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ORIGINAL ARTICLE

Geochemical processes and multivariate statistical analysis for the assessment of groundwater quality in the Swarnamukhi River basin, Andhra Pradesh, India

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Abstract With rapid increase of human population, swift growth of industries and intensive irrigation activities, groundwater quality is being increasingly endangered by agricultural chemicals and indiscriminate disposal of urban and industrial wastes. Hence, in water management, assessment of groundwater quality is as important as quantity especially in the arid and semi-arid regions. Evaluation of hydrogeochemical parameters and solute acquisition process controlling water chemical composition was studied by collecting 66 groundwater samples in pre-monsoon and post-monsoon seasons in the Swarnamukhi River basin, Andhra Pradesh, India. Geologically, the study area comprises granite and granitic gneisses, quartzite and alluvium. The total dissolved solids classification reveals that majority of the groundwater samples are desirable for drinking, and all are useful for irrigation purposes. Major ion chemistry reveals the ionic dominance pattern among cations and anions is in the order: $Na > Ca > Mg > K$ and $Cl > HCO_3 > NO_3 > SO_4 > CO_3 > F > PO_4$ in both the seasons. 85 and 89 % of samples are very hard water in pre- and post-monsoon, respectively which needs softening for domestic uses. 48 and 42 % and 34 and 41 % of the samples of the study area are found having sodium (200 mg/l) and nitrate content (50 mg/l) in pre- and post-monsoon seasons, respectively, more than permissible limits which is not good for human consumption. Natural and anthropogenic sources of the solutes have been categorized with the help of different ionic ratios, plots and correlation matrix. Potential salinity sources include deep saline upcoming and wastewater infiltration. Salinity mapping shows brackish to fresh brackish water predominance in the study area. The plot of major ion in the Piper diagram reveals that majority of samples belongs to mixed type followed by Na–Cl facies. Four principal components were extracted from chemical data to explain the major sources and processes responsible for chemical characteristics of groundwater. It shows that silicate weathering, agricultural runoff (fertilizer input), municipal wastewater infiltration play a vital role in the enrichment of ionic constituents. Average water quality index shows that majority of the samples are good to permissible for drinking purpose. Various irrigation indices show good to permissible use of groundwater in agricultural activities. As per the LSI and RSI values, groundwater of the area is considered very aggressive and substantial corrosion is possible.

Keywords Geochemical processes · Groundwater quality · Swarnamukhi River · Salinity · Principal component analysis · Industrial use · AWQI

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Introduction

Water is not only the essence of life but also the single most crucial factor determining the quality of life of the people. The climate change and increasing disruptions in the rainfall patterns, temperature and soil moisture directly impacted the water availability and its quality for drinking, livestock use, agriculture and various other purposes.

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Groundwater is the primary source of water for drinking, domestic, agricultural and industrial uses in many countries and its contamination is recognized as one of the most serious problems in India (Raju et al. 2011; Singh et al. 2015a). The latest trends reflect the reserves heading toward depletion and deterioration of quality in many parts of the world (Raju 2007; Jianhua et al. 2009; Khairy and Janardhana 2013; Thivya et al. 2013; Raju et al. 2014; Toumi et al. 2015). Water scarcity leads to a multitude of problems of walking kilometers to fetch water for domestic purposes, lack of access to freshwater resources and impediments in agricultural processes. In addition to water decline, pollution of water resources further enhance the problems and put up more pressure on the already stressed out available fresh water resources (Reddy et al. 2000). Water quality is determined by the solutes and gases dissolved in the water, as well as the matter suspended in and floating on the water. Water quality is a consequence of the natural physical and chemical state of the water as well as any alterations that may have occurred as a consequence of human activity. In the hydrosphere, most of the water is in very saline oceans as well as tied up in glacial ice forms. Hence, that leaves relatively small quantities of surface and groundwater for potential freshwater sources. Moreover, much of the water on and in the continents is not sternly fresh. Once precipitation reaches the ground, it reacts with soil, rock and organic debris and dissolving chemical materials besides from any pollution generated by human activities. Water quality must be a consideration when evaluating water supplies to domestic, irrigation and industrial purposes. To date, the assessment of the qualitative status of groundwater is based almost exclusively on chemical parameters of the water. In various parts of the world, numerous studies have been carried out to assess the geochemical characteristics of groundwater affected by contamination from human activities such as sewage effluents, agricultural fertilizers and ion-exchange, evapotranspiration and water–rock interactions which results in an increase of the ion concentration making water unfit for drinking and agricultural purpose (Jiang et al. 2009; Raju 2012; Raju et al. 2012; Abdesselam et al. 2013; Khashogji and El Maghraby 2013; Alaya et al. 2014; Iranmanesh et al. 2014; Kim et al. 2015; Singh et al. 2015b). Determination of groundwater composition and its interpretation is of utmost importance for the evaluation of its suitability for domestic, irrigation and industrial uses.

The source of about 80–90 % of drinking and irrigation water is from groundwater resources in the semi-arid region of the Swarnamukhi River basin, Andhra Pradesh. However, this water resource is facing problems of fast decline due to overexploitation and quality risk in many areas where the exposure to pollution from domestic and agriculture fertilizers in shallow groundwater aquifers make the water unsuitable for human consumption. Few studies were carried out related to land use/land cover pattern, groundwater potential zone demarcation, groundwater table depth and quality analysis in the Swarnamukhi River basin (Jasmin et al. 2010; Bhupal and Reddy 2013), but whole River basin had not been studied properly for its hydrogeochemical processes and suitability of groundwater quality for various purposes. The aims of this study were to characterize the influences of water–rock interaction and anthropogenic activities on the hydrogeochemistry and suitability of groundwater for drinking, irrigation and industrial purpose in Swarnamukhi River basin, Andhra Pradesh, India.

Study area

The study area has been located in the Chittoor and Nellore districts of Andhra Pradesh state, bounded by latitudes 13°25′30″–14°08′30″N and longitudes 79°07′39″–80°11′0″E (Fig. 1). The Swarnamukhi is an ephemeral east flowing river has a drainage area of 3225 km² and length of about 192 km with dendritic to sub-dendritic type of drainage pattern. Chittoor district has two major pilgrimage spots Tirupati and Sri Kalahasti which are fast urbanizing centers resulting in setting up of universities, industries and commercial locations. Annual average rainfall of the study area is around 934 mm with a contribution of southwest monsoon 47 % and northeast monsoon 42 %. The summer temperature touches 38–46 °C and winter temperatures ranges around 12–18 °C. River rises at an elevation of 300 m in Eastern Ghat ranges near Pakala village in the Chandragiri Taluk, flowing in a northeast to southeast directions in Srikalahasti and Thottambedu taluks in Chittoor district and passing through the famous Tirupati hills, joining finally the Bay of Bengal in Gudur taluk of Nellore district in Andhra Pradesh of India. Around 11 % of the Swarnamukhi River basin lies in Nellore district. This independent river has no major tributaries and therefore its flow depends only on rainfall in its upper catchment (CGWB 2013) and it runs generally in north eastern direction. Around 30 % of land area in Chittoor is covered by forests and Tirumala hills.

Geology and hydrogeology

The study area has been located in semi-arid zone and is underlain by formations of archaean, proterozoic and quaternary ages. The oldest rocks in the area belong to Migmatite Complex, represented by migmatised quartzofelspathic gneiss, exposed in northeastern part. Older
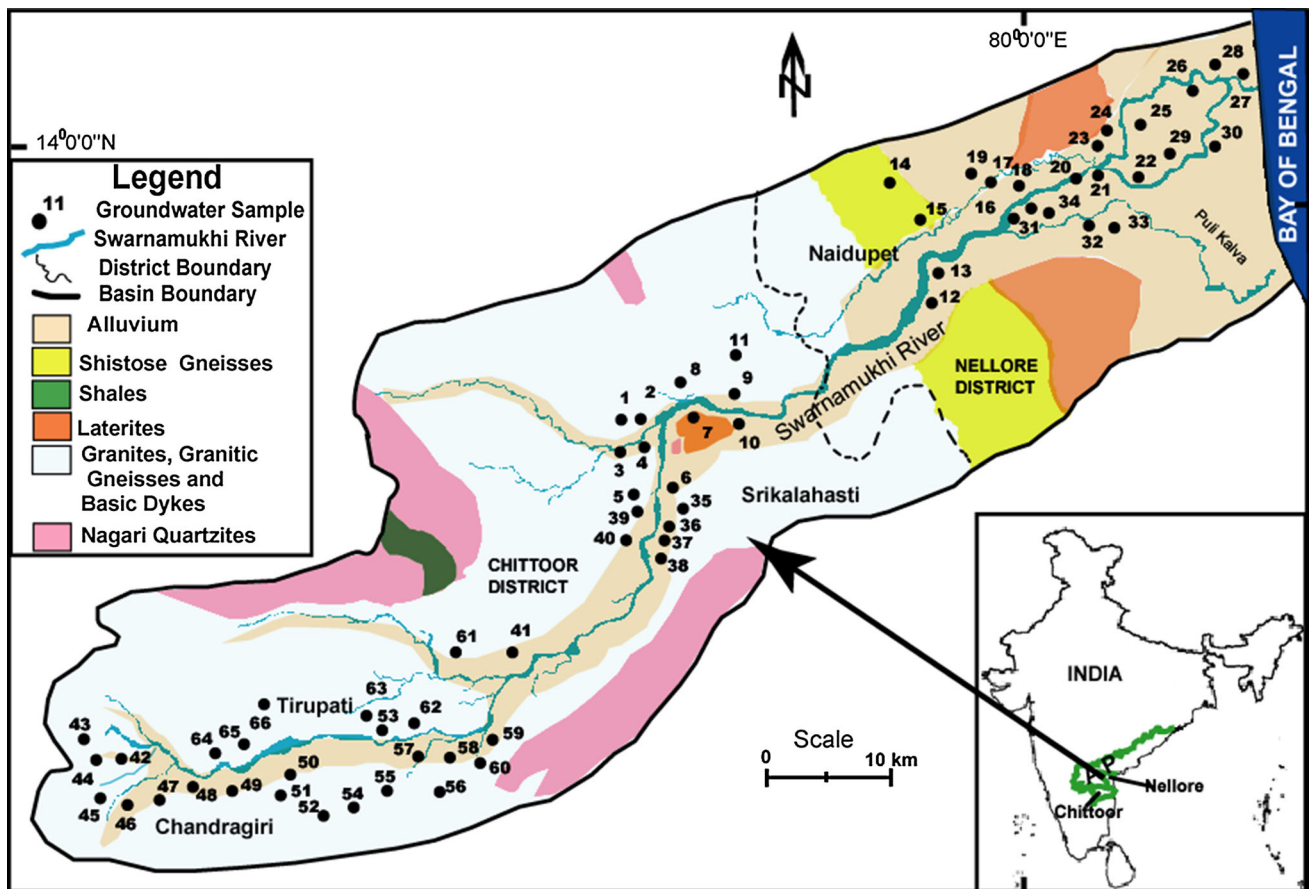
Fig. 1 Physiographic, geological and groundwater sample location map of the Swarnamukhi River basin

metamorphics comprise amphibolites, hornblende-talc-mica-schist, fuchsite quartzite, calc-silicate rock, marble and banded ferruginous quartzite. These older metamorphics occur as enclaves within Peninsular Gneissic complex (PGC) which comprises a complex assemblage of gneissic variants and granitic rocks. The rocks of Gondwana super group occur nonconformably over the PGC in southeastern part of the Chittoor district, represented by Satyavedu Formation (Under Gondwana) and comprise mottled, ferruginous quartzite and conglomerate with plant fossils. Laterite cappings occur over Gondwana formations. Large tracts of alluvium found along the major stream of Swarnamukhi river belong to recent age. So, the major rock types prevailing in the study area are granitic gneiss, shales, quartzites, laterites and sandstones (Fig. 1). The major soil types profound in the study area are red loamy, red sandy, black clay, black loamy, black cotton, black sandy, red clayey, lateritic sandy and alluvial soils.

Ground water occurs under unconfined conditions in weathered portion and semi-confined to confined condition occurs in fractures, joints at deeper depths. Ground water in weathered formations is developed by dug wells. For irrigation purposes, the dug wells are circular or rectangular in shape with 30–60 m^2. The average discharge of energized wells ranges from 18 to 30 m^3/day. However, during monsoon period, the discharge varies from 80 to 200 m^3/day and during summer 10 to 50 m^3/day. The bore wells are drilled down to 120 m depth with 160 m diameter. The alluvium is confined to mostly river banks and stream courses with varying width and depth. Ground water development in this formation is mostly by filter points and dug wells. In hard rocks, the specific capacity of the bore wells ranges 0.13–11.38 m^3/h/m drawdown. The transmissivity ranges 30–150 m^2/day with a maximum value 825 m^2/day. Among the un-consolidated formations river alluvium, i.e. in deltaic area ground water occurrence is controlled by landforms and also in this area a lot of heterogeneity in hydrogeological conditions exist both spatially and vertically. In Swarnamukhi delta, fresh water is generally limited to a depth of 15 m. Most of the coastal alluvium aquifers are saline. Palaeochannels are favourable locations for fresh water potential aquifers. Net annual ground water availability is around 153857 MCM (CGWB 2013).

