

# Quality assessment and hydrogeochemical characteristics of groundwater in Agastheeswaram taluk, Kanyakumari district, Tamil Nadu, India

Srinivas Y.<sup>1</sup>, Hudson Oliver D.<sup>1\*</sup>, Stanley Raj A.<sup>2</sup>, and Chandrasekar N.<sup>1</sup>

<sup>1</sup> Centre for GeoTechnology Manonmaniam Sundaranar University

<sup>2</sup> Vel Tech Dr. RR & Dr. SR Technical University, Avadi, Chennai

\* Corresponding author, E-mail: hudson2612@gmail.com

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**Abstract** The present study investigates the hydrogeochemical characteristics of groundwater quality in Agastheeswaram taluk of Kanyakumari district, Tamil Nadu, India. A total of 69 groundwater samples were collected during pre- and post-monsoon periods of 2011–2012. The groundwater quality assessment has been carried out by evaluating the physicochemical parameters such as pH, EC, TDS,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  for both the seasons. Based on these parameters, groundwater has been assessed in favor of its suitability for drinking and irrigation purpose. Dominant cations for both the seasons are in the order of  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$  while the dominant anions for post monsoon and pre monsoon have the trends of  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$  and  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ , respectively. Analytical results observed from various indices reveal that the groundwater quality is fairly good in some places. Analytical results of few samples show that they are severely polluted and incidentally found to be near the coasts, estuaries and salt pans in the study area. The Gibbs plot indicates that the majority of groundwater samples fall in rock dominant region, which indicates rock water interaction in the study area. The United States salinity (USSS) diagram shows that the groundwater is free from sodium hazards but the salinity hazard varies from low to very high throughout the study area. This reveals that the groundwater is moderately suitable for agricultural activities. The observed chemical variations in pre-monsoon and post-monsoon seasons may be the effect to rock-water interactions, ion-exchange reactions, and runoff of fertilizers from the surrounding agricultural lands.

**Key words** groundwater quality; geochemical analysis; seasonal variation; Agastheeswaram taluk; India

## 1 Introduction

In recent decades, utilization of groundwater has increased at an alarming rate worldwide. Exploitation of groundwater has increased greatly, particularly for irrigation, industrial and drinking purposes in large parts of the India due to frequent failures of monsoon, which in turn affects the surface water sources such as rivers and lakes. Rapid urbanization and industrialization also tremendously increase the groundwater demand. Now it is recognized that the quality of the groundwater is just as important as its quantity. Over exploitation of groundwater can affect both quantity and quality of groundwater. Exploitation of groundwater must be regulated to avoid sea water incursion by that we can maintain the quality and quantity of groundwater for our current and future needs. Natural and anthropogenic effects include local climate, geology and irrigation practices. The assessment and clas-

sification of groundwater based on its quality can be done by analyzing its chemical characteristics. Variations in ion chemistry of groundwater are used to identify geochemical processes that control the groundwater quality. Ion exchange reaction is the process of replacement of ions absorbed from the surrounding aquifers by ions in the solution. The nature of the rock formations, topography, soils, atmospheric precipitation, quality of the recharged water and sub-surface geochemical process are some of the parameters affecting groundwater quality (Todd, 1980; Fetter, 1994). Rising of groundwater levels with an increasing trend of salinity may be because of the dissolution of rocks or mineral salts (Ballukraya and Ravi, 1995; SubbaRao, 2008; Latha and Rao, 2012). So many geochemical works are carried out in India and several parts of the world to find out the suitability of groundwater for drinking, irrigational and other domestic purposes (Ramesh and Elango, 2012; Raju et

al., 2011; Subramani et al., 2005; Srinivasamoorthy et al., 2010). Similar types of studies were carried out in the Kanyakumari district by Subramanian (2011), Perumal and Thamarai (2008). But this study predicts the overall groundwater quality and hydrogeochemical characteristics of Agastheeswaram taluk which was not focused in the earlier studies. The aim of the study is to assess the geochemical processes controlling the water composition and to assess the spatial distribution of various hydrogeochemical parameters for suitability of groundwater resources.

## 2 Study area

The study area is in Kanyakumari district, located in the southern tip of India (Fig. 1). The total region of Agastheeswaram taluk covers 279.4 km<sup>2</sup>. It lies between the latitude 77°18'45" E to 77°35'15" E and 8°4' N to 8°13'45" N longitude. The land use pattern of Agastheeswaram taluk (Table 1) shows that the majority of the area are cultivated lands (CGWB, 2008). Nagercoil, the administrative head quarter of Kanyakumari district is the 12<sup>th</sup> largest city of Tamilnadu State, is situated in the study area. The highest temperature is attained in the month of May as 35.93°C. The lowest temperature is noted as 23.85°C in January (CGWB, 2008). The overall water level variation suggests that it increases from October to December and decreases from February to September. A slight increasing tendency is seen during July because of southwestern monsoon rain. However, water level conditions of the district for the duration of what

went before years are in declining trend (PWD, 2005).

## 3 Geology and hydrogeology

The study area is underlain by crystalline rocks like gneiss and charnockite of the Archaean age. Along the coast sands of recent origin are noticed. The geology map (Fig. 2) of the study area is obtained from Geological survey of India (GSI, 2005). The peninsular gneisses occupy the largest area in the district. The general trend of the strike of this area is in the N-NW to S-SE direction. Garnetiferous silliminate, graphite gneiss and garnet biotite gneiss are the two major group identified in Kanyakumari district. The stratigraphical succession of geological formations in the study area is listed in Table 2. The charnockite group rocks are well exposed around Rajakamangalam areas. Charnockite group mainly consists of charnockite, pyroxene granulite and their associated migmatites. Charnokites are also exposed within the gneiss as bands and lenses. Near Kanyakumari calcareous limeshell of sub recent origin is noticed. The west coast of India which starts from Kanyakumari in our study area up to Muttom is covered by thick lateritic soil dotted with a few rocky outcrops. The general sand types seen along the coast are bay deposits or lateral deposits of sand, zircon, rutile, illemanite and garnet. The straight west coast line continuing without any break is itself suggestive of faulted one and the faulting would have taken place during the Pliocene period.

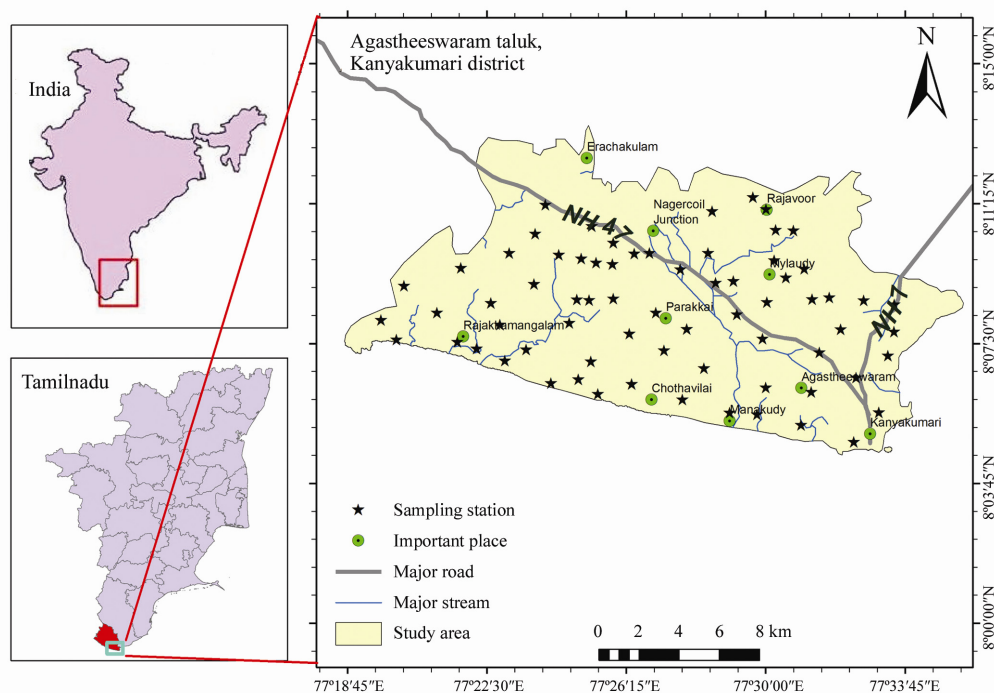


Fig. 1. Location map of the study area showing the sampling stations.

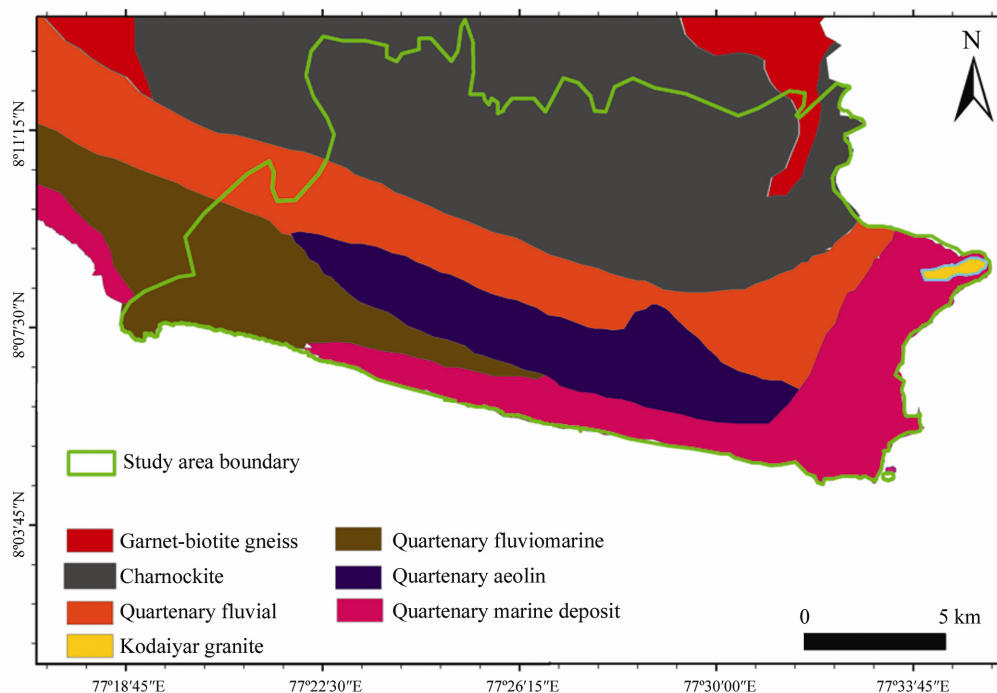


Fig. 2. Thematic map depicting the geology of the study area.

