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Urbanisation impact of groundwater quality in Cuddalore District, East Coast of India

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The study area enjoyed artesian conditions few decades back but at present frequent failure of monsoon and over exploitation threatens the quantum of groundwater. Further, urbanization, extensive agricultural and industrial activities has deteriorated the quality of groundwater. The study was carried out to identify the sources responsible for the change in quality of groundwater as well as to evaluate the suitability of water to irrigation. Results of the study illustrates that the seasonal effect does not change the order of abundance of both cations and anions, but it changes the concentration of various ions present in the groundwater. Geochemical nature of water is determined using piper diagram wherein the results show the predominance of CaMgCl and $CaHCO_3$ types. Equiline diagrams were applied to evaluate the relationship between various ions present in these waters. Results of Gibb's diagram show that the mechanism of the chemical budget of this water is mainly due to rock-water interaction. The geochemical data was interpreted using Kelly's ratio, Magnesium ratio, SAR and Wilcox diagram and the results shows that about 70% of the groundwater is suitable for irrigation.

Key words: Groundwater, water quality, suitability to irrigation, hydrogeochemistry.

INTRODUCTION

In recent decades, groundwater exploitation has increased greatly, particularly for agricultural and domestic purposes, since many regions have only insufficient rainfall which is further worsened by the frequent failures and variability in the occurrence of monsoon. Due to rapid growth of population and the accelerated pace of industrialization, demand for fresh water has been increased tremendously. Rapid urbanization followed by overexploitation of groundwater and improper waste disposal, has affected the quantity and quality of groundwater. Groundwater quality is as important as the quantity. Poor quality of water adversely affects the plant growth and human health (Hem, 1991; Karanth, 1997). According to World Health Organization reports, about 80% of all the diseases in human beings are caused by water. Moreover, the restoration of the contaminated water to its natural composition is a difficult

task. Hence regular monitoring of water sources and halting the entry of pollutants into the water body are highly necessitated. Understanding its importance, numerous studies on groundwater quality with regard to drinking and irrigation purposes have been carried out in different parts of the country (Majumdar and Gupta, 2000; Khurshid et al., 2002; Sreedevi, 2004; Subba and John, 2005). In addition to the anthropogenic activities, water quality also depends upon the geochemical properties of groundwater. Chemical composition of groundwater directly relies on the chemistry of water in the recharge area as well as on various geochemical processes that are occurring in the subsurface. These geochemical processes accounts for the spatio-temporal variations in groundwater chemistry (Matthess, 1982). Groundwater composition evolves from rock-water interaction and internal mixing among different groundwater along-flow paths in the subsurface (Wallick and Toth, 1976; Toth, 1984).

Chemical reactions such as weathering, dissolution, precipitation, ion exchange and reverse ion-exchange

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processes commonly take place in the sub-surface. To identify and characterize the processes that are responsible for the chemical budget of groundwater, hydrogeochemical study finds an important place. Detailed study on the role played by the contaminants in soil and water were carried out by several authors (Kolpin et al., 1998; Srinivasa Rao et al., 1997; Subba et al., 1998; Elango et al., 2003; Barco et al., 2008). Study of chemical composition of major ions gains importance since it explains the origin of the ions in groundwater and the level of contamination by natural as well as anthropogenic sources (Woo et al., 2000; Gowd, 2005; Jalali, 2005; Rajmohan and Elango, 2005; Subba, 2006; Valdes et al., 2007). Ratios and diagrams like SAR, Kellys ratio, magnesium ratio, Gibb's and Wilcox diagram are used to find out the nature of the water and its suitability to irrigation. Many authors have used these diagrams to check whether the water is useful for irrigation (Gowd, 2005; Singh et al., 2008; Subramani et al., 2005).

In the present work, the groundwater samples belonging to the tertiary sandstone aquifer of Cuddalore district is being studied. This sandstone is separated from the upper alluvial formation by impervious clay layer and hence over exploitation of urbanisation process, industrial activities, agriculture activities and frequent failure of monsoon has resulted in the increase in demand and contamination of the aquifer. This potential aquifer is also facing threat from anthropogenic activities and its quality is deteriorating at an alarming threat. Under these circumstances a comprehensive hydro-geochemical study is necessary to assess, identify and evaluate the chemical processes that affect the groundwater quality of this study area. But it is still possible to protect our societies and economics from their severity by providing better information, improved planning and better adopted climate-resilient crops and infrastructure and also to make groundwater safe for human consumption, sustainable and the study area is accessible to all. In the present study, a detailed investigation was carried out with the objectives to identify hydrogeochemical processes and their relation with the groundwater quality.

Study area

The study area, viz., Cuddalore District lies on the East Coast of Southern India, bounded on the north, south and west by Villupuram, Nagapattinam and Perambalur districts and on the east by Bay of Bengal. River Vellar and River Coloroon flows in the southern boundary of this region. The district lies between 78° 42' and 80° 12' east latitude and 12° 27' 30" and 11°10' 45" north longitude. Major part of the region is covered by Archean Rock of the gneiss family, resting on the three great groups of sedimentary rocks belonging to different geological periods and overlying each other in regular succession from the coast on the east to the hills on the west. Most

part of the district is a flat plain sloping very gently to the sea on the east. Hills are found only on the southwestern border. River Gadilam rises in the eastern part of Tirukoilur district, flows through Cuddalore. The principal river of the region is the Pennar or the Ponnaiyar. The river flows across the boundary between Cuddalore and Villupuram taluks and empties itself into the Bay of Bengal. River Ponnaiyar and the Gadilam are connected by a river course called the Malattar, which serves to carry the surplus water of the former into the latter. It flows on the Southern boundary of Chidambaram taluk for 36 miles and joins the Bay of Bengal.

