ORIGINAL ARTICLE

Fluoride occurrence and mobilization in geo-environment of semi-arid Granite watershed in southern peninsular India

Sakambari Padhi · D. Muralidharan

Abstract Plausible forms of fluoride (F) responsible for the persistence of fluoride toxicity in ground water of a granitic terrain of semi-arid region, which is the main source of drinking water, have been studied. The study area in Anantapur District of Andhra Pradesh, India, is one of the chronic regions with excess fluoride in groundwater and the region is under transformation into aridity due to poor rainfall and over-exploitation of groundwater. Geochemical analysis of soil, groundwater, and rock samples of the study area revealed the presence of other toxic elements also in addition to fluoride which need to be addressed in drinking water sector in near future. Soil fluoride leaching experiments demonstrated the probable mode of mobilization of F into the groundwater through natural recharge process during monsoon. Analysis of saturation indices indicates that the fluorite solubility alone is not attributable to the high fluoride content in groundwater. The groundwater flow controls fluoride mobilization in the study area as it is evidenced through fluoride concentration and electrical conductivity increase from catchment to downstream region. Creation of lesser fluoride groundwater sources through rainwater harvesting and artificial recharge of groundwater in catchment areas is suggested as a long-term sustainable safe drinking water strategy.

Keywords Granites · Fluoride · Groundwater · Geochemistry · Anantapur District · India

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Introduction

High-fluoride in groundwater has been reported from many parts of the world (Edmunds and Smedley 2005). In India, it is established that fluorosis is endemic (Meenakshi and Maheshwari 2006; Rao and Devadas 2003; Jacks et al. 2005) and is associated with high concentrations of F in drinking water in rural areas of semi-arid to arid regions (Singh and Dass 1993). Sixteen out of 23 districts of Andhra Pradesh State in India are reported to be F endemic. Among these 16 districts, the stressed groundwater resources coupled with high fluoride content make the Anantapur District into a critical stage where the groundwater is the principal drinking water source. The concentration of F in the groundwater samples is in the range of 2.59–6.53 mg/l and is found to exceed the permissible limits of 1.5 mg/l set by WHO (2004).

Deeper groundwater exploitation and the aridity condition accelerated the fluorosis problem over this region compelling the planners to take alternate expensive measures of river water transportation for drinking water supply from far distances or opting for water treatment technological solutions in non-amicable rural conditions. The main objectives of this study are to (1) find the source and occurrence of fluoride in the groundwater, (2) understand the mechanisms controlling the groundwater chemical composition which influences the status of fluoride in groundwater, and (3) find a solution for development of safe drinking water sources on a sustainable basis.

Chemical and physical characteristics of soils and rock samples were carried out to understand the F contributions from them to groundwater. Hydro-geochemical classification of groundwater was done by using Piper diagram (Piper 1944, 1953; Back 1961; Back and Hanshaw 1965; Walton 1991; Rafique et al. 2009). Saturation index (SI) of

calcite and fluorite and Gibbs' boomerang diagram (Gibbs 1970, 1992) were used to understand the fluoride geochemistry and the dissolution status of F into groundwater.

Geohydrology of the study area

The study area falls in Anantapur District bounded between 13°–15°N latitude and 76°–78°E longitude, in the southwestern part of Andhra Pradesh, India (Fig. 1). This area experiences an arid climate with large water deficit (Rao and Devadas 2003). It witnesses recurrent droughts and famine, and it is the driest district of Andhra Pradesh, with an average rainfall of <560 mm. The semi-arid to arid type of climate, characterized by dryness of air, lesser development of surface runoff, scarce precipitation, high evaporation, and heavy winds is the principal factor that controls the physics and chemistry of the soil (Raju et al. 1979).

Younger intrusive rocks consisting of pink granite with pegmatite and quartz veins are the major rocks seen in the study area. These pink granites constitute hill ranges and occur as medium-grained, large linear bodies flesh pink in color, with predominant pink feldspar, quartz, and epidote veins. They have been highly subjected to weathering thereby increasing the susceptibility for erosion and transportation. They possess principal fluorine-bearing minerals of acid-soluble minerals such as fluorite in the form of irregular grains along the boundaries of felsic and mafic minerals and in the form of thin veins. Fluroapatite also occurs as inclusions (Ramam and Murthy 1997; Raju et al. 1979).

