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ORIGINAL ARTICLE

Origin of high fluoride in groundwater of the Tuticorin district, Tamil Nadu, India

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Abstract

This paper reports the results of higher F^- and HCO_3^- concentrations and its response to high pH level in a hard rock terrain in Tamil Nadu, India. About 400 groundwater samples from the study area were collected from a period of four different seasons and analysed for F^-, HCO_3^- and other major cations and anions. The key rationale for the higher fluoride and bicarbonate in the study area is the soaring rate of the leaching fluoride-bearing minerals and weathering processes. Fluoride and HCO_3^- ranges from BDL to 3.30 mgl^{-1} and 12 to 940 mgl^{-1}, its concentrations are lower for the period of SWM and it increases during POM and reaches to a maximum in PRM. Higher dissolution is observed in the NEM season due to rainfall impact. Spatial distribution and factor score show that the higher concentrations of F^- and HCO_3^- are eminent in the northern and central zone of the study area due to the impact of lithology. The higher values in pCO_2 versus HCO_3^- plot indicate higher residence time which favours more water–rock interactions, which further increase the F^- concentrations in groundwater. HCO_3^- is linearly correlated with F^- which indicates that these ions were consequent from the weathering influences. At the same time, poor correlation of F^- with pH could possibly be due to the increase of alkalinity follow-on from the swell of bicarbonate level with very low Ca^{2+} that promotes increase in F^-concentration in the groundwater.

Keywords Fluoride · Bicarbonate · Water–rock interactions · Weathering processes · Lithology · India

Introduction

Growing groundwater contamination causes not only the deterioration of water quality but also make threats to human health, the stability of aquatic ecosystems, economic improvement and social wealth. The cause for the poor quality of groundwater is attributable to variety of reasons including interaction between water, soluble minerals, salts, and anthropogenic pollution (Codling et al. 2014; Subba Rao et al. 2016). Despite the intricate hydro and biogeochemical issues, the quantity of fresh ground water is limited. Besides the major components in water

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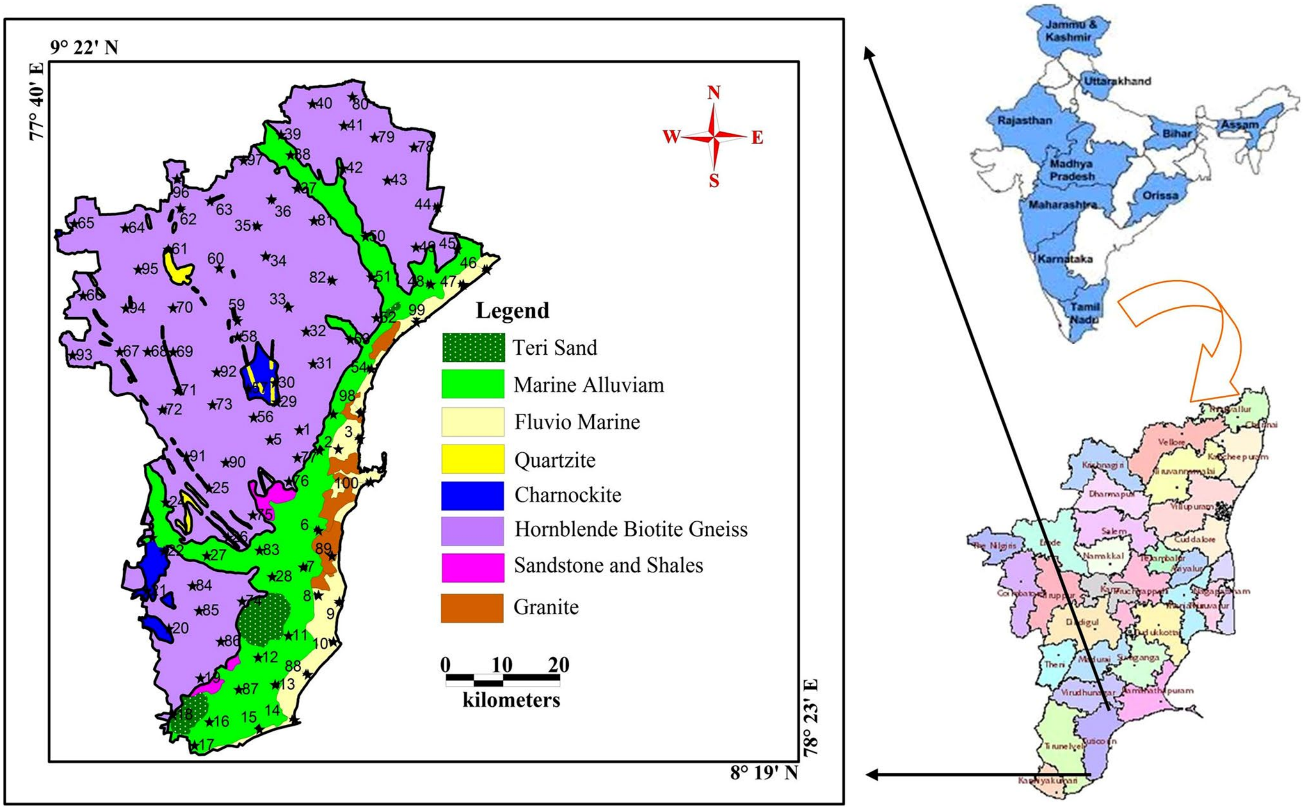

Fig. 1 Location and geology map of the study area

namely Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, HCO_3^-, and Cl^-, the secondary components include F^-, K^+, PO_4^{3-}, NO_3^- and CO_3^{2-} (Chidambaram et al. 2013). Fluoride and bicarbonate becomes toxic if it occurs in drinking water, and the maximum acceptable limit of F^- and HCO_3^- are 1.5 and 125 to 350 mgl^{-1}, respectively, as per WHO standards (2004). Fluorine has unenthusiastic effects on human health when its intake levels are either too high or too low. High fluoride level can cause negative effects on human health, such as dental fluorosis, skeletal fluorosis, impaired thyroid function, and lower intelligence in children (Edmunds and Smedley 2013). Alkalinity in natural groundwater is mainly derived from the dissolution of carbonate minerals and CO_2 present in the atmosphere and in the soil above the water table (Gao et al. 2016a, b). The fluoride in groundwater shows variation with respect to the lithounits of the study area. High concentration of F^- is seen in groundwater from hard rock, fluvial as well as alluvial aquifers, which might be derived from minerals such as micas, apatite, fluorite, soil dust, chemical stimulant, clay and shale (Naseem et al. 2010; Manikandan et al. 2014; Li et al. 2015). Hence, fluoride problems are predisposed to arise in hard rock and sedimentary aquifer where these minerals are rich in the country rocks.

Generally, fluoride show negative correlations with calcium and magnesium concentrations and positive correlation with bicarbonate concentrations in groundwater (Chae et al. 2006; Gao et al. 2011; Subba Rao et al. 2016). Higher levels of dissolved fluoride are usually related with high pH and Na^+–HCO_3^- type waters, while the temperature and depth of groundwater can also play vital roles (Chae et al. 2007). Ion exchange has been found to influence fluoride levels through both base exchange, which reduces calcium concentrations (Edmunds and Smedley 2005; Chae et al. 2006) and anion exchange, in which OH^- in groundwater replaces F^- on certain clay minerals or weathered micas (Guo et al. 2007). Thermodynamics computation indicated that some of this high fluoride groundwater is supersaturated with respect to fluorite, fluorapatite and hydroxyl-apatite (Singaraja et al. 2012; Chidambaram et al. 2012; Li et al. 2015). The overuse of fertiliser on the soil for agricultural activities would also be the possible source for the high fluoride and bicarbonate content in groundwater (Singaraja et al. 2012; Gao et al. 2016a, b). It is also implicit that the similar lithology from the nearby district and furthermore hard rock terrains are usually reported to have high concentrations of fluoride and bicarbonate in groundwater (Chidambaram et al. 2012; Manikandan et al. 2014). In addition, higher concentrations of F^- and HCO_3^- could possibly come from hornblende biotite

Table 1 Maximum, minimum and average of the chemical constituents in groundwater representing all four seasons (all values in mgl^{-1} except EC in µS/cm and pH)