The district has many hazardous industries, which are classified as "Red" by Tamil Nadu Pollution Control Board. There are 551 industrial units in this area classed under highly polluting industries including sugar mills, distilleries, pesticides, fertilisers, thermal power plants, dye manufacturing, pharmaceuticals and tanneries. River Uppanar is a heavily polluted estuary situated in Cuddalore district which receives a bulk amount of industrial effluents from the industrial complex and municipal sewage from the Cuddalore old town. This indiscriminate effluent discharge leads to the frequent 'fish kills' in this estuary. The liquid waste from the aforementioned industrial complex discharged without standard treatments has caused heavy pollution of water and air in the surrounding industrial areas. The existing 25 units produce 6516 m^3/d of Industrial effluent and 380 m^3/d of sewage. When the new 28 units are completed, an additional 7835 m^3/d of trade effluent and 149 m^3/d of sewage will be produced. Keeping in view of the industrial and urbanization expansion of the region as well as the groundwater potential, the region is chosen as the study area of the present research work (Figure 1).

METHODOLOGY

Groundwater samples were collected using random sampling method from 36 representative bore wells during August 2008 and February 2009. The samples were collected and stored in new polyethylene bottles and preserved at 4°C. About one litre of water samples were collected for physical and chemical examinations from each location and half litre water samples were collected from the same locations in separate bottles and few drops of HNO$_3$ were added for the analysis of trace elements. Samples were analyzed within a short period of time so as to get more reliable analytical results. EC and pH of water samples were measured in the field immediately after the collection of samples using pH and electrical conductivity meters (Model: 5061 Pen EC meter). Before each measurement, pH meter (Model: Orion, 330) was calibrated with reference to buffer solution of pH=4 and 7. Total dissolved solids (TDS) were determined by evaporation method (Hem, 1991). Phosphate (PO$_4$) analyses of the water samples were carried out by reacting the phosphate ion with ammonium molybdate leading to the formation of coloured phosphoammoniummolybdate complex which could be easily estimated using spectrophotometer (Rowell, 1994). Sulphate was analysed using the turbidimetric method (Clesceri et al., 1998). Ca^{2+} and Mg^{2+} were determined titrimetrically using standard EDTA. Chloride was estimated by AgNO$_3$ titration (APHA, 1995). Sodium (Na) and potassium (K) were determined using flame photometer. Flouride (F) was determined using
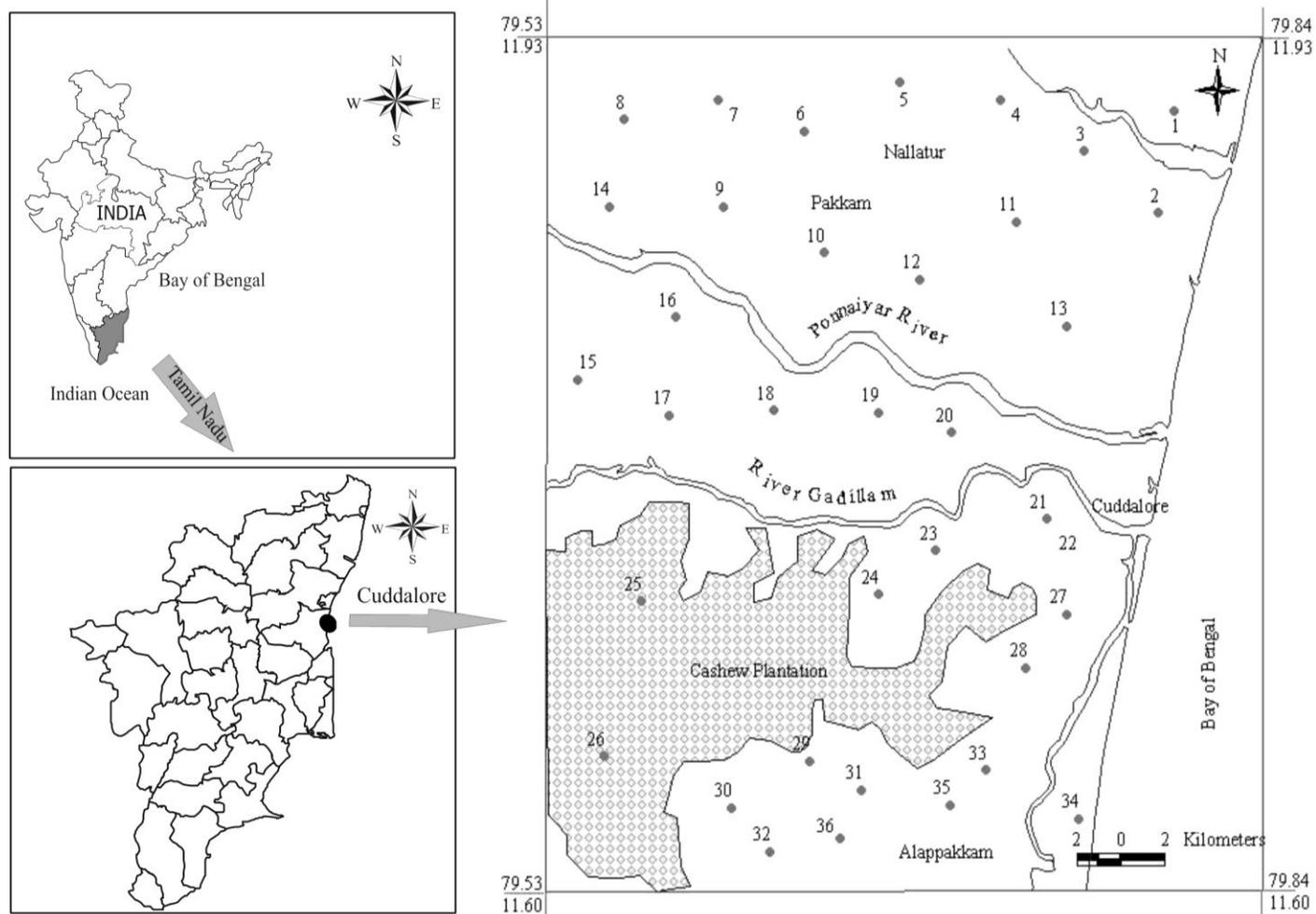
Figure 1. Sampling locations of the study area.

