

# Hydrogeochemical characteristics of Karst Aquifer from a semi-arid region of Southern India and impact of rainfall recharge on groundwater chemistry

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**Abstract** The highly heterogeneous and anisotropic property of karst aquifers is a result of the dissolution and karstification of carbonate rocks. Hydrogeochemical evolution and possible water–rock interaction is therefore discussed through spatial and temporal variations in physico–chemical variables of groundwater. Samples were collected both from spring and bore wells. Dissolution of carbonate minerals is the main source of major ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$ ) in the water. Agricultural activities cause an increase in the concentration of pollution-related ions (nitrates, sulphates, chlorides, etc.). The variability of water chemistry was discussed in terms of different processes like dilution and water–rock interactions, etc. The study reveals a pronounced seasonal hydrochemical variation in the limestone aquifer. In general, the karst groundwater is of Ca–Mg– $\text{HCO}_3$  type. Hydrogeochemical signature also helped to analyse the recharge types in the area. The semi-arid climate of the area also contributes to the increase of concentration of certain ions.

**Keywords** Hydrogeochemistry · Karst aquifer · Semi-arid · Southern India

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## Introduction

Physico–chemical parameters of groundwater provide specific information about the karst aquifers and their heterogeneity and act as a means to characterise the karst system regarding its structure and behaviour. A number of studies have used the physico–chemical properties of karst waters (e.g. Shuster and White 1971; Ternan 1972; Scanlon 1990; Perrin et al. 2003; Vesper et al. 2003; Karimi et al. 2005; Krawczyk and Ford 2006; Moral et al. 2008; Wu et al. 2009; etc.). The hydrochemical data helps to reveal the groundwater flow, its residence time, interaction and exchange of chemical components, transport properties, vulnerability etc. (Wicks and Engeln 1997; Lang et al. 2006). The chemical signature of water has been interpreted in terms of recharge conditions (Scanlon and Thrailkill 1987; Mayer 1999; Hess and White 1988; Vervier 1990), nature of groundwater storage (Williams 1983), quick flow and matrix flow (Blavoux and Mudry 1983) and tributary mixing (Perrin et al. 2006). Water chemistry significantly contributes to the conceptualization of the aquifer hydrogeology and helps in understanding the mineralogical and hydrological processes operating in the aquifer system (Glynn and Plummer 2005).

A number of inter-related processes and factors govern the physico–chemical characteristics of karst groundwater. The proportion of calcite and dolomite minerals in the rock and their dissolution kinetics are one of the basic factors. Partial pressure of  $\text{CO}_2$  ( $\text{PCO}_2$ ) is an important factor that determines the dissolution equilibrium (Plummer et al. 1978; Buhmann and Dreybrodt 1985). The quality of recharging water, chemical composition of parent rock, geochemical processes, residence time, water and soil–rock interactions etc. affect the water chemistry and its evolution with time (Jeong 2001; Wu et al. 2009). The nature of recharge and the degree of karstification along with the anthropogenic activities are additional factors responsible for the chemical variation in

groundwater (Karimi et al. 2005; Ford and Williams 2007). The concentrated recharge rapidly transports sediments, pesticides, fertilisers and bacteria which adversely affect the geochemical processes.

Spatial and temporal variability of karst water chemistry has also been studied worldwide (e.g. Mayer 1999; Perrin et al. 2003; Musgrove and Banner 2004) and these studies have been interpreted in terms of structure, nature and location of chemical inputs, nature of different reactions and mixing processes occurring in the system etc. for the water resource management and protection of the karst aquifers. No such detailed research is available about the hydrogeochemical characteristics of karst aquifers of India which are also major groundwater-bearing rocks (e.g. Dar et al. 2014). The objective of this paper is to understand the source of major ions in karst water and also the processes modifying the groundwater chemistry in relation to space and time, for which a karstified area from Proterozoic Cuddapah basin of southern India was chosen.

## Study area

The study area lies in the central part of the Cuddapah Basin of southern India (Fig. 1) and covers an area of more than 100 km<sup>2</sup>. About 17 % of the basin is occupied by the carbonate rocks (Dar et al. 2011). The climate is typically semi-arid with long, hot and dry summers (day temperature reaching 45 °C) and a well-defined monsoon season with a mean annual rainfall of ~709 mm. Annual rainfall makes only 38.8 % of total annual potential evapotranspiration demand, which indicates an aridity index of 0.38.

Detailed geology of this karstified area is discussed in Dar et al. (2011). The karstified aquifer is a part of 100–200-m thick Narji Formation of the Kurnool Group. Owk shale and Paniam quartzite overlay the limestone towards west and form the Uppalapadu plateau (Fig. 1). The aquifer geometry is complex and is tectonically compartmented into different units (Fig. 2). Major part of the limestone is overlain by a thin (less than a metre) veneer of black and mixed soil with thickness increasing towards north. Black soil has more clay content (73.76 %) than mixed soil (Dar et al. 2011). Groundwater recharge occurs by concentrated allogenic and autogenic types through the dissolution features and diffuses recharge through the soil and epikarst zone. The limestone becomes confined towards the east by the overlying impervious shale. Regional groundwater flow is generally towards southeast (Fig. 1). Surface drainage consists of the temporary Pal-Eru stream, a tributary of the Kundu River. Towards the south, karst features (sinkholes) are widespread through which the surface drainage gets lost in the form of sinking streams. Natural vegetation is scarce and comprises of scattered shrubs. Agriculture occurs as rain-fed crops towards the south and

irrigated crops (paddy) towards north due to the available surface water from the Owk reservoir for canal irrigation.