	Temp °C	pH	TDS	EC	Ca^{2+}	Mg^{2+}	Na^+	K^+	F^-	Cl^-	HCO_3^-	NO_3^-	PO_4^-	SO_4^{2-}	H_4SiO_4
Pre-monsoon															
Avg	32.35	7.57	1843.33	2878.23	100.54	78.62	424.56	45.55	0.53	922.83	318.88	7.02	0.52	72.55	61.75
Max	35.90	9.20	16731.21	26240.00	1600.00	1248.00	3980.00	520.50	3.30	10812.25	940.20	148.00	12.00	456.00	125.00
Min	27.60	6.80	204.62	308.80	4.00	4.80	14.80	0.50	BDL	35.45	36.60	0.51	BDL	1.00	1.25
Southwest monsoon															
Avg	29.82	7.83	1587.91	2504.24	109.68	96.31	308.72	32.29	0.45	705.84	160.95	7.22	0.14	70.95	42.01
Max	31.61	9.40	13906.94	21794.00	500.00	895.00	4250.00	293.00	2.70	9052.50	536.80	148.20	1.02	274.00	75.76
Min	28.22	6.80	312.25	461.00	29.00	9.00	10.00	2.00	BDL	35.45	12.20	0.71	BDL	2.00	3.67
Northeast monsoon															
Avg	28.45	7.33	1369.40	2141.60	86.38	54.99	283.03	38.09	0.47	545.15	316.46	6.74	0.27	48.94	52.19
Max	29.60	8.60	9283.70	14598.00	560.00	296.00	3400.00	196.00	2.90	5276.00	915.00	129.00	4.35	248.00	99.78
Min	27.00	6.00	261.81	417.00	8.00	2.40	20.00	1.00	BDL	35.45	61.00	0.15	BDL	1.43	2.00
Post-monsoon															
Avg	31.82	7.67	1484.23	2357.86	81.37	50.04	365.27	25.42	0.46	636.04	267.86	4.34	0.21	37.78	12.21
Max	35.80	8.80	19365.68	30200.00	608.00	559.20	6812.00	218.50	2.43	10989.50	683.20	57.00	3.21	324.00	15.20
Min	29.30	6.95	253.92	372.00	4.00	2.40	14.70	0.83	BDL	35.45	50.40	0.23	BDL	1.00	2.00

gneiss (HBG) and charnockites subjected to weathering in hard rock terrain (Singaraja et al. 2012; Manivannan et al. 2010; Subba Rao et al. 2016).

In India, several states face problems due to the high F^- and HCO_3^- content in groundwater. It is well-known that F^- and HCO_3^- contaminations are present in the groundwater in the various districts of Tamil Nadu State, India. Tuticorin district in Tamil Nadu is one such big area where high concentrations of fluoride and bicarbonate are present in groundwater. However, no major studies have been conducted till date in this area. In the present study, an attempt is made to correlate the chemical ions and geological sequence to identify the origin and geochemical processes prevailing in high fluoride and bicarbonate groundwater in Tuticorin district of Tamil Nadu. Another objective of the study is to understand the spatial variations and saturation index of fluoride and bicarbonate minerals in groundwater.

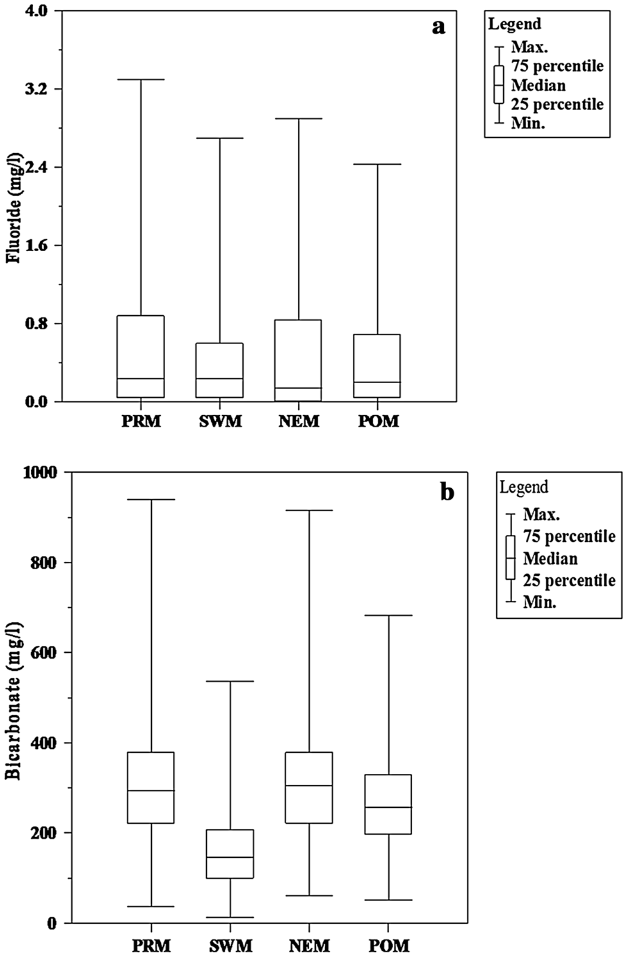

Fig. 2 Box plot for the maximum, minimum, and average of the chemical constituents in groundwater during PRM and POM (all values in mg l^{-1} except pH)

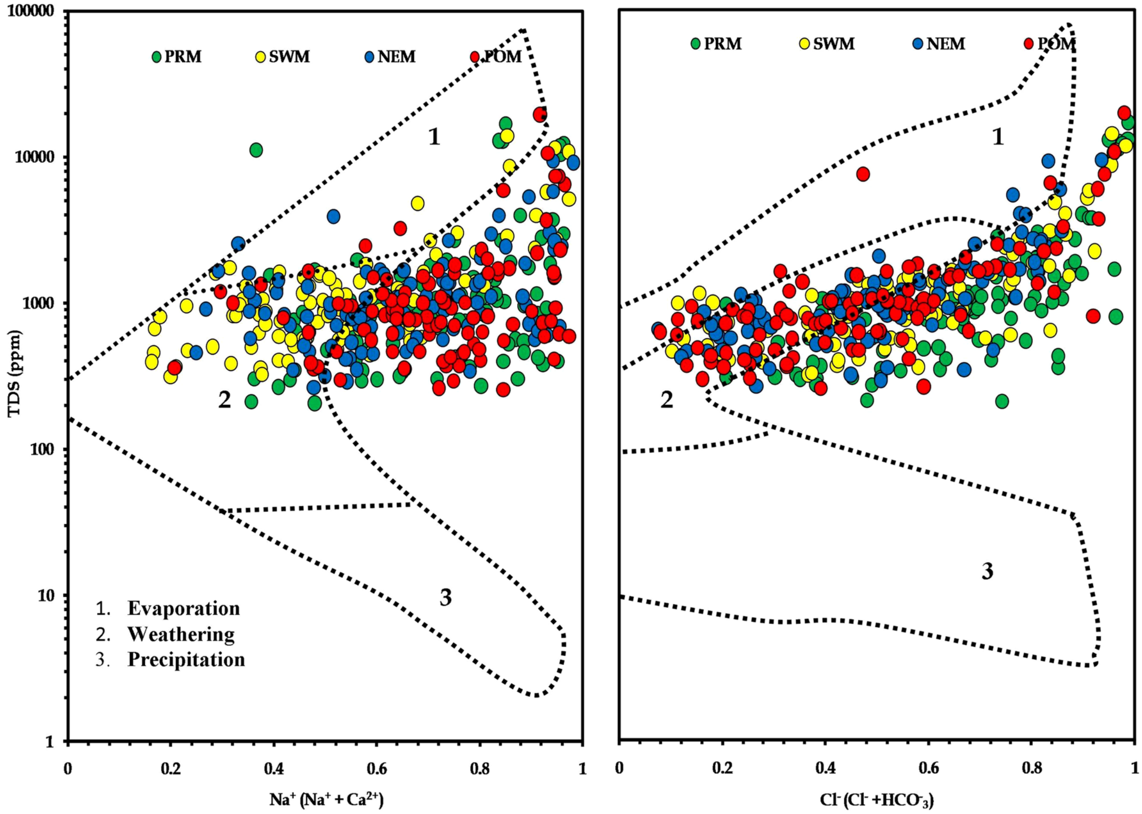

Fig. 3 Major ion chemistry showing nature of water (fields after Gibbs 1970)

Description of study area

The study area, lying between latitude 8°19′ to 9°22′N and longitude 77°40′ to 78°23′E with a total area of 4620 Km^2 (Fig. 1) is situated in southeast part of Tamil Nadu, India. Geologically, five most important lithounits are present in this area, hornblende biotite gneiss, charnockite, quartzite, granite, and alluvial and fluvial plains (Fig. 1). The sandstone and teri sands form small patches in the study area. Three major rivers such as Tambraparani, Vaiparand and Karamanaiyar are draining within the study area. The area experiences a tropical climate with a yearly rainfall that ranges between 570 and 740 mm (CGWB 2009). The V.O. Chidambaram port and hurriedly rising industrial region consisting of major and small-scale industries (SIPCOT) are developing in the fluvial region of the study area (Singaraja et al. 2012).