SPADNS method. Nitrate concentration is determined using UV–Visible spectrophotometer at a wavelength of 220nm (APHA, 1995). All concentrations are expressed in milligrams per liter (mg/L). High purity analytical reagents were used throughout the study, and chemical standards (Merck, Germany) for each element were prepared separately.

RESULTS AND DISCUSSION

Chemistry of groundwater

The analytical results of the chemical analysis and the statistical parameters such as minimum, maximum, mean and standard deviation are presented in Table 1.

The pH values of groundwater of the study area ranges from 6.5 to 7.4 which lies in the range of slightly acidic to alkaline. pH values of all stations are found to be well within the WHO prescribed limit of 6.5 to 8.5. During pre-monsoon, concentration of salinity (TDS) ranges from 210.21 to 2356.9 mg/L with a mean of 942.75 mg/L and

in the case of post-monsoon, TDS varies from 230 to 1920 with a mean of 751.1 mg/L. The groundwater classifications of Freeze and Cherry (1979) and Davis and DeWiest (1966) are presented in Tables 2 and 3, respectively.

As per the TDS classification (Fetter, 1990), nearly one-third and one-fifth of groundwater samples during pre-monsoon and post-monsoon periods belong to brackish type (TDS>1,000 mg/L). Results clearly demonstrates the seasonal effect in the groundwater samples as there is a considerable decrease in the concentration of ions during post-monsoon period due to the dilution of water. In the study area, concentration of cations of pre-monsoon water samples viz., Ca^{2+}, Mg^{2+}, Na^+, K^+ ions ranged from 20 to 240; 2.4 to 131.3; 11.5 to 437; 1.95 to 75.07 mg/L with a mean of 78.3, 33.5, 144.89 and 20.6 mg/L, respectively. The ionic concentrations (based on mmol/L) are 28.49, 20.06, 47.61 and 3.84%. The order of abundance is Na^+ > Ca^{2+} > Mg^{2+} > K^+. In the case of anions, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-

Table 1. Statistical parameters of analytical data.

Parameter (mg/L)	Pre-monsoon				Post-monsoon			
	Minimum	Maximum	Mean	S.D	Minimum	Maximum	Mean	S.D
pH	6.5	7.40	7.01	0.22	6.6	7.30	7.02	0.19
EC (µS/cm)	330	3700.00	1479.72	739.67	143.52	1198.08	468.68	215.37
TDS	210.21	2356.90	942.75	470.97	230	1920.00	751.08	345.14
Ca	20	240.00	78.33	43.95	17.8	168.00	68.68	33.29
Mg	2.432	131.33	33.54	23.25	5.8	112.80	27.60	18.80
Na	11.5	437.00	144.89	99.87	13.8	355.40	106.06	73.08
K	1.955	75.07	20.64	19.10	2.2	55.40	15.00	12.13
HCO_3	85.4	652.70	328.65	153.17	88.5	524.70	272.19	111.76
CO_3	0	0.00	0.00	0.00	0	0.00	0.00	0.00
SO_4	10.56	264.00	94.04	57.87	12.2	188.40	69.07	40.20
Cl	14.18	764.08	191.02	163.13	18.9	582.20	135.27	120.29
NO_3	0	111.60	26.12	28.10	1.8	88.40	19.17	21.03
PO_4	0.02	3.31	0.42	0.62	0.05	2.20	0.31	0.40
Fluoride	0.05	27.00	1.19	4.44	0.05	1.80	0.29	0.35
Silica	10.6	66.50	34.55	15.90	11.2	37.90	22.89	8.10

Table 2. Groundwater classifications after Freeze and Cherry (1979).

S/N	Type of water	TDS (range)	Number of samples percentage	Percentage of samples
1	Fresh water type	0-1000	23	64
2	Brackish water type	1000-10,000	13	36
3	Saline water type	10,000-100,000	…	…
4	Brine water type	>100,000	…	…

Table 3. Groundwater classifications after Davis and DeWiest (1966).

S/N	Suitability of water	TDS (range)	Number of samples percentage	Percentage of samples
1	Desirable for drinking	Up to 500	7	19.4
2	Permissible for drinking	500-1000	16	44.4
3	Useful for irrigation	Up to 3000	13	36.1
4	Unfit for drinking and irrigation	>3000	…	…

ranged from 85.4 to 652.7, 10.56 to 264, 14.18 to 794.08 and 0 to 111.6 mg/L with a mean of 328.65, 94.04, 191.02 and 26.12 mg/L, respectively. The ionic concentrations (based on mmol/L) are 40.32, 14.67, 40.89 and 4.12%. The order of abundance is $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$. In the case of post-monsoon, concentration of cations in the water samples viz., Ca^{2+}, Mg^{2+}, Na^+, K^+ ions ranged from 17.8 to 168; 5.8 to 112.8; 13.8 to 355.4; 2.2 to 55.4 mg/l with a mean of 68.7, 27.6, 106.1 and 27.6 mg/L, respectively. The ionic concentrations (based on mmol/L) are 32.1, 21.2, 43.1 and 3.6%. The order of abundance is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. In the case of anions, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- ranged from 88.5 to 524.7, 12.2 to 188.4, 18.9 to 582.2 and 1.8 to 88.4

mg/L with a mean of 272.2, 69.1, 135.3 and 19.2 mg/L, respectively. The ionic concentrations (based on mmol/L) are 44.51, 14.35, 38.06 and 3.08%. The order of abundance is $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$.