Materials and methods

Field work

To understand the water quality of the study area, 66 groundwater samples were collected in May (pre-monsoon) and January (post-monsoon) 2014 from dugwells and borewells and locations were fixed by GPS (Oregon 600). Samples were taken in properly rinsed 250 ml poly-ethylene bottles (presoaked in acid wash for 24 h. and rinsed several times with distilled water). General parameters such as pH, EC, TDS and depth to water table were measured immediately at the time of sampling using a multi parameter ion meter (pH/Cond 340i SET 1).

Laboratory analysis

The physicochemical parameters were determined using the standard analytical methods (APHA 2005): hardness, alkalinity, Ca, CO_3, HCO_3 and Cl were analyzed with titrimetric method and Mg was determined with calculation method. Na and K was analyzed using flame photometer (Elico Model CL 378). F was estimated using ion analyzer (Thermo scientific Orion-4 star) with an ion-selective electrode. SO_4, SiO_2, NO_3 and PO_4 were determined by spectrophotometry method (UV 3200 double beam spectrophotometer, Labindia).

Data treatment

The analytical precision for the accurate measurements of ions was determined by calculating electrical neutrality (EN %) which is acceptable at ±5 % (Appelo and Postma 1999). All the samples have EN % values within ±5 % in pre- and post-monsoon.

$$\text{Electrical Neutrality} = \sum \text{Cation} + \sum \text{Anion} / \sum \text{Cation} - \sum \text{Anion} \times 100$$

The analytical data obtained were processed for detailed geochemical and statistical analysis. AqQA 1.1 software package was used for different hydrogeochemical facies identification. Statistical analysis was carried out by Stat Soft STATISTICA 6 and Microsoft Excel-2010. Principal component analysis has been carried out with the help of IBM SPSS Statistics 19. Study area, geological map and spatial distribution maps of parameters were prepared with the help of Arc GIS 9.3, Globber Mapper and Adobe Illustrator 10. The Gibbs plot, Wilcox (1948) diagram, USSL (1954) diagram and Doneen permeability index plot (1964) were made using Microsoft excel-2010 and Adobe Illustrator 10. Salinity mapping and hydrogeochemical facies distribution maps were prepared by Golden software Surfer 11.

Total hardness and various water indices used to classify groundwater suitability for irrigation and industrial purposes are calculated using the formula:

$$\text{Total Hardness} = 2.5 \, \text{Ca} + 4.1 \, \text{Mg} \, (\text{mg/l as CaCO}_3)$$

Average water quality index (AWQI) permits the reduction of large data of physico-chemical parameters to a single unit. Thus, to understand the water quality for human consumption, index has been calculated through following steps (Soltan 1999; Kumar et al. 2014). In the primary step, important parameters assigned a weight (w_i) according to their relative importance to potability. The maximum weight 5 assigned to NO_3, TDS, Cl, F and SO_4 due to their importance in water quality and human health. In the later step, relative weight (W_i) calculated as:

$$W_i = w_i \Big/ \sum_{i=1}^{n} w_i$$

where w_i = weight of each parameter and n = number of parameters

Then, quality rating scale (q_i) for each parameter is assigned as:

$$q_i = (C_i/S_i) \times 100$$

where C_i = concentration of ith parameter and S_i = standard of ith parameter (mg/l)AWQI for n parameters can be calculated using the following equation:

$$\text{AWQI} = \sum_{i=1}^{n} q_i/n$$

Irrigation water quality indices are determined using the following formulas; all units are in meq/l:

Percent Sodium (%Na) $= (Na + K)/(Ca + Mg + Na + K) \times 100$
Sodium Adsorption Ratio (SAR) $= Na/\sqrt{[(Ca + Mg)/2]}$
Residual Sodium Carbonate (RSC) $= (CO_3 + HCO_3) - (Ca + Mg)$
Permeability Index (PI) $= [Na + \sqrt{(HCO_3)}/Ca + Mg + Na] \times 100$
Kelly's Ratio (KR) $= Na/(Ca + Mg)$
Magnesium Hazard (MH) $= (Mg/Ca + Mg) \times 100$

Industrial water quality indices are determined using the following formulas; all units are in mg/l:

Langelier Saturation Index (LSI) $= pHw - pHs$

where pHw = measured pH and pHs $= (9.3 + A + B) - (C + D)$; $A = (\log_{10}[\text{TDS}] - 1)/10$; $B = -13.12 \times \log_{10}(°C + 273) + 34.55$; $C = \log_{10}[Ca^{2+} \text{ as CaCO}_3] - 0.4$ and $D = \log_{10}[\text{Alkalinity as CaCO}_3]$

$$\text{Ryznar Stability Index (RSI)} = 2(\text{pHs}) - \text{pHw}$$

$$\text{Corrosivity Ratio (CR)} = (\text{Cl}/35.5) + (\text{SO}_4/48)$$
$$/[(\text{CO}_3 + \text{HCO}_3)/50]$$

Results and discussion

General parameters

Physico–chemical parameters were analyzed for ground-water samples have been summarized in Table 1. pH is a measurement of activity of the free, un-complexed hydrogen ion which may lead to precipitation, co-precipitation and sorption processes that alter the chemical composition and reaction rates. pH ranges 6.4–8.6 (mean 7.2) in pre- and 6.4–8.8 (mean 7.3) for post-monsoon which depicts slightly alkaline nature of groundwater due to the influx of HCO_3^- ions in the groundwater aquifer from percolation of rain water through soil (Alam et al. 2011). Total hardness (mg/l as $CaCO_3$) of groundwater is ranging from 191 to 1146 (mean 512.5) for pre- and 100 to 1176 (mean 542.7) for post-monsoon. Conductance measurement provides an indication of ion concentration. EC (µS/cm) ranges 216–5080 (mean 1721.9) in pre- and 293–4140 (mean 1525.8) in post-monsoon. TDS (mg/l) ranges 120–2822.2 (mean 956.6) in pre- and 163–2300 (mean 847.7) in post-monsoon. The low TDS content in the groundwater of the study area could be either a result of short residence time with the underground rocks or the slow weathering of granitic or granitic gneiss terrain.

Cation chemistry

Among major analysed cationic concentrations (mg/l): sodium is the dominating ion ranges 43.1–459.7 (mean 203.9) and 7.7–456.6 (mean 180.1) followed by calcium ranges 38–306 (mean 115.8) and 18–234 (mean 93.7), magnesium ranges 12–172.7 (mean 54.4) and 13.4–226.7 (mean 74.9) and potassium ranges 0.8–277 (mean 15) and 0.3–200.7 (mean 10.1) in pre- and post-monsoon, respectively. Among cationic concentrations (meq/l), Na predominates by constituting 44 and 40 % of total cation followed by Ca constitute 32 and 25 %, Mg constitute 23 and 33 % and K constitute 2 and 1 % of total cations in pre- and post-monsoon, respectively. In this groundwater system, Na is the dominant cation that exceeds the threshold of dominance (meq/L >50 %) in 31 and 23 % of the samples followed by Ca (5 and 2 %) and Mg (0 and 6 %) in pre- and post-monsoon, respectively. So, hydrogeochemistry reveals that the order of cation abundance is Na > Ca > Mg > K in both seasons.

Anion chemistry

Among major analysed anion concentrations (mg/l): bicarbonate is the dominant ion ranges 120–1104 (mean 593.8) and 72–960 (mean 471.2) followed by chloride ranges 140–1200 (mean 338.8) and 96–1140 (mean 344.6), nitrate ranges 0–142.7 (mean 41.9) and 0–150 (mean 47.4), sulphate ranges 4.5–63.1 (mean 26.9) and 1.6–106.2 (mean 27.4), carbonate ranges 0–39.3 (mean 2.9) and 0–31.5 (mean 0.7), fluoride ranges 0–1.9 (mean 0.4) and 0.02–2.2 (mean 0.5) and phosphate ranges 0–1.9 (mean 0.1) and 0–1.3 (mean 0.1) in pre- and post-monsoon, respectively. Among the anionic concentrations (meq/l), Cl constitute 48 and 52 % of total anion apart from HCO_3 (45 and 40 %), NO_3 (3 and 4 %), SO_4 (3 and 3 %) and less than 1 % of total anions contributed by F, PO_4 and CO_3 in pre- and post-monsoon, respectively. Cl is the dominant anion that exceeds the threshold of dominance (i.e. meq/L >50 %) in 39 and 55 % followed by HCO_3 (32 and 14 %) in pre- and post-monsoon samples, respectively. Hydrogeochemistry reveals that the order of anion abundance is $Cl > HCO_3 > NO_3 > SO_4 > CO_3 > F > PO_4$ in pre- and post-monsoon. In general, mineral weathering, dissolution and base-exchange processes control the levels of ionic concentrations in groundwater.

The spatial distribution of total hardness in the investigated area clearly shows that high levels of hardness confined mainly to extreme southwest and few patches are found in central and northeast part in both the seasons (Fig. 2). High Ca, Mg, HCO_3 and Cl in groundwater are the probable reason for the hardness in basin. Nitrate spatial distribution plot shows wide variation in its concentration infers point and non-point sources (Fig. 2). High nitrate contamination is predominant in southwest part which consists of fast urbanizing Tirupati town. Poor sewerage, leakage of human excreta from septic tanks and locally unmanaged solid waste disposal sites could have result in slug like motion of water during infiltration in groundwater. Few patches of nitrate pollution have also been observed in the central and northeast part might be due to high agricultural activities and domestic sewage. Application of N-fertilizers on irrigation land as crop nutrients along the Swarnamukhi River course may be responsible for nitrate pollution in the groundwater due to leaching by applied irrigation water.

Origin of solutes

Natural sources

Ca/Mg ratio is used to determine the sources of Ca and Mg into the groundwater. Ratio of 1, indicates dolomite dissolution, 1–2 indicate calcite dissolution dominance and >2

Table 1 Statistical summary of chemical constituents, water indices and ionic ratios in the Swarnamukhi River basin

Parameter	Pre-monsoon			Post-monsoon		
	Range	Mean	SD	Range	Mean	SD
Ca^{2+}	38 to 306	115.78	45.81	18 to 234	93.70	50.83
Mg^{2+}	12 to 172.73	54.40	32.24	13.4 to 226.65	75.00	35.50
Na^+	43.1 to 459.7	204	106.51	7.7 to 456.6	180.10	96.25
K^+	0.8 to 277	15.02	37.06	0.3 to 200.7	10.09	26.10
CO_3^{2-}	0 to 39.34	2.934	9.32	0 to 31.47	0.72	4.30
HCO_3^-	120 to 1104	593.80	245.63	72 to 960	471.20	205.97
$SO4^{2-}$	4.46 to 63.05	26.85	14.13	1.6 to 106.2	27.362	17.66
Cl^-	140 to 1200	338.77	182.33	96 to 1140	344.64	171.51
PO_4^{3-}	0 to 1.93	0.08	0.28	0 to 1.30	0.12	0.19
F^-	0 to 1.9	0.36	0.32	0.02 to 2.2	0.48	0.35
NO_3^-	0 to 142.7	41.85	27.44	0 to 150	47.36	25.72
SiO_2	0.033 to 25.82	10.83	6.24	12.6 to 58.55	42.31	9.15
Hardness	190.84 to 1146.12	512.45	208.33	100 to 1176	542.70	222.68
Alkalinity	98.4 to 954.48	489.97	203.32	59 to 787.2	387.24	167.71
pH	6.37 to 8.58	7.21	0.56	6.44 to 8.75	7.25	0.39
EC	216 to 5080	1721.97	986.37	293 to 4140	1525.83	840.30
TDS	120 to 2822.22	956.65	547.98	163 to 2300	847.69	466.83
Na%	16.31 to 80.92	45.45	13.22	4.98 to 73.92	41.41	13.83
SAR	0.85 to 11.96	4.03	1.78	0.17 to 9.01	3.43	2.21
RSC	−14.89 to 13.54	−0.42	3.55	−14 to 8.14	−3.10	4.08
KR	0.19 to 3.57	0.95	0.48	0.04 to 2.47	0.79	0.62
MH	15.86 to 81.18	42	13.70	26.80 to 86.13	57.37	12.25
PI	37.72 to 93.94	61.65	15.35	4.27 to 87.75	54.44	12.72
LSI	−2.86 to 0.02	−1.37	0.50	−3.29 to −0.60	−1.59	0.60
RSI	8.22 to 12.15	9.94	0.85	9.13 to 13.10	10.36	0.76
CR	0.32 to 3.61	0.98	0.72	0.40 to 4.01	1.28	0.60
Gibbs I	0.27 to 0.81	0.49	0.11	0.30 to 0.82	0.56	0.46
Gibbs II	0.28 to 0.93	0.58	0.15	0.11 to 0.93	0.62	0.12
Ca/Mg	0.23 to 5.31	1.63	–	0.16 to 2.73	0.86	–
$HCO_3/HCO_3 + SO_4$	0.86 to 0.99	0.94	–	0.49 to 0.99	0.92	–
$Ca + Mg/HCO_3$	0.15 to 1.58	0.59	–	0.24 to 2.20	0.80	–
Na/Cl	0.29 to 2.45	0.96	–	0.06 to 1.69	0.82	–
Na/Ca	0.78 to 17.59	3.5	–	0.22 to 27.40	4.48	–
K/Cl	0.00 to 0.63	0.04	–	0.00 to 0.48	0.03	–
Mg/Ca	0.19 to 4.31	0.83	–	0.37 to 6.21	1.68	–
AWQI	16 to 451	61	–	13 to 334	60	–
HCO_3/SiO_2	6.7 to 33,454.5	699.5	–	1.84 to 41.34	11.55	–

