

# Physicochemical parameters and their sources in groundwater in the Thirupathur region, Tamil Nadu, South India

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**Abstract** This study reports physicochemical characteristics and their sources in groundwater in Thirupathur region in Tamil Nadu, India. For this purpose, groundwater samples were collected and analysed using standard methods. A wide seasonal variation was showed for the majority of the samples; higher concentration was observed in the pre-monsoon season. Concentration of fluoride was quite alarming in many locations. Groundwater is found to be dominated by  $\text{Na}^+$ ,  $\text{Ca}^+$ ,  $\text{HCO}_3$  and  $\text{Cl}^-$ . Gibbs plot showed the dominance of rock–water interaction. Geology of the area in comparison with the results obtained in the chemical cross plots showed the dominance of silicate weathering, with a minor contribution from the cation exchange. Other processes such as evaporation dissolution of carbonate and gypsum were proved to be ineffective. However, dissolution of fluoride minerals present in the geological formation is the major source of fluoride in groundwater.

**Keywords** Physicochemical parameters · Groundwater · Thirupathur · Tamil Nadu · India

## Introduction

Accessibility to a safe and reliable source of water is essential for sustainable development. The reliability of the water for various purposes depends on the chemical and

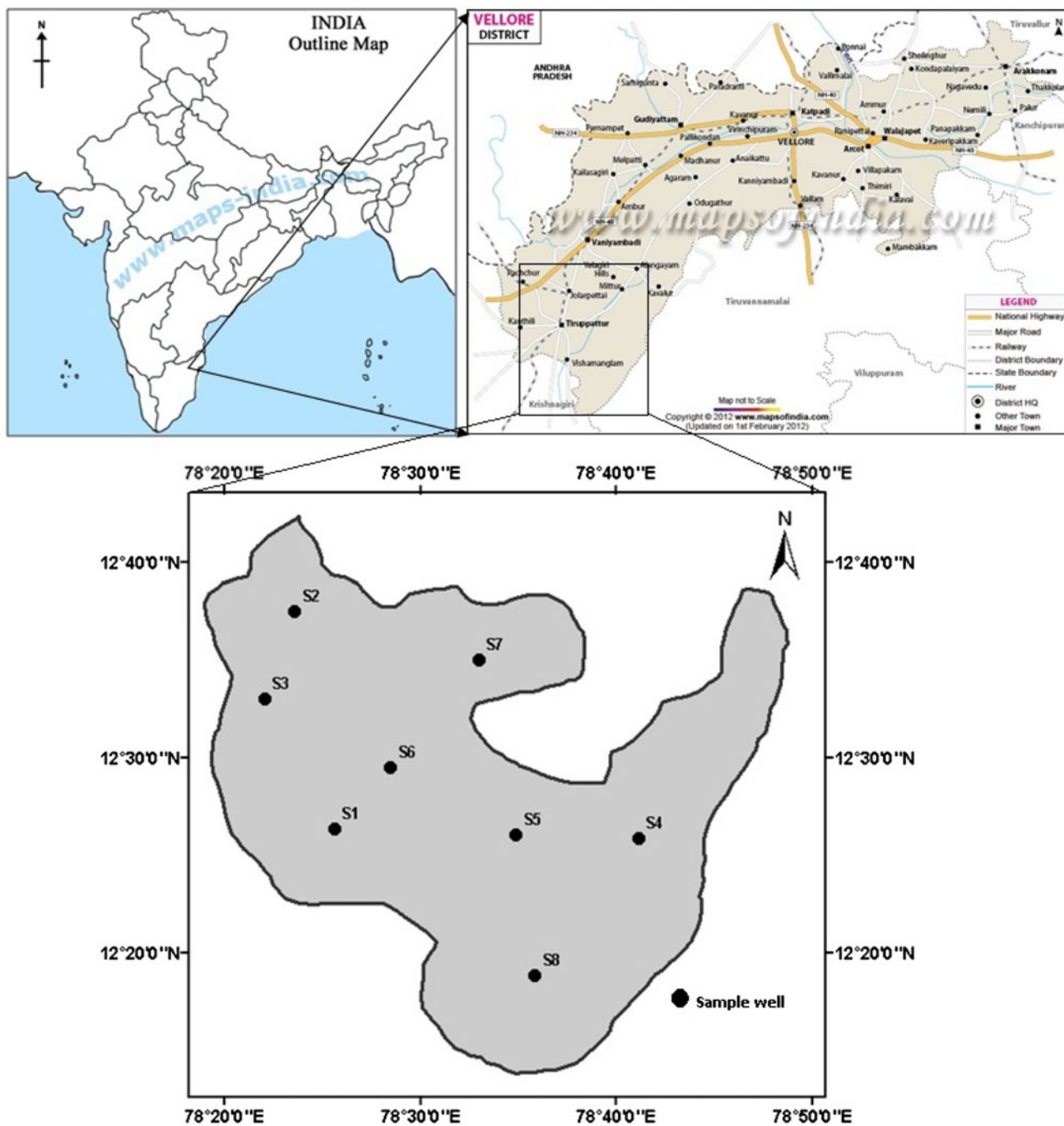
physical quality of water. Groundwater chemistry is mainly controlled by natural as well as anthropogenic factors. Chemical composition of geologic formations affects the hydrochemical characteristics of groundwater during their circulation in the subsurface (Elango et al. 2003). This underground passage through the pore spaces and weathered zones may alter the natural composition of the groundwater by the action of various hydrochemical processes (Rajmohan and Elango 2004). In other words, composition of water can reveal the various processes in groundwater. Groundwater chemistry can be modified by a variety of anthropogenic sources. These include point sources, such as waste disposal facilities, industrial pollution, wastewater treatment works, on site sanitation, cemeteries, and many others (Amoako et al. 2011). Systematic assessment of the physicochemical parameters, their sources and controlling hydrochemical processes are essential in maintaining the sustainable ecosystem.

