

High-fluoride groundwater

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Abstract Fluoride (F^-) is essential for normal bone growth, but its higher concentration in the drinking water poses great health problems and fluorosis is common in many parts of India. The present paper deals with the aim of establishment of facts of the chemical characteristics responsible for the higher concentration of F^- in the groundwater, after understanding the chemical behavior of F^- in relation to pH, total alkalinity (TA), total hardness (TH), carbonate hardness (CH), non-carbonate hardness (NCH), and excess alkalinity (EA) in the groundwater observed from the known areas of endemic fluorosis zones of Andhra Pradesh that have abundant sources of F^- -bearing minerals of the Precambrians. The chemical data of the groundwater shows that the pH increases with increase F^- ; the concentration of TH is more than the concentration of TA at low F^- groundwater, the resulting water is represented by NCH; the TH has less concentration compared to TA at high F^- groundwater, causing the water that is characterized by EA; and the water of both low and high concentrations of F^- has CH. As a result, the F^- has a positive

relation with pH and TA, and a negative relation with TH. The operating mechanism derived from these observations is that the F^- is released from the source into the groundwater by geochemical reactions and that the groundwater in its flowpath is subjected to evapotranspiration due to the influence of dry climate, which accelerates a precipitation of $CaCO_3$ and a reduction of TH, and thereby a dissolution of F^- . Furthermore, the EA in the water activates the alkalinity in the areas of alkaline soils, leading to enrichment of F^- . Therefore, the alkaline condition, with high pH and EA, and low TH, is a more conducive environment for the higher concentration of F^- in the groundwater.

Keywords Groundwater · Alkaline environment · Fluoride · Precambrian terrain

Introduction

India has two acute health problems due to the influence of higher concentrations of fluoride (F^-) and arsenic (As) in the drinking water. The health problems, arising as a result of F^- -contamination, are far more widespread than those of As-contamination in India (Muralidharan et al. 2002). The ever-increasing demand for groundwater coupled with lack of assessment of its quality for

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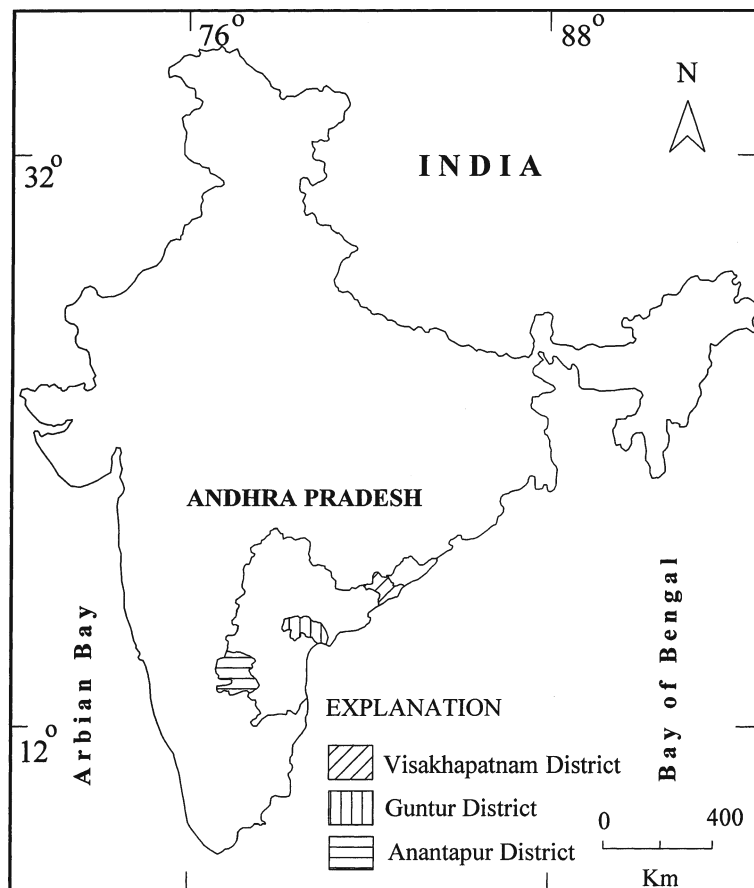
potable purpose, before its use, makes the situation worse. Therefore, more than 60 million people drink F^- -contaminated groundwater and the number affected by fluorosis is estimated at 2 to 3 million in many states, including Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamilnadu, and Uttar Pradesh, in India (Jacks et al. 1993, 2005; Athavale and Das 1999; Susheela 1999; Chakraborti et al. 2000; Muralidharan et al. 2002; Pillai and Stanley 2002; Ayoob and Gupta 2006).