Materials and method

Sample collection and analysis

A total of about 400 groundwater samples were collected covering most of the geological formations representing the entire district during pre-monsoon (PRM), southwest monsoon (SWM), northeast monsoon (NEM) and post-monsoon (POM). The physico-chemical parameters like pH, electrical conductivity (EC), temperature of groundwater were measured in situ using hand-held instruments (Eutech make). The F^- was analysed using the Orion Ion selective electrodes and HCO_3^- by titration method; Cl^-, SO_4^{2-}, PO_4^-, NO_3^-, H_4SiO_4, Ca^{2+}, Mg^{2+}, Na^+ and K^+ were analysed using the ion chromatograph (IC, Metrohm 861). The accuracy of analysis of major ions was checked by error percentage computation and it was found to be less than 10% (Hem, 1985). In this study, saturation indices (SI) of fluoride and carbonate minerals were calculated by WATEQ4F (Hammarstrom et al. 2005) software. The correlation and factor analyses were computed using Statistical Package of Social Studies (SPSS) version 17 and spatial diagram were constructed using Arc GIS software.

Results and discussion

The maximum, minimum, and average values of various chemical constituents in the groundwater samples collected from the study area is shown in Table 1.

The ascending order of cations and anions concentrations areas follows: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $Cl^- > HCO_3^- > SO_4^{2-} > H_4SiO_4 > NO_3^- > F^- > PO_4^{3-}$ during all the seasons. The pH ranges from 6 to 9.40 indicating that the groundwater is changing from slightly acidic to alkaline nature. The lowest pH is observed in NEM but highest in PRM. EC ranges from 310 to 30,200 µS/cm in the study area. In all seasons, higher electrical conductivities were noted along the coastal region which was possibly due to seawater intrusion (Singaraja et al. 2012). TDS in the groundwater samples varies between 205 and 19,370 mgl^{-1} and higher concentrations are found during PRM followed by SWM, POM and NEM. Water temperatures have a wide distribution in all the seasons which ranges from 28 to 36 °C.

The Ca^{2+} concentration in the groundwater ranges from 4 to 1600 mgl^{-1}. It is higher in SWM and lower during POM. The Ca^{2+} may be derived from calcite, hornblende and plagioclase minerals. Mg^{2+} concentration ranges from 2.4 to 1248 mgl^{-1} in the groundwater samples of the study area. Relatively higher concentration of Mg^{2+} is observed in the SWM season and lesser during POM season. Higher levels of Mg^{2+} in groundwater is seen in HBG and charnockite region located along the western part of the study area that have Mg^{2+} affluent pyroxene as the predominant mineral (Chidambaram et al. 2012). Also, the higher level of Mg^{2+} seen along the coastal zone perhaps may be because of the influence of seawater intrusion (Subba Rao et al. 2012; Singaraja et al. 2014). Na^+ concentration ranges from 10 to 6212 mgl^{-1} which is higher in the PRM and lesser in NEM. The main sources of Na^+ in groundwater are hornblende biotite gneiss, charnockite, plagioclase feldspar rock types seen along the western part of the region (Srinivasamoorthy et al. 2009; Thivya et al. 2013; Venkatramanan et al. 2013) as well as seawater intrusion along the coastal region (Thilagavathi et al. 2014). K^+ concentration ranges between 0.5 and 520 mgl^{-1} with higher values observed in POM. At a few locations, abnormalities are seen irrespective of seasons possibly due to weathering and urban landfill leaching (Thivya et al. 2015; Selvam et al. 2016).

Cl^- is the leading ion among anions during all the seasons, and its higher values are noted in the coastal zone, may be because of seawater intrusion (Srinivasamoorthy et al. 2008; Chidambaram et al. 2013). Its concentration ranges from 35.5 to 10,990 mgl^{-1}; higher values are prominent in PRM groundwater samples. SO_4^{2-} concentration ranges from 1 to 456 mgl^{-1}, and the highest concentration is observed in PRM and lesser in POM. Higher concentrations of SO_4^{2-} mainly derived from evaporate minerals such as gypsum and anhydrite, which are sulphates of magnesium and sodium. It would also possibly migrate to groundwater from salt pan activities happening along the eastern part of the study area (Chandrasekharan et al. 1997). Nitrate ranges from 0.2 to 148 mgl^{-1}, which is noted to be higher in PRM. The concentration of silica (H_4SiO_4) ranges from 1.2 to 125 mgl^{-1}, higher values are observed during PRM compared to other seasons. Higher concentration of H_4SiO_4 in groundwater is chiefly attributable to the weathering of silicate minerals (Prasanna et al. 2010). PO_4^{3-} concentration ranges from BDL to 12 mgl^{-1}; higher values are seen during PRM. SO_4^{2-} and PO_4^{3-} in the groundwater may also arise from the use of fertilisers. In addition, it can also come from apatite mineral found in HBG and charnockite (Brindha et al. 2012; Chidambaram et al. 2012). One of the reasons for the high bicarbonate in the study area is the high rate of the dissociation of H_2CO_3 (Rafique et al. 2015). HCO_3^- concentration ranges from 1 to 940 mgl^{-1}, with higher values in PRM samples followed by NEM, POM and SWM. It is attributed to carbonate chemical weathering process (Mondal and Singh 2004; Li et al. 2015). It is also noted that the higher values of HCO_3^- in the groundwater controls the mineral dissolution processes (Thivya et al. 2015). Fluoride concentration ranges from BDL to 3.3 mgl^{-1}, with higher values in PRM season followed by NEM, POM and SWM. Hornblende biotite gneiss is one of the most important sources

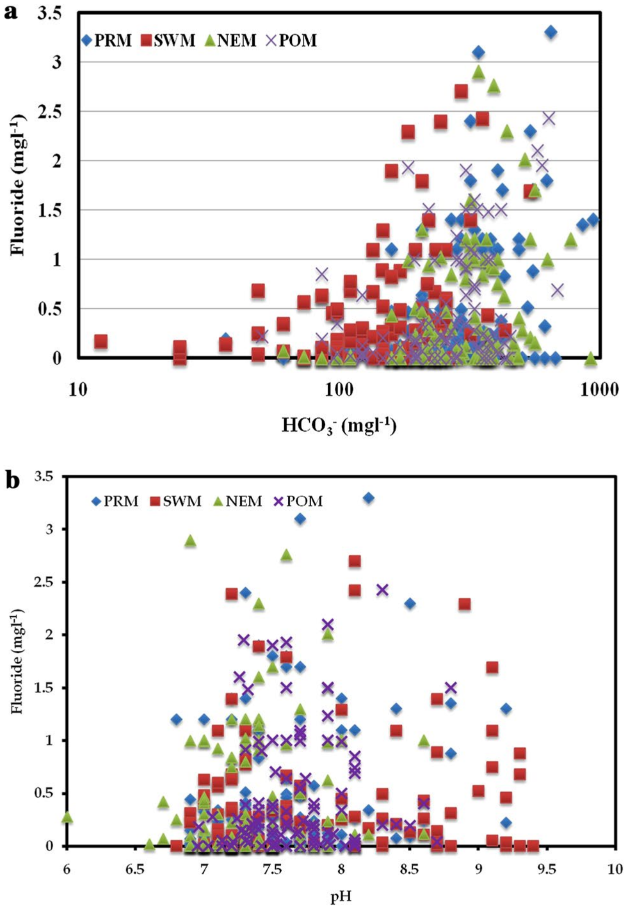

Fig. 4 **a** Variation of F^- concentrations with HCO_3^- and **b** F^- concentrations with pH in groundwater samples from Tuticorin district

