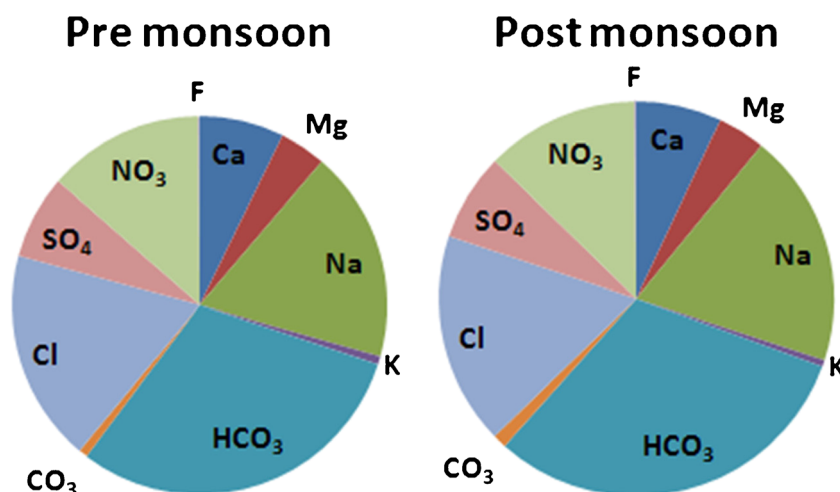
Fig. 3 Physicochemical ion concentration for irrigation water standards in pre- and post-monsoon seasons (FAO 1985)



————— Permissible Limit for Irrigation

Fig. 3 (continued)

Fig. 4 Mean concentration of major ions during pre- and post-monsoon seasons



weathered zone into groundwater by monsoon recharge (Subba Rao 2003).

Statistical analysis

Pearson's correlation matrix (Table 4) for pre-monsoon samples showed a significant moderate (M) negative correlation coefficient between pH and Ca^{2+} ($r = -0.57$) and NO_3^- ($r = -0.51$), a significant moderate (M) positive correlation between pH and CO_3^{2-} ($r = 0.65$), and a significant weak (W) negative correlation between pH and Mg^{2+} ($r = -0.48$). During the post-monsoon (Table 5) period, pH showed a significant strong negative correlation coefficient between pH and Ca^{2+} ($r = -0.71$), a significant moderate negative correlation with EC ($r = -0.51$), TDS ($r = -0.50$), Mg^{2+} ($r = -0.66$), Cl^- ($r = -0.52$), and NO_3^- ($r = -0.64$), a significant moderate positive correlation with CO_3^{2-} ($r = 0.51$), and a significant weak (W) negative correlation between K^+ ($r = -0.43$) and SO_4^{2-} ($r = -0.42$). The negative correlation indicates that pH was decreased with increasing EC, TDS, K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , and NO_3^- in groundwater and vice versa. The positive correlation indicates that the pH was increased with increasing CO_3^{2-} in groundwater.

EC showed a perfect (P) significant positive correlation with TDS ($r = 1.0$), Cl^- ($r = 0.97$), and SO_4^{2-} ($r = 0.93$), a significant strong (S) positive correlation coefficient between EC with Na^+ ($r = 0.80$), Mg^{2+} ($r = 0.83$), Ca^{2+} ($r = 0.75$), HCO_3^- ($r = 0.71$), and NO_3^- ($r = 0.76$), and significant moderate (M) positive correlation between EC with K^+ ($r = 0.50$) during pre-monsoon. In post-monsoon, EC showed that a perfect significant positive correlation with TDS ($r = 1.0$), Cl^- ($r = 0.98$), and SO_4^{2-} ($r = 0.91$) and a significant strong positive correlation were noticed between EC with Na^+ ($r = 0.82$), Mg^{2+} ($r = 0.84$), HCO_3^- ($r = 0.75$), a significant moderate (M) positive correlation

between EC with Ca^{2+} ($r = 0.69$) and NO_3^- ($r = 0.69$), and a significant weak positive correlation with K^+ ($r = 0.48$). All major ions are showing a similar trend (“ r ” values) with EC and TDS in pre- and post-monsoon seasons. Therefore, a significant positive relationship of the major ions together with EC and TDS is expected and suggests their contribution to major geochemical processes through mineralogical influence (Tay et al. 2017).

In pre-monsoon, Na^+ showed a perfect significant positive correlation with HCO_3^- ($r = 0.92$) and a significant strong positive correlation with Cl^- ($r = 0.72$) and SO_4^{2-} ($r = 0.76$); however, there was a significant weak positive correlation with Mg^{2+} ($r = 0.37$). During post-monsoon, Na^+ showed a perfect significant positive correlation with HCO_3^- ($r = 0.93$), a significant strong positive correlation with Cl^- ($r = 0.78$) and SO_4^{2-} ($r = 0.82$), and a significant weak positive correlation with Mg^{2+} ($r = 0.42$) and F^- ($r = 0.39$).

In pre-monsoon, K^+ showed a significant strong positive correlation with NO_3^- ($r = 0.70$), a significant moderate positive correlation with Mg^{2+} ($r = 0.52$) and Ca^{2+} ($r = 0.58$), and a significant weak positive correlation with Cl^- ($r = 0.46$) and SO_4^{2-} ($r = 0.38$). In post-monsoon, K^+ showed a significant strong positive correlation with NO_3^- ($r = 0.70$) and a significant moderately positive correlation with Mg^{2+} ($r = 0.53$) and Ca^{2+} ($r = 0.54$).

In pre-monsoon, Mg^{2+} showed a significant strong positive correlation with Ca^{2+} ($r = 0.88$), Cl^- ($r = 0.86$), SO_4^{2-} ($r = 0.75$), and NO_3^- ($r = 0.84$). In post-monsoon, Mg^{2+} showed a significant strong positive correlation with Ca^{2+} ($r = 0.87$), Cl^- ($r = 0.86$), SO_4^{2-} ($r = 0.75$) and NO_3^- ($r = 0.85$).

In pre-monsoon, Ca^{2+} showed a significant strong positive correlation with Cl^- ($r = 0.79$) and NO_3^- ($r = 0.87$), a significant moderate positive correlation with SO_4^{2-} ($r = 0.69$), and a significant weak negative correlation with F^- ($r = -0.41$). In post-monsoon, Ca^{2+} showed a significant strong positive

Table 4 Pearson's correlation matrix for hydrogeochemical data for pre-monsoon season