The WHO's recommendation has placed an upper limit at 1.50 mg L^{-1} for F^- in the potable water (WHO 1984). However, the fluorosis in India is observed at the concentration of F^- more than 1.20 mg L^{-1} and the dental caries at the concentration of F^- less than 0.60 mg L^{-1} in the drinking water (ISI 1983). Since the drinking of water with

F^- is threatening the health of millions of people, the establishment of facts of the chemical characteristics responsible for the higher concentration of F^- in the groundwater from the known areas of endemic fluorosis zones is an important aspect. These chemical characteristics could help as indicators to decipher the fluorosis zones. An attempt is, therefore, made to establish the relation of F^- with pH, total alkalinity (TA), total hardness (TH), carbonate hardness (CH), non-carbonate hardness (NCH), and excess alkalinity (EA).

To illustrate this objective, the areas of Visakhapatnam, Guntur, and Anantapur Districts, Andhra Pradesh, India, are selected (Fig. 1), where people have suffered from fluorosis for a long time. This could reach the scientific community to bring out the F^- -toxicity into better focus for taking remedial measures.

Fig. 1 Location of the study areas



Study area

The studied areas of Visakhapatnam, Guntur, and Anantapur Districts (Fig. 1) experience a dry climate, with average monthly temperatures of 15°C to 41°C. Average annual rainfall is about 870 mm, mostly falling during the south-west monsoon. Average annual potential evapotranspiration is about 1,700 mm. Red sandy clay soils occur at Visakhapatnam and black cotton soils at Anantapur and Guntur. The soils are of mostly alkaline and contain CaCO₃ precipitates, locally known as kankar.

The areas are mainly underlain by the rocks of Precambrians. The rocks include granite gneisses, charnockites, and sand khondalites. The first two rocks occur at Guntur, the first one at Anantapur and the last one at Visakhapatnam. The granite gneisses are light pink to grey; medium to coarse grained; and consist of orthoclase, microcline, hornblende, biotite, fluorite, and magnetite. The charnockites are fine to coarse grained and are represented by black grey variety, which are made of orthoclase and plagioclase feldspars, hypersthene, apatite, ilmenite, and magnetite. The khondalites are of pink variety, showing medium to coarse grained, which have mineral assemblages of feldspar, garnet, sillimanite, biotite, apatite, and opaques. Basic dykes and veins of pegmatite and quartzite occur in the country rocks. Modal composition of F⁻-bearing minerals of the rocks is shown in Table 1.

Rainfall is the direct recharge source and the usage of water for land use activities, domestic and agriculture purposes, is the indirect additional recharge source of groundwater. Groundwater occurs in the weathered and fractured rocks.

Table 1 Modal composition of (wt.%) of F⁻-bearing minerals

F ⁻ -bearing minerals	Modal composition (wt.%)
Apatite	0.20–1.50
Biotite	Trace–3.90
Muscovite	Trace–1.95
Hornblende	0.21–8.22
Fluorite	0.10–0.70

Source: Subba Rao (1984), John Devadas (1998), Subba Rao et al. (1998)

Irrigation is intensive and long-term. Application of unlimited agricultural fertilizers for higher crop yields is a common practice.