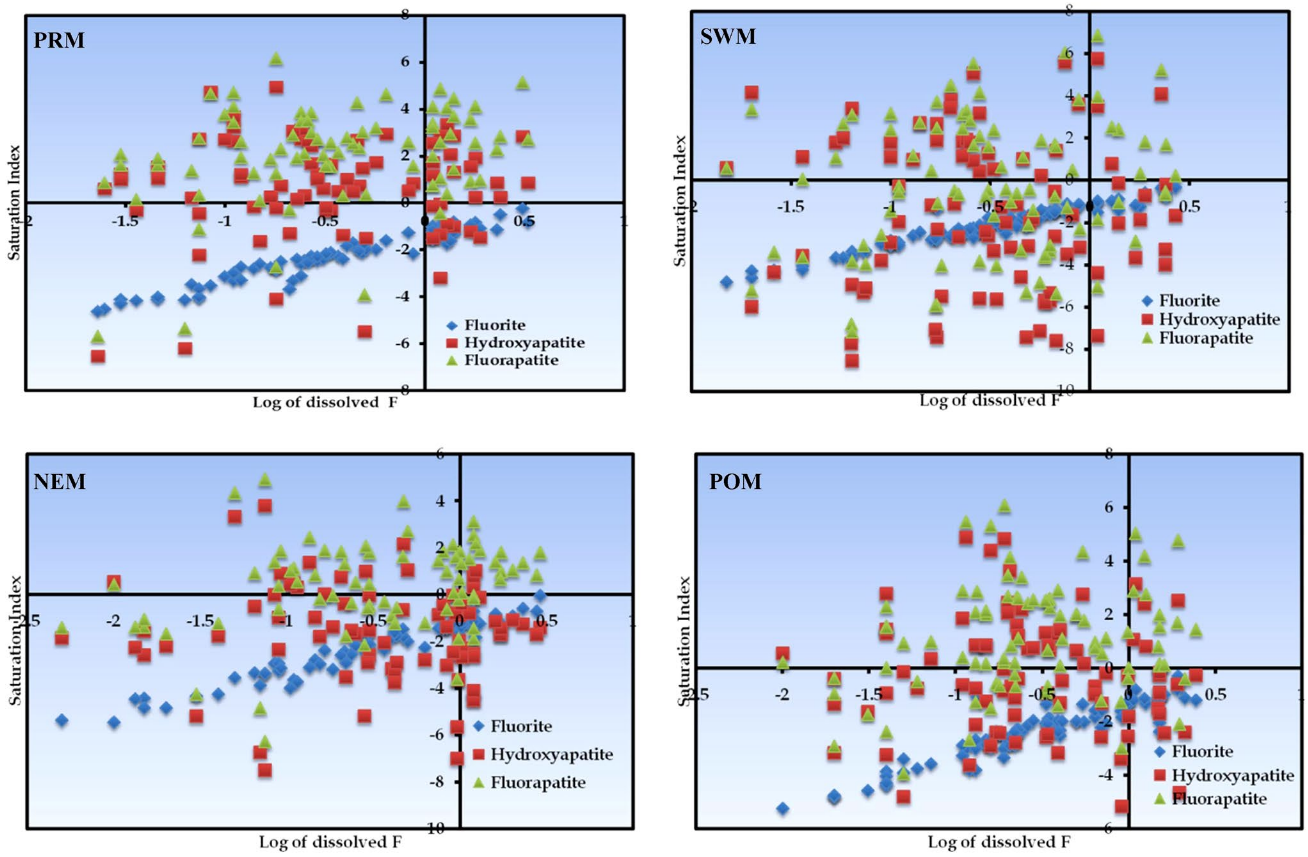

Fig. 5 Variation of saturation index of different fluoride minerals with dissolved F^- for samples representing different seasons

of F^- in the groundwater (Chidambaram et al. 2013). The lithological influences in the dissolution of fluoride ions in groundwater are studied by Manikandan et al. (2014). The higher concentrations of fluoride in groundwater could be due to the weathering as well as leaching of biotite, hornblende, apatite and mica minerals (Srinivasamoorthy et al. 2008; Chidambaram et al. 2013). The seasonal variation of fluoride and bicarbonate is shown in Fig. 2. It is seen that most of the samples fall above the median value during PRM, NEM and POM, but there is not much variation during SWM. Fluoride concentration beyond the WHO drinking water limit is observed during PRM (9%), SWM (7%) and NEM and POM (6%). In the case of bicarbonate, majority of the samples are above the WHO permissible limit like PRM (33%), SWM (4%), NEM (37%) and POM (22%). For inferring the dominant controls on water quality, the data are plotted on Gibbs diagrams (Gibbs1970) (Fig. 3). These plots suggest that groundwater in the study area is closely influenced by weathering, although some samples appear to reflect only the influence of evaporation. This finding suggests that the groundwater chemistry is largely controlled by weathering and precipitation of lower solubility minerals, as evaporation causes salinity to increase.

The origin of high fluoride in groundwater

In all seasons, F^- is found to be positively correlated with HCO_3^- with significant correlation coefficient (Fig. 4). Maximum values are observed in PRM. Figure 4 shows that high concentration of F^- are observed in both low and high pH conditions that may be attributed to weathering of biotite minerals from HBG. In addition, alkaline pH conditions are favourable for the dissolution of F^- into groundwater (Chidambaram et al. 2012; Subba Rao et al. 2012; Singaraja et al. 2014). At lower pH conditions, groundwater containing dissolved HCO_3^- in the form of H_2CO_3 reacts with the minerals and releases H^+, F^-, cations and HCO_3^-, according to the equation given below.

$$\begin{aligned}&(\mathrm{Na})_2(\mathrm{Ca},\ \mathrm{Mg},\ \mathrm{Fe})_3\mathrm{Al}_2\mathrm{Si}_6\mathrm{O}_{20}(\mathrm{OH})_4\\&\quad+\ \mathrm{H_2O}\ +\mathrm{H_2CO_3}\\&\quad\rightarrow\left(\mathrm{Ca},\mathrm{Mg_3Fe_3}\right)\ \mathrm{Al_3Si_5O_{20}(OH)}\\&\quad+\mathrm{F}^-+\ \mathrm{Na}^+ +\ \mathrm{H}^+ +\ \mathrm{HCO}_3^-\end{aligned}$$

At higher pH conditions, hydrolysis takes place which releases $(OH)^-$ along with cations and fluoride according to the equation given below.

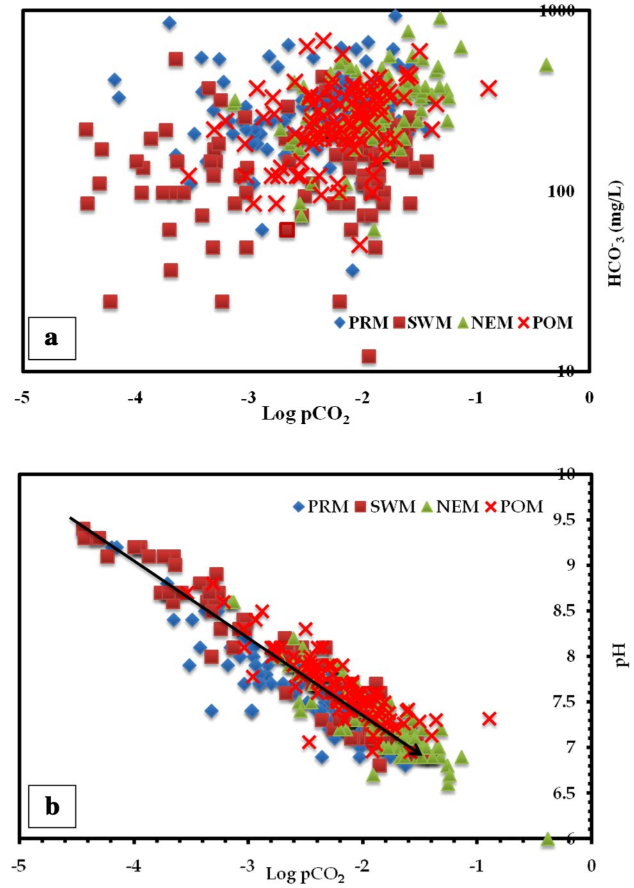

Fig. 6 **a** Log pCO_2 versus HCO_3^- and **b** Log pCO_2 versus pH relationship of groundwater samples for different seasons

$$
\begin{aligned}
&(Na)_2(Ca, Mg, Fe)_3Al_2Si_6O_{20}(OH)_4 + H_2O \\
&\quad \rightarrow (Mg_3Fe_3)\ Al_3Si_5O_{20}(OH) \\
&\quad + OH^- + F^- + Na^+ + Ca^{2+} + Mg^{2+} + HCO_3^-
\end{aligned}
$$

