

A study on the high fluoride concentration in the magnesium-rich waters of hard rock aquifer in Krishnagiri district, Tamilnadu, India

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Received: 16 February 2012 / Accepted: 31 October 2012
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Abstract Excess fluoride in groundwater affects the human health and results in dental and skeletal fluorosis. Higher concentration of fluoride was noted in hard rock terrain of the south India, in the Krishnagiri district of Tamilnadu. The region has a complex geology ranging from ultra basic to acid igneous rocks, charnockite and gneissic rocks. Thirty-four groundwater samples were collected from this study area and analysed for major cations and anions along with fluoride. The order of dominance of cations is $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ and the anions in the following order $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$. It is found that nearly 58 % of the samples have more fluoride ranging from 1 to 3 mg/L. It is also noted that high fluoride waters correspond to magnesium water types. This is due to the release of fluoride from the magnesium-bearing minerals like, biotite, hornblende, etc., or weathering of apatite/hydroxyapatites found in charnockites.

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Keywords Groundwater · Excess fluoride · High magnesium water · Weathering

Introduction

Water is a prime natural resource and essential for life on earth. About 80 % of the diseases in the world are due to the poor quality of drinking water (WHO 1984). The occurrence of fluoride in groundwater is mainly due to natural or geogenic contamination and the source of contamination of often complex and site specific ([Handa 1975](#); [Saxena and Ahmad 2002](#)). Dissolution of fluoride ions from the fluoride bearing minerals and contributes to higher fluoride concentrations in groundwater ([Suttie 1969](#); [Jubb et al. 1993](#); [Schultheiss and Godley 1995](#)). Fluoride-rich groundwater has been associated with diverse geological settings and lithologies. These include not only the interaction with granitic rocks ([Kim and Jeong 2005](#); [Valenzuela-Vasquez et al. 2006](#)), but also the geothermal waters associated to basaltic rocks ([Gaciri and Davies 1993](#); [Hurtado and Gardea-Torresdey 2004](#)). Groundwater is the main source of intake of F^- even though food items like tea also contribute substantial amount of F^- ([Cao et al. 2000](#)). Small concentration of F^- is essential for normal development and strengthening of bones and for the formation of dental enamel ([Bell 1970](#); [Fung et al. 1999](#); [Shomar et al. 2004](#)). Although F^- is thought to be beneficial for tooth formation and as a mouth antibacterial, excessive fluoride may cause dental as well as skeletal fluorosis and other adverse health effects ([Fordyce et al. 2007](#)). Excessive F^- intake causes dental enamel to lose its luster into either mild form of dental fluorosis, which is characterized by white, opaque areas on tooth surface, or into severe form of dental

fluorosis, which is characterized by yellowish brown to black stains on the teeth (Choubasia and Sompura 1996). Application of phosphatic fertilisers to the soils may also cause a potential F^- risk in groundwater quality (Loganathan et al. 2006). Fluorosis is now a worldwide problem. Reports for high F^- (>1.5 mg/L) in Mexico, suggest that its presence in groundwater is of concern mainly in the federal States of San Luis Potosí (Carrillo-Rivera et al. 2002); Jalisco (Hurtado and Gardea-Torresdey 2004), Sonora (Valenzuela-Vasquez et al. 2006) and northernmost Baja California (Soto-Rojas et al. 2004). It is also reported in nearly 20 developing countries like Argentina, USA, Algeria, Libya, Turkey, Iran, China, Australia, South Africa, Kenya, Iraq, Sri Lanka, Canada, Thailand, New Zealand, Japan and India. (Mameri et al. 1998). Excessive fluoride concentrations in ground water have been reported in India, where 17 states are facing fluoride problem (Yadav and Khan 2010). Endemic fluorosis remains a challenging and extensively studied national health problem in India. The high concentrations of fluoride in groundwater in India have resulted due to the dissolution of fluorite, apatite, micas, amphiboles with the OH, F group and topaz from the local bedrock (Handa 1975; Chidambaram 2000). Handa (1975) noted the general negative correlation between fluoride and calcium concentration in groundwater of India.

Many studies report on the prevalence of high fluoride content in various water bodies in different parts of India (Siddiqui 1955; Jolly et al. 1973; Teotia and Teotia 1991; Susheela 1993; Karthikeyan et al. 1996; Manivannan et al. 2010). In India, at present, it has been estimated that fluorosis is prevalent in 17 states of India (Tables 1 and 2). The safe limit of fluoride in drinking water is 1.0 mg/L (WHO 1984). The endemic fluorosis reported in different parts of India is chiefly of geochemical origin (Chidambaram et al. 2012). The Krishnagiri district contains minerals with higher amounts of fluoride (CGWB 2009). Hence, it is important to understand their distribution and concentration on the groundwater of the district. The dissolution of fluoride from primary minerals can increase the concentration of dissolved fluoride in groundwater, which is the only source of the town's drinking water (Manikandan et al. 2011). The variation

of ionic concentration with respect to space and time gives a definite idea about the characterisation of hydrochemical process, recharge and discharge region and region with higher ionic concentration. Hence, this study was designed in such a way to address major issues in determining the hydrogeochemical processes and factors controlling fluoride in water chemistry. This study also attempts to highlight the relationship between fluoride in groundwater and the geology of different aquifers along with their spatial variations.

Study area

Krishnagiri district is bounded by Vellore and Thiruvannamalai districts in the East, Karnataka state in the west, State of Andhra Pradesh in the North and Dharmapuri district in the south, covering about 5,143 km². This district is elevated from 300 to 1,400 m above the mean sea level. It is located between 11° 12'N to 12° 49'N latitude, 77° 27'E to 78° 38'E longitude. Eastern part of the district experiences hot climate and Western part has a contrasting cold climate. The average rainfall is 830 mm per annum. Cauvery River flows in the south western boundary of the study area. Dodda Halla is the most important tributary of Cauvery draining the rugged terrain in the north western part of the district. Ponnaiyar is the major river draining the district and is ephemeral in nature. After flowing for a short distance in an easterly direction, it again follows the district boundary before entering the neighbouring Dharmapuri district (Fig. 1). Physiographically, most of the area is occupied by flat to gently sloping land (about 300 to 1,400 m amsl) with soil cover. The northeastern and extreme southwestern parts are occupied by NW–SE running low hills and ridges (about 300 m to 1,400 m amsl).

Groundwater generally occurs under phreatic conditions in the weathered mantle and under semi-confined conditions in the fractured zones at deeper levels. The thickness of weathered zones in the district ranges from less than a meter to more than 15 m. The yield of large diameter dug wells in the district, tapping the weathered mantle of crystalline rocks ranges from 100 to 500 lpm. These wells normally sustain pumping for 2 to 6 h per day, depending upon the local topography and characteristics of the weathered mantle (CGWB 2009). The depth to water level (DTW) during pre-monsoon ranged between 0.5 and 9.9 m bgl in the district and it ranged between 2 and 9.9 m bgl during post monsoon and the average DTW is >5 m bgl in the entire district, except for a few isolated pockets.