Physicochemical parameters as well as hydrochemistry were studied by many researchers to assess the characteristics of groundwater (Sanchez Martos et al. 1999; Subba Rao et al. 2002; Bhardwaj and Singh 2010). Major ion chemistry of the groundwater in the Ejina basin was studied by Jianhua et al. (2009). This study reported the dominance of gypsum halite dissolution and evaporation processes are predominantly controlling the groundwater quality. A series of factors, such as refreshing by recharge waters, concentration by evaporation, dissolution of evaporites, and mixing with older and more saline ground water were identified as the sources of major chemical characteristics of the groundwater in arid regions of Namibia (Shanyengana et al. 2004). Rim-Rukeh et al. (2007) studied the physicochemical properties of both surface and groundwater in the Niger delta and reported severe health effects on human beings by the consumption of contaminated water. Physicochemical

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**Fig. 1** Location map of the study area showing sampling points

parameters of the Sutlej River in India were studied by Jindal and Sharma (2011). They concluded that two stretches out of three were not suitable for human consumption. Abdul Jameel and Sirajudeen (2006) evaluated the sources of physicochemical parameters and their present level in groundwater in the Pettavaithalai area in Tamil Nadu and reported groundwater contamination due to high human, industrial and agricultural activities.

This study was carried out in the Thirupathur region in the Vellore district of Tamil Nadu. This is typical hard rock terrain with tropical climate. Groundwater is the major source of water for drinking and domestic purposes. However, this area is listed under the overexploited regions in Tamil Nadu state. On this background, we carried out this study with an objective to evaluate the status of the physicochemical parameters and their specific sources in

**Table 1** Physicochemical parameters in the groundwater of the study area (post-monsoon)

Long	Lat	ID	pH	EC	TDS	Ca	Mg	Na	K	Cl	SO <sub>4</sub>	CO <sub>3</sub>	HCO <sub>3</sub>	F	NO <sub>3</sub>
78.48	12.42	S1	8.6	1,300	875	12	46	248	4	163	173	65	258	1.75	8
78.44	12.61	S2	8.1	1,350	869	28	36	242	5	162	154	0	414	1.69	8
78.47	12.55	S3	8.3	1,300	783	28	63	163	10	199	152	28	226	1.15	6
78.69	12.43	S4	8.3	1,250	724	26	51	196	9	142	76	54	305	0.26	4
78.58	12.43	S5	8.4	1,250	787	22	55	198	9	158	69	62	348	2.15	9
78.48	12.49	S6	8.7	1,720	1,027	24	62	276	4	241	175	53	367	2.45	2
78.55	12.58	S7	8.6	1,220	718	18	31	194	30	216	73	36	214	0.53	3
78.70	12.37	S8	8.8	1,960	1,231	16	51	396	5	164	127	135	595	2.75	9

All the ions as well as TDS were measured in mg/l, while EC measured in  $\mu\text{S/cm}$  pH is unitless

**Table 2** Physico chemical parameters of the study area (pre-monsoon)

Long	Lat	ID	pH	EC	TDS	Ca	Mg	Na	K	Cl	SO <sub>4</sub>	CO <sub>3</sub>	HCO <sub>3</sub>	F	NO <sub>3</sub>
78.48	12.42	S1	7.7	3,330	1,845	184	156	269	3	922	74	0	305	0.52	19
78.44	12.61	S2	9	1,180	728	20	32	216	2	124	86	66	311	1.49	6
78.47	12.55	S3	8.5	1,350	839	32	62	179	5	216	192	18	226	1.12	5
78.69	12.43	S4	8.7	1,410	941	32	56	228	4	191	269	36	232	1.41	2
78.58	12.43	S5	7.8	3,150	1,709	168	175	200	3	922	77	0	159	0.45	19
78.48	12.49	S6	8.8	1,680	1,079	16	55	308	2	252	202	72	336	1.75	1
78.55	12.58	S7	8.2	2,430	1,491	116	73	288	6	585	80	0	128	0.5	63
78.70	12.37	S8	9	1,430	887	14	33	274	5	78	187	45	439	1.66	7

All the ions as well as TDS were measured in mg/l, while EC measured in  $\mu\text{S/cm}$  pH is unitless

the groundwater of the region. This is a vital step in future groundwater developments in this region.

