Evaluation of the seasonal variation on the geochemical parameters and quality assessment of the groundwater in the proximity of River Cooum, Chennai, India

L. Giridharan · T. Venugopal · M. Jayaprakash

Abstract The seasonal variations of the chemical budget of ions were determined from the hydrochemical investigation of the groundwater. Though the effect of monsoon does not change the order of abundance of cations, but it does change the concentration of various ions and it is found that there was a considerable change in the case of all major ions. The unique characteristic of the ground water is the linear relationship among the principal ions. Hydrochemical characteristics of ions in the groundwater were studied using 1:1 equiline diagrams. The nature of the water samples were determined using the piper diagram. The correlation studies and R-mode factor analysis were carried out on the various groundwater parameters. The study of factor scores reveals the extent of influence of each factors on the overall water chemistry at each sampling stations. The trace metal concentration in the water was determined. The quality of the groundwater in the study area has been assessed using Percent sodium, SAR and Wilcox diagrams. The groundwater results of the premonsoon shows the dominance of excessive evaporation, silicate weathering and anthropogenic activities whereas in postmonsoon, dilution predominates over that of other factors.

Keywords Groundwater chemistry ·
Quality assessment · R-mode factor analysis ·
Seasonal variation

Introduction

Studies on the geochemical processes that control groundwater chemical composition in and around the river course may lead to improved understanding of hydrochemical systems in such areas. Such studies contribute to effective management and utilization of the groundwater resources. Exploitation of groundwater has increased greatly, particularly for agricultural purpose. Poor quality of water adversely affects the plant growth and human health. Urban rivers have been associated with water quality problems and the practice of discharging untreated domestic and industrial waste into the water course has emerged (Hall 1984). High population density in Chennai increases the pressure on the drainage system and sewage treatment plants. The existing system does not cope up with the heavy domestic discharge which leads to the present level of degradation of Cooum River. The problems are associated with the quantity, quality and temporal distribution of the waste produced effected by different sources and is aggravated further by routing these directly into the catchment areas of the river. Various

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authors were studied on the groundwater quality in different parts of the country with respect to drinking and irrigation purposes (Subba Rao et al. 1999; Majumdar and Gupta 2000; Khurshid et al. 2002; Sreedevi 2004; Subba Rao and John Devadas 2005).

The chemical alteration of the ground water depends on several factors, such as interaction with solid phases, residence time of ground water, seepage of polluted river water, mixing of groundwater with pockets of saline water and anthropogenic impacts (Stallord and Edmond 1983; Dethier 1988; Faure 1998; Umar and Absar 2003; Umar et. al. 2006). In this study, the ground water in the proximity of river Cooum is taken for geochemical analysis. In the upper part of the river, it was found that many agricultural activities are being carried out. Among various fertilizers, nitrate and phosphate fertilizers are found to be in use in the upper part of the river. Many nitrogenous fertilizers are converted into mobile nitrates by natural processes which contaminates the nearby water bodies more profusely (Freeze and Cherry 1979, Walter et al 1975). The influence of the heavily polluted Cooum river on the adjacent aquifer through percolation is highly expected. It has been observed that the ground water near the river is used by the residents settled adjacent to the bank of the river.

Hence in order to assess the level of pollution and to conduct a geochemical study in these waters, ground water samples are collected near the river at various locations. 23 sample stations were chosen for ground water samples (within 100 m from the river course) for analysis. In the present work, an attempt has been made on the evaluation of interrelated hydrogeochemical processes and the various factors that contribute to the chemistry of water. The role of various factors in groundwater can be understood better by applying multivariate analysis on the chemical parameters. Statistical methods of analysing hydrochemical data, such as principal component factor analysis, can be a useful tool in identifying the likely factors that cause the variations in hydrochemical composition. Factor analytical technique is successfully applied on the geochemical data of the groundwater by many other authors to sort out the hydrogeological and hydrogeochemical processes (Dawdy and Feth 1967; Hitchon et al. 1971; Lawrence and Upchurch 1983; Seyhan et al. 1985; Usunoff and Guzman (1989); Razack and Dazy 1990; Ruiz et al. 1990).

Factor scores were examined to identify the stations which are most affected and also the chemical variations in these waters due to seasonal changes. Ashley and Lloyd (1978) used the factor analytical tool to identify the hydrogeological process in the Santiago basin of Chile and the Derbyshire Dome of England, Briz-kishore and Murali(1992) have delineated the areas prone to salinity hazard in Chitravati watershed of India, Syed Munaf Ahmed et al. (2005) used the multivariate factor analytical technique to assess the water quality and source of contamination in a irrigation project at Al-Fadhli, Saudi Arabia.

It is to be mentioned that the groundwater samples were collected during September 2005, 9 months after the Sumatra-Andaman tsunami which occurred on 26 December 2004 and the seasonal variation of the groundwater Geochemistry near the river Cooum was carried out. The sea water intruded into the river Cooum up to 0.5 km during tsunami and the mouth of the river which was closed for most part of the year got opened and the polluted sewage water were flushed out but this phenomena was only a temporary effect and the river water got back into its originality within 3–4 months. The effect of tsunami in the present study which had been carried out well after the restoration period was expected to be negligible.

Study area

In this study, the groundwater in the vicinity of river Cooum is taken for Geochemical analysis (Fig. 1). River Cooum originates from Kesavaram dam, Kesavaram village at about 48 km west of Chennai. Though river Cooum originates from this dam, the excess water from the Cooum tank (79.82° latitude and 13.02° longitude) joins this course at about 8 km and this is considered as the head of the river Cooum. Throughout the river stretch in the upper part of the river, it was found that many agricultural activities are being carried out. The river receives a sizeable quantity of sewage from its neighborhood after it reaches Vanagaram near Chennai. It flows through Kancheepuram, Tiruvallur and Chennai districts for a distance of about 68 km and after flowing through the heart of the Chennai city, it enters into the Bay of Bengal. This river is almost stagnant and do not carry enough water except during rainy season (NE-monsoon). Chennai city receives
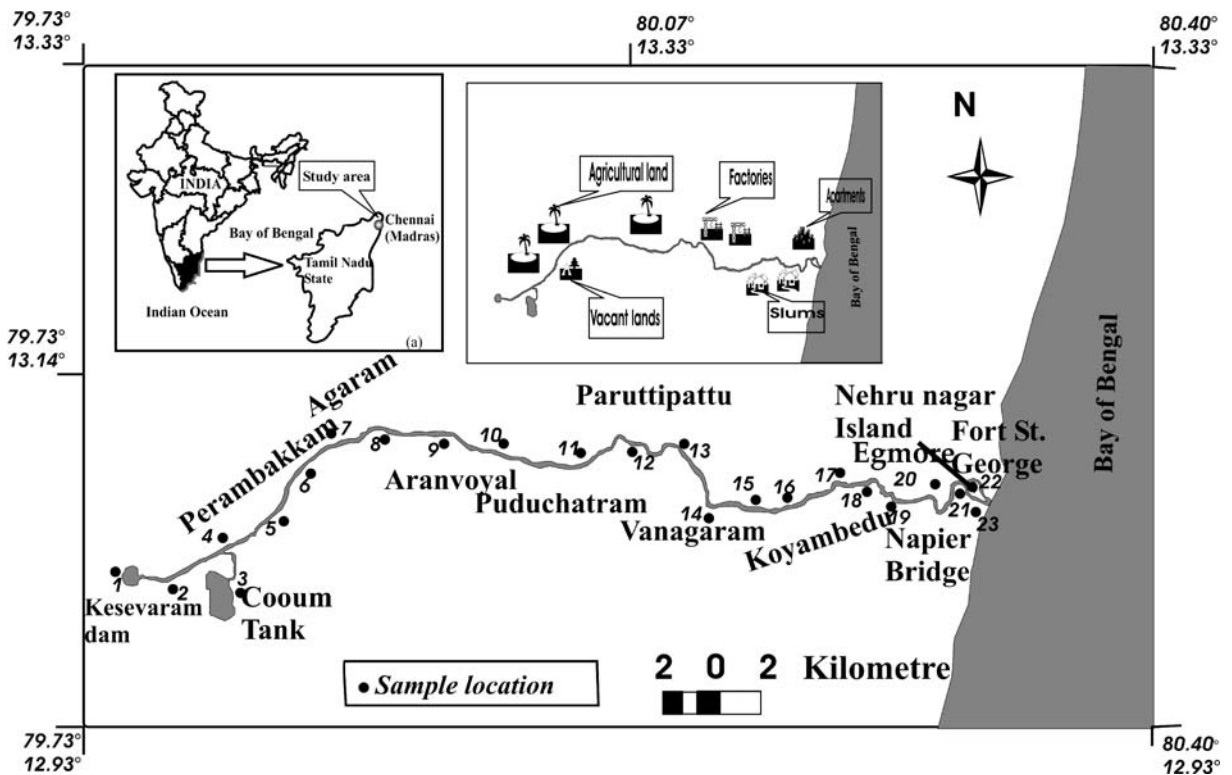
Fig. 1 Sample location and river Cooum map