Methodology

Groundwater samples were collected from 39 dug wells (depth range of 3 to 12 m) during the pre- and post-monsoons of 1997 (Anantapur), 2001 (Guntur), and 2006 (Visakhapatnam; Fig. 1). They were analyzed for pH, TA (as CaCO₃), TH (as CaCO₃), and F⁻, following the standard procedures of APHA (1992). The CH, NCH, and EA were computed, using TA and TH (Chow 1974; ISI 1963): the criterion followed was (a) the values, which were lowest (among TA and TH), were placed under CH, (b) when the value of TA was greater than those of TH, the difference (TA – TH) value was considered as EA, and (c) when the TH was greater than the TA, the difference value (TH – TA) was considered as NCH.

The chemical data was used to understand the relationship of F⁻, with other chemical parameters, as they represent the overall dissolved chemical constituents of groundwater. For example, pH decides the rate of dissolution of ions, TA measures the CO₃²⁻ and HCO₃⁻ ions, TH denotes the Ca²⁺ and Mg²⁺ ions, CH characterizes the combination of Ca²⁺ and Mg²⁺ of CO₃²⁻ and HCO₃⁻ ions, NCH represents the association of Ca²⁺ and Mg²⁺ of Cl⁻, SO₄²⁻, and NO₃⁻ ions, and EA expresses the compound of NaHCO₃.

Results

Since the main objective of this paper is to establish the facts of the chemical characteristics responsible for the identification of higher concentration of F⁻ in the groundwater, after understanding the chemical behavior of F⁻ in relation to pH, TA, TH, CH, NCH, and EA in the groundwater observed from the known areas of endemic fluorosis zones, the chemical data is classified into three groups on the basis of F⁻ concentration prescribed for the drinking water (ISI 1983): (a) less than the desirable limit (<0.60 mg L⁻¹), (b)

Table 2 Summary of the results of F⁻ in relation to pH, TA, TH, CH, NCH, and EA of pre-monsoon groundwater

F ⁻ (mg L ⁻¹)	pH	TA	TH	CH	NCH	EA	TA:TH	TA:F ⁻	TH:F ⁻	Number of samples
Range	Mean	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	ratio	ratio	ratio	
Less than the desirable limit of F ⁻ (<0.60 mg L ⁻¹)										
<0.30	0.30 (0.03)	255 (3.05)	465 (4.62)	255 (3.05)	210 (2.01)	-	0.57 (0.08)	850.00 (10.41)	1,500.00 (9.33)	3
0.30–0.60	0.55 (0.05)	296 (4.45)	455 (3.56)	296 (4.45)	159 (1.89)	-	0.65 (0.06)	538.18 (9.36)	827.27 (10.41)	4
Desirable limit of F ⁻ (0.60–1.20 mg L ⁻¹)										
0.60–0.90	0.81 (0.05)	311 (5.30)	414 (6.06)	311 (5.30)	103 (1.96)	-	0.75 (0.07)	383.95 (8.26)	511.11 (11.63)	5
0.90–1.20	1.10 (0.04)	386 (4.60)	398 (5.10)	386 (4.60)	12 (1.10)	-	0.97 (0.09)	350.91 (9.12)	361.82 (8.16)	7
More than the desirable limit of F ⁻ (>1.20 mg L ⁻¹)										
1.20–1.50	1.45 (0.06)	429 (7.74)	324 (6.53)	324 (6.53)	-	105 (1.84)	1.32 (0.08)	295.87 (8.16)	223.45 (9.37)	9
>1.50	1.75 (0.08)	465 (8.81)	315 (6.44)	315 (6.44)	-	150 (1.06)	1.48 (0.06)	265.71 (7.49)	180.00 (8.16)	11

Error analyses in terms of standard deviation are expressed in parentheses

Table 3 Summary of the results of F⁻ in relation to pH, TA, TH, CH, NCH, and EA of post-monsoon groundwater

