

# Assessment of groundwater quality with special emphasis on fluoride contamination in crystalline bed rock aquifers of Mettur region, Tamilnadu, India

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**Abstract** Groundwater samples were collected from Mettur taluk of Salem district, Tamilnadu, India for two different seasons (pre-monsoon and post-monsoon) and analyzed for fluoride ion along with other chemical parameters. The major litho units of the study area are Charnockites, peninsular gneiss, and calc gneiss of meta-sedimentary group. The fluoride concentration ranges from 0.1 to 2.8 mg/L and 0.4 to 4.0 mg/L during pre-monsoon (PRM) and post-monsoon (POM) seasons, respectively. Results showed that collected water samples were contaminated by the presence of fluoride ion. During PRM and POM, 21% and 56% of samples recorded higher fluoride when compared with Indian Drinking Water Standard (1 mg/L) and (9% and 35%) of samples recorded higher fluoride when compared with World Health Organization tolerance limit (1.5 mg/L). The ratio of Na/Ca indicates high sodium content in groundwater enhances the dissolution of fluoride at higher pH. Hydrogeochemical facies indicates water-rock interaction as main source for high fluoride in groundwater. A positive correlation between pH, Mg, and *F* indicates high alkaline nature of water promotes

fluoride leaching from source rocks into ground water. Factor analysis indicates hydro-geochemical processes like weathering, ion exchange, and anthropogenic contributes to groundwater chemistry. The saturation index indicates dissolution and precipitation contributes fluoride dissolution along with mixing.

**Keywords** Fluoride · Hydrofacies · Spatial distribution · Correlation · Factor analysis · Saturation indices

## Introduction

Fluorine is widely distributed in the environment and ranks 13th among the other elements in order of abundance in the earth's crust. Fluorine has the highest electro-negativity and most reactive among all known elements. Fluoride ion occurs in natural waters commonly in concentrations less than 1.0 mg/l and seldom outside the range from 0.01 to 10.0 mg/l. The problem of excessive fluoride in ground water in India was first reported in 1937 in the state of Andhra Pradesh (Short et al. 1937). In India, approximately 62 million people including 6 million children suffer from fluorosis because of consumption of water with high fluoride concentrations (Susheela 1999a, b). Seventeen states in India have been identified as endemic for fluorosis of which Tamilnadu is one along with 23 out of 28 districts are prone to fluorosis in drinking water (Misra et al. 2006). Groundwater is a major source of human intake of fluoride, including its subsequent incorporation into food items. The main source of fluoride in groundwater is considered to be fluoride-bearing minerals such as fluorospar, fluorapatite, cryolite, and hydroxylapatite in rocks (Farooqi et al. 2007)

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by prolonged water-rock interactions (Carrillo-Rivera et al. 2002). The amount of  $F$  occurring naturally in groundwater is governed principally by climate, composition of the host rock, and hydrogeology. Some anthropogenic activities such as use of phosphatic fertilizers, pesticides and sewage and sludge, depletion of groundwater table, etc., for agriculture have also been indicated to cause an increase in  $F$  concentration in groundwater (EPA 1997; Ramanaiah et al. 2006). Fluoride in groundwater evokes considerable interest due to its unique character as regards to its impact on physiological system of living beings. Due to excessive fluoride intake, enamel loses its luster. Dental fluorosis is characterized by discoloration in the form of spots or horizontal streaks on the tooth surface. Skeletal fluorosis occurs when fluoride deposits in the joint of neck, knee, and shoulder bones and makes it difficult to move or walk. Besides skeletal and dental fluorosis, excessive consumption of fluoride may lead to muscle fiber degeneration, low hemoglobin levels, excessive thirst, headache, skin rashes, nervousness, depression, etc. (Meenakshi 2006). Table 1 summarizes potential health effects associated with long-term ingestion of fluoride-bearing waters as described by Dissanayake (1991).

Many investigations have been made related to origin and hydrogeochemistry of high fluoride in groundwater from different parts of the world (Moghaddam and Fijani 2008; Salve et al. 2008; Tirumalesh et al. 2007; Sreedevi et al. 2006; Nanyaro et al. 1984; Kundu and Mandal 2008; Farooqi et al. 2007; Jacks et al. 1993; Valenzuela-Vasquez et al. 2006; Kumar and Syed 1989; Srinivasamoorthy et al. 2007; Babulal et al. 2003; Ramamohana Rao et al. 1996; Carrillo-Rivera et al. 2002; Rukah and Alsokhny 2004; Kim and Jeong 2005; Karro et al. 2006; Gizaw 1996; Ozsvath 2006 and Guo et al. 2007). In these researches, groundwater samples were obtained from dug/bore wells and examined for fluoride ions and high fluoride have been identified to be originated from water–rock interaction and anthropogenic sources like application of fertilizers, industrial effluents, and household domes-

tic effluents. The study area Mettur taluk in Salem district is marked as one of the prevalent fluoride zones in Tamilnadu, India due to occurrence of diverse rock types which include higher fluoride-bearing minerals (RGNDWM 1993). The major exposure of the study area are peninsular gneiss, charnockites and calc gneiss which have been marked for widespread fluoride-bearing minerals indicating their accessibility to water by weathering along with leaching process. Mica content is significantly noted in peninsular gneiss and apatite is noted in charnockites which are the sources of fluoride into the groundwater (Srinivasamoorthy et al. 2008a, b). Hence, it is essential to discriminate fluoride-vulnerable zones and to identify major geochemical process controlling the incidence of fluoride in the groundwater of study area. Hence, in the present study, an attempt has been made to discuss about the fluoride concentration with respect to major lithology, relation of fluoride with other ions, correlation, factor analysis, and spatial distribution of fluoride ions.