In general, higher concentration of ions in the groundwater occurs due to weathering of silicate rocks and from anthropogenic activities. Evaporation leads to the concentration of ions thereby increasing the chemical budget of groundwater. If the dominant process in the groundwater chemistry is evaporation, assuming that no precipitation of compound occurs, then the Na/Cl ratio would be unchanged (Jankowski and Acworth, 1997). In these cases, the plot of Na/Cl versus EC would give a horizontal line, which is an effective indicator of

concentration by evaporation and evapo-transpiration. In cases where the halite dissolution is responsible for the high concentration of sodium, the Na/Cl molar ratio should be approximately equal to 1, whereas a ratio greater than 1 is typically interpreted as Na released from a silicate weathering reaction (Meybeck, 1987). In the study area, the molar ratio of Na/Cl for groundwater samples of the study area generally ranges from 0.46 to 3.83 and 0.48 to 3.88 during pre-monsoon and postmonson periods, respectively. As most of the samples have Na/Cl molar ratio above 1 indicating that silicate weathering is the major process which is prevalent in this region. The excess of Na is attributed from silicate weathering (Stallard and Edmond, 1983).

The study of Ca/Mg ratio of groundwater suggests the nature of reaction mechanism that is predominant in these waters. The ratio Ca/Mg = 1 indicates dissolution of dolomite, whereas a higher ratio is indicative of greater calcite contribution (Maya and Loucks, 1995). Higher Ca/Mg molar ratio (>2) indicates the dissolution of silicate minerals, which contribute calcium and magnesium to groundwater. The results of premonsoon samples demonstrates nearly 47% of the samples have a ratio between 1 and 2 indicating the dissolution of calcite, while 31% of the samples are found to be >2 which indicates the effect of silicate minerals. In the case of post-monsoon, 44% of the samples have ratio between 1 and 2 while 30% of the samples are found to be >2 indicating that the seasonal effect does not have much influence over the weathering reaction occurring in the region.

Chemical characteristics of major ions

The plot of equilines (Figure 2) for the various ions shows the characteristics of the ions and their affinities. The plot of Na + K vs Cl during pre-monsoon shows that most of the values fall above and on the equiline suggesting that the alkali ions are balanced by the Chloride ions. Moreover, the ratio between the Na+K with respect to the total cation is 0.51 and the ratio between the Cl and total anion is also found to be 0.41 indicating that most of the alkali ions are balanced by the chlorides. Among the alkalis, Na is dominant and the concentration of potassium is apparently low. Relatively, the natural origin of potassium in water usually arises from the chemical weathering and subsequent dissolution of minerals of local igneous rocks and sedimentary rocks as well as silicate and clay minerals (Howari and Banat, 2002). The study area does not support the weathering and subsequent enrichment of potassium in these waters and hence its concentration is found to be about one tenth of the concentration of sodium. The low contribution of K may also be due to the greater resistance of K to weathering and its fixation in the formation of clay minerals (Sarin et al., 1989). The plot of Na + K vs Cl also

illustrates that some of the points lie above the equiline suggesting some excess alkali ions in this water. Ca+Mg vs HCO_3+SO_4 diagram reveals that the alkaline earth metal ions are balanced by the bicarbonate and sulphate anions and this plot also shows that some of the points lying below the 1:1 equiline indicating some excess HCO_3+SO_4 in these water. The excess alkali ions present in the water is compensated by these anions. The ratio of Na + K with TC is 0.51 and that of Ca + Mg with TC is 0.49 clearly showing the dominance of alkalis over the alkaline earth metal ions. The ratio of $HCO_3 + SO_4$ with TA is 0.51 and that of Cl with TA is 0.41 indicating the dominance of bicarbonate and sulphate ions among the anions. HCO_3^- ions in groundwater normally arises from the reaction of carbonate ions with water molecules releasing hydroxyl ions into the water, thereby increasing the pH of the water which becomes alkaline. Cl- ion concentration in groundwater normally arises from three sources viz., saline water entrapped in the sediments since the time of their deposition (connate water), solution of halite and related minerals in evaporate deposits and solution of dry fallout from the atmosphere especially in the arid region (Walker et al., 1991).

During post-monsoon, Na+K Vs Cl plot demonstrates that except two samples, all the samples fall above and on the equiline suggesting that though most of the alkali metal ions are balanced by chloride ions, still there exists some excess alkali ions in the groundwater. The plot of Ca+Mg vs HCO_3+SO_4 illustrates that most of the ions are located below the 1:1 equiline which suggests the excess bicarbonate and sulphate ions over that of the alkaline earth metal ions. The excess alkali ions present in the water is balanced by this excess bicarbonate and sulphate ions. Ratio of Na+K with TC is found to be 0.44 and Ca+Mg with TC ratio is observed to be 0.56 reflecting that there is an inversion of ratios during post-monsoon suggesting a clear dominance of alkaline earth metal ions over that of alkali ions. The ratio of HCO_3+SO_4 with TA is 0.63 and that of Cl with TA is 0.34 indicating the dominance of bicarbonate and sulphate ions over that of chloride ions in this region.