F ⁻ (mg L ⁻¹)	pH	TA	TH	CH	NCH	EA	TA:TH	TA:F ⁻	TH:F ⁻	Number of samples
Range	Mean	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	ratio	ratio	ratio	
Less than the desirable limit of F ⁻ (<0.60 mg L ⁻¹)										
<0.30	0.30 (0.05)	268 (2.08)	470 (2.47)	268 (2.08)	202 (1.84)	-	0.57 (0.04)	893.33 (12.50)	1,566.67 (12.27)	2
0.30–0.60	0.57 (0.06)	299 (3.39)	466 (3.80)	299 (3.39)	167 (2.63)	-	0.69 (0.06)	524.56 (6.41)	817.54 (7.12)	3
Desirable limit of F ⁻ (0.60–1.20 mg L ⁻¹)										
0.60–0.90	0.85 (0.06)	336 (5.55)	448 (4.52)	336 (5.55)	112 (1.52)	-	0.75 (0.09)	395.29 (7.33)	527.06 (9.25)	3
0.90–1.20	1.14 (0.04)	398 (6.27)	436 (7.13)	398 (6.27)	38 (1.09)	-	0.91 (0.08)	349.12 (6.69)	382.46 (4.08)	6
More than the desirable limit of F ⁻ (>1.20 mg L ⁻¹)										
1.20–1.50	1.47 (0.08)	436 (7.49)	315 (6.12)	315 (6.12)	-	121 (1.15)	1.38 (0.08)	296.60 (4.10)	214.29 (3.09)	11
>1.50	1.81 (0.09)	517 (8.62)	305 (5.96)	305 (5.96)	-	212 (2.36)	1.70 (0.09)	285.64 (5.56)	168.51 (4.44)	14

Error analyses in terms of standard deviation are expressed in parentheses

the desirable limit (0.60 to 1.20 mg L⁻¹), and (c) more than the desirable limit (>1.20 mg L⁻¹). Accordingly, the chemical parameters are arranged, taking the average values of the groundwater samples in each season (Tables 2 and 3).

The chemical data of groundwater shows that there is an increase in pH (from 7.0 to 8.5), TA (from 255 to 517 mg L⁻¹), and TA:TH (from 0.57 to 1.70), and a decrease in TH (from 470 to 305 mg L⁻¹), TA:F⁻ (from 850 to 266), and TH:F⁻ (1,567 to 169), with an increase of F⁻ (from 0.30 to 1.81 mg L⁻¹) in the pre- and post-monsoons, being a dominant of pH, TA, TA:TH, TA:F⁻, and TH:F⁻ in the latter season (Tables 2 and 3).

It is noted that the groundwater exhibits a higher concentration of NCH, with increasing from 159 to 210 mg L⁻¹ at less than the desirable limit of F⁻ (Tables 2 and 3). Very low concentration of NCH, with decreasing from 112 to 12 mg L⁻¹, is observed at the desirable limit of F⁻. The groundwater is associated with an increase of EA from 105 to 212 mg L⁻¹ at more than the desirable limit of F⁻. The CH increases from 255 to 398 mg/l up to the desirable limit of F⁻ and decreases from 324 to 305 mg L⁻¹ beyond the desirable limit of F⁻. Significantly, while the TA:F⁻ decreases gradually from 850 to 266 (more than three times), the TH:F⁻ reduces steeply from 1,567 to 169 (more than nine times), with an increase of F⁻ from 0.30 to 1.81 mg L⁻¹ (six times).

To have a clear understanding of affinity among the chemical characteristics for the higher concentration of F⁻ in the groundwater, a relation between F⁻ and pH, TA, TH, CH, NCH, EA, TA:F, TA:TH, and TH:F⁻ is illustrated in Figs. 2 and 3. The F⁻ has a positive relation with pH ($r = 0.98$ to 0.99), TA ($r = 0.98$ to 0.99), and TA:TH ($r = 0.96$ to 0.99), and a negative relation with TH ($r = -0.92$ to -0.98), TA:F ($r = -0.89$ to -0.90), and TH:F⁻ ($r = -0.86$ to -0.90) in the pre- and post-monsoons. The F⁻ shows a positive relation with CH and an inverse relation with NCH, where the groundwater has F⁻ at less than the desirable limit and also at the desirable limit. The relation between F⁻ and CH is observed to be negative, and the relation between F⁻ and EA is found to be positive, where the groundwater has F⁻ at more than the desirable limit.

