

Fluoride occurrence in the groundwater in a coastal region of Andhra Pradesh, India

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Abstract Fluoride (F^-) content varies from 0.60 to 1.80 mg/L in the coastal region between Chirala and Ongole of Andhra Pradesh, India. It exceeds the threshold limit of 1.20 mg/L in 20 % of the total groundwater samples. The aim of the present study is to assess the controlling factors of F^- content. The study area experiences a dry climate and is underlain by Charnockite Group of rocks over which the river and coastal alluvium occur. The results of the study identify the four factors that control the high F^- content. First one is related to alkalinity, leading to active dissolution and leaching of F^- -bearing minerals, which supports the positive correlation of F^- with pH and HCO_3^- . A longer water residence time in the clays is the second factor, which activates not only solubility and dissolution of F^- -bearing minerals, but also anion exchange between F^- and OH^- . Third factor is a result of higher Na^+ due to impact of saline water, ion exchange between Na^+ and Ca^{2+} , and precipitation of $CaCO_3$. This reduces the Ca^{2+} content, causing dissolution of CaF_2 to maintain the chemical equilibria, which is supported by positive correlation between Na^{2+} and F^- . The influence of anthropogenic activities is the last factor, which acts as an additional source of F^- . Thus, the shallow groundwater shows higher content of F^- and the hydrogeochemical

facies also support this hypothesis. The study suggests the remedial measures to reduce the F^- content.

Keywords Fluoride · Groundwater · Coastal region · Prakasam district · Andhra Pradesh · India

Introduction

Groundwater is a major source for drinking as well as for agricultural and industrial use. In India, the people suffer mainly from two health disorders due to occurrences of fluoride (F^-) and arsenic (As) in drinking water. Relatively, the health implications caused by F^- -contamination are far more wide spread than those of As contamination in the country (Subba Rao 2011). Approximately, 62 million people, including 6 million children suffer from fluorosis in the country due to consumption of F^- -contaminated water (Susheela 1999). The endemic fluorosis is prevalent in many states, including Andhra Pradesh, Bihar, Delhi, Gujarat, Haryana, Karnataka, Madhya Pradesh, Maharashtra, Odisha, Punjab, Rajasthan, Tamil Nadu, Telangana (a part of erstwhile Andhra Pradesh) and Uttar Pradesh in the country.

Many investigations on geochemistry of F^- -bearing groundwater have been carried out in different parts of the world. A detailed study on geochemistry and genesis of F^- -containing groundwater in different geological formations of India has been done by Handa (1975), Sahu and Karim (1989), Jacks et al. (1993, 2005), Datta et al. (1996), Agrawal et al. (1997), Gupta et al. (1999, 2005), Das et al. (2003), Chakraborti et al. (2000), Bhosle et al. (2001), Ray et al. (2000), Madhavan and Subramanian (2002), Muralidharan et al. (2002), Ayoob and Gupta (2006), Misra and Mishra (2006), Kundu and Mandal (2009a, b), Raju

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et al. (2009) and Vikas et al. (2009). Jha and Jha (1982) explain the natural sources as responsible for F^- contamination in India that causes serious health problems. Ramesam and Rajagopalan (1985) report that the degree of weathering and the leachable F^- in a hard rock terrain is more important in deciding F^- content in the water rather than the mere presence of F^- -bearing minerals in the bulk rocks/soils. Fluoride-bearing minerals (fluorite, apatite, biotite, hornblende, etc.) present in hard rock terrains (basalts, granites, gneisses, schists, charnockites, khondalites, etc.) and anthropogenic sources (chemical fertilizers, sewage, sludge, etc.) in India are mainly responsible for higher content of F^- in groundwater with a combination of higher rate of evaporation and longer interaction of water with aquifer materials under alkaline environment (Ramamohana Rao et al. 1993; Wodeyar and Sreenivasan 1996; Chatterjee and Mohabey 1998; Subba Rao et al. 1998a, b, 2012; Sumalatha et al. 1999; Kundu et al. 2001; Saxena and Ahmed 2003; Subba Rao 2003, 2009, 2011; Subba Rao and John Devadas 2003; Subba Rao and Rao 2003; Sujatha 2003; Bhagavan and Raghu 2005; Sreedevi et al. 2006; Madhnure et al. 2007; Shaji et al. 2007; Srinivasamoorthy et al. 2008, 2012; Ramachandran et al. 2012; Reddy et al. 2010; Deepu and Shaji 2011; Chidambaram et al. 2013; Manikandan et al. 2014). All these studies state that high F^- and very low Ca^{2+} and Mg^{2+} or inverse relation between F^- and Ca^{2+} or Mg^{2+} in water are a result of higher Na^+ (due to impact of saline water), prior precipitation of $CaCO_3$ from water and a limited incorporation of F^- in $CaCO_3$ structure so that there is always a net balance of F^- in solution. They also discuss the role of clays that facilitate active solubility and dissolution of F^- -containing minerals, and also activate anion exchange between F^- and OH^- . Further, they also explain that high F^- groundwater is associated with high HCO_3^- , Na^+ , K^+ , SO_4^{2-} and NO_3^- ions. Gao et al. (2007, 2013) point out the processes of F^- activity reduction and the change of ratio $Na^+:Cl^-$ in the groundwater induced by intrusion of saline water, which favours dissolution of F^- -bearing minerals at the salt lake area of Yuncheng basin, Northern China. Singaraja et al. (2013), Subba Rao et al. (2014a, b) and Surya Rao et al. (2015) state that the higher Na^+ and pH causing factor for release of F^- into the groundwater is due to the influence of saline water in coastal aquifers of South India.