All ions, TDS and HCO_3/SiO_2 in mg/l, EC in µS/cm, Hardness and Alkalinity in mg/l as $CaCO_3$, pH unitless, Ca/Mg, $Ca+Mg/HCO_3$, Mg/Ca and Na/Ca in mmol/l, Gibbs ratio, HCO_3/HCO_3+SO_4, Na/Cl and K/Cl in meq/l

reflects an effect of silicate minerals (Raju et al. 2015). The Ca/Mg ratio varies 0.23–5.31(mean 1.63) and 0.16–2.73 (mean 0.86) (Table 1) in pre- and post-monsoon season, respectively. 44 and 30 % groundwater samples depicts calcite weathering dominance, and 25 and 67 % shows dolomite weathering dominance in the study area in pre- and post-monsoon season, respectively (Fig. 3a). 31 and

3 % of the samples showing >2 Ca/Mg ratio which indicates silicate weathering is dominant process for the contribution of Ca and Mg ions in pre- and post-monsoon, respectively. HCO_3/SiO_2 ratio is used to understand the type of dominance in the groundwater system. Silica in the groundwater can be released by silicate weathering but not by dissolving carbonate, Hence, HCO_3/SiO_2 <5 illustrates
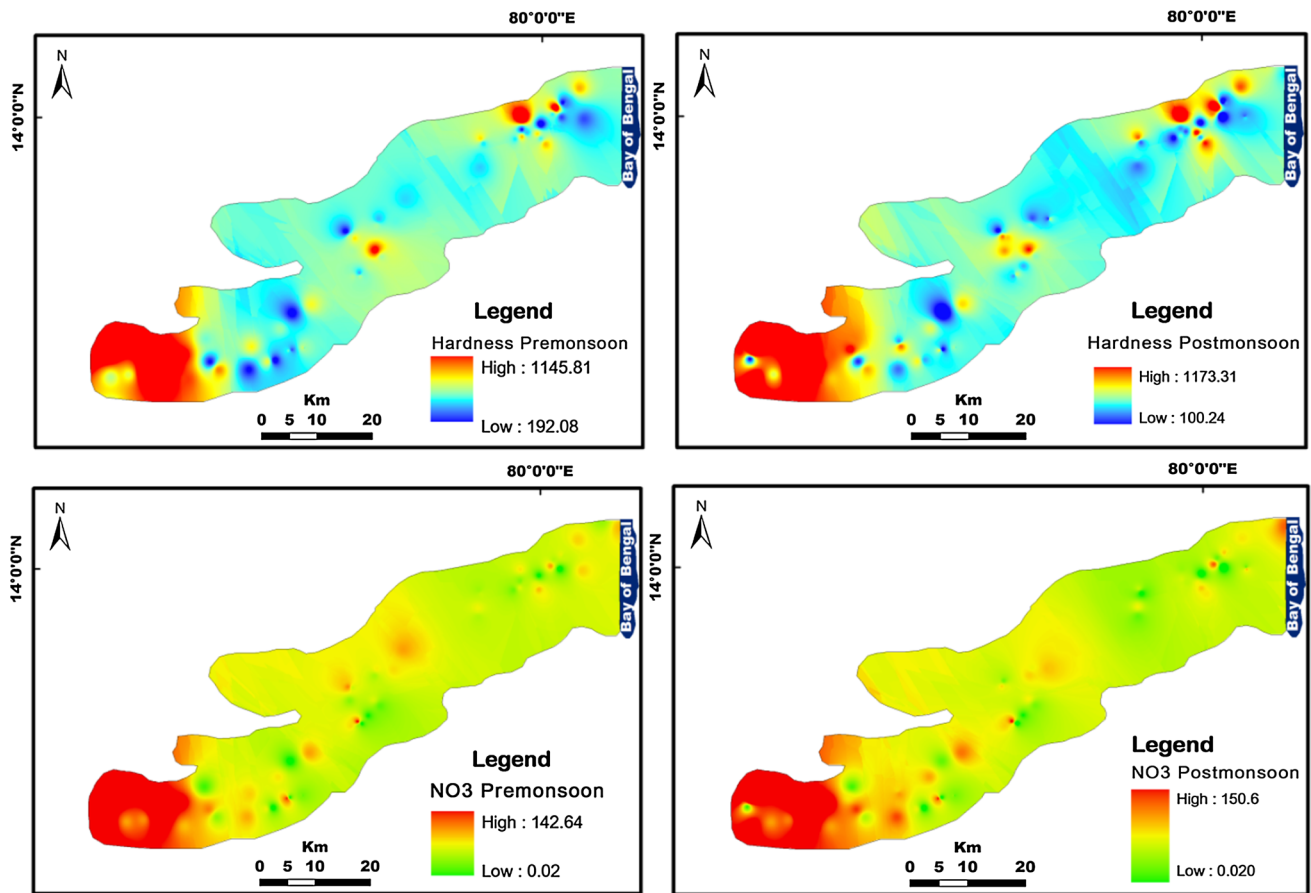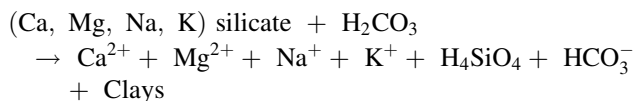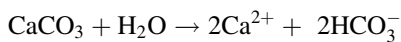
Fig. 2 Spatial distribution of hardness and nitrate concentration

silicate weathering, while ratio >10 represent carbonate weathering (Hounslow 1995). The HCO_3/SiO_2 ratio (mean 699.5 in pre- and 11.55 in post-) evidently demonstrating the dominance of carbonate over silicate weathering in both seasons.

The carbonate and silicate weathering/dissolution reactions are:

$$CaCO_3 + H_2O \rightarrow 2Ca^{2+} + 2HCO_3^-$$

$$\begin{aligned}(Ca, Mg, Na, K)\ silicate\ &+\ H_2CO_3 \\ \rightarrow\ Ca^{2+} +\ Mg^{2+} +\ &Na^+ +\ K^+ +\ H_4SiO_4 +\ HCO_3^- \\ +\ &Clays\end{aligned}$$

Correlation study shows that there is positive correlation exist between Ca–HCO_3 ($r = 0.22$ in pre- and $r = 0.47$ in post-), Mg–HCO_3 ($r = 0.64$ in pre- and $r = 0.53$ in post-) which supports the carbonate weathering process (Table 2). Ca–Mg has positive correlation ($r = 0.33$ in pre- and $r = 0.48$ in post-) depicting that dolomite is providing Ca and Mg in the groundwater in both the seasons. If gypsum is the major source for Ca in groundwater it will dissociate Ca and SO_4 in equal concentration. There is a positive correlation between Ca–

SO_4 ($r = 0.25$) in pre- and negative correlation ($r = -0.04$) in post-monsoon indicating gypsum dissolution as source for Ca mainly in pre-monsoon groundwater. Positive and good correlation of Ca–Cl ($r = 0.56$ in pre- and $r = 0.45$ in post-) and Mg–Cl ($r = 0.54$ in pre- and $r = 0.73$ in post-) indicate the presence of $CaCl_2$ and $MgCl_2$ minerals for the contribution of Ca, Mg and Cl ions in the groundwater. The positive relation between Mg and Na ($r = 0.31$ in pre- and $r = 0.44$ in post-) demonstrate that silicate weathering process providing both ions in groundwater. The relative ratio of $HCO_3/(HCO_3 + SO_4)$ in most of the groundwater samples (>0.5) signifies carbonic acid weathering as major proton producer. The presence of kankar carbonates in the alluvial sediments could have favored the carbonate weathering process in the study area (Raju et al. 2011). If Ca, Mg, HCO_3 and SO_4 are derived from dissolution of calcite, dolomite and gypsum minerals then all samples should exist on 1:1 line. As indicated, alkaline earths are in excess over $HCO_3 + SO_4$ in majority of the samples (Fig. 3b). Thus, the excess positive charge would be balanced by Cl, the only other major anion or reverse ion exchange also shifts the points to left.

Fig. 3 Ionic plots of chemical constituent relationships from natural sources
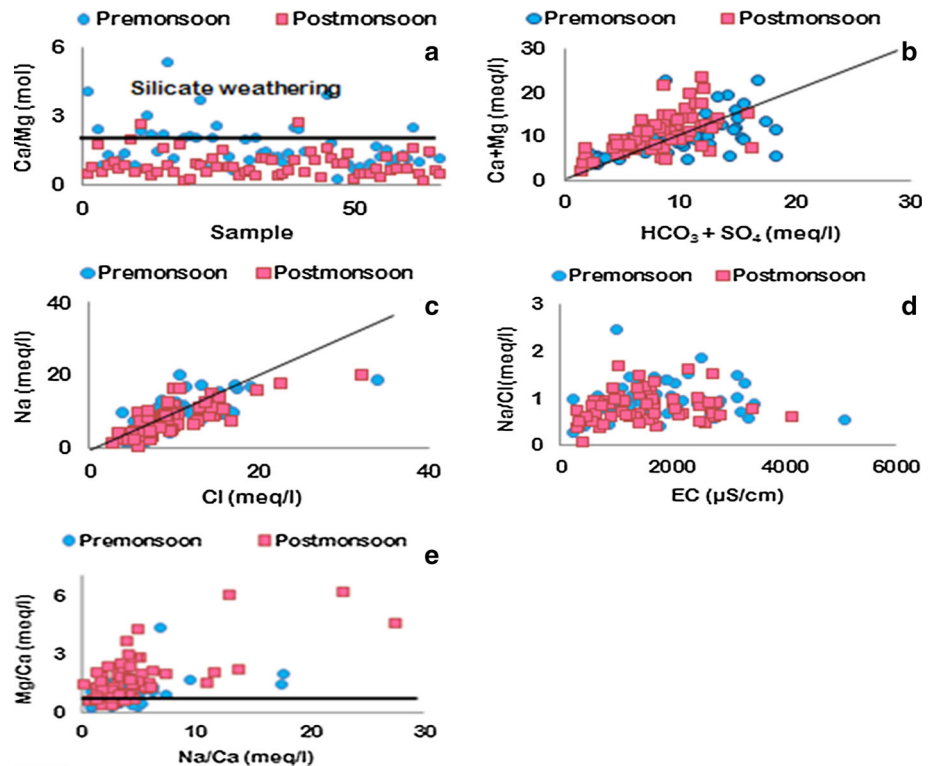
Na–Cl relationship is used to identify its source and mechanism of acquiring the salinity and saline intrusions in semi-arid regions (Sami 1992). Halite (NaCl) dissociate to Na and Cl in equal proportion to enrich the groundwater. A very good positive correlation exist between Na–Cl ($r = 0.73$ in pre- and $r = 0.77$ in post-) indicating dissolution chloride salts as probable source for Na and Cl in groundwater. Na/Cl >1 is used to account for silicate weathering contribution of Na (Meybeck 1987). Around 39 and 21 % samples shows Na/Cl ratio >1 indicating the silicate weathering as one of the probable source apart from halite in the enrichment of Na in pre- and post-monsoon season, respectively. Plotting of Na and Cl shows more points are towards Cl side and few points fall on the equiline depicting halite dissolution (Fig. 3c). The Na–Cl plot indicates that most of the post-monsoon samples lie slightly above the equiline. The excess of Na is attributed to silicate weathering (Stallard and Edmond 1983), while the pre-monsoon samples lay below the line indicating that the addition of Cl may be due to the halite dissolution during water–rock interactions. In the plot of Na/Cl vs EC (Fig. 3d), the Na/Cl shows a decreasing trend with increasing EC, indicating Na released from silicate weathering process. It also displays that evaporation is not playing the predominant part as ionic source. The higher bicarbonate values in groundwater supported the above relation due to reaction of plagioclase feldspar minerals with carbonic acid which may be one of the reasons for

increase of EC (Jankowski and Acworth 1997) in both the seasons. Na–HCO$_3$ ($r = 0.60$ in pre- and $r = 0.65$ in post-) relation shows that greater part of HCO$_3$ is originated from carbonate and silicate rock dissolution resulting in Na–HCO$_3$ water type. Albite (NaAlSi$_3$O$_8$) may contribute Na in groundwater. The reaction is as follows:

$$NaAlSi_3O_8 + H_2CO_3 + H_2O$$
$$\rightarrow Na^+ + HCO_3^- + 2H_4SiO_4 + Al_2Si_2O_5(OH)_4$$
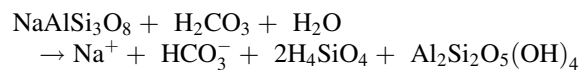
Na/Ca >1 indicates Ca deficiency probably due to precipitation of CaCO$_3$ or ion exchange process. The ratio (mean 3.50 in pre- and 4.48 in post-) signifies that if the contribution of dissolved ions is mainly from common source (Na$_2$SO$_4$, K$_2$SO$_4$, NaCl and KCl), the alkali elements should increase simultaneously with an increase of Cl and SO$_4$ in groundwater. Relationship between Mg/Ca and Na/Ca molar ratio for groundwater ($r = 0.51$ in pre- and $r = 0.71$ in post-) is illustrated in Fig. 3e. From the correlation between Mg/Ca and Na/Ca molar ratio shows that majority of groundwater samples are below Mg/Ca = 0.8 lines in the pre-, but in most of the samples in post-monsoon depicts ratio more than 0.8 line. This is probably due to equilibrium of groundwaters simultaneously with calcite and dolomite (Han and Liu 2004) in pre- whereas mainly dolomite contributing in post-monsoon. The water equilibrated together with calcite and dolomite under room temperature gives an ideal molar Mg/Ca ratio of about 0.8 (Appelo and Postma 1996). K/Cl >0.2 indicates potash