Discussion

A positive relation of pH and TA with F⁻ (Fig. 2a and b) and a negative relation of TH with F⁻ (Fig. 2c) clearly indicate a greater affinity of F⁻ with pH and TA rather than with TH. The relation of F⁻ with pH is in response to silicate mineral dissolution and potentially also degassing of CO₂. Similar relation between F⁻ and TA leads to a more conducive to mobilization of F⁻. Higher concentration of F⁻ with lower concentration of TH is explained, as the Ca²⁺ and Mg²⁺ ions in the TH precipitate as carbonates and/or involves in ion exchange of Ca²⁺ with Na⁺ (Gaciri and Ad Davis 1993; Hem 1991).

As TA increases and TH decreases with F⁻ (Fig. 2b and c), there is a positive relation between TA:TH in relation to F⁻. The difference in decreasing of TA:F⁻ (more than three times; Fig. 3c) and TH:F⁻ (more than nine times; Fig. 3d) with increasing of F⁻ (six times) is because of the concentration of F⁻ increases more with a decrease of TH:F⁻ than those with a decrease of TA:F⁻. A negative relation of F⁻ with CH (Fig. 2d) and a positive relation of F⁻ with EA (Fig. 3a) at more than the desirable limit of F⁻ is caused by high TA compared to TH. Here, as TA is more than TH, the excess value of TA is considered as EA and the lowest value of TH as CH (Tables 2 and 3). A positive relation of F⁻ with CH and a negative relation of F⁻ with NCH at less than the desirable limit and also at the desirable limit of F⁻ are because the groundwater has low TA compared to TH. Here, as TA is less than TH, the lowest value of TA is considered as CH and the excess value of TH as NCH.

The recharge water falling on the land gets enriched in CO₂ from soil, air, and biochemical reactions of bacteria and organic matter during its downward movement, which is caused for the higher concentration of carbonates in the groundwater (Eqs. 1 and 2), resulting in an increase in pH and subsequent over-saturation of CaCO₃. The formation of kankar in the studied areas indicates a long history of evaporation, leading to a precipitation of CaCO₃, under the influence of dry climatic condition, so that the soils become alkaline, with higher concentration of sodium. Besides, the carbonates can also derive from the dissolution of