bulk of its rainfall from this monsoon. The period October to December is referred to as Northeast Monsoon season over Tamil Nadu.

It has been observed that in the upper part of the river, there is no settlement along the bank of the river and hence, this part is not polluted by domestic effluents. But due to intense agricultural activities in the upper part of the river, the chance of pollution due to fertilizers and pesticides is highly expected. Now-a-days, fertilizers play a vital part in the crop growth. The bulk use of these fertilizers leaves behind unused wastes that are driven off by rain and enters into the river, which may percolate into the adjacent ground-water. Several studies have reported that the release of nitrates from agricultural activities contaminated the groundwaters (Mukherjee and Pandey 1994; Chandu et al 1995; Prasad 1998; Pacheco 2001). In the middle and lower stretch of the river, the domestic sewage water was directed into the river and it was found that the river is highly contaminated and appears as a sewage water stream.

Geology of the River Basin

The major part of the river Basin of Cooum is covered by alluvium soil with tertiary and Gondwana rocks at depth. The alluvium soil varies from 10 to 20 m thickness and is mostly granular. In the down stream area of the river Basin coastal sand predominates while the middle part and upper parts are dominated by sand and silt. Charnockites are also found in some part of the basins. The Geological succession of the basin is given as.

Group	Age	Lithology
Quaternary	Sub Recent	Soil, alluvium (Sand and silt)
Tertiary	Pleistocene	Black Clay
	Eocene to Pliocene	Sand Stone and Shale fossil ferrous
Mesozoic	Lower Cretaceous to Lower Jurassic	Brown Sand stone
		Silt, Stone grey and black shale
Azoic	Precambrian	Charnockite, Granite, Gneiss

Methodology

Ground water samples were collected during September 2005 and February 2006 representing pre- and post-monsoon seasons to evaluate the seasonal variations in chemical compositions. The water samples were collected from wells adjacent to the river at a depth of 10 to 20 ft. The samples were collected in new 1-l HDPE bottles pre-washed with dilute hydrochloric acid and rinsed three to four times with the water sample before filling it to capacity and then labelled accordingly. The samples were stored at a temperature below 4°C prior to analysis in the laboratory. For collection, preservation and analysis of the samples, the standard methods (Rainwater and Thatcher 1960; Brown et al. 1970; AWWA 1971; Hem 1985; APHA 1995) were followed. EC and pH of water samples were measured in the field immediately after the collection of the samples using pH and SEC meters. Before each measurement, the pH meter was calibrated with reference buffer solution of pH=4. Na^+ and K^+ were measured by using a flame photometer (Model: Systronics Flame Photometer 128). Silica content was determined by Molybdate Blue method using UV-Visible spectrophotometer. Total dissolved solids (TDS) were measured by evaporation and calculation methods (Hem 1991).

Ca^{2+} and Mg^{2+} were determined titrimetrically using standard EDTA. Chloride was estimated by $AgNO_3$ titration. Sulphate was analysed using the turbidimetric method (Clesceri et al. 1998). Nitrate, nitrite, phosphate, fluoride were analysed using UV-Visible spectrophotometer (Rowell 1994). Standard solutions for the above analysis were prepared from the respective salts of Analytical Reagent grade. Trace metals were determined by Graphite Furnace Atomic Absorption Spectrophotometer (Perkin-Elmer AAnalyst 700). Multi element Perkin-Elmer standard solutions were used for the estimation of trace metals.

Results and discussion

Chemistry of groundwater

The analytical results of the chemical analysis and the statistical parameters such as minimum, maximum, mean, standard deviation and t-test of groundwater are presented in Table 1 for both premonsoon and postmonsoon. The salient features of the hydro-chemistry of the ground water are as follows:

The pH values of groundwater is acidic ranging from 6.11 to 6.91 with an average value of 6.53 during premonsoon. However during the postmon-

Table 1 Summary statistics of the analytical data

Parameters (mg/l)	Premonsoon					Postmonsoon					T	R
	Mininum	Maxixmum	Mean	σ	Var	Minimum	Maximum	Mean	σ	Var		
pH	6.11	6.91	6.53	1.81	3.26	7.88	8.92	8.25	0.28	0.08	−5.84	S
EC (μS/cm)	1,250	4,870	2,640	1.13	1.28	1.31	3.06	1.94	0.53	0.28	3.68	S
TDS	798	3116	1,690	724.51	524,916.1	838	1,960	1,239.26	339.74	115,420.5	3.68	S
$Ca2+$	94	240	150.48	39.17	1535	48	152	109.13	25.82	667	5.61	S
$Mg2+$	3.6	100.8	32.52	25.08	629	19.2	115.2	56.16	22.07	487	−3.57	S
$Na+$	52.2	786.29	276.91	199.73	39892	40.15	412	200.78	106.23	11,285	2.05	N
$K+$	1.4	74.36	21.45	18.88	356	1.7	23.6	7.04	6.27	39	4.14	S
HCO_3^-	128.9	732	365.18	178.41	31,829	97.6	549	238.63	92.6	8,575	3.60	S
SO_4^{2-}	188.7	262.8	230.01	17.69	313	13.16	186	119.92	47.97	2,301	10.55	S
Cl^-	120	1130	444.93	300.33	90198	232	790	390.35	138.27	19,119	1.14	N
F-	0.48	2.5	1.2	0.56	0.31	0.11	0.68	0.32	0.17	0.03	6.89	S
NO_3^-	0.15	59.26	12.6	16.34	267	2	22.38	10	5.84	34	0.73	N
NO_2^-	0.01	9.65	0.91	2.31	5.3	0.12	5.11	1.52	1.47	2.2	-1.34	N
PO_4^{3-}	0.73	10.34	3.16	3.28	11	0.01	0.64	0.23	0.19	0.04	4.32	S
$SiO2$	24.8	29.8	28.36	1.26	1.6	15.20	28.60	24.96	3.38	11	4.21	S

t stands for *t*-test critical two-tail – 2.07 σ – standard deviation Var – variance