Reverse ion exchange study

In a groundwater reaction medium, the plot of Ca+Mg vs $HCO_3^-+SO_4$ is expected to fall close to the 1:1 equiline if the dissolution reactions of calcite, dolomite, gypsum are dominant in the system. Chemical reactions due to ion exchange tend to shift the points to the right of the equiline due to an excess of $SO_4 + HCO_3$ (Cerling et al., 1989; Fisher and Mulican, 1997). If there is a large excess of Ca+Mg over that of SO_4+HCO_3 ions, then the points will shift to the left side of the equiline due to the occurrence of reverse ion exchange reactions. In the study area, the plot of Ca+Mg vs $HCO_3^-+SO_4$ shows that some of the values fall above the equiline suggesting that
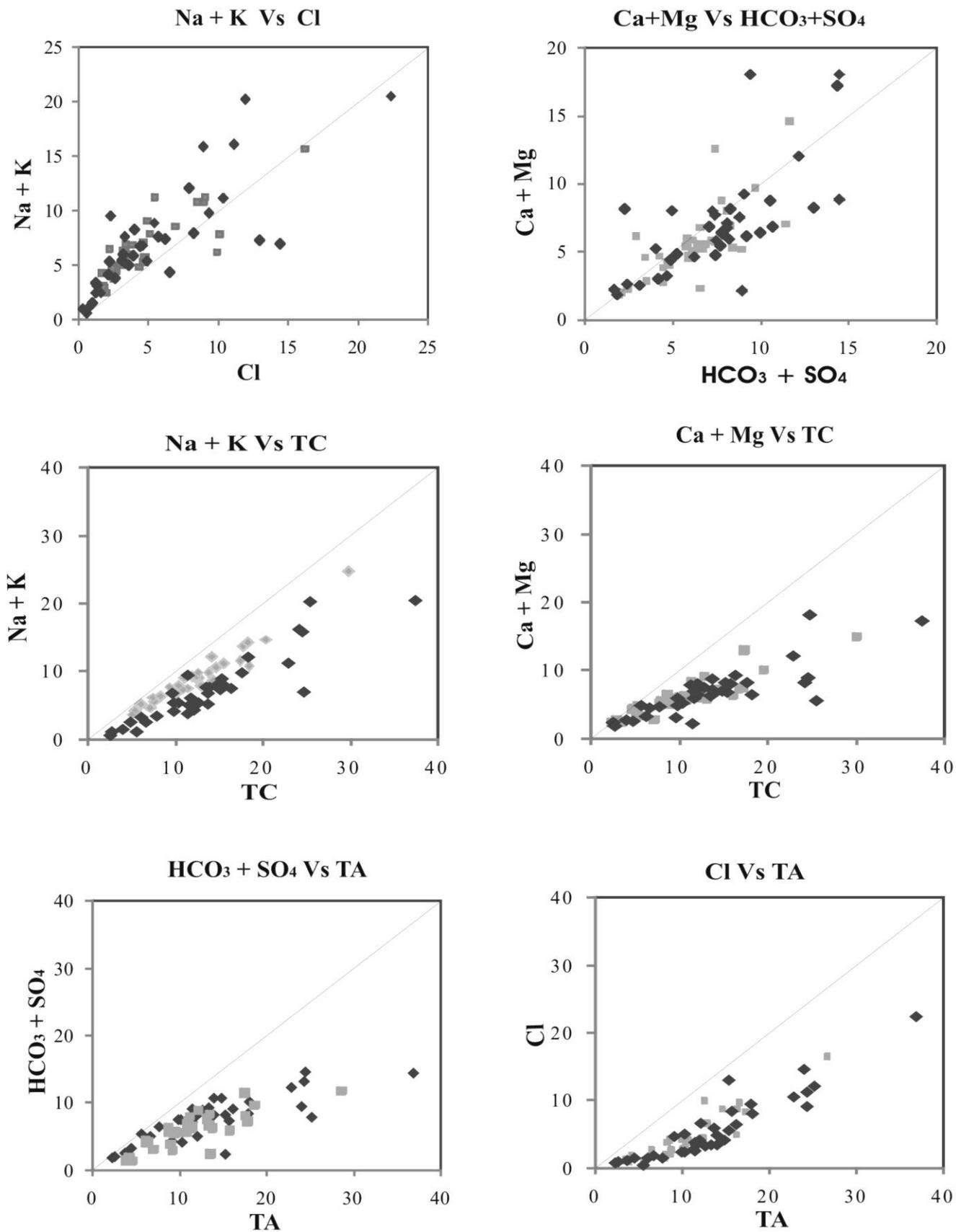
Figure 2. 1:1 Equiline diagrams.
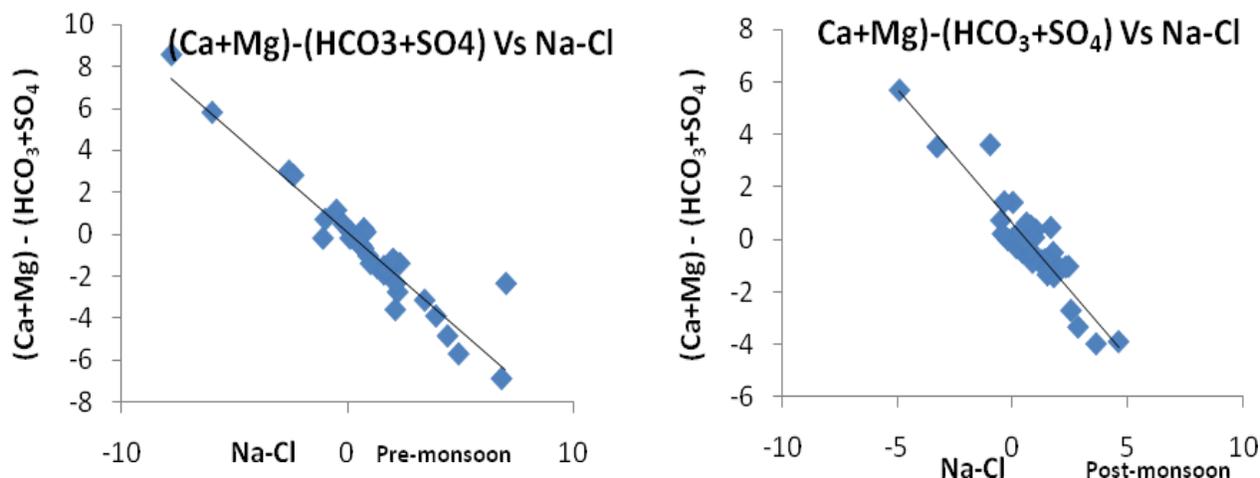
Figure 3. Diagrams depicting the reverse ion exchange chemistry.