In southern peninsular India, rainwater harvesting is practiced through tanks for agricultural activities. In Andhra Pradesh alone, 80,000 tanks exist with 0.7 million hectares under irrigation (Pradan 1997). These tanks indirectly contribute to groundwater recharge through

Fig. 1 Location map showing the study watershed area
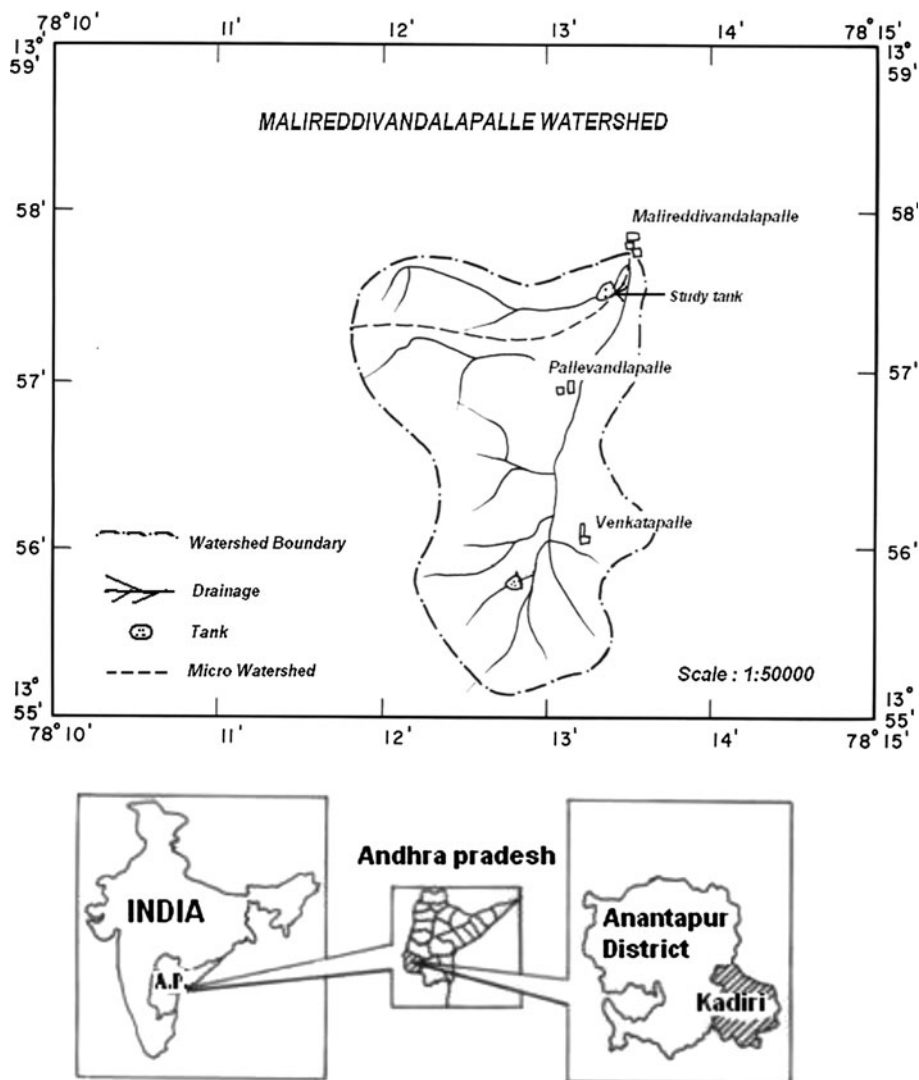
percolation of water from their beds. As these traditional water harvesting structures are old enough to accumulate silts, to study the influence of these interception structures, we have selected the study area with a tank of age more than 150 years. Due to poor inflow into this tank, the groundwater is mainly used as a source for agricultural activities in the area and it is being exploited through dug wells and boreholes.

Source of fluorine in the environment

Fluorine in the study area is almost wholly contributed by the granites and accessory minerals present in association with pegmatitic rocks. The inducement of Fluorine to the water environment through anthropogenic activities is negligible as this area is located in region of extreme backwardness (Raju et al. 1979).