The regional geology of the study area is hard rock: gneisses, granites and basic rocks, alluvium and colluviums.

Table 1 Range of fluoride concentration in groundwater of India and associated severity of fluorosis (Agrawal et al. 1997)

Region/state	Range of fluoride concentration (mg/L)	Severity of fluorosis
Northwest India	0.4–19	Severe
Central India	0.2–10	Moderate
South India	0.2–20	Severe
Deccan Province	0.4–8	Moderate

Table 2 Status of fluoride level (Meenakshi and Maheshwari 2006)

States	Districts	Range of fluoride concentration (mg/L)
Assam	Karbianglong, Nagaon	0.1–18.1
Andhra Pradesh	All districts Except Adilabad, Nizambad, West Godavari, Visakhapatnam, Srikakulam, Vijianagaram	0.11–20.0
Bihar	Palamu, Daltonganj, Gridh, Gaya, Rohlas, Gopalganj, Paschim, Champaran	0.6–8.0
Delhi	Kanjwala, Nijafgarh, Alipu	0.4–10.0
Gujarat	All district except Dang	1.58–31.0
Haryana	Rewari, Faridabad, Karnal, Sonipat, Jind, Gurgaon, Mohidergarh, Rohtak, kurukshetra, Kaithal, Bhiwani, Sirsa, Hisar	0.17–24.7
Jammu and Kashmir	Doda	0.05–4.21
Karnataka	Dharwad, Gadag, Bellary, Belgam, Raichur, Bijapur, Gulbarga, Chitradurga, Tumkur, Chikmagalur, Manya, Bangalore, Mysore	0.2–18.0
Kerala	Palghat, Allepy, Vamanapuram, Allapuzha	0.2–2.5
Maharashtra	Chandrapur, Bhandara, Nagpur, Jalgaon, Bukduna, Amravati Akola, Yavatmal, Nanded, Sholapur	0.11–10.2
Madya Pradesh	Shivpuri, Jabua, Mandla, Dindori, Chhindwara, Dhar Vidhisha, Seoni, Sehore, Ralsen and Bhopal	0.08–4.2
Orissa	Phulbani, Koraput, Dhenkanal	0.6–5.7
Punjab	Mansa, Faridcot, Bhatinda, Muktsar, Moga, Sangrur, Freozpur, Ludhiana, Amritsar, Patila, Ropar, Jallandhar, Fatehgarh Sahib	0.44–6.0
Rajasthan	All the 32 districts	0.2–37.0
Tamilnadu	Salem, Periyar, Dharmapuri, Coimbatore, Thiruchirappalli, Vellore, Madurai, Virudunagar	1.5–5.0
Uttar Pradesh	Unnao, Agra, Meerat, Aligarh, Mathura, Raibarell, Allahabad	0.12–8.9
West Bengal	Birbhum, Bhardaman, Bankura	1.5–13.0

A major portion of the Krishnagiri district consists of quartzofelspathic gneiss and followed by charnockites in the south western part of the study area (Fig. 1). The eastern part of the district is mainly composed of syenites, granite felsite and epidote hornblende gneiss. There are also patches of basic, ultrabasic and mafic rocks. Amphibolite patches are noted in the northern part of the district. Quartz reef is hosted by both hornblende schist of the region and the champion gneiss (quartzofelspathic gneiss). The area also comprises of gold mineralisation with molybdenum in quartz veins (GSI 2009). The epigenetic gold mineralisation is mainly confined to the shear and the silicified zones in the quartz sericite schist (champion gneiss) occurring in association with amphibolite. The region is also associated with minerals like pyrite, pyrrhotite, arsenopyrite and chalcopyrite. Near Bargur, the gold mineralisation has been recorded in the amphibolite band occurring within the gneiss (GSI 2009). This region forms a significant part of the southern granulite terrain of India associated with the metallogeny and metallic minerals with gold mineralisation in the Archean greenstone belts of Veppanapalli and Bargur sectors.

Methodology

A total of 34 groundwater samples were collected from bore wells of different depths (10–65 m) representing the major formations (Fig. 2). Sampling was done at definite intervals in a grid pattern. Each sample was collected in acid-washed polyethylene 250-ml bottles. Samples were filtered using 0.45 μm Millipore filters. The bottle was tightly capped to protect samples from atmospheric CO_2 , adequately labelled and stored at room temperature. Precaution was also taken to avoid samples agitation during transfer to the laboratory for measurement. The collected samples were analysed for F^- , major, and minor ions by using the standard procedures (APHA 1995). Analysis of water samples were carried in detail for different ions like HCO_3^- by titrimetry; Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , H_4SiO_4 , Ca^{2+} , Mg^{2+} , Na^+ and K^+ by ion chromatograph (Metrohm-861); F^- , EC and pH were measured by Orion Ion Electrodes using standard procedures (APHA 1995) to understand the geochemical behaviour. The roles played by other ions than those considered are less significant in the charge balance calculation. The fluoride concentrations in the ground waters were plotted spatially by using Map info 8.5, GIS software to identify the fluoride plume in the study area.