### Description of the study area

The present study area, Thirupathur, is located in the Vellore district in Tamil Nadu. A detailed map of the study area with groundwater sample points is shown in Fig. 1. The study area enjoys a tropical climate with a range of temperature from 18.2 to 36.8 °C. The highest temperature is observed during May and the lowest in December. Both southwest and northeast monsoons are contributing to the annual normal rainfall (949.8 mm). The contribution of southwest monsoon and northeast monsoon ranges from 45 to 52 and 30 to 43 %, respectively. Heavy rains are often associated with depressions and storms, which generally occur in the Bay of Bengal during the NE monsoon. Structural hills and the residual hills are observed at the SE part of the region. Geologically, the sub-basin is covered by Peninsular Gneisses, charnockites and embraces a variety of granitic rocks, such as massive and porphyritic biotite granite, biotite gneiss of foliated varieties. They are massive, coarse grained granites containing quartz, feldspars in varying proportions with biotite and hornblende as the common ferromagnesium minerals (Rajmohan and

Elango 2004). Calcite and dolomite are present in the sediments at certain patches. Groundwater occurs under phreatic conditions in weathered, fractured, jointed and faulted portions of crystalline rocks. Thickness of the weathered zone varies from less than a meter to about 15 m in the area depending on the topography. The pore spaces developed in the weathered portions act as a shallow granular aquifer and form potential water-bearing zones. The depth of wells in this region reaches 10 m. Most of the wells in the hard rock region are large diameter dug wells. Generally, the water level in the crystalline formations is 6–9 m below ground level. In high summer period, many wells dried up occasionally.

### Materials and methods

Extensive geological and hydrogeological survey was conducted prior to the sampling campaign. Special care has been given to those areas where the contamination was expected. The wells, which would have dried up in the summer season, were avoided. Based on this study, eight representative bore wells were selected for sampling. Samples were collected from the same wells for post-monsoon (January 2010) and pre-monsoon (July 2010) period. Sampling was carried out using pre-cleaned

polythene bottles. Collected samples were preserved at 4 °C and taken into the laboratory for analysis. Electrical conductivity (EC) and pH were measured as in situ. Chemical parameters were determined by the standard methods recommended in American Public Health Association (APHA 1995).  $\text{HCO}_3$ , Cl, Ca and Mg were determined by titration.  $\text{SO}_4$  was determined by UV–visible spectrophotometer. A flame photometer was employed in the analysis of Na and K. Extreme precision was maintained throughout the analysis. The ion balance error was calculated and all the samples show an error of  $\pm 5\%$ .

## Results and discussion

Physicochemical parameters of individual groundwater samples for the post- and pre-monsoon season are given in Tables 1 and 2. Range of pH in the groundwater samples was 8.1–8.8 (post-monsoon) and 7.7–9 (pre-monsoon), with a general alkaline nature. The permissible limit of pH for drinking water is 6.5–8.5 (WHO 2011). However, 38 % of the samples from both seasons exceeded the maximum permissible limit. Electrical conductivity (EC) of post-monsoon samples was in the range of 1,220–1,960  $\mu\text{S}/\text{cm}$ . The majority of the samples (75 %) were within the permissible limit 1,500  $\mu\text{S}/\text{cm}$ , i.e., TDS value is  $<1,000$  mg/l (WHO 2011). In the pre-monsoon season, 50 % of the samples showed an EC greater than 1,500  $\mu\text{S}/\text{cm}$ . Moreover, all the samples exceeded the permissible limit showed an elevated concentration of Cl in the groundwater and this suggesting the possibility of anthropogenic inputs.

Sodium is an important ion in the earth's crust, especially in hardrocks like granites and gneisses in the form of plagioclase feldspar (Srinivasamoorthy et al. 2008; Krishna Kumar et al. 2009) Concentration of sodium is ranged between 163 and 396 mg/l in the post-monsoon period. Four samples (50 %) exceeded the permissible limit of 200 mg/l. Although in the pre-monsoon season, concentration of Na varied from 179 to 308 mg/l and six samples (75 %) exceeded the permissible limit. All samples showed an increment in concentration during the pre-monsoon season except S8. This variation hints complex hydrogeochemical processes occurring in the study area. Potassium is a major constituent of most of the silicate minerals and their alteration product, clay. Calcium and magnesium are mainly originated from the carbonate minerals, such as calcite and dolomite. Magnesium can also originate from the ferro-magnesium minerals, such as olivine, garnet and also from silicate families like amphiboles and pyroxenes. In the post-monsoon season, potassium concentration varied from 4 to 30 mg/l. For the pre-monsoon season, it was in the range of 2 to 6 mg/l. For both seasons, K concentrations were well within the permissible limit 12 mg/l