Table 4. Statistical results of various ratios of groundwater samples.

Parameter	Pre-monsoon				Post-monsoon			
	Minimum	Maximum	Mean	S.D	Minimum	Maximum	Mean	S.D
CA1	-2.938	6.186	-0.331	1.270	-3.088	0.483	-0.579	0.715
CA2	-0.776	2.441	-0.062	0.600	0.234	2.338	0.785	0.414
Gibb's ratio 1	0.215	0.904	0.608	0.153	0.284	0.764	0.560	0.137
Gibb's ratio 2	0.160	0.903	0.446	0.168	0.160	0.836	0.410	0.165
Kelley's ratio	0.188	4.381	1.052	0.835	0.233	2.012	0.801	0.404
% Na	15.625	79.654	44.46	13.35	18.042	64.443	40.20	11.91
SAR	0.674	16.353	5.074	3.306	1.397	3.877	2.326	0.552
RSC	-9.800	5.200	-1.200	3.000	-7.556	2.895	-1.243	2.113
Magnesium ratio	3.704	69.136	40.84	13.40	7.852	64.642	39.32	11.62
Permeability index	38.719	105.326	67.39	13.06	40.589	98.237	65.77	10.99

the reverse ion exchange process has occurred. During pre-monsoon, the plot of Na–Cl versus (Ca+Mg)–(HCO$_3$+SO$_4$) (Figure 3) shows a slope of -0.94 which is nearly equal to -1.0 indicating that Ca, Mg and Na concentrations are interrelated through reverse ion exchange. Chloro alkaline indices (CAI 1 and CAI 2; Table 4) are negative that confirms the aforementioned fact. In the post-monsoon, plot of Na–Cl versus (Ca+Mg)–(HCO$_3$+ SO$_4$) (Figure 3) shows a slope of -1.02 which is nearly equal to -1.0 indicating that Ca, Mg and Na concentrations are interrelated through reverse ion exchange. Chloro alkaline index (CAI 1; Table 4) is negative confirms the aforementioned fact and the results fall in the same line as that of pre-monsoon. In the study area, the water table is generally high, which increases the contact surface area of the water, so there is an exchange of sodium in groundwater with calcium and magnesium in these soils.

Hydrochemical facies

The hydrochemical types of the groundwater were identified and characterized from the distribution of sample positions on the Piper diagram where concentration is assigned in % meq/L (Figure 4). The evolution of hydrochemical parameters of groundwater can be better understood by plotting the concentration of major cations and anions in the piper diagram. Piper diagram shows that most of the groundwater samples analysed fall in the field of mixed CaMgCl. During post-monsoon, most of the groundwater samples fall in the field of CaHCO$_3$ and mixed CaMgCl. The dominant anion of the groundwater changes from bicarbonate to sulphate to chloride with a corresponding increase in the TDS. From the plot, it is observed that alkalis (Na$^+$ and K$^+$) exceed the alkaline earths (Ca^{2+} and Mg^{2+}) and Cl$^-$ exceeds the other anions.
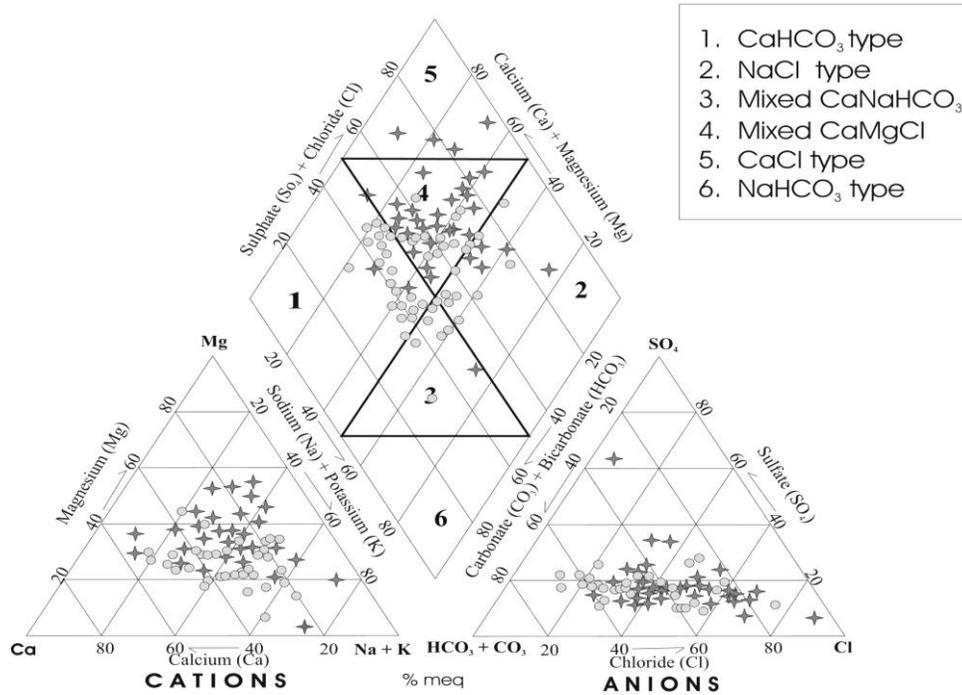
Figure 4. Piper diagram depicting hydrochemical facies.
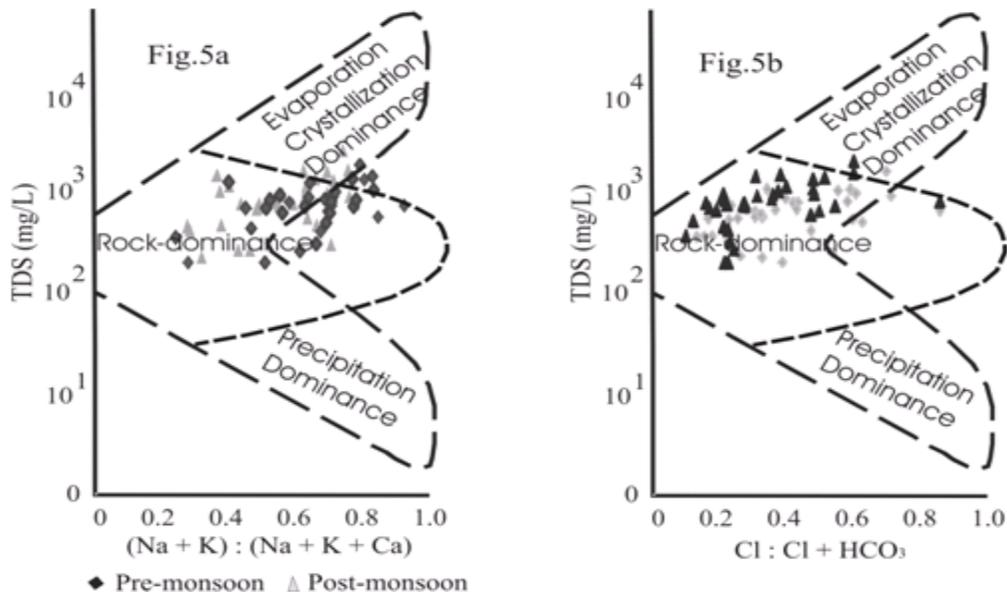
Figure 5. Diagram depicting the mechanism controlling groundwater quality.