**Table 1 Land use details**

Sample No.	Land use particular	Area (km <sup>2</sup> )	% to geographical area
1	Barren and uncultivable lands	12.870	4.605
2	Land put to non-agriculture use	77.020	27.566
3	Cultivable waste	0.070	0.025
4	Present pastures & other grazing lands	0.040	0.014
5	Current fallows	1.560	0.557
6	Other fallow lands	1.810	0.646
7	Net vegetation area	174.500	62.454
8	Constructions and other lands	11.550	4.133
	Total geographical area	279.400	100

**Table 2 Stratigraphical succession of geological formations**

Era	Age	Lithology
Quaternary	Recent	Sand
Cenozoic	Middle Miocene	Warkalai sandstones
Archaean		Peninsular gneisses, charnickites, khondalites, granites and pegmatites

The Kanyakumari district has a different type of drainage pattern having perennial streams flowing towards south and southwest directions. All the major rivers draining in the Kanyakumari district originate from the western Ghats and flow towards the southwest directions. The major river flowing in the study area, the Agastheeswaram taluk is Pazhayar River. Pazhayar River originates from Mahendragiri hills north to Arumanallur village at an altitude of 1300 m above the sea level and drains along Boothapandi,

Tirupathisaram of Thovalai taluk and also through the towns Nagercoil and Agastheeswaram of Agastheeswaram taluk and confluences with the Indian Ocean near Manakudy which is nearly 12 km away from Nagercoil. Pazhayar River is benefitted by both southwest and northeast monsoons and forms a vital source for surface water irrigation by covering a vast area as the river water being taken away to different regions through channels.

Some of the geomorphic formations in the study

area are structural hills, pediments, coastal plains, valleys and water bodies (Fig. 3). Pediments and structural hills are run off zones and hence have poor potential regions. The valleys have a good infiltration—recharge zone which has a medium groundwater potential zone. The coastal plains are characterized by beaches and sand dunes comprising of medium to fine sandy windblown particles, which is also a good groundwater potential zone. For agricultural developments almost the entire shallow aquifer zone is tapped in the study area. Groundwater occurs in almost all the geological formations like crystalline rocks, sedimentary formations and quaternary alluvium and beach sands. The groundwater occurrence in hard rock region is limited to the weathered mantle with the thickness 10 to 35 m below ground level. The weathered thickness in hard rock regions is discontinuous both in space and depth. Hence the groundwater potentiality is influenced by the intensity of weathering. In the sedimentary formations having alluvial deposits the water table is very shallow which is up to the maximum depth of 10 m (PWD, 2005).

#### 4 Methodology

Totally 69 groundwater samples were collected from dug wells and bore wells during January and June of 2012 representing both the post monsoon and pre-monsoon seasons respectively. Samples were collected after 10 minutes of pumping and stored in 1 liter plastic cans which were pre-cleaned (acid-washed) and thoroughly rinsed with distilled water. Each of the collected groundwater samples was analyzed for the physico-chemical parameters as pH, electrical conductivity, bi-carbonate, chloride, sulfate, calcium, magnesium, sodium and potassium using the standard procedures as per APHA (1989). The hydrogen ion concentration (pH) and electrical conductivity were measured using Eutech digital portable meters *in-situ*; the instruments are calibrated as manufacturer guidelines. The pH meter was calibrated using the buffer solutions of pH 4.01, 7, 10.01 and the EC meter was calibrated using the conductivity buffer solutions having conductivity 84 and 1408  $\mu\text{S}/\text{cm}$ . Calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) were estimated by ethylene diamine tetra acetic acid (EDTA) titration. Bicarbonate ( $\text{HCO}_3^-$ ) was determined by using acid titrimetric method. Concentrations of sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) were estimated using flame photometer. Chloride ( $\text{Cl}^-$ ) concentration was measured using argentometric ( $\text{AgNO}_3$ ) titration. Spectrophotometer was employed to determine the sulphate ( $\text{SO}_4^{2-}$ ) concentration. Total hardness (TH) was calculated from the values of the calcium and magnesium ion concentrations by the following equation (Todd, 1980).

$$\text{TH} = 2.497 \text{ Ca}^{2+} + 4.115 \text{ Mg}^{2+} \text{ (mg/L)} \quad (1)$$

The accuracy of the obtained results was verified by calculating the ion-balance error (Mandel and Shifan, 1981) which was found to be around 10%.

### 5 Results and discussion

#### 5.1 Hydrogeochemical processes

The ionic concentrations were plotted in Piper diagram (Piper, 1944) to characterize geochemical nature of the groundwater in the study area. On the basis of Piper diagram (Fig. 4) it is detected that for both the seasons the alkaline earth elements ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) exceed the alkali elements ( $\text{Na}^+ + \text{K}^+$ ) even though  $\text{Na}^+$  is the leading cation in the study area. Also strong acids ( $\text{SO}_4^{2-} + \text{Cl}^-$ ) exceed the weak acids ( $\text{CO}_3^{2-} + \text{HCO}_3^-$ ) in the post-monsoon and both the acids had balanced levels in the pre-monsoon period. The anion triangle shows that  $\text{Cl}^-$  is the dominating ion next with  $\text{HCO}_3^-$  in the case of post-monsoon and  $\text{HCO}_3^-$  is the dominant anion in pre-monsoon season. But sulphate ion is completely non dominant in both seasons. In the cation triangle the majority of samples fall into no dominant region for both seasons but comparing all other cations,  $\text{Na}^+$  is found to be the major cation. Major water types are  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ - $\text{Cl}^-$ - $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ - $\text{HCO}_3^-$ .

Three important natural mechanisms controlling the major ion chemistry of the groundwater like atmospheric precipitation, rock weathering and evaporation were plotted by Gibbs (1970). Gibbs present two plots, i) TDS versus  $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$  and ii) TDS versus  $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ . Both the plots are plotted for both the seasons (Fig. 5) and it is found that majority of the samples fall into the rock dominant region which shows that the rock weathering is the leading chemical process in the study area. Weathering of different sources of rocks produces different combinations of cations and anions in the groundwater (Garrels and Mackenzie, 1967). Next to rock weathering, majority of samples falls into evaporation dominant area. This shows that the anthropogenic activities also play a key role in the chemical composition of the groundwater in the study area.

Several factors increasing the ionic ratios in the groundwater were discussed. Characterization of ionic ratios of potential source is also necessary to be identified. The salinity and mechanism of acquiring salinity can be identified by plotting  $\text{Na}^+$ - $\text{Cl}^-$  scatter plots (Sami, 1992). A good correlation of sodium and chloride were obtained (Fig. 6a, b), which shows that the groundwater is controlled by rock-water interaction which would likely to be from calcium and magne-

sium silicate weathering. The Gibbs plots confirm this process. The lower  $\text{Na}^+/\text{Cl}^-$  is because of cationic exchange of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  which replaces the  $\text{Na}^+$  ions in the study area. The plot of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus  $\text{HCO}_3^-$  (Fig. 6c, d) marks the upper limit in the post-monsoon season, showing that the carbonate weathering is dominant. The  $\text{Na}^+ + \text{K}^+$  was plotted against  $\text{Cl}^-$  (Fig. 7a, b), showing the silicate weathering is dominant in pre-monsoon season. The excess of

$\text{Na}^+ + \text{K}^+$  by  $\text{Cl}^-$  corresponds to silicate weathering (Stallard and Edmond, 1983). The relationship between EC and  $\text{Na}^+/\text{Cl}^-$  in the groundwater was plotted and it gave the evidence of evaporation. The scatter diagram of EC versus  $\text{Na}^+/\text{Cl}^-$  (Fig. 7c, d) shows that the trend line is inclined with the increasing EC, indicating that the evaporation is not the dominant process. But the same result was given by Gibbs diagram (Fig. 5) which justifies this result.