S Significant, *N* non-significant, *R* result

soon, the pH of groundwater was found to be alkaline ranging from 7.88 to 8.92 with a mean of 8.25. Concentration of salinity (TDS) ranges from 798 to 3,116 mg/l in premonsoon and 838 to 1,960 mg/l in postmonsoon. There is a considerable amount of dilution of concentration of ions during the postmonsoon due to precipitation. Higher concentration of TDS is observed in the groundwater near the lower part of the river basin which is near to the Bay of Bengal ocean. The intrusion of sea water into the ground water would have increased the salinity of the adjacent aquifers. As per the TDS classification (Fetter 1990) most of the groundwater samples collected during the premonsoon and postmonsoon periods belong to brackish type (TDS>1,000 mg/l). The groundwater classifications of Freeze and Cherry, 1979 and Davis and DeWiest, 1966 are presented in Tables 2 and 3. During premonsoon, the concentration of cations Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions ranged from 94 to 240; 3.6 to 100.8; 52.2 to 786.29 and 1.4 to 74.36 mg/l with a mean of 150.48, 32.52, 276.91 and 21.45 respectively. The ionic concentrations (based on mmol/l) are 21.24, 7.57, 68.13 and 3.07%. The order of abundance is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. But during postmonsoon the concentration of cations Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions ranged from 48 to 152; 19.2 to 115.2; 40.19 to 412 and 1.7 to 23.6 mg/l with a mean of 109.13, 56.16, 200.78 and 7.41 mg/l respectively. The ionic concentrations (based on mmol/l) are 19.52, 16.56, 62.62 and 1.29%. The order of abundance is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. Though the effect of monsoon does not change the order of abundance of cations, but it does change the concentration of various ions and it is found that there is a considerable change in the case of all major ions. Similarly in the case of anions during premonsoon, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-

Table 2 Groundwater classification (Freeze and Cherry, 1979)

Sl. no.	Type of water	TDS (range)	%	
			Premonsoon	Postmonsoon
1	Fresh water type	0–1,000	17	35
2	Brackish Water type	1,000–10,000	83	65
3	Saline water type	10,000–100,000	0	0
4	Brine water type	>100,000	0	0

Table 3 Groundwater classification (Davis and DeWiest, 1966)

Sl. no.	TDS (range)	Suitability of water	%	
			Premonsoon	Postmonsoon
1	Up to 500	Desirable for Drinking	0	0
2	500–1,000	Permissible for drinking	17	35
3	Upto 3,000	Useful for irrigation	78	65
4	Above 3,000	Unfit for drinking and irrigation	5	0

ranges from 128.9 to732, 188.7 to 262.8, 120 to 1,130 and 0.15 to 59.26 mg/l with a mean of 365.18, 230.01, 444.93 and 12.6 mg/l respectively. The ionic concentrations (based on mmol/l) are 28.45, 10.94, 59.65 and 0.97%. The order of abundance is $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$. During postmonsoon, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, ranged from 97.6 to 549, 13.16 to186, 232 to 790, 2.0 to 22.38 mg/l with a mean of 238.63, 119.92, 390.35, 10.0 respectively. The ionic concentrations (based on mmol/l) are 23.95, 7.64, 67.42 and 0.99%. The order of abundance is $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$.

The seasonal variation of constituents in the groundwater of the study area are shown in Fig. 2. As far as anions are concerned, the seasonal effect on the concentration of ions is significant except that of nitrates. Fluorides varied from 0.48 to 2.5 mg/l with a mean of 1.20 mg/l and during postmonsoon it varied from 0.02 to 0.68 with a mean of 0.32 mg/l. Hence the demonstration of monsoon over the dilution of the concentration of fluorides is obvious. The variation in the range of silica concentration during both the seasons is only narrow. During premonsoon, it varied from 25.8 to 29.8 mg/l with a mean of 28.36 mg/l and in postmonsoon, it ranges from 15.2 to 28.6 with a mean of 24.96 mg/l. T-test was performed to determine the effect of monsoon on the chemical constituents/variables present in the groundwater. The results show that Na^+, Cl^-, NO_2^- and NO_3^- are found to be non-significant with respect to seasonal changes. Standard deviation results show that the TDS values exhibit high variability in both pre and postmonsoon periods. The cause of this variability may be due to the difference in the chemical constituents of the groundwater near the fresh water river (upper course)
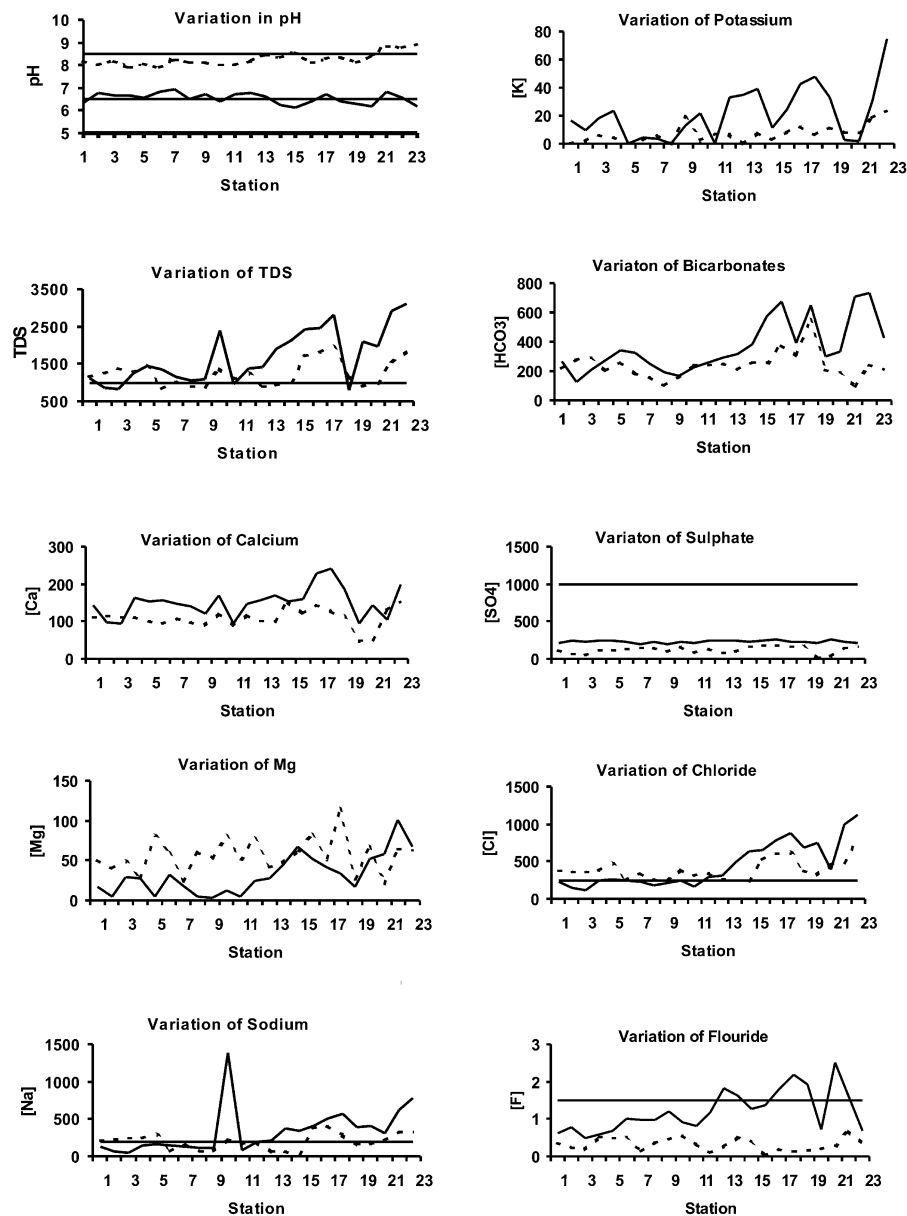
Fig. 2 Seasonal variation of constituents

and the groundwater near the saline estuarine water (lower course). The above fact is substantiated by the high standard deviation values of the sodium and chloride ions.