In Andhra Pradesh, the highest F^- -affected villages are approximately 195 in Prakasam district (Eenadu 2013). The first case of endemic fluorosis in the country was reported as long as 1937 in the district (a part of erstwhile Guntur district; Shortt et al. 1937). There are so many unnoticed F^- -contaminated groundwater areas in the district, in which the coastal region of Chirala-Ongole is no exception (Fig. 1). The controlling factors of F^- content in

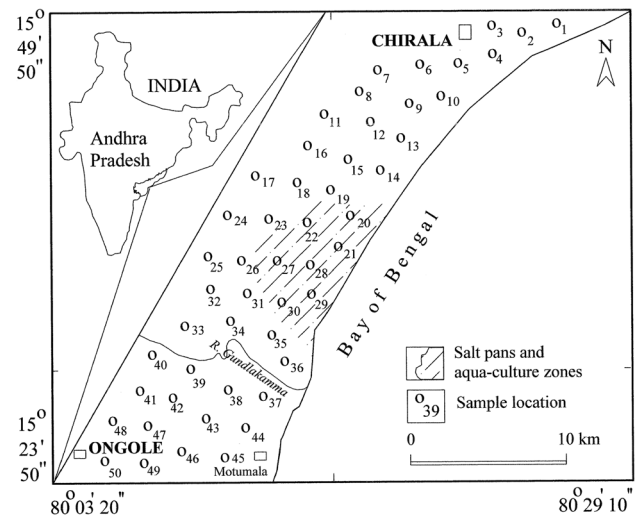


Fig. 1 Location of the coastal region between Chirala and Ongole, Prakasam District, Andhra Pradesh, India

the groundwater are not uniform in any area. Thus, the coastal region between Chirala and Ongole is chosen for the present study to assess the controlling factors of F^- -bearing groundwater and also to suggest the suitable remedies to reduce the F^- -content in the drinking water before one can act intelligently towards the aim of improvement in water quality as well as in health conditions.

Study area

Location

The study area lies in between $80^{\circ}29'10''$ – $80^{\circ}03'20''$ East and $15^{\circ}23'50''$ – $15^{\circ}49'50''$ North with a linear patch extending for about 10 km from the sea coast and covering nearly 40 km in the north–south direction along the coast (Fig. 1). It covers an area of 400 km^2 . The area experiences a dry climate, with an annual average temperature of 19.7° to 41.7° C and receives an annual rainfall of about 900 mm. The southwest monsoon (June to September) contributes 44 % (396 mm), the northeast monsoon (October to December) 50 % (450 mm) and the non-monsoon (January to May) the remaining 6 % (54 mm) of the total rainfall. Cyclones/depressions are not uncommon. The river *Gundalakamma* drains the area (Fig. 2).

Geology

The slope of the study area is gentle towards the southeast. The soils are of silty clay, sand and black cotton types. The sand is dominant in the northern part. The proportion of clay content (silty clay and black cotton soils) increases

towards the southern part from the northern part. The occurrence of *kankar* (concretion of CaCO_3) in the soil zone is a characteristic feature of dry climate. The southern part of the study area is underlain by Charnockite Group of rocks of the Archaean and the rest of the part by the river and coastal alluvium of the Recent (Fig. 3). Apatite, hornblende and biotite are the main F^- -bearing minerals in the host rocks, which occur in and around Ongole.