## Methodology

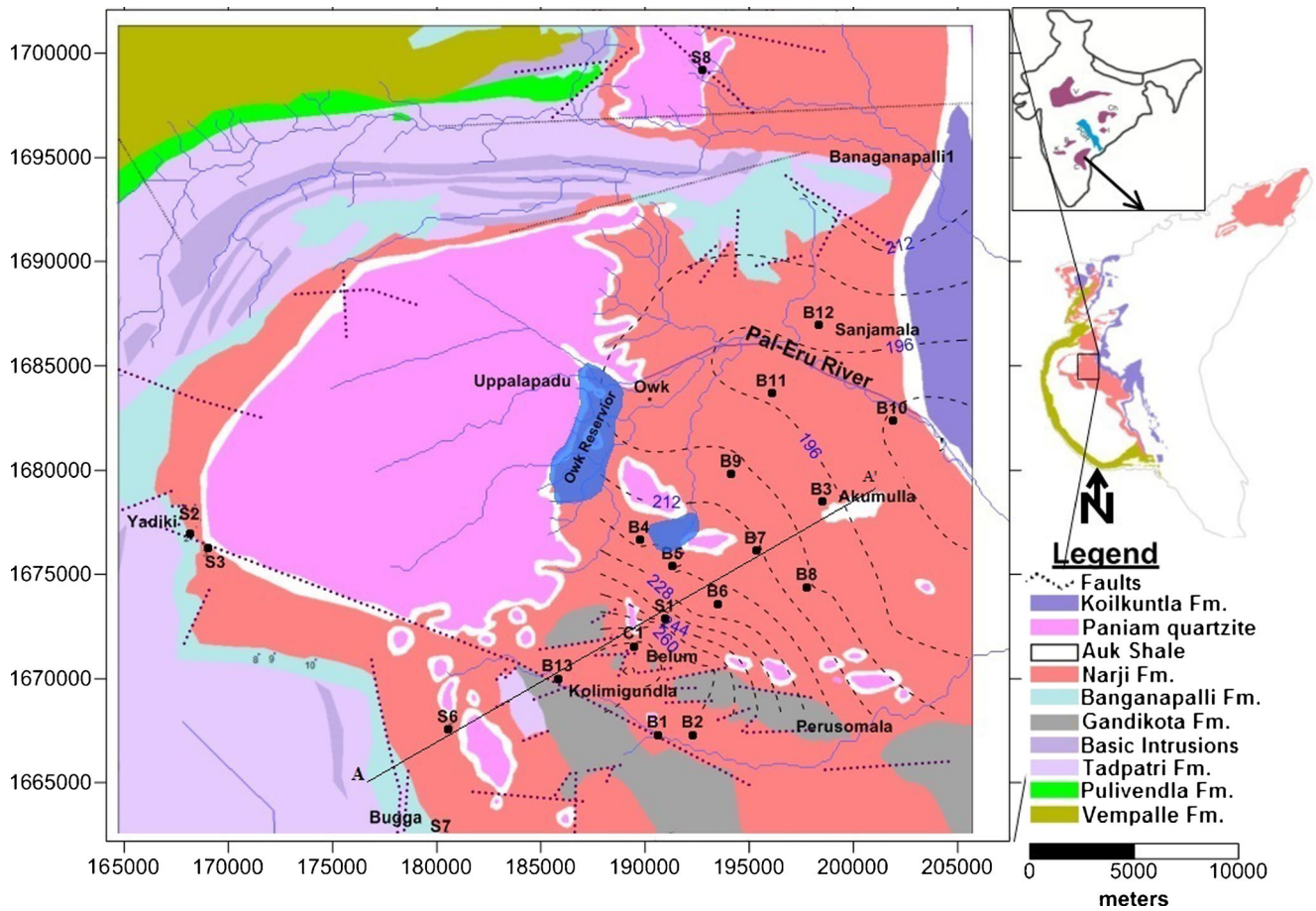
Groundwater samples analysed for chemistry include 13 from bore wells, 6 from springs and 1 from the deepest point in the Belum cave. The springs, namely Belum (S1), Kona (S2 and S3) and Yaganti (S8) were also monitored continuously but infrequently for a period of 3 years (2009–2011). At these spring locations, discharge of the out flowing water was also measured during each field survey using a measurable bucket and a stopwatch. Water samples were analysed for physical and chemical characteristics for pre-monsoon (PRM-2011) season while, in post-monsoon (POM-2011) season, the number of samples was reduced to 12 because of inaccessibility to some of the sample locations. Permanent springs at Kona (S2 and S3) and Yaganti (S8) and the temporary springs (S6 and S7) are hydrogeologically separate from the rest of the samples (Fig. 1). S7 is highly contaminated due to human interactions. The in situ measurement of electrical conductivity (EC), pH and water temperature was carried out with a portable field conductivity and pH metre. The unfiltered samples were analysed for bicarbonates by titration with 0.1-M HCl to a pH of 4.5 within a few days. The anions were analysed with an ion chromatograph Dionex DX 600 from the filtered samples. The detection limit was about 1 µmol/L and usual precision of 5 %. Cations were measured with an ICP-OES Jobain-Yvon with the same detection limit and precision except for Ca and Mg, due to conditioning of samples (oversaturation regarding to carbonates). All the samples were analysed within 1 month after collection.

The basic statistical analysis was done for the samples of same location for both seasons. Few samples were also neglected which were most affected by anthropogenic activities. The analysis was done using MS Excel and the data plotting was done in Golden Grapher software. In order to check the quality of the analysis, the ionic balance was computed for each sample. The charge balance error of analysis (acceptable range 0–5 %) was found to be below 2 %. The linear regression of cation sum to anion sum gives  $R^2=0.9$  (Fig. 3).

## Results

### Spatial variability of water chemistry

The Piper (Piper 1953) diagram shows a large variability in the water chemistry of the area. During PRM season, 67 % of the samples fall in the Ca triangle and the rest of the samples did not show any dominant signature (Fig. 4a). Among



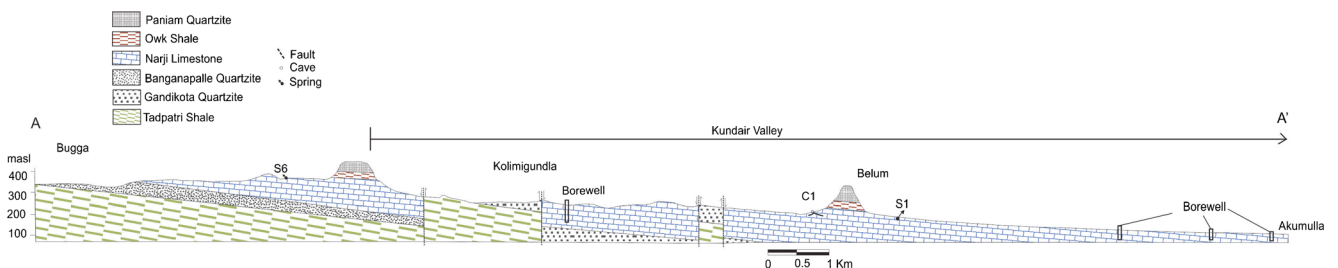
**Fig. 1** Geological map of the karstified area. Three karstified formations of Cuddapah Basin are also shown (modified after GSI 1997). Black dashed contours represent the water level in masl. Spring (represented by

S) and bore well (B) samples are represented by solid circles. Major surface drainage is shown by blue lines

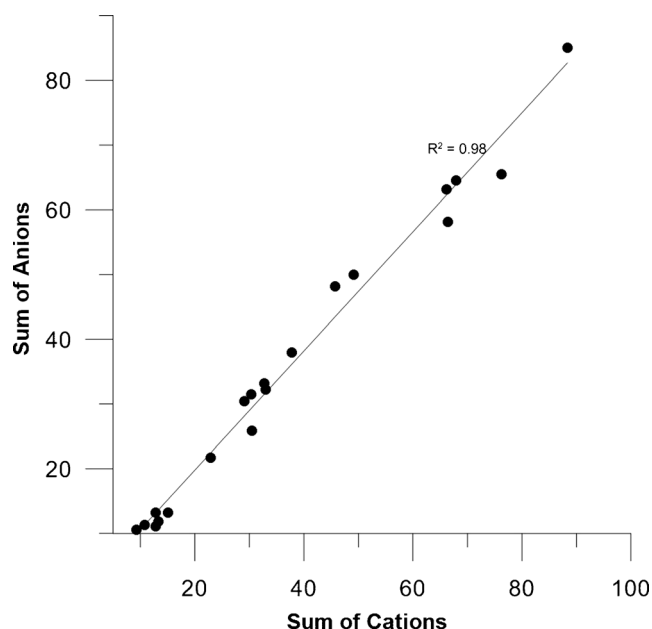
anionic species, 33 % of samples are Cl type, 33 % bicarbonate type and the rest of the samples show mixed character. During POM season (Fig. 4b), 92 % of the samples shift towards the Ca type in case of cationic species and 33 % towards carbonate type and 67 % show a mixed nature in case of anionic species.