Table 2 Correlation matrix for the groundwater samples of pre- (italics) and post-monsoon (bold)

	Ca^{2+}	Mg^{2+}	K^+	Na^+	CO_3^{2-}	HCO_3^-	Cl^-	F^-	PO_4^{3-}	SO_4^{2-}	NO_3^-	pH	EC
Ca^{2+}	*1*												
	1												
Mg^{2+}	*0.33*	*1*											
	0.48	**1**											
K^+	*−0.26*	*0.04*	*1*										
	0.01	**−0.02**	**1**										
Na^+	*0.14*	*0.31*	*0.28*	*1*									
	0.15	**0.44**	**0.29**	**1**									
CO_3^{2-}	*−0.33*	*−0.13*	*0.32*	*0.21*	*1*								
	−0.15	**−0.05**	**−0.06**	**−0.14**	**1**								
HCO_3^-	*0.22*	*0.64*	*0.34*	*0.60*	*0.07*	*1*							
	0.47	**0.53**	**0.38**	**0.65**	**−0.18**	**1**							
Cl^-	*0.56*	*0.54*	*0.08*	*0.73*	*−0.04*	*0.29*	*1*						
	0.45	**0.73**	**0.08**	**0.77**	**−0.15**	**0.47**	**1**						
F^-	*−0.10*	*0.01*	*−0.03*	*0.12*	*0.12*	*0.15*	*−0.08*	*1*					
	0.01	**0.14**	**−0.08**	**0.16**	**−0.07**	**0.25**	**0.08**	**1**					
PO_4^{3-}	*−0.23*	*−0.14*	*0.86*	*0.21*	*0.31*	*0.16*	*0.04*	*−0.07*	*1*				
	−0.04	**−0.08**	**0.75**	**0.28**	**−0.04**	**0.18**	**0.11**	**−0.08**	**1**				
SO_4^{2-}	*0.25*	*0.20*	*−0.15*	*0.26*	*−0.23*	*0.18*	*0.26*	*0.12*	*−0.16*	*1*			
	−0.04	**−0.05**	**−0.04**	**0.28**	**−0.07**	**0.03**	**0.10**	**0.03**	**−0.02**	**1**			
NO_3^-	*0.48*	*0.36*	*0.13*	*0.23*	*−0.06*	*0.42*	*0.25*	*0.02*	*0.10*	*0.06*	*1*		
	0.58	**0.22**	**0.19**	**0.26**	**−0.07**	**0.44**	**0.26**	**0.06**	**0.14**	**0.02**	**1**		
pH	*−0.22*	*−0.12*	*0.17*	*0.30*	*0.62*	*0.08*	*0.07*	*0.21*	*0.18*	*−0.12*	*−0.12*	*1*	
	−0.42	**−0.09**	**−0.06**	**0.04**	**0.52**	**−0.03**	**−0.19**	**0.08**	**−0.06**	**0.19**	**−0.29**	**1**	
EC	*0.50*	*0.67*	*0.25*	*0.77*	*0.04*	*0.63*	*0.83*	*−0.02*	*0.08*	*0.22*	*0.44*	*0.12*	*1*
	0.58	**0.67**	**0.26**	**0.83**	**−0.19**	**0.75**	**0.89**	**0.07**	**0.19**	**0.15**	**0.48**	**−0.19**	**1**

feldspar dissolution for the K in groundwater. K/Cl ratio (mean 0.04 in pre- and 0.03 in post-) indicates silicate weathering is not playing the significance role in providing potassium in the aquifer system.

Anthropogenic sources

Variation in EC or TDS is mainly related to land use pattern and pollution (Gillardet et al. 1999). Ions like PO_4, NO_3, Na and Cl are mostly derived from different anthropogenic sources like agricultural fertilizer excess input, runoff, animal excreta, municipal and industrial sewage waste (Jalali 2009). These factors can be related to the EC variation in the groundwater and can be used to indicate the influence of human activities on the water chemistry (Han and Liu 2004). Relationships between various ions (Na, Cl and NO_3) and EC are presented in the Fig. 4a–c. Strong and significant positive correlation between EC and Ca ($r = 0.50$ in pre- and $r = 0.58$ in post-), Mg ($r = 0.67$ in pre- and $r = 0.67$ in post-), Na

($r = 0.77$ in pre- and $r = 0.83$ in post-), HCO_3 ($r = 0.63$ in pre- and $r = 0.75$ in post-), Cl ($r = 0.83$ in pre- and $r = 0.89$ in post-) and NO_3 ($r = 0.44$ in pre- and $r = 0.47$ in post-), suggests the influence of human activities to a significance level in providing these ions to groundwater of the study area (Table 2).

Nitrate in groundwater is an anthropogenic pollutant contributed by seepage of irrigation water from agricultural field where nitrogenous fertilizers are used, industrial effluents, human and animal wastes through biochemical activity of nitrifying bacteria (Nitrosomonas and Nitrobacter) (Raju et al. 2011). Fertilizers have major constituent of N along with minor components of Ca and Mg as plant nutrients which result in positive relation between NO_3–Ca ($r = 0.48$ in pre- and $r = 0.58$ in post-) and NO_3–Mg ($r = 0.36$ in pre- and $r = 0.22$ in post-). This implies that excess fertilizer retained in the soil after plant uptake, infiltrate into the groundwater system which eventually increase NO_3, Ca and Mg. Significant relation of PO_4–K ($r = 0.86$ in pre- and $r = 0.75$ in post-) indicating
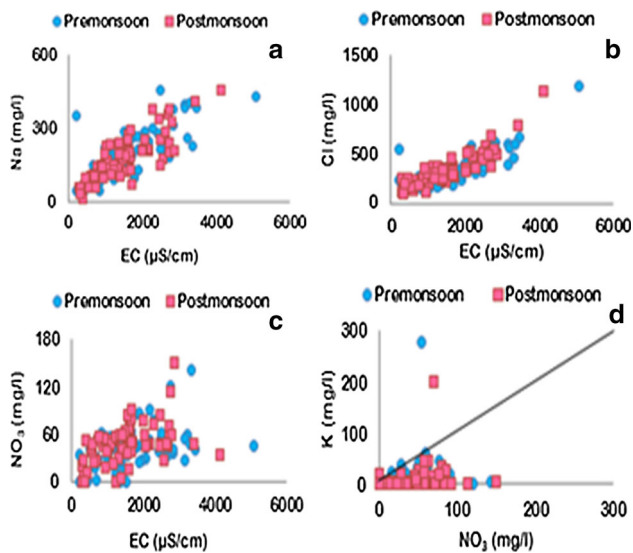
Fig. 4 Ionic plots of chemical constituent relationships from anthropogenic sources

the fertilizer as probable source in the enrichment of PO_4 and K in the aquifer system. Soil acidification from N-fertilizer application occurs due to the proton (H^+) generation in nitrification further supported by negative correlation between pH and NO_3 ($r = -0.12$ in pre- and $r = -0.30$ in post-). Plot of NO_3-K clearly indicate that most of the samples are below the 1:1 line i.e. towards NO_3 suggesting domestic sewage, septic tanks effluents and agricultural activities contribute these ions to the groundwater system (Fig. 4d).

Comparisons of ionic ratios for potential salinity sources and salinity mapping

Important ionic ratios [Na/Cl, SO_4/Cl, K/Cl, Mg/Ca, Ca/(HCO_3 + SO_4)] have been compared to understand the possible source of salinity of the groundwater (Table 3). Modification of the geochemical characteristics of saline water is probably due to water–rock interaction with processes of ion exchange, adsorption on clay minerals and carbonate-dissolution-precipitation reactions (Kumar et al.

2009; Raju et al. 2015). Salinity in the aquifer is largely from sea-water intrusion (coastal areas), deep saline water upcoming (due to overexploitation of aquifer), agricultural return flows (excess fertilizer input and its runoff) and finally wastewater infiltration (municipal and industrial discharge). If salinization source is only from seawater intrusion then Mg/Ca ionic ratio will be >5 which is the direct indicator of seawater contamination (Metcalf and Eddy 2000). Relative to seawater, the saline groundwater has relatively low Na/Cl, low Mg/Ca and high Ca/(HCO_3 + SO_4) ratios. The groundwaters of the study area is characterized by slightly higher SO_4/Cl ratios (>0.05), is attributed to the application of gypsum fertilizers in irrigation practices (Vengosh et al. 2002). The chemical signatures of groundwater contamination due to urban domestic wastewater is discernible because sewage effluent has a relatively high Na/Cl (>1), high K/Cl (>0.02) and a high SO_4/Cl (0.09) ratio (Ghabayen et al. 2006). These ratios are attributed to applications of sodium chloride salts and domestic wastewater sewage characteristics.

The comparison of the Na/Cl ratio shows that the potential source of high salinity is due to seawater intrusion and wastewater infiltration in both the seasons of the study area. The Swarnamukhi River finally joins in the Bay of Bengal and sea water intrusion in the eastern part of the study area may be due to the overexploitation of groundwater in the coastal aquifers. The pre-monsoon Na/Cl ratio found higher in comparison to post-monsoon which indicate the man-made impact of pollution. This is supported by slightly high SO_4/Cl ratio in pre- and post-monsoon seasons corroborate that there is some impact from agriculture return flows. It is also observed in the alkaline and saline white patches in some parts of the area during summer season due to high evapo-transpiration process. The correlations between K and other major ions has no significant relation except PO_4 ($r = 0.86$ in pre- and 0.75 in post-) which reveals that the source of K is from anthropogenic activities. This finding supports by comparison of K/Cl ratio establish pretty higher and equivalent to wastewater infiltration. Mg/Ca ratio in groundwater samples shows upcoming process accountable in post-monsoon. Ca/(HCO_3 + SO_4) ratio clearly shows the high

Table 3 The comparative ionic ratio of potential salinization sources

Ratio (meq/l)	Seawater intrusion	Deep saline upcoming	Agricultural return flow	Wastewater infiltration	Mean	
					Pre	Post
Na^+/Cl^-	0.86–1	<0.8	–	1.1	0.96	0.80
SO_4^{2-}/Cl^-	0.05	∼0.05	≫0.05	0.09	0.07	0.07
K^+/Cl^-	0.019	<0.019	–	≫0.02	0.04	0.03
Mg^{2+}/Ca^{2+}	>5	>1	–	–	0.83	1.68
$Ca^{2+}/(HCO_3^- + SO_4^{2-})$	0.35–1	>1	–	–	0.66	0.61

impact of seawater on the freshwater aquifers in both the seasons. It can be concluded that deep saline upcoming and wastewater infiltration are the major factors as well as agriculture return flow and seawater intrusion play significant role in the contribution of increasing salinity of groundwater in the study area.

The water quality (salinity) varies within the river basin in space as well as with the depth of the occurrence groundwater depending upon water–rock interactions and anthropogenic impacts. On the basis of the groundwater suitable for the drinking needs, the salinity is analysed and groundwater of the area broadly characterized into four classes: fresh, fresh brackish, brackish and brackish salt and the spatial distribution of salinity categories are shown in Fig. 5. Stuyfzand (1989) has classified, on the basis of Chloride (meq/l), groundwater into eight classes: extremely fresh (<0.14), very fresh (0.14–0.85), fresh (0.85–4.23), fresh brackish (4.23–8.46), brackish (8.46–28.21), brackish salt (28.21–282.06), salt (282.06–564.13) and hyperhaline

(>564.13). Brackish water and fresh brackish waters categories are predominantly spread in entire river basin in which former is dominating in the eastern part and latter is dominating in central to western regions of the area in both the seasons. Intermittent patches of brackish salt water class found in northeastern part of the area in both the seasons which needs remedy before using for drinking or irrigation purposes.