### Study area

The study area (Fig. 1) occupies North Western part of Salem district in Tamilnadu and lies between North Latitudes 11°30' and 12°00' and East Longitudes 77°45' and 78°00' with a Total extent of 777.15 km<sup>2</sup>. The southern part of the area contain hill ranges and high land areas where eastern part is low lying due to the flow of river Cauvery. The study area receives scanty rainfall (804.3 mm) both by northeast and southwest monsoons. It is entirely underlined by Archaean crystalline metamorphic complexes. The rocks of this group are highly weathered, jointed, and covered by recent valley fills and soil covers at site-specific locations. A wide range of rock types occur, formed by tectonic and magmatic activities during Precambrian period resulting in complicated structure and geology. The geology of the study area is composed of charnockites, peninsular gneiss, and calc gneiss of meta-sedimentary group. Hills, undulating plains, plateaus, pediments, and bazadas are the mixture of geomorphic units identified in the study area with topographic low due NS trend. The main drainage of the study area is by river Cauvery which flows North to South with a subdentric drainage pattern. Groundwater in the study area occurs in weathered portions of rocks along joints and fractures. The occurrence and movement of groundwater in a hard rock terrain are restricted to fissures and joints in unweathered portion and porous zones of weathered formations. The weathered layer in gneiss varies from 2.2 to 50 m and in charnockite thickness ranges between 5.8 and 55 m. At contacts of

**Table 1** Effects of fluoride ingestion on human health

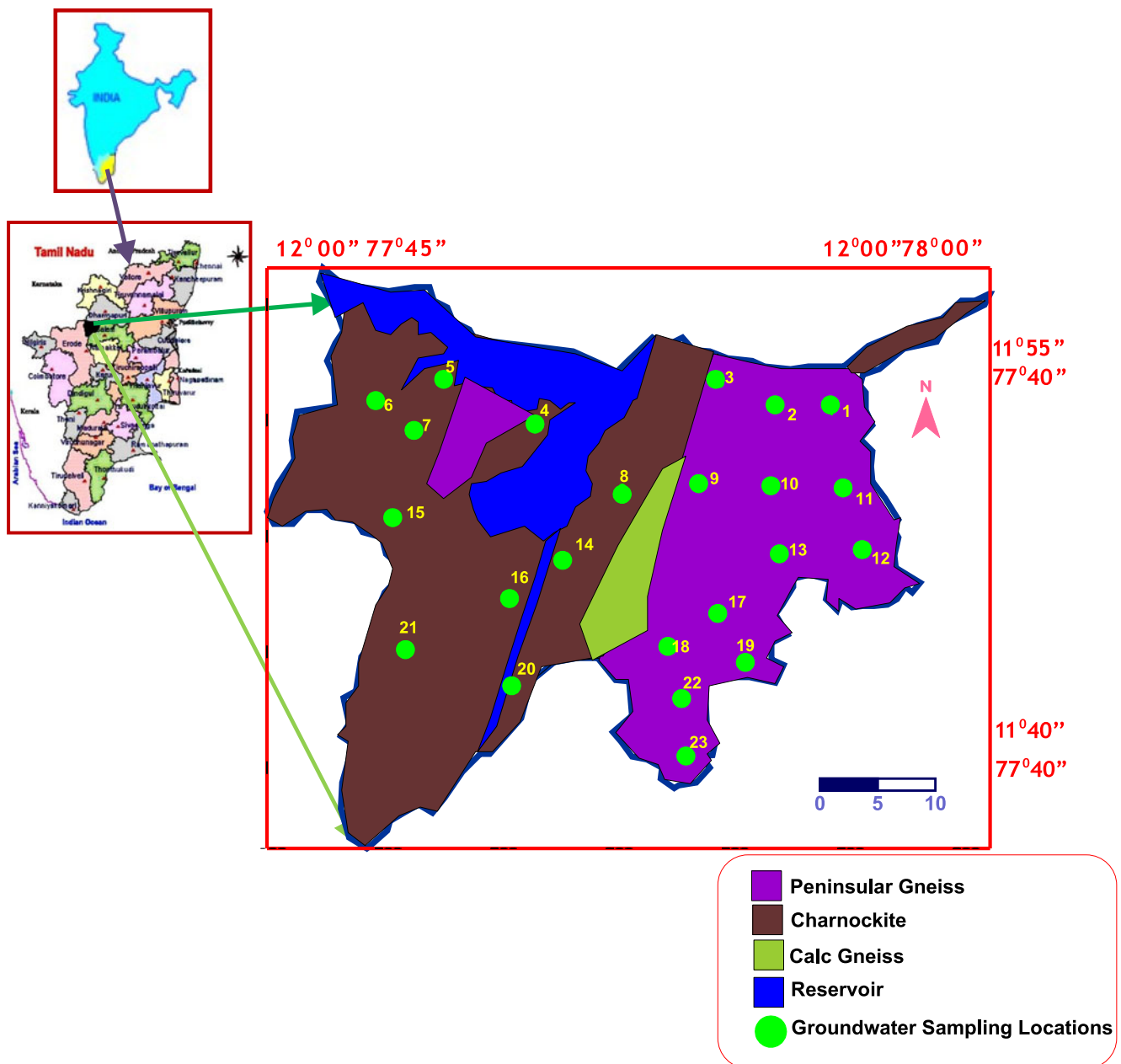
Fluoride concentration (mg/L)	Effect on human health
<0.5	Conducive to dental caries
0.5–1.5	Promotes development of strong bones and teeth
1.5–4.0	Promotes dental Fluorosis in children
>4.0	Promotes dental and skeletal Fluorosis
>10	Crippling skeletal Fluorosis, cancer

gneiss and charnockites, thickness was from 9.0 to 90.8 m (Srinivasamoorthy et al. 2008a, b).

### Materials and methods

To assess water chemistry under natural conditions, 46 representative groundwater samples representing major lithology of study area was collected for two seasons pre- and post-monsoon (June and December) from long-term groundwater observation wells and drinking

wells. Each sample was collected in acid-washed polyethylene 1,000 ml bottle with strict adherence to the sampling protocol as described by Robin 2002. Samples were filtered using a 0.45- $\mu$ m cellulose acetate filter membrane. The bottles were tightly capped to protect samples from atmospheric CO<sub>2</sub>, adequately labeled, and preserved in the refrigerator until they were taken to the laboratory for measurement. Precaution was also taken to avoid sample agitation during transfer to the laboratory. Before taking readings, pumping was carried out until the meter readings were stable for each