The karst waters do not show any major type. Ca–HCO<sub>3</sub>–Cl type waters are represented by 42 % of samples. S8 is of Ca–HCO<sub>3</sub> type, S2 and S3 are of Ca–Cl type in which average Ca<sup>2+</sup>+Mg<sup>2+</sup>+HCO<sub>3</sub><sup>-</sup> constitutes 83 % of total ions, B7 is Ca–Na–Cl type, B13 is of Ca–Na–HCO<sub>3</sub>–Cl type and B11 of Na–HCO<sub>3</sub> type. All springs lie in the field of Ca<sup>2+</sup>+Mg<sup>2+</sup> >70 %.

From the diamond field of the Piper diagram, no major water groups were distinguished. However, spring waters from Belum (S1), Kona (S2 and S3), Rati (S6) and bore well (B13) can be separated into a major group. The springs S2 and S3 are less affected by human activities and are hydrogeologically separated from the rest of the samples. The reason for very high concentration of certain ions in B7 is not known; however, the sample was collected from a village hand pump which could have a large human influence. B11 and B12 are located in agriculturally cultivated area. C1 has a large human impact and is fed by sewage from the cave area.



**Fig. 2** Geological cross-section along the karstic terrain, showing the Narji limestone aquifer and location of some springs and bore wells



**Fig. 3** Plot of sum of cations vs. sum of anions for the samples analysed

During POM season, majority of the samples shift towards the Ca–HCO<sub>3</sub>–Cl type water (Fig. 4b). S8 fall in the pure Ca–HCO<sub>3</sub> type field and do not show any change in water type during POM season. In the case of samples B2 and B13, HCO<sub>3</sub><sup>-</sup> ions get exchanged and water becomes a Ca–Cl type during POM season.

#### Seasonal (PRM-POM) water chemistry variation

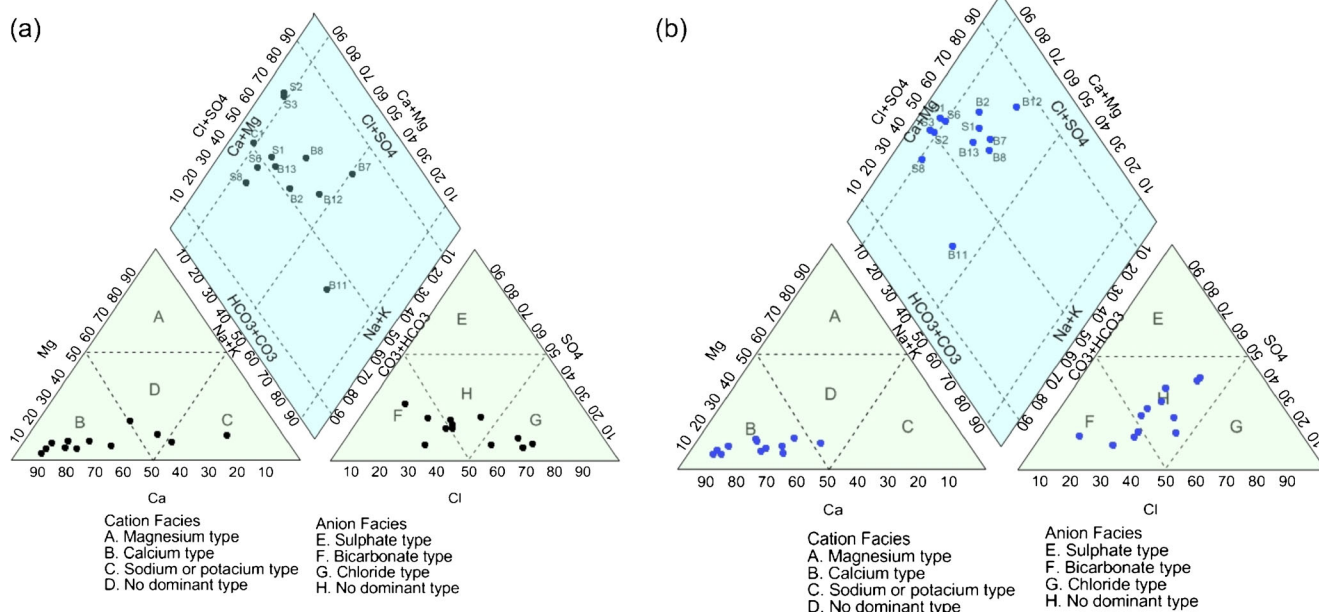
The chemical variation from PRM to POM season is quite clear in most of the samples. The difference in concentration

of chemical parameters from PRM to POM (PRM-POM/PRM and expressed as percent) for the springs and wells is also studied.

All the springs showed an increase in Ca<sup>2+</sup> concentration in POM season except S6 which discharges from the top most (epikarst) layer of the aquifer and shows a large variation in flow during PRM to POM season. It also remains dry for most of the PRM months (Dar 2014). Mg<sup>2+</sup> ion decreases in all the springs except S3. A very high increase was observed in the concentration of Ca<sup>2+</sup>, Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> in S3. An increase in Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> was also observed in spring waters during POM season. Decrease in EC, total dissolved solids (TDS) and T is also observed in majority of the samples. The springs S2 and S3 showed very large increase in Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, TH. The springs are separated in terms of hydrogeological setup than rest of the samples. All the bore wells showed a decrease in Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> except B7.

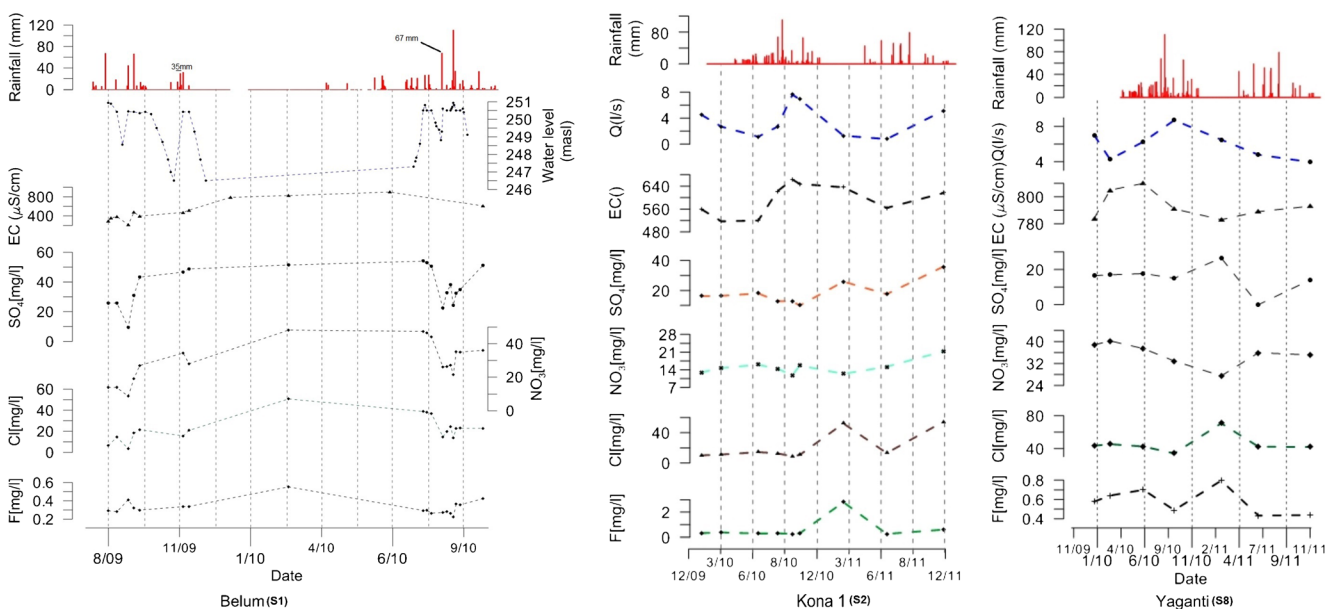
#### Temporal variability of water chemistry