Solute attainment process and hydrogeochemical facies

The term hydrogeochemical facies is used to describe the bodies of groundwater in an aquifer that differ in their chemical composition and thus are the function of lithology, solution kinetics and flow pattern of the aquifer. Based on the relative dominance of major ions in terms of their reactive values (meq/l), groundwater samples have been classified into six hydrochemical facies which are Na–Cl (32 and 35 %), Na–HCO₃ (31 and 20 %), Ca–Cl (17 and

Fig. 5 Groundwater salinity characterization of Swarnamukhi River basin
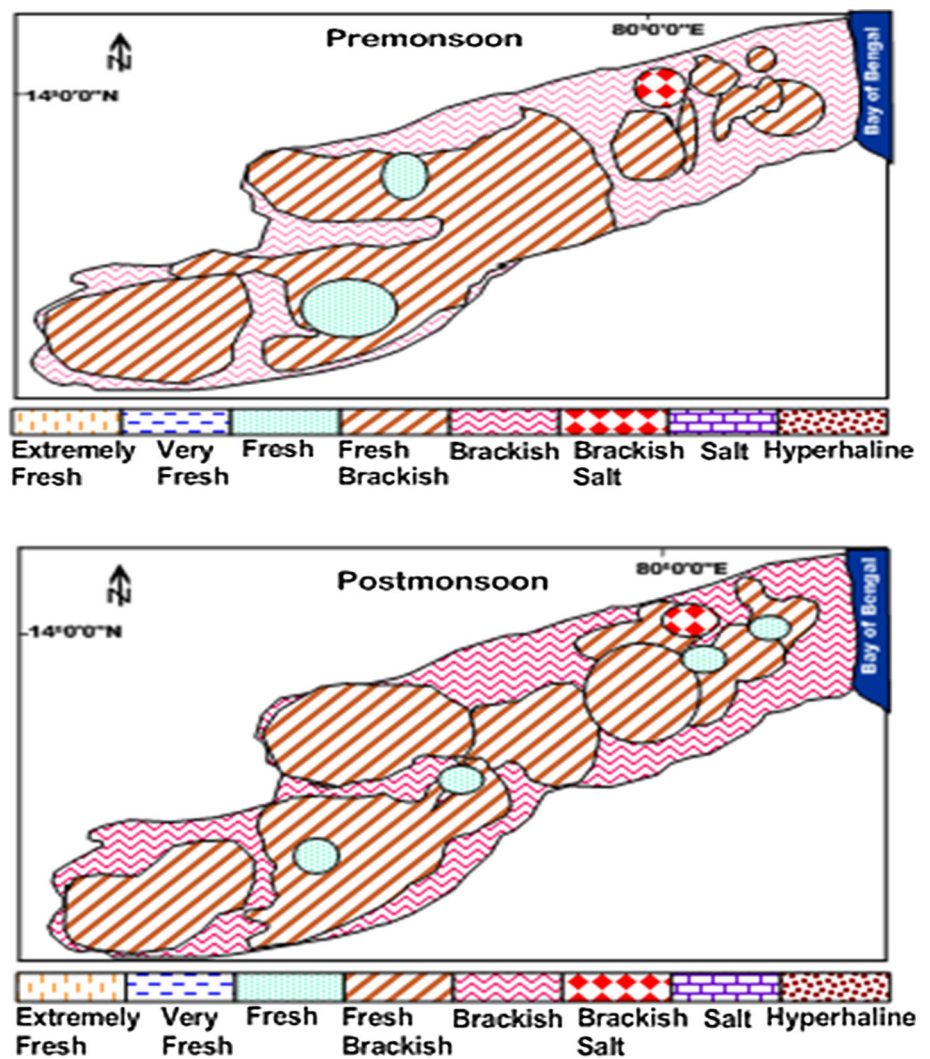
12 %), Mg–Cl (5 and 24 %), Ca–HCO$_3$ (14 and 1 %) and Mg–HCO$_3$ (1 and 8 %) in pre- and post-monsoon, respectively (Fig. 6). The spatial distribution of hydrogeochemical facies depicts that majority of the area is dominated by sodium chloride facies (Fig. 7). Na–Cl water facies is distributed mainly in northeast side close to the Bay of Bengal, highly urbanized and intensive agricultural central regions of the study area. Na–Cl facies exist in areas where groundwater movement is restricted with very low flushing action by recharge due to over-drafting of groundwater from the aquifer and the contribution of overflowing domestic waste and stagnant water pools. Na–HCO$_3$ type water is distributed unevenly throughout the area implying active flushing of the aquifer by fresh water. In such hydrogeochemical environment, ion exchange processes would have taken place and Ca + Mg taken up from the recharging water in return for adsorbed Na in the clay lenses and releases sodium in the groundwater. Most of Na–HCO$_3$ type water is observed in and around Srikalahasti and Naidupet town areas which may be attributed to the recharge from the Swarnamukhi river.

Patches of Ca–Cl facies have been observed in extreme southwest, central and northeast parts in pre- whereas it confined to southwest and central parts in post-monsoon. This may be due to dilution effect and ion exchange process between Na, Mg and Ca. At higher salinities, direct ion exchange may create Ca–Cl waters due to the removal of Na from solution in exchange of Ca in solid surfaces or result of the process of mixing between younger, fresher water with more saline older water (Adams et al. 2001). More patches of Mg–Cl found in extreme northeast part or coastal parts in post- rather than in pre-monsoon indicate high Mg might be due to ion exchange of Mg minerals with Na and Ca. Small pockets of Ca–HCO$_3$ facies observed in southwest, central and north eastern parts in pre-, but restricted to only central part in post-monsoon. The conversion of Ca–HCO$_3$ to Ca–Cl may be due to rainwater infiltration of dissolved chloride salts occur in the soils
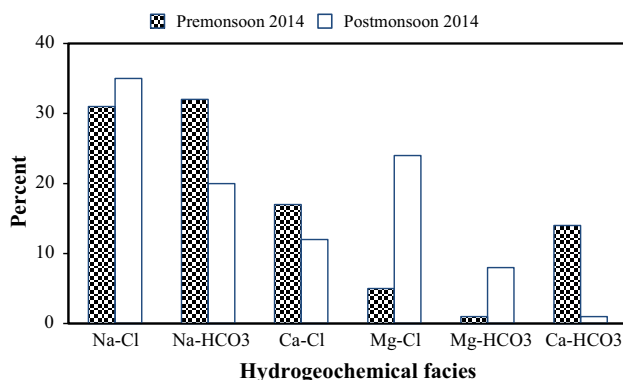
during the post-monsoon season. Spatial distribution of Mg–HCO$_3$ is observed mainly in south western and central parts in post-monsoon which is attributed to ion exchange and water–rock interactions.

The geochemical evolution of groundwater can be understood by plotting the concentrations of major cations and anions in the Piper tri-linear diagram (Piper 1944). The plot (Fig. 8) showed that 59 and 62 % of groundwater samples fall into the no dominant type, whereas 34 and 27 % falls in domain of sodium and potassium type, 7 and 2 % in calcium type cation facies in pre- and post-monsoon, respectively. In anion facies, it is observed that 56 and 68 % of these groundwater samples fall into the chloride type, 32 and 13 % into the bicarbonate type and remaining in the no dominant type (Table 4). The plot of chemical data on middle diamond shaped trilinear diagram reveals that majority of groundwater samples fall in the fields of 1, 4 and 9 suggesting that alkaline earth exceeds alkalies, strong acids exceeds weak acids and none of the cation and anion pairs exceed 50 % in both the seasons. From the data plots, it is apparent that the total hydrochemistry is dominated by alkaline earths and strong acids. Piper diagram shows that majority (49 % in pre- and 70 % in post-) of groundwater samples are of mixed type. High Na concentrations suggesting that Ca–Na ion exchange might be an important geochemical process for the occurrence of 26 and 18 % Na–Cl type water in pre- and post-monsoon, respectively. Ca–Mg–HCO$_3$ (22 % in pre- and 7 % in post-) water type may be due to mineral dissolution, direct ion exchange and recharge by freshwater. In groundwater monitoring programs, Ca rich waters have more significance as they are more susceptible to contamination and are unsuited of the location of waste disposal sites. Few samples also show the Ca–Mg–SO$_4$ (3 % in pre- and 5 % in post) water facies which indicate the movement of water from recharge to discharge area. Therefore, the geochemical classification of groundwater chemistry in the Piper's diagram indicates that the origin of dissolved solids in the groundwater is through the geochemical processes and its quality is subsequently altered by the influence of anthropogenic activities.

The Gibbs diagram is widely used to establish the relationship of water composition and aquifer lithological characteristics (Gibbs 1970) and proposed two diagrams which are related to the ratios of cations (Na+K/Na+K+Ca) and anions (Cl/Cl+HCO$_3$) against TDS. The cation ratios varies 0.28–0.93 in pre- and 0.11–0.93 in post-monsoon and anion ratios varies from 0.27 to 0.81 in pre- and 0.30 to 0.82 in post-monsoon (Table 1). The clustering of data points suggest chemical weathering of rock forming minerals (60 % in pre- and 71 % in post-) and evaporation (40 % in pre- and 29 % in post-) are dominant factors controlling the groundwater chemistry in the study area

Fig. 6 Histograms showing seasonal hydrogeochemical facies

Fig. 7 Spatial distribution of hydrochemical type of groundwater
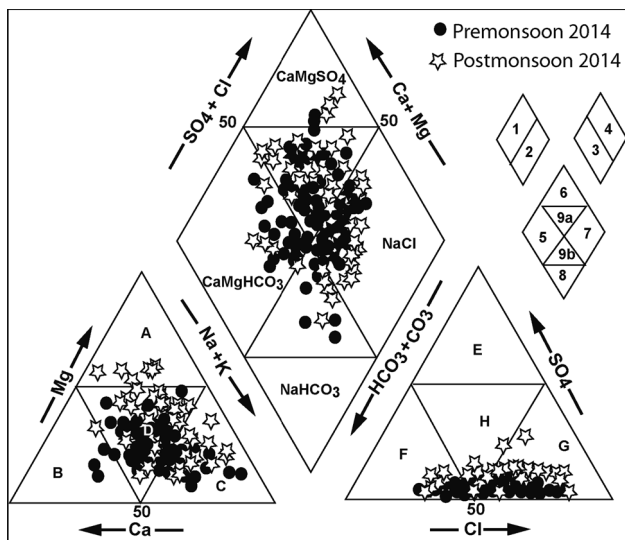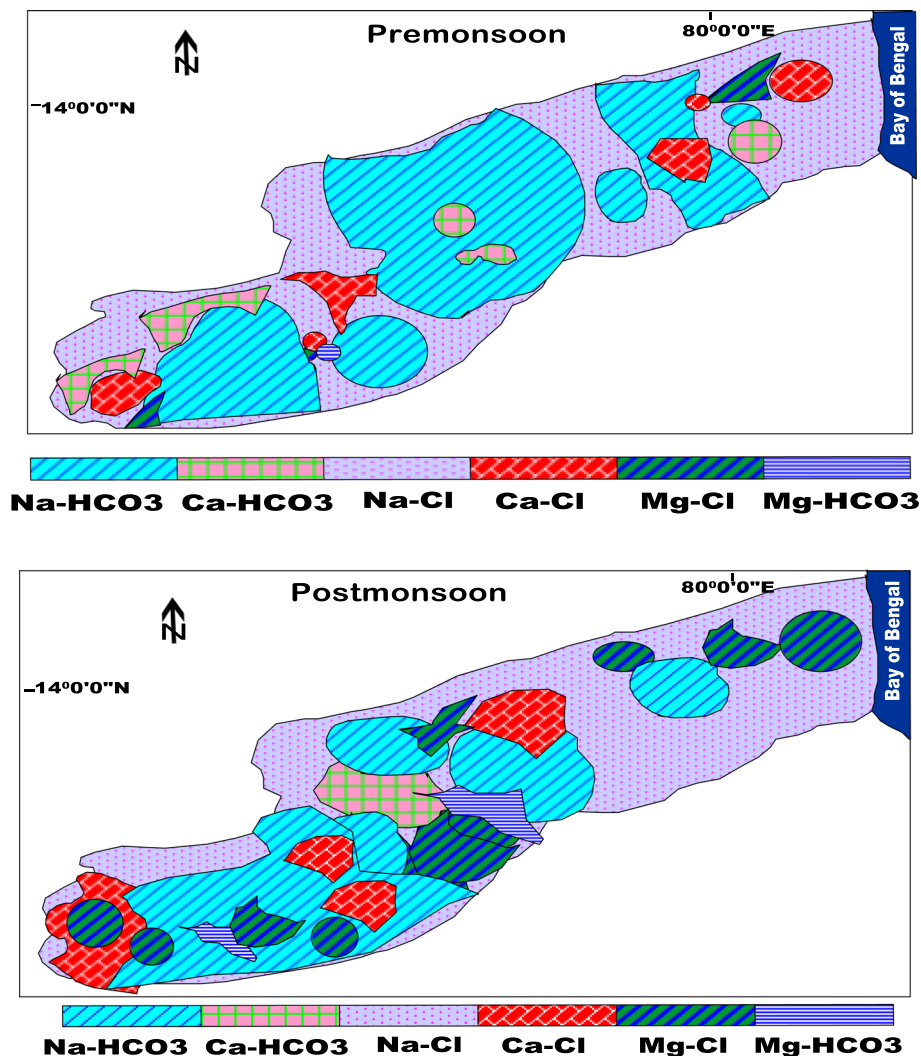

Fig. 8 Relative ionic composition of groundwater (after Piper 1944)

(Fig. 9). In pre-monsoon, number of samples fall in the evaporation zone which suggests these waters are controlled by evaporation subsequent accumulation of salts in the soils. Intensive agricultural activities i.e. long-term farming practices can increase the weathering and erosion of soil may be responsible in a higher TDS content (Srinivasamoorthy et al. 2014).