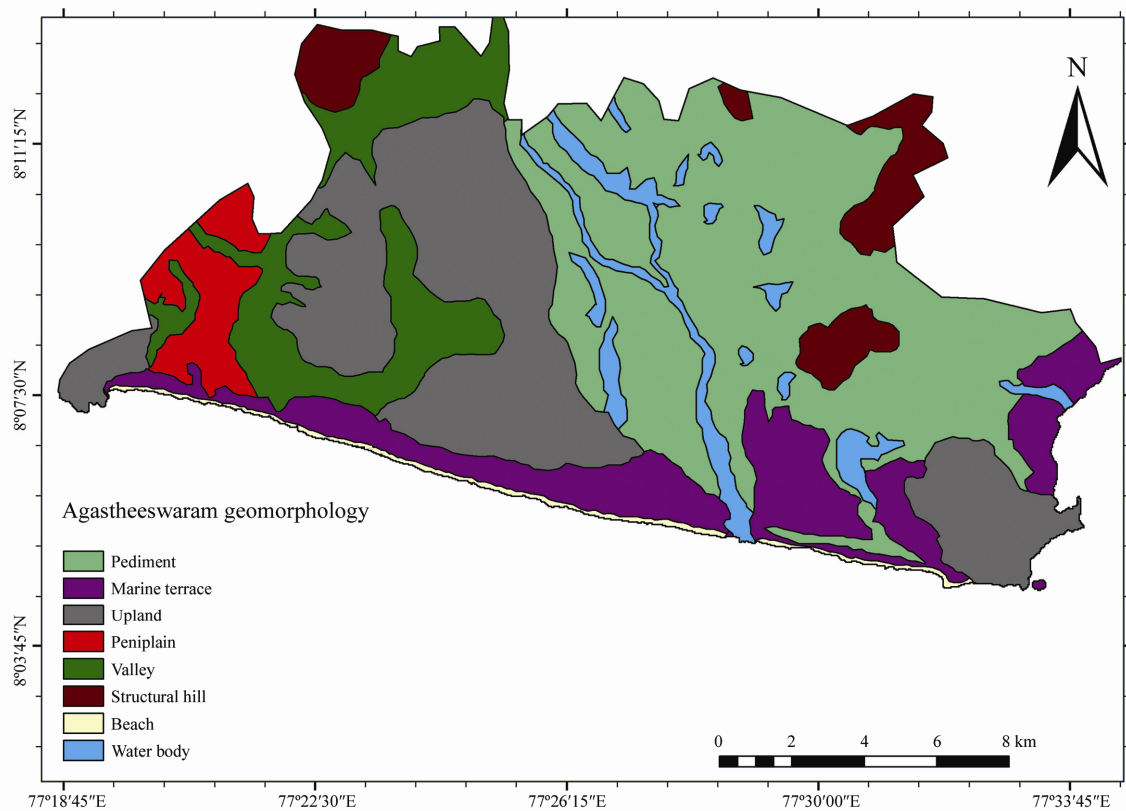


Fig. 3. Thematic map depicting the geomorphology of the study area.

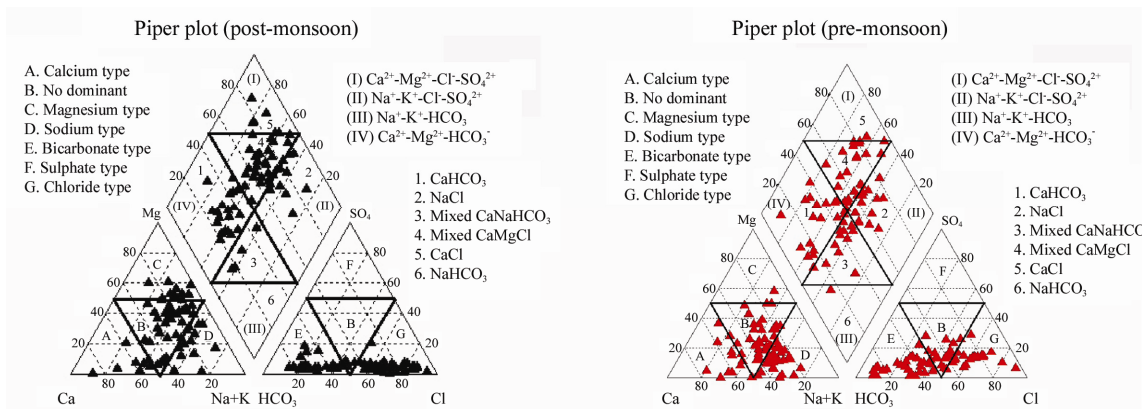


Fig. 4. Piper diagram illustrating the chemical composition of groundwater. (a) Post monsoon; (b) pre monsoon.

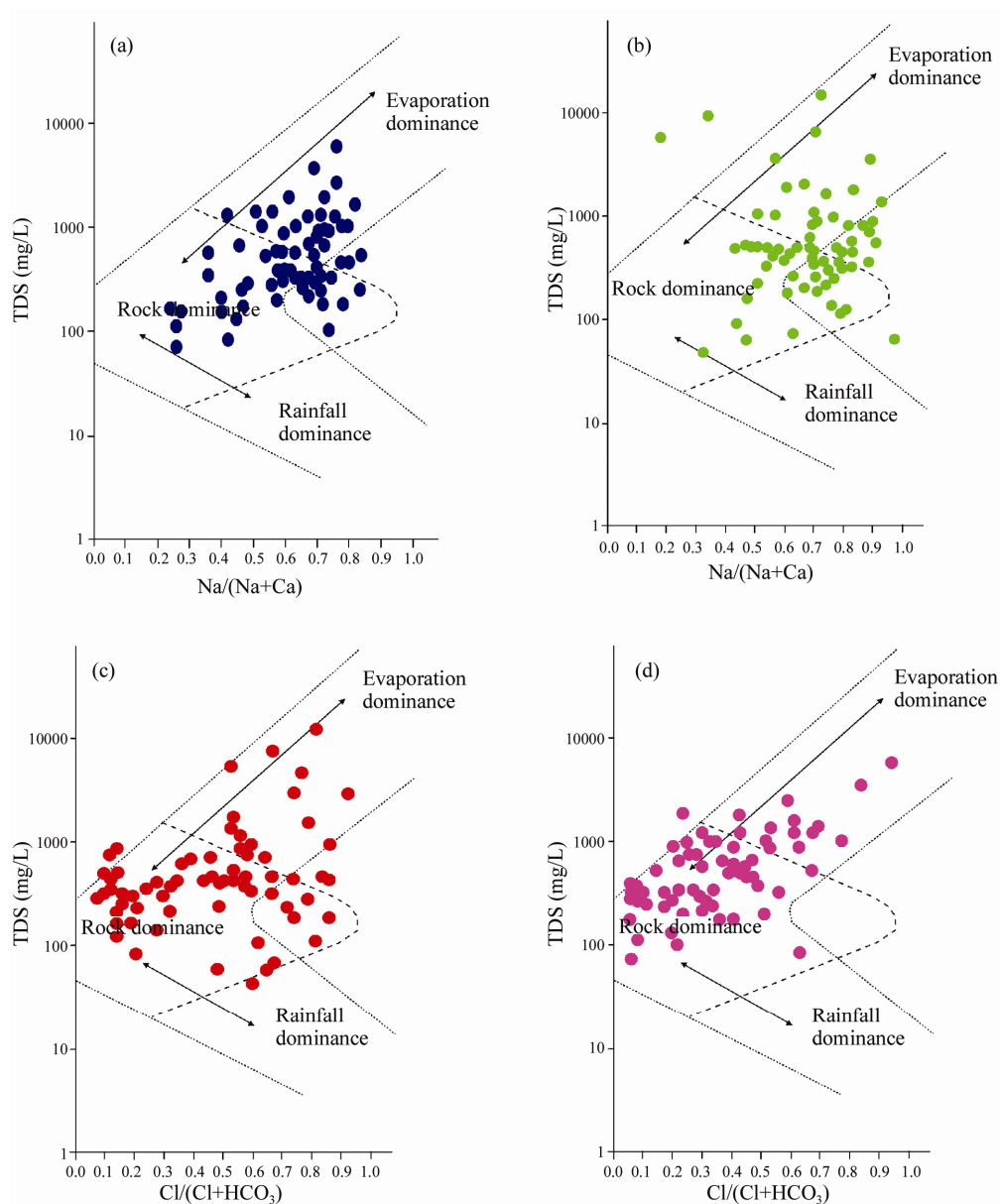


Fig. 5. Gibbs diagram showing the mechanisms controlling the chemistry of groundwater. (a) Major cations vs. TDS for post monsoon; (b) major cations vs. TDS for pre monsoon; (c) major anions vs. TDS for post monsoon; (d) major anions vs. TDS for pre monsoon.

## 5.2 Drinking water quality analysis

Depending upon some specific standards the groundwater quality can be determined for its suitability for different purposes. In our study the standards were derived from standards of World Health Organization (WHO, 1997) and Bureau of Indian Standards (BIS, 1991) guidelines to assess the drinking water quality of the groundwater. The ranges of chemical parameters and their comparison with the WHO and the Indian standards for drinking for the post monsoon (Table 3a) and pre monsoon (Table 3b) were presented. The pH of the groundwater samples ranges from 6.35 to 8.74 with an average of 7.87 for the post monsoon which shows that the majority of the

groundwater samples are slightly alkaline in nature. But in the pre-monsoon period the pH values of the groundwater ranges from 5.63 to 7.9 with an average of 6.9 shows slightly acidic. Total dissolved solids (TDS) in the groundwater varies from 48 to 17024 mg/L with a mean of 1243 mg/L in the post-monsoon period and the variation in pre-monsoon period was between 73 and 6406 mg/L with an average of 767 mg/L. 46% of the samples exceeds the desirable limit of 500 mg/L of both the WHO and BIS standards for both the seasons. The saline water seepage from nearby sea, estuaries and salt pans and intrusion of waste water from the surrounding agricultural lands may be the reason for increasing TDS in the study area. The groundwater classification based on TDS is



present in Table 4. The abundance of cations is generally in the order  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$  for both seasons. In some samples because of saline intrusion the cation  $\text{Na}^+$  dominates  $\text{Ca}^{2+}$ . Even though the concentrations of the ions change, there is no change in the order of abundance. The  $\text{Na}^+$  ion concentrations range from 16 to 795 mg/L with a mean value 138 mg/L and 8 to 338 mg/L with an average of 121 mg/L for post monsoon and pre monsoon, respectively. The higher concentration of sodium in the groundwater may be because of cation exchange reaction and some human activities (Ramkumar et al., 2012). The  $\text{Ca}^{2+}$  ionic concentration for the post monsoon varies from 2 to 2291 mg/L with an average of 124 mg/L where as for the pre monsoon the concentration of  $\text{Ca}^{2+}$  is in the range of 22 to 196 mg/L with a mean value of 86 mg/L. In the post monsoon, the magnesium concentration varies from 0.6 to 1067 mg/L with an average of 73 mg/L. For the pre monsoon  $\text{Mg}^{2+}$  concentration ranges from 1.26 to 220 mg/L with an average of 41 mg/L. The reason for higher  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations is the cationic exchange of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with  $\text{Na}^+$ , i.e.,  $\text{Na}^+$  ions are replaced with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Jacob et al., 1999). The mean values of  $\text{K}^+$  concentrations in the groundwater are 22 and 29 for post and pre monsoon, respectively. High concentration of potassium in the groundwater may be due to the weathering of silicate minerals from igneous and metamorphic rocks (Karnath, 1987). The percolation of excessive potassium fertilizers and manures into the groundwater used in the surrounding agricultural fields is also a reason for the increase of potassium values.