The intra-site variability of chemical parameters from 2009–2011 for S1, S2 and S8 is shown in Fig. 5. Spring S1 shows sharp changes in flow and chemistry during monsoon months. For most of the time, the spring remains in non-flowing condition and gets a large influence from human activities. During high rainy events, the discharge reaches up to 50 L/s which sharply decrease after rainfall. The peak flow follows immediately after rainfall which sustains for few (3 to 4) days after rainfall (Dar 2014) and shows sharp decrease in the water chemistry due to fast dilution from fresh rain water. From Fig. 5, it is observed that in 2009, a rainfall event of 35 mm lead to the water level rise of ~4 m in a few days. The same



**Fig. 4** Hydrochemical facies showing the spatial variability of spring and bore well waters on Piper diagram **a** PRM and **b** POM samples





**Fig. 5** Intra-site temporal variability of physico-chemical parameters in springs (S1, S2 S8). Water level was used for Belum spring (S1) whereas discharge was compared for Kona 1 (S2) and Yaganti (S8) springs

sharp response was observed in year 2010, when a single rainfall event of ~67 mm (Fig. 5) caused a 3-m rise in water level in the well and a large variation in water chemistry. During the periods of high recharge, ionic concentrations decreased to lower values but increased sharply during non-flowing conditions. Thus, dilution effect, rapid transit time and short residence time are the main reasons for such sharp decrease in chemistry during monsoon months. The catchment area of the spring gets faster recharge as the area shows high karstification degree (Dar et al. 2011). The intra-site temporal variability of different constituent was observed by comparing the coefficient of variation (CV) in percentage. The most sensitive spring is S1 which shows high variability in discharge and chemistry than other springs. The fluctuations in chemistry of S2 and S8 are not sharp and indicate a longer residence time of groundwater. The mineralogical controls and longer residence time may be responsible for the production of Ca–Mg–HCO<sub>3</sub> type water in S2 and S8 springs. S1 and S6 (epikarst spring) are more sensitive to EC, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions (Fig. 6).

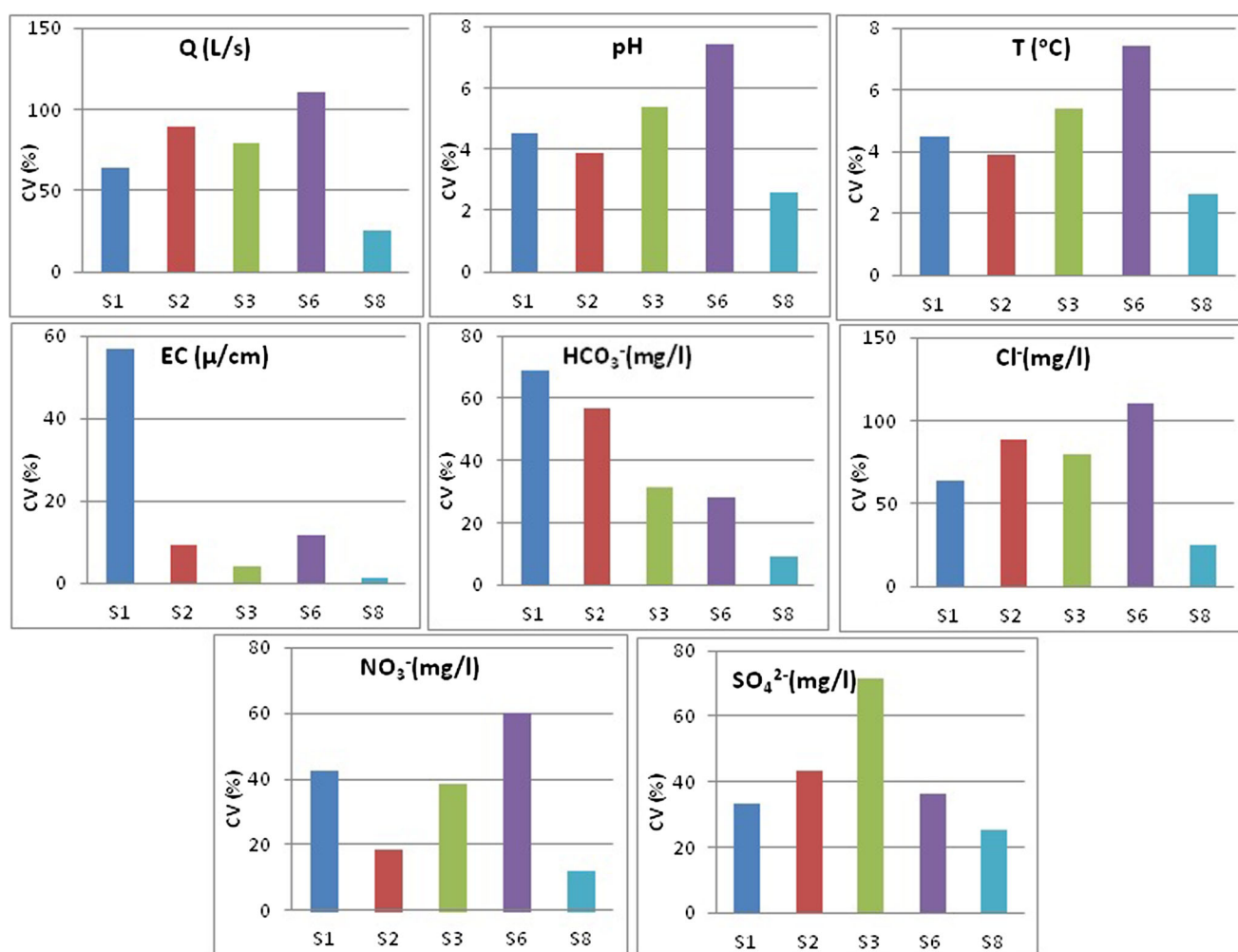
**Discussion**

The results from major ion data were used to understand the seasonal, temporal and spatial changes in groundwater chemistry of the karst aquifer. The data for physico-chemical parameters summarised in Table 1 shows a wide variation. Chemical parameters were divided into dissolution related (Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>) and agriculture and land use-related (Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) parameters. For springs and bore

wells during PRM and POM season, the mean and CV is given in Table 2. Agriculture-related parameters show more variability during both seasons.

Groundwater is mildly acidic to slightly alkaline in nature and shows no marked decrease from PRM to POM seasons. Karst water show high temperatures during PRM and POM seasons. EC values range between 538–2013 and 422–1,703 µS/cm during PRM and POM seasons with mean values of 1,141.7 and 942.5 µS/cm, respectively. The EC values of majority of the samples remain above 500 µS/cm during both seasons, which indicates that the waters remain saturated with respect to CaCO<sub>3</sub> (Jacobson and Langmuir 1974). The slight decrease in temperature, EC and TDS during POM season is due to the fresh recharging water that dilutes the more mineralized stored water. The dilution effect is also found by the decrease of Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> during POM season.