Statistical screening of water quality data

Principal component analysis (PCA) is a multivariate data analytic technique which reduces a large number of variables to a small one, without sacrificing too much of the information. In the PCA, varimax with kaiser normalization rotation was applied to find components that can be more easily explained in terms of hydrochemical or anthropogenic processes as it increases the participation of the variables with higher contribution and reduce those

Table 4 Hydrogeochemical classification of groundwater

Piper diagram's hydrogeochemical facies classification (Fig. 8)		Pre	Post
	Characteristics	Pre	Post
Diamond			
1	Alkaline earths exceeds alkalies	64	79
2	Alkalies exceed alkaline earths	36	21
3	Weak acids exceed strong acids	32	11
4	Strong acids exceed weak acids	68	89
5	Carbonate hardness exceeds 50 %	22	7
6	Non-carbonate hardness exceeds 50 %	3	5
7	Non-carbonate alkali exceeds 50 %	26	18
8	Carbonate alkali exceeds 50 %	–	–
9	None of the ion pairs exceed 50 %	49	70
Cation field			
A	Magnesium type	–	9
B	Calcium type	7	2
C	Sodium and potassium type	34	27
D	No dominant type	59	62
Anion field			
E	Sulphate type	–	–
F	Bicarbonate type	32	13
G	Chloride type	56	68
H	No dominant type	12	19
Wilcox diagram classification (Fig. 11)			
	Excellent to good	17	20
	Good to permissible	42	46
	Permissible to doubtful	7	6
	Doubtful to unsuitable	22	25
	Unsuitable	12	3
US Salinity Laboratory classification (Fig. 12)			
C1S1	Low salty and low Na and used for every soil	3	–
C2S1	Medium salty and low Na, drainage should be good	14	21
C3S1	High salty and low Na, require drainage or dangerous for soil	56	62
C4S1	Very salty and low Na, require rich drainage, used for every soil	14	12
C4S2	Very salty and medium Na, require rich drainage otherwise dangerous for soil	12	9

with lesser contributions. PCA results comprising the four rotated loadings, eigenvalues and % variance and cumulative are summarized in Table 5. The PC1 is related to the largest eigenvalue and is able to explain the greatest amount of variance in the data set and so forth. The cumulative variances explained by the four components were 73.45 and 70.52 % in pre- and post-monsoon, respectively. The parameters with loadings >±0.50 is considered significant. The scree plot is a graphical mode in which sorted eigenvalues are plotted in their decreasing order, found four components where the eigenvalue is greater than one to explain the maximum variance of data. Scree plots and spatial distribution of chemical variables in 3D (x–y–z) plot of three components obtained has been presented in Fig. 10.

Component 1: natural and anthropogenic

Five of major water quality parameters (Ca, Mg, Na, Cl and NO_3) were significantly positively loaded on component 1 explained with 37.71 % in pre- and 38.88 % variance in pre- and post-monsoon season, respectively and these ions are mainly responsible for high EC, TDS and hardness in groundwater in both the seasons (Table 5). Ca, Mg and Na are derived from incongruent dissolution of respective feldspar minerals in groundwater indicates the water–rock interaction factor. The high concentration of Na, Cl and NO_3 in the groundwater mostly derived from agricultural fertilizers, animal waste, municipal and industrial sewage and can be attributed to the anthropogenic activities. The high concentration of Cl

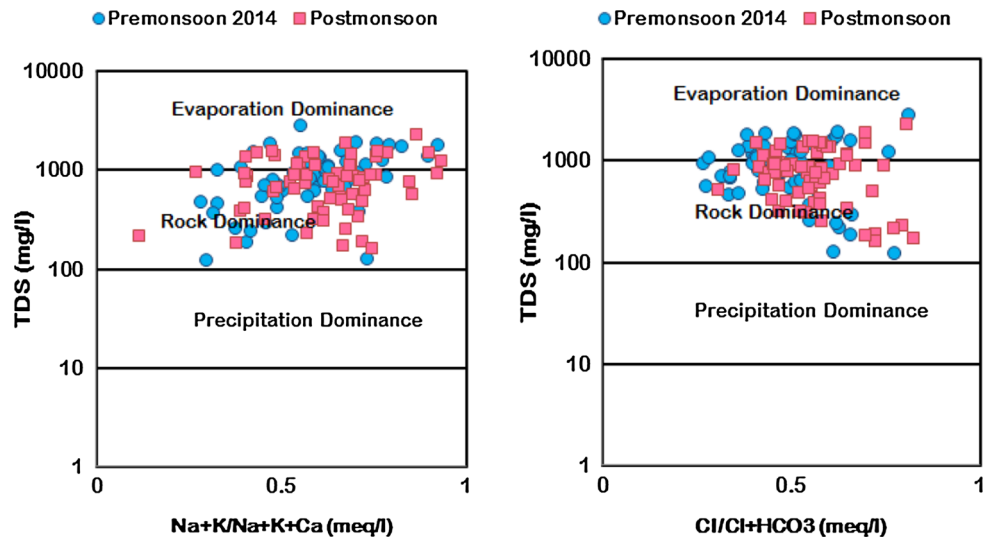**Fig. 9** Mechanism controlling the chemistry of groundwater (after Gibbs 1970)

Table 5 Rotated component matrix of chemical variables for pre- and post-monsoon seasons

| Variables	1		2		3		4	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post
Ca^{2+}	**0.75**	**0.64**	−0.30	−0.10	−0.29	−0.34	−0.10	0.45
Mg^{2+}	**0.72**	**0.80**	−0.08	−0.18	−0.17	0.08	0.41	0.08
Na^+	**0.58**	**0.73**	0.30	0.34	0.36	0.02	0.29	−0.44
K^+	0.04	0.10	**0.92**	**0.92**	0.12	−0.01	0.15	0.06
CO_3^{2-}	−0.07	−0.07	0.22	−0.03	**0.81**	**0.84**	0.05	0.26
HCO_3^-	0.48	**0.71**	0.26	0.31	−0.01	−0.03	**0.75**	0.08
Cl^-	**0.87**	**0.90**	0.07	0.02	0.13	−0.08	−0.11	−0.18
F^-	−0.21	0.07	−0.27	−0.12	0.27	0.06	**0.61**	**0.84**
PO_4^{3-}	−0.06	0.03	**0.91**	**0.90**	0.12	−0.03	0.01	0.00
SO_4^{2-}	0.17	0.12	−0.14	−0.03	−0.26	−0.05	**−0.52**	**−0.72**
NO_3^-	**0.51**	**0.50**	0.10	0.20	−0.20	−0.21	0.31	0.44
Si	−0.37	0.15	−0.28	0.09	−0.04	−0.33	**0.72**	**0.57**
pH	0.01	−0.12	0.03	−0.01	**0.88**	**0.85**	0.07	−0.29
EC	**0.90**	**0.95**	0.17	0.20	0.14	−0.12	0.20	−0.10
TDS	**0.90**	**0.95**	0.17	0.20	0.14	−0.12	0.20	−0.10
Hardness	**0.87**	**0.89**	−0.22	−0.18	−0.27	−0.14	0.21	0.31
Eigenvalue	6.03	6.22	2.98	2.01	1.48	1.82	1.26	1.23
% Variance	37.71	38.88	18.63	12.58	9.22	11.34	7.89	7.72
% Cumulative	37.71	38.88	56.34	51.46	65.56	62.80	73.45	70.52

Bold values are with significance level alpha = 0.05

in groundwater can also results from salts commonly added to animal feed to enhance the feed flavors and maintain cation–anion balance in the diet (Goff 2006) and it is supported by one of the major Na–Cl water facies in the study area. In post-monsoon, HCO_3 shows higher loading apart from above ions which supports the hypothesis of carbonate and silicate weathering activity and fresh water recharge from rainfall/or surface water to groundwater.

Component 2: anthropogenic

Component 2 with higher loading of K and PO_4 explained with 18.63 and 12.58 % of variance in pre- and post-monsoon seasons, respectively. Significant positive loadings observed in K and PO_4 with lesser percentage of variation in both the seasons. The occurrence of K in groundwater may be from granitic rocks consists of feldspars (orthoclase and plagioclase), mica, pyroxene and

Fig. 10 Scree and 3D (x–y–z) plots of three principal components
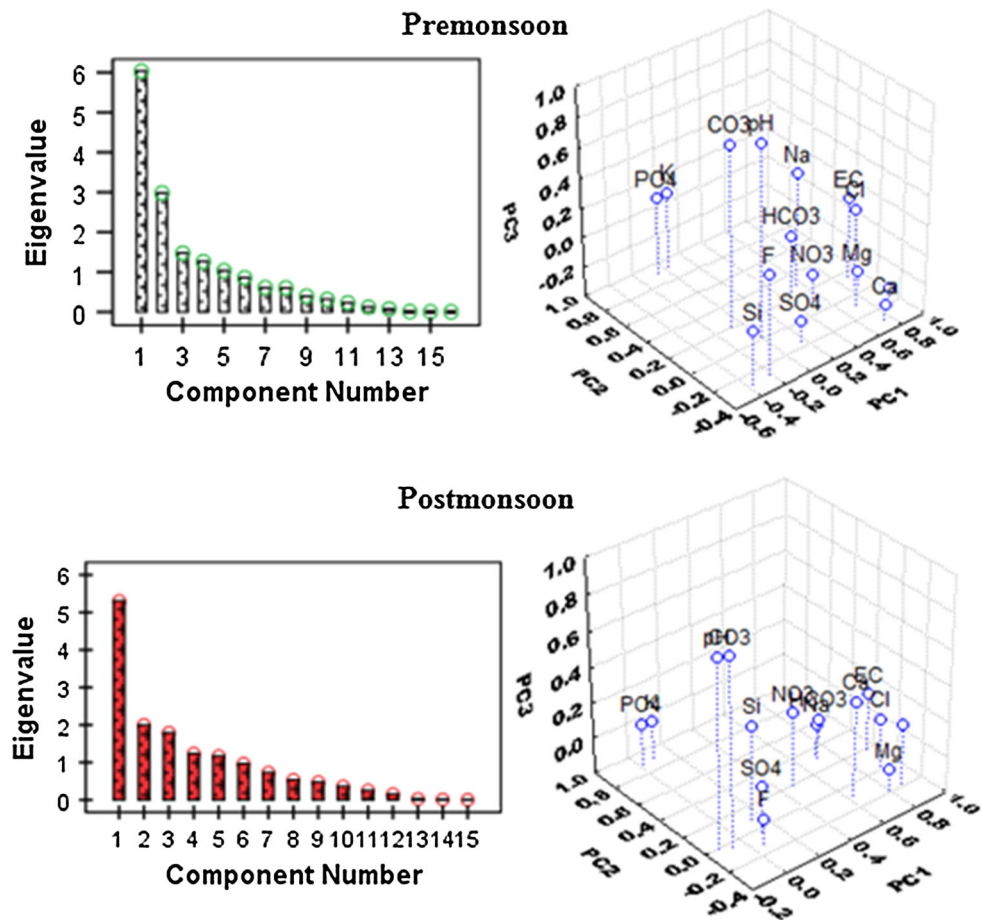
quartz in the studied area. There is no known geogenic source of PO_4 in the groundwater. Long-term fertilization of coarse-textured alluvial soil could increase K and PO_4 downward movement due to comparatively lesser adsorption and higher leaching capacity. Apart from fertilizers, other possible sources for increasing PO_4 and K in the study area are irrigation return flow containing their excess amount, municipality waste or sewage and decomposition of organic matter (Khashogji and Maghraby 2013).

Component 3: natural

The positive loadings of pH and CO_3 explained with 9.22 and 11.34 % of variance in pre- and post-monsoon, respectively. The average pH of both the season was greater than 7. Alkalinity of water may be due to dissolution of carbonate mineral (lime kankar) in the study area. Thus, it can be termed as natural process responsible for the occurrence of carbonate ions in the groundwater for both the seasons. Decomposition of organic matters in soil system also results in higher concentration of carbonates in the study area.

Component 4: fluoride and silica enrichment

It reflects the loading of HCO_3, F, SO_4 and Si with 7.89 and 7.72 % of variance in pre- and post-monsoon, respectively. Fluorite (CaF_2) is the main solid phase fluoride found in granites, granitic gneisses and pegmatites of semi-arid climate (Handa 1975). The hydrolysis of alumino–silicate minerals creates HCO_3, which can enhance fluorite dissolution as below in an alkaline medium.

$$CaF_2 + 2HCO_3^- \leftrightarrow CaCO_3 + 2F^- + H_2O + CO_2$$

Thus, activity of F is directly proportional to the amount of HCO_3. Intensive and long-term irrigation is also an important factor that causes weathering and leaching of F from the soils/weathered rocks. There exist positive loading of F and Si, suggesting the silicate weathering and fluoride leaching into the groundwater. Silicon was loaded with small percentage of variation due to the presence of Si in most of the rocks of the study area. This result is supported by the granitic rocks consist of quartz, feldspars and pyroxenes. Negative loading of SO_4 indicating its lesser role played in controlling the hydrogeochemistry and also

may represent the variations in agricultural management such as using different fertilizers in the studied area.