(WHO 1993). Calcium concentrations for the post-monsoon season were in the range of 12–28 mg/l, where as it showed a range 14–184 mg/l in the pre-monsoon season. Permissible limit of Ca in the drinking water is 75 mg/l (WHO 1993). Approximately, 37.5 % of the pre-monsoon samples exceeded the permissible limit, while all the samples in post-monsoon season were well within the guideline value. The level of magnesium was ranged from 31 to 63 and 32 to 175 mg/l in the post- and pre-monsoon seasons, respectively. The results show that 75 % of the pre-monsoon samples and 62.5 % of the post-monsoon samples were exceeded the permissible limit 50 mg/l. This variation in concentration of Ca and Mg is due to the seasonal changes in the rock–water interactions during pre- and post-monsoon periods. An increase in the concentration was observed for Ca and Mg during the pre-monsoon period. The possible explanation for the elevated concentration of Ca and Mg in the groundwater during the pre-monsoon season may be due to the increased residence time of the groundwater due to sluggish flow (Han et al. 2010).

Carbonates in the pre-monsoon season ranged between 0 and 65 mg/l and it showed a range 0–135 mg/l during post-monsoon period. The bicarbonate concentration was ranged between 128 and 439 and 214 and 535 mg/l during the pre- and post-monsoon seasons, respectively. The major origin of these ions are largely depends on the carbonate dissolution and silicate weathering. Weathering of silicate minerals may be the dominant process in the study area in the absence of carbonate minerals. Similar results were reported from the nearby areas (Rajmohan and Elango 2004; Subramani et al. 2010). However, there is no standard guideline value available for  $\text{CO}_3$  and  $\text{HCO}_3$  in drinking water. Chloride is a common toxicity in water, which adds salty taste and cause damage to the pipe networks. It is not absorbed by the soil, which results in its free movement. Plants will take high chloride water and deposit on the leaves. This may cause leaf burn and drying of leaf tissues (Ayers and Westcot 1994; Vasanthavigar et al. 2010). Chloride concentration in the study area for post-monsoon season was in the range of 142–241 mg/l, whereas 78–922 mg/l in the pre-monsoon season. A wide range of seasonal variation was exhibited by chloride in the study area with 50 % of the samples exceeded the permissible limit 250 mg/l in the pre-monsoon season. In the well number S5, concentration of Cl increased six times that of the post-monsoon period. In the tropical region high temperature during summer may concentrate the groundwater Cl due to evaporation (Beaucaire et al. 1999). The other reason may be the recirculation of irrigation water and/or water logging.

Sulphates originate from numerous sources including natural as well as industrial effluents; however, the highest



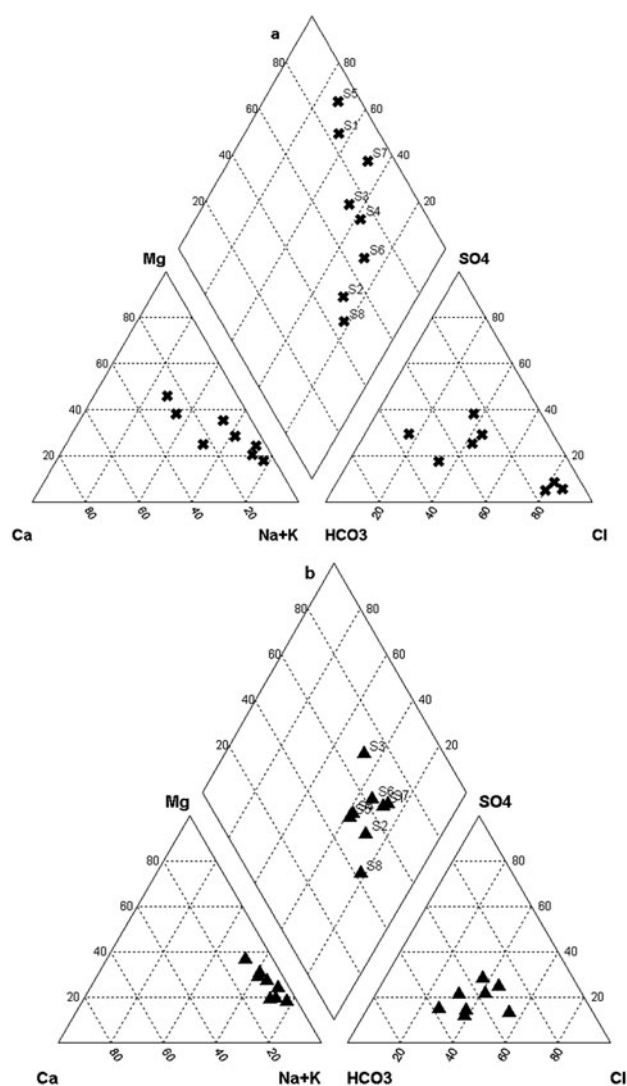
levels usually occur in groundwater are from natural mineral sources, including barite ( $\text{BaSO}_4$ ), epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (Greenwood and Earnshaw 1984). Sulphate of the study area varied from 73 to 175 and 74 to 269 mg/l during the post- and pre-monsoon seasons, respectively. One sample from the pre-monsoon period showed exceedingly high concentration than the permissible limit 250 mg/l (WHO 1993). Higher concentration  $\text{SO}_4$  may cause gastrointestinal irritation particularly when Mg and Na are also present in drinking water resources (Suthar et al. 2009).