The major anion abundance for the post monsoon is in the order  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ . In pre monsoon the order of anion abundance changes as  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . The  $\text{HCO}_3^-$  ion concentrations vary from 24 to 716 mg/L with an average value of 267 mg/L and 12 to 622 mg/L with a mean value 178 mg/L for the post monsoon and pre monsoon, respectively. The bicarbonates in groundwater may be due to the oxidation and decomposition of organic pollutants (Sadhana, 1994) and because that  $\text{CO}_2$  reacts with soil and releases  $\text{HCO}_3^-$  into the groundwater (Tyagi et al., 2009; Vasanthavigar et al., 2010). The chloride concentrations in the groundwater have mean values of 363 and 123 mg/L for the post-monsoon and pre-monsoon seasons, respectively. The chlorine in the groundwater originates from both the natural and anthropogenic sources like runoff containing inorganic fertilizers, animal feeds, irrigation drainage and seawater intrusion in coastal area (O'Brien and Majewski, 2002; Aghazadeh et al., 2011). Comparing with pre-monsoon, the post-monsoon season samples show high values for chloride. This may be because of the increased rate of percolation domestic sewage and irri-

gation return flow. Leaching of saline residues from the soil may also increase the chloride ion concentration in the groundwater (Appelo and Postma, 1993). Chloride concentration in groundwater gives the evidence of surface contamination (Prasanna et al., 2011). As the surface contamination is less in the pre-monsoon season, there is a reduction of chloride concentration.

The sulphate concentration in the groundwater for the post monsoon varies from 1.5 to 115 mg/L with an average of 36 mg/L and for pre monsoon it varies from 0.45 to 155 mg/L with an average of 42 mg/L. The increase of sulphate is mainly by the influence of agricultural activities (Ramkumar et al., 2012). The hardness of the groundwater may be due to the leaching of calcium and magnesium ions into groundwater (Srinivasamoorthy et al., 2011). The hardness of the water increases its boiling point and it has no remarkable effects on human beings. The classification of the groundwater based on hardness is presented in Table 4. The surface water from the river or channel flowing near the groundwater station will have a direct relation with the chemical combinations of the groundwater to a small extent (Li et al., 2005). The channel and rivers in the study area also have an influence in the groundwater chemistry of the samples. These streams with domestic sewages and agricultural wastes percolated in the groundwater and it drastically changes the ion concentrations in the groundwater (Jameel and Hussain, 2012).

### 5.3 Irrigation water quality analysis

In addition to the chemical characteristics of the groundwater, irrigation is also based on factors like soil texture and composition, crops grown and the irrigation practices in that area (Srinivasamoorthy et al., 2011). Percent sodium (Na%), sodium absorption ratio (SAR) and residual sodium carbonate (RSC) are some of the parameters decide water quality for irrigation in a region.

#### 5.3.1 Sodium percent

Classifying the groundwater for irrigation based on its sodium content is important. The sodium in water reacts with the soils and reduces its permeability which in turn affects the irrigation (Srinivasamoorthy et al., 2013). The sodium content in groundwater can be expressed in the term percent sodium (Na%). The sodium percentage can be calculated using the formula,

$$\text{Na}\% = (\text{Na}^+ + \text{K}^+) / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+) \times 100 \quad (2)$$

where all the concentrations are reported in meq/L.

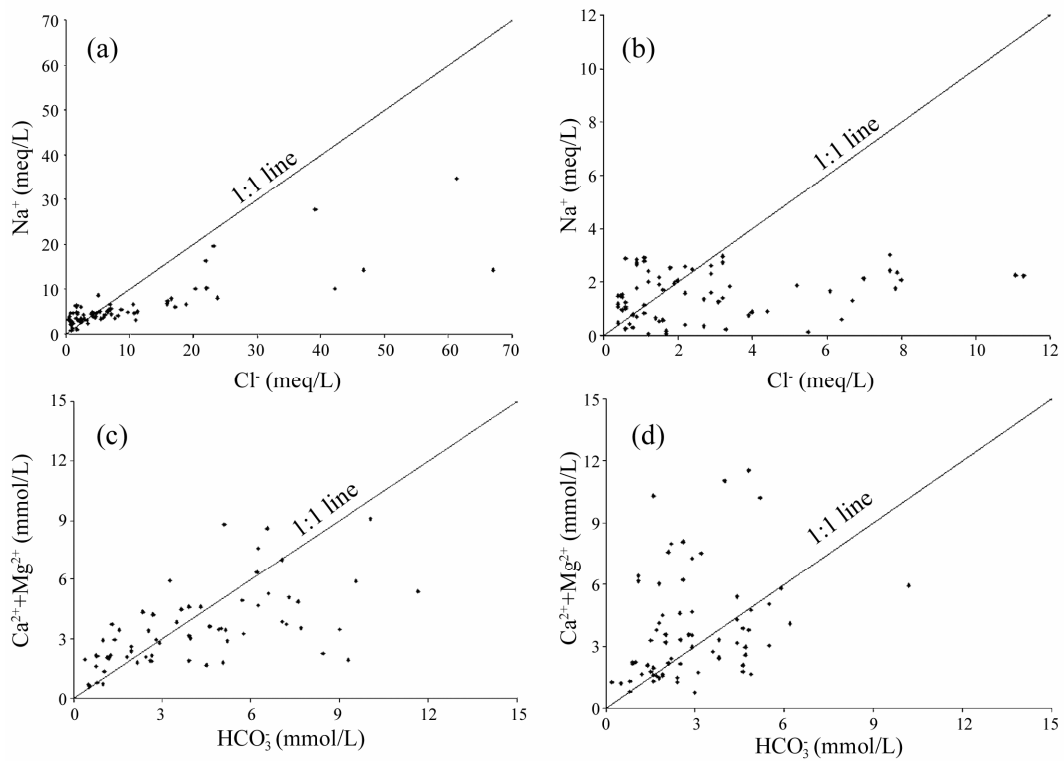


Fig. 6. Ion scatter diagrams for groundwater in the study area. (a)  $\text{Na}^+$  versus  $\text{Cl}^-$  scatter plot for post monsoon; (b)  $\text{Na}^+$  versus  $\text{Cl}^-$  scatter plot pre monsoon; (c)  $\text{HCO}_3^-$  versus  $(\text{Ca}^{2+}+\text{Mg}^{2+})$  plot for post monsoon; (d)  $\text{HCO}_3^-$  versus  $(\text{Ca}^{2+}+\text{Mg}^{2+})$  plot for pre monsoon.

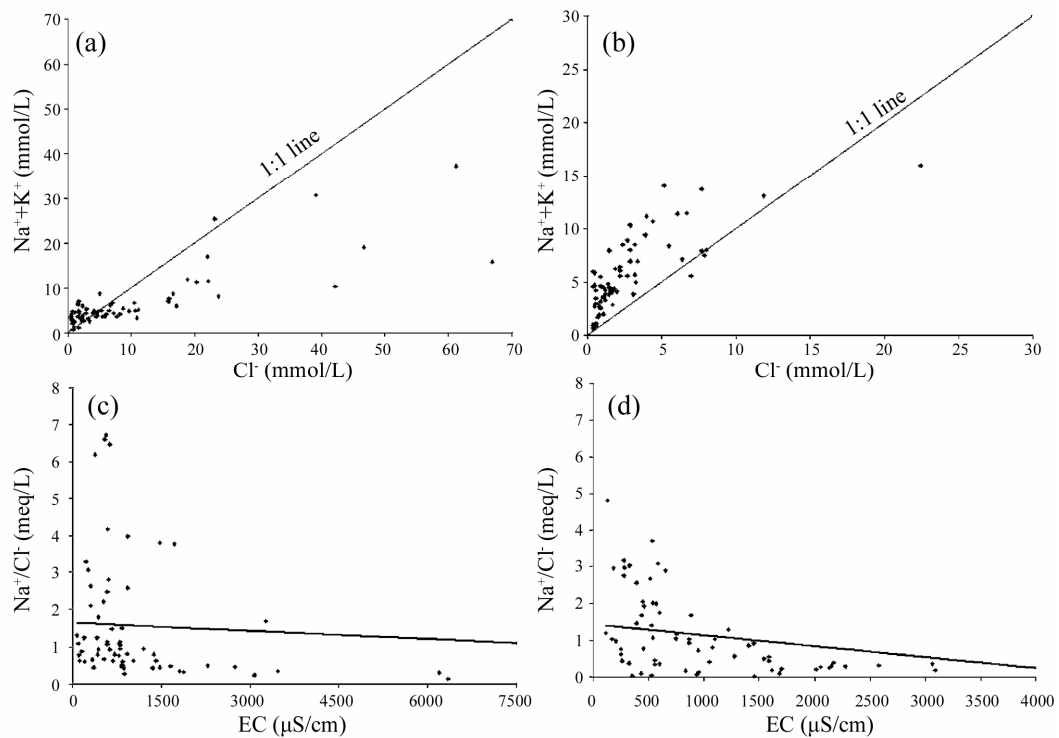


Fig. 7. Ion scatter diagrams for groundwater in the study area. (a)  $\text{Cl}^-$  versus  $(\text{Na}^++\text{K}^+)$  plot for post monsoon; (b)  $\text{Cl}^-$  versus  $(\text{Na}^++\text{K}^+)$  plot for pre monsoon; (c)  $\text{EC}$  versus  $\text{Na}^+/\text{Cl}^-$  plot for post monsoon; (d)  $\text{EC}$  versus  $\text{Na}^+/\text{Cl}^-$  plot for pre monsoon.