| Variables | pH | EC (µS/cm) | TDS (mg/L) | Na ⁺ (mg/L) | K ⁺ (mg/L) | Mg ²⁺ (mg/L) | Ca ²⁺ (mg/L) | Cl ⁻ (mg/L) | SO ₄ ²⁻ (mg/L) | HCO ₃ ⁻ (mg/L) | CO ₃ ²⁻ (mg/L) | NO ₃ ⁻ (mg/L) | F ⁻ (mg/L) |
|--------------------------------------|----------|------------|------------|------------------------|-----------------------|-------------------------|-------------------------|------------------------|--------------------------------------|--------------------------------------|--------------------------------------|-------------------------------------|-----------------------|
| pH | <i>I</i> | -0.320 | -0.318 | 0.058 | -0.281 | -0.478 | -0.567 | -0.318 | -0.230 | -0.044 | 0.653 | -0.511 | 0.258 |
| EC (µS/cm) | <i>I</i> | <i>I</i> | 1.000 | 0.798 | 0.500 | 0.827 | 0.748 | 0.971 | 0.929 | 0.711 | 0.005 | 0.759 | -0.063 |
| TDS (mg/L) | <i>I</i> | <i>I</i> | <i>I</i> | 0.797 | 0.502 | 0.827 | 0.749 | 0.972 | 0.929 | 0.710 | 0.005 | 0.760 | -0.064 |
| Na ⁺ (mg/L) | 0.058 | 0.798 | 0.797 | <i>I</i> | 0.184 | 0.373 | 0.220 | 0.718 | 0.756 | 0.919 | 0.251 | 0.315 | 0.263 |
| K ⁺ (mg/L) | -0.281 | 0.500 | 0.502 | 0.184 | <i>I</i> | 0.523 | 0.579 | 0.458 | 0.380 | 0.178 | -0.162 | 0.696 | -0.318 |
| Mg ²⁺ (mg/L) | -0.478 | 0.827 | 0.827 | 0.373 | 0.523 | <i>I</i> | 0.878 | 0.863 | 0.751 | 0.305 | -0.169 | 0.837 | -0.279 |
| Ca ²⁺ (mg/L) | -0.567 | 0.748 | 0.749 | 0.220 | 0.579 | 0.878 | <i>I</i> | 0.790 | 0.691 | 0.166 | -0.222 | 0.873 | -0.414 |
| Cl ⁻ (mg/L) | -0.318 | 0.971 | 0.972 | 0.718 | 0.458 | 0.863 | 0.790 | <i>I</i> | 0.933 | 0.573 | -0.009 | 0.720 | -0.120 |
| SO ₄ ²⁻ (mg/L) | -0.230 | 0.929 | 0.929 | 0.756 | 0.380 | 0.751 | 0.691 | 0.933 | <i>I</i> | 0.636 | -0.036 | 0.628 | -0.022 |
| HCO ₃ ⁻ (mg/L) | -0.044 | 0.711 | 0.710 | 0.919 | 0.178 | 0.305 | 0.166 | 0.573 | 0.636 | <i>I</i> | 0.122 | 0.294 | 0.344 |
| CO ₃ ²⁻ (mg/L) | 0.653 | 0.005 | 0.005 | 0.251 | -0.162 | -0.169 | -0.222 | -0.009 | -0.036 | 0.122 | <i>I</i> | -0.224 | 0.120 |
| NO ₃ ⁻ (mg/L) | -0.511 | 0.759 | 0.760 | 0.315 | 0.696 | 0.837 | 0.873 | 0.720 | 0.628 | 0.294 | -0.224 | <i>I</i> | -0.376 |
| F ⁻ (mg/L) | 0.258 | -0.063 | -0.064 | 0.263 | -0.318 | -0.279 | -0.414 | -0.120 | -0.022 | 0.344 | 0.120 | -0.376 | <i>I</i> |

Values in italics are significantly different from 0 at a significance level of 0.05

Table 5 Pearson's correlation matrix for hydrogeochemical data for post-monsoon season

| Variables | pH | EC (µS/cm) | TDS (mg/L) | Na ⁺ (mg/L) | K ⁺ (mg/L) | Mg ²⁺ (mg/L) | Ca ²⁺ (mg/L) | Cl ⁻ (mg/L) | SO ₄ ²⁻ (mg/L) | HCO ₃ ⁻ (mg/L) | CO ₃ ²⁻ (mg/L) | NO ₃ ⁻ (mg/L) | F ⁻ (mg/L) |
|--------------------------------------|----------|------------|------------|------------------------|-----------------------|-------------------------|-------------------------|------------------------|--------------------------------------|--------------------------------------|--------------------------------------|-------------------------------------|-----------------------|
| pH | <i>I</i> | -0.506 | -0.504 | -0.120 | -0.432 | -0.661 | -0.713 | -0.524 | -0.420 | -0.113 | 0.507 | -0.639 | 0.300 |
| EC (µS/cm) | <i>I</i> | <i>I</i> | 1.000 | 0.824 | 0.476 | 0.839 | 0.689 | 0.979 | 0.911 | 0.753 | -0.109 | 0.685 | 0.084 |
| TDS (mg/L) | -0.504 | 1.000 | <i>I</i> | 0.825 | 0.472 | 0.839 | 0.688 | 0.980 | 0.912 | 0.753 | -0.109 | 0.684 | 0.084 |
| Na ⁺ (mg/L) | -0.120 | 0.824 | 0.825 | <i>I</i> | 0.184 | 0.418 | 0.182 | 0.779 | 0.820 | 0.932 | 0.182 | 0.226 | 0.393 |
| K ⁺ (mg/L) | -0.432 | 0.476 | 0.472 | 0.184 | <i>I</i> | 0.534 | 0.535 | 0.402 | 0.367 | 0.284 | -0.195 | 0.703 | -0.110 |
| Mg ²⁺ (mg/L) | -0.661 | 0.839 | 0.839 | 0.418 | 0.534 | <i>I</i> | 0.873 | 0.863 | 0.749 | 0.343 | -0.335 | 0.845 | -0.150 |
| Ca ²⁺ (mg/L) | -0.713 | 0.689 | 0.688 | 0.182 | 0.535 | 0.873 | <i>I</i> | 0.724 | 0.523 | 0.142 | -0.364 | 0.864 | -0.428 |
| Cl ⁻ (mg/L) | -0.524 | 0.979 | 0.980 | 0.779 | 0.402 | 0.863 | 0.724 | <i>I</i> | 0.902 | 0.669 | -0.156 | 0.663 | 0.012 |
| SO ₄ ²⁻ (mg/L) | -0.420 | 0.911 | 0.912 | 0.820 | 0.367 | 0.749 | 0.523 | 0.902 | <i>I</i> | 0.734 | -0.208 | 0.495 | 0.046 |
| HCO ₃ ⁻ (mg/L) | -0.113 | 0.753 | 0.753 | 0.932 | 0.284 | 0.343 | 0.142 | 0.669 | 0.734 | <i>I</i> | 0.194 | 0.164 | 0.457 |
| CO ₃ ²⁻ (mg/L) | 0.507 | -0.109 | -0.109 | 0.182 | -0.195 | -0.335 | -0.364 | -0.156 | -0.208 | 0.194 | <i>I</i> | -0.310 | 0.376 |
| NO ₃ ⁻ (mg/L) | -0.639 | 0.685 | 0.684 | 0.226 | 0.703 | 0.845 | 0.864 | 0.663 | 0.495 | 0.164 | -0.310 | <i>I</i> | -0.290 |
| F ⁻ (mg/L) | 0.300 | 0.084 | 0.084 | 0.393 | -0.110 | -0.150 | -0.428 | 0.012 | 0.046 | 0.457 | 0.376 | -0.290 | <i>I</i> |

Values in italics are significantly different from 0 at a significance level of 0.05