Total dissolved solids (TDS) in the groundwater vary from 370.9–1,557.8 mg/L during PRM and 304.7–1317.9 mg/l during POM season. The TDS values of well waters are generally higher (mean 1,373 and 484 mg/l) than the spring waters (mean 1,021 and 465 mg/L, respectively) during PRM and POM season (Tables 1, 2 and 3). Ca<sup>2+</sup> is higher during POM (average value is 111.8 mg/L). The increase of Ca<sup>2+</sup> during POM season in majority of springs except S6 could be due to more dissolution by the recharging water. Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> are higher in PRM season. Higher HCO<sub>3</sub><sup>-</sup> was observed during PRM which varies from 236–710 (mean value 410.6 mg/L). While in POM season, the values range from 121.4–458.4 with a mean of 210.3 mg/L. All the parameters, except Ca<sup>2+</sup> are high during PRM than POM season, which



**Fig. 6** Temporal variability as indicated by the coefficient of variation CV in percentage of physico-chemical parameters in karst springs

**Table 1** Statistical results of the physico-chemical analysis of spring and bore well waters of the karst area. T in °C and EC in microsiemens per centimetre and other concentrations in milligram per litre. Ca<sup>2+</sup>/Mg<sup>2+</sup> is in molar ratio. Number of samples is given in braces

|                                    | PRM 2011 (11) |          |          |        | POM 2011 (11) |          |        |        |
|------------------------------------|---------------|----------|----------|--------|---------------|----------|--------|--------|
|                                    | Min           | Max      | Mean     | CV     | Min           | Max      | Mean   | CV     |
| T                                  | 28.30         | 32.50    | 30.01    | 4.94   | 25.20         | 30.50    | 27.92  | 6.59   |
| pH                                 | 6.79          | 7.67     | 7.24     | 3.21   | 7.22          | 7.93     | 7.48   | 3.04   |
| EC                                 | 538.00        | 2,013.00 | 1,141.75 | 43.88  | 442.00        | 1,703.00 | 942.55 | 48.55  |
| TDS                                | 370.95        | 1,557.86 | 826.81   | 49.64  | 304.76        | 1,317.95 | 677.81 | 54.02  |
| Ca <sup>2+</sup>                   | 34.88         | 123.38   | 73.26    | 35.44  | 48.03         | 245.22   | 111.81 | 46.59  |
| Mg <sup>2+</sup>                   | 16.82         | 53.81    | 27.60    | 45.43  | 3.70          | 21.12    | 9.96   | 57.03  |
| Na <sup>+</sup>                    | 34.13         | 406.10   | 139.46   | 81.91  | 11.94         | 206.49   | 53.06  | 116.75 |
| K <sup>+</sup>                     | 2.31          | 31.77    | 9.68     | 84.75  | 0.27          | 14.90    | 3.49   | 143.72 |
| HCO <sub>3</sub> <sup>-</sup>      | 236.11        | 710.63   | 410.59   | 38.84  | 121.39        | 458.37   | 210.29 | 48.37  |
| F <sup>-</sup>                     | 0.39          | 1.56     | 0.93     | 35.21  | 0.19          | 1.40     | 0.65   | 57.98  |
| Cl <sup>-</sup>                    | 13.07         | 368.22   | 135.33   | 88.16  | 32.28         | 248.32   | 100.03 | 76.69  |
| NO <sub>3</sub> <sup>-</sup>       | 4.39          | 120.40   | 27.42    | 113.57 | 28.23         | 119.33   | 51.89  | 47.08  |
| SO <sub>4</sub> <sup>2-</sup>      | 2.85          | 131.02   | 54.60    | 82.82  | 22.02         | 160.06   | 53.17  | 72.82  |
| TH                                 | 211.03        | 131.02   | 54.60    | 82.82  | 164.74        | 658.63   | 320.36 | 40.69  |
| Ca <sup>2+</sup> /Mg <sup>2+</sup> | 0.39          | 4.45     | 1.99     | 59.87  | 1.70          | 21.93    | 8.94   | 64.10  |

**Table 2** Mean and coefficient of variation of different ions in spring and bore well samples during PRM and POM. Mean is expressed in milligram per litre and CV as percentage. Number of samples is given in parenthesis

|                |     |      | Dissolution related |                  |                               | Agriculture, land use related |                |                 |                              |                               | EC   |
|----------------|-----|------|---------------------|------------------|-------------------------------|-------------------------------|----------------|-----------------|------------------------------|-------------------------------|------|
|                |     |      | Ca <sup>2+</sup>    | Mg <sup>2+</sup> | HCO <sub>3</sub> <sup>-</sup> | Na <sup>+</sup>               | K <sup>+</sup> | Cl <sup>-</sup> | NO <sub>3</sub> <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> |      |
| Springs (5)    | PRM | Mean | 73.6                | 20               | 320                           | 64.8                          | 6.34           | 62.3            | 14.2                         | 36.1                          | 702  |
|                |     | CV   | 33.9                | 16.6             | 19.1                          | 41.8                          | 48.1           | 96.5            | 47.2                         | 134                           | 20.8 |
|                | POM | Mean | 137                 | 6.81             | 176                           | 21.7                          | 1.81           | 107             | 63.9                         | 36.7                          | 675  |
|                |     | CV   | 46                  | 45.9             | 26.5                          | 28.6                          | 58.9           | 82.4            | 49                           | 26.8                          | 14.4 |
| Bore wells (6) | PRM | Mean | 87.2                | 28.6             | 437                           | 135                           | 13.2           | 121             | 67.7                         | 55                            | 1526 |
|                |     | CV   | 25.1                | 30               | 36.9                          | 56                            | 62.6           | 84.9            | 111                          | 80.7                          | 30.6 |
|                | POM | Mean | 96.7                | 14.8             | 252                           | 106                           | 9.76           | 143             | 44.5                         | 71                            | 1381 |
|                |     | CV   | 39.7                | 40.8             | 49.7                          | 72.1                          | 120            | 87.6            | 22.7                         | 67                            | 65.9 |

indicates the more mineralized water during PRM season and dilution effect due to fresh rainfall recharging water. However, simple dilution cannot explain this variability, therefore, equilibrium with respect to calcite could also be a controlling factor (Toran and White 2005). F<sup>-</sup> varies from 0.4–1.6 and 0.2–1.4 mg/L during PRM and POM seasons, respectively. Cl<sup>-</sup> is higher in PRM season (average value 135 mg/L) than POM (average 100 mg/L). Nitrate concentrations are also high in the area (mean 27–51 during PRM and POM season). In karst areas, agriculture contributes nitrate as a common groundwater contaminant derived from leaching processes from plant nutrients, animal waste and nitrate fertilisers (Freeze and Cherry 1979; Peterson et al. 2000; Kingsbury and Shelton 2002). It can be correlated with the percent of agriculture in the area (e.g. Boyer and Pasquarell 1996). High nitrate concentration (above 20 mg/l) is also due to the influence of human activities (Spalding et al. 1993). SO<sub>4</sub><sup>2-</sup> is higher in PRM season (mean 54.6 mg/L) than POM

season (mean 53.2 mg/L). Agriculture usually contributes higher concentrations of sulphates (Langmuir 1971). High sulphate values are frequently found in carbonate waters. However, the carbonate rocks of the area rarely contain measurable concentrations of sulphur minerals (few beds with pyrite crystals) (Kumar 1983). Thus, it can be concluded that agricultural-related parameters (nitrates, sulphates and potassium) are derived from fertilisers, liquid sprays and manures applied on the agricultural areas, mostly paddy which is grown for the whole year particularly in the northern areas where canal water is supplied from the Owk Reservoir. Both the seasons record higher concentration of total hardness (hard water >200 mg/L of CaCO<sub>3</sub>) which is the effect of dissolution process in carbonate rocks. In semi-arid climates, the return flow from paddy is also believed to contribute relative amount of ions to the groundwater where high evaporation causes enrichment of ions as observed by high TDS values (Tizro and Voudouris 2007).