These equations indicate that elevated HCO_3^- contents favour F^- release from the hard rock aquifer matrix into the groundwater. The HBG and charnockites present in the study area contains mica, quartz, calcite and feldspar. The F^- present in the mineral will be desorbed into the groundwater ,when the HCO_3^- concentrations are high because of HCO_3^- which is a strong competitor for sorption (Gao et al. 2011). In few samples at high pH, OH^- could release F^- ions and result in the sorption of F^- into the aquifers (Jacks et al. 2005). The release of high concentration of fluoride into groundwater at higher pH ranges may also be due to anthropogenic sources.

Generally, it is seen that the HCO_3^- and F^- concentrations are lesser during SWM and it increases during POM and reaches to a maximum in PRM and then they get diluted during NEM (Fig. 4). This leads to the interpretation that higher dissolution and dispersivity of F^- is observed in the NEM season due to the impact of rainfall.

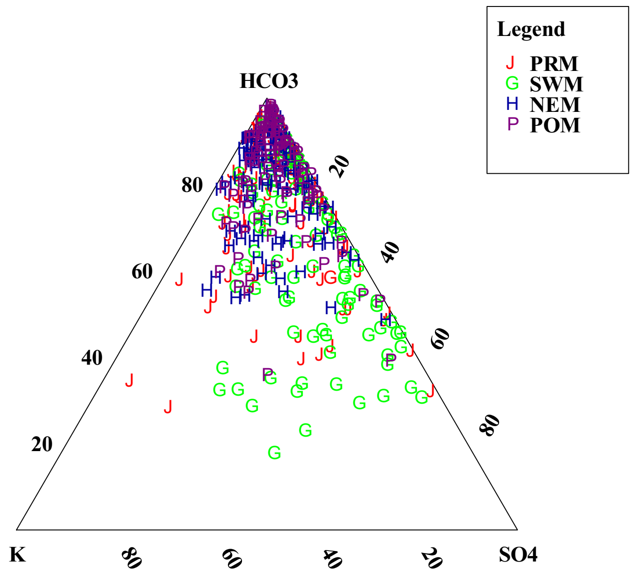

Fig. 7 Relative HCO_3^-, K^+ and SO_4^{2-} contents of waters of the study area

Fluoride-bearing minerals

The association of F^- ion to the saturation index (SI) of different F^- bearing minerals like fluorite [CaF_2], fluorapatite [$Ca_5(PO_4)_3$ (OH)] and hydroxyl-apatite [Ca_5 $(PO_4)_3F$] are studied. The calculated saturation indices (SI) values for fluorite minerals and log of dissolved concentration of fluoride are shown in Fig. 5. Most of the groundwater samples were saturated or over-saturated with respect to the dissolved concentration of fluoride. Initially, SI increases simultaneously with the F^- concentration, until F^- concentration reached a value of 6 due to long residence time of water–rock interaction which lead to the release of F^- from fluorine-bearing minerals (Rafique et al. 2015; Li et al. 2015). Saturations show fluorapatite dominance followed by hydroxyl-apatite and fluorite. F^- when released into the system, it readily adsorbs on to the apatite and makes it fluorapatite, later the $(OH)^-$ in the hydroxyl-apatite are preferred by F^- and at the end, a separate compound namely fluorite is formed. There is a clear linear relationship between F^- concentration and SI of fluorite irrespective of the seasons (Edmunds and Smedley 2005; Rafique et al. 2015).

Relationship between pCO_2 and HCO_3^-

The pCO_2 values in the groundwater ranges from −4.19 to −1.43 during PRM, −4.43 to −1.43 during SWM, −3.14 to

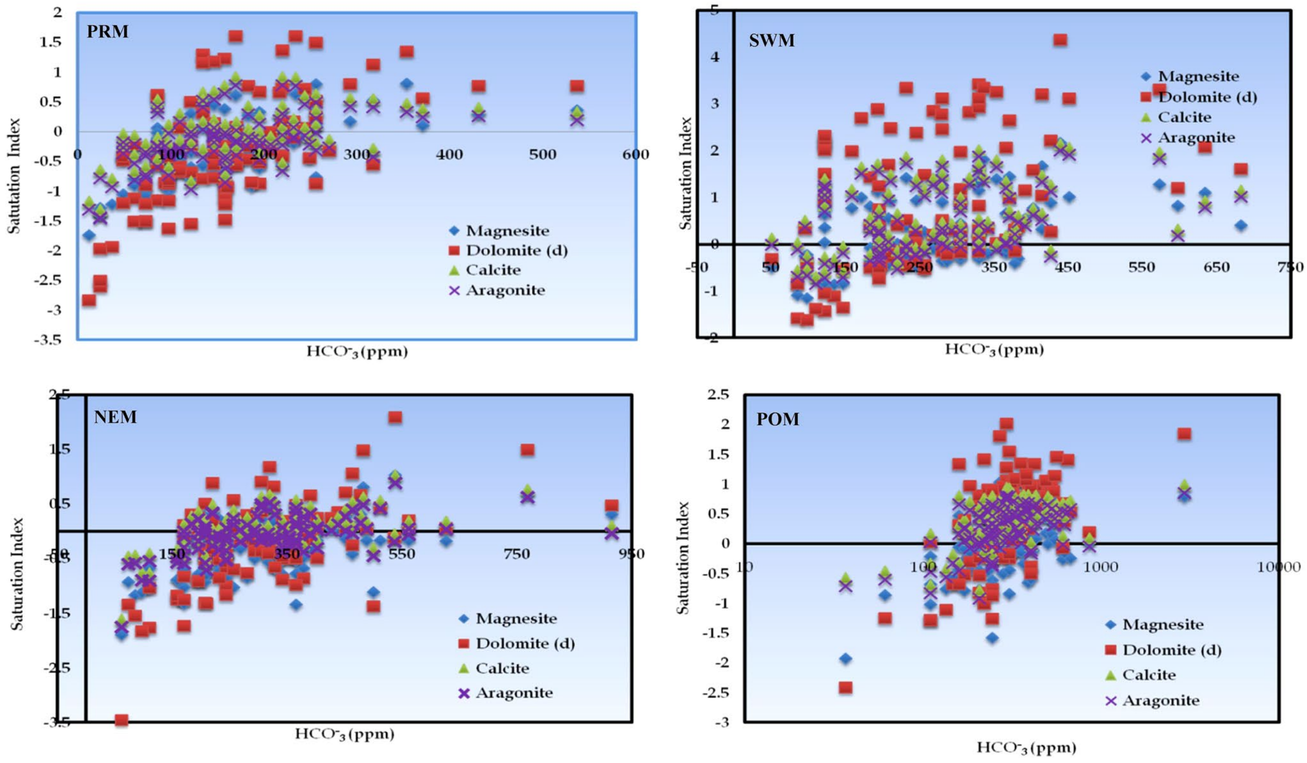

Fig. 8 Variation of saturation index of different carbonate minerals with HCO_3 for samples collected during different seasons

– 0.38 and – 3.53 to – 0.89 during NEM and POM seasons, respectively, indicating an increase in pCO_2 with increase in bicarbonate (Fig. 6). The increase is found in all the groundwater samples irrespective of season. The higher values of pCO_2 also indicate longer residence times (Prasanna et al. 2010). Water with a high pCO_2 of around – 2 indicates deep circulation of groundwater with a lesser amount of atmospheric contact or higher saturation of carbonate minerals. This results from the interaction of minerals present in the rocks through which it flows (Ayoob and Gupta 2006; Chidambaram et al. 2012). It is also evident that log pCO_2 values linearly decreases with pH indicating fresh water recharge or less atmospheric interaction with the system (Chidambaram et al. 2013). The higher values of log pCO_2 coincide with the lesser values of pH indicating rock–water interactions. The pH increases from 6 to 9.4 (Fig. 6), this progressive increase of H^+ concentration and log pCO_2 values indicate less interaction of the groundwater system with the atmosphere. The ion exchange reactions occur by the exchange of H^+ ions in the host rock. In all seasons, the groundwater remains as HCO_3^- type. From the Fig. 7, it is clear that there is a shift from $Na^+ + K^+$ to Ca^{2+} and Cl^- to HCO_3^- type (Manivannan et al. 2010; Singaraja et al. 2014). These imply that higher pCO_2 leads to higher bicarbonate concentrations in the groundwater, which in turn enhances the release of F^- due to higher rock–water interactions under long residence time.