**Fig. 1** Location, geology, and water sample locations

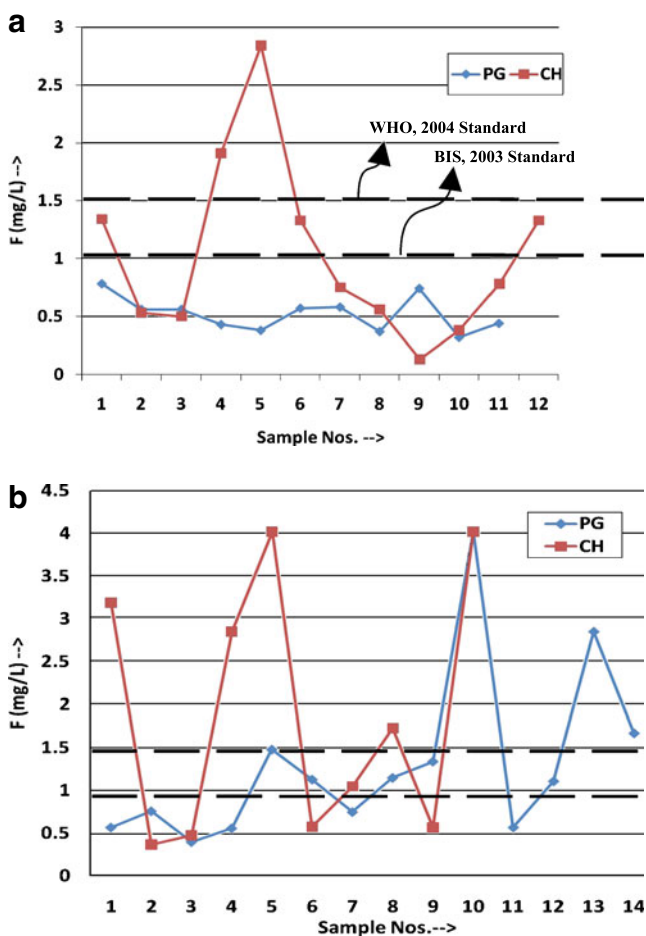
parameter. Samples were analyzed in the laboratory for the major ions chemistry using standard methods APHA 1995 and Srinivasamoorthy et al. (2008a, b). Calcium (Ca) and magnesium (Mg) were determined titrimetrically using standard EDTA. Chloride (Cl) was determined by standard  $\text{AgNO}_3$  titration. Bicarbonate ( $\text{HCO}_3$ ) by titration with HCl. Sodium (Na) and potassium (K) by flame photometry. Electrical conductivity (EC), pH, and total dissolved solids (TDS) were measured by Water Quality Analyzer. Sulfate ( $\text{SO}_4$ ), phosphate ( $\text{PO}_4$ ), and silicate ( $\text{H}_4\text{SiO}_4$ ) was determined by spectrophotometer. Nitrate ( $\text{NO}_3$ ) and fluoride (F) were analyzed by using ion-sensitive electrode. Care was taken that the pH, EC,  $\text{HCO}_3$ , and Ca were analyzed within 24 h of sampling. The quantity controls of the measurements consisted of duplicate samples. Correlation analysis among various parameters was done with SPSS statistical software package and geochemical reaction simulation model WATQ4F (Plummer et al. 1976) has been used to determine the solubility of equilibrium for fluoride. Using the approach of Hounslow (1995), the analysis accuracy was checked for the water samples by using the charge balance and TDS/EC ratio. The charge balance values for all the samples vary by about 5–10%, which indicates that the analysis results are good. TDS/EC ratios for most of the samples range from 0.55 to 1.0 which is in the range of attention value.

## Results and discussion

Groundwater in general was alkaline in nature, and higher EC values were noted during pre-monsoon (PRM) season.  $\text{HCO}_3$  in the study area was higher during post-monsoon (POM) (543.0 mg/L) due to weathering of silicates. The concentration of Cl was higher in POM (1,057.0 mg/L) indicating leaching from upper soil layers due to industrial and domestic activities and dry climates (Herman Bouwer 1978).  $\text{SO}_4$  was higher in PRM (219.0 mg/L) indicating breaking of organic substances from topsoil/water, leachable sulfate preset in fertilizer, and other human influences (Miller 1979; Craig and Anderson 1979).  $\text{NO}_3$  was higher in PRM (76.2 mg/L) indicating leaching of organic substances from weathered soil (Table 2). The general dominance of anion was in the order of  $\text{Cl} > \text{HCO}_3 > \text{SO}_4 > \text{NO}_3 > \text{PO}_4$ . For cations, Na was higher in PRM (400.0 mg/L) indicating weathering from plagioclase bearing rocks. K was lesser in both the seasons indicating its lower geochemical mobility. Ca and Mg were higher in PRM (153.0 and 177.0 mg/L) indicating the weathering from primary mineral sources. The general dominance of cations was in the order of  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$ . The concentration of  $\text{H}_4\text{SiO}_4$  was higher in POM (36.5 mg/L) indicating the existence of alkaline environment and abundance of silicate minerals in the study area. The F concentration ranges from 0.1 to

**Table 2** Statistics of water chemistry from the study area

Constituents	Range of observed values		Mean		Median		Standard deviation	
	PRM	POM	PRM	POM	PRM	POM	PRm	POM
Ca	5.8–153.0	2.0–44.6	53.9	11.2	47.9	7.7	41.4	9.2
Mg	21.6–177.0	8.79–91.3	76.7	51.3	62.4	49.1	39.6	25.9
Na	72.0–400.0	73.9–296.0	156.1	133.2	136	124	72.3	56
K	1.3–49.3	1.29–128.0	17.1	27.9	14	25.1	13.9	26.6
Cl	35.4–823.0	79.5–1057.0	302.2	337.3	257	284	203.9	208.3
$\text{HCO}_3$	205.0–447.0	142.0–542.0	340	308.3	341.0	274.0	69.8	98.1
$\text{SO}_4$	19.7–219.0	2.35–17.7	105.3	10.7	99.1	9.2	64.5	5.2
pH	7.0–8.0	7.2–8.4	7.5	7.6	7.5	7.7	0.3	0.3
EC	1882.8–9094.1	1613.2–5677.6	4154	2786.5	3798.5	2436.4	1635.8	948.8
$\text{PO}_4$	0.0–7.7	0.0–7.7	0.8	0.8	0.3	0.3	1.5	1.5
$\text{NO}_3$	1.2–76.2	3.7–27.3	37.4	8.2	35.9	6.8	20.3	5.2
F	0.1–2.8	0.4–4.0	0.8	1.4	0.6	1.1	0.6	1.1
$\text{H}_4\text{SiO}_4$	1.6–22.4	10.8–36.5	16.4	24.2	16.8	23.2	4.6	8.0
TDS	1,205.0–5,820.2	1,032.4–3,633.7	2658.6	1783.4	2431	1559.3	1046.9	607.2
$\text{HCO}_3/\text{Cl}$	0.4–12.4	0.45–4.42	1.9	1.2	1.3	0.9	2.4	0.9
$\text{Na}/\text{Cl}$	0.3–2.0	0.23–1.17	0.7	0.47	0.6	0.4	0.4	0.2
$\text{Na}/\text{Ca}$	1.0–28.4	6.15–16.47	5.4	16.4	3.2	12.4	6.7	10.5
$\text{HCO}_3/\text{Ca}$	2.2–35.5	10.92–175.50	10.5	41.4	8.5	33.7	7.9	34.1