Groundwater quality

Gibbs ratio

The mechanism of chemical reactions leading to the change in the composition of groundwater and source of the dissolved ions in the groundwater can be understood by Gibbs diagram (Gibbs, 1970). It is a plot of $(Na^++K^+)/(Na^++K^++Ca^{2+})$ vs TDS and $Cl^-/(Cl^-+HCO_3^-)$ vs TDS. Figure 5 shows that about 90% of the water samples during both pre-monsoon and post-monsoon falls in the rock dominance region. The Gibbs' diagrams

Wilcox Diagram
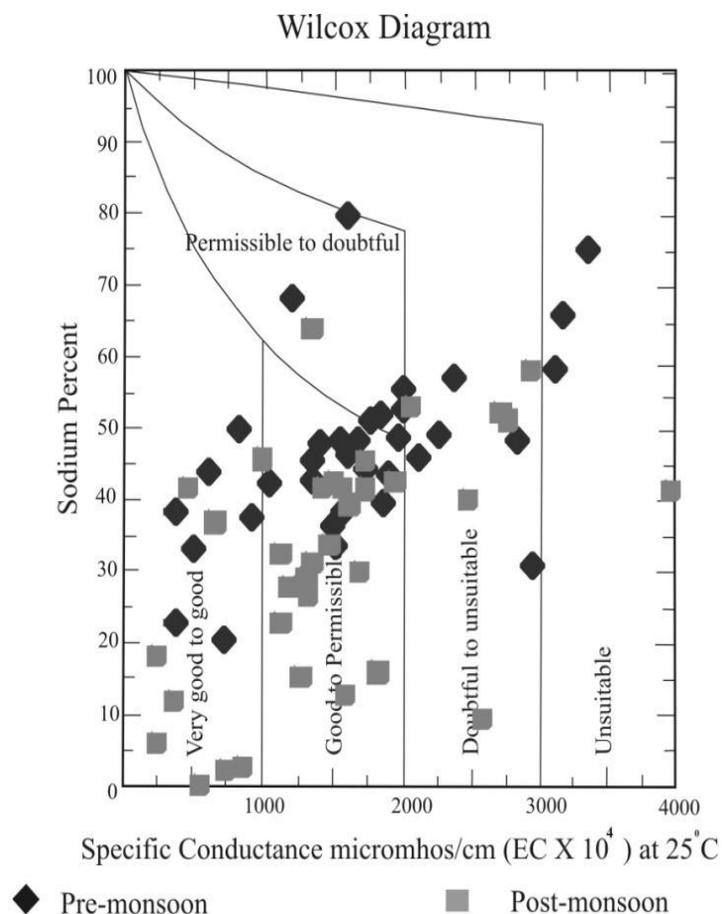
Figure 6. Specific conductance and percent sodium relation for rating irrigation water.

suggest that rock-water interaction in the groundwater leading to the chemical weathering of the rock forming minerals is the main process which contributes to the chemical budget of this water. It is interesting to note that both the cation and anion plots clearly illustrate the occurrence of weathering reaction in the study area. The variation of Gibb's ratio with premonsoon and post-monsoon is given in Table 4.

Kelley's ratio

The extent of suitability of groundwater for irrigation can easily be evaluated using Kelley's ratio. Sodium measured against calcium and magnesium was considered by Kelley (1951) for calculating Kelley's ratio. Groundwater having Kelley's ratio more than one is generally considered as unfit for irrigation. Kelley's ratio varies form 0.19 to 4.38 with a mean of 1.05 and for post-monsoon, the values ranges from 0.23 to 2.01 with a mean of 0.80 (Table 4). According to Kelley's ratio, during pre-monsoon, 33% of the samples are found to be unfit

for irrigation. In the case of post-monsoon, 36% of the samples have Kelley's ratio greater than one suggesting that only 64% of the samples are suitable for irrigation.