**Table 3** Difference in ionic concentration in percentage from PRM to POM season, (PRM–POM/PRM×100). Positive values indicate a decrease in concentration and negative values indicate an increase in concentration during POM season. Springs are indicated by “S” symbol in figures

| Spring/<br>bore well | Dissolution related |                  |                               | Agriculture and land use related |                |                 |                              |                               |      |    |     |    |
|----------------------|---------------------|------------------|-------------------------------|----------------------------------|----------------|-----------------|------------------------------|-------------------------------|------|----|-----|----|
|                      | Ca <sup>2+</sup>    | Mg <sup>2+</sup> | HCO <sub>3</sub> <sup>-</sup> | Na <sup>+</sup>                  | K <sup>+</sup> | Cl <sup>-</sup> | NO <sub>3</sub> <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | TH   | EC | TDS | T  |
| Belum (S1)           | -68                 | 69               | 55                            | 56                               | 73             | -79             | -247                         | -526                          | -21  | 15 | 15  | 7  |
| Kona (S2)            | -93                 | 78               | 65                            | 63                               | 92             | -968            | -612                         | -1,118                        | -44  | 3  | 3   | 0  |
| Kona (S3)            | -196                | -28              | -14                           | 10                               | -15            | -1,097          | -1,435                       | 88                            | -147 | 23 | 23  | 0  |
| Rati (S6)            | 29                  | 78               | 40                            | 83                               | 81             | 82              | -148                         | 70                            | 39   | -7 | -7  | 15 |
| Yaganti (S8)         | -79                 | 67               | 35                            | 61                               | 79             | 9               | -130                         | 7                             | -20  | 0  | 0   | 7  |
| B2                   | 35                  | 69               | 80                            | 79                               | -70            | 35              | 16                           | 7                             | 49   | 56 | 56  | 12 |
| B7                   | -117                | 48               | -20                           | 41                               | -33            | -3              | 81                           | 46                            | -34  | 23 | 23  | 2  |
| B8                   | -4                  | 41               | 33                            | 19                               | 18             | -16             | -53                          | 9                             | 4    | 0  | 0   | -1 |
| B11                  | 2                   | 57               | 20                            | 19                               | 72             | 76              | 57                           | -83                           | 33   | 21 | 28  | 12 |
| B12                  | -245                | 61               | 53                            | 67                               | 97             | 37              | -133                         | 56                            | -26  | 15 | 15  | 12 |
| B13                  | -24                 | 81               | 72                            | 78                               | 97             | 67              | -402                         | -85                           | 25   | 45 | 45  | 0  |

Bore well samples B11 and B12 show a large influence on water chemistry from agriculture as they were collected from paddy fields. Average concentration of agriculture-related parameters in these samples is very high ( $\text{Na}^+$  355,  $\text{Cl}^-$  299,  $\text{NO}_3^-$  113,  $\text{SO}_4^{2-}$  183 mg/l). C1 sample has a large human influence caused by sewage effluent (near Belum Cave entrance) as observed by very high concentration of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  and hence, was not used for statistical analysis.

The Kona springs (S2 and S3) are less affected by the human activities and are in a different hydrogeological configuration separated from the rest of the samples. S2 is a permanent spring showing less variability in discharge and chemistry (Fig. 6) whereas S3 and S6 flow with less than a litre per second discharge round the year. The discharge of the spring S2 (Fig. 5) as well as S3 do not show any marked seasonal and temporal variability which could be due to diffuse recharge and diffuse flow in these springs (Dar 2014). Spring waters except S1 and S6 are colourless and odourless throughout the year. S1 flows with a high turbidity during monsoon months. It carries a lot of sediments collected from the highly karstified areas through sink holes. S6 discharges from the epikarst layer of the aquifer and shows very high concentration of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  during PRM season which decreases in the POM months. In case of S1, B2 and B13, the area is hydrogeologically more complex than the other area. The area possesses a number of surface and sub-surface karst features. Concentrated recharge is the main contributor of the groundwater along with diffuse recharge through the soil cover. The area is mostly used for rain-fed agriculture along with some isolated paddy and vegetable fields. S1 has a large human influence as the spring is located within a village and possibly connected underground through conduits with the Belum cave stream (C1 sample). S8 is also a permanent spring from the same limestone but has no hydrological connectivity with the rest of the sampled points.

Spatially, the borehole samples from the northern area show higher concentrations in agriculture-related parameters compared to the ones located in the southern area. The reason for this high concentration is that the northern area is largely cultivated for paddy crop round the year. The water showed very high nitrate concentration. In karst areas, nitrate is a common groundwater contaminant coming from agricultural sources (Kingsbury and Shelton 2002) and linearly correlated with the percent of agriculture (e.g. Boyer and Pasquarell 1996). Seventy-three percent of samples showed an increase in concentration of nitrates and 45 and 33 % showed an increase in  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , respectively. Before the onset of monsoon, a large part of the area is prepared for crop cultivation by ploughing the soils and adding seeds and fertilisers. This can be related to the release of more agriculture-related chemicals from the soils by the recharging water. High concentration of nitrates during POM months can be due to moist

soil conditions that are suitable for nitrification of soil organic-N (Kingsbury 2008).

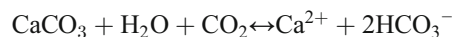
#### Hydrochemical evolution

To assess the chemical evolution of groundwater from PRM to POM season LL-diagram (Langelier and Ludwig 1941) was plotted for equivalent ratios of ions (Fig. 7). The diagram shows a broader scatter and samples fall in all the major fields during PRM. The central part of the diagram is occupied by majority of the samples which depicts mixed chemical characteristics. The plot (Fig. 7) shows that the groundwater is influenced by dissolution of gypsum/anhydrite (indicated by I), carbonate dissolution (II) and silicate dissolution (III). Most of the samples are dominated by the carbonate and silicate dissolution. B7 is dominated by gypsum dissolution however; gypsum/anhydrite dissolution is unlikely process as no sulphate minerals are present in the rocks except few beds of pyrite crystals (Kumar 1983). About 58 % of samples are of bicarbonate alkali type in character.

During POM, a completely different scenario is observed. A significant shift towards the upper half of the diagram is observed in which bicarbonates and major alkali are the dominant ions. Interaction with  $\text{CO}_2$  is also observed during POM season. S1, S6, B2 and B13 samples are located in highly karstified area. During POM season B7, B12, B8, S2 and S3 shift towards the chlorite-sulphate-alkali water type by an increase in  $\text{Cl}^- + \text{SO}_4^{2-}$  and  $\text{Na}^+ + \text{K}^+$  concentration. B8 and B12 are affected by agricultural practices of the area and B7 is influenced by humans as the sample was collected from village hand pump.