Natural nitrate levels in the naturally occurring groundwater do not exceed 4–9 mg/l for nitrate and 0.3 mg/l for nitrite (USEPA 1987). Fertilizer application, septic tank uses, animal farming atmospheric deposition, and industrial and wastewater discharges, are the possible sources of  $\text{NO}_3$  in groundwater (Liu et al. 2005). In the present study, concentration of nitrate was ranged between 2 and 9 mg/l in the post-monsoon season, whereas 1 and 63 mg/l in pre-monsoon season. One well in the pre-monsoon season exceeded the permissible limit 45 mg/l (WHO 1993) at Katter area, indicating the origin from agricultural fertilizers.

Important factor that determines the concentration of fluoride in groundwater is availability and the solubility of F minerals, pH, temperature, anion exchange capacity of aquifer materials, type of geological materials and residence time, porosity, structures, depth, groundwater age, the concentration of carbonates and bicarbonates in the water (Apambire et al. 1997; Kim and Jeong 2005). The permissible range of fluoride in groundwater is 0.6–1.2 mg/l, with an extendable limit up to 1.5 mg/l (BIS 1992). In Thirupathur area concentration of fluoride (0.26–2.75 mg/l) was exceeded the permissible limit in 62.5 % the samples during post-monsoon season and 25 % samples in the post-monsoon season (0.45–1.7 mg/l), respectively. Intake of high fluoride groundwater will lead to dental fluorosis, skeletal fluorosis, deformation of ligaments and bending of the spinal column (Handa 1975; Rukah and Alsokhny 2004)

#### Groundwater types

Groundwater types were analysed by a Piper diagram (Piper 1944). Four types water samples, Ca–Cl, Na–Cl, Ca–Na– $\text{HCO}_3$  and mixed Ca–Mg–Cl, were identified in the groundwater samples of the study area. During the post-monsoon season, most of the samples were plotted in Na–Cl type field in the piper diagram, except sample number S8. Sample number S8 showed the Ca Na– $\text{HCO}_3$  type of water. Pre-monsoon samples were scattered over the above mentioned four types; however, majority of them were NaCl type. Sample number S5 behaved slightly different