Table 6 Eigenvalues, percent of variance, cumulative eigenvalue, and cumulative percent variance for the PAC of pre- and post-monsoon groundwater samples

| Factor | Pre-monsoon | | | | Post-monsoon | | | |
|--------|-------------|---------------------|-----------------------|--------------------------------|--------------|---------------------|-----------------------|--------------------------------|
| | Eigenvalue | Percent of variance | Cumulative eigenvalue | Cumulative percent of variance | Eigenvalue | Percent of variance | Cumulative eigenvalue | Cumulative percent of variance |
| 1 | 7.313 | 56.250 | 7.31255 | 56.25038 | 7.416 | 57.044 | 7.41572 | 57.04400 |
| 2 | 2.647 | 20.360 | 9.95931 | 76.61007 | 2.871 | 22.081 | 10.28624 | 79.12490 |
| 3 | 1.180 | 9.073 | 11.13881 | 85.68317 | 0.864 | 6.650 | 11.15070 | 85.77461 |
| 4 | 0.644 | 4.955 | 11.78296 | 90.63813 | 0.679 | 5.223 | 11.82975 | 90.99810 |
| 5 | 0.477 | 3.670 | 12.26000 | 94.30769 | 0.488 | 3.751 | 12.31736 | 94.74895 |
| 6 | 0.326 | 2.511 | 12.58643 | 96.81871 | 0.355 | 2.729 | 12.67208 | 97.47751 |
| 7 | 0.174 | 1.340 | 12.76057 | 98.15822 | 0.134 | 1.028 | 12.80569 | 98.50533 |
| 8 | 0.116 | 0.895 | 12.87698 | 99.05366 | 0.113 | 0.865 | 12.91820 | 99.37079 |
| 9 | 0.068 | 0.525 | 12.94517 | 99.57821 | 0.048 | 0.372 | 12.96650 | 99.74235 |
| 10 | 0.049 | 0.376 | 12.99402 | 99.95396 | 0.028 | 0.215 | 12.99451 | 99.95780 |
| 11 | 0.004 | 0.027 | 12.99758 | 99.98139 | 0.004 | 0.035 | 12.99901 | 99.99239 |
| 12 | 0.002 | 0.019 | 12.99999 | 99.99991 | 0.001 | 0.008 | 12.99999 | 99.99994 |
| 13 | 0.000 | 0.000 | 13.00000 | 100.00000 | 0.000 | 0.000 | 13.00000 | 100.00000 |

correlation with Cl^- ($r = 0.72$) and NO_3^- ($r = 0.86$), a significant moderate positive correlation with SO_4^{2-} ($r = 0.52$), and a significant weak negative correlation with CO_3^{2-} ($r = -0.36$) and F^- ($r = -0.43$).

In pre-monsoon, Cl^- showed a significant perfect positive correlation with SO_4^{2-} ($r = 0.93$), a significant strong positive correlation with NO_3^- ($r = 0.72$), and a significant moderate positive correlation with HCO_3^- ($r = 0.57$). In post-monsoon, Cl^- showed a significant perfect positive correlation with SO_4^{2-} ($r = 0.90$) and a significant moderate positive correlation with HCO_3^- ($r = 0.67$) and NO_3^- ($r = 0.66$).

In pre-monsoon, SO_4^{2-} showed a significant moderate positive correlation with HCO_3^- ($r = 0.64$) and NO_3^- ($r = 0.63$). In post-monsoon, SO_4^{2-} showed a significant moderate positive correlation with HCO_3^- ($r = 0.73$) and NO_3^- ($r = 0.50$). In pre-monsoon, HCO_3^- showed a significant weak positive correlation with F^- ($r = 0.34$). In post-monsoon, HCO_3^- showed a significant weak positive correlation with F^- ($r = 0.46$). In

post-monsoon, NO_3^- showed a significant strong negative correlation with F^- ($r = -0.38$).

Principal component analysis

Table 6 presents the eigenvalues, the percentage of variance, the cumulative eigenvalue, and the cumulative percentage of variance of pre- and post-monsoon groundwater samples. The scree plot graphs are used to identify the number of principal components (PCs) of the primary data structure (Ayla 2015). The vertical axis of the plots represents the eigenvalues, while the horizontal axis shows the factors. The factor that indicates an enormously accelerated quick dropoff on the chart gives the number of the essential factors. The horizontal lines demonstrate that the individual contributions of other variances brought by the factors come close to one another (Ayla 2015; Buyukozturk 2002). The eigenvalue greater than or

Fig. 5 Scree plot graph for components with its eigenvalues during pre- and post-monsoon seasons

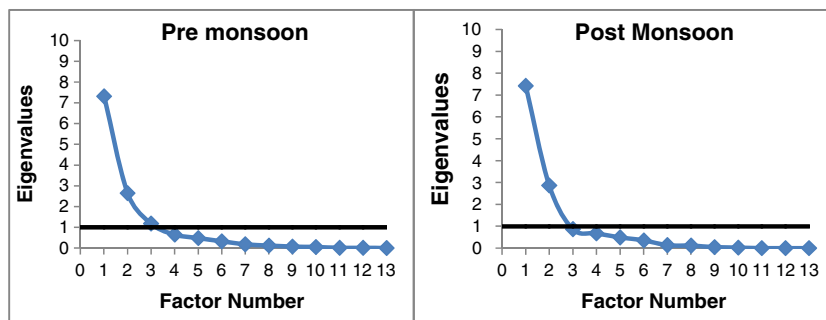


Table 7 Factor loading after varimax rotation in pre- and post-monsoon groundwater samples

| Variable | Three-factor model explaining 94.3% of the total variance in pre-monsoon | | | Two-factor model explaining 94.7% of the total variance in post-monsoon | |
|-------------------------------|--|-----------|-----------|---|-----------|
| | Factor 1 | Factor 2 | Factor 3 | Factor 1 | Factor 2 |
| pH | -0.365 | 0.005 | 0.833 *** | -0.126 | 0.020 |
| EC | 0.739 ** | 0.641 ** | -0.042 | 0.829 *** | 0.019 |
| TDS | 0.740 ** | 0.640 ** | -0.041 | 0.830 *** | 0.019 |
| Na ⁺ | 0.277 | 0.931 *** | 0.170 | 0.962 *** | 0.189 |
| K ⁺ | 0.333 * | 0.113 | -0.093 | 0.180 | -0.028 |
| Mg ²⁺ | 0.906 *** | 0.175 | -0.162 | 0.463 * | -0.076 |
| Ca ²⁺ | 0.884 *** | 0.048 | -0.225 | 0.243 | -0.305 * |
| Cl ⁻ | 0.824 *** | 0.524 ** | -0.024 | 0.800 *** | -0.047 |
| SO ₄ ²⁻ | 0.729 ** | 0.603 ** | -0.028 | 0.893 *** | -0.068 |
| HCO ₃ ⁻ | 0.140 | 0.940 *** | -0.002 | 0.902 *** | 0.279 |
| CO ₃ ²⁻ | -0.013 | 0.108 | 0.928 *** | 0.038 | 0.190 |
| NO ₃ ⁻ | 0.730 ** | 0.176 | -0.225 | 0.217 | -0.165 |
| F ⁻ | -0.183 | 0.207 | 0.074 | 0.224 | 0.921 *** |

Significant factor loadings are bold faced (*weak 0.50–0.30; **medium 0.50–0.75; ***strong > 0.75) (Liu et al. 2003)

equal to 1 will be accepted, which indicates that the contribution factor is significant.

The three-factor model for pre-monsoon and the two-factor model for post-monsoon were identified with eigenvalues greater than 1 (Fig. 5). Therefore, the first three factors with an eigenvalue sum of 11.1 in pre-monsoon and the first two factors with a total eigenvalue sum of 10.3 in post-monsoon show a significant effect on the variability of the groundwater chemistry (Table 7).

The total variance of the water quality among the studied wells in pre-monsoon is 85.63% of the first three PCs, and 79.12% of the first two PCs in post-monsoon. In pre-monsoon, the first factor (F1) explains 56.75% of the total variance, where Mg²⁺ (0.906), Ca²⁺ (0.884), and Cl⁻ (0.824) have strong positive weights. Pearson's correlation coefficient matrix also shows that Mg²⁺ has a significant strong positive correlation with Ca²⁺ ($r=0.88$) and Cl⁻ ($r=0.86$). The occurrence of these ions in groundwater is mainly due to dissolution from the host rock (Tay et al. 2017; Aksever and Buyuksahin 2017). The main source of Mg²⁺, Ca²⁺, and Cl⁻-bearing minerals occurring in the host rock is hornblende [Ca₂(Mg, Fe, Al)₅(Al, Si)₈O₂₂(OH)₂] and feldspathoid sodalite [Na₈(Cl₂(Al SiO₄)₆)] (Hem 1970).