**Fig. 2** **a** Comparison of fluoride concentration with WHO 2004 and BIS 2003 standards during PRM. **b** Comparison of fluoride concentration with WHO 2004 and BIS 2003 standards during POM

2.8 mg/L and 0.4 to 4.0 mg/L during PRM and POM seasons, respectively. The concentration of fluoride found in the ground water samples was higher in (21% and 56%) during PRM and POM when compared with the Indian Drinking Water Standard of maximum permissible limit of 1.0 mg/L (BIS 2003; Fig. 2a and b). The values of fluoride in (9% and 35%) of samples during PRM and POM were higher than the maximum tolerance limit (1.5 mg/L) recommended by World Health Organization (WHO 2004). Ingestion of water with fluoride concentration above >1.5 mg/L causes Fluorosis (Madhnure et al. 2007). High degree of weathering, easy accessibility of circulating water to the weathered rocks due to intensive and long-time irrigation are responsible for the leaching of fluoride from their parent minerals present in soils and rocks. Further concentration has been brought about due to semi-arid climate of the region and long residence time of groundwater in the aquifer (Wodeyar and Sreenivasan 1996). The influence of local lithology and soil aided by

other factors like very low freshwater exchange due to the arid climate of the regions (average daily temperature 28°C and average rainfall of 804.3 mm) is responsible for higher concentration of fluoride in the groundwater of the region. Higher concentration was noted in charnockites followed by peninsular gneiss due to presence of dominant fluoride-bearing minerals like apatite, hornblende, and biotite which has enhanced the fluoride concentration. Higher concentration of fluoride was noted in charnockites due to the easy accessibility of fluoride minerals due to the higher degree of weathered zone thickness in charnockites than peninsular gneiss.

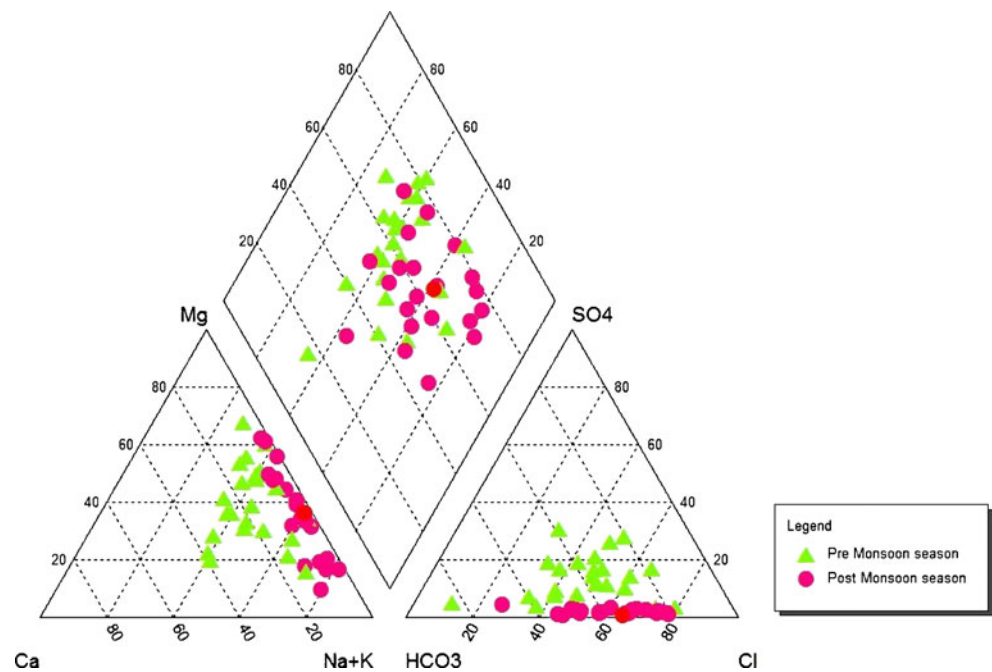
In order to identify possible combinations, ratio values of important variables were selected. The ratio of  $\text{HCO}_3/\text{Cl}$  during PRM and POM were found in the range of 0.37–12.4 and 0.45–4.4 (Table 2). The average ratio value of 1.9 and 1.19 indicates dominance of carbonate ions from silicate weathering, whereas values less than one indicate domination of chloride ion in the study area. The  $\text{Na}/\text{Cl}$  ratio was observed in the range of 0.2–2.0 and 0.4–4.4. The lower average ratio 0.66 and 1.1 indicates modification of sodium carbonate water by dissolution or mixing with sodium chloride, whereas increase in chloride may be due to local recharge (Dhiman and Keshari 2006). The ratio value of  $\text{Na}/\text{Ca}$  was observed in the range of 1.02–28.3 and 6.1–46.5. The increase in average 5.4 and 16.4 ratios may be due to lowering calcium activity whereby high sodium activates the dissolution of fluoride-bearing minerals at higher pH in groundwater system (Shaji et al. 2007). The  $\text{HCO}_3/\text{Ca}$  ratio was observed in the range of 2.1–35.4 and 10.9–175.5, with an average of 10.5 and 41.3, which indicate favorable chemical condition for fluoride dissolution (Saxena and Ahmed 2003).