Chemical characteristics of major ions

The plot of equilines (Fig. 3a–l) for both the seasons show a marked difference. In premonsoon, the plot of Na + K vs Cl show that most of the values fall on the equiline and suggest that the alkali is balanced by the

Chloride ions and also the ratio between the Na + K and total cation is 0.54 and the ratio between the Cl and total anion is also found to be 0.54 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. The natural source of potassium in water usually originates from the chemical weathering and subsequent dissolution of minerals of local igneous rocks such as feldspars (orthoclase and microcline), mica and sedimentary rocks as well as silicate and clay minerals (Howari
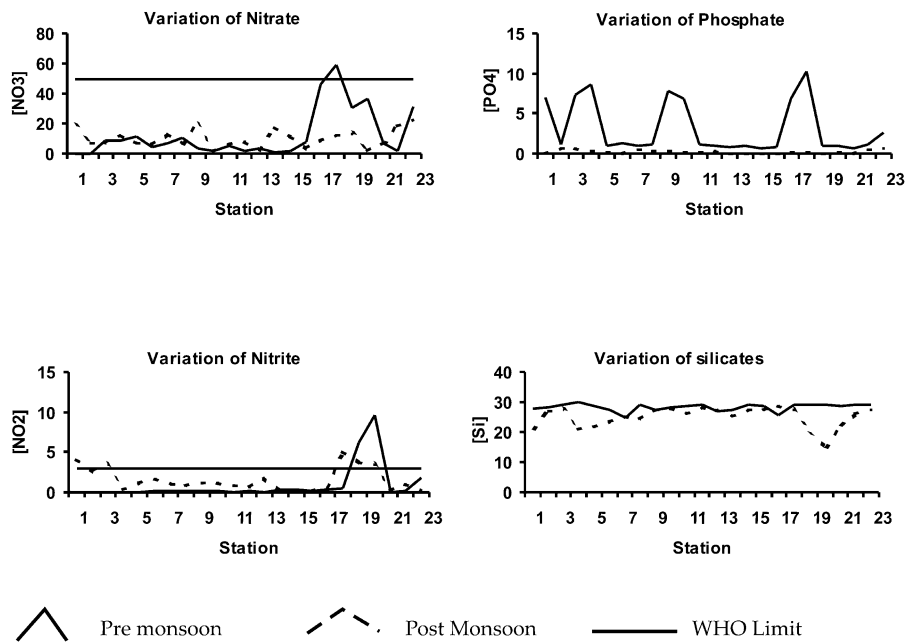
Fig. 2 (continued)

and Banat 2002). Since these minerals are not abundant in the study area, potassium concentration in these waters is only 1/10th of the concentration of Sodium and 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 high ratio of Na + K vs Z^+ suggest that silicate weathering may to some extent contribute to the total cation. And also it is seen that the Na + K and Cl values increases gradually from west to east in which the river flows. It may be noted that in the down stream area, the value of alkali and Chloride ions are high indicating that the contribution from the Saline water intrusion anthropogenic activities such as the effluents from industries and the domestic sewage directed into the river would have increased the concentration of these ions in the river water. Moreover the stagnancy of the water in the river increases the residence time of these ions facilitating high percolation into the adjoining aquifers. The excess of Ca + Mg over the HCO_3 suggest that bicarbonate alone could not balance these cations and the remaining alkaline earth metal ions would have been balanced by sulphate anions. Moreover, In comparison with the ratio of 0.25 for HCO_3 vs TA, the ratio of SO_4 vs TA is 0.19 reflecting that the contribution of both anions is almost equal.

In Postmonsoon, the plot of Na + K Vs Cl shows that most of the points are below 1:1 lines suggesting that there is excess of Cl over Na + K. And also the plot of Ca + Mg vs HCO_3 + SO_4 shows that most of the points lie above the 1:1 equiline indicating that the excess chloride ions are balanced by the alkaline earth metal ions. The ratio of Na + K with TC is 0.45 and that of Ca + Mg with TC is 0.55 which indicates that there is an inversion of ratio during postmonsoon clearly showing the dominance of alkaline earth metal ions over the alkalis. As in premonsoon, the concentration of sodium predominates over that of potassium. The ratio of HCO_3 + SO_4 with TA is 0.36 and that of Cl with TA is 0.63 indicating that there is an increase in the concentration of chloride ions in postmonsoon. Cl^- ion concentration in groundwater normally arises from three sources viz., ancient seawater entrapped sediments, dissolution 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). The high concentration of chloride in the study area does not seem to arise from the above factors but it may be caused by anthropogenic activities and may also from the leaching of saline residues of the soil by the action of rainwater during postmonsoon (Subba Rao, 2002).

Fig. 3 1:1 equiline diagrams
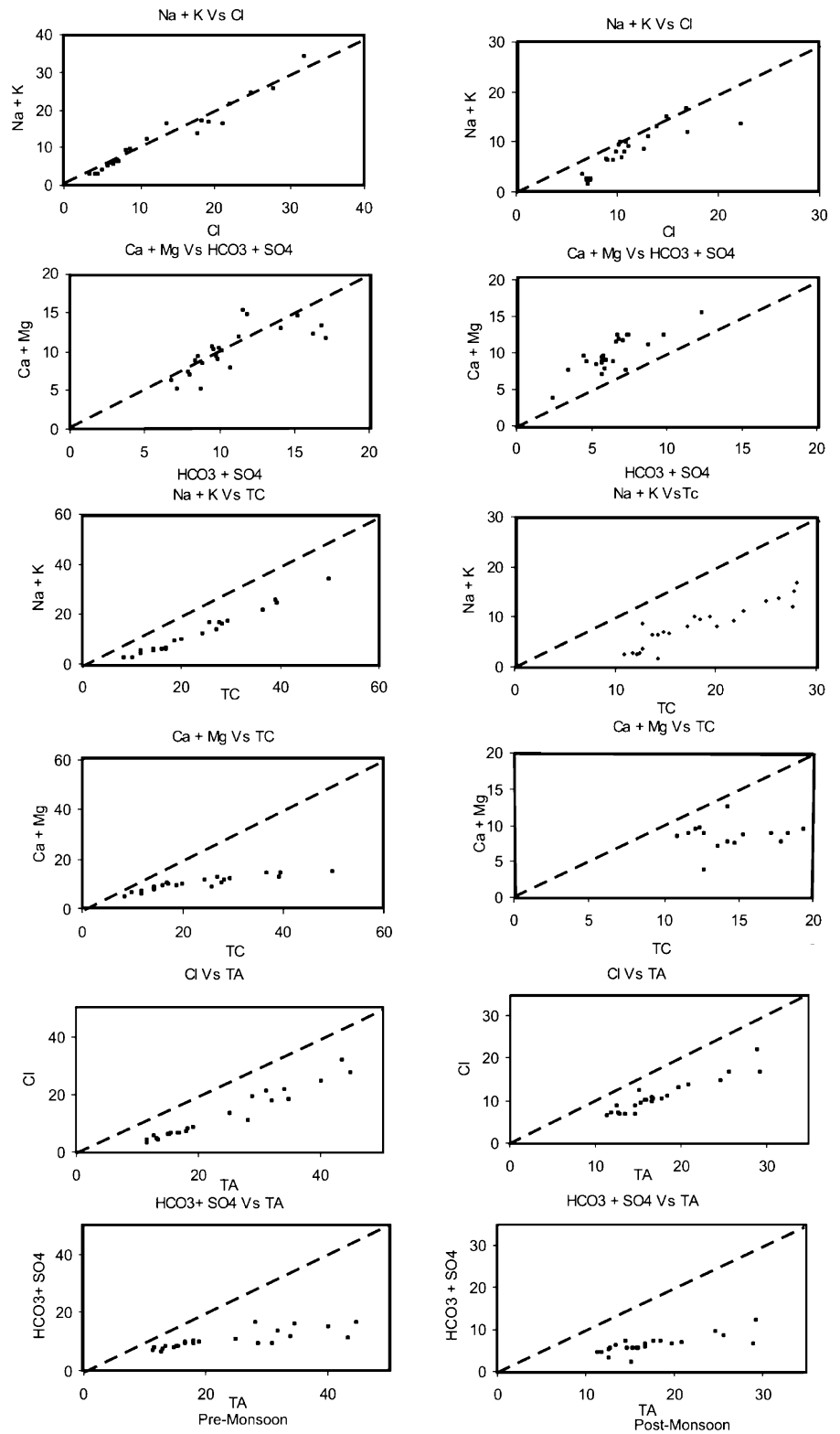
Hydrochemical facies

The evolution of hydrochemical parameters of groundwater can be understood by plotting the concentration of major cations and anions in the piper diagram Fig. 4. The plot shows that most of the groundwater samples analysed during the premonsoon and postmonsoon fall in the field of NaCl, mixed CaMgCl types and NaCl, mixed CaMgCl, CaCl types of water respectively. 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.