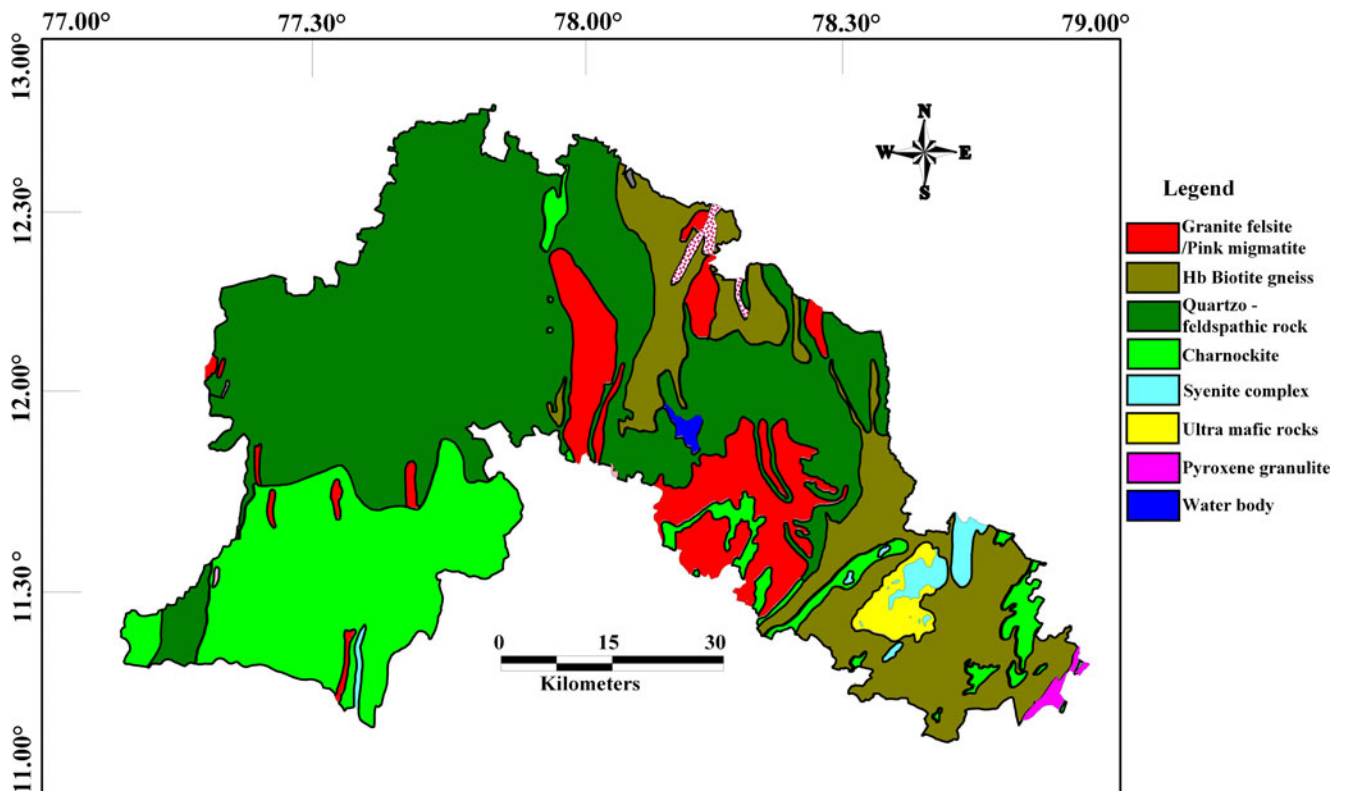


Fig. 1 Geology map of the study area

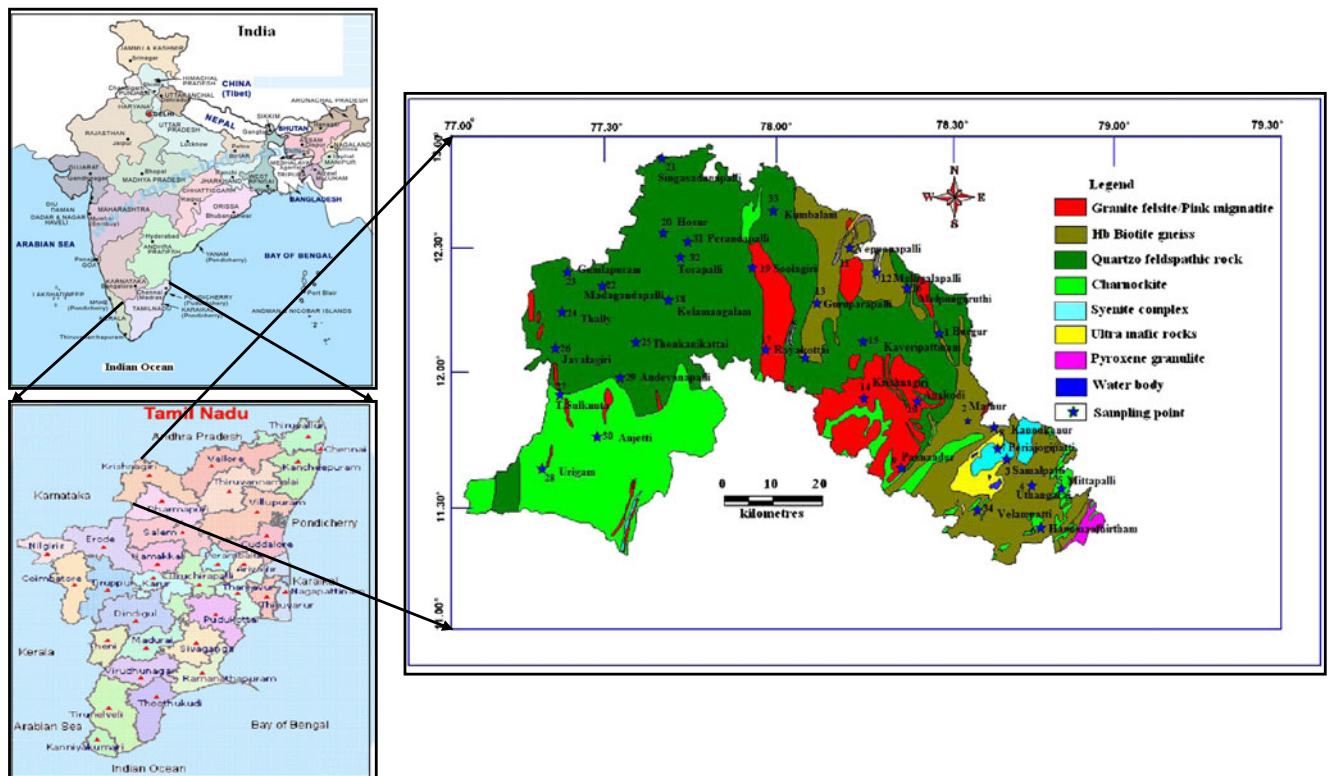


Fig. 2 Sampling location map of the study area

Results and discussion

The average, minimum and maximum values for different ions are given in (Table 3). The groundwater in the study area is generally odourless and colourless in most of the places. The average temperature at the time of sampling varies from 25 to 31 °C. The order of dominance of cations is $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ and that of anions $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$.

Fluoride concentrations frequently are proportional to the degree of water–rock interaction because fluoride primarily originates from the geology (Gizaw 1996; Banks et al. 1995; Dowgiałło 2000; Frengstad et al. 2001; Carrillo-Rivera et al. 2002). It is also reported that fluoride in groundwater is negatively related to anthropogenic contaminants that may infiltrate from the land surface (Pertti and Backman 1995; Kim and Jeong 2005). Fluorite (CaF_2) has generally been considered a dominant source of groundwater fluoride, especially in granitic terrains (Deshmukh et al. 1995; Shah and Danishwar 2003). The study area is divided into four categories—(1) safe area ($\text{F}^- < 1$ mg/L), (2) area prone to dental fluorosis ($\text{F}^- 1\text{--}3$ mg/L), (3) area prone to stiffness of bones ($\text{F}^- 3\text{--}4$ mg/L), and (4) area prone to skeletal fluorosis ($\text{F}^- > 4$ mg/L). The lower limit for dental fluorosis has been taken as 1.0 mg/L, as incidences of dental fluorosis in the country have been reported beyond this level (Chaturvedi et al. 1990; Apambire et al. 1997). The lower limit for skeletal fluorosis was taken as 3.0 mg/L (Raju et al. 2009).