### Hydro facies

Dissolution and deposition of fluoride is controlled by chemical type of groundwater. Hence, major ion chemistry of groundwater is examined by using Piper (1994) trilinear diagram to identify chemical alteration in groundwater. The Piper diagram consists of two lower triangular fields and a central diamond-shaped field. All the three fields have incorporation of major ions only. The triangular fields are plotted separately with epw values of cations ( $\text{Ca}+\text{Mg}$ ) alkali earth, ( $\text{Na}+\text{K}$ ) alkali,  $\text{HCO}_3$  weak acid, and ( $\text{SO}_4+\text{Cl}$ ) strong acid. Water facies can be identified by projection of plots in the central diamond-shaped field as per the classifications made by Karanth (1987). Hydrogeochemical facies interpretation is a useful tool for determining the flow pattern, origin of chemical histories of groundwater masses (Fig. 3). During PRM, majority of samples clusters in the  $\text{Ca}-\text{Na}-\text{Cl}-\text{HCO}_3$ ,



**Fig. 3** Hydrochemical facies classification of groundwater from the study area



Mg-Na-Cl-HCO<sub>3</sub>, Na-Cl-HCO<sub>3</sub>, Mg-Na-Ca-HCO<sub>3</sub>, Na-Mg-HCO<sub>3</sub>-Cl, Ca-Na-Mg-Cl-HCO<sub>3</sub>, Na-Ca-Mg-Cl-SO<sub>4</sub>-HCO<sub>3</sub>, Mg-Na-Cl-SO<sub>4</sub>-HCO<sub>3</sub>, Na-Mg-Ca-HCO<sub>3</sub>-Cl-SO<sub>4</sub>, and Na-Mg-Cl-HCO<sub>3</sub> zones. Lower fluoride (<1.0 mg/L) are confined to Ca-Na-Cl-HCO<sub>3</sub>-Cl and Mg-Na-Cl-HCO<sub>3</sub> types and higher fluoride (>1.0 mg/L) is due to Mg-Ca-Cl-HCO<sub>3</sub>, Na-Mg-HCO<sub>3</sub>-Cl, Na-Mg-Cl-HCO<sub>3</sub>, and Na-Cl-HCO<sub>3</sub> zones indicating effective dissolution of fluoride from litho units of the study area. During POM, samples cluster in Na-Mg-HCO<sub>3</sub>-Cl, Mg-Na-HCO<sub>3</sub>-Cl, Na-HCO<sub>3</sub>-Cl, Mg-Na-Cl-HCO<sub>3</sub>, Na-Mg-Cl-HCO<sub>3</sub> and Na-Cl-HCO<sub>3</sub> facies indicating calcium and magnesium replaced by Na ions and Cl and HCO<sub>3</sub> enrichment in anion indicates the transformation of facies from hard calcium bicarbonate type to alkaline mixed bicarbonate type along the flow path which favors higher mobility of fluoride ions (>1.5 mg/l) into the groundwater system (Pickering et al. 1988). The Na-K-Cl-HCO<sub>3</sub>, Na-Cl-HCO<sub>3</sub>, Mg-Na-HCO<sub>3</sub>, and Na-Mg-Cl-HCO<sub>3</sub> type facies indicates the mixing of young waters due precipitation which has considerably reduced the fluoride concentration (0.05–1.5 mg/L).

### Gibbs plot

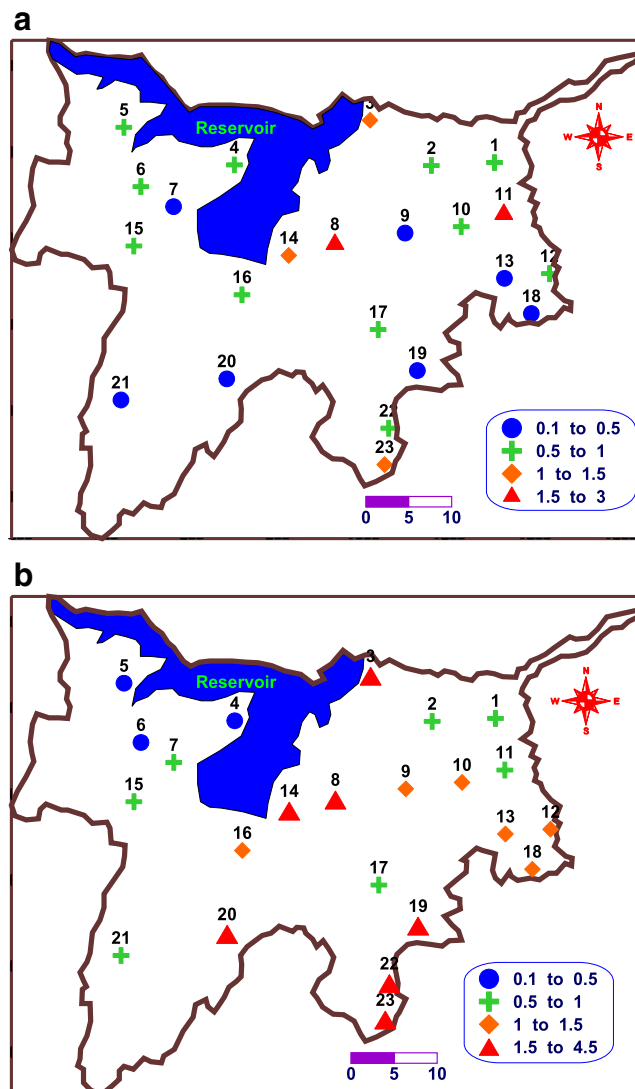
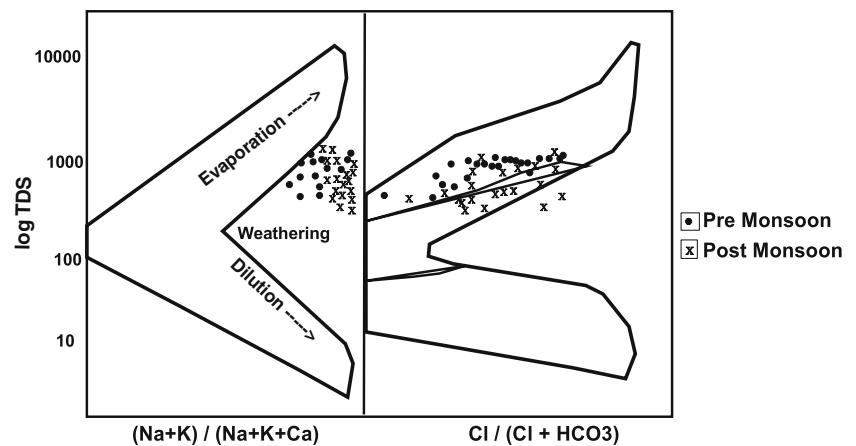
Since the study region experiences dry and semiarid climatic condition, evaporation may also contribute to changes in water chemistry in the study region. Hence, to identify and to differentiate the influences of rock-water interaction, evaporation and precipitation process, and mechanisms affecting the chemistry of groundwater from the study area, Gibbs (1970) plot representing the ratios of