#### Chemical reactions

The source of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in carbonate waters is generally the dissolution of calcite and dolomite minerals of the rocks. Thus, chemical composition of water is used to infer the processes of mineral dissolution and water-rock interaction. The general equilibrium reaction of limestone dissolution, if dolomite part is negligible is expressed as



According to the equation, the dissolution of calcite releases equivalent charge ratio of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ . Thus, the samples should fall along 1:1 line which is not observed due to a large scatter about 1:1 line. This disequilibrium (Fig. 8) indicates that  $\text{Mg}^{2+}$  is also added to the groundwater system in suitable amounts from another source (e.g. Wu et al. 2009). It has been documented that, Narji limestone contains significant concentration of dolomite (average carbonates ~60.5 % as  $\text{CaCO}_3 + \text{MgCO}_3$  and average CaO and MgO ~34.6 and ~0.5 %, respectively) (Kumar 1983). Hence, the chemical



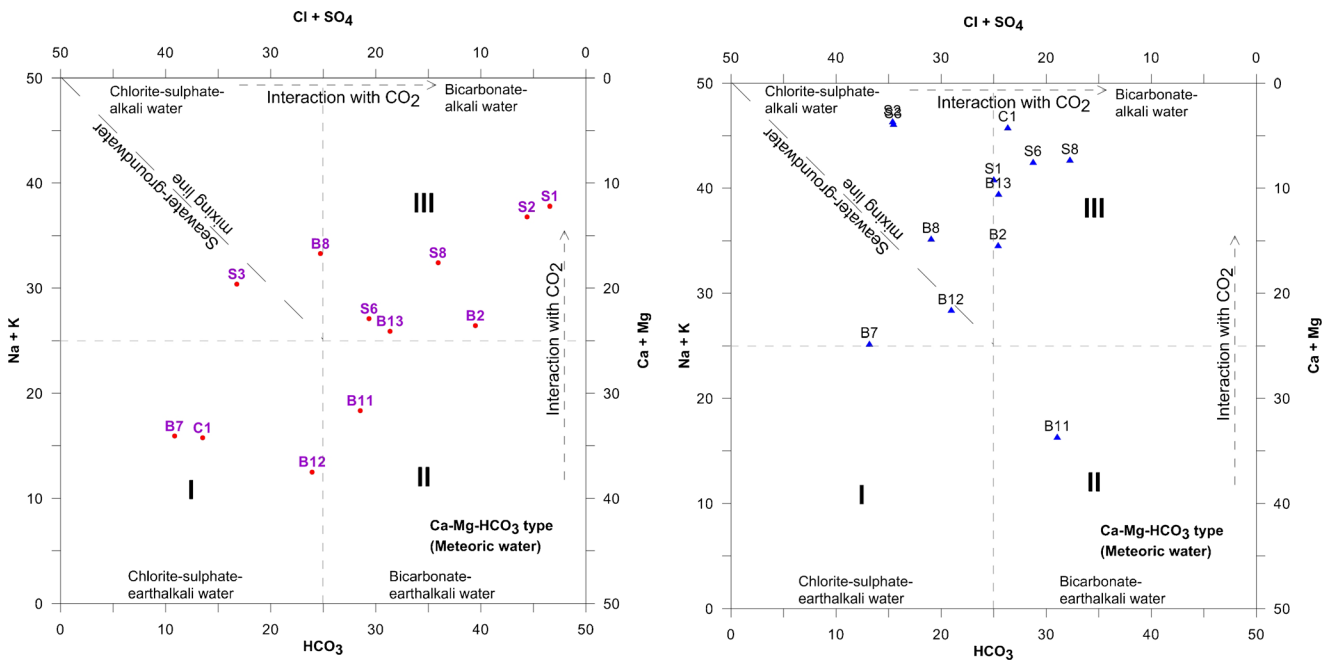
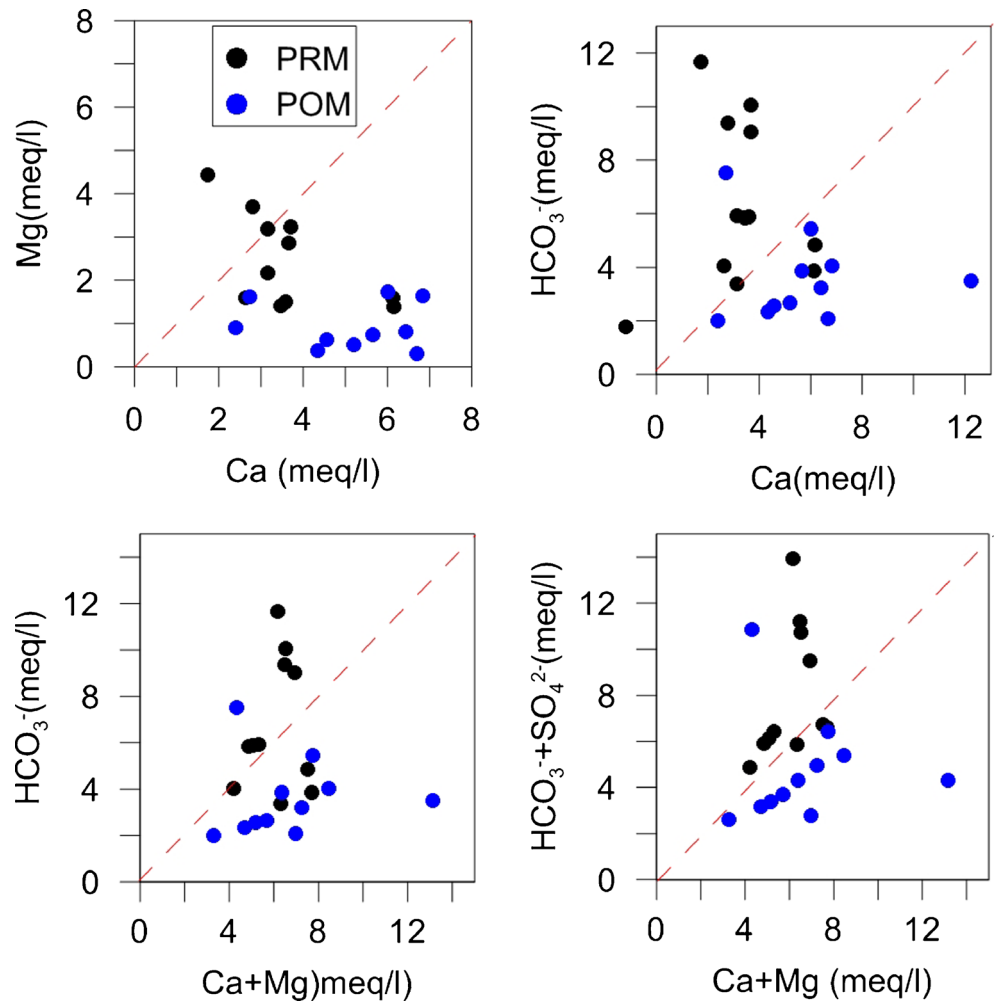
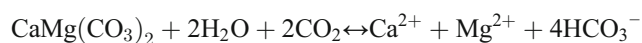


Fig. 7 Hydrogeochemical evolution of groundwater during PRM and POM using LL-diagram

Fig. 8 Scatter plots between various cations and anions that can indicate the possible nature of equilibrium reactions between rock and water in the area during PRM (black dots) and POM (blue dots). Little scattering is observed between  $Ca^{2+}+Mg^{2+}$  vs  $HCO_3^- + SO_4^{2-}$



reactions that control the water chemistry in this aquifer could be expressed as;



Therefore, dissolution of this impure carbonate rock results in the increase of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  content in groundwater. A plot of molar ratio of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  to the  $\text{HCO}_3^{2-} + \text{SO}_4^{2-}$  showed that 70 % of samples lie close to 1:1 line during PRM and 66 % during POM season which reflects that  $\text{Ca}^{2+} + \text{Mg}^{2+}$  equilibrates the  $\text{HCO}_3^- + \text{SO}_4^{2-}$  concentration. During POM the sample show a good correlation but fall below 1:1 equiline. The possible reason for such behaviour could be due to increased concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.