The principal fluorine-bearing minerals of these rocks are fluorite, fluorapatite, hornblende, mica, and epidote. Owing to its favorable dissolution properties, fluorite (CaF_2) seems to be the main mineral that controls the fluoride geochemistry in the environment (Apambire et al. 1997). High-degree weathering of fluoride-bearing younger granites and semi-arid to arid climates favored fluoride release and enrichment. The chemistry of the fluoride ions released into the groundwater is found to be not essentially controlled by the degree of saturation of fluorite (CaF_2) and calcite ($CaCO_3$) alone in our study area, but earlier studies reported that the degree of saturation of fluorite and calcite controls the fluoride release into groundwater (Handa 1975; Nordstrom and Jenne 1977; Gaciri and Davies 1993). The environmental factors also govern the distribution of fluoride in natural waters, which is dependent on the amount of fluorine in the source rocks, soils, duration of contact of water with rocks and soils, temperature, rain fall, vegetation, and oxidation–reduction reactions.

Materials and methods

Soil samples from 10 cm below the surface were collected from ten sites (three samples were collected inside the tank from different locations, five samples from upstream and two samples from down stream of the tank) and were packed in polyethylene packets. The locations of soil samples collected are shown in Fig. 2.

For textural analysis, 100 g of sample was taken and washed with deionized water with 53 micron sieve. Fractions <53 microns were considered as silt and clay and the fractions >53 microns were subjected to a Vibratory Sieve-Shaker to find the various grain sizes. Studies were also carried out for F to leach at room temperature using another 100 g of dried soil samples, soaked in a beaker containing
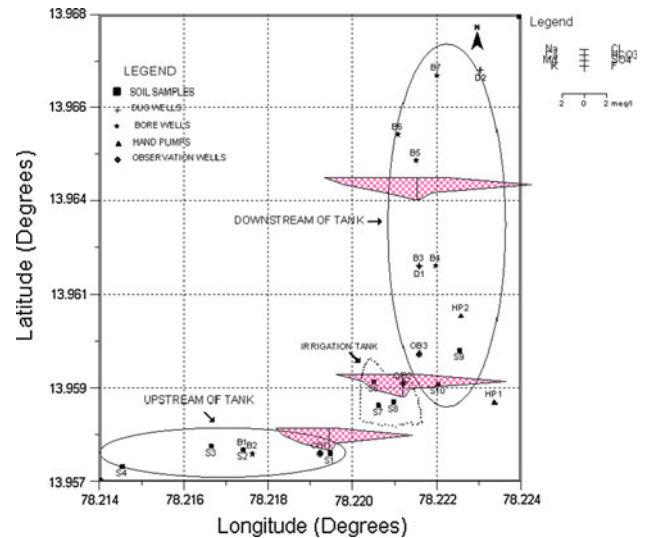

Fig. 2 Location map showing the sampling sites along with the spatial distribution of average chemical composition for upstream, downstream and inside the tank

400 ml of deionized water, continuously mixed by stirring at every 30 min for about 6 h, and left for 24 h for each site. The supernatant leachate was then analyzed for F, pH, conductivity, major and trace elements. pH and electrical conductivity (Ec) were measured using a pH meter (HACH, Model pH 10101) and conductivity meter (LaMOTTE CON 5), respectively. Total concentration of Ca, Mg, Na, K, and other trace elements were analyzed by inductively coupled plasma mass spectrometry (ICPMS), after acidifying the supernatant liquid to pH < 2 using ultra pure nitric Acid. Water-soluble F of the first leachate was analyzed by a UV–VIS Spectrophotometer. Fluoride is colorless and will not absorb any light wave in the UV–VIS range. However, a method developed by Hach Company to analyze fluoride in water uses a SPADNS reagent to the solution and determines the fluoride concentration by absorbance at 580 nm. This method is accepted by the US EPA and is equivalent to EPA's method 340.1 for drinking water and wastewater. This method is also recommended by the APHA (1985). Total leachable F was calculated following elutriation process by subjecting the same soil sample for leaching through a number of cycles till the F level in the aliquot is less than the detectable limit. X-ray fluorescence (XRF) spectroscopy studies were also carried out for the determination of major oxides in the soil.