Table 4 shows that most of the samples fall within the 1–3 mg/L (58 %) then followed by 3–4 mg/L concentration (26.47 %). Hence, it is evident that the people of the region are prone to dental fluorosis and subsequently the stiff and brittleness of bone and joints are noted in this region. Even few samples of values higher than 4 mg/L are noted in Samalpatti and Periyajogipatti. In these regions, few people with inability to stand straight were witnessed. Only about 11 % of the samples collected were below the permissible limit.

Piper

The piper plot shows two dominant water types as Mg^{2+} and Na^+ type in cations (Fig. 3) and HCO_3^- is dominant in anions.

Compared with Na-HCO_3 type groundwater, Ca-HCO_3 type groundwater is known to generally contain lower fluoride (Lee et al. 1997). Its hydrochemistry is characterized by increased Ca^{2+} ion concentration with increasing total dissolved solid due to the gradual dissolution of carbonate minerals or Ca^{2+} bearing plagioclase in aquifer materials (Yun et al. 1998a and b; Kim and Chon 2001; Sujatha 2003). The Na-HCO_3 type groundwater are generally enriched in fluoride and sodium ions, due to the dissolution of silicates as well as the removal of Ca^{2+} by calcite precipitation and cation exchange (Chae et al. 2005; Kim and Jeong 2005). It is interesting to note that higher F^- was noted in the Mg^{2+} -dominant water type with Mg-Na-HCO_3 . This may be due to the process of hydrolysis which has resulted in the release of F^- from the Mg^{2+} bearing minerals like biotite, hornblende, etc., or weathering of apatite/hydroxyapatites found in charnockites. Shahid Naseem et al. (2010) shows that the dissolved constituents of groundwater, mainly Na^+ , K^+ and Mg^{2+} , may be considered as an evidence of granite–water interaction. He also stated that the positive correlation matrix between F-SiO_2 , F-Na and F-Mg reflect that flouriferous groundwater originates from granitic rocks. The samples are arranged according to the increasing order of F^- content (Table 5) and they are grouped as group I (< 1 mg/L), group II (1–2 mg/L), group III (2–3 mg/L), group IV (3–4 mg/L) and group V (> 4 mg/L) along with their water types for further discussion. It is clearly witnessed that two water types are dominant Na^+ and Mg^{2+} type, but in both the types the dominant anion is HCO_3^- . Since HCO_3^- is the dominant anion the process of weathering or dissolution may be the prominent process (Srinivasamoorthy et al. 2008; Prasanna et al. 2008). Enrichment of fluoride in groundwaters may also result due to the process of evaporation (Jacks et al. 2005), the process of evaporation is generally reflected by the dominance of Cl^- ion in groundwater and the absence of this water type rules out the possibility of this process. Table 5 shows the percentage of dominance of these two water types; the percentage of dominance of Mg^{2+} water type increases with increase in fluoride (i.e. > 2 mg/L), but in the range of 1–2 mg/L of fluoride ion concentration Na^+ dominant water type is noted. It is also interesting to note that there are representations of the two major water types; type A ($\text{Mg-Ca-Na-HCO}_3\text{-Cl}$) and type B ($\text{Mg-Na-Ca-HCO}_3\text{-Cl}$) in both groups, group I (< 1 mg/L) and

Table 3 Maximum, minimum, average of the chemical constituents present in groundwater of the study area ($n=34$)

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	HCO_3^-	SO_4^{2+}	NO_3^-	F^-	pH	EC	TDS
Maximum	99.387	130.46	220.6	96.2	292.7	644.4	153.67	197.1	5.45	7.8	3,880	2,087
Minimum	31.228	21.161	31.4	16.5	49.59	195.2	10.758	21.94	0.5	6.3	703	357.5
Average	57.993	67.907	118.1	46.6	130.8	416.7	65.601	76.53	2.6	7.064	1,841	967.4083

All values are in milligrams per liter except pH; EC is in microsiemens per centimeter

EC electrical conductivity, TDS total dissolved solids

Table 4 Level of fluoride content in drinking water and corresponding effects on human health (Chaturvedi et al. 1990)

Corresponding effects on human health	Fluoride concentration (mg/L)	Sample no.	% of the samples
safe limit	< 1	5, 15, 26, 33	11.76
Dental fluorosis	1–3	2, 4, 8, 9, 12, 13, 14, 17, 18, 21–24, 27, 29–32	58.82
stiff and brittle bones/ joints	3–4	1, 6, 9, 10, 16, 19, 25, 28, 34	26.47
Deformities in knees; crippling fluorosis; bones finally paralyzed resulting in inability to walk or stand straight	>4	3, 7	5.88

group V (>4 mg/L). The representation of water type A in both the categories are represented in a stiff diagram and it shows that in group I (sample nos. 26 and 33) have lesser concentration of Mg^{2+} in the sample (Fig. 4a and b) but with regard to percentage it is higher. In group V (sample nos. 3 and 7) the quantity of Mg^{2+} and HCO_3^- are higher and comparatively Ca^{2+} is lesser (Fig. 5a and b). Hence, it clearly shows that the water type with higher Mg^{2+} concentration have more relation to high F^- groundwaters.

Saturation indices Log (IAP/KT) was calculated by WATEQ4F geochemical model for those minerals and other solids stored in the model data book for which the dissolved constituents are reported in the groundwater analysis. Solubility equilibrium hypothesis were tested by computing ion

activity product (IAP) from the activities of uncomplexed ions based on the stoichiometries of minerals and other solids in the WATEQ4F data base. The activity product are then compared to the solubility product (KT) for the same solid phases to the assumption that certain dissolved constituents in groundwater are in equilibrium with particular minerals and amorphous solids (Deutsch et al. 1982). Indices log (IAP/KT) were calculated to determine, if the water is in thermodynamic equilibrium log (IAP/KT=0), oversaturated log (IAP/KT>0) or undersaturated log (IAP/KT<0) with respect to certain solid phases (Truesdell and Jones 1974).