Trace metals in groundwater

Seasonal variation of trace metals (Cu, Co, Zn, Fe, Pb and Cr) was evaluated in the groundwater samples of the study area. The Cu values ranging from 0.019 to 0.098 mg/l with an average value of 0.055 mg/l during premonsoon. However during the postmonsoon, the values ranging from 0.004 to 0.054 with a mean of 0.031. Both in pre and postmonsoon, the concentration of Cu is well within the WHO allowed limit of 2 mg/l. The concentration of cobalt during premonsoon ranges from 0.009 to 0.090 mg/l with a mean of 0.032 and the postmonsoon shows 0.004 to 0.021 with a mean of 0.010 mg/l. Zinc ranges from 0.004 to 0.087 with a mean of 0.037 mg/l during premonsoon and postmonsoon demonstrates 0.001 to 0.074 with a mean of 0.022 mg/l. The concentration of Zinc in these waters during both the seasons has not crossed the prescribed limit of 3 mg/l. In the case of iron, the concentration of Fe in many of the stations is higher than the WHO permitted limit of 0.3 mg/l. The average value during pre and postmonsoon is 0.809 and 0.438 mg/l respectively. Pb values during premonsoon is ranging from 0.08 to 0.567 with a mean of 0.284 mg/l and the values of postmonsoon ranges from 0.032 to 0.658 with a mean of 0.275. Lead is usually found in low concentration in natural waters because Pb containing minerals are less soluble in water. Concentration of lead in natural water increases mainly through anthropogenic activities Almost all stations show the concentration of Pb higher than the WHO allowed limit of 0.01 mg/l which may create health hazards. The value of Cr ranges from 0.01 to 0.09 with an average value of 0.056 during premonsoon and 0.012 to 0.254 with an average value of 0.064 during postmonsoon. Many stations shows higher value than the prescribed limit of 0.05 mg/l, which is mainly attributed by the anthropogenic activities. Since the concentration of Cr in the study area is found to be high, it may create some health problems.

Fig. 4 Piper diagram depicting hydrochemical facies
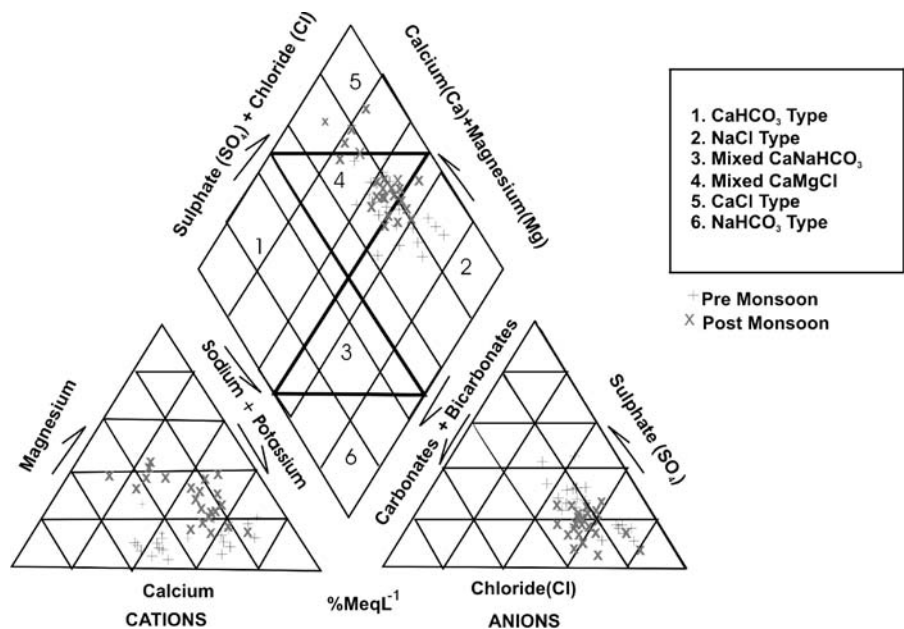
Groundwater quality

In the study area, the assessment of groundwater quality was carried out in order to identify its suitability to drinking and irrigation purposes. The major factors which decides the quality of the groundwater in the study area is agricultural activities near the upper stretch of the river, rock-water interaction, anthropogenic activities at the middle part of the river and saline water intrusion near the confluence point. Except at few stations, the pH (6.1–8.9) of the groundwater samples during pre- and post-monsoons is within the safe limits (6.5–8.5) prescribed for drinking water by ISI (1983) and WHO (1984). Except at few stations, the concentration of TDS (798 to 3,116 mg/l) is more than the recommended limit of 1000 mg/l allowed (ISI 1983; WHO 1984) in all groundwater samples during both the seasons which may cause gastrointestinal irritation to the consumers. The concentration of Na in both the pre and postmonsoon periods shows high values in groundwaters near the downstream. This excess sodium in water is unsuitable for patients suffering from hypertension or congenial heart diseases and also from kidney problems. In order to assess the groundwater suitability to irrigation Percent sodium, SAR and Wilcox diagrams (Fig. 5) are evaluated. Wilcox (1955) used % sodium and specific conductance in evaluating the suitability of groundwater to irrigation. Sodium-percentage determines the ratio of sodium to the total cations viz., sodium, potassium, calcium and magnesium. The results shows that the groundwater near the upstream is good for irrigation and the contamination is found to be high near the downstream. During premonsoon, 39% of the groundwater values falls under the unsuitable region; 17% falls in the region of doubtful to unsuitable; 44% shows good to permissible for irrigation. Postmonsoon results shows 52% of the groundwater values illustrate good to permissible; 16% falls in the region of doubtful to unsuitable; 12% of the groundwater are unsuitable for irrigation. This may be due to the increased anthropogenic activities near the downstream owing to intense settlements along the bank of the river, directing the domestic sewage into the river and saline water intrusion.

Another important tool commonly used to assess the degree of suitability of water to irrigation is Sodium Absorption Ratio (SAR). It has been found that the magnitude of absorption of Na^+ by soils has a direct relationship with SAR. Higher concentration of Na^+ in soils saturates the ion-exchange complex with Ca^{2+} resulting in deflocculation and impermeability and cultivation in such soils becomes very difficult (Subba Rao 2006). The SAR concentration ranges from 1.58 to 36.21 with a mean of 8.00 for premonsoon and from 0.91 to 9.83 with a mean of 5.12 in postmonsoon. The results shows that 11 samples in pre monsoon and 10 samples in post-monsoon shows SAR values greater than 6. Groundwater containing SAR values greater than 6 have higher concentration of Na^+ relative to the concentration of Ca^{2+} reflecting that these water is not suitable for irrigation.