**Table 3a Ranges of chemical parameters and their comparison with the WHO and the Indian standards for drinking water (post monsoon)**

Chemical parameter	Concentration of ions		Range of standards (Desirable to permissible)		Sample well numbers exceeding permissible limits	
	Range	Mean	WHO (1997)	BIS (1991)	WHO (1997)	BIS (1991)
pH	6.35–8.74	7.87	7.00–9.20	6.50–9.20	3–5, 12, 55, 65	65
TDS (mg/L)	48–17024	1243	500–1500	500–2000	40, 43, 51–54, 60–62, 68	51–54, 60–62, 68
Ca <sup>2+</sup> (mg/L)	2–2290	124	75–200	75–200	51, 53, 54, 61, 62	51, 53, 54, 61, 62
Mg <sup>2+</sup> (mg/L)	0.60–1067	73	30–150	30–100	40, 51, 52, 61, 62	17, 32, 40, 51, 52, 59, 61–63, 69
Na <sup>+</sup> (mg/L)	16–795	138	50–200	-	16, 40, 43, 51–54, 61, 62	-
K <sup>+</sup> (mg/L)	1.30–225	22	10–12	-	16, 17, 19–21, 37, 38, 43, 51–54, 59–63	-
HCO <sub>3</sub> <sup>-</sup> (mg/L)	24–716	267	300–600	300–600	43, 52, 61, 62	43, 52, 61, 62
SO <sub>4</sub> <sup>2-</sup> (mg/L)	1.50–115	36	200–600	200–400	Within limit	Within limit
Cl <sup>-</sup> (mg/L)	18–3624	363	250–600	250–1000	16, 40, 43, 49, 51–54, 60–62	40, 51–53, 61
TH (mg/L)	60–5992	609	100–500	300–600	29, 32, 40, 43, 51–54, 59–63, 69	40, 51–54, 59–63, 69

**Table 3b Ranges of chemical parameters and their comparison with the WHO and the Indian standards for drinking water (pre monsoon)**

Chemical Parameter	Concentration of ions		Range of standards (Desirable to permissible)		Sample well numbers exceeding permissible limits	
	Range	Mean	WHO (1997)	BIS (1991)	WHO (1997)	BIS (1991)
pH	5.63–91	6.9	7.0–9.2	6.5–9.2	1–4, 6, 8–11, 16, 21, 24, 26, 27, 29, 30, 32, 38–40, 43, 44, 48, 49, 57–59, 61, 64–66	1–4, 6, 9, 11, 29, 39, 57, 58, 64, 66
TDS (mg/L)	75–6406	767	500–1500	500–2000	30, 43, 40, 51, 52, 56	40, 51, 52
Ca <sup>2+</sup> (mg/L)	20–196	86	75–200	75–200	Within limit	Within limit
Mg <sup>2+</sup> (mg/L)	1.26–220	41	30–150	30–100	40	29, 30, 40, 48, 69
Na <sup>+</sup> (mg/L)	8–338	121	50–200	-	21, 30, 38, 40, 43, 51, 52, 56	-
K <sup>+</sup> (mg/L)	2–151	29	10–12	-	1, 3, 14, 16–18, 20, 21, 29, 31, 36–38, 40, 54, 56, 59, 60, 63, 69	-
HCO <sub>3</sub> <sup>-</sup> (mg/L)	12–622	178	300–600	300–600	43	43
SO <sub>4</sub> <sup>2-</sup> (mg/L)	0.45–155	42	200–600	200–400	Within limit	Within limit
Cl <sup>-</sup> (mg/L)	16–1526	123	250–600	250–1000	51, 52	52
TH (mg/L)	75–1157	382	100–500	300–600	12, 14, 17, 21, 29, 30, 32, 40, 42, 43, 48, 49, 51, 52, 54, 63, 69	12, 14, 29, 30, 40, 42, 43, 48, 49, 51, 52, 54, 63, 69

The classification of groundwater based on the Na% by Wilcox (1955) is presented in Table 4. Wilcox diagram (Wilcox, 1955) was drawn with electrical conductivity (EC) and percent sodium (Na%) to sort the groundwater based on its suitability for irrigation (Fig. 8). Irrespective of the seasons majority of the samples fall into the excellent to good and good to permissible regions. Less than 10 percentages of samples fall into the doubtful to unsuitable and unsuitable regions. In these regions the soils have high EC and Ca<sup>2+</sup> and Mg<sup>2+</sup> ions replaces Na<sup>+</sup> ion when absorbed by the clay particles, which reduces the permeability and internal drainage and makes the soil hard and unfit for irrigation (Zhu et al., 2010).

### 5.3.2 Alkalinity hazard

The alkali or sodium hazard to groundwater is found by determining the sodium absorption ratio (SAR). The SAR was calculated using the following formula (Karnath, 1987):

$$SAR = Na^+ / \sqrt{Ca^{2+} + 4Mg^{2+}} \quad (3)$$

where all concentrations are expressed in meq/L.

The classification of groundwater based on SAR values is presented in Table 4. The salinity hazard to groundwater is measured with its electrical conductivity (EC). The salinity in the groundwater originates

mainly due to weathering of the rocks, leaching from the topsoil and some anthropogenic activities along with climate also had a minor influence. The classification of groundwater for irrigation purposes can be obtained by sketching the United States salinity diagram (USSL, 1954). The USSL diagrams for both the seasons (Fig. 9) are plotted by taking salinity hazard (EC) and alkalinity hazard (SAR) in X and Y axes respectively. The USSL diagrams show 85% of samples for both the post and pre monsoons fall into the C2S1 and C3S1 regions, showing a medium to high salinity in the groundwater of the study area. Other areas are affected by very high salinity. A salt tolerance cropping can be done in those areas which are affected by high salinity.

### 5.3.3 Residual sodium carbonate (RSC)

Residual sodium carbonate is another parameter used to classify groundwater for irrigation purposes. The RSC in groundwater is mainly due to the water have higher concentration of bicarbonate ions, which precipitates  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions as their carbonates and increases the  $\text{Na}^+$  ions which increases the sodium carbonate in the groundwater (Srinivasamoorthy et al., 2013). The RSC was calculated by the following equation (Eaton, 1950),

$$\text{RSC} = (\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{2+} + \text{Mg}^{2+}) \quad (4)$$

all of the concentrations are expressed in meq/L.

The classification of groundwater for irrigation based on the RSC values is presented in Table 4. According to this classification 71% of samples are within doubtful limit with  $\text{RSC} < 2.5$  for post monsoon and 91% of samples are within the doubtful limit for pre-monsoon season which shows that the residual sodium carbonate decreases in the pre-monsoon period.

### 5.3.4 Ion exchange

The concentration of ions in groundwater varies when there is an exchange with the ions of its aquifer environment during the periods of residence and movement (Latha and Rao, 2012). Chloroalkaline indices 1 and 2 were calculated for groundwater samples from the study area and suggested the ion exchange taking place in the groundwater (Prasanna et al., 2011). They were calculated using the following formulas:

$$\text{CAI 1} = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)] / \text{Cl}^- \quad (5)$$

$$\text{CAI 2} = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)] / (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-) \quad (6)$$

where the concentration of ions is in meq/L.

**Table 4** Classification of groundwater on the basis of Na%, SAR, EC, RSC, TH and TDS

Parameters	Range	Water class	Number of samples	
			POM	PRM
Na% (after Wilcox, 1955)	<20	Excellent	2	3
	20–40	Good	32	21
	40–60	Permissible	32	37
	60–80	Doubtful	3	8
	>80	Unsuitable	-	-
Alkalinity Hazard (SAR) after Richard (1954)	<10	Excellent	68	69
	10.0–18	Good	1	-
	18–26	Doubtful	-	-
	>26	Unsuitable	-	-
EC	<250	Excellent	8	6
	250–750	Good	30	28
	750–2000	Permissible	21	23
	2000–3000	Doubtful	1	7
RSC after Richard (1954)	<1.25	Good	41	62
	1.25 – 2.50	Doubtful	8	5
	> 2.50	Unsuitable	20	2
TH (Sawyer et al., 2003)	<75	Soft	3	-
	75–150	Moderately hard	2	7
	150–300	Hard	23	27
	>300	Very hard	41	35
TDS (USGS, 2000)	<1000	Fresh	54	52
	1000–3000	Saline	9	14
	3000–10000	Moderately saline	4	3
	>10000	Highly saline	2	-

Both the indices, CAI 1 and CAI 2 are negative if there is an exchange of calcium or magnesium in the groundwater with sodium and potassium in the aquifer material, and if there is a reverse ion exchange both indices will be positive (Schoeller, 1965). The obtained results show that 58% of samples show positive for both indices during the post-monsoon period and only 7% of samples show positive in the pre-monsoon

period. These observed results from the collected samples show that the reverse cationic exchange is the leading process in the post monsoon and normal ion exchange is the leading process in the pre-monsoon season.