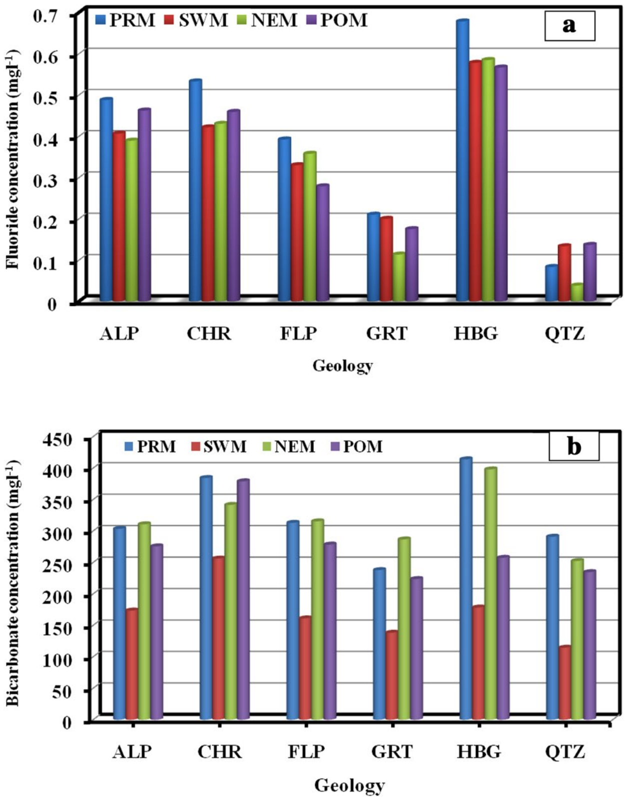

Fig. 9 **a** F^- and **b** HCO_3^- versus geology for different seasons in the study area

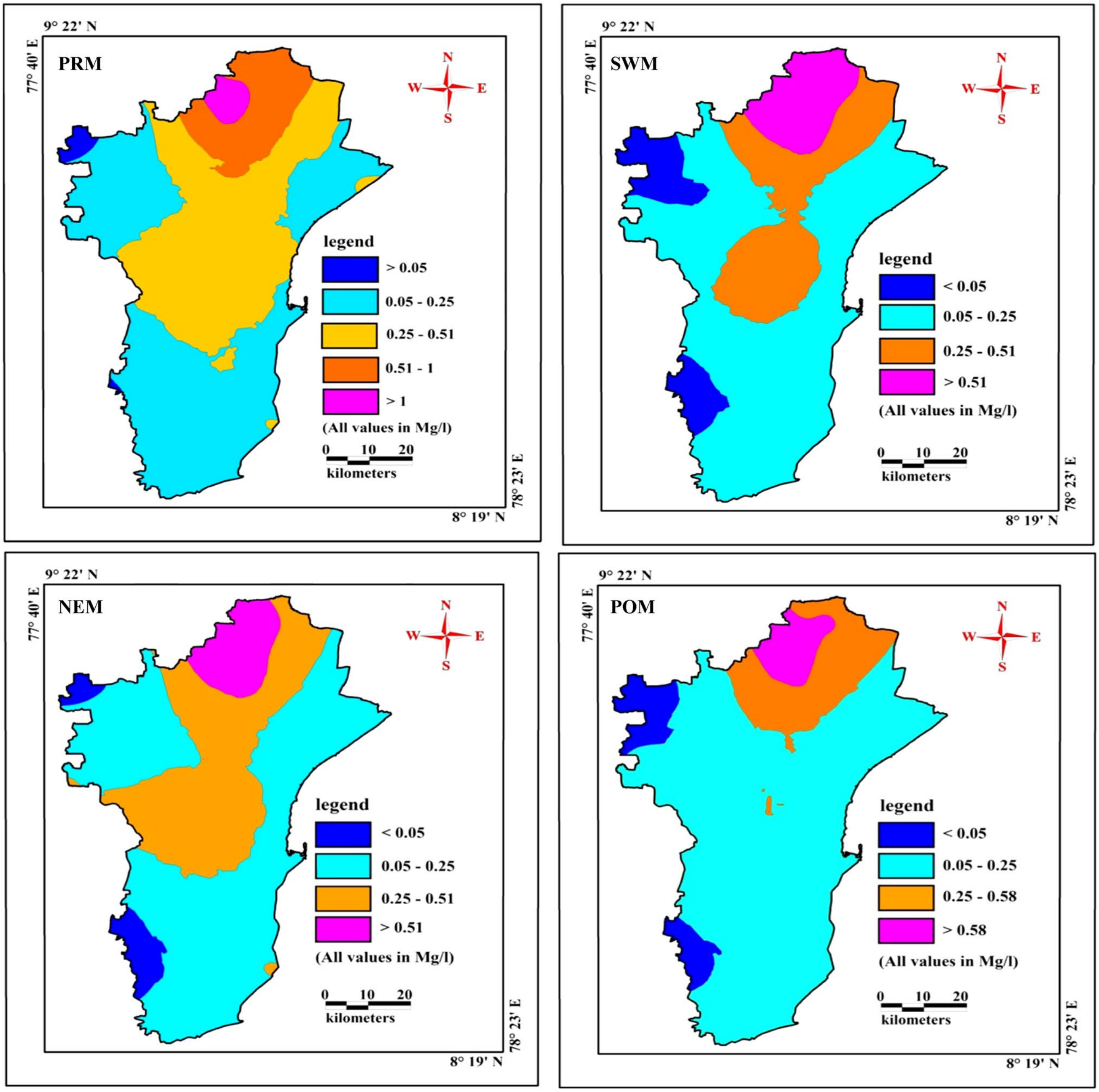

Fig. 10 Spatial distribution of F^- during different seasons

SI of carbonate minerals

Saturation index for minerals such as magnesite ($MgCO_3$), aragonite ($CaCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) were calculated. Saturation index of carbonate minerals are plotted against the concentration of HCO_3^- (in mgl^{-1}) (Fig. 8). The saturation state of carbonate minerals are in the following orders: $SI_C > SI_A > SI_D > SI_M$ during PRM and NEM. $SI_D > SI_C > SI_D > SI_M$ during SWM and $SI_C > SI_D > SI_A > SI_M$ during POM season, respectively. SI of all carbonate minerals increases with increase in HCO_3^- during all seasons, due to increased groundwater recharge and subsequent dilution of chemical constituents present in groundwater. They form near saturation to saturation state. Excess of HCO_3^- may result in stoichiometric dissolution of calcite and ion exchange (Gomez et al. 2006). A few samples show under saturation, which may be due to non-availability of cations (Ca^{2+} and Mg^{2+}) which might have been removed from the aqueous system due to the process of cation exchange (McNab et al. 2009; Li et al. 2015). The