Correlation studies

The correlation coefficient values exhibiting + 1 or -1 between the variables reveals that there exist strong correlation and the value at zero indicates no relationship between them. In general, the Geochemical parameters showing correlation coefficient >0.7 are considered to be strongly correlated whereas value between 0.5 and 0.7 shows moderate correlation. In this study, the relationship between various elements has been studied. The correlation matrix (Tables 4 and 5) shows high values of positive and negative correlations among various elements. The chemical budget of ions in the groundwater of the study area depends on the factors such as anthropogenic activities, rock-water interactions, river water seepage and saline water intrusions. During premonsoon, Mg^{2+} and Na^+ are strongly correlated with HCO_3. Ca^{2+} also have positive correlation with HCO_3. The positive correlation of silicates with Ca and Na during premonsoon reveals that the long residence time of the stagnant river water facilitates the rock-water interaction and hence the silicate weathering. Na^+ is strongly correlated with Cl^- in both the seasons. During premonsoon, the variation of Na^+ with Cl^- is related to nitrate but in postmonsoon, the variation is unrelated to nitrate reflecting that some contribution from the anthropogenic activities is expected in premonsoon and the dissolution of dispersed halite would have contributed to the water chemistry during postmonsoon. The saline water intrusion into the groundwater near the lower part of the river at the confluence point also increases the concentration of theses ions in the water. During both the seasons, the major exchangeable ions Na–Ca and

Fig. 5 Wilcox diagram
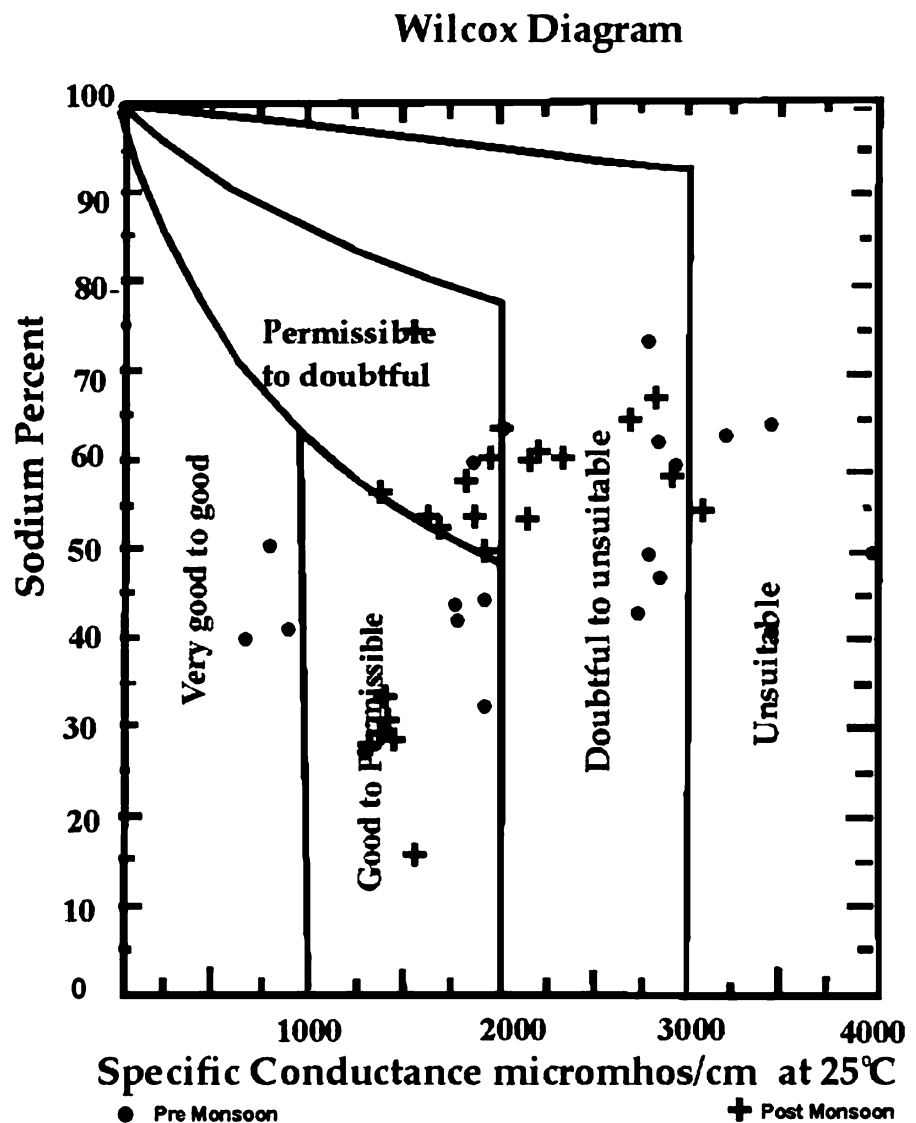
Na–Mg correlate positively. It can therefore be postulated that the concurrent increase/decrease in the composition of ions in these waters is predominantly due to the result of dissolution/precipitation reaction and concentration effects.

Moreover, in groundwater, three different sets of strong relationships exist between major cations and anions (Douglas and Leo 1977). They are:

1. The highly competitive relationship between ions having same charge but a different valence number e.g. Ca^{2+} and Na^+

2. The affinity between ions having different charges but the same valence number e.g. Na^+ and Cl^-.

3. The non-competitive relationship between ions having the same charge and same valence number e.g. Ca^{2+} and Mg^{2+}.

On the above basis and from the results of the correlation coefficient matrix (Tables 4 and 5), the correlation of ions in groundwater samples in pre-monsoon is as follows:

1. Highly competitive ion relationship:. Ca^{2+} with Na^+, K^+; Mg^{2+} with Na^+ have high positive correlation. SO_4^{2-} with HCO_3^-, F^-; Mg^{2+} with K^+ have low positive correlation.

2. Affinity ion relationship: Na^+ with Cl^-, NO_3^-, HCO_3^-, F^-; K^+ with Cl^-, NO_3^- have significant

Table 4 Correlation coefficient matrix – premonsoon

	pH	Ec	TDS	Ca	Mg	Na	K	HCO3	SO4	Cl	F	NO3	NO2	PO4	Sil
pH	1.00														
Ec	−0.01	1.00													
TDS	−0.01	1.00	1.00												
Ca	0.22	0.47	0.47	1.00											
Mg	0.00	0.75	0.75	0.09	1.00										
Na	−0.04	0.85	0.85	0.52	0.76	1.00									
K	0.27	0.57	0.57	0.65	0.39	0.73	1.00								
HCO3	0.15	0.73	0.73	0.30	0.80	0.69	0.27	1.00							
SO4	0.16	0.22	0.22	0.28	0.24	0.16	0.15	0.37	1.00						
Cl	−0.09	0.83	0.83	0.47	0.76	0.99	0.67	0.68	0.10	1.00					
F	0.20	0.34	0.34	0.46	0.34	0.44	0.26	0.62	0.39	0.39	1.00				
NO3	−0.24	0.43	0.43	0.61	0.14	0.61	0.45	0.24	0.01	0.63	0.30	1.00			
NO2	−0.59	0.05	0.05	−0.08	0.13	0.30	0.00	−0.06	−0.23	0.38	−0.02	0.47	1.00		
PO4	0.20	0.09	0.09	0.34	−0.21	−0.03	0.28	−0.14	−0.19	−0.03	−0.09	0.35	−0.20	1.00	
Sil	−0.21	0.44	0.44	0.28	0.32	0.44	0.19	0.34	−0.11	0.43	0.54	0.23	0.22	−0.29	1.00

correlation. Ca^{2+} with SO_4^{2-}; Mg^{2+} with SO_4^{2-}; Na^+ with NO_2^-; K^+ with HCO_3^-, F^- have low positive correlation.

3. Non-Competitive ion relationship: Na^+ with K^+; HCO_3^- with Cl^-, F^-; Cl^- with NO_3^- have significant correlation. HCO_3^- with NO_3^-; Cl^- with F^-, NO_2^-; F^- with NO_3^- have low positive correlation.

The correlation of ions in groundwater samples in Postmonsoon is as follows:

1. Highly competitive ion relationship: Low positive correlation exists between Ca^{2+} with Na^+ and K^+; Mg^{2+} with Na^+; HCO_3^- with SO_4^{2-}; SO_4^{2-} with Cl^-, NO_3^-.

2. Affinity ion relationship: Ca^{2+} with SO_4^{2-}; Na^+ with Cl^-, HCO_3^-; K^+ with Cl^-, NO_3^-, have significant correlation. Negative correlation exists between Na^+ with F^-; K^+ with HCO_3^-, NO_2^-.