Magnesium ratio

The quantum of magnesium present in water would adversely affect the soil quality rendering it unfit for cultivation. Magnesium ratio with more than 50% is considered as harmful and unsuitable for irrigation. Szabolcs and Darab (1964) proposed magnesium hazard (MH) value for irrigation water is given as:

$$MH = Mg^{2+}/(Ca^{2+} + Mg^{2+}) * 100$$

Table 4 reveals that during pre-monsoon, 31% of samples showed magnesium ratio > 50% reflecting that 69% of the wells in the study area are suitable for irrigation. In the case of postmonsoon, only 22% of samples showed magnesium ratio greater than 50%

suggesting that the dilution effect due to precipitation increases the suitability of groundwater to irrigation.

Wilcox diagram

To evaluate the suitability of groundwater to irrigation, Wilcox (1955) used % sodium and specific conductance values of the groundwater. The salts, besides affecting the growth of the plants directly, also affect soil structure, permeability and aeration, which indirectly affect plant growth (Singh et al., 2008). Sodium-percentage determines the ratio of sodium to the total cations viz., sodium, potassium, calcium and magnesium. All concentration values are expressed in equivalents per million in Figure 6. Percent sodium is calculated as follows:

% Na = [(Na+K)*100]/(Ca+Mg+Na+K)]

Wilcox diagram (Figure 6) illustrates that during pre-monsoon, 62.2% of groundwater in the study area is found to be suitable for irrigation. The remaining 27.8% of the groundwater samples falls in the field of doubtful to unsuitable and unsuitable. In the case of post-monsoon, 68% of the groundwater samples falls into the good suitable region and the remaining 22% of the values falls into the field of doubtful to unsuitable region.

Sodium absorption ratio (SAR)

Sodium absorption ratio is used to evaluate the suitability of groundwater to irrigation as it gives a measure of alkali/sodium hazard to crops. Sodium hazard is also usually expressed in terms of the sodium adsorption ratio (SAR). SAR is determined from the ionic ratio of sodium to calcium and magnesium. The alkaline earth metal ions are important since they tend to counter the effects of sodium to calcium and magnesium. These ions are vital since they tend to counter the effects of sodium. The physical structure of the soil gets breakdown when water containing high SAR is used continuously. Adsorption of sodium occurs on the surface of the soil particles. On drying, the soil then becomes hard and compact and increasingly impervious to water penetration. SAR clearly indicates the degree to which irrigation water tends to enter into cation-exchange reactions in soil. SAR is a vital parameter for the determination of the suitability of irrigation since it is responsible for the sodium hazard of soil (Nagarajah et al., 1988). Sodium absorption ratio (SAR) which is given by the relation (Karanth, 1997):

$$SAR = Na^+/\{(Ca^{2+} + Mg^{2+})/2\}^{1/2}$$

All ionic concentrations are expressed in epm. Groundwater could be classified on the basis of sodium adsorption ratio (SAR) as excellent (10), Good (10-18).

Doubtful (18-26) and unsuitable (>26) (Sadashivaiah et al., 2008).

SAR concentration of pre-monsoon ranges from 0.674 to 16.353 with a mean of 5.074. During post-monsoon, SAR varies from 1.39 to 3.88 with a mean of 2.33. The results of SAR demonstrate that the groundwater of the study area is found to be good for irrigation.

Conclusions

In the present work, groundwater quality of the study area has been evaluated using various techniques and the temporal effect on the chemical budget of the water has also been evaluated and characterized. TDS values indicate that nearly one-third and one-fifth of groundwater samples during pre-monsoon and post-monsoon periods belong to brackish type. Results clearly demonstrates the seasonal effect in the groundwater samples as there is a considerable decrease in concentration of ions due to dilution of water during post-monsoon period. In general, the concentrations of cations and anions are high in the pre-monsoon ground water indicating excessive evaporation, silicate weathering and anthropogenic activities. Considerable decrease in concentration of cations and anions in the postmonsoon water samples indicates that the dilution factor predominates over the leaching factor. Na/Cl molar ratio above 1 indicates that silicate weathering is the major process prevalent in this region. Higher Ca/Mg molar ratio (>2) indicates the dissolution of silicate minerals, which contribute calcium and magnesium to groundwater.

This study has demonstrated the bonding affinities of various ions present in the water and the variation in the chemical composition of groundwater according to the water types. The study on the hydrochemical characteristics of the major ions in these waters shows that in premonsoon, the alkalis and the alkaline earth metals are found to be balanced by chlorides and bicarbonates and sulphates respectively. Based on Gibbs' ratios of water samples plotted against total dissolved solids, water samples from pre and post-monsoon seasons fall in the rock dominance area indicating the rock-water interaction predominates the water chemistry of these groundwaters.

Plot of Na–Cl versus (Ca + Mg)–(HCO3 + SO4) shows a slope of -0.94 which is nearly equal to -1.0 indicating that Ca, Mg and Na concentrations are interrelated through reverse ion exchange. Piper diagram shows that most of the groundwater samples analysed fall in the field of mixed CaMgCl. During post-monsoon, most of the groundwater samples fall in the field of CaHCO$_3$ and mixed CaMgCl. According to Kelley's and Magnesium ratio, about 60 to 70% of the groundwater samples are found to be suitable for irrigation. Wilcox diagram also substantiates and shows that about 62 and 68% of groundwater samples during pre-monsoon and post-monsoon are found to be suitable for irrigation.

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