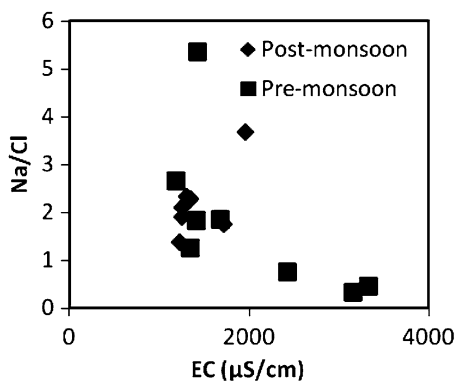
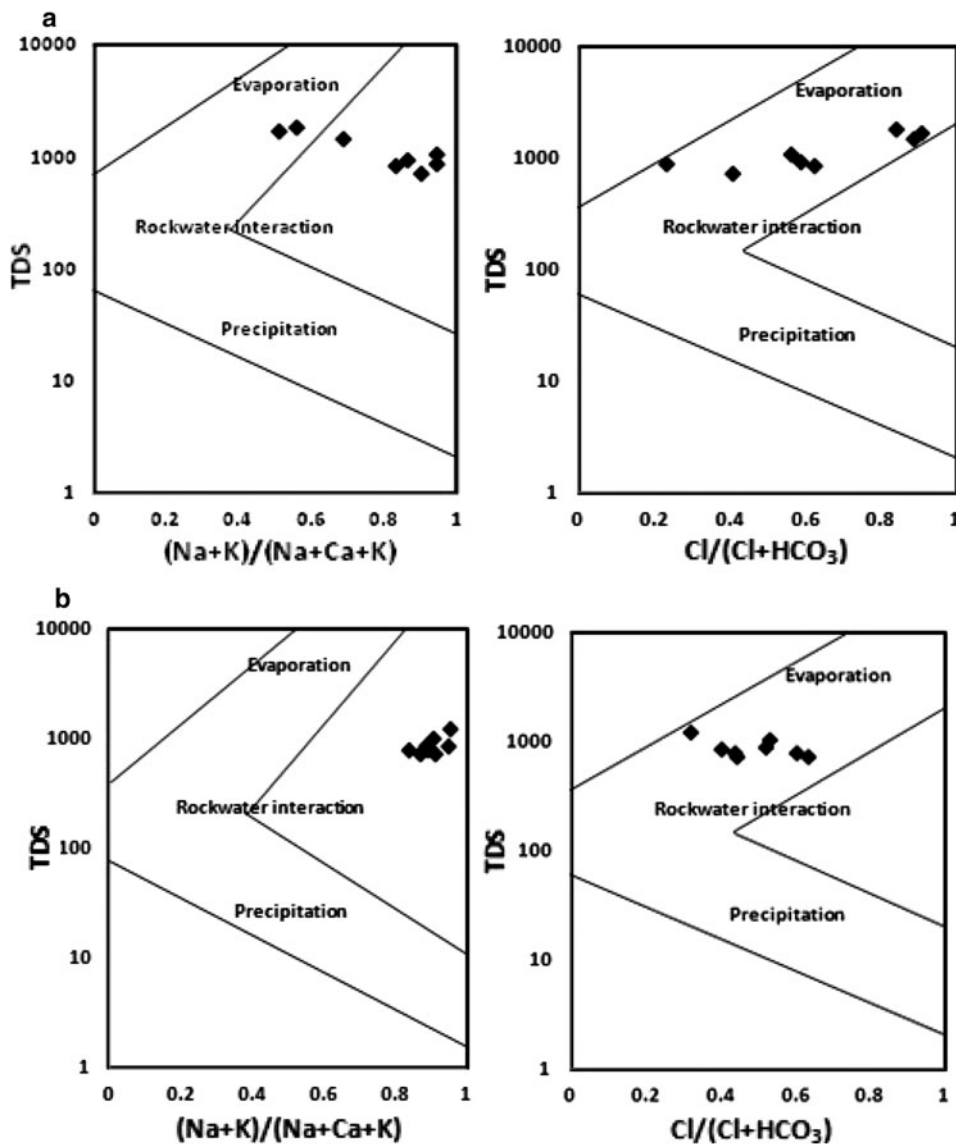
**Fig. 2** Piper trilinear diagram shows hydrogeochemical facies for groundwater of the study area. **a** Pre-monsoon, **b** post-monsoon

by showing Ca–Cl type. Piper trilinear diagram for the groundwater in the study area is given in Fig. 2.

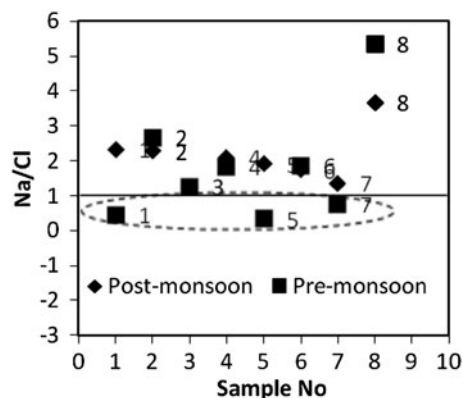
Factors controlling the hydrochemical parameters and their sources

Effect of the natural processes like evaporation, rock water interaction and precipitation were assessed by Gibb's plot (Gibbs 1970; Fig. 3a, b). For the post-monsoon period, all the samples fall in the rock–water interaction field (Fig. 3b). This suggests that weathering and subsequent dissolution of the minerals present in the groundwater may be the dominant process in the study area. However, for the further confirmation of the results obtained from Gibb's diagram, plots of EC versus Na/Cl were drawn. This plot is often considered as an effective indicator of the evaporation process (Jankowski and Acworth 1997). In an

**Fig. 3** Gibbs plot shows the geochemical process in the study area. **a** Pre-monsoon, **b** post-monsoon



**Fig. 4** Plot shows the relation between EC versus Na/Cl



**Fig. 5** Plot showing Na/Cl ratio

evaporation dominated groundwater, this plot will yield a horizontal trend line. In the pre-monsoon season, Na/Cl was decreased with an increase EC while increased in the

post-monsoon season (Fig. 4). This indicates that evaporation is not a dominant process affecting the groundwater chemistry. The ratio of Na/Cl plotted in Fig. 5 show that

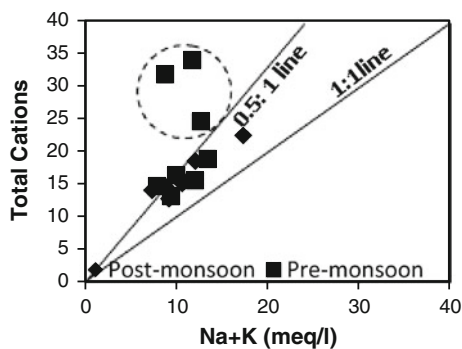


Fig. 6 Plots shows the relation between (Na + K) and total cation

most of the samples in the pre-monsoon and the entire samples in post-monsoon have the Na/Cl ratio >1. Mayback (1987) reported that the Na/Cl >1 is an indication of the origin of Na from the silicate weathering.