These ions are strong contributors to salinity in the groundwater.

EC (0.739), TDS (0.740), SO₄²⁻ (0.729), and NO₃⁻ (0.730) have medium positive weights. Pearson's correlation coefficient matrix also shows that EC has a significant perfect positive correlation with TDS ($r=1$) and SO₄²⁻ ($r=0.929$) and a significant strong positive correlation with NO₃⁻ ($r=0.759$). The association of EC, TDS, SO₄²⁻, and NO₃⁻ reflects the influence of geogenic processes increased through human-induced activities such as fertilizers and animal feedings (Bhuiyan et al. 2016; Barzegar et al. 2017). The cause of SO₄²⁻ in groundwater is due to decomposition and oxidation of sulfur-bearing minerals in crystalline rocks (Jeziarski et al. 2006), and NO₃⁻ is due to leaching of organic and inorganic fertilizers from agricultural land by infiltration of precipitation, irrigation water, animal waste, and leakage from the sewers (Hem 1985). The study reveals that F1 is influenced by both geogenic and anthropogenic activities (Ayla 2015).

The second factor (F2) explains 20.36% of the total variance, where Na⁺ (0.931) and HCO₃⁻ (0.940) have strong positive weights. Pearson's correlation coefficient matrix also shows that Na⁺ has a significant perfect positive correlation with HCO₃⁻ ($r=0.919$). The occurrence of these ions in groundwater is mainly due to weathering of

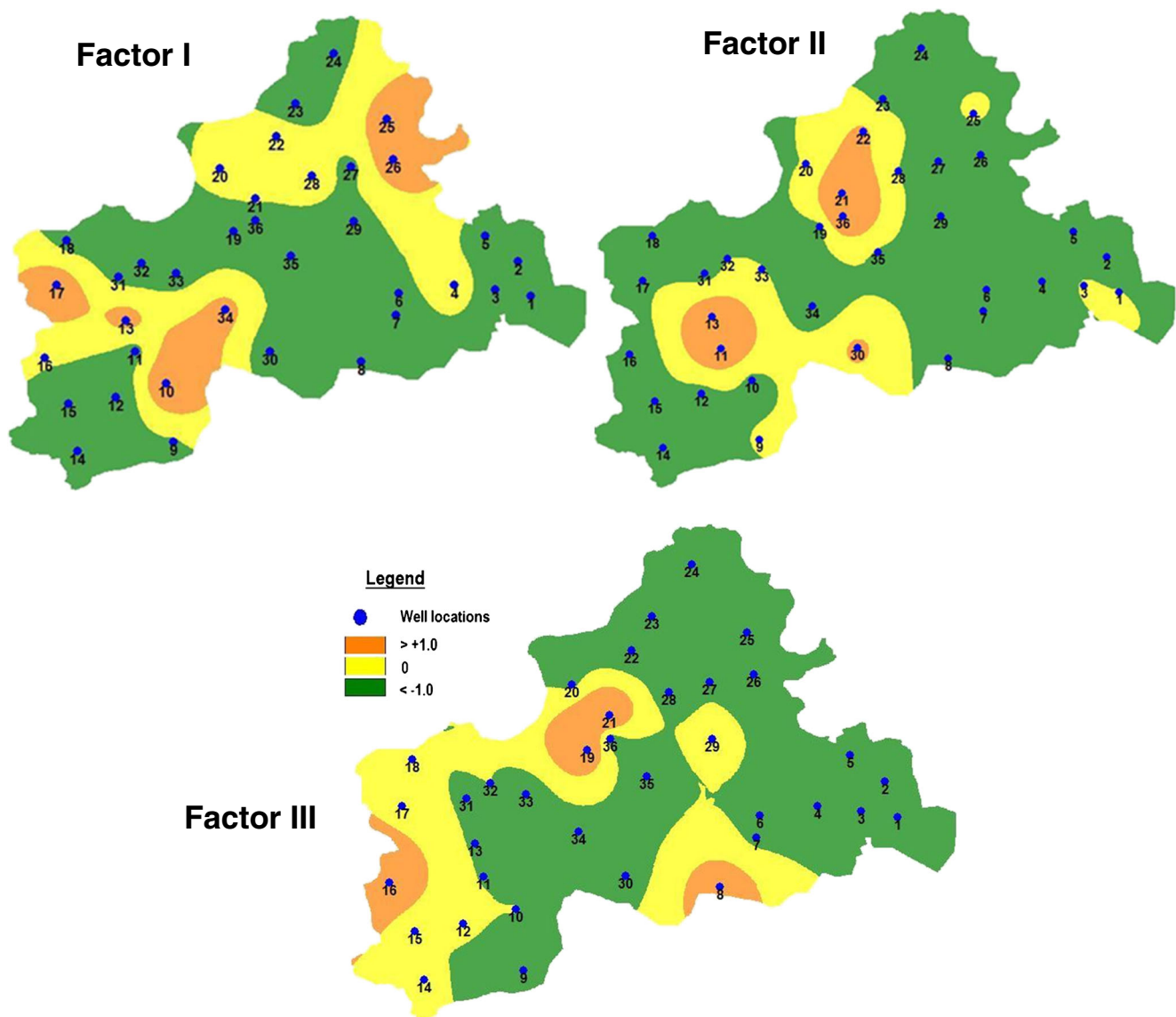
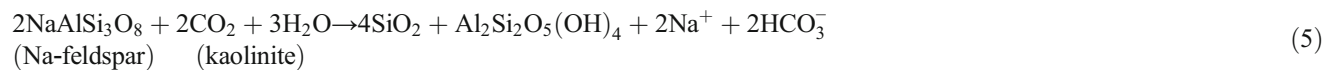


Fig. 6 Factor scores after varimax rotation for factors I, II, and III in pre-monsoon

the minerals like Na-feldspar in the host rock (Ahada and Suthar 2017; Hamzah et al. 2017). The following equation



explains the dissolution process of Na-feldspar in the groundwater.

EC (0.641), TDS (0.640), SO_4^{2-} (0.603), and Cl^- (0.524) have medium positive weights in the second factor. Pearson's correlation coefficient matrix also shows that Na^+ has a significant strong positive correlation with EC ($r=0.798$), TDS ($r=0.797$), SO_4^{2-} ($r=0.756$), and Cl^-

($r=0.718$). The occurrence of these ions in groundwater is mainly due to weathering and alteration of secondary minerals in the host rock.