Na:(Na+Ca) and Cl:(Cl+HCO<sub>3</sub>) as a function of TDS was used (Fig. 4). Samples from both seasons fall in rock dominance zone suggesting precipitation induced chemical weathering along with dissolution of rock-forming minerals. Therefore, the concentrations of major ions in groundwater and the mineralogy of different rocks have been used to determine the source of these major ions to the groundwater and their relation to regional geology and weathering processes.

### Spatial distribution

The spatial distribution of fluoride in the groundwater (Fig. 5a and b) was attempted to identify regions and locations of widespread fluorosis. During PRM, fluoride (<0.5 mg/l) was noted in 30% of the samples in seven locations (7, 9, 13, 18, 19, 20, and 21) and concentration (0.5–1.00 mg/L) was observed in 48% of samples in 11 locations (1, 2, 4, 5, 6, 10, 12, 15, 16, 17, and 22). Concentrations ranging from 1.0 to 1.5 mg/L were observed in 13% of samples in three locations (3, 14, and 23). Higher concentration (1.5–3 mg/L) was observed in 9% of samples in two locations (8 and 11). In general, fluoride was higher in both litho units. During POM, fluoride (<0.5 mg/L) was noted in 14% of the samples in three locations (4, 5, and 6) and concentration (0.5–1.00 mg/L) was observed in 30% of samples in seven locations (1, 2, 7, 11, 15, 17, and 22). Concentrations ranging from 1.0 to 1.5 mg/L were observed in 26% of samples in six locations (9, 10, 12, 13, 16, and 18). Higher concentration (1.5–4.5 mg/L) was observed in 30% of samples in seven

**Fig. 4** Gibbs plot for the groundwater samples from the study area



**Fig. 5** a Spatial distribution of fluoride during PRM season. b Spatial distribution of fluoride during POM

locations (3, 8, 14, 19, 20, 22, and 23). In general, higher fluoride was observed in both litho units. During PRM, enhanced concentrations of fluoride ( $>1.5$  mg/L) were confined to inferior samples (9%) but during POM higher concentrations were confined to further samples (30%) indicating the function of infiltrated rainwater which dissolves additional fluoride ions from source rocks. In general, seasonal fluctuations were noted higher when compared with lithological influence during both the seasons.

### Statistical analysis

Numerical analysis of hydrogeochemical data has been attempted to determine the geochemical parameters of groundwater (Lawrence and Upchurch 1982). Correlation and factor analysis are widely used in statistical or numerical concepts for parametric classification of modeling studies (Balasubramanian et al. 1985). Statistical data generally provide a better representation than graphical data because (1) there are a finite number of variables that can be considered, (b) variables are generally limited by convention to major ions, and (c) superior relationships may be deduced by use of certain procedures.

### Correlation matrix

The correlation matrix of groundwater samples collected from study area is shown in Tables 3 and 4. During PRM, correlation of fluoride with other ions was observed relatively not dependent except fluoride and pH. A positive correlation between pH and fluoride indicates, high alkaline nature of water promotes leaching of fluoride and thus, increases fluoride in ground water. The ionic radius of

**Table 3** Correlation matrix for the water samples during PRM season

Variables	Ca	Mg	Na	K	Cl	HCO <sub>3</sub>	SO <sub>4</sub>	pH	EC	PO <sub>4</sub>	NO <sub>3</sub>	F	H <sub>4</sub> SiO <sub>4</sub>	TDS
Ca	1.00													
Mg	−0.13	1.00												
Na	0.07	0.34	1.00											
K	0.50	0.47	0.44	1.00										
Cl	0.35	0.73	0.68	0.77	1.00									
HCO <sub>3</sub>	0.25	0.17	−0.03	0.34	0.04	1.00								
SO <sub>4</sub>	0.16	0.04	0.34	−0.13	0.15	−0.33	1.00							
pH	−0.25	0.16	0.04	−0.10	0.09	−0.41	0.39	1.00						
EC	−0.03	0.07	0.75	0.12	0.29	0.04	0.41	−0.01	1.00					
PO <sub>4</sub>	−0.19	0.00	0.05	0.05	−0.16	0.21	−0.19	−0.27	0.18	1.00				
NO <sub>3</sub>	−0.07	−0.10	0.14	0.10	−0.06	0.06	−0.26	−0.16	0.24	0.49	1.00			
F	0.00	−0.35	−0.15	−0.33	−0.28	−0.19	0.15	0.41	0.00	−0.15	−0.14	1.00		
H <sub>4</sub> SiO <sub>4</sub>	0.26	0.18	0.01	0.01	0.22	0.02	0.17	0.13	0.09	−0.29	0.01	−0.20	1.00	
TDS	0.07	0.22	0.82	0.27	0.47	0.09	0.43	0.00	0.98	0.14	0.21	−0.07	0.14	1.00

fluoride (0.136 nm) was same as that of hydroxyl ion which can be easily substituted for one another from water at high pH (Sreedevi et al. 2006; Gupta et al. 2006). Good correlation was also observed between ions like Ca-K, Mg-K, Mg-Cl, Na-K, Na-Cl, Na-EC, Na-TDS, K-Cl, TDS-Cl, SO<sub>4</sub>-EC, SO<sub>4</sub>-TDS, EC-TDS, and PO<sub>4</sub>-NO<sub>3</sub> indicating dissolution of ions into the groundwater through ion exchange, weathering, and/or oxidation reduction reaction along with anthropogenic activities (Subba Rao 2002). During POM, good correlation was observed between Mg and F indicating leaching of fluoride from sources rocks. Good positive correlation was also observed between Ca-Na, Ca-Cl, Ca-HCO<sub>3</sub>, Mg-SO<sub>4</sub>, Na-Cl, Na-HCO<sub>3</sub>, Na-EC, Cl-EC, and HCO<sub>3</sub>-EC indicating once again the action of same sources identified during the PRM season.