Water samples from drinking and irrigation wells (both open shallow wells and bore wells) were collected from different locations in the upstream and downstream of the study tank (Fig. 2). Three permanent observation wells were developed through drilling, one each in upstream, inside the tank, and downstream of the tank to study the groundwater levels and chemical characteristics. Collected groundwater samples were filtered and stored in polyethylene bottles,

which were initially washed thoroughly with distilled water and then with the water sample itself. One more set of samples from each location was collected and acidified to pH < 2 by adding ultrapure concentrated Nitric acid for major and trace element analysis. Physical parameters like pH and electrical conductivity (Ec) were measured in field itself using a pH meter and a conductivity meter, respectively. Total dissolved solids (TDS) were computed by multiplying Ec with 0.64 (Hem 1985). Acidified samples were analyzed for Ca, Mg, Na, K, and other trace elements through ICPMS. Total alkalinity, CO_3^{2-}, and HCO_3^- were calculated by titrimetric method using 0.01639 N H_2SO_4 (Skougstad et al. 1974). Fluoride concentration of water samples was determined by the SPADNS method and Sulfate was determined by SulfaVer 4 method as recommended by APHA (1985), using spectrophotometer. Chloride concentration (mg/l) was also estimated using standard $AgNO_3$ titration method with potassium chromate as indicator (Skougstad et al. 1974).

Rock samples from the aquifer depth of three permanent observation wells collected while drilling were subjected to XRF analysis for major oxides and total fluorine.

Results and discussions

Analysis of soil, water, and rock samples

The analytical data for the water samples and soil aqueous extracts is presented in Table 1 with statistical measures such as range and mean with standard deviation. The soil leachate is alkaline in nature with pH varying from 7.8 to 8.9 and with electrical conductivity ranging from 113.5 to 287.0 µS/cm, whereas the groundwater conductivity varied from 604 to 1765 µS/cm over the study region. Tank soils contain the maximum percentage of silt and clay (67.83%) as compared with the upstream and downstream soils (Table 2). The total leachable fluoride concentration of the soil samples varied from 11.68 to 62.74 mg/l, while groundwater fluoride varied from 2.59 to 6.53 mg/l only. Soils have higher percentage of Al_2O_3 as compared with CaO and MgO.

The pH of the groundwater with a narrow range of 7.9–9.0 similar to that of soil leachate is observed. Total alkalinity of groundwater varies from 438 to 918 mg/l, whereas bicarbonate concentration varied from 110 to

Table 1 Geochemical parameters of groundwater (n = 15) and first soil aqueous extract (n = 10)

Parameter	Ground water samples (n = 15)		Soil aqueous extracts (10–20 cm) (n = 10)	
	Range	[a]Mean	Range	[a]Mean
pH	7.9–9.0	8.56 ± 0.3	7.8–8.9	8.23 ± 0.3
TDS (mg/l)	399.9–1138	637.7 ± 215.8	73–185.1	120.87 ± 29
Ec (µS/cm)	604–1765	988.7 ± 334.5	113.5–287	187.4 ± 45.7
Na (mg/l)	92.3–314.4	163.3 ± 59.7	39.1–79.4	56.9 ± 11.7
K (mg/l)	2.7–10.3	5.99 ± 2.5	0–8.1	5.7 ± 2.3
Ca (mg/l)	38.7–221.7	116.0 ± 51.5	12.2–141	35.9 ± 37.6
Mg (mg/l)	22.4–80.5	47.2 ± 15.5	1.8–9.1	4.6 ± 2.1
F (mg/l)	2.59–6.53	3.9 ± 1.1	3.56–18.8	11.5 ± 5.3
Cl^- (mg/l)	21.2–195	74.3 ± 51.9		
Alk. (mg/l)	438–918	606.9 ± 117.9		
HCO_3^-(mg/l)	370–900	574.4 ± 158.1		
CO_3^-(mg/l)	0–162	78.2 ± 45.0		
SO_4^- (mg/l)	20–75	53.9 ± 22.9		
Total leachable Fluoride concentration of the soil samples (n = 10) of study area				
F (mg/l)	11.7–62.7	30.8 ± 16.2		

[a] Mean values with standard deviation

Table 2 Average values of silt–clay percentage with major oxides for soil samples, TDS and F for first soil water extract and groundwater samples

Sites	Water samples		Soil leachate		Soil samples				
	F (mg/l)	TDS (mg/l)	F (mg/l)	TDS (mg/l)	Texture (<50 μ) (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)
Upstream	3.3	423	7.9	114	26.14	8.9	1.3	0.11	1.22
Inside the tank	4.7	497	13.4	122	67.83	13.8	2.8	1.64	1.8
Downstream	4.1	723	15.5	135	33.85	9.5	1.9	0.43	1.26

755 mg/l. Chloride ranging from 21.2 to 195 mg/l and sulfate ranging from 20 to 75 mg/l were found in groundwater of the study area. Average values of TDS and fluoride for the groundwater and soil water extracts in the upstream, in-tank and downstream area are listed in Table 2.