The sub-surface geology reveals fine, fine to medium and medium sand at depths of less than 0.50, 0.50–16 and 16–22 m from the ground surface, respectively, at Chirala; and fine sand with clay from a depth of less than 3 m, followed by fine to medium sand with clay, quartzite pieces with clay and *kankar*, gravel with sand and clay, and clay with fine sand from depths of 3–10, 10–34, 34–64 and 64–174 m from the surface, respectively, at Motumala

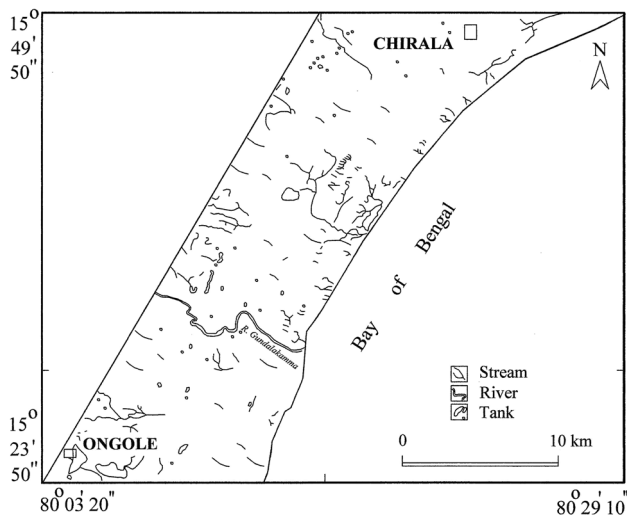


Fig. 2 Drainage of the study area

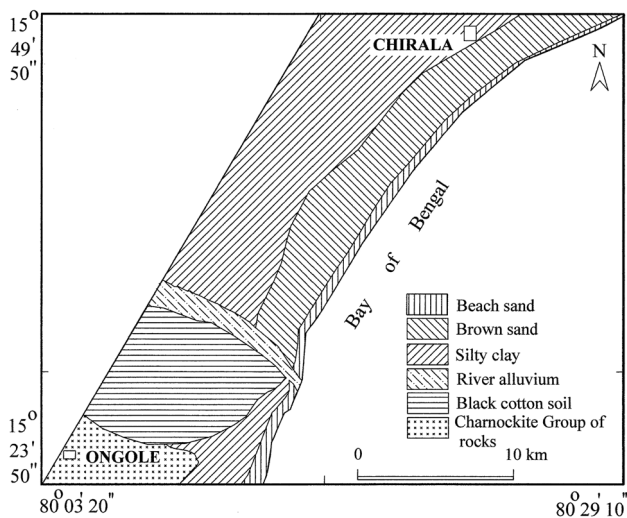


Fig. 3 Geology map of the study area

(CGWB 2002). As per the well owners, the depth of weathering varies from 1 to 5 m and fracturing extends up to depth of 30 m, which are not uniform in their horizontal and vertical variation.

Hydrogeology

Groundwater is used for drinking and irrigation purposes in the study area. It occurs under unconfined and semi-confined to confined conditions. The water level varies from 7.50 to 13.60 m below ground level (bgl) and the direction of water flow being towards the eastern side (Fig. 4). The occurrence of sand in the northern part develops a good drainage conditions by virtue of its high hydraulic conductivity, while in the southern part the content of clay increases gradually from the northern part, which forms a sluggish drainage condition due to its low hydraulic conductivity. In addition to this, the presence of rocks in the southern part has low hydraulic conductivity, because of limited weathered and fractured portions, which form a poor drainage conditions. The yield is from 215 to 300 m^3/day in filter points/tube wells observed from the area of river alluvium, while it is from 40 to 100 m^3/day in bore wells in the area of rock terrain (CGWB 2013). The transmissivity is in the range of 30–1400 m^2/day in the former area, while it is 1–12 m^2/day in the latter area. It indicates that the movement of groundwater flow is slow in the rock terrain.

Sources of pollution

Dry climate and the occurrence of clay in the soil zone as well as in the sub-surface at different depths cause salinity (which occurs naturally in the geological formations) in the

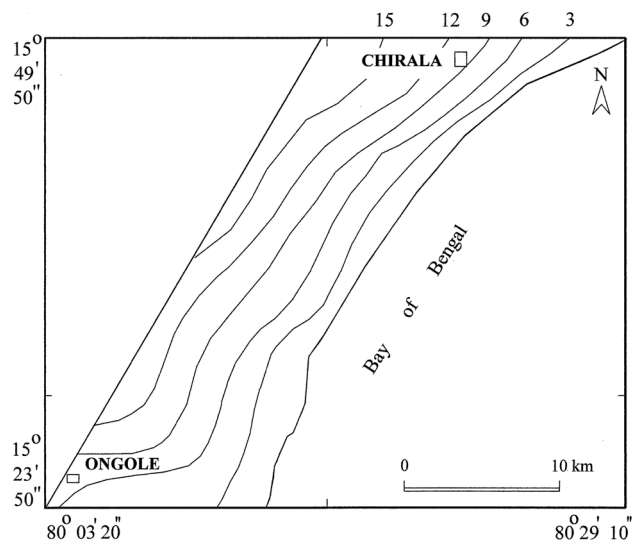


Fig. 4 Depth to groundwater level (m bgl) in the study area

study area (Subba Rao 2014; Subba Rao et al. 2014a, b). Irrigation is intensive and long-term practice, leading to groundwater contamination due to irrigation return flows. Applications of agricultural fertilisers like nitrogen, phosphate and potash varieties, and soil amendments (gypsum) are unlimited for higher crop growth of tobacco, paddy, cotton, groundnut, pulses, etc., causing a deterioration of groundwater quality. Salt pans and aqua-cultural activities are dominant in the central part of the study area (Fig. 1), which are the sources of salinity in the groundwater. Sanitary facilities, such as dumping of domestic wastes and leakage of septic tanks, are poor. They also cause groundwater pollution.