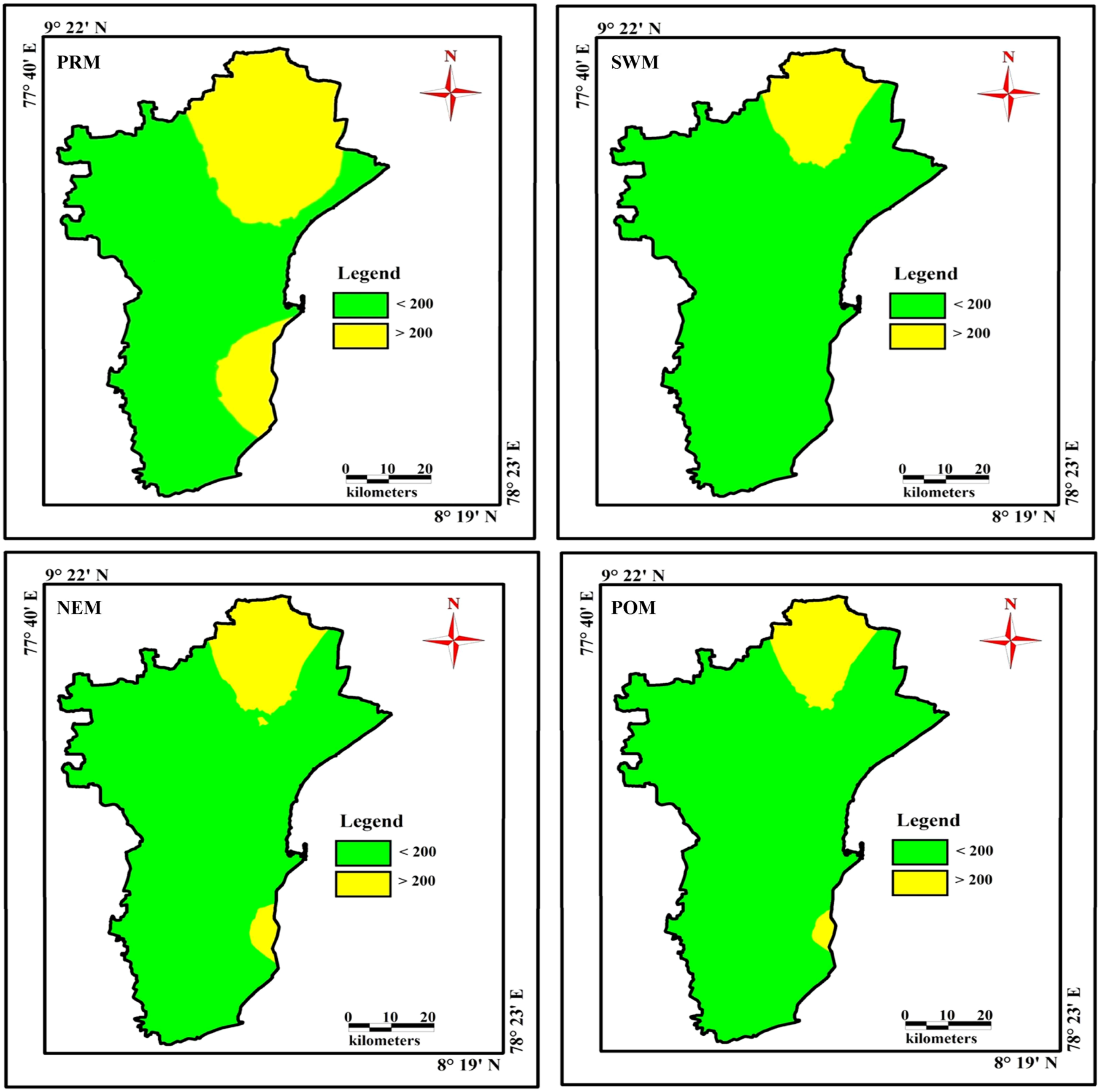

Fig. 11 Spatial distribution of HCO_3^- during different seasons

carbonate minerals generally attain saturation when the concentration of HCO_3^- reaches nearly 300 mgl^{-1}. It is interesting to note that the majority of samples attain saturation after this concentration, which may be due to the low flow conditions with high pCO_2 value and extent of weathering by the parent material (Rosa Cidu and Luca Mereu 2007). It is also appealing to the order of dominance that are under saturation is $SI_{Mg} > SI_{Do}$ and $Si_C < SI_{Ar}$ but $SI_{Mg} < SI_{Do}$ and $Si_C > SI_{Ar}$ are the state of saturation. It may be due to the preferential addition of Mg to $CaCO_3$ and formation of new Ca $Mg(CO_3)_2$, which results in the increase of SI_{Do} in the saturation state than the other carbonate minerals. The saturation of magnesite requires 2 Mg atoms to form an $MgCO_3$ compound. So, the first available free magnesium tends to join with existing calcite to form dolomite or it forms new dolomite. It may due to overall precipitation reaction that proceeds as below (Davis et al. 1997).

1. $CaCO_3 + Mg^{2+} \rightarrow CaMg\left(CO_3\right)_2$

2. $Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \rightarrow CaMg(CO_3)_2$

Occurrence of high F^- and HCO_3^- groundwater

The order of dominance of average fluoride concentration in various lithounits in all the seasons is as follows: hornblende biotite gneiss > charnockite > alluvial plain (river deposited) > fluvial plain (coastal deposited) > quartzite > granite (Fig. 9). The bicarbonate dominance during all the seasons is as follows: hornblende biotite gneiss > charnockite > fluvial plain (coast deposited) > alluvial plain (river deposited) > quartzite > granite (Fig. 9). Lithologically, the highest F^- and HCO_3^- contents in the groundwater occurred in the hornblende biotite gneiss areas of the study area. The spatial variations of the F^- and HCO_3^- concentrations are presented in Figs. 10 and 11. Physiographically, the highest F^- and HCO_3^- contents in groundwater occur in the northern part of the Tuticorin District due to HBG and charnockites geology (Manivannan et al. 2010; Manikandan et al. 2014). In the northern part of the Tuticorin District, the groundwater flow paths are longer and hence will have longer residence time and higher degree of rock–water interactions. This leads to higher concentrations of most of the elements in the groundwater including F^- and HCO_3^-. In other parts, the groundwater flow paths are comparatively shorter, residence time is lower and there is a less time of contact between water and minerals. It is also noted that F^- and HCO_3^- concentrations in alluvial and fluvial plain are typically low. But, higher concentrations of F^- observed in these parts may be attributable to the mud, dust, industrial discharge, chemical fertilisers as well as the sources of clays, biotite and apatite at higher rate of evaporation (Subba Rao 2009). Significant HCO_3^- concentrations are noted in the western and the eastern parts along the alluvial and fluvial region. The source of HCO_3^- in non-calcareous aquifers are derived by two different processes, one is when CO_2 mixes with water, it forms carbonic acid which decreases the pH of groundwater

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^-.$$

Second, the bicarbonate is derived when CO_2 dissolves in water. This forms HCO_3^-, which is a pH buffer. Hence, groundwater with high HCO_3^- concentrations will have relatively high pH

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+.$$

Also, it is noted that the spatial distribution of HCO_3^- coincides with that of F^- concentration in the study area.

Relationship in support of fluoride and bicarbonate concentration

Factor analysis

Using factor analysis, four factors were taken for PRM, SWM and POM seasons and five factors for the NEM (Table 2). Liu et al. (2003) classified the absolute factor loadings values as 0.3–0.5 (weak), 0.5–0.75 (moderate) and > 0.75 (strong), respectively. Fluoride concentration signifies as the third factor during PRM with 10.82 percentage of variance (PV). SWM results reveal that the second factor with 12.93 PV is represented by F^-. The F^- factor is represented as the fourth factor with 9.38 PV during NEM and again as second factor by 12.16 PV during POM. High F^- and HCO_3^- groundwater at Tuticorin District displayed distinctive major ion chemistry. Generally, higher loading of F^- and HCO_3^- with relatively negative or low loading of other ions (Table 2), particularly Ca^{2+}, Mg^{2+}, Na^{2+}, K^{2+}, pH and SO_4^{2-} concentrations may be due to increasing weathering process with dissolution of fluorine-bearing minerals and the desorption of exchangeable F^- from the loess. Long-term water–rock interactions may lead to the release of F^- from fluorine-bearing minerals (Rafique et al. 2015; Gao et al. 2016a, b). In this area, hard rocks, such as HBG and charnockite, contained abundant fluorine-bearing minerals, including fluorite, biotite, hornblende and apatite (Singaraja et al. 2014). As one of the major fluorine-bearing natural minerals, fluorite dissolves rapidly under natural conditions (Fig. 5). Because the fluorine-bearing minerals are sparingly soluble, the presence of high F^- concentrations in the groundwater require a long residence time, which is possible in the northern parts of Tuticorin District (Singaraja et al. 2015).