Table 3 lists the values for major oxides and total fluorine analysis of the rock samples collected from the aquifer depth of three observation wells, which shows total fluorine in the range of 193–460 ppm. Similar to the soils, oxides of Al is found to be predominating in rocks also.

Fluoride in groundwater

Bicarbonate

Studies carried out by Muralidharan (2009) in the same region over a period of 2 years indicated that the pH of the groundwater remains reasonably static. As the pH of the groundwater remains reasonably constant, any increase or decrease in the bicarbonate concentration will be accompanied by increase or decrease in the concentration of fluoride (Handa 1975). Groundwaters with high F concentration are reported to be of Na–HCO$_3$ types with low Ca concentrations under alkaline pH environ. Also studies have shown positive correlations between F and both HCO$_3$ and Na in high-F groundwater environ and an inverse relationship between F and Ca concentrations in fluorite-saturated groundwater (Handa 1975; Kundu et al. 2001; Wang and Cheng 2001; Smedley et al. 2002; Edmunds and Smedley 2005). Attempt on correlation matrix for the chemical parameters as presented in Table 4 shows a positive

correlation with Na and HCO$_3$ with correlation coefficients of 0.63 and 0.62, respectively. A negative or poor correlation is seen with Ca and Mg with correlation coefficients of −0.09 and 0.35, respectively. The correlation matrix analysis brought out probable reasoning for persistence of high fluoride in groundwater of the study area.

Saturation index

As fluorite is the main fluorine-bearing mineral in the study area, the saturation indices for fluorite (CaF$_2$) and calcite (CaCO$_3$) in groundwater samples are calculated using AquaChem software interlinking PHREEQC (Parkhurst and Appelo 1999) and are plotted in Fig. 3a. The saturation indices indicated that majority of groundwater in the study area is oversaturated with respect to calcite and is saturated with fluorite. As solubility of calcite and fluorite are interdependent (Kundu et al. 2001), low calcite solubility and deficiency of calcium ion in the groundwater might have caused the persistence of high F concentration and its mobility in groundwater of the study area. Also prevailing alkaline conditions facilitate additional fluorite to dissolve by allowing calcite precipitation (Handa 1975). Jacks et al. (1993) found that high fluoride waters are generally saturated with fluorite, calcite, and dolomite in groundwater environs similar to that of our study area.

Hydrochemical facies

Fluoride concentration in groundwater generally depends upon the chemical characteristics of groundwater. Trilinear (Piper) diagram has been used for understanding the type

Table 3 Average values for major oxides and total fluorine in rock samples of aquifer depths

Rock samples (aquifer depth)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	MgO (%)	CaO (%)	Total F (ppm)
Upstream of tank	13.03	2.0	6.71	3.2	194.8
Inside the tank	14.01	2.91	9.8	2.38	193.1
Downstream of tank	13.17	6.1	8.37	5.62	460.2