The saturation index of minerals like dolomite, magnesite and calcite were plotted against (Fig. 6) the F^- concentration

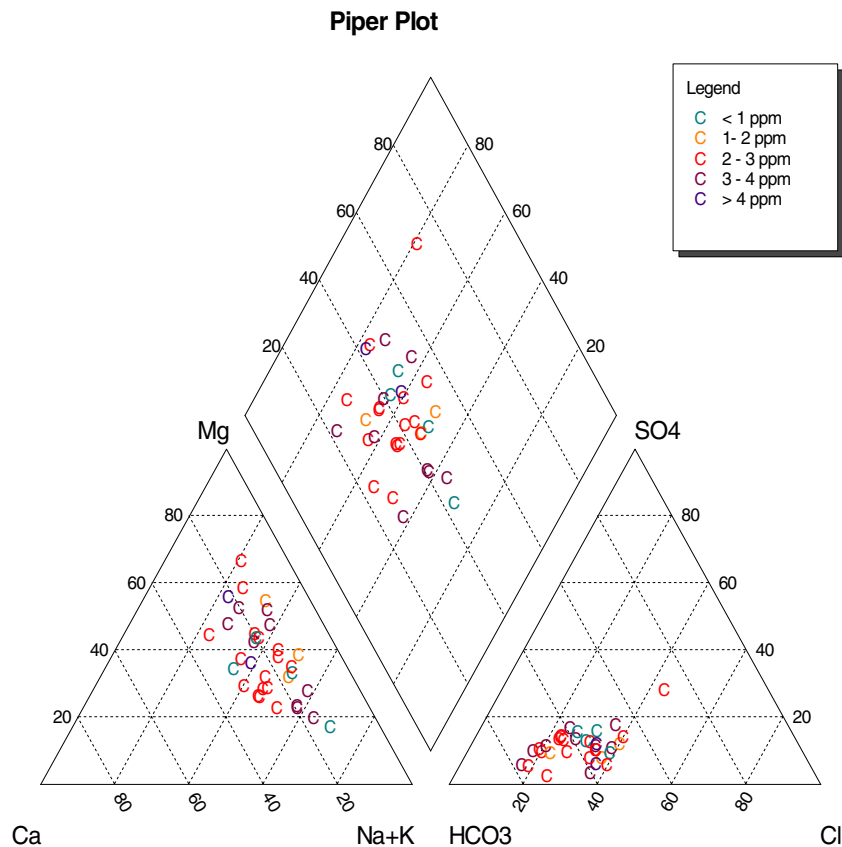
Fig. 3 Piper plot representation

Table 5 Dominance of fluoride ions and its relation to Mg²⁺-rich water types (in percentage)

Groups	Sample no	Water type	Fluoride (mg/L)	% of dominant water type
V (>4 mg/L)	3	Mg-Ca-Na-HCO ₃ -Cl	5.45	100 %Mg ²⁺ dominant
	7	Mg-Na-Ca-HCO ₃ -Cl	4.58	
IV (3–4 mg/L)	10	Mg-Na-HCO ₃ -Cl	3.88	67 % of Mg ²⁺ dominant water type
	25	Mg-Ca-Na-HCO ₃ -Cl	3.65	
	28	Mg-HCO ₃	3.64	
	6	Mg-Na-HCO ₃	3.59	
	11	Na-Mg-Ca-HCO ₃ -Cl	3.45	
	16	Na-Mg-HCO ₃	3.37	
	19	Mg-Na-Ca-HCO ₃ -Cl	3.37	
	1	Na-Mg-HCO ₃ -Cl	3.26	
	34	Mg-Na-HCO ₃ -Cl	3.05	
	III (2–3 mg/L)	14	Na-Ca-Mg-HCO ₃ -Cl	
32		Mg-Na-Ca-HCO ₃ -Cl	2.76	
20		Mg-Cl-SO ₄ -HCO ₃	2.67	
21		Na-Mg-HCO ₃ -Cl	2.65	
8		Na-Mg-HCO ₃ -Cl	2.61	
9		Mg-Na-HCO ₃ -Cl	2.57	
22		Na-HCO ₃ -Cl	2.49	
31		Na-Ca-Mg-HCO ₃ -Cl	2.39	
4		Na-Mg-Ca-HCO ₃ -Cl	2.38	
13		Mg-Na-HCO ₃	2.36	
24		Na-Ca-Mg-HCO ₃	2.36	
12		Mg-Na-Ca-HCO ₃	2.35	
23		Mg-Na-HCO ₃	2.32	
29		Mg-Ca-HCO ₃ -Cl	2.21	
27		Mg-HCO ₃	2.19	
18		Mg-Ca-Na-HCO ₃	2.15	
II (1–2 mg/L)	17	Na-Mg-HCO ₃ -Cl	1.8	100 % Na ⁺ dominant water type
	30	Na-Mg-HCO ₃	1.69	
	2	Na-Mg-HCO ₃ -Cl	1.37	
I (0–1 mg/L)	26	Mg-Ca-Na-HCO ₃ -Cl	0.9	50 %Mg ²⁺ dominant water type
	15	Na-HCO ₃ -Cl	0.8	
	5	Na-Mg-HCO ₃ -Cl	0.6	
	33	Mg-Na-Ca-HCO ₃ -Cl	0.5	

and it was understood that the increase of dolomite saturation was noted with the increase of the F⁻ concentration and no definite trend was noted with saturation index of calcite and magnesite. This indicates there is a positive relation between the SI of magnesite and F⁻ concentration.

The geology of this area is chiefly composed of peninsular gneiss and charnockites which consists of biotite and hornblende and apatites (Fig. 1). The F⁻-rich waters are characterized by high concentrations of Na⁺ and Mg²⁺ along low concentrations of Ca²⁺. Low Ca²⁺ results from the intense cation exchange reaction between Ca²⁺ and Na⁺ (Sarma and Rao 1997). High HCO₃⁻ concentrations and alkaline pH promote the precipitation of Ca²⁺ as calcite (Sarma and Rao 1997), and all of the studied groundwaters are saturated with those

minerals. Fluoride ions are adsorbed by clays in acidic solution; however, they are desorbed in alkaline solution. Thus, an alkaline pH is favourable for F⁻ dissolution (Sexena and Ahmed 2003). The groundwater samples were weakly acidic to near neutral, with pH 6.3 to 7.8. In groundwaters, however, low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride-bearing minerals. The absence of calcium in solution allows higher concentrations to be stable (Edmunds and Smedley 1996). High fluoride concentrations may therefore be expected in groundwaters from calcium-poor aquifers and in areas where fluoride-bearing minerals are common. Fluoride concentrations may also increase in groundwaters in which cation exchange of sodium for calcium occurs (Edmunds and Smedley 1996).