The third factor (F3) explains 9.07% of the total variance, where pH (0.833) and CO_3^{2-} (0.928) show strong positive

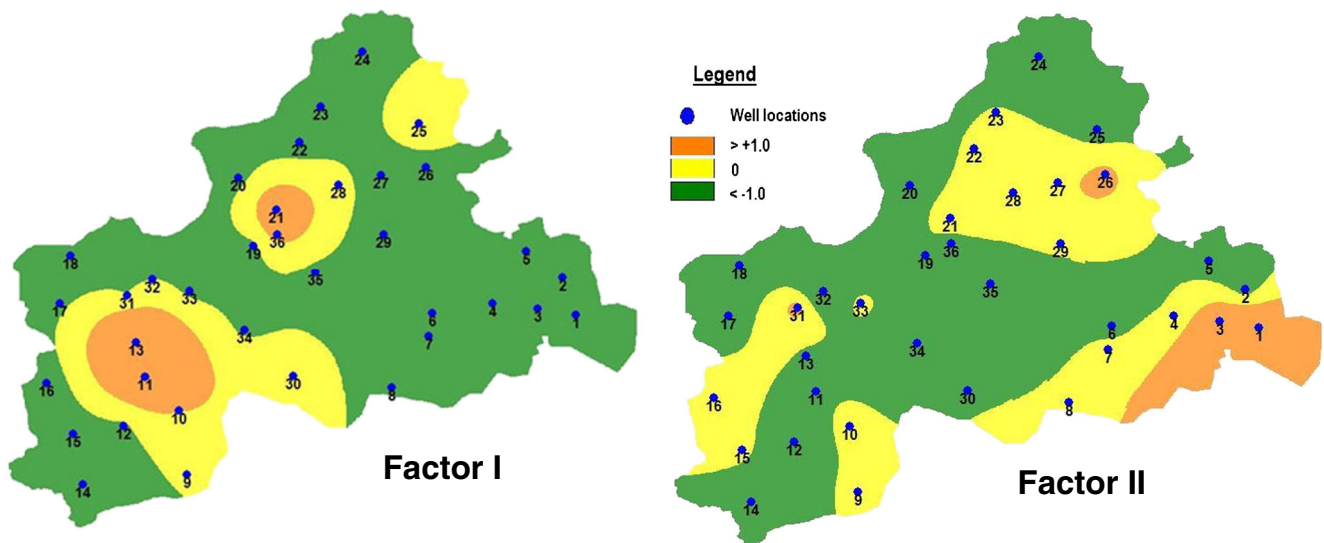


Fig. 7 Factor scores after varimax rotation for factors I and II in post-monsoon

weights. Pearson's correlation coefficient matrix also shows that the pH has a significant moderate positive correlation with CO_3^{2-} ($r=0.653$). The pH of water plays an essential role in the dissolution of CO_3^{2-} from the soil zone and lithology. The CO_3^{2-} ions can react with and neutralize two hydrogen ions (H^+) and release the HCO_3^- ions into the water (see, Eqs. 6 and 7).



The study reveals that F2 and F3 are influenced by geogenic origins.

In post-monsoon, F1 explains 57.04% of the total variance, where EC (0.829), TDS (0.830), Na^+ (0.962), Cl^- (0.800), SO_4^{2-} (0.893), and HCO_3^- (0.902) have strong positive weights. Pearson's correlation coefficient matrix also shows that EC has a significant perfect positive correlation with TDS ($r=1.00$),

Cl^- ($r=0.979$), and SO_4^{2-} ($r=0.911$) and a significant strong positive correlation with Na^+ ($r=0.824$) and HCO_3^- ($r=0.753$). The contribution of these ions in groundwater is mainly due to rainfall recharge during the monsoon season (Subba Rao 2003; Isa et al. 2017). Generally, in arid and semi-arid regions during dry and pre-monsoon seasons, a high rate of evapotranspiration occurs due to low freshwater exchange. It may cause precipitation of salts, temporarily in the top layers of the soil. In the subsequent rainfall, the infiltrating waters carry the salts, resulting in greater salinity. During the monsoon season, rock-water interaction, chemical weathering (Na-feldspar weathering), and ion exchange by infiltrating recharge waters subsequently dissolve ions in water. The results indicate that in post-monsoon the quality of groundwater is controlled by geogenic activities (Subba Rao 2003; Bencer et al. 2016).

In post-monsoon, F2 explains 22.08% of the total variance, where F^- (0.921) shows a strong positive weight. F^- is

Fig. 8 Trilinear diagram for representing analysis of groundwater quality during pre- and post-monsoon seasons (after Piper 1944)

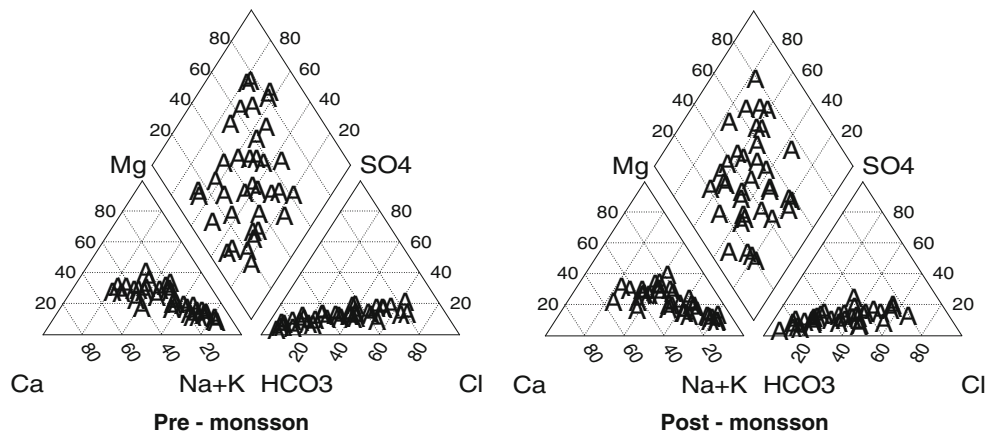


Table 8 Gibbs ratio and chloroalkaline indices of pre-monsoon groundwater samples

| Sample no. | Water type | TDS | Gibbs ratio I | Gibbs ratio II | C.A.I.—I | C.A.I.—II |
|------------|---|------|---------------|----------------|----------|-----------|
| 1 | Na-HCO ₃ | 730 | 0.16 | 0.91 | -5.54 | 0.81 |
| 2 | Na-HCO ₃ | 393 | 0.08 | 0.83 | -10.68 | -0.35 |
| 3 | Na-HCO ₃ -Cl | 890 | 0.26 | 0.87 | -2.81 | 2.65 |
| 4 | Ca-Mg-Na-Cl-HCO ₃ | 1220 | 0.61 | 0.41 | 0.40 | 10.69 |
| 5 | Ca-Na-Mg-HCO ₃ | 439 | 0.09 | 0.50 | -4.78 | 0.17 |
| 6 | Na-Ca-Mg-HCO ₃ -Cl-NO ₃ | 740 | 0.38 | 0.73 | -1.72 | 2.32 |
| 7 | Na-Mg-Ca-HCO ₃ | 443 | 0.09 | 0.71 | -6.45 | 0.05 |
| 8 | Na-HCO ₃ -CO ₃ | 649 | 0.24 | 0.89 | -3.75 | 1.33 |
| 9 | Na-Ca-Mg-HCO ₃ -Cl | 1170 | 0.49 | 0.73 | -0.76 | 7.20 |
| 10 | Na-Mg-Ca-Cl | 2270 | 0.81 | 0.58 | 0.32 | 27.60 |
| 11 | Na-HCO ₃ -Cl | 2290 | 0.47 | 0.84 | -1.31 | 15.78 |
| 12 | Na-HCO ₃ | 381 | 0.11 | 0.79 | -7.19 | -0.19 |
| 13 | Na-Cl-HCO ₃ | 2970 | 0.62 | 0.79 | -0.46 | 29.52 |
| 14 | Na-Ca-Mg-HCO ₃ -NO ₃ | 393 | 0.19 | 0.54 | -2.72 | 0.36 |
| 15 | Na-Mg-Ca-HCO ₃ -Cl | 1040 | 0.49 | 0.72 | -0.69 | 5.52 |
| 16 | Na-Ca-HCO ₃ -CO ₃ | 680 | 0.30 | 0.71 | -2.28 | 1.81 |
| 17 | Na-Ca-Mg-Cl | 2710 | 0.79 | 0.55 | 0.21 | 29.79 |
| 18 | Ca-Na-Mg-HCO ₃ | 530 | 0.30 | 0.48 | -1.04 | 1.45 |
| 19 | Na-HCO ₃ -CO ₃ | 670 | 0.15 | 0.89 | -7.07 | 0.58 |
| 20 | Na-Ca-Mg-Cl-HCO ₃ | 1460 | 0.65 | 0.62 | -0.08 | 12.69 |
| 21 | Na-Cl-HCO ₃ | 2340 | 0.58 | 0.92 | -1.07 | 21.04 |
| 22 | Na-Mg-HCO ₃ -Cl | 2090 | 0.48 | 0.73 | -0.57 | 14.74 |
| 23 | Na-Ca-HCO ₃ | 590 | 0.19 | 0.70 | -3.35 | 0.75 |
| 24 | Ca-Mg-Na-HCO ₃ -Cl-NO ₃ | 1020 | 0.49 | 0.38 | 0.03 | 5.33 |
| 25 | Ca-Na-Mg-Cl-NO ₃ -HCO ₃ | 2710 | 0.66 | 0.47 | 0.14 | 22.91 |
| 26 | Ca-Mg-Na-Cl | 1950 | 0.71 | 0.32 | 0.48 | 19.29 |
| 27 | Na-Mg-Ca-HCO ₃ | 720 | 0.20 | 0.70 | -2.52 | 1.31 |
| 28 | Na-Mg-Ca-Cl-HCO ₃ -NO ₃ | 1650 | 0.56 | 0.64 | -0.37 | 11.13 |
| 29 | Mg-Na-Ca-HCO ₃ | 420 | 0.11 | 0.56 | -3.99 | 0.20 |
| 30 | Na-HCO ₃ -Cl | 1340 | 0.46 | 0.80 | -1.02 | 9.11 |
| 31 | Na-HCO ₃ -Cl | 720 | 0.27 | 0.87 | -2.37 | 2.05 |
| 32 | Na-HCO ₃ -Cl | 760 | 0.39 | 0.78 | -0.88 | 3.64 |
| 33 | Na-HCO ₃ -Cl | 740 | 0.33 | 0.84 | -2.16 | 2.46 |
| 34 | Ca-Mg-Na-Cl | 1640 | 0.75 | 0.35 | 0.46 | 15.43 |
| 35 | Na-Ca-HCO ₃ -Cl | 820 | 0.41 | 0.52 | -0.33 | 4.53 |
| 36 | Na-HCO ₃ -Cl | 2100 | 0.45 | 0.92 | -1.62 | 14.18 |