**5.4 Seasonal variations**

The seasonal variation of major chemical parameters in the groundwater is spatially depicted in the figures (Figs. 10–13) prepared using the ArcGIS 9.2 software. The spatial diagrams show the variation of the different chemical parameters spatially over the study area. The total ionic budget is found to be more in the post-monsoon season when compared with the pre-monsoon season. The total dissolved solids spatial maps show that there is no major change in the overall distribution of the TDS. But comparing with the post-monsoon season, the TDS is considerably less the post-monsoon season. The sodium distribution maps are also similar in both seasons. Comparing both the seasons, the sodium concentration is low in the pre-monsoon season. In the case of K spatial maps the overall distribution illustrates that the distribution of potassium is higher in the pre-monsoon season. In majority of wells the potassium is found to be higher than the permissible limits.

Calcium in groundwater of the study area is generally within the permissible limits the case of both the seasons. In the post monsoon season fewer wells in the southern side of the study area show very high concentrations of calcium. Mg distribution maps also depict that majority of the samples in the study area have permissible amounts of magnesium except two or three samples. Sum of calcium and magnesium content is expressed as the hardness of the groundwater. The hardness of the groundwater may be mainly from surface water (Hounslow, 1995), which shows that anthropogenic activities is also the reason for high calcium and magnesium concentrations.

In the case of anions, chloride concentration is higher in the post-monsoon season. The southern side regions near Manakudy and the upper central region around the Nallur are showing higher concentration of chloride crossing the permissible limits. But in pre-monsoon season, majority of the samples are within the desirable limit. Only a smaller area near Manakudy has higher concentration of chloride. Few of the ground water samples has comparatively elevated concentrations of  $K^+$ ,  $Na^+$ , and  $Cl^-$  in both seasons. This may possibly because of anthropogenic pollution (Li S-L et al., 2005). The rainwater is also a major source for chloride ions in the groundwater (Hounslow, 1995).

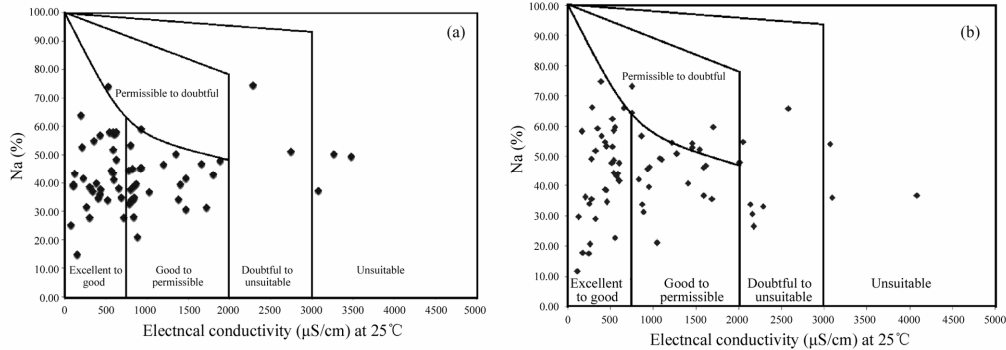


Fig. 8. Rating of groundwater samples by Wilcox diagram on the basis of EC and %Na. (a) Post monsoon; (b) pre monsoon.

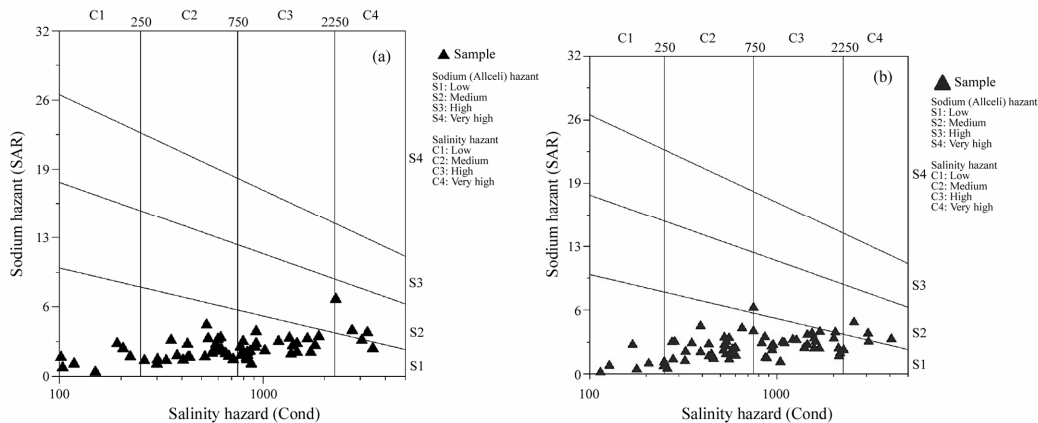


Fig. 9. Salinity and alkalinity hazard of groundwater samples depicted in USSL Diagram. (a) Post monsoon; (b) pre monsoon.

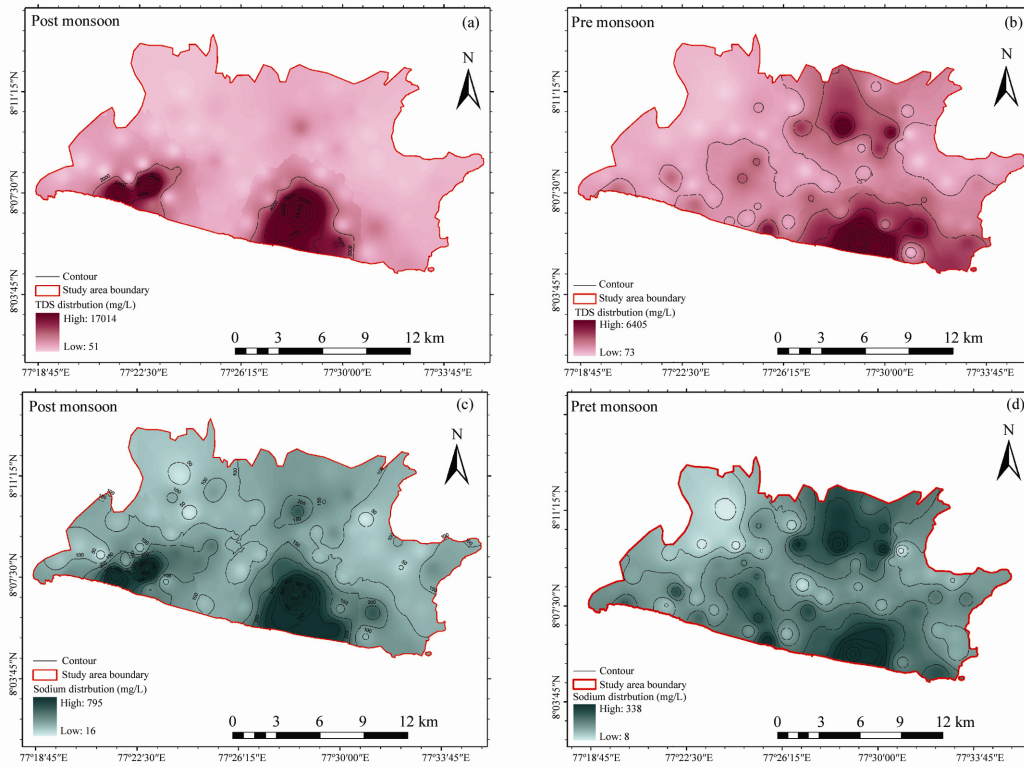


Fig. 10. (a) Spatial distribution of total dissolved solids (TDS) in the study area for post monsoon; (b) spatial distribution of total dissolved solids (TDS) in the study area for pre monsoon; (c) spatial distribution of sodium ( $\text{Na}^+$ ) in the study area for post monsoon; (d) spatial distribution of sodium ( $\text{Na}^+$ ) in the study area for pre monsoon.