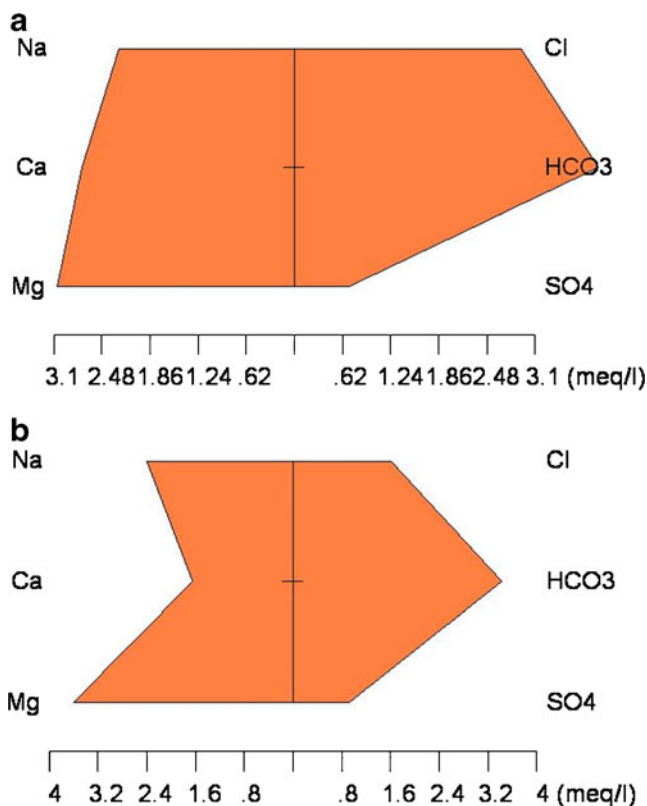


Fig. 4 a Stiff diagram representing the major concentration of cations and anions in (meq/L) for the sample number of 26. b Stiff diagram representing the major concentration of cations and anions (in milliequivalents per liter) for the sample number of 33

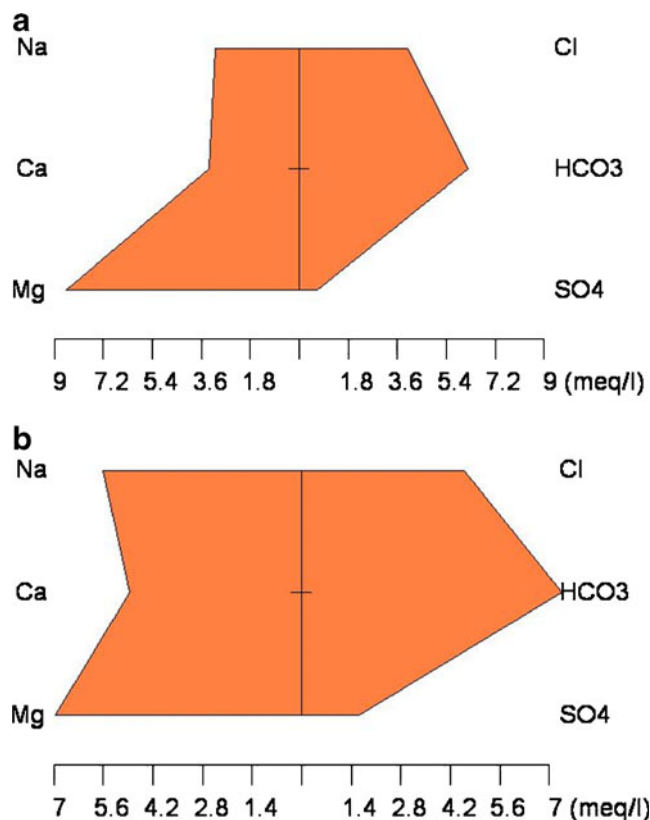
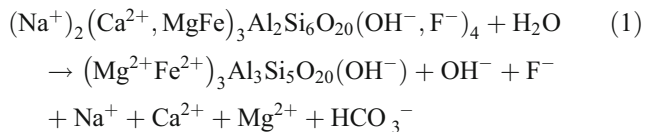


Fig. 5 a Stiff diagram representing the major concentration of cations and anions in (meq/L) for the sample number of 3. b Stiff diagram representing the major concentration of cations and anions in (in milliequivalents per liter) for the sample number of 7

pH and F⁻

pH of the groundwater samples in the study area ranges from 6.3 to 7.8. There are higher concentrations of fluoride at alkaline pH (Fig. 7) and this is mainly due to the process of dissolution and weathering of rock forming minerals like hornblende, biotite, etc. In these regions with hornblende biotite gneiss and biotite undergoes weathering to vermiculite. The dissolution takes place, where water with dissolved HCO₃⁻ in the form of H₂CO₃ acts on the mineral and releases OH⁻, F⁻, cation and HCO₃⁻



In this scenario, the Ca²⁺ released from the dissolution can combine with F⁻ and can result in a lesser concentration in solution. Hence, the water with higher fluoride concentration might have been derived from source rock of lesser Ca²⁺ content and probably higher Na⁺. The higher concentrations of Mg²⁺ may be due to weathering of the Mg²⁺-rich minerals like micas or amphiboles

group of minerals or the higher Mg²⁺ might be due to the weathering of enstatite in charnockites and the F⁻ due to the dissolution of apatite/hydroxyapatite in charnockites. It is interesting to note that the higher fluoride concentration is noted in the charnockite region and the contact between the peninsular gneiss and other acidic intrusions. The higher Mg-F associations are noted in the

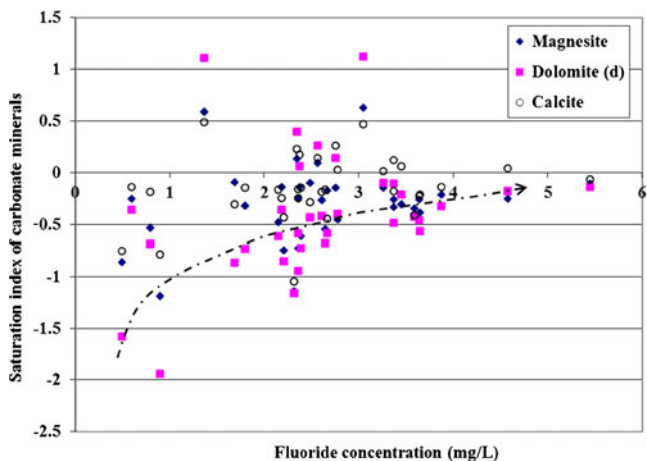
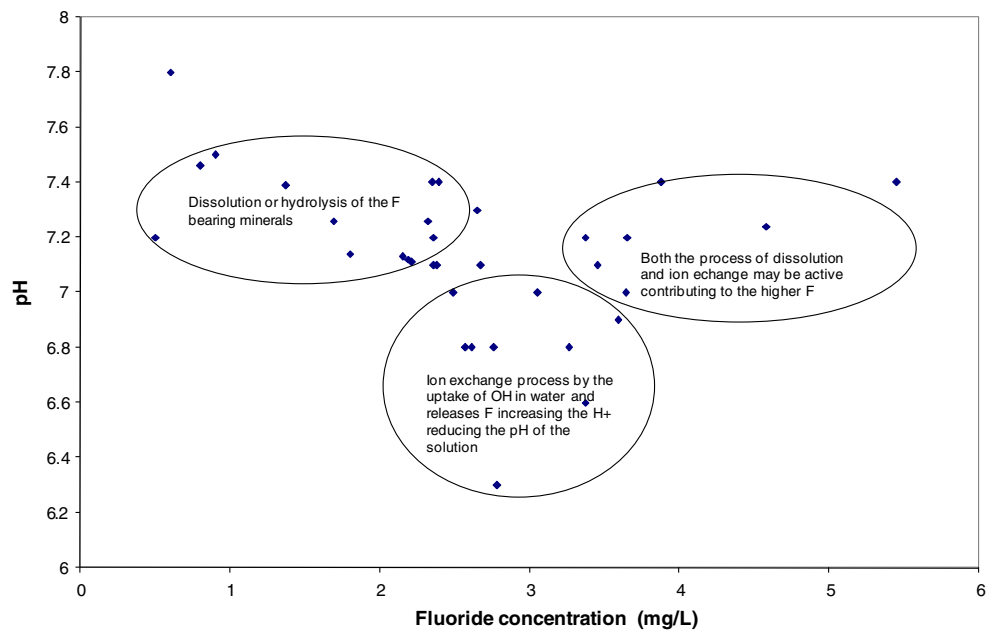