### Factor analysis

After computation of correlation matrix, the correlation coefficient measures of interrelationship for all pairs of constituents are determined. The factors with Eigen values larger than 1.0 were selected and rotated iteratively by the Varimax method (Davis 1986), which maximizes the variance of the factor. For factor loadings, a high loading was defined as greater than 0.75, and a moderate loading was defined as 0.40–0.75. Loadings of less than 0.4 were considered insignificant (Mor et al. 2006). A total of three factors were identified which control the groundwater quality (Tables 5 and 6). During PRM, factor I represent 23.8% of variance with representations of Na, SO<sub>4</sub>, EC, and TDS resulting from influx of these ions by dissolution from

**Table 4** Correlation Matrix for the water samples during POM season

Variables	Ca	Mg	Na	K	Cl	HCO <sub>3</sub>	SO <sub>4</sub>	pH	EC	PO <sub>4</sub>	NO <sub>3</sub>	F	H <sub>4</sub> SiO <sub>4</sub>	TDS
Ca	1.00													
Mg	0.03	1.00												
Na	0.63	−0.15	1.00											
K	0.20	−0.22	0.11	1.00										
Cl	0.97	0.09	0.68	0.23	1.00									
HCO <sub>3</sub>	0.44	0.28	0.40	0.06	0.37	1.00								
SO <sub>4</sub>	0.30	0.42	0.32	0.17	0.31	0.22	1.00							
pH	−0.05	0.04	0.08	−0.27	−0.04	−0.06	−0.06	1.00						
EC	0.88	0.13	0.69	0.24	0.88	0.62	0.32	0.14	1.00					
PO <sub>4</sub>	−0.21	0.22	−0.11	−0.27	−0.25	0.07	0.31	0.24	−0.22	1.00				
NO <sub>3</sub>	0.27	0.20	0.08	0.14	0.31	0.10	−0.17	−0.18	0.27	−0.14	1.00			
F	−0.32	0.42	−0.20	−0.11	−0.25	−0.08	−0.01	0.10	−0.23	−0.20	−0.09	1.00		
H <sub>4</sub> SiO <sub>4</sub>	−0.05	0.09	0.12	0.11	−0.04	0.04	0.23	−0.34	−0.02	−0.01	0.31	−0.12	1.00	
TDS	0.88	0.13	0.69	0.24	0.88	0.62	0.32	0.14	1.00	−0.22	0.27	−0.23	−0.02	1.00



**Table 5** Factor analysis for water samples during PRM

Variables	Factor 1	Factor 2	Factor 3
Ca	−0.06	0.57	0.07
Mg	0.26	0.61	0.05
Na	0.87	0.28	−0.02
K	0.26	0.74	0.36
Cl	0.48	0.81	−0.01
HCO <sub>3</sub>	−0.05	0.27	0.62
SO <sub>4</sub>	0.45	0.04	−0.66
pH	0.09	−0.03	−0.73
EC	0.95	0.11	−0.01
PO <sub>4</sub>	0.29	−0.41	0.63
NO <sub>3</sub>	0.34	−0.33	0.52
F	−0.07	−0.38	−0.49
H <sub>4</sub> SiO <sub>4</sub>	0.02	0.41	−0.22
TDS	0.95	0.11	−0.01
Total	3.34	2.67	2.43
% of variance	23.84	19.09	17.38
Cumulative %	23.84	42.93	60.31

parent rocks like charnockites and gneisses along contribution from precipitation and deposition from dust materials. Factor II is represented by Ca, Mg, K, and Cl with 19.09% of variance, indicating sources from ion exchange and contribution from weathering processes and anthropogenic input into the groundwater system by leaching from industrial effluents. Factor III is represented by SO<sub>4</sub>, Ph, and *F* with 17.3% of variance indicating dissolution and leaching from fluoride-bearing minerals (apatite, hornblende, mica, etc.) from the

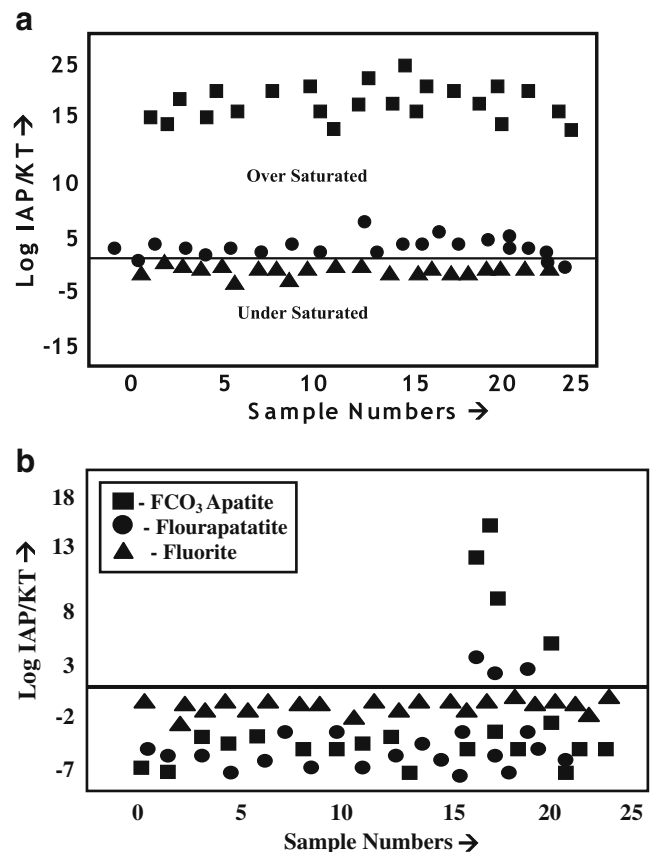
**Table 6** Factor analysis for water samples during POM