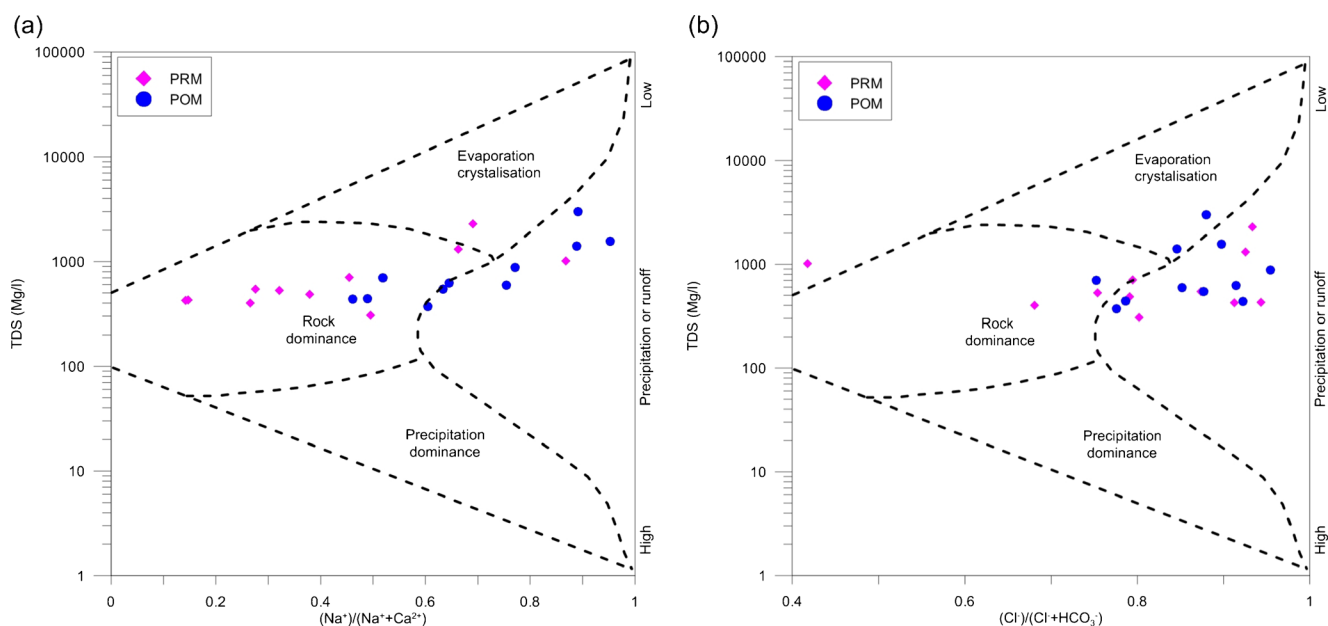
Gibbs' ratio (Gibbs 1970) were plotted separately for major cations ( $\text{Na}^+/\text{Na}^+ + \text{Ca}^{2+}$ ) and major anions ( $\text{Cl}^-/\text{Cl}^- + \text{HCO}_3^-$ ) vs. log TDS for PRM and POM samples (Fig. 9a, b). The plots indicate that the chemistry of water is controlled predominantly by the chemical interaction between rock and groundwater. Few samples lying close to evaporation end indicate that it also has a significant effect on groundwater chemistry during both seasons. A  $\text{Ca}^{2+}/\text{Mg}^{2+}$  molar ratio in spring and well waters is highly variable and is generally high during POM season.  $\text{Ca}^{2+}/\text{Mg}^{2+}$  molar ratios vary from 0.39–4.45 during PRM season with an average value of 1.99. During POM months, the value increases to an average value of 8.9. High ratio (more than two) is usually attributed to the calcite ( $\text{CaCO}_3$ ) weathering (Mayo and Loucks 1995) and an increase in ratio from PRM to POM seasons can indicate the release of more  $\text{Mg}^{2+}$  ions (dolomite dissolution) from the rock or increase in silicate weathering (Katz et al. 1998). The

fresh water has a high  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio while, older water will show lower  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio. Thus, the variation in  $\text{Ca}^{2+}/\text{Mg}^{2+}$  molar ratio seems to be related to the rock weathering in the area. Hence, it can be deduces that the dissolution of calcite and dolomite are the dominant geochemical processes with a little dissolution from silicate minerals.

$\text{Na}^+/\text{Cl}^-$  ratio is a widely used indicator in many groundwater studies (Magaritz et al. 1989) where a greater ratio indicates that  $\text{Na}^+$  may get released from silicate weathering (Mayback 1987) and a lower ratio indicates higher concentration of chloride due to evaporation process (Jankowski and Acworth 1997). Average value of the ratio is 2.2 during PRM and 1.3 during POM season. It was observed that majority of the samples showed an increase in EC with increase in  $\text{Na}^+/\text{Cl}^-$  ratio which can be related to the effect of high evaporation in the area (e.g. El-Sayed et al. 2012). This evaporative effect is also indicated by the Gibbs diagrams as the sample fall towards evaporation side and a higher concentration of chloride which indicate a source from evaporation process (Jankowski and Acworth 1997).

## Conclusion

The physico–chemical variables showed a significant statistical difference between PRM and POM seasons. The spatial variability in water chemistry is clearly observed.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  are directly related to the water–rock interaction (solution processes) and are derived from dissolution of limestone possessing little  $\text{MgCO}_3$  content. High concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  suggests the anthropogenic sources dominated by the application of fertilisers and manures in



**Fig. 9** Plot showing the mechanism that controls the chemistry of groundwater (after Gibbs 1970), **a** for cations and **b** for anions

agricultural areas. The seasonal changes in agricultural activities and vegetation growth cause possible variations in  $p\text{CO}_2$  which also modifies the solution processes. Weathering of clastic rocks is believed to contribute little sodium and potassium ions. The less contaminated spring waters are emerging from hydrogeologically different conditions where soils and vegetation is almost absent and have little human influence.

Based on the above discussion, it is obvious that groundwater has encompassed many hydrogeochemical processes. The original chemical signature of groundwater gets modified to a great degree during post-monsoon season by recharging monsoon water. Water seems to have acquired majority of the ions dominantly through water–rock interaction and mixing processes mainly dilution. The mixing of different types of recharging waters (concentrated and diffuse) also causes variation in groundwater chemistry.

Physical process, like evapotranspiration, also led to the concentration of certain ions particularly in agriculture-dominated areas. Dumping of domestic waste directly in karst depressions (common practice in the area) could also be the cause of anthropogenic sources.

The results discussed therefore, indicate that karst dissolution, land use and anthropogenic effects are likely factors that lead to the variability in water chemistry of the karstified Narji limestone. This study needs further improvements to understand fully the hydrochemical processes by incorporating detailed chemical investigations of frequent water samples, rock material and soils. These investigations will be useful for the characterisation of the aquifer flow system and to know the control of karst heterogeneities on groundwater flow for an efficient management of its water resources.

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