Silicate weathering normally results in the elevation of Na and K concentration in groundwater. Influence of silicate weathering can be explained by the relation between Na + K and total cations (TC) (Subramani et al. 2010), which is presented in Fig. 6. The relation between Na + K and TC show that in the post-monsoon season, all the samples were plotted on or below the Na + K = 0.5 TC line. This indicates the dominance of silicate weathering in the groundwater. However, in the pre-monsoon season, three samples showed a less Na + K ratio, suggests the other sources of Na and K or the effect of Ca/Na cation exchange. Dominance of HCO<sub>3</sub> and the higher Na/Cl ratio confirms the higher control of silicate weathering than other hydrogeochemical processes in groundwater of the study area. Similar results were reported by Rajmohan and Elango (2004) from Palar and Cheyyar river basins. However, in the pre-monsoon season, three samples (sample numbers 1, 3 and 7) showed a lesser Na/Cl ratio than 1, suggests some other source of Na in the groundwater, i.e., silicate weathering. Geologically, the study area comprises of gneisses and charnockites as country rock with abundance of potash and plagioclase feldspars. These groups are comparatively more susceptible than quartz for weathering. This is a major source for Na and K in the groundwater.

Although Ca and Mg in groundwater are originated mainly by the dissolution of carbonate minerals, a fair amount of Ca and Mg can also contribute by silicate weathering. In this case, the relation between Ca + Mg and TC will be 0.59: 1 (Subramani et al. 2010). Figure 7 illustrates the relation between Ca + Mg versus TC for the study area. This plot behaves more or less in the same way as the Na + K versus TC plot. The same three sample in pre-monsoon season deviated from the proposed ratio line, suggests the other origin for Ca and Mg. However, it is evident from the plot that, all other samples were influenced by silicate weathering.

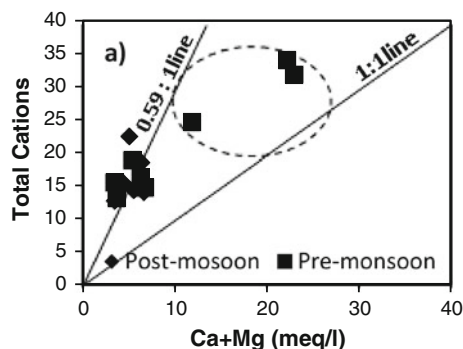


Fig. 7 Plot shows the relation between (Ca + Mg) and total cation

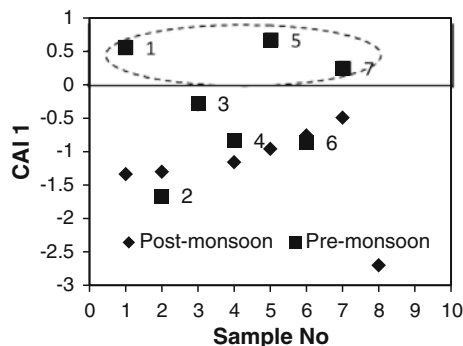


Fig. 8 Distribution of CAI 1 in the study area

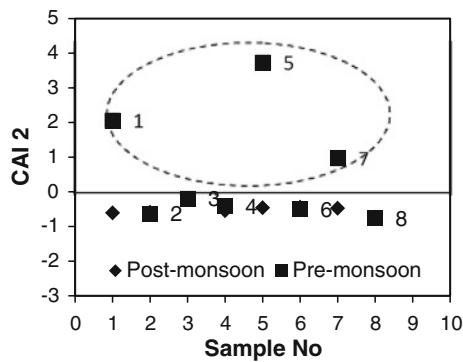
Ion exchange is a major process which controls the hydrochemistry. Effect of ion exchange on the groundwater chemistry was evaluated by the Chloro alkaline indices (CAI 1 and 2) suggested by Schoeller (1967). CAI 1 and 2 is calculated using the Eqs. 1 and 2.

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

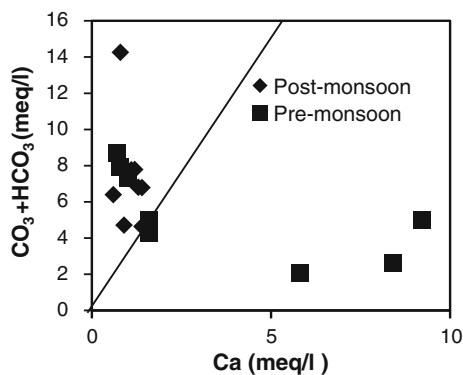
$$CAI\ 2 = [Cl^- (Na^+ + K^+)] / [(SO_4 + HCO_3 + CO_3 + NO_3)] \tag{2}$$

In the ion exchange process, Ca and Mg from the groundwater will be exchanged with the Na and K from the host rock. In this case, both the indices will yield negative values. Although for a reverse exchange process, the indices will be positive (Nagaraju et al. 2006; Ishaku et al. 2011). In the preset study, all the samples in post-monsoon season showed negative value for both indices, suggests that the normal ion exchange process is more prominent. However, three samples in the pre-monsoon season, showed positive values for both indices, thus reverse ion exchange process is acting on these locations. CAI 1 and 2 for the studies are is shown in Figs. 8 and 9.