released to the soil and groundwater, through weathering of the primary minerals (Rama Rao 1982; Sudheer Kumar et al. 2017). The study reveals that F1 and F2 in post-monsoon are influenced by geogenic processes.



Factor scores for the pre- and post-monsoon seasons were plotted on the maps (Figs. 6 and 7). The extreme positive factor score (> +1.0) reflects the most affected area. The negative factor scores (< -1.0) demonstrates the area unaffected by the process representing that factor, and near-zero scores reflect an area affected, but to an average degree, by the chemical process of the particular factor. Most of the area comes under negative factor scores; it indicates that geogenic processes like

weathering, dissolution, and ion exchange from host rock have not reached the maximum.

Understanding the hydrogeochemical evolution of groundwater

The major cation and anion concentrations were plotted on the Piper trilinear diagram to understand the hydrogeochemical evolution of groundwater in the study area (Piper 1944). The trilinear diagram of Piper is very useful in bringing out the chemical relationship in groundwater. Figure 8 shows the typical classification of hydrogeochemical facies for groundwater in pre- and post-monsoon seasons in the study area (Tables 8 and 9). Based on the Piper classification, most of the groundwater samples are identified as of sodium bicarbonate ($\text{Na}^+ - \text{HCO}_3^-$) type. Alkalies ($\text{Na}^+ + \text{K}^+$) exceed alkaline earths

Table 9 Gibbs ratio and chloroalkaline indices of post-monsoon groundwater samples

| Sample no. | Water type | TDS | Gibbs ratio I | Gibbs ratio II | C.A.I.—I | C.A.I.—II |
|------------|---|------|---------------|----------------|----------|-----------|
| 1 | Na-HCO ₃ | 730 | 0.19 | 0.91 | -5.20 | 1.12 |
| 2 | Na-HCO ₃ | 389 | 0.09 | 0.82 | -11.98 | -0.32 |
| 3 | Na-Mg-HCO ₃ -Cl | 1240 | 0.50 | 0.83 | -1.08 | 7.82 |
| 4 | Ca-Na-Mg-Cl-HCO ₃ | 1130 | 0.63 | 0.42 | 0.33 | 10.64 |
| 5 | Na-Ca-Mg-HCO ₃ | 454 | 0.14 | 0.51 | -3.84 | 0.40 |
| 6 | Na-Ca-Mg-Cl-NO ₃ -HCO ₃ | 990 | 0.58 | 0.55 | -0.42 | 5.79 |
| 7 | Na-Mg-Ca-HCO ₃ | 444 | 0.15 | 0.71 | -3.52 | 0.52 |
| 8 | Na-HCO ₃ | 540 | 0.17 | 0.90 | -6.02 | 0.37 |
| 9 | Na-Ca-Mg-HCO ₃ -Cl | 1070 | 0.47 | 0.74 | -0.90 | 6.94 |
| 10 | Na-Mg-Ca-Cl-HCO ₃ | 1900 | 0.71 | 0.60 | 0.16 | 22.20 |
| 11 | Na-HCO ₃ -Cl-SO ₄ | 1910 | 0.46 | 0.94 | -1.54 | 13.29 |
| 12 | Na-Ca-HCO ₃ | 590 | 0.25 | 0.75 | -2.69 | 1.45 |
| 13 | Na-Cl-HCO ₃ | 3010 | 0.71 | 0.81 | -0.31 | 35.91 |
| 14 | Na-Ca-Mg-HCO ₃ -NO ₃ | 455 | 0.29 | 0.52 | -1.46 | 1.04 |
| 15 | Na-Mg-Ca-HCO ₃ -Cl-NO ₃ | 880 | 0.48 | 0.72 | -0.84 | 4.84 |
| 16 | Na-Ca-HCO ₃ | 610 | 0.26 | 0.69 | -2.66 | 1.38 |
| 17 | Na-Ca-Mg-Cl-HCO ₃ | 850 | 0.54 | 0.63 | -0.38 | 5.59 |
| 18 | Ca-Na-Mg-HCO ₃ | 429 | 0.24 | 0.48 | -1.80 | 0.83 |
| 19 | Na-HCO ₃ | 640 | 0.14 | 0.88 | -7.05 | 0.51 |
| 20 | Na-Ca-Mg-HCO ₃ -Cl | 471 | 0.28 | 0.67 | -1.84 | 1.33 |
| 21 | Na-HCO ₃ -Cl | 1940 | 0.49 | 0.92 | -1.29 | 16.32 |
| 22 | Na-Mg-HCO ₃ | 630 | 0.24 | 0.82 | -3.27 | 1.24 |
| 23 | Na-Ca-HCO ₃ | 471 | 0.20 | 0.75 | -4.26 | 0.54 |
| 24 | Ca-Na-Mg-Cl-HCO ₃ | 980 | 0.50 | 0.32 | 0.16 | 6.34 |
| 25 | Ca-Na-Mg-Cl-NO ₃ | 2660 | 0.69 | 0.51 | 0.13 | 26.21 |
| 26 | Na-Mg-Ca-HCO ₃ -Cl | 760 | 0.41 | 0.62 | -0.59 | 4.16 |
| 27 | Na-Mg-HCO ₃ | 690 | 0.24 | 0.72 | -1.68 | 1.83 |
| 28 | Na-Mg-Ca-Cl-HCO ₃ -NO ₃ | 1830 | 0.62 | 0.62 | -0.17 | 15.24 |
| 29 | Na-Mg-Ca-HCO ₃ | 640 | 0.25 | 0.64 | -2.14 | 1.45 |
| 30 | Na-Ca-HCO ₃ -Cl | 1190 | 0.46 | 0.77 | -1.01 | 8.29 |
| 31 | Na-HCO ₃ -Cl | 810 | 0.39 | 0.89 | -1.66 | 4.35 |
| 32 | Na-Ca-HCO ₃ -Cl | 690 | 0.38 | 0.66 | -1.13 | 3.26 |
| 33 | Na-HCO ₃ -Cl | 730 | 0.34 | 0.83 | -2.01 | 2.75 |
| 34 | Ca-Mg-Na-Cl-NO ₃ | 1700 | 0.78 | 0.36 | 0.48 | 18.71 |
| 35 | Ca-Na-HCO ₃ -Cl | 760 | 0.42 | 0.47 | -0.30 | 4.79 |
| 36 | Na-Cl-HCO ₃ | 1510 | 0.52 | 0.88 | -1.29 | 11.74 |