Materials and methods

Water samples from 50 open dug wells were collected in half-litre polythene bottles, after the bottles were soaked in 1:1 HCl for 24 h and were rinsed with distilled water followed by deionised water, during summer 2011 (Fig. 1). The bottles were tightly capped without air gap. Immediately, after collection of the water, the samples are shifted to laboratory for the chemical analysis, following the standard water quality procedures (APHA 1999).

The values of pH and electrical conductivity (EC) were measured in the field, using their portable meters (Systronics make). The EC was used to calculate the total dissolved solids (TDS), following the procedure suggested by Hem (1991). Total hardness (TH) as CaCO_3 and calcium (Ca^{2+}) were estimated by volumetric titrations, using standard EDTA. Bicarbonate (HCO_3^-) and chloride (Cl^-) were analysed volumetrically, using standard HCl and AgNO_3 , respectively. Magnesium (Mg^{2+}) was computed, taking the difference between TH and Ca^{2+} . Sodium (Na^+) and potassium (K^+) were analysed using flame photometer. Sulphate (SO_4^{2-}), nitrate (NO_3^-) and fluoride (F^-), using turbidimetric, colorimetric and ion-selective electrode methods, respectively. All chemical variables (except pH) are expressed in milligrams per litre (mg/L) and also in milliequivalents per litre (me/L).

The analytical precision for the chemical variables was determined by the ionic balance computed between cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and F^-) as $100 \times (\text{cations} - \text{anions}) / (\text{cations} + \text{anions})$. This is within the acceptable limit of $\pm 5\%$ (Deutsch 1997).

Results and discussion

The pH varies from 7.2 to 8.2, being an average of 7.81 (Table 1), indicating an alkaline nature of groundwater. The TDS ranges from 850 to 3380 mg/L and its average is

1745.80 mg/L. The groundwater belongs to fresh (TDS <1000 mg/L) in 22 % and brackish (TDS 1000–10,000 mg/L; Fetter 1990) in 78 % of the total samples. The concentrations (mg/L) of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and F^- vary from 30 to 75, 40–180, 165–746, 8–110, 310–550, 180–1325, 12–232, 39–123 and 0.60–1.80 with an average of 48.60, 80.90, 399.12, 29.34, 429.00, 623.30, 88.40, 51.84 and 0.98, respectively.

As per the TDS classification (Table 2; Fig. 4), two hydrogeochemical facies, viz., $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$: $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ (where the TDS is less than 1000 mg/L) and $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$: $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ (where the TDS is more than 1000 mg/L) are observed from the study area. The facies is useful for determining the flow pattern and origin of chemical histories of groundwater masses. Thus, the pH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and F^- increase with the increase of TDS (Fig. 5).

A higher Na^+ indicates dissolution of minerals and/or soil salts as well as the influence of anthropogenic and marine sources (Todd 1980; Stallard and Edmond 1983; Subba Rao 2002, 2014; Subba Rao et al. 2014a, b). A dominance of HCO_3^- favours mineral dissolution (Stumm and Morgan 1996). An abundance of Cl^- is a result of leaching from soils and the influence of domestic wastes, salt pans, aqua-cultural activities, etc. (Todd 1980; Subba Rao 2014). Further, the solubility of Na^+ and Cl^- is high (Hem 1991; Drever 1997). Sulphate and NO_3^- are the sources of soils, evaporites, fertilisers, domestic wastes, leakage of septic tanks, etc. (Todd 1980; Drever 1997; Subba Rao 2014). Ferromagnesian minerals and manmade activities (salt pans and aqua-cultural activities) are responsible for higher Mg^{2+} than Ca^{2+} in the groundwater (Hem 1991; Drever 1997; Subba Rao 2014; Subba Rao et al. 2014a, b). A lower K^+ indicates its lower geochemical mobility and its absorption on clays (Hem 1991; Drever 1997). Fluoride minerals, agro-chemicals, etc., are the sources of F^- in the groundwater (Ayoob and Gupta 2006; Ahmed 2014; Rao et al. 2014).