Average Water Quality Index (AWQI)

World Health Organization (1997) standards, assigned weight (w_i) and relative weight (W_i) for each physico-chemical parameters are shown in Table 6. The AWQI = 0 depicts that all pollutants are absent and AWQI = 100 when all pollutants reach their permissible limits. Values of AWQI exceeding 100 indicate that water has serious pollution problems. AWQI has values of 16–451 (mean 61) and 13–334 (mean 60) in pre- and post-monsoon seasons, respectively. Thus, around 93 and 95 %

of the water samples are safe for drinking purpose in pre- and post-monsoon, respectively.

Evaluation of groundwater quality

Suitability for drinking and domestic purposes

The water used for drinking purpose should be free from colour, turbidity and microorganisms (Karanth 1997). Chemically, the water should be soft with less dissolved solids and free from poisonous constituents. The range of hydrochemical parameters of groundwater of the parts of study area and their comparison with the prescribed specification of World Health Organization (WHO 1997) is summarized in Table 7, to evaluate the suitability of groundwater for drinking, domestic and public health uses. It is observed that majority of the hydrochemical parameters exceed the permissible limits prescribed by WHO in the study area. Majority (59 % in pre- and 83 % in post-) of groundwater samples have permanent or non-carbonate hardness (total hardness in excess of alkalinity) which can not be removed by boiling due to the presence of strong acids. Increased hardness in post-monsoon may be due to excess leaching of Ca and Mg ions into the groundwater (Raju et al. 2012). According to Sawyer and Mc Cartly (1967) classification (Table 8), 85 and 89 % are very hard in pre- and post-monsoon, respectively. Based on the classification of TDS content, 17 and 11 % of the samples are exceeding the prescribed limit making water unfit for drinking in pre- and post-monsoon, respectively. According to Davis and De Wiest (1966) classification of TDS, all

Table 6 Water quality parameters with WHO (1997) standards and assigned weights

Parameter	WHO	w_i	W
TDS	1500	5	0.12
Bicarbonate	600	1	0.02
Chloride	600	5	0.12
Sulphate	600	5	0.12
Phosphate	0.1	1	0.02
Nitrate	50	5	0.12
Fluoride	1.5	5	0.12
Calcium	200	3	0.07
Magnesium	150	3	0.07
Sodium	200	4	0.09
Potassium	12	2	0.05
Silicate	17	2	0.05
$\sum$		41	0.97

Table 7 Comparison of chemical parameters with WHO standards for drinking water use

Parameter (mg/l)	Range		WHO (1997)	% Samples		Hazardous effects
	Pre	Post		Pre	Post	
pH	6.37–8.58	6.44–8.75	9.2	–	–	Taste, damages mucous membrane of eyes, nose, mouth, abdomen, anus, etc.
TDS	120–2822	163–2300	1500	17	11	Kidney stones, gastrointestinal irritation
TH	190–1146	100–1176	500	46	49	Urolithiasis, anencephaly, arthritis, arthropathies
TA	98–954	59–787	–	–	–	Alkaline taste and eye irritation
Ca^{2+}	38–306	18–234	200	5	3	Kidney stones and gastro-intestinal irritation
Mg^{2+}	12–172	13.4–226	150	1	3	Laxative agent
Na^+	43–459	7.7–456	200	48	42	Heart problems, renal and circulatory diseases
K^+	0.8–277	0.3–200	12	27	18	Laxative effects
HCO_3^-	120–1104	72–960	600	46	40	–
SO_4^{2-}	4.4–63	1.6–106	600	–	–	Bitter taste, gastrointestinal irritation, intestinal disorders
Cl^-	140–1200	96–1140	600	7	5	Salty taste, injurious who have heart and kidney diseases
F^-	0–1.9	0.02–2.2	1.5	3	2	Dental and skeletal fluorosis
NO_3^-	0–142	0–150	50	34	41	Blue baby syndrome, gastric carcinomas, disorders of alimentary canal, respiratory and nervous system

samples are desirable to permissible for drinking purpose and agricultural use in both the seasons. Based on Freeze and Cherry (1979) classification of TDS, 39 and 71 % of groundwater fall in freshwater category, 61 and 29 % samples categorised as brackish water in pre- and post-monsoon season, respectively (Table 8).

Most of the Ca and Mg values are within the permissible limit in both the seasons. Undesirable effect produced beyond the permissible limits of Ca and Mg is encrustation in water supply and has an adverse effect on domestic use. 48 and 42 % of Na and 27 and 18 % of K of samples are exceeding the limits in pre- and post-monsoon, respectively in the area. The analytical data shows that bicarbonate in 46 and 40 % of samples are above the standard in pre- and post-monsoon, respectively. Few samples (7 % in pre- and 5 % in post-) are above the standard of chloride. Nitrate in 41 and 34 % of the samples are above the prescribed value of 50 mg/l in pre- and post-monsoon, respectively. This depicts the nitrate contamination in the study area which could lead to blue baby syndrome and various body cancers. Fluoride is the ion whose lower (<0.6 mg/l) and higher concentration (>1.5 mg/l) is significant to health view point. It is required for preventing dental caries and normal development of bones but at the same time become curse by forming dental and skeletal fluorosis. Almost all the groundwater samples are within the permissible limits of fluoride except in two villages (Nadavatturur and Balavaripalem), but no case of fluorosis has been reported yet. Sulfate in all samples are within the permissible limit in both the seasons. High sulfate content in combination with excess of Mg may result in corrosion of metals in the distribution system, particularly in waters having low alkalinity.

Suitability for irrigation purposes

Factors responsible for the suitability of groundwater for irrigation are soil type, quality of groundwater and salt tolerance characteristics of the soil. Effects of dissolved salts on soils cause changes in soil structure, permeability and aeration. The values of hydrochemical parameters of groundwater used to determine irrigation suitability are %Na, SAR, RSC, EC, permeability index, Kelly's Index and magnesium hazard are summarized in Table 1. Knowledge of water quality for irrigation use is critical to understanding what management practices are necessary for sustainable productivity.

Sodium percent (%Na)

Sodium concentration is important in classifying irrigation water because it reacts with soils to reduce its permeability (Wilcox 1948). Sodium content is usually expressed in terms of percent sodium (%Na). The calculated value of percent sodium ranges from 16.3 to 80.9 % (mean 45.5 %) and 4.98 to 73.92 % (mean 41.4 %) in pre- and post-monsoon, respectively. The high Na% in pre-monsoon might be due to long residence time of water, dissolution of minerals from lithological composition and chemical fertilizers (Latha and Rao 2012). A maximum of 60 % sodium is allowed in the irrigated water, of which majority of samples (84 % in pre- and 92 % in post-) are permissible for irrigating the crop. The chemical quality of groundwater samples was studied from plots of sodium percent and electrical conductivity on the Wilcox diagram (Fig. 11). According to this plot, majority of the samples falls (42 % in pre- and 46 % in post-) in good to permissible category followed by doubtful to unsuitable category (Table 4). The crop yields are generally low in lands irrigated with waters belonging to doubtful to unsuitable category. This is probably due to the presence of excess sodium salts, which causes osmotic effect on soil–plant system. When the concentration of sodium is high in irrigation water, sodium ions tend to be adsorbed by clay particles, displacing Mg and Ca ions, this exchange process of Na in water for Ca and Mg in soil causing deflocculation (dispersion of clay particles) and impairment of tilth which reduces the permeability and eventually results in soil with poor internal drainage. Hence, air and water circulation is restricted during wet conditions and such soils are usually hard when dry (Saleh et al. 1999; Raju et al. 2009).

Salinity and alkalinity hazard

Higher EC in water creates a saline soil with low permeability and hard texture. On the basis of EC, irrigation water is classified into four salinity hazard zones (Table 8). Majority of the samples (56 % in pre- and 58 % in post-) belongs to high salinity hazard zone. The degree to which irrigation water tends to enter into cation exchange reactions in soil can be indicated by the sodium adsorption ratio. If water used for irrigation is high in sodium and low in calcium, the cation exchange complex may become saturated with sodium, which can destroy the soil structure owing to dispersion of clay particles. The SAR ranges 0.85–11.96 (mean 4.03) in pre- and 0.17–9.01 (mean 3.43) in post-monsoon. All the samples belong to excellent category in pre- and post-monsoon except one sample of Tiruchanuru village in pre-monsoon which falls in good category. A more detailed irrigation suitability analysis was made by plotting the USSL diagram (USSL 1954) in which EC is taken as salinity hazard and SAR is taken as alkalinity hazard. According to USSL plot, majority of the samples (56 % in pre- and 62 % in post-) fall in C3S1 category of high salinity and low alkalinity water which require proper drainage otherwise is dangerous for soil

Table 8 Classification of groundwater for different uses using various water quality indices

Parameter	Range	Classification	% Sample exceeding limit	
			Pre	Post
Classification for domestic use				
TDS (Davis and De Wiest 1966)	<500	Desirable for drinking	22	27
	500–1000	Permissible for drinking	37	44
	1000–3000	Useful for agriculture	41	29
	>3000	Unfit for drinking and irrigation	–	–
TDS (Freeze and Cherry 1979)	<1000	Fresh water	39	71
	1000–10,000	Brackish water	61	29
	10,000–100,000	Saline water	–	–
	>100,000	Brine water	–	–
Hardness (Sawyer and Mc Cartly 1967)	<75	Soft	–	–
	75–150	Slightly hard	–	2
	150–300	Moderately hard	15	9
	>300	Very hard	85	89
Classification for irrigation use				
Na %	0–20	Excellent	2	5
	20–40	Good	31	46
	40–60	Permissible	51	41
	60–80	Doubtful	14	8
	>80	Unsuitable	2	–
SAR	0–10	Excellent	98	100
	10–18	Good	2	–
	18–26	Fair	–	–
	>26	Poor	–	–
RSC	<1.25	Good	76	92
	1.25–2.5	Medium	7	2
	>2.5	Bad	17	6
EC	<250	Low salinity hazard (good)	3	–
	250–750	Medium salinity hazard (moderate)	14	21
	750–2250	High salinity hazard (poor)	56	58
	>2250	Very high salinity hazard (V. poor)	27	21
Kelly's ratio	<1	Suitable	65	77
	1–2	Marginal suitability	32	18
	>2	Unsuitable	3	5
Mg hazard	<50	Suitable for irrigation	75	33
	>50	Harmful for irrigation	25	67
PI	Class I	Max. permeability	93	92
	Class II	75 % of Max. permeability	7	8
	Class III	25 % of Max. permeability	–	–
Classification for industrial use				
LSI	Negative	Safe	98	100
	Positive	Unsafe	2	–
	Neutral	Safe	–	–
RSI	<5.5	Heavy scale	–	–
	5.5–6.2	Moderate scale	–	–
	6.2–6.8	Neutral water	–	–
	6.8–8.5	Aggressive water and corrosion is likely	2	
	>8.5	Very aggressive water and corrosion is possible	98	100
CR	<1	Safe zone	66	41
	>1	Unsafe zone	34	59
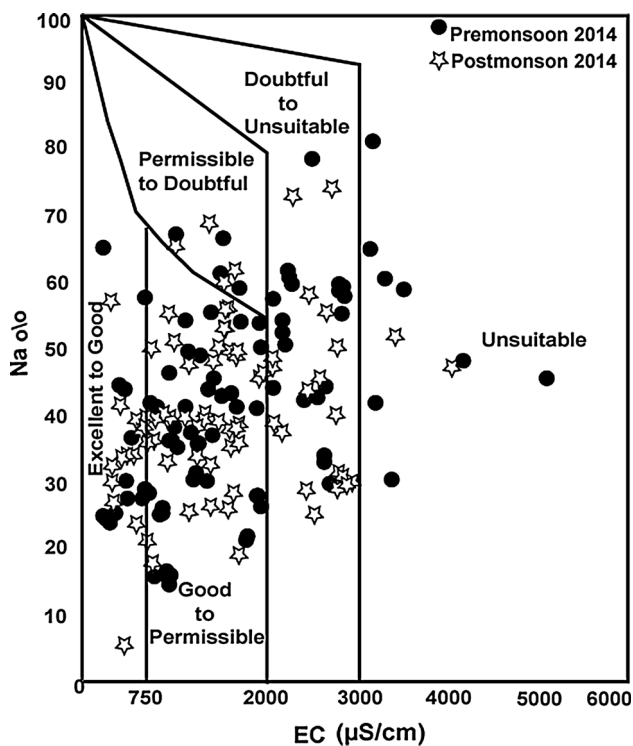
Fig. 11 Rating of groundwater on the basis of EC and %Na (after Wilcox 1948)

Fig. 12 Rating of groundwater in relation to salinity and sodium hazard (after USSL 1954)

(Fig. 12). Around 14 % in pre- and 21 % in post-monsoon samples belongs to C2S1 category shows medium salinity and low alkaline water which is suited for all plants but drainage should be good (Table 4). However, few (12 % in pre- and 9 % in post-) samples belong to C4S2 category implying very high salinity and medium alkalinity hazard water. This type of water is not suitable for irrigation under ordinary condition but may be used under very special circumstances and can be used only for plants with good salt tolerance (Rasouli et al. 2012).