3. Non-Competitive ion relationship: HCO_3^- with Cl^- shows positive correlation. Ca^{2+} with Mg^{2+};

Table 5 Correlation coefficient matrix – postmonsoon

	pH	Ec	TDS	Ca	Mg	Na	K	HCO3	SO4	Cl	F	NO3	NO2	PO4	Sil
pH	1.00														
Ec	0.18	1.00													
TDS	0.18	1.00	1.00												
Ca	0.11	0.63	0.63	1.00											
Mg	−0.03	0.49	0.49	0.31	1.00										
Na	0.14	0.90	0.90	0.37	0.27	1.00									
K	0.53	0.36	0.35	0.22	−0.01	0.34	1.00								
HCO3	−0.08	0.71	0.71	0.47	0.68	0.49	−0.02	1.00							
SO4	−0.04	0.47	0.47	0.72	0.28	0.26	0.19	0.27	1.00						
Cl	0.44	0.90	0.90	0.45	0.32	0.86	0.50	0.43	0.35	1.00					
F	0.05	−0.22	−0.22	0.06	−0.02	−0.22	0.08	−0.32	0.04	−0.18	1.00				
NO3	0.39	0.19	0.19	0.39	−0.12	0.07	0.60	−0.03	0.31	0.27	0.32	1.00			
NO2	−0.21	0.10	0.10	−0.12	0.20	0.03	−0.22	0.39	−0.20	−0.01	−0.30	−0.04	1.00		
PO4	0.06	0.30	0.30	0.32	−0.07	0.29	0.33	0.01	−0.12	0.27	0.01	0.28	0.04	1.00	
Sil	0.08	0.38	0.38	0.64	0.28	0.17	0.19	0.38	0.37	0.20	−0.07	0.08	−0.30	0.31	1.00

Na^+ with K^+; HCO3$^-$ with NO_2^-; Cl^- with NO_3^-; F^- with NO_3^- shows low positive correlation.

Factor analysis

Factor analysis is a multivariate technique designed to analyse the interrelationships within a set of variables. The factors are chosen in such a way that reduces the overall complexity of the data by taking advantages of inherent interdependencies (Davis 2002). In this work, R-mode factor analysis is chosen which provides several positive features that allows inter-pretation of the data set more scientifically. In order to evaluate the variables belonging to a specific chem-ical process and also to find out the dominance and contribution of the major elements in terms of the total data set, Factor loadings Communalities and Eigen values (Tables 6 and 7) are being examined.

The first four factors of the premonsoon and five factors of the postmonsoon accounts for about 80% of variance showing eigenvalues >1 have been extracted from the principal factor matrix after varimax rota-tion. Factor 1 of the premonsoon which explains 44% of the total variance has high loadings in the ions Mg, Na, Cl, K and HCO_3. The percentage abundance of the above variables indicates that their source of origin may be expected from silicate weathering, percolation of adjacent polluted river water and to a lesser extent from atmospheric precipitation. Sporadic occurrence of alkaline and saline soils in the river basin may contribute these ions to the adjacent aquifers through dissolution and percolation. More-over, the poor correlation of the above variables with pH reflects that alteration in the pH of these waters has no significant effect over these ions. The upper course of the river is almost dry and water can be seen only in the lower course of the river and the almost stagnant water in this part increases the residence time of the ions in the water which facilitates seepage into the nearby aquifers. This explains why factor I which has 44% loadings is highly significant near the downstream. Factor I of the postmonsoon which explains 38% of the total variation has high loading in the ions Cl, Na and HCO_3. The surface run off of the saline soils during storm would have increased these ions in the nearby watersheds and the ground-water may get concentrated with these ions through seepage and hence this factor may be termed as precipitation and chemical weathering factor.

Factor 2 of the premonsoon accounts for 15% of the total variance is an anthropogenic factor which contains variables NO_3, PO_4, Ca and K. During postmonsoon, factor 2 is found to be a nitrate factor with variables NO_3, NO_2 and Ca. The nitrate/nitrite ions have no significant lithologic source in the studied area and it must be associated with surface runoff of the fertilizers remains in the soil which percolates into the groundwater.

Factor 3 of the premonsoon accounts for about 10% of the total variance is explicitly a nitrate factor containing the variables HCO_3 and NO_3. During postmonsoon, the loading of silicates is found to be high replacing the nitrates along with HCO_3 and SO_4. The effect of precipitation and chemical weathering could have determined the variation among the variables.

Factor 4 of the premonsoon which explains 7.5% of the total variation is a fluoride factor. pH is positively correlated with fluorides indicating that an increase in pH increases the dissolution of F^- ions. But the lithology of the study area has no significant fluoride bearing minerals and hence it is logical to assign the high fluoride to the anthropogenic activity and to a lesser extent to the chemical weathering. During postmonsoon, factor 4 is found to be a nitrite factor which may be attributed to the anthropogenic activities of that area.

Factor 5 of postmonsoon which accounts for 7.2% of variance is explicitly a phosphate factor. The effect of precipitation and subsequent dissolution of the fertilizer remains in the soil would have increased the concentration of these ions in the river water which would have percolated into the nearby aquifers.

Factor scores

The study of factor scores reveals the extent of influence of each factors on the overall water chemistry at all locations of sampling stations. Fig. 6a,b depicts the downstream variations in the magnitude of all factors controlling the groundwater chemistry.

In premonsoon, factor 1 is least significant near the origin and it gradually contributes to the water chemistry starting from the station 14 to the ground-water near the confluence point. In the case of postmonsoon, the pattern is almost similar with only two positive scores at the upstream and factor 1

Table 6 Eigen values and factor loadings – premonsoon

Rotated Component Matrix(a)

| Variables | Component | | | |
	Factor I	Factor II	Factor III	Factor IV
pH	$5.854E-03$	0.177	-0.812	$4.213E-02$
Ec	0.903	0.251	$3.927E-03$	0.143
TDS	0.903	0.250	$3.342E-03$	0.142
Ca	0.216	0.789	-0.136	0.412
Mg	0.925	-0.180	$-2.542E-03$	0.127
Na	0.859	0.342	0.198	0.238
K	0.529	0.642	-0.122	$4.930E-02$
HCO_3	0.782	$-6.180E-02$	-0.183	0.423
SO_4	0.184	$-5.686E-02$	-0.441	0.468
Cl	0.855	0.320	0.275	0.194
F	0.229	0.180	-0.125	0.866
NO_3	0.263	0.730	0.448	0.193
NO_2	0.106	$3.586E-02$	0.878	$3.289E-02$
PO_4	$-8.085E-02$	0.728	-0.208	-0.401
Sil	0.291	$1.781E-02$	0.371	0.628
Eigen values	6.583	2.205	1.941	1.237
% Variance	43.889	14.700	12.939	8.248
Cumulative %	43.889	58.588	71.528	79.776

played a major role only at the downstream stations. This leads to the conclusion that precipitation and chemical weathering, saline water intrusion played a major role at the downstream.