In the present study area (Table 1), the concentration of F^- exceeds 1.20 mg/L in 20 % of the total groundwater samples (18, 20–24, 28, 29, 49 and 50). According to ISI (2012) and WHO (2008), the desirable and permissible limits of F^- in drinking water are 1.00 and 1.50 mg/L, respectively. However, the recommended limit of F^- in the water depends on the climatic conditions of an area (USPHS 1987), because the amount of water consumed and the amount of F^- ingested is influenced primarily by air temperature. Thus, the higher the air temperature, the lower is the allowable concentration of F^- . On the other hand, the intake of F^- below 0.50 mg/L causes dental caries (WHO 2008), while it is above 1.00 mg/L resulting

Table 1 Chemical composition of groundwater

S. no.	pH	TDS (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	F ⁻ (mg/L)
1	7.4	850	30	40	165	12	450	180	12	21	0.6
2	7.5	950	35	55	173	12	430	220	56	29	0.7
3	7.3	930	40	60	165	14	410	210	45	33	0.6
4	8.2	990	45	55	185	14	460	195	56	46	0.8
5	7.6	960	40	50	190	17	440	215	58	48	0.8
6	7.9	980	50	40	205	13	450	200	55	51	0.9
7	8.2	980	40	45	210	9	450	195	61	50	0.9
8	7.9	960	35	40	220	8	440	225	43	49	0.8
9	8.0	970	40	45	200	12	460	190	71	54	0.9
10	7.6	1000	45	50	190	12	430	240	62	44	0.8
11	7.8	1000	45	50	202	11	430	230	46	52	0.7
12	7.9	1230	45	70	230	19	420	360	66	44	0.7
13	7.3	1430	40	70	290	23	390	460	83	56	0.9
14	7.5	1610	40	60	360	24	380	565	86	44	0.8
15	7.2	1490	50	55	342	27	310	535	92	59	0.6
16	7.4	1430	40	60	321	33	360	505	67	29	0.7
17	7.9	1830	40	80	430	29	450	675	84	36	1.0
18	8.2	1870	40	105	631	61	440	1020	136	82	1.3
19	7.6	2150	70	85	482	34	350	810	110	63	0.9
20	8.1	2930	40	115	720	59	480	1140	153	110	1.6
21	8.2	3055	70	200	600	24	440	1325	84	63	1.4
22	8.2	3000	60	165	676	83	520	1065	210	116	1.6
23	8.2	2930	50	100	735	61	520	1165	185	86	1.5
24	8.3	2600	50	120	625	39	540	990	190	62	1.6
25	8.1	2080	40	85	480	58	450	750	90	66	1.0
26	7.6	2665	40	115	610	92	340	1025	210	75	0.9
27	8.2	3120	70	155	690	36	490	1300	120	54	1.2
28	8.2	3190	75	195	733	62	550	1210	189	96	1.8
29	8.2	3380	75	190	746	110	530	1315	232	123	1.7
30	7.6	2670	40	110	670	39	350	1080	230	66	0.9
31	7.4	2535	50	80	710	26	310	1110	94	43	0.8
32	7.5	1950	50	70	475	18	360	780	53	35	0.8
33	7.3	1560	50	60	360	17	350	590	45	47	0.7
34	8.2	1760	50	80	380	23	480	600	49	33	1.0
35	7.9	1820	50	70	429	39	400	640	56	26	1.0
36	8.1	2015	40	85	480	36	410	765	109	49	1.1
37	8.2	1755	60	55	417	19	430	670	59	49	1.0
38	7.4	1690	50	60	400	10	320	640	53	43	0.8
39	7.6	1500	55	60	350	14	370	565	12	46	0.7
40	7.4	1235	35	75	260	28	310	425	68	36	0.6
41	7.4	1230	55	50	265	26	310	380	96	43	0.6
42	7.7	1430	65	80	324	19	390	525	54	46	0.9
43	7.6	1560	75	70	310	11	410	520	110	21	0.8
44	8.0	1690	75	80	394	23	440	630	61	36	1.0
45	7.9	1625	30	55	390	16	380	610	56	51	0.9
46	7.8	1365	60	80	296	18	420	460	49	33	0.8
47	7.8	1300	40	75	295	32	480	370	110	38	0.8

Table 1 continued

S. no.	pH	TDS (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	F ⁻ (mg/L)
48	7.4	1370	30	70	310	16	390	500	33	40	0.8
49	8.2	1240	60	75	285	10	430	365	49	51	1.4
50	8.2	1430	30	50	260	19	550	425	24	19	1.8
Mean	7.81	1745.80	48.60	80.90	399.12	29.34	429.00	623.30	88.40	51.84	0.98
SD	0.34	716.67	12.90	39.52	182.17	22.37	64.17	346.30	56.30	22.89	0.33
CV	4.35	41.05	26.54	48.85	45.64	76.24	14.96	55.56	63.69	44.16	33.67

SD standard deviation, CV coefficient of variation

in fluorosis (USPHS 1987). Therefore, the lowest and highest desirable limits of F⁻ are considered as 0.60 and 1.20 mg/L, respectively, in the present study area.