Residual sodium carbonate

The residual sodium carbonate (RSC) was calculated to determine the hazardous effects of carbonate and bicarbonate on the quality of groundwater for irrigation purposes. When the excess carbonate (residual) concentration becomes too high, the carbonate combines with Ca and Mg to form scale which settles out of the water. The RSC ranges from −14.89 to 13.54 (mean −0.42) in pre- and from −14 to 8.14 (mean −3.10) in post-monsoon. A high value of RSC in water leads to an increase in the adsorption of sodium in soil (Eaton 1950). Based on the classification, it is observed that majority of the samples (76 % in pre- and 92 % in post-) are good for irrigation purpose. Only few samples (17 % in pre- and 6 % in post-) are categorized as bad water for agriculture use because of higher
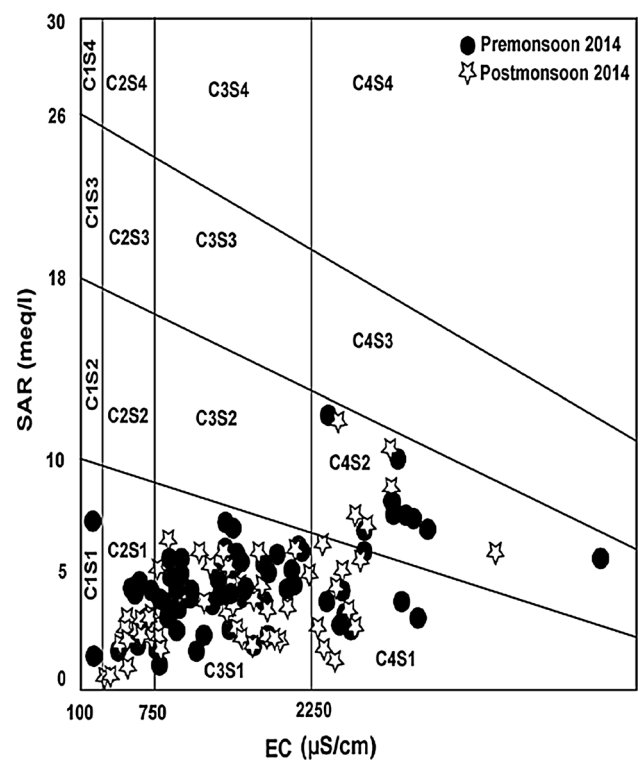
RSC (>2.5 meq/l) and result in formation of scales on agricultural field soil.

Permeability index

WHO uses a criterion for assessing the suitability of water for irrigation based on the permeability index. Doneen (1964) has developed the diagram based on the PI to classify irrigation waters for soils of medium permeability. Permeability index of the area varies 37.72–93.94 (mean 61.65) and 4.27–87.75 (mean 54.44) in pre- and post-monsoon, respectively. Based on the Doneen's chart classification (Fig. 13), 93 and 92 % of samples fall in class I (maximum permeability), and 7 and 8 % in class II (75 % of permeability) in pre- and post-monsoon, respectively. This implies that groundwater in the study area is of very good to suitable for irrigation uses in both season without noticeable variation.

Kelly's index

Sodium measured against Ca and Mg was considered by Kelly (1940) and Paliwal (1967) to calculate this parameter. Kelly's ratio >1 indicates an excess level of sodium in water which is unsuitable and <1 is suitable for irrigation uses. It ranges from 0.19 to 3.57 (mean 0.95) in pre- and

0.04–2.47 (mean 0.79) in post-monsoon season. Therefore, according to Kelly's ratio, majority of samples (65 % in pre- and 77 % in post-) are suitable for irrigation purpose, however, three locations (Tiruchanuru, Gajulamandyam and Molakandriga) suffer from the excess sodium in water which make water unsuitable for irrigation purpose (Table 8).

Magnesium hazard

Szabolcs and Darab (1964) had proposed a magnesium hazard for assessing the suitability of water quality for irrigation. Normally, a high level of Mg is caused by exchangeable Na in irrigated soils. An increased proportion of Mg relative to Ca increases sodication in soils which causes the dispersion of clay particles thus damages soil structure and decreases the relative hydraulic conductivity of soils as Mg behaves like Na (Rasouli et al. 2012). Thus, productivity in soils being irrigated with high Mg water found to be low. The yield of barley, wheat, maize and sugar beets are significantly reduced when the Mg/Ca ratio in the soil water is >1. In the present study, the MH is varied 15.86–81.18 (mean 42) in pre- and 26.80–86.13 (mean 57.37) in post-monsoon. If MH exceeds the value of 50, the water associated with such a value is considered to be harmful and hence is unsuitable for irrigation, because it adversely affects the crop yield. Around 25 and 67 % samples are above 50 in pre- and post-monsoon, respectively (Table 8) which

Fig. 13 Doneen permeability index plot (Doneen 1964)

reveals the unsuitability of irrigation water in the study area especially in post-monsoon probably due to ion exchange process.

Suitability for industrial purposes

Water is considered safe for industrial use if it is neither scale-forming nor scale-removing in nature. The water saturation index is used to assess whether water is precipitating out, dissolving or in equilibrium with calcium carbonate. Indices like LSI, RSI and CR has been calculated to understand groundwater industrial suitability (Table 1).

Langelier saturation index (LSI)

The Langelier saturation index (LSI) is used to determine the need for calcium carbonate precipitation scale control in water sources containing a TDS concentration of less than 10,000 mg/l (ASTM 1998). It is the difference between the water's measured pH (pHw) and the calculated pH when that water is in equilibrium with calcium carbonate (pHs). Scaling and corrosion are common process problems found in domestic and industrial applications where water or wastewaters are in contact with other materials. The scaling of metallic surfaces by calcium carbonate is related to the type of rocks in contact with groundwater. LSI is probably the most widely used indicator of cooling water scale potential. Positive LSI values suggest that water is supersaturated with respect to calcium carbonate and scale formation may occur; negative values suggest that water is undersaturated which has a tendency to remove existing calcium carbonate protective coatings in pipelines and equipment; neutral value indicate that solution is at equilibrium provides an indication of the degree of saturation of water with respect to calcium carbonate and it is neither scale forming nor scale removing (Tchobanoglous et al. 2003). One of the major problems of high calcium waters is the formation of scales in industrial boilers. The LSI value varies from −2.86 to 0.02 (mean −1.37) in pre- and from −3.29 to −0.60 (mean −1.56) in post-monsoon. The calculated results show all most all water samples have negative LSI values indicate that the solution is under-saturated with calcium carbonate (i.e. CaCO$_3$ dissolves) during both the seasons, except one location where CaCO$_3$ depositing in post-monsoon season (Table 8; Fig. 14a). The positive LSI values (Saini et al. 2006) indicate encrustation tendency due to CaCO$_3$ precipitation and hence need for moderate treatment of the water to prevent scaling. The increased levels of scaling can be harmful and can cause corrosion of water pipes and release of toxic metals to the water system.
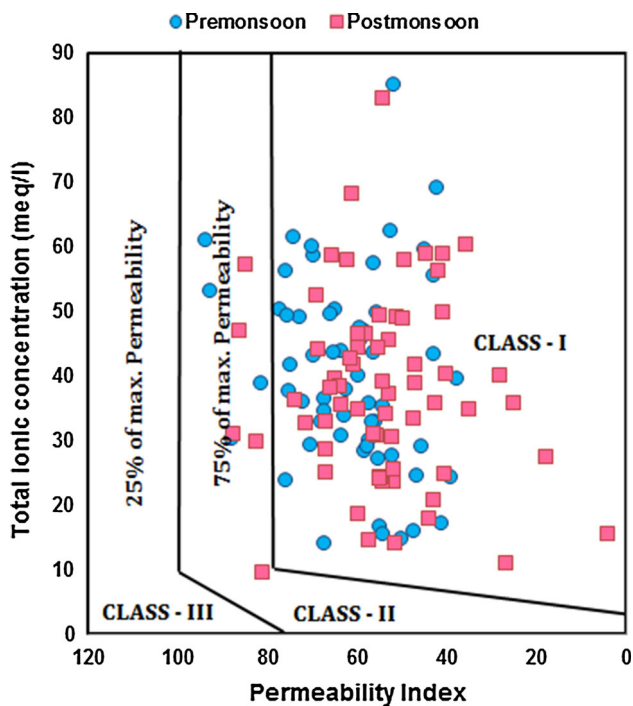
Ryznar stability index (RSI)

Ryznar (1944) proposed modification of the langelier index and it is an alternative method to the LSI for computing calcium carbonate scale formation. The criteria for interpreting the value of RSI are presented in the Table 8 and saturation index values of the groundwater samples are shown in Fig. 14b. According to RSI value, one sample in pre-monsoon season does not protect against corrosion and the rest of the samples were found to dissolve $CaCO_3$ (corrosive) which is in good agreement with the LSI results. The groundwater samples of the study area are considered very aggressive and substantial corrosion is possible. The RSI index value varies 8.22–12.15 (mean 9.94) in pre- and 9.13–13.10 (mean 10.36) in post-monsoon.

Corrosivity ratio

It defines the susceptibility of groundwater to corrosion and is expressed as ratio of alkaline earths to saline salts in groundwater. Ratio ranges 0.32–3.61 (mean 0.98) in pre- and 0.40–4.01 (mean 1.28) in post-monsoon. 66 and 41 % of samples in pre- and post-monsoon, respectively have a ratio of <1 and thus are safe to use whereas 34 and 59 % of groundwater samples in pre- and post-monsoon, respectively have ratio >1 indicating its unsuitability to use. The effect of corrosion is loss in the hydraulic capacity of pipes (Table 8). Groundwater which has CR values greater than 1, noncorrosive pipes (polyvinylchloride) should be used for water supply instead of metal pipes (Fig. 14c).

Conclusion

The groundwater of the study area are slightly alkaline in nature. Majority of the groundwater samples are moderately hard to very hard waters in both the seasons. In this groundwater system, Na (31 % in pre- and 23 % in post-) and Cl (39 % samples in pre- and 55 % in post-) are dominant ion that exceeds the threshold of dominance (i.e. meq/L >50 %). Ca/Mg molar ratio signifies calcite weathering as dominant source in pre- and dolomite weathering in post-monsoon for the ionic constituent in the groundwaters. The spatial distribution of hydrochemical facies shows that majority of the area is dominated by Na–Cl facies. Deep saline water upcoming and wastewater infiltration are the primary factors along with agricultural return flow and sea water intrusion which play momentous role in increasing salinity of the groundwater. According to Cl classification, brackish water is distributed all over the study area followed by the fresh brackish water. Piper diagram shows that majority (49 % in pre- and 70 % in
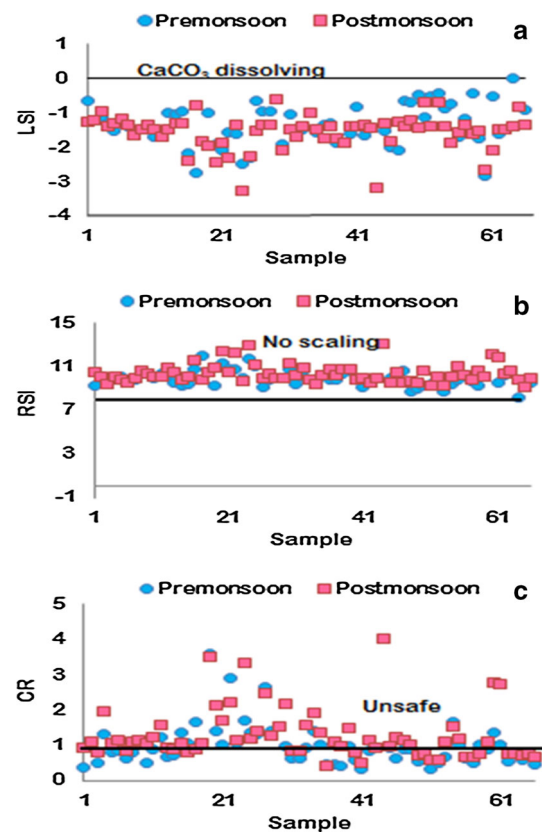

Fig. 14 Calcium carbonate precipitation potential for the groundwater

post-) of groundwater samples are of mixed type waters. Gibbs plot suggest chemical weathering of rock forming minerals and evaporation are dominant factors controlling the groundwater chemistry. Four components were inferred from the principal component analysis noticeably infers the water rock interaction and municipal wastewater discharge in PC1, agricultural fertilizer input in PC2, CO_3-pH relation in PC3, and fluoride and silica enrichment in PC4 as major factors in the groundwater system. AWQI calculation reveals that groundwater is less polluted with various natural and anthropogenic activities and majority of the samples are good to permissible for drinking purpose. The groundwater usage for domestic purposes has been limited due to the excessive permissible limit of TDS, TH, Na, HCO_3 and NO_3 in the study area. Wilcox diagram reveals the majority (42 % in pre- and 46 % in post-) of the samples are good to permissible for irrigation, though some samples are unsuitable as well. According to USSL diagram, majority of the samples (56 % in pre- and 62 % in post-) fall in C3S1 category of high salinity and low alkalinity water which require proper drainage otherwise it damages the irrigation crops. The low calcium carbonate saturation, as per the LSI and RSI, in the groundwaters of the study area is safe for metallic pipes, industrial boiler

and other related uses. CR demonstrating high rate of localized corrosion (59 % in pre- and 34 % in post-) may weaken the water pipes and may add toxic heavy metals to the groundwaters.

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