Table 4 Correlation matrix of physico-chemical parameters of groundwater

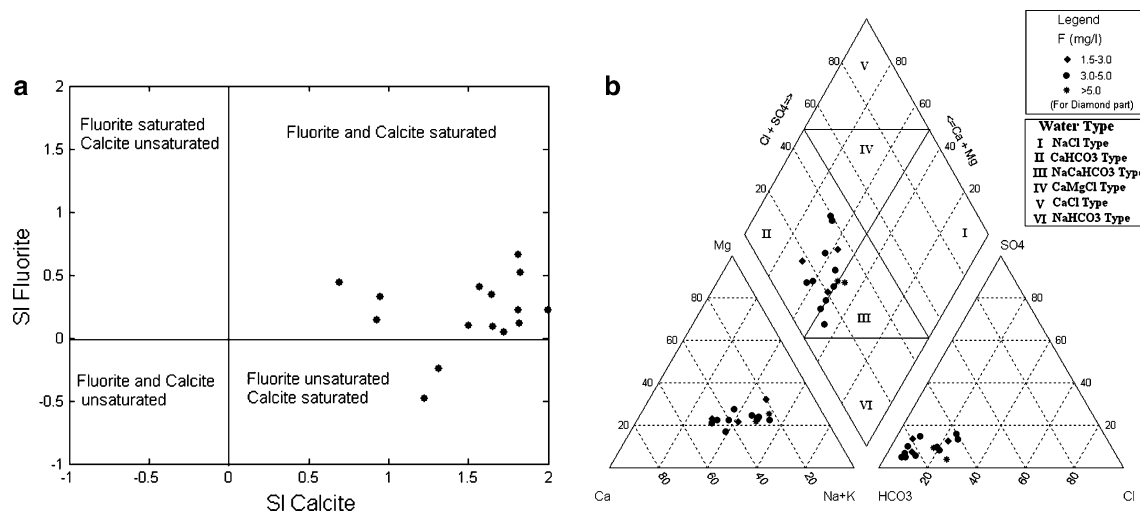|	pH	Ec	TDS	Na	K	Ca	Mg	F	HCO$_3$	Cl	SO$_4$
pH	1.00	0.146	0.146	0.137	0.348	0.02	0.09	0.05	0.115	0.12	0.243
Ec		1.00	1.00	0.953	0.652	0.614	0.948	0.487	0.756	0.989	0.421
TDS			1.00	0.953	0.652	0.614	0.948	0.487	0.756	0.989	0.421
Na				1.00	0.77	0.396	0.884	0.628	0.857	0.924	0.321
K					1.00	0.166	0.612	0.499	0.656	0.619	0.242
Ca						1.00	0.622	−0.09	0.128	0.614	0.502
Mg							1.00	0.356	0.725	0.947	0.471
F								1.00	0.626	0.469	−0.07
HCO$_3$									1.00	0.717	0.113
Cl										1.00	0.4
SO$_4$											1.00

Fig. 3 a Plot of saturation index for Calcite and Fluorite. b Trilinear (Piper) diagram for the major ions of groundwater samples

of groundwater and draw inference on fluoride presence (Srivastava and Ramanathan 2008). Sodium bicarbonate type of groundwater is found to favor fluoride dissolution (Handa 1975). The piper diagram for the water samples of the study area is shown in Fig. 3b. Based on the piper classification, groundwater of the area is of bicarbonate type, where the alkali earth metals (Ca, Mg) and the alkaline elements (Na, K) are more or less equal, while bicarbonates exceed sulfate and chloride. The analysis using Piper diagram has not brought out clear picture of fluoride dissolution process.

Gibbs' diagram

Gibbs (1970) proposed a diagram to provide genetic information from the composition of river water which includes three distinct fields, namely precipitation dominance, evaporation dominance, and rock dominance areas. The geochemical character of groundwater in an aquifer is similarly dependent upon the chemistry of the infiltrating water (precipitation/surface water), water depth (evaporation), and rock–water interaction in the aquifer (rock dissolution and rock type). Gibbs' diagram could also be extended to provide genetic information from groundwater chemistry. The Gibbs ratio: I—Na/(Na + Ca) for cations and ratio: II—Cl/(Cl + HCO₃) for anions of water samples of the study area were plotted separately against the respective total dissolved solids (TDS) in Fig. 4a, b, respectively. Ratios I and II for the groundwater of the study area varied from 0.42 to 0.73 and 0.04 to 0.2, respectively. The plots of these ratios with respect to TDS, as shown in Fig. 4a, b, display that the groundwater samples of the study area fall in the rock weathering (rock-water interaction) zone and in the evaporation zone. The
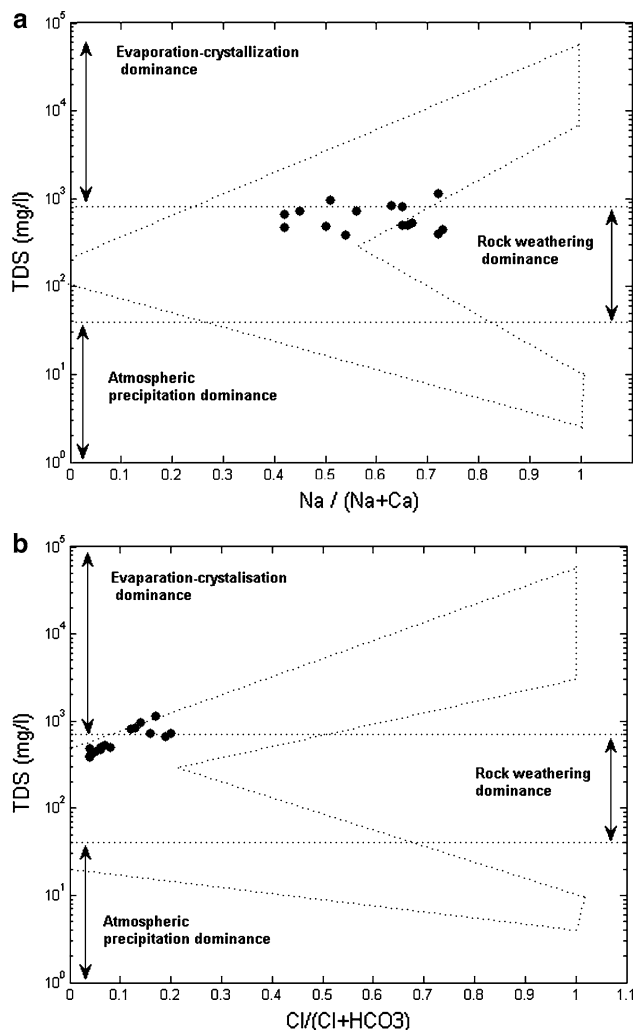