From Table 1, it is noted that the concentration of F⁻ (0.60–1.80 mg/L) is not uniform in the study area. For example, the F⁻ content varies from 0.60 to 0.90 mg/L in 64 % of the groundwater samples (1 to 16, 19, 26, 30–33, 38–43 and 45–48); from 0.90 to 1.20 mg/L in 16 % of the groundwater samples (17, 25, 27, 34–37 and 44); from 1.20 to 1.50 mg/L in 8 % of the groundwater samples (18, 21, 23 and 49); and from 1.50 to 1.80 mg/L in the remaining 12 % of the groundwater samples (20, 22, 24, 28, 29 and 50). It is also observed that the pH, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, SO₄²⁻ and NO₃⁻ follow a similar trend of F⁻ (Table 2).

For assessing the factors that control the F⁻ content in the groundwater, understanding the influences of climate, slope, soil cover, lithology, anthropogenic activity and marine source on spatial distribution of F⁻ is very essential. Figure 6 shows the spatial distribution of F⁻ content in the study area. It indicates a progressive increase of F⁻ from 0.60 to 0.90, 0.90–1.20, 1.20–1.50 and 1.50–1.80 mg/L towards the southern part from the northern part. Significantly, the higher concentration of F⁻ (1.20–1.80 mg/L) is observed from the central and southern parts.

Dry climate is known to increase both the solubility and the rate of dissolution of soil salts and/or rock minerals. In addition to this, the climate also increases the rate of evaporation. The slope of the study area is gentle, which leads to slow movement of water. It causes a longer contact time of water with the aquifer material, thereby increasing the solubility of ions. The sand aquifer occurs mainly in the northern part, which reflects the higher rate of water circulation due to its high hydraulic conductivity. Thus, it supports a lesser solubility of ions. The increase of clay content from the northern to the southern part tends to slow water movement, because of its low hydraulic conductivity. This not only causes the increase of ions solubility, but also supports anion exchange. The occurrence of the Charnockite Group of rocks in the southern part (especially

in and around Ongole) shows low weathered and fractured portions, thereby causing a low hydraulic conductivity. In addition to this, the rocks contain the F⁻-bearing minerals (apatite, hornblende and biotite). The influences of salt pans and aqua-cultural activity on the groundwater system are dominant in the central part, while the impact of domestic wastes, leakage of septic tanks and agro-chemicals on the groundwater body is predominant in the remaining part. Thus, the soil–rock–water interaction appears as a prime geogenic factor for a source of F⁻ and the influences of anthropogenic activities as a supplementary factor for further increase of F⁻ in the groundwater system. This hypothesis is explained below, using binary diagrams, for understanding the factors that control the F⁻ content in the groundwater in the study area.

The F⁻ is plotted against pH, HCO₃⁻ and Ca²⁺ (Figs. 7, 8, 9). The F⁻ shows a significant positive correlation (*r*) with pH (*r* = 0.75) and HCO₃⁻ (*r* = 0.64), while it has a poor positive relation with Ca²⁺ (*r* = 0.32). Further, the pH has a good positive correlation with HCO₃⁻ (*r* = 0.78; Fig. 10), as the infiltrated water reacts with soil CO₂, which forms H₂O₃, resulting HCO₃⁻ and thereby causing a pH (Berner and Berner 1987). On the other hand, the incongruent dissolution of rock weathering causes a release of HCO₃⁻ (Drever 1997). This indicates a prevailing condition of alkalinity (caused by HCO₃⁻ only here) in the groundwater, which promotes a mineral dissolution (Stumm and Morgan 1996). Further, an easy accessibility of circulating water caused by rainwater and/or intensive and long-term irrigation practices in the soil and/or weathered zone stimulates the alkalinity more effectively (Wodeyar and Sreenivasan 1996; Subba Rao 2003, 2011; Madhnure et al. 2007). Thus, the alkaline water activates the leaching of F⁻-bearing minerals (apatite, hornblende and biotite) present in the host rocks. As a result, the chemical relations obviously indicate a greater affinity of F⁻ with HCO₃⁻ rather than with Ca²⁺. Further, it appears that the residence time of water in the aquifer zone could be high, because of the gentle slope and the occurrence of clays in the soil zone as well as in the sub-surface at