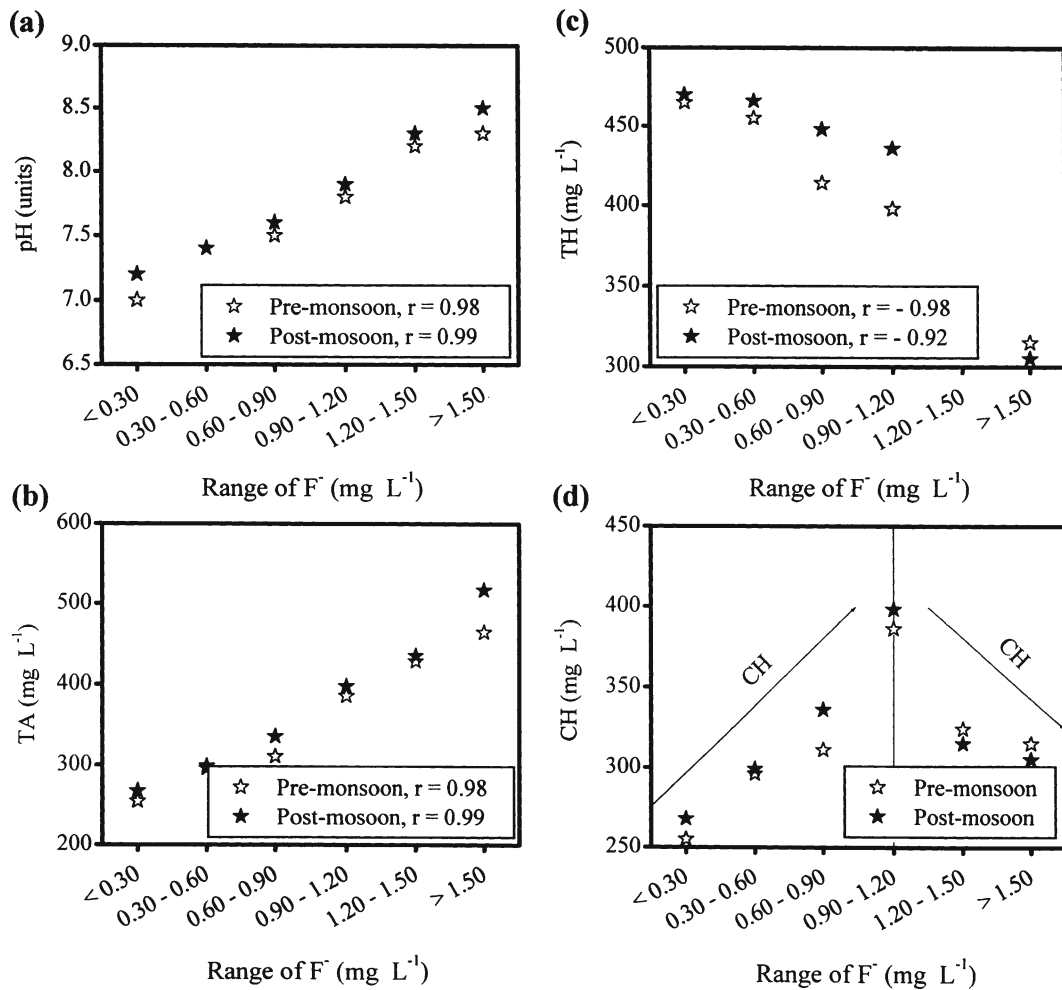
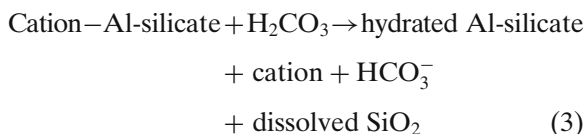


Fig. 2 Relation of F⁻ with **a** pH, **b** TA, **c** TH, and **d** CH

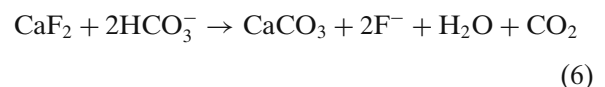
silicate minerals by the action of H₂CO₃ (Eq. 3). The CaCO₃ present in the studied areas can also get dissolved as shown in Eqs. 4 and 5.



While the F⁻-bearing minerals, apatite, biotite, muscovite, hornblende and fluorite, in the country

rocks (Table 1) are the principal sources of F⁻ in the groundwater, the application of agricultural fertilizers, phosphate variety, is the supplementary source of F⁻ in the water. Besides, the clay minerals can also be responsible for the concentration of F⁻ in the groundwater due to the exchange between F⁻ and OH⁻ ions (Hem 1991).

As the alkaline water activates the processes of dissociation and dissolution of F⁻ from the soils and weathered rocks (Ramamohana Rao et al. 1993; Saxena and Ahmed 2001; Gupta et al. 2005), with a simultaneous precipitation of CaCO₃, there is a reduction in TH (in terms of Ca²⁺ and Mg²⁺ ions) and a dissolution of CaF₂ (Eqs. 6 and 7).