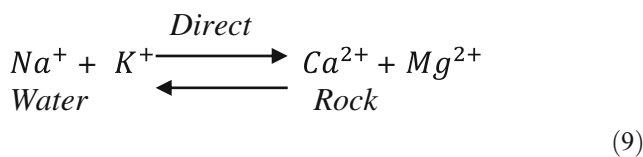
(Ca²⁺ > Mg²⁺) and weak acids (CO₃²⁻ + HCO₃⁻) exceed strong acids (SO₄²⁻ + Cl⁻).

Understanding the mechanism controlling the chemistry of groundwater

The quality of groundwater is controlled by several factors such as the physical situation of the aquifer, bedrock mineralogy, and weather condition. Gibbs ratios of the water samples are plotted against their respective values of total dissolved solids for anions and cations separately (Tables 8 and 9). The Gibbs (1970) diagram shows three distinct fields, namely, precipitation dominant area, evaporation dominant area, and rock–water interaction dominant area. The graphs indicate that almost all the water samples in both seasons either for cations or anions fall in the rock dominance field (Fig. 9).

Index of base exchange

Control on the dissolution of undesirable elements in waters is impossible during the subsurface runoff, but it is essential to know the various changes undergone by water during the travel (Pojasek 1977 and Johnson 1979). In the evaluation of the ion exchange or base exchange, chloroalkaline indices can be either positive or negative depending on whether the exchange of Na⁺ and K⁺ from water for Mg²⁺ and Ca²⁺ in rock is observed as a direct or vice versa as reverse as shown below.



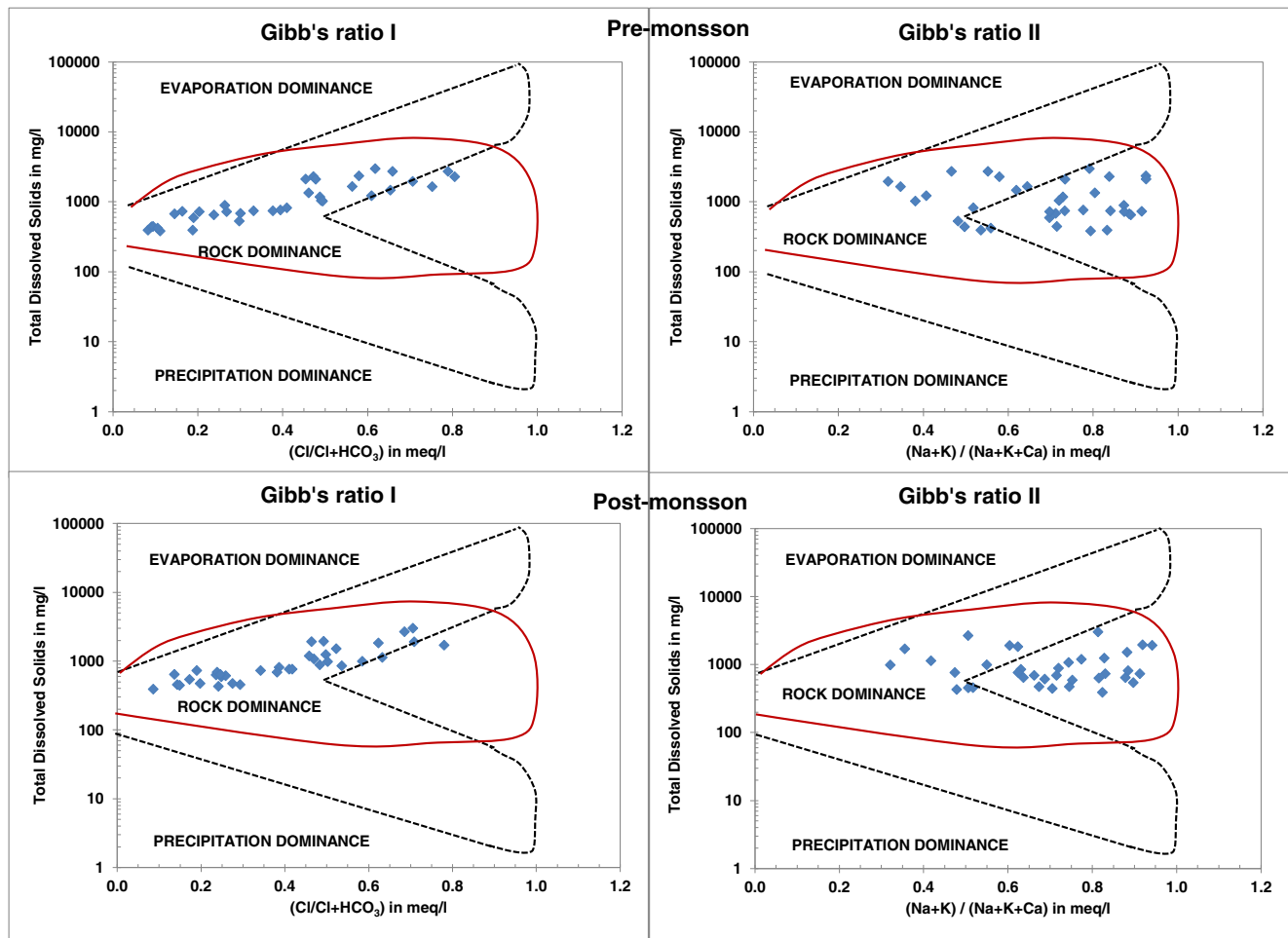


Fig. 9 Mechanism controlling the chemistry of groundwater during pre- and post-monsoon seasons (after Gibbs 1970)

Chloroalkaline indices for pre- and post-monsoon waters are calculated and given in Tables 8 and 9. The CAI calculations show that 81 and 86% of samples are negative ratios in pre- and post-monsoon. This ratio indicates an indirect base exchange reaction. CAII calculations show that 94 and 97% of samples are positive in pre- and post-monsoon (Fig. 10). It shows a direct base exchange reaction.

Conclusion and recommendations

Principal component analysis, Gibbs ratio, and index of base exchange were concurrently applied to the hydrochemical data of groundwater samples to identify

the primary sources that control groundwater chemistry. The results revealed that the dominance of cations in groundwater is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and that of anions is $HCO_3^- > Cl^- > NO_3^- > SO_4^{2-} > CO_3^{2-} > F^-$. Based on the Piper classification, most of the groundwater samples are identified as of sodium bicarbonate ($Na^+-HCO_3^-$) type. Alkalies ($Na^+ + K^+$) exceed alkaline earths ($Ca^{2+} > Mg^{2+}$), and weak acids ($CO_3^{2-} + HCO_3^-$) exceed strong acids ($SO_4^{2-} + Cl^-$). The nature of the groundwater is near-neutral to weakly alkaline.