Fig. 4 a Gibb's diagram of ratios of Na/(Na + Ca) versus TDS. b Gibb's diagram of ratios of Cl/(Cl + HCO₃) versus TDS

predominance of rock–water interaction processes probably indicates that the geo-chemistry of groundwater over the area is due to influence of weathered rocks in groundwater fluctuation zone and fractured zones.

Fluoride contribution from soil

Flouride toxicity is caused not only by the drinking water source having high fluoride content, but also by crops grown over soils enriched with fluoride and/or irrigated with fluoride-rich groundwater. On analysis, the total water leachable fluoride of the soil samples is found to vary from 11.68 to 62.74 mg/l and the presence of leachable soil fluoride requires a better understanding of fluoride mobilization in the environment. A similar study for the Nalgonda district of Andhra Pradesh (Rao et al. 1993) having similar granites and climate conditions also shows high water-soluble soil F content. Also leachability of soil fluoride is influenced by the chemical nature of the soil in addition to pH (Wang et al. 2002). A high value of pH facilitates the release of F from soil into water by exchange of OH^- with the exchangeable F in soil and fixed F in the crystal lattice of F-bearing minerals because of the similar chemical characteristics of F and OH^- (Jacks et al. 2005). It was found that the presence of silt and clay in soil enhances adsorption and leaching of F, as F is found to be bonded to the clay structure (Madhavan and Subramanian 2002). Figure 5 shows the relation of increase in total leachable F of soil with increase in percentage of silt and clay with a correlation coefficient of 0.85 for the study area. The analysis shows that the soils over the study area play a major role in mobilization of fluoride in the environment.
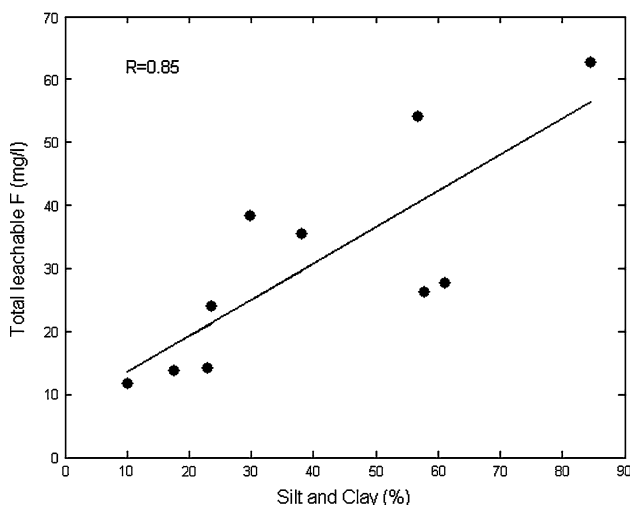

Fig. 5 Relation between total leachable F of soil and silt–clay content

XRF analysis of the soil samples indicated that the soil samples contain higher percentage of Al_2O_3 and lower percentage of CaO and MgO (Table 2). Such high F in soil of the study area is attributable to the high F saturation adsorbing capacity due to presence of high Al_2O_3 of the soil and favored the leaching of F from soil because of low CaO and MgO (Wang et al. 2002). As the accumulated soils in the tank bed are fine textured and are enriched with Al_2O_3 with low CaO and MgO as compared with the upstream and downstream areas, the total leachable fluoride concentration of the tank soil is found to be very high as compared with soils from other areas. It is expected that the interception through such tanks accumulates the fluoride and enhances the release of F into the groundwater through percolation of tank water during storage as a point pollution source.