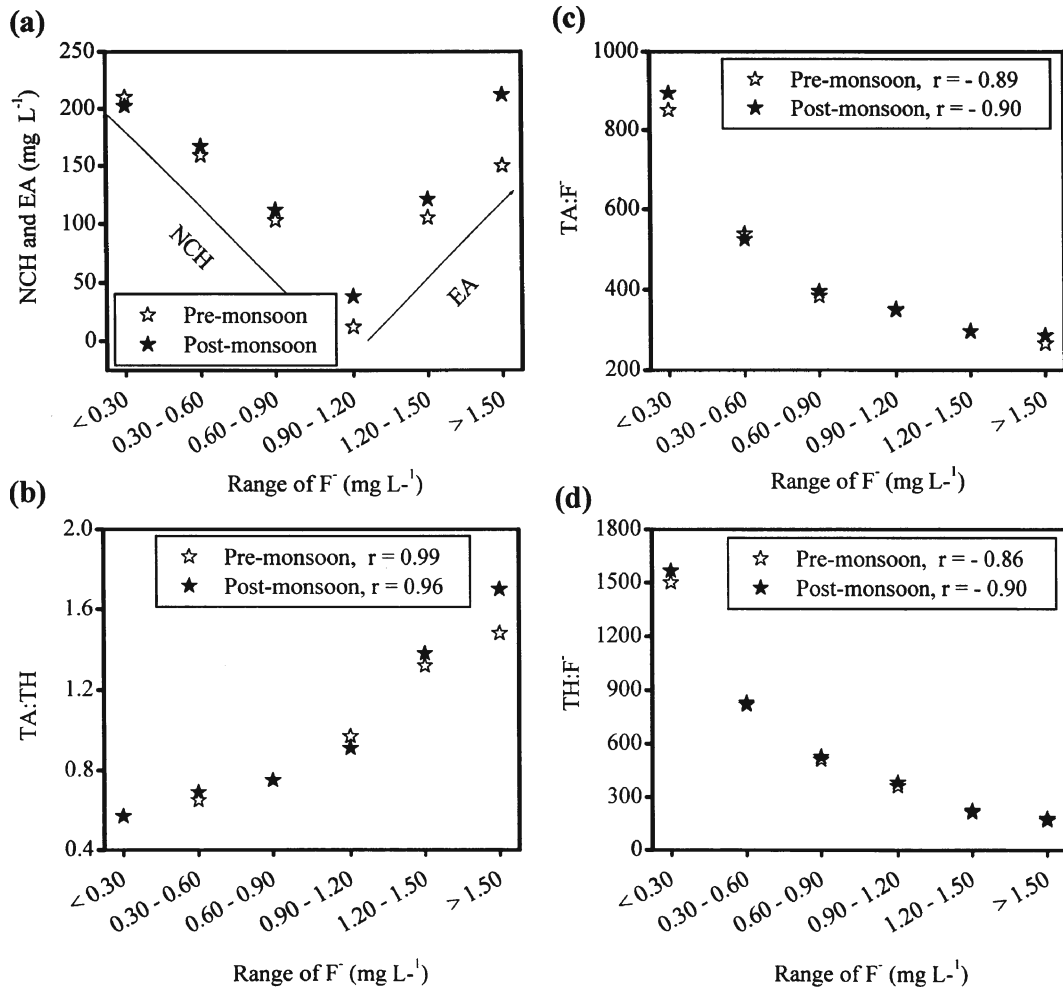
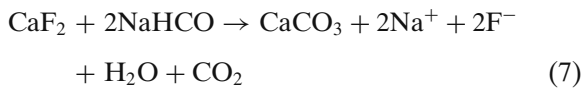


Fig. 3 Relation of F⁻ with **a** NCH and EA, **b** TA:TH, **c** TA:F⁻, and **d** TH:F⁻



The outline of the operating mechanism derived from the above discussion is that F⁻ is mainly released from the F⁻-bearing minerals during the downward movement of infiltrating recharge water through the land surface by geochemical reactions and that the groundwater in its pathway is subjected to evapotranspiration due to the influence of dry climate, resulting a precipitation of CaCO₃ and a reduction in the activity of TH so that there is a dissolution of F⁻. Furthermore, the EA activates the alkalinity in the presence of alkaline soils, causing the higher concentration of F⁻ in the groundwater. This operating mechanism

could be more active during the post-monsoon groundwater, resulting higher values of pH, TA, EA, and F⁻ than those in the pre-monsoon groundwater. Therefore, there is a positive relation of F⁻ with pH, TA, and EA, and a negative relation of F⁻ with TH and NCH, as a whole.