Factor 2 of premonsoon also shows least significant contribution at the origin and there is a gradual increase in the factor scores downstream. This trend indicates that the contribution of water chemistry becomes

Table 7 Eigen values and factor loadings – postmonsoon

Rotated Component Matrix(a)

| Variables | Component | | | | |
	Factor I	Factor II	Factor III	Factor IV	Factor V
pH	0.399	-0.193	0.527	-0.368	$-6.524E-02$
Ec	0.878	0.405	$6.238E-02$	0.175	$8.939E-02$
TDS	0.877	0.407	$6.222E-02$	0.176	$9.013E-02$
Ca	0.289	0.835	0.222	$4.003E-02$	0.190
Mg	0.340	0.452	-0.104	0.437	-0.310
Na	0.901	0.127	$-2.020E-02$	$2.852E-02$	0.107
K	0.433	$-5.661E-03$	0.645	-0.266	0.216
HCO_3	0.537	0.442	-0.213	0.542	$-7.457E-02$
SO_4	0.198	0.759	0.214	$-5.430E-02$	-0.276
Cl	0.928	0.142	0.232	$-3.177E-02$	$3.366E-02$
F	-0.413	0.177	0.561	$-7.968E-02$	-0.126
NO_3	$5.464E-02$	0.161	0.890	$7.095E-02$	0.184
NO_2	$7.732E-02$	-0.265	$-7.172E-02$	0.894	$8.089E-02$
PO_4	0.179	$8.921E-02$	0.160	$4.362E-02$	0.915
Sil	0.149	0.751	-0.125	-0.230	0.351
Eigen values	5.688	2.470	1.707	1.147	1.081
% Variance	37.922	16.470	11.379	7.646	7.205
Cumulative %	37.922	54.392	65.771	73.417	80.622
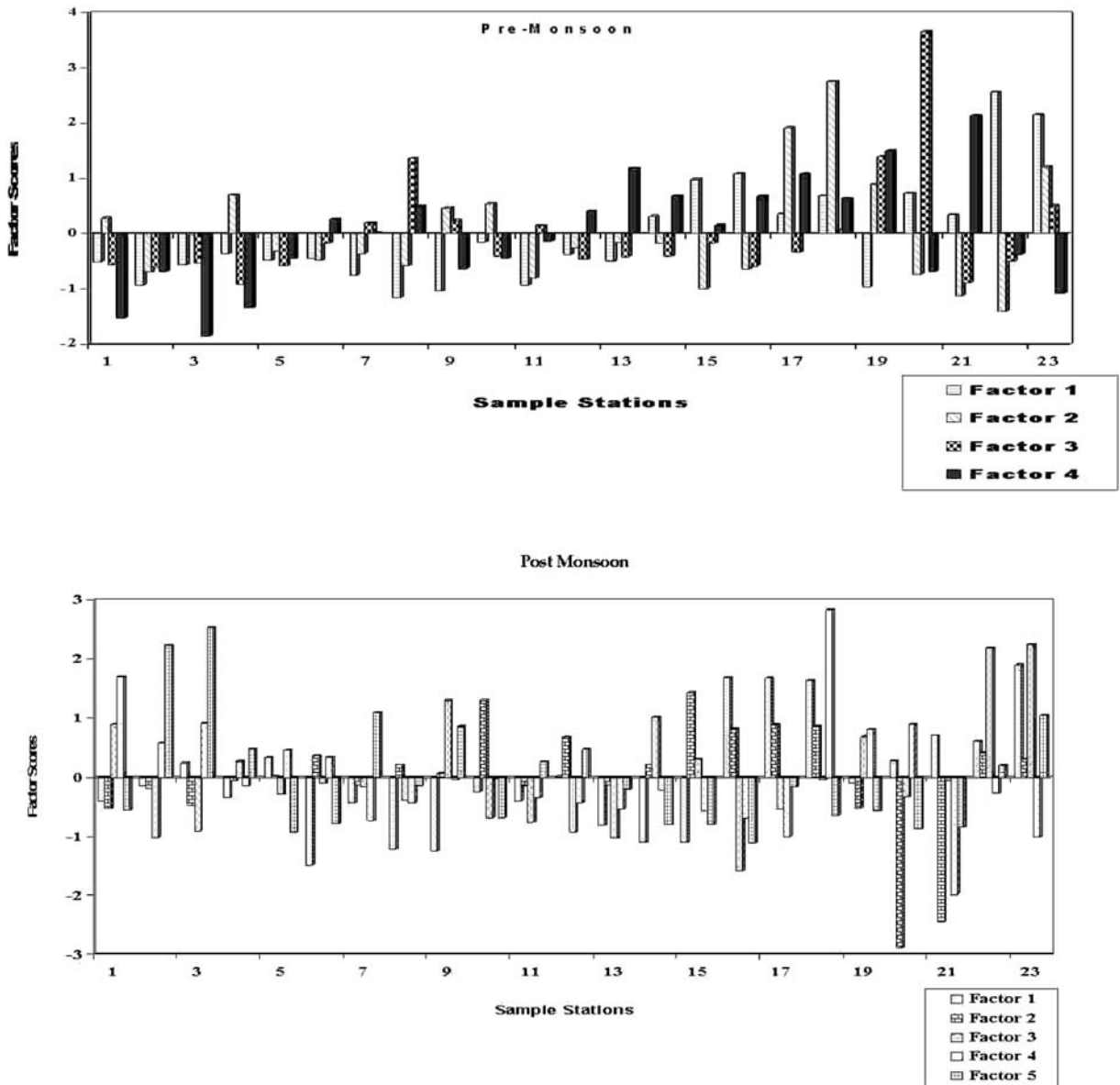
Fig. 6 Factor scores bar diagram

gradually significant. The distribution pattern of this factor leads to the conclusion that the anthropogenic activities predominate over the precipitations and the associated silicate weathering. Postmonsoon scores show a distinct pattern. Though it also shows no significant contribution near the origin but starting from station 6 to station 18, it gradually contributes to the water chemistry and this observed pattern is in line with the expected anthropogenic activities.

Factor 3 of premonsoon has not shown much significance except at stations 8, 19 and 20. During

postmonsoon, the scores shows significant values at about eight stations and it shows high values only at the downstream. Contribution from precipitation and silicate weathering would have decided the premonsoon values and leaching due to heavy storm as well as saline water intrusion gains importance in postmonsoon.

In factor 4, the premonsoon value gradually shows significant values starting from station 6 to station 21. During postmonsoon, the scores show high values at the origin and it has been inferred that there is no

significance in the aquifers near the middle course of the river. The effect of monsoon is obvious from the trend shown in this factor and hence it could be concluded that rainfall and its associated dissolution and seepage would have contributed to this factor.

Factor 5 of postmonsoon is significant at the upstream from station 2 to station 12. It has been observed that there is much agricultural activities in these areas which may lead to the increased concentration of phosphate ions in the soil which in turn increases the concentration of these ions in the groundwater.

Conclusion

The hydrochemistry of the groundwater varies in relation to different water-rock interactions, intrusion of polluted river water, anthropogenic activities and seepage of seawater near the coast. The results indicates that the groundwater composition in the study area is affected on a regional scale by agricultural activities in the aquifers near the upper part of the river course and in the middle part by seepage of the polluted river water and in the lower part, the saline water intrusion has gained significance. The premonsoon values indicate that most of the groundwater belongs to the brackish type and it has been found that much of dilution has occurred during the postmonsoon where the TDS values were significantly lowered. Moreover the TDS values of the ground water are higher than the permissible limit for both the pre and postmonsoon samples. The fluoride and nitrate concentrations of premonsoon ground water samples are higher than the WHO permissible limits in certain places but got diluted in postmonsoon. 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 but in the case of postmonsoon the effect of monsoon is found to be obvious. The results on the concentration of trace metals shows that Pb and Cr are found to be higher than the prescribed limit. The quality assessment studies shows that the groundwater near the upper part of the river is good for irrigation. During premonsoon, 44% of the groundwater is found

to be suitable for irrigation and 52% is found to be suitable in postmonsoon. From the correlation studies, competitive and non-competitive ion relationship between the major ions was demonstrated. The factor analysis of the major ion chemistry of the groundwater reveals three prevalent factors operating in these waters. The major factors which explain the various loadings are precipitation and chemical weathering and anthropogenic. The results of factor scores reflect the extent of influence of each factors on the water chemistry at various sample stations. The significance of these factors at various regions of the groundwater indicates the major contributors to the chemical budget of ions at that region. The results shows that near the upstream of the river, the groundwater is affected by the agricultural activities and in the downstream both anthropogenic and chemical weathering factors are found to be significant. In general, the concentrations of cations and anions are high in the premonsoon 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.

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