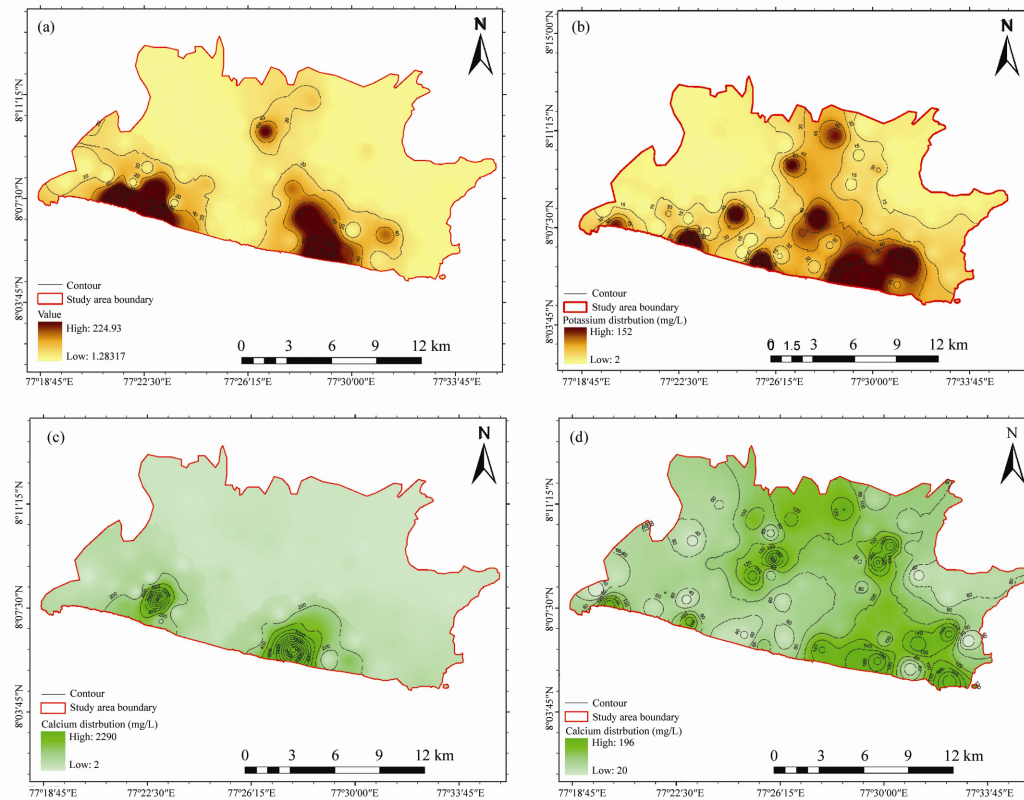


Fig. 11. (a) Spatial distribution of potassium ( $\text{K}^+$ ) in the study area for post monsoon; (b) spatial distribution of potassium ( $\text{K}^+$ ) in the study area for pre monsoon; (c) spatial distribution of calcium ( $\text{Ca}^{2+}$ ) in the study area for post monsoon; (d) spatial distribution of calcium ( $\text{Ca}^{2+}$ ) in the study area for pre monsoon.

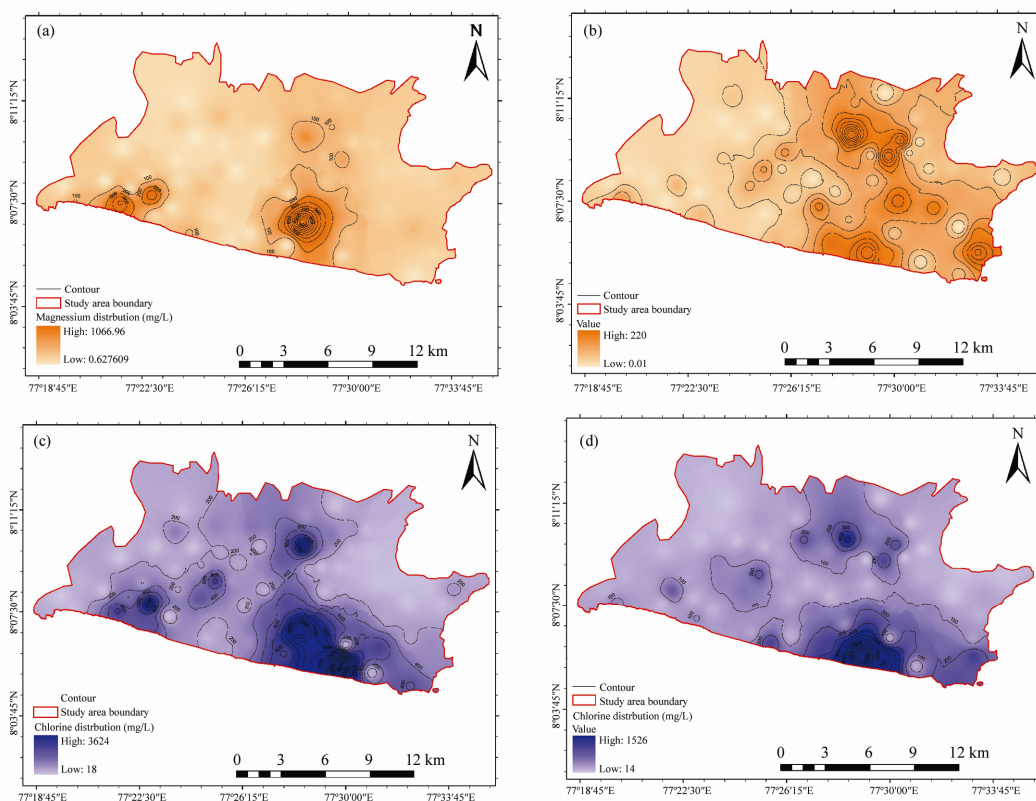


Fig. 12. (a) Spatial distribution of magnesium ( $Mg^{2+}$ ) in the study area for post monsoon; (b) spatial distribution of magnesium ( $Mg^{2+}$ ) in the study area for pre monsoon; (c) spatial distribution of Chloride ( $Cl^-$ ) in the study area post monsoon; (d) spatial distribution of Chloride ( $Cl^-$ ) in the study area pre monsoon.

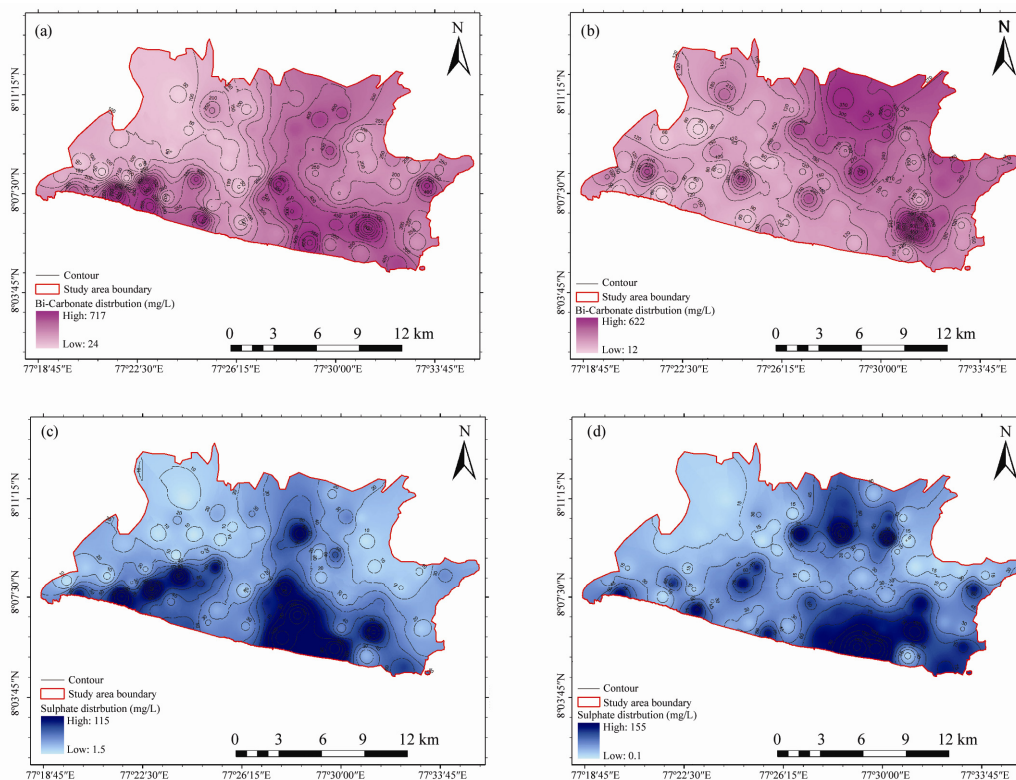


Fig. 13. (a) Spatial distribution of bi-carbonate ( $HCO_3^-$ ) in the study area for post monsoon; (b) spatial distribution of bi-carbonate ( $HCO_3^-$ ) in the study area for pre monsoon; (c) spatial distribution of sulphate ( $SO_4^{2-}$ ) in the study area for post monsoon; (d) spatial distribution of sulphate ( $SO_4^{2-}$ ) in the study area for pre monsoon.

In the spatial maps of sulphate distribution, there are no notable changes the concentration of sulphate during both seasons. In both seasons, groundwater from the south and central parts were found to have more sulphate ions, and this may be due to the irrigation return flow. The bicarbonate ion distribution maps show that majority of the samples from the study area are having a desirable amount of bicarbonate in the groundwater. But in the post-monsoon season  $\text{HCO}_3^-$  ion is the dominant anion, which is found to be more in the central, east and southern parts of the study area.

From the overall spatial analysis, the regions around Manakudy and Nallur in the southern side and upper central region of the study area were seemed to be highly contaminated in both seasons. The saline intrusion around Manakudy and the runoff of excess fertilizers from the surrounding agricultural lands and percolation of domestic sewage in Nallur may be the reasons for the contamination of groundwater of these areas. The bicarbonate concentration is higher in central and northwestern side of the study area may be because of rock water interaction.

## 6 Conclusions

The quality assessment of groundwater in Agastheeswaram taluk shows it is slightly alkaline during the post-monsoon and it is slightly acidic in the pre-monsoon season. The order of cationic abundance is  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$  except few samples where  $\text{Ca}^{2+}$  replaces  $\text{Na}^+$  in the post monsoon season by cationic exchange reactions. The hydrogeochemistry also reveals the order of anionic supremacy  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$  in the post monsoon and the trend changed as  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$  in the pre-monsoon, due to the carbonate weathering in the pre-monsoon season. The groundwater usage for drinking purposes is restricted in the wells 40, 41, 51, 52, 54, 61, 68 and 69 representing the areas Nallur, Koilvilai, Manakudy, Puthalam, Rajakkamangalam, Pallam and Thengamputhoor respectively of Agastheeswaram taluk because of high contents of TDS,  $\text{Na}^+$ , and  $\text{Cl}^-$  and hardness. High salinity with medium sodium hazard at some locations shows that the groundwater is not suitable for regular agricultural activities. Soils affected with high salinity and alkalinity hazards require gypsum/lime treatment to improve permeability by base exchange. The observed chemical variations in both seasons may be because of rock-water interactions, ion-exchange reactions and percolation of agricultural waste water from the surrounding agricultural fields. In general the groundwater from majority of the areas in the study area is suitable for domestic and irrigation usage and some needs remedial measures.