Variables	Factor 1	Factor 2	Factor 3
Ca	0.93	−0.10	0.11
Mg	0.08	0.86	0.09
Na	0.77	−0.08	0.00
K	0.21	−0.31	0.47
Cl	0.92	−0.08	0.13
HCO <sub>3</sub>	0.60	0.32	0.06
SO <sub>4</sub>	0.36	0.62	0.15
pH	0.12	0.11	−0.77
EC	0.98	0.01	0.04
PO <sub>4</sub>	−0.16	0.55	−0.30
NO <sub>3</sub>	0.22	−0.01	0.55
F	−0.28	0.36	−0.08
H <sub>4</sub> SiO <sub>4</sub>	−0.06	0.22	0.73
TDS	0.98	0.01	0.04
Total	4.93	1.83	1.80
% of Variance	35.24	13.08	12.88
Cumulative%	35.24	48.32	61.20

litho units and soils. During POM, factor I is influenced by Cl, Ca, Na, EC, and HCO<sub>3</sub> with 35.2% of variance, once again indicating the influence of anthropogenic and lithological activities. Factor II represented by H<sub>4</sub>SiO<sub>4</sub> and K ions with 13.0% of variance indicating weathering from charnockites, gneisses, and leaching from agricultural wastes. Factor III with a total variance of 12.8% represents the domination of SO<sub>4</sub>, Mg, and *F* ions, indicating impact of anthropogenic activities like residential water softeners or agricultural activities and leaching from fluoride-bearing minerals. In general, different hydro-geochemical processes like weathering, ion-exchange, and anthropogenic inputs are the key factors that determine the groundwater chemistry in the study area. At most, factor analyses substantiate the findings of previous sections and provide greater confidence in data interpretation.

### The saturation indices

The quality of groundwater depends on the mineralogy, reactivity of drift materials, and the degree of equilibrium that has been attained between water and rock (Robin



**Fig. 6** **a** Saturation indices for groundwater samples during PRM season. **b** Saturation indices for groundwater samples during POM season

2002). The hydrochemical equilibrium conditions controlling the groundwater were therefore studied with the program WATEQ4F. The saturation index (SI) of groundwater samples with respect to mineral precipitation is expressed by:  $SI = \log (IAP/K_{sp})$  where IAP is ion activity of the solution;  $K_{sp}$  is equilibrium constant of the reaction considered at temperature  $T$ . The saturation indices describe quantitatively the deviation of water from equilibrium with respect to dissolved minerals. If the water is exactly saturated with the dissolved mineral, SI equals to zero. Positive values of SI indicate saturation, and negative ones indicate undersaturation (Appelo and Postma 1996; Drever 1988). During PRM,  $FeCO_3$  apatite was over saturated, fluorapatite was in equilibrium and fluorite was undersaturated. During POM, effect of dilution by undersaturated nature is well noted in all the fluoride minerals (Fig. 6a and b). It is observed that fluorides in groundwater are mainly due to dissolution of apatite and fluoride bearing minerals which plays a significant role in determining the water chemistry of the study area. Fluoride chemistry of the region is highly influenced by dissolution and precipitation along with mixing apart from anthropogenic activities.

## Conclusion

The study area Mettur region forms a part of Salem district of Tamilnadu, India with a total spread of 777.15 km<sup>2</sup> area. It is entirely underlined by Archaean crystalline metamorphic complexes. Important rocks like peninsular gneiss, charnockites, and calc gneiss are exposed in the study area. Groundwater in the study area occurs in weathered portions of rocks along joints and fractures. The study area is marked as one of the prevalent fluoride zones in Tamilnadu, due to occurrence of fluoride-bearing minerals in the litho units. Mica content is significantly noted in peninsular gneiss and apatite is noted in Charnockites. The present study is an attempt to demarcate fluoride-vulnerable zones and to identify major geochemical process controlling the incidence of fluoride in the groundwater of study area. The  $F$  concentration ranges from 0.1 to 2.8 mg/L and 0.4 to 4.0 mg/L during PRM and POM seasons, respectively. The concentration of fluoride in 50% of the samples was higher when compared with BIS and WHO standards. Majority of samples during PRM fall in optimal and deficit zones and during POM majority of samples clusters in optimal and Fluorosis zone. The higher ratio of Na/Ca indicates dissolution of fluoride minerals at higher pH and the  $HCO_3/Ca$  ratio indicate the chemical condition favoring dissolution of fluoride ions. The hill piper diagram indicates low fluoride (<1.0 mg/l) are confined to Ca-Na-Cl- $HCO_3$ -Cl and Mg-Na-Cl- $HCO_3$ , and higher fluoride (>1.0 mg/l) is

due to Mg-Ca-Cl- $HCO_3$ , Na-Mg-  $HCO_3$ -Cl, Na-Mg-Cl- $HCO_3$ , and Na-Cl- $HCO_3$  zones due to effective dissolution of fluoride ions from the litho units of the study area. During POM facies changes from hard calcium bicarbonate type to alkaline-mixed bicarbonate type along the flow path favors mobility of fluoride ions. Gibbs plot indicate the influence of precipitation-induced chemical weathering along with dissolution of rock-forming minerals. The spatial distribution of fluoride indicates lower concentration of fluoride during PRM than POM due to aggressive nature of in filtering rainwater to dissolve additional fluoride ions. A positive correlation was observed between fluoride and pH values during PRM indicating alkaline nature of the water promotes leaching of fluoride. During POM, good correlation was observed between Mg and  $F$  indicating leaching of fluoride from sources rocks. Three factors were extracted during PRM and POM indicating the combined action of hydrogeochemical processes like weathering, ion exchange, and anthropogenic inputs are the key factors that determine the groundwater chemistry in the study area. The saturation indices during PRM indicates apatite as over saturated, fluorapatite as equilibrium and fluorite was undersaturated. During POM, all the fluoride minerals show undersaturation indicating the effect of dilution. In general, fluoride chemistry of the region is highly influenced by dissolution and precipitation along with mixing apart from anthropogenic activities.

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