Considerable research has been carried out to understand the processes of dissolution, ion exchange, and evaporation as the main contributors to have a high F⁻ in the groundwater (Handa 1975; Nordstrom and Jenne 1977; Ramesam and Rajagopalan 1985; Gupta et al. 1986; Fuhong and Shuqin 1988; Gaciri and Ad Davis 1993; Jacks et al. 1993, 2005; Ramamohana Rao et al. 1993; Wodeyar and Sreenivasan 1996; Apambire et al. 1997; Subba Rao et al. 1998; Saxena and Ahmed

2001, 2003; Gupta and Deshpande 2003; Subba Rao 2003, 2009; Subba Rao and John Devadas 2003; Edmunds and Smedley 2005; Chae et al. 2007; Jain 2005; Kim and Jeong 2005; Amini et al. 2008).

The chemical data has been summarized in relation to classification of F^- allowed for the potable water to quantify the chemical characteristics responsible for the higher concentration of F^- in the groundwater based on the above discussion as shown below (Table 4):

1. The groundwater of less than the desirable limit of F^- (Group I) is characterized by pH less than 7.5, TA less than 300 mg L^{-1} , TH more than 450 mg L^{-1} , NCH more than 150 mg L^{-1} , TA:TH less than 0.70, TA: F^- more than 500, and TH: F^- more than 600.
2. The groundwater, which is associated with the desirable limit of F^- (Group II), shows pH between 7.5 and 8.0, TA between 300 and 400 mg L^{-1} , TH between 325 and 450 mg L^{-1} , NCH less than 150 mg L^{-1} , TA:TH between 0.70 and 1.00, TA: F^- between 300 and 500, and TH: F^- between 300 and 600.
3. The groundwater of more than the desirable limit of F^- (Group III) has pH more than 8.0, TA more than 400 mg L^{-1} , TH less than 325 mg L^{-1} , EA more than 100 mg L^{-1} , TA:TH more than 1.00, TA: F^- less than 300, and TH: F^- less than 300.

Table 4 Generalized chemical characteristics of F^- -bearing groundwater

Chemical character	Average value		
	Group I	Group II	Group III
pH (units)	<7.5	7.5–8.0	>8.0
TA (mg L^{-1})	<300	300–400	>400
TH (mg L^{-1})	>450	325–450	<325
NCH (mg L^{-1})	>150	<150	–
EA (mg L^{-1})	–	–	>100
TA:TH ratio	<0.70	0.70–1.00	>1.00
TA: F^- ratio	>500	300–500	<300
TH: F^- ratio	>600	300–600	<300

Group I denotes the groundwater with less the desirable limit of F^- . Group II denotes the groundwater with the desirable limit of F^- . Group III denotes the groundwater with more than the desirable limit of F^-

Therefore, the groundwater characterized by high pH, TA, and EA, and low TH can be taken into account as chemical characteristics to identify the higher concentration of F^- in the groundwater.

Conclusions

The present paper concludes from the chemical data of the groundwater observed from the known areas of endemic fluorosis zones of Andhra Pradesh, India, where the F^- -bearing minerals are abundant, that the high F^- in the groundwater ($>1.20 \text{ mg L}^{-1}$) is characterized by pH more than 8.0, TA more than 400 mg L^{-1} , and EA more than 100 mg L^{-1} , and TH less than 325 mg L^{-1} compared to the chemical characters of pH less than 8.0, TA less than 400 mg L^{-1} , and TH more than 325 mg L^{-1} of the low F^- groundwater ($<1.20 \text{ mg L}^{-1}$), as the F^- -bearing minerals can mainly dissolve more rapidly under the influence of alkaline condition in the presence of alkaline soils. This study would be an important practical use to assess the driving forces responsible for the mobilization of higher concentration of F^- in the groundwater.

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