Groundwater movement

The average values of TDS (mg/l) and F (mg/l) of first leachate of soil water extract and groundwater are grouped into their geomorphological locations and are presented in Table 2. The analysis shows an increase in fluoride levels of groundwater from upstream to downstream area. It implies that the hydrological process of groundwater movement from recharge area to downstream area is as expected in general. Relatively, high level of fluoride in groundwater below the tank area supported the influence of leaching of fluoride from soils. The observed trend of F enrichment along the expected direction of groundwater flow is in concurrence with the trend of increase in dissolved solids from recharge to discharge areas (Gaciri and Davies 1993).

Stiff diagrams (Stiff 1951) are used to compare the ionic composition of water samples between different locations, depths, or aquifers. The stiff diagram is a polygon created from three horizontal axes extended on both sides of a vertical axis. Cations and anions are plotted on the left and right sides with respect to the vertical axis in meq/l, respectively. In order to understand the fluoride mobilization over the study area, we have included one more horizontal axis to cover the fluoride and potassium. A greater extent from the vertical axis represents larger ionic concentration. The stiff diagrams for the average concentrations of major cations and anions including fluoride concentration for upstream, downstream, and in tank well of the study area are shown in Fig. 2 depicting the well locations. The stiff diagrams depicted the evolution of groundwater chemistry from the upstream part of the watershed to the downstream area with the increase in the concentrations of major cations and anions along the expected direction of groundwater flow.

F in rocks

In order to understand the F mobilization in groundwater, rocks of the area were analyzed as it is expected to be the main contributing factor of fluorine in environment. Studies showed that the availability of leachable fluoride in a terrain is more important in the contamination of fluoride in groundwater rather than the mere presence of fluoride-bearing minerals in the bulk rocks (Ramesam and Rajagopalan 1985; Sahu and Karin 1989), whereas studies also showed that the rock types influence the mobility of F ion (Xu et al. 2006).

In order to understand the fluoride mobilization, we have attempted to calculate the mobility index of F using Perelman (1967) method. The mobility of an element expressed in terms of coefficient of aqueous migration (k) can be quantitatively estimated by

$$k = \frac{100 \times w}{t \times r}$$

where w is the concentration of the element in water (mg/l), t is the total dissolved solids (mg/l), and r is the concentration of the element in rock (%). Using the above formula, we determined the coefficient of aqueous migration (k) of F to be 40.0 for upstream, 48.9 for in-tank, and 12.3 for downstream using the data of rock analysis carried out for the rock samples collected from aquifer depths and respective groundwater analysis (Tables 2, 3). According to Rose et al. (1979), the values of k are in the range of highly mobile element ($k > 10$) group. Moreover, the lower k value in downstream with respect to upstream and tank areas also imply less F mobility in downstream relative to upstream and tank areas.

Conclusions

Integrated geochemical studies on rock, soil, and water brought out an understanding of the causative factors for the persistence of fluoride in groundwater at higher levels over the study area. The physico-chemical conditions of soil, such as alkaline nature, high Al_2O_3, and low CaO and MgO favored adsorption and leaching of F into the groundwater. Interception structures such as tanks, though they facilitate in increasing the water resource availability, indirectly influence the hydrochemistry of groundwater with fluoride toxicity in arid to semi-arid regions.

The chemical kinetics of the water samples is found to be controlled basically by the weathering and water–rock interaction. Fluorite (CaF_2) solubility is not the only factor controlling the F concentration in the study area. The aridity influence on persistence of high fluoride in groundwater is seen clearly. That the soils contain high leachable fluoride and higher mobility of F from rocks is also observed. The gradational increase of F in groundwater from upstream to downstream parts of the study area is attributable to the mobilization as part of hydrological process. The study helps understand the prevailing hydro-geological conditions and concludes that the drinking water sources need to be located on upstream part of the watershed area to have minimum concentration of fluoride in groundwater. Further, it is preferable to have number of rainwater harvesting structures in upstream areas having less soil thickness to harvest the rainwater having low concentration of fluoride. The percolation of fluoride-free water may ultimately dilute the existing groundwater fluoride concentration and sustain the availability of groundwater sources for safe drinking water supply.

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