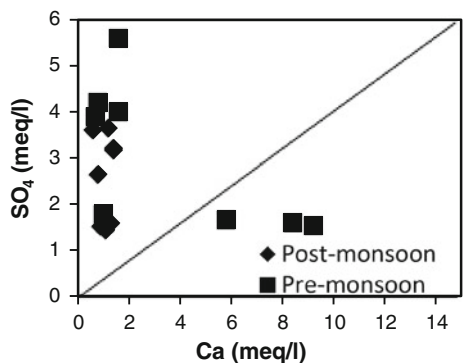
Sources of alkalinity were evaluated using a relation between Ca, HCO<sub>3</sub> and CO<sub>3</sub>. In the case of dissolution of carbonates, water samples will show a 1:2 relation. The results of this plot (Fig. 10) show that few samples fall on the 1:2 line. These samples are affected by the dissolution of calcite present in the sedimentary formation. Figure 11



**Fig. 9** Distribution of CAI 2 in the study area



**Fig. 10** Plot shows the relation between Ca and  $(\text{CO}_3 + \text{HCO}_3)$



**Fig. 11** Plot shows the relation between Ca and  $\text{SO}_4$

illustrates the relation between calcium and sulphate, which is often used to study the dissolution of gypsum (Jalali 2005). However, in the present there is no significant relation between these ions, suggests that dissolution of gypsum is not at all contributing to the hydrochemistry.

Major source of fluoride in groundwater is geological formations through which water circulate. Fluoride content in groundwater originates primarily from the dissolution of fluoride-rich minerals of the bedrock. Fluoride-rich minerals are fluorite, apatite, Mica, amphiboles, clay and villiaumite. In the study area, the major source of F is gneissic and charnockitic rocks (Sajil Kumar 2012). It is observed that the F concentration was higher during the post-monsoon

than the pre-monsoon. This is may be due to the formation of calcium fluoride ( $\text{CaF}_2$ ) in the pre-monsoon season and its deposition, induced by the higher residence time. A relatively high concentration of Ca in the pre-monsoon than post-monsoon season is supporting this argument.

## Conclusions

This study investigated the physicochemical properties of the groundwater to understand the status of water quality and also detect the sources of contamination. Four types of water were identified, which are Ca–Cl, Na–Cl, Ca–Na– $\text{HCO}_3$  and mixed Ca–Mg–Cl in which Na–Cl type was observed in 50 % of the samples. All the samples were alkaline in nature and a higher value was shown in 38 % of the samples. In general, all the parameters showed a higher concentration in the pre-monsoon season except  $\text{F}^-$ . High fluoride concentration (up to 2.75 mg/l) exceeding the guideline value 1.5 mg/L was observed in 62.5 % of the post-monsoon season. A lower F concentration in the pre-monsoon season may be due to the precipitation of  $\text{F}^-$  as  $\text{CaF}_2$ . High TDS values are observed in the pre-monsoon season, with 50 % of samples exceeding the permissible limit 1,000 mg/l in the case of Na; 50 % of the post-monsoon and 75 % of the pre-monsoon samples were exceeded the drinking water guideline 200 mg/L. K and Ca concentrations were under the permissible limit, except three samples during pre-monsoon season exceeding the permissible level of Ca 75 mg/l. Mg concentration in the study area with exceeded in the 62.5 % of pre- and 75 % in post-monsoon season. Since the study area does not have carbonate rocks in the geological formations, the origin of ca and Mg may be attributed to the weathering of silicate minerals. Bicarbonate was the dominant anion that imparting alkalinity to groundwater, this is supporting the alkaline pH in the study area. Chloride concentration was within the limit during post-monsoon and showed higher concentration with 50 % samples exceeded the permissible limit during pre-monsoon. Sulphate was under the guideline value and nitrate was higher in one sample near the agricultural field. Fluoride posing serious problems especially in the post-monsoon season with 62.5 % of the samples exceeded the permissible limit 1.5 mg/l. Evaluation of the source of ions and controlling process were carried out initially with Gibbs plot and later with bivariate plots of ionic ratios. Rock–water interaction was identified as the major process in the study area. Further investigation on the rock–water interaction was indicate the dominance of silicate weathering on the other processes in contributing the ions such as Na, Ca, Mg,  $\text{HCO}_3$ , etc. The odd behaviour of few samples from the normal silicate weathering process was attributed to the cation exchange process in the study



area. However, the origin of fluoride was largely controlled by the fluoride rich minerals in the hard rocks of the study area. This study provides a baseline for the groundwater chemistry in Thirupathur region, which will help the water resources managers to focus on the specific contaminant sources and its mitigation.

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