Table 2 Mean chemical composition of groundwater in different zones

Zone (Figure 1)	TDS range (mg/L)	pH	TDS (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	F ⁻ (mg/L)	Na ⁺ : Cl ⁻ (mg/L)	HCO ₃ ⁻ : Ca ²⁺ (mg/L)	Water quality
I	<1000	7.76	960.91	40.45	48.18	199.36	12.18	416.67	209.09	51.36	43.36	0.77	1.47	3.38	Fresh
II	1000–1500	7.64	1360.00	46.54	66.92	301.38	21.85	449.00	451.92	61.77	41.54	0.87	1.03	3.17	Very low brackish
III	1500–2000	7.80	1726.67	50.83	70.42	414.67	24.17	419.33	661.67	70.67	41.92	0.90	0.97	2.70	Low brackish
IV	2000–2500	7.93	2081.67	50.00	85.00	480.67	42.67	423.33	775.00	103.00	59.33	1.00	0.96	2.78	Moderate brackish
V	2500–3000	7.91	2761.43	47.14	115.00	678.00	57.00	437.14	1082.14	181.71	79.71	1.27	0.97	3.05	High brackish
VI	>3000	8.20	3186.25	72.50	185.00	692.25	58.00	502.50	1287.50	156.25	84.00	1.53	0.83	2.28	Very high brackish