Fig. 6 Saturation index

Fig. 7 Relation between pH and fluoride



groundwaters of acid igneous rocks (Shahid Naseem et al. 2010).

At higher pH hydrolysis takes place, where OH^- is released into the system with more cations and fluoride. The release of fluoride in the natural system is mainly due to the process of ion exchange or due to the process of selective

sorption of OH^- to the surface of clay minerals and the release of the adsorbed F^-



Moreover, groundwaters with high HCO_3^- and Na^+ content are usually alkaline and have relative high OH^- content,

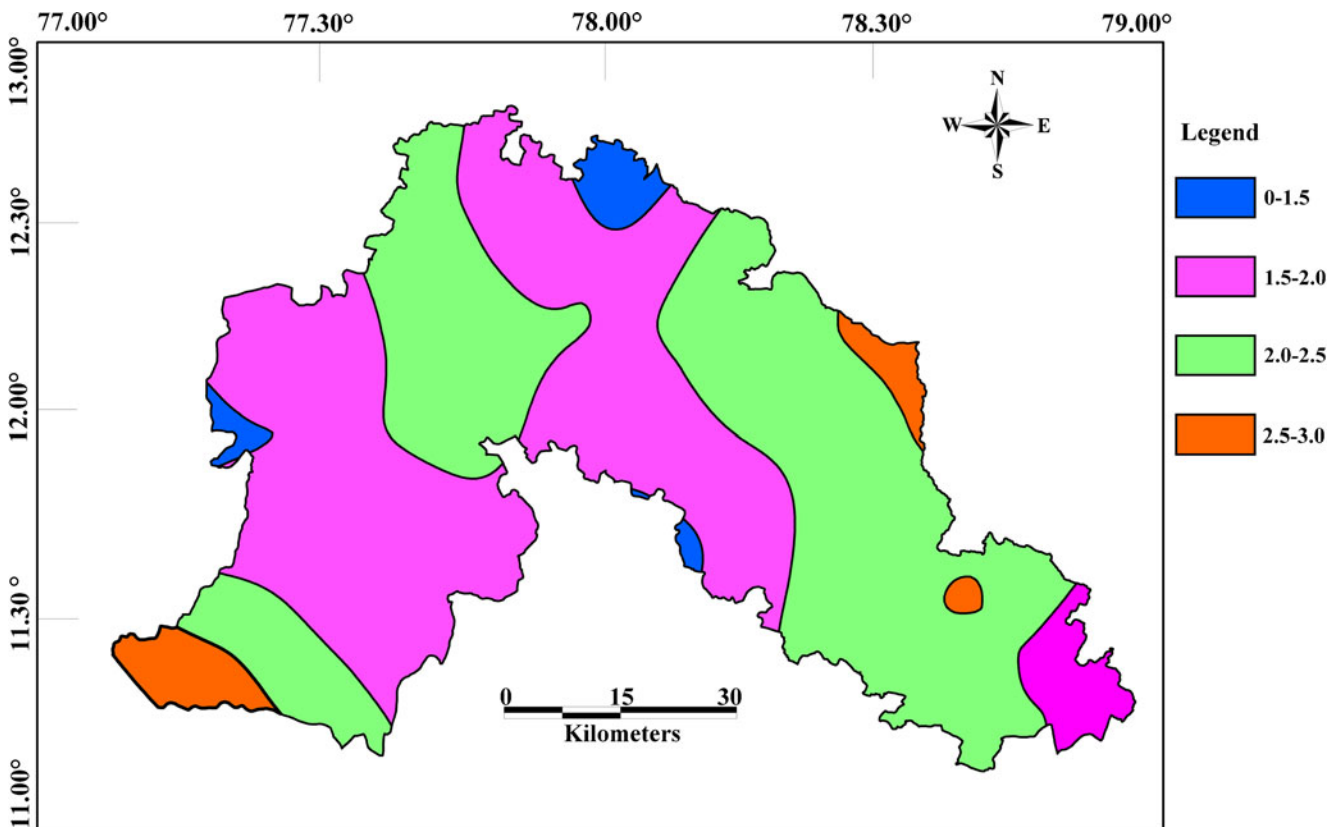


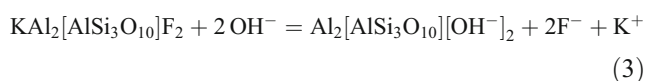
Fig. 8 Spatial distribution of fluoride (in mg/L)

Table 6 Range of fluoride concentration (in milligrams per liter) in groundwater

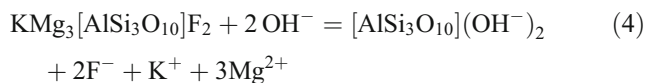
Fluoride concentration (mg/L)	Area (km ²)	Area %
0–1.5	151.69	2.95 %
1.5–2.0	2393.2	46.5 %
2.0–2.5	2370.5	46.59 %
2.5–3.0	227.77	4.43 %

so the OH⁻ can replace the exchangeable F⁻ of fluoride-bearing minerals, increasing the F⁻ content in groundwater. The reactions are basically as follows:

Muscovite:



Biotite:



The hydrogeochemical parameters analysed shows that high HCO₃⁻ and Na⁺ occurs in the dominant, complex weathering of alkali feldspars (Srinivasamoorthy et al.

2008) as a result of silicate mineral hydrolysis. Chidambaram et al. (2012) found that the occurrence of groundwater with high HCO₃⁻ and Na⁺ concentration due to water–rock interactions is also one of the important reasons for fluoride release from the aquifer matrix into groundwater. This higher Na⁺ may be exchanged for the H present in the clay/ weathered matrix in the host rock thereby increasing the pH (Manivannan et al. 2011) and resulting in the dominance of Mg²⁺-rich water type.