Principal component analysis extracted a three-factor model for pre-monsoon and a two-factor model for post-monsoon. In pre-monsoon, F1 explains 56.75% of the total variance, where Mg^{2+} , Ca^{2+} , and Cl^- have strong positive weights.

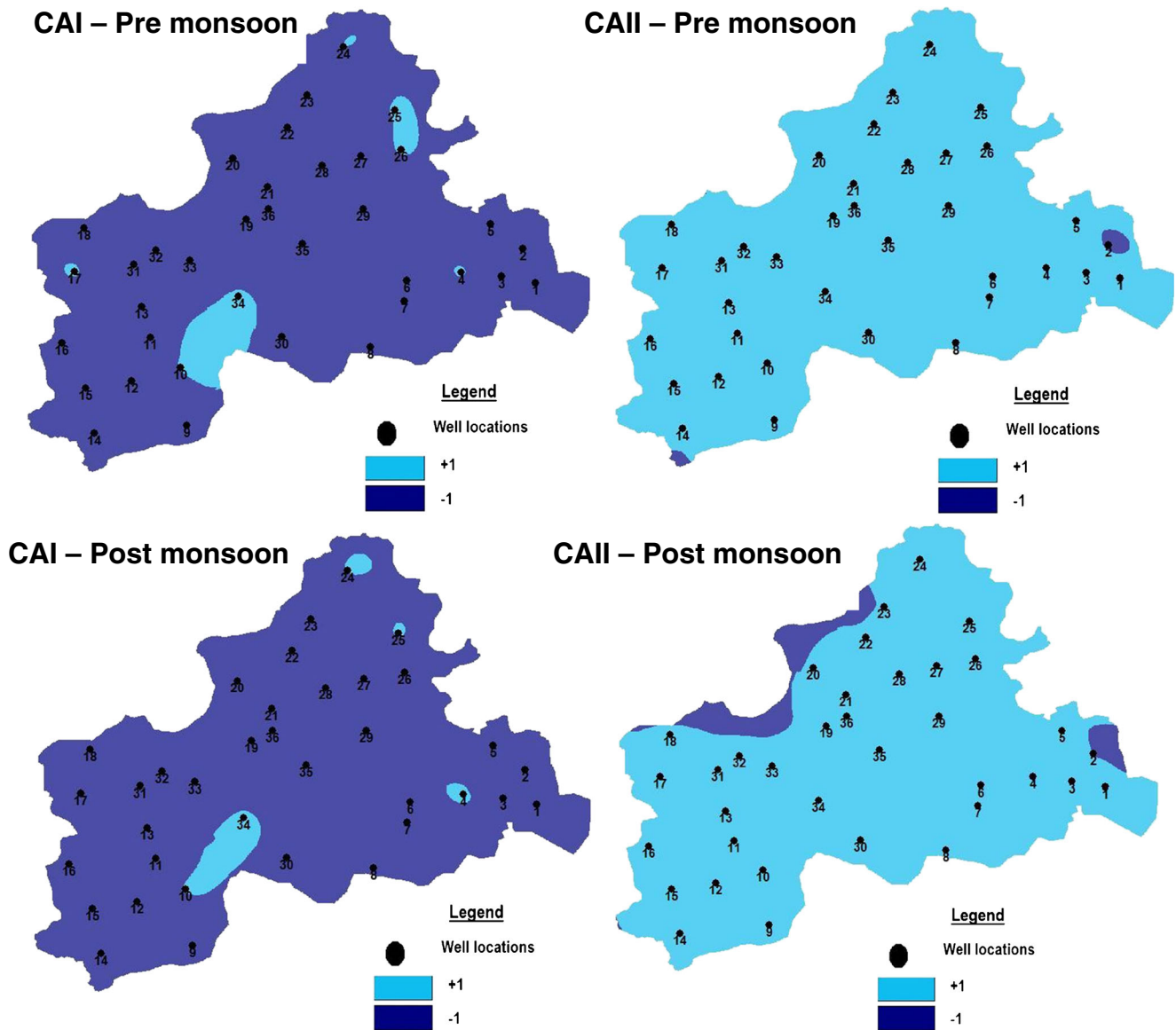


Fig. 10 The chloroalkaline indices I and II during pre- and post-monsoon

Pearson's correlation coefficient matrix also shows that Mg^{2+} has a significant strong positive correlation with Ca^{2+} and Cl^- . The occurrence of these ions in groundwater is mainly due to dissolution from the host rock. EC, TDS, SO_4^{2-} , and NO_3^- have medium positive weights, and Pearson's correlation coefficient matrix also shows that EC has a significant perfect positive correlation with TDS and SO_4^{2-} and a significant strong positive relationship with NO_3^- . The study reveals that F1 is influenced by both geogenic and anthropogenic activities. F2 explains 20.36% of the total variance, where Na^+ and HCO_3^- have strong positive weights. Pearson's correlation coefficient matrix also shows that Na^+ has a significant perfect

positive correlation with HCO_3^- . The occurrence of these ions in groundwater is mainly due to weathering of the minerals like Na-feldspar in granites and gneisses. EC, TDS, SO_4^{2-} , and Cl^- have medium positive weights, and Pearson's correlation coefficient matrix also shows that Na^+ has a significant strong positive correlation with EC, TDS, SO_4^{2-} , and Cl^- . The occurrence of these ions in groundwater is mainly due to weathering and alteration of secondary minerals in the host rock. F3 explains 9.07% of the total variance, where pH and CO_3^{2-} show strong positive weights. Pearson's correlation coefficient matrix also shows that pH has a

significant moderate positive correlation with CO_3^{2-} . The pH of water plays an important role in the dissolution of CO_3^{2-} from the soil zone and lithology. The study reveals that F2 and F3 are totally influenced by geogenic processes.

In post-monsoon, F1 explains 57.04% of the total variance, where EC, TDS, Na^+ , Cl^- , SO_4^{2-} , and HCO_3^- have strong positive weights. Pearson's correlation coefficient matrix also shows that EC has a significant perfect positive correlation with TDS, Cl^- , and SO_4^{2-} and a significant strong positive correlation with Na^+ and HCO_3^- . The contribution of these ions in groundwater is mainly due to rainfall recharge during the monsoon season. The results indicate that in post-monsoon the quality of groundwater is controlled by geogenic processes. F2 explains 22.08% of the total variance, where F^- shows a strong positive weight. F^- is released to soil and groundwater, through weathering of the primary minerals. The study reveals that F1 and F2 in post-monsoon are influenced by geogenic processes.

According to Gibbs classification, all the groundwater samples of both seasons either for cations or for anions fall under the rock dominance field. CAI indices show that 81 and 86% of samples are negative ratios in pre- and post-monsoon. This ratio indicates the indirect base exchange reaction among the studied groundwater samples. CAII indices show that 94 and 97% of samples are positive in pre- and post-monsoon. It shows a direct base exchange reaction. The overall study indicates that geogenic processes in the study area control the groundwater chemistry.

Most of the groundwater samples are exceeding their maximum permissible limits of drinking and irrigation standards. Mainly, F^- and NO_3^- concentrations are alarming and may pose risks to the health of the people using it for drinking purposes in the study area. It may cause illness, skeletal fluorosis, renal disorders, and gastrointestinal problems due to the high concentration of F^- and NO_3^- . Defluorinating and denitrifying the groundwater with the help of cost-effective methods needs to be practiced in a large extent to reduce the F^- and NO_3^- concentration of groundwater before using it for domestic purposes.

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