## References

- Aghazadeh N., Nojavan M., and Mogaddam A.A. (2011) Effects of road-deicing salt (NaCl) and saline water on water quality in the Urmia area, northwest of Iran [J]. *Arabian Journal of Geosciences*. **5**, 565–570.
- Appelo C.A.J. and Postma D. (1993) *Geochemistry, Groundwater and Pollution* [M]. Rotterdam: AA Balkema.
- APHA (1989) *Standard Methods for the Examination of Water and Waste Water* (19<sup>th</sup> edition) [Z]. American Public Health Association. Washington, DC.
- Ballukraya P.N. and Ravi R. (1995) Hydrogeology of Madras City aquifer [J]. *Journal of the Geological Society of India*. **45**, 87–96.
- BIS (1991) *Indian Standard Specification for Drinking Water* [Z]. IS:10500, Bureau of Indian Standards.
- CGWB (2008) *Technical Report, Central Ground Water Board* [R].
- Eaton F.M. (1950) Significance of carbonate in irrigation waters [J]. *Soil Science*. **69**, 123–133.
- Fetter C.W. (1994) *Applied Hydrogeology* (Third edition) [Z]. pp.310. Macmillan College Publication, New York.
- Garrels R.M. and Mackenzie F.T. (1967) *Origin of the Chemical Compositions of Some Springs and Lakes* (ed. Stumm W.). Equilibrium concepts in natural water systems [J]. *Journal of the American Chemical Society*. 222–242.
- Gibbs R.J. (1970) Mechanisms controlling world's water chemistry [J]. *Science*. **170**, 1088–1099.
- GSI (2005) *Geology and Mineral Map of Kanyakumari District* (eds. Sundaram R., Ranganathan M., and Vasudevan D.) [Z]. Geological Survey of India.
- Hounslow A.W. (1995) *Water Quality Data—Analysis and Interpretation* [C]. pp.56. Lewis publishers, USA.
- Jameel A.A. and Hussain A.Z. (2012) Monitoring the quality of groundwater on the bank of Uyyakondan channel of River Cauvery at Tiruchirappalli, Tamil Nadu—India [J]. *Environmental Monitoring and Assessment*. **183**, 103–111.
- Karnath K.R. (1987) *Groundwater Assessment, Development and Management* [C]. Tata McGraw Hill, New Delhi.
- Li Siliang, Liu Congqiang, Tao Faxiang, Lang Yunchao, and Han Guilin (2005) Carbon biogeochemistry of ground water, Guiyang, Southwest China [J]. *Ground Water*. **43**, 494–499.
- Mandel and Shiftan (1981) *Ground Water Resources Academic* [C]. pp.269. New York.
- O'Brien J.E. and Majewski J.C. (2002) Effects of deicing salt on groundwater characteristics [J]. *Environmental Letters*. **8**, 303–313.
- Perumal S.B. and Thamarai P. (2008) Groundwater quality after Tsunami in coastal area of Kanyakumari, South Tamilnadu, India [J]. *International Journal of Applied Environmental Sciences*. **3**, 37–55.
- Piper A.M. (1944) A graphic procedure in the geochemical interpretation of water analysis [J]. *Transactions—American Geophysical Union*. **25**, 914–923.
- Prasanna M.V., Chidambaram S., Senthil Kumar G., Ramanathan A.L., and Nainwal H.C. (2011) Hydrogeochemical assessment of groundwater in Neyveli Basin, Cuddalore District, South India [J]. *Arabian Journal of Geosciences*. **4**, 319–330.
- PWD (2005) *Groundwater Perspectives: A Profile of Kanyakumari District*,

- Tamil Nadu [Z]. Tamil Nadu Public Works Department, India.
- Raju N.J., Shukla U.K., and Ram P. (2011) Hydrogeochemistry for the assessment of groundwater quality in Varanasi: A fast-urbanizing center in Uttar Pradesh, India [J]. *Environmental Monitoring and Assessment*. **173**, 279–300.
- Ramesh K. and Elango L. (2012) Groundwater quality and its suitability for domestic and agricultural use in Tondiar River Basin, Tamil Nadu, India [J]. *Environmental Monitoring and Assessment*. **184**, 3887–3899.
- Ramkumar T., Venkatraman S., Anithamary I., and Ibrahim S.M.S. (2012) Evaluation of hydrogeochemical parameters and quality assessment of the groundwater in Kottur blocks, Tiruvarur district, Tamilnadu, India [J]. *Arabian Journal of Geosciences*. **6**, 101–108.
- Richards L.A. (1954) *Diagnosis and Improvement of Saline and Alkali Soils* [C]. pp.160. U.S. Department of Agriculture Handbook 60, Washington.
- Sadhana C. (1994) Water pollution from mass bathing in River Mandakini during Chitrakoot Deepawali mela 1993 [J]. *Indian Journal of Environmental Protection*. **14**, 758–765.
- Sami K. (1992) Recharge mechanisms and geochemical processes in a semi-arid sedimentary basin, Eastern Cape, South Africa [J]. *Journal of Hydrology*. **139**, 27–48.
- Sawyer C.N., Mccarty P.L., and Parkin G.F. (2003) *Chemistry for Environmental Engineering and Science*. (5<sup>th</sup> edition). [M]. pp.752. McGraw-Hill, New York.
- Schoeller H. (1965) Qualitative evaluation of groundwater resources. In *Methods and Techniques of Groundwater Investigations and Development* [M]. pp.54–83. UNESCO, Paris.
- Srinivasamoorthy K., Nanthakumar C., Vasanthavigar M., Vijayaraghavan K., Rajivgandhi R., Chidambaram S., Anandhan P., Manivannan R., and Vasudevan S. (2011) Groundwater quality assessment from a hard rock terrain, Salem District of Tamilnadu, India [J]. *Arabian Journal of Geosciences*. **4**, 91–102.
- Srinivasamoorthy K., Vasanthavigar M., Vijayaraghavan K., Sarathidasan R., and Gopinath S. (2013) Hydrochemistry of groundwater in a coastal region of Cuddalore District, Tamilnadu, India: Implication for quality assessment [J]. *Arabian Journal of Geosciences*. **6**, 441–454.
- Stallard R.F. and Edmond J.M. (1983) Geochemistry of the Amazon River. The influence of the geology and weathering environment on dissolved load [J]. *Journal of Geophysical Research-Atmospheres*. **88**, 9671–9688.
- Subba Rao N. (2008) Factors controlling the salinity in groundwaters from a part of Guntur District, Andhra Pradesh, India [J]. *Environmental Monitoring and Assessment*. **138**, 327–341.
- Subramani T., Elango L., and Damodarasamy R. (2005) Groundwater quality and its suitability for drinking and agricultural use in Chithar River Basin, Tamil Nadu, India [J]. *Environmental Geology*. **47**, 1099–1110.
- Subramanian A. (2011) Ground water quality assessment of Nagercoil Town [J]. *Journal of Environment and Earth Science*. **1**.
- Latha S. and Rao N. (2012) An integrated approach to assess the quality of groundwater in a coastal aquifer of Andhra Pradesh, India [J]. *Carpathian Journal of Earth and Environmental Sciences*. **66**, 2143–2169
- Jacob C.T., Azariah J., and Roy A.G.V. (1999) Impact of textile industries on River Noyyal and riverine groundwater quality of Tirupur, India [J]. *Pollution Research*. **18**, 359–368.
- Todd D.K. (1980) *Groundwater Hydrology* (2<sup>nd</sup> edition) [M]. Wiley, New York.
- Tyagi S.K., Datta P.S., and Pruthi N.K. (2009) Hydrochemical appraisal of groundwater and its suitability in the intensive agricultural area of Muzaffarnagar District, Uttar Pradesh, India [J]. *Environmental Geology*. **56**, 901–912.
- USGS (US Geological Survey) (2000) *Classification of Natural Ponds and Lakes* [Z]. Department of the Interior, Washington DC.
- USRSL (US Regional Salinity Laboratory) (1954) *Diagnosis and Improvement of Saline and Alkali Soils* [Z]. pp.1–160.
- Vasanthavigar M., Srinivasamoorthy K., Vijayaragavan K., Rajiv Ganthi R., Chidambaram S., Anandhan P., Manivannan R., and Vasudevan S. (2010) Application of water quality index for groundwater quality assessment: Thirumanimuttar Sub-basin, Tamilnadu, India [J]. *Environmental Monitoring and Assessment*. **171**, 595–609.
- WHO (1997) *Guideline for Drinking Water Quality (Recommendations)* [Z]. (Vol. 1, 2<sup>nd</sup> ed). Geneva.
- Wilcox L.V. (1955) *Classification and Use of Irrigation waters*. USDA, Circular 969, Washington DC, USA.
- Zhu Gaofeng, Su Yonghong, Huang Chunlin, Qi Feng, and Liu Zhiguang (2010) Hydrogeochemical processes in the groundwater environment of Heihe River Basin, Northwest China [J]. *Environmental Earth Sciences*. **60**, 139–153.