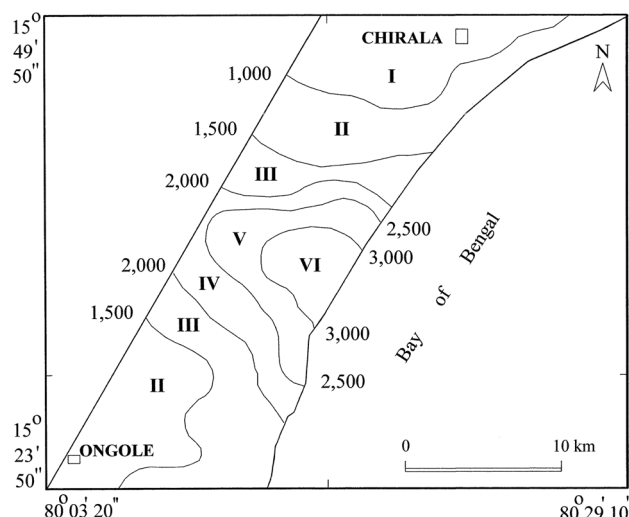


Fig. 5 Spatial distribution of TDS (mg/L) in the study area

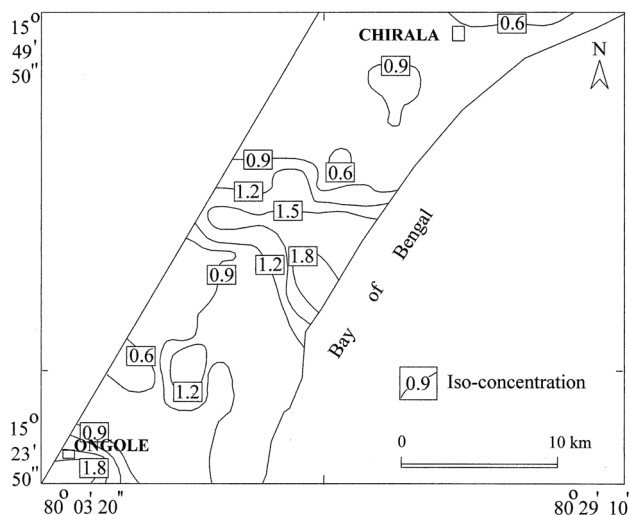


Fig. 6 Spatial distribution of F⁻ content (mg/L) in the study area

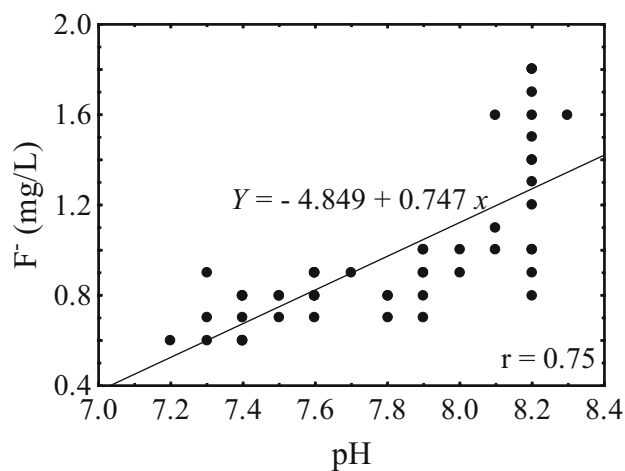


Fig. 7 Correlation between pH and F⁻

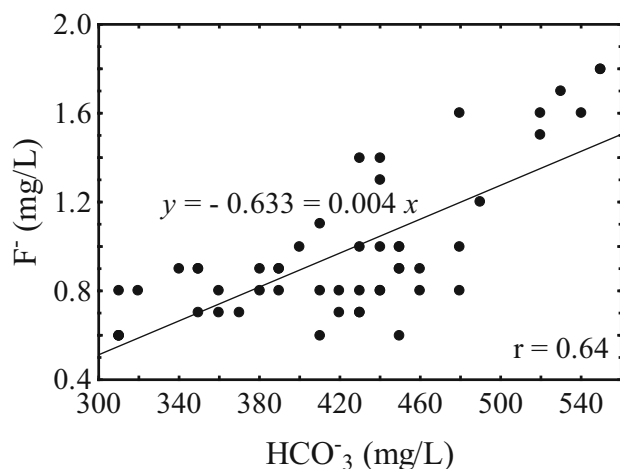


Fig. 8 Correlation between HCO_3^- and F^-

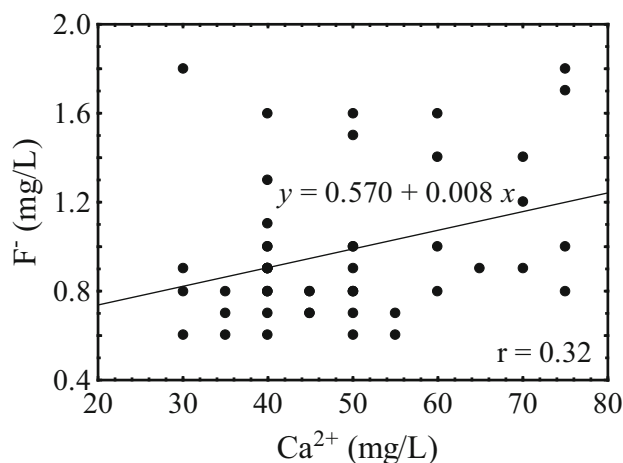


Fig. 9 Correlation between Ca^{2+} and F^-

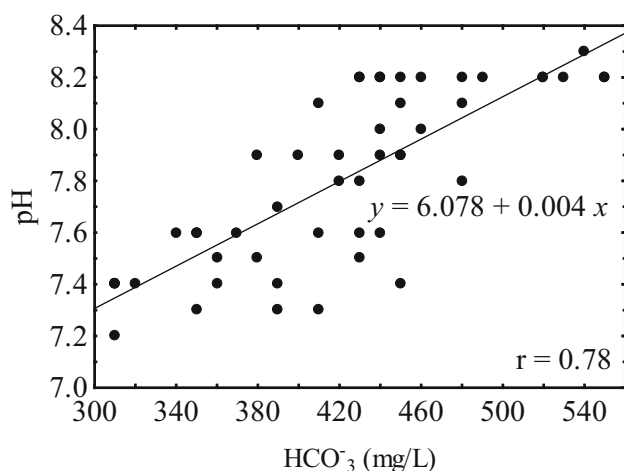


Fig. 10 Correlation between HCO_3^- and pH

different depths in the study area. This facilities not only active solubility and dissolution of F^- -bearing minerals, but also activate anion exchange between F^- and OH^- (Robinson and Edgington 1946; Hem 1991), which favours the increase of F^- content in the groundwater. Therefore, the F^- shows a good correlation with pH and HCO_3^- (Figs. 7, 8) as well as a poor relation with Ca^{2+} (Fig. 9). Similar correlation trends are also observed from other regions, which are discussed in the review literature.

Influences of saline water, chemical activity (ion exchange) and climate (evaporation) also play an important role for increasing F^- content in the groundwater. An insignificant correlation between Na^+ and Ca^{2+} ($r = 0.38$; Fig. 11) is observed from the groundwater due to increase of Na^+ caused by ion exchange between Na^+ and Ca^{2+} , and decrease of Ca^{2+} (Gao et al. 2007, 2013; Singaraja et al. 2013; Subba Rao et al. 2014a, b; Surya Rao et al. 2015). Impacts of saline water (used for salt pans and aquacultural activities), domestic wastes, leakage of septic tanks and clays are responsible for additional source of Na^+ (Todd 1980; Hem 1991; Subba Rao 2014; Subba Rao et al. 2014a, b). On the other hand, the solubility of F^- is low and its dissolution rate is slow (Nordstrom and Jenne 1977). But the solubility of F^- increases with the increase of Na^+ in the groundwater (Apambire et al. 1997; Gao et al. 2007, 2013; Singaraja et al. 2013; Surya Rao et al. 2015). Further, the dry climate increases the rate of solubility and dissolution of minerals present in the host rocks (Hem 1991). It also increases the rate of evaporation, which rises the pH levels due to loss of CO_2 along with water (Handa 1975). This causes a precipitation of CaCO_3 . The occurrence of *kankar* in the soil zone further supports this hypothesis so that the groundwater in the study area shows an oversaturation with respect to solid phase of CaCO_3 (Table 3). This also causes in reduction in Ca^{2+}