Spatial distribution of fluoride

The occurrence of F⁻ in groundwater is mainly due to natural or geogenic contamination and the source of contamination often unknown (Handa 1975; Saxena and Ahmad 2002). The water–rock interaction assessment can be used as a tool to assess the geogenic input of fluoride from fluoride minerals in the deep groundwater aquifers (Saxena and Ahmed 2001). The study area is chiefly composed of epidote hornblende gneiss and charnockite; both these rock types are major contributors for F⁻ in groundwater. The apatite/fluorapatite in charnockites is also major contributors of this ion (Ramanathan 1956; Chidambaram 2000). However, its solubility in fresh water is low and furthermore its dissolution rate is remarkably slow (Nordstrom and Jenne 1977). Few researchers suggested that high fluoride concentrations in groundwater are likely a

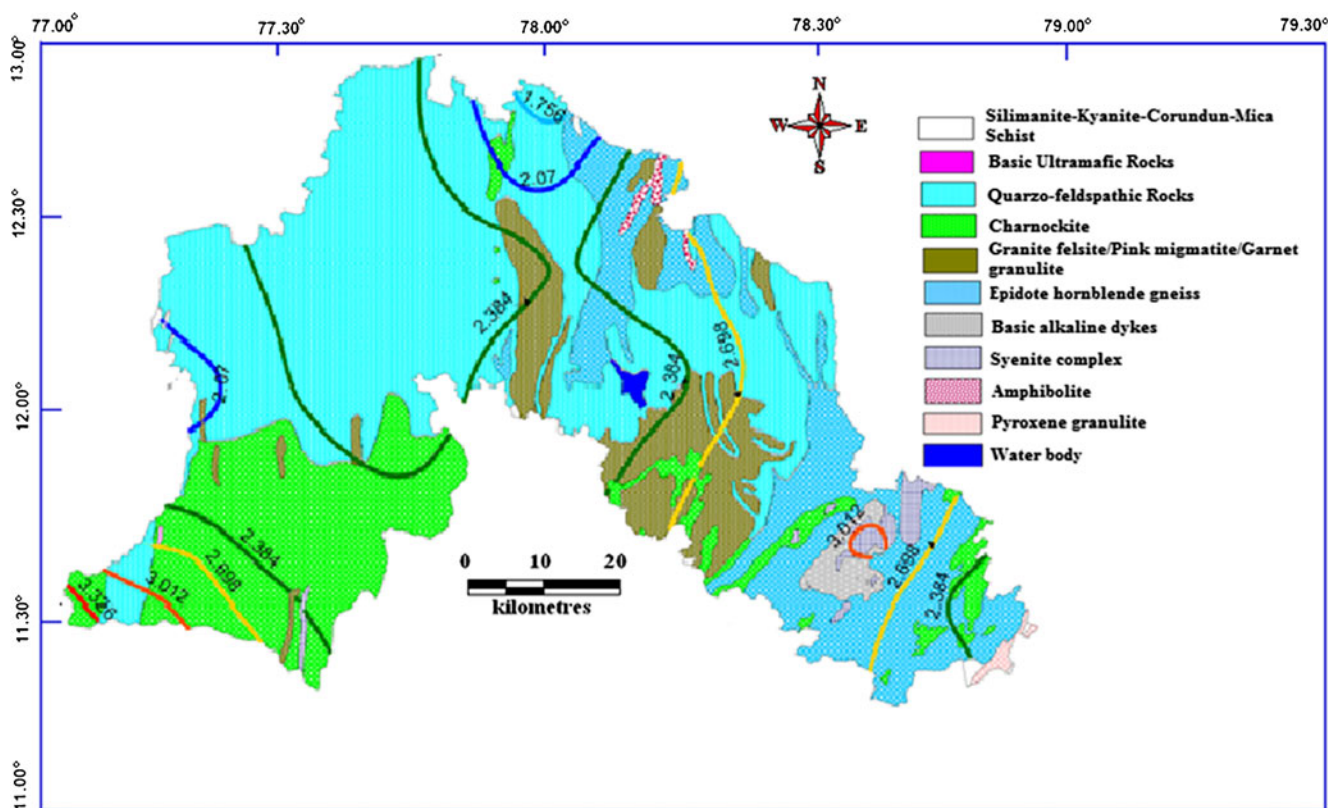


Fig. 9 Integration of fluoride concentration (mg/L) contour on geology map of the study area

result of the dissolution of Biotite, which may contain significant fluorine at the OH^- sites of their octahedral sheet (Nordstrom et al. 1989; Li et al. 2003).

Figure 8 shows that higher nearly about 50 % of the study area is shared by 1.5–2.0 mg/L range and the rest by 2.0–2.5 mg/L (Table 6). The overlay of the fluoride contour over the geology of the region (Fig. 9) shows that most of the region has an average value of 2.3 mg/L in the peninsular gneissic region (hornblende biotite gneiss). A very minor spatial representations of <1.5 mg/L region was noted in the northern part of the study area. The regions with values >2.5 mg/L were noted near the contact between the granite felsite, syenite complex and the epidote hornblende gneiss. As the study area is a hard rock terrain the water is stored in the interconnected fractures and in deep fissures. The increase of temperature and residence time with increasing depth will also enhance the dissolution of fluorine-bearing minerals in rocks (Nordstrom et al. 1989; Sexena and Ahmed 2003).

The higher concentrations are noted in the south western and the south eastern part of the study area. The order of the median fluoride concentration with respect to geology is as follows: metamorphic rocks \geq granitoids \geq complex rock (Chae et al. 2007). It can be concluded that the fluoride concentration of groundwater from the metamorphic rocks, granitoids, and complex rock is higher. According to Perti and Backman (1995), granite contains 0.05–0.14 % of fluorine, which is much higher than in other types of rock (0.01–0.05 %). Since the study area is entirely composed of hard rock, the distributions of F^- found in the hard rocks are generally related to the depth of the aquifer. The water table in the study area occurs in deeper conditions. The higher fluoride concentrations are typically observed in deeper wells as well as in granitic and gneissic aquifers, a trend which has been commonly recognized by many studies on groundwater in granitic setting (White et al. 1963; Yun et al. 1998a; Chidambaram et al. 2003).

Conclusion

The groundwater samples of the study area (88 %) show F^- concentration above the permissible limit. The piper facies shows that domination of the Mg^{2+} water type has higher F^- than Na^+ type. The near-alkaline pH may result in the hydrolysis of minerals like biotite and hornblende in the gneiss to enhance the Mg^{2+} in the groundwater and the release of Mg^{2+} from the enstatite present in charnockite may also increase the Mg^{2+} concentration in groundwater. The increase of F^- concentration with SI of dolomite also shows a closer affinity of this ion to Mg^{2+} . The contour overlay on the geology of the region shows that higher fluoride is noted in the contact between the charnockite and the quartzofelspathic gneiss in

the southwestern part of the study area and the region adjoining to the syenite intrusion.

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