Table 2 Summary of fluoride represented factors during different periods of the study

Seasons	PRM	SWM	NEM	POM
Total number of factors	4	4	5	4
Fluoride Factor	3	2	4	2
pH	0.17	0.29	0.10	0.04
Ca^{2+}	0.02	−0.06	−0.01	−0.08
Mg^{2+}	−0.01	0.04	0.06	−0.05
Na^+	0.02	−0.09	0.00	0.08
K^+	0.08	0.08	−0.07	−0.02
Cl^-	−0.02	−0.09	−0.06	0.00
HCO_3^-	0.80	0.84	0.55	0.81
NO_3^-	−0.03	−0.04	−0.10	0.07
PO_4^-	0.02	0.14	−0.05	−0.07
F^-	0.85	0.80	0.92	0.81
SO_4^{2-}	0.17	0.20	0.20	0.10
H_4SiO_4	−0.06	−0.06	0.08	0.22

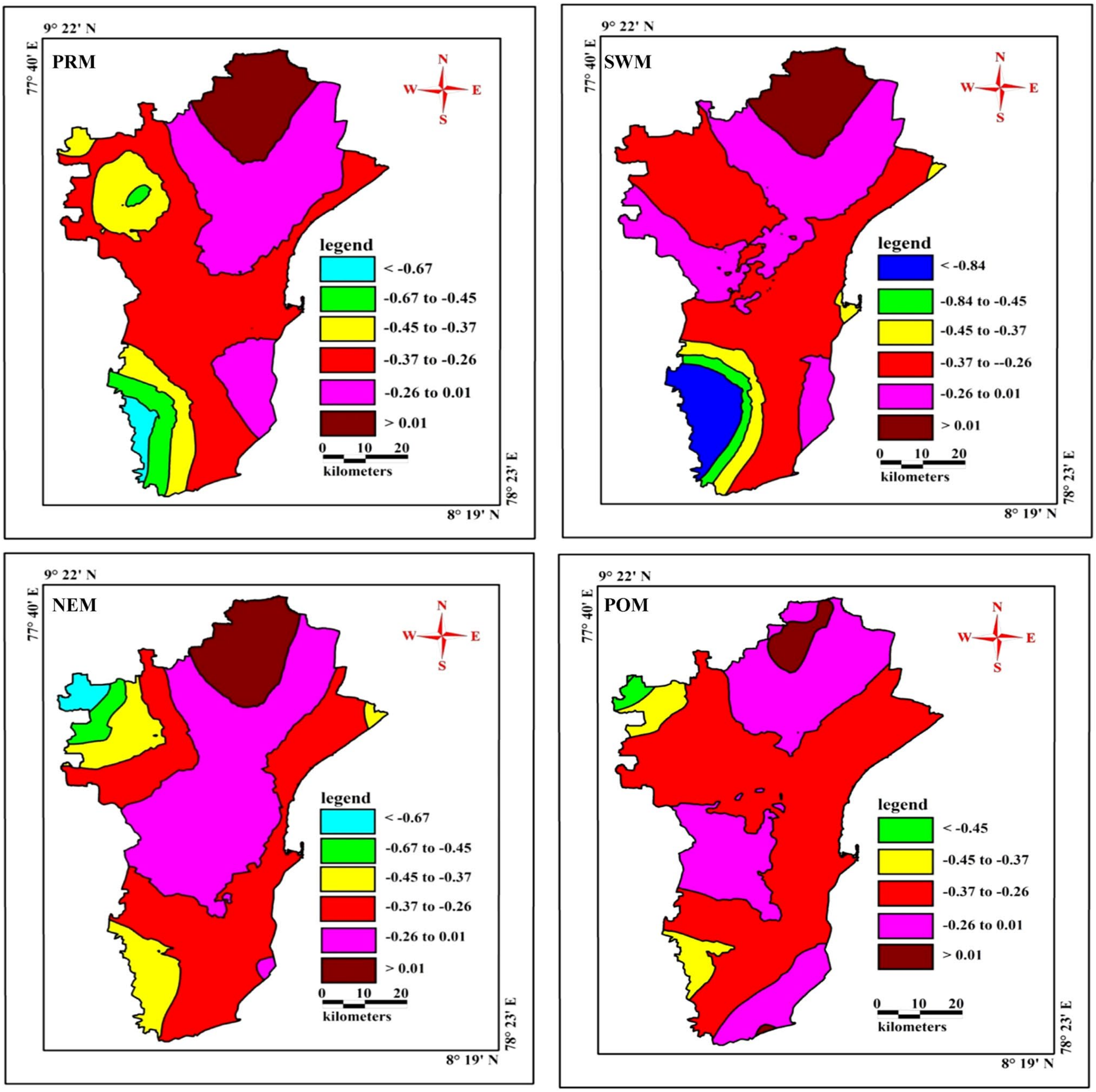

Fig. 12 Spatial distribution of F^- and HCO_3^- factor score during different seasons

Particularly, in all the seasons, HCO_3^- is positively correlated with F^- and higher factor scores are established in northern part of the study area suggesting that the minerals dissolve in the groundwater (Chidambaram et al. 2012; Singaraja et al. 2013). In addition, pH and F^- is weak correlation as increase of alkalinity is attributable to the swell of bicarbonate ions, these ions control on pH values ,Hence, the alkalinity inversely relationship of the pH level during all the seasons (Subba Rao et al. 2003; Singaraja et al. 2014). F^- and HCO_3^- concentrations have negative loading with respect to calcite and lower Ca^{2+} concentrations allowed additional fluorite to dissolve, further increasing F^- concentrations in groundwater. Hence, cation exchange promotes the release of F^- from the groundwater at Tuticorin District (Singaraja et al. 2016). Agricultural activity is unlikely a major source of F^- in the study area, given the insignificant correlation between F^- and NO_3^-concentrations in groundwater (Chatterjee and Mohabey 1998; Singaraja et al. 2015). Figures 10 and 11 clearly indicate that elevated HCO_3^- contents favoured F^- release from the aquifer matrix into groundwater. Spatial distribution of F^- and HCO_3^- values corresponds to the hydrogeochemical active zone (Fig. 12) resulting from the factor scores, possibly due to the migration of these ions from the similar source.

Conclusion

The above study provides evidence on the major difference in the chemical composition of groundwater with respect to F^- and HCO_3^- concentration during all the seasons. Higher F^- and HCO_3^- are noted in PRM, followed by NEM, SWM and low levels in POM, which is as a result of dilution effect after monsoon periods. It is also interesting to note that pCO_2 increases with HCO_3^-, due to longer residence time and the dissolution of minerals from the host rocks. Majority of the PRM, POM and NEM samples show evidence of higher pCO_2 values and log pCO_2 values linearly decrease with pH. Higher pH shows lesser pCO_2, which is more significant during SWM seasons, indicating fresh water recharge or less atmosphere interaction. The spatial distribution of F^- and HCO_3^- signify that the higher concentrations are seen along the hornblende biotite gneiss and charnockite rocks which lies in the northern part of the region indicating lithological control in the distribution of fluorides and bicarbonates during all the seasons. The F^- concentration in groundwater is controlled by degree of weathering, longer flow paths, higher residence time and more time of contact between water and minerals in the study area. The source of HCO_3^- in groundwater is due to mixing of CO_2 with groundwater forming carbonic acid which decreases the pH of groundwater and bicarbonate is derived when CO_2 dissolves in water forming HCO_3^- in relatively high pH condition. Fluoride shows a positive correlation with HCO_3^-, but poor correlation with pH, Ca^{2+} and Mg^{2+} during all seasons. It is attractive to note that increase of bicarbonate ions control the pH level in groundwater, and consequently the increase in alkalinity with low pH and Ca^{2+} levels due to cation exchange promotes the release of F^-. Poor correlation between F^- and NO_3^- concentrations indicate agricultural activity as an unlikely source of F^- in groundwater in the study area. Spatial distribution of F^- and HCO_3^- values corresponds to the hydrogeochemical active zone resulting from the factor scores, possibly due to the migration of these ions from the similar source. Since most of the groundwater is having high F^- concentration, it is recommended that regular groundwater monitoring and integrated management should be established for the safe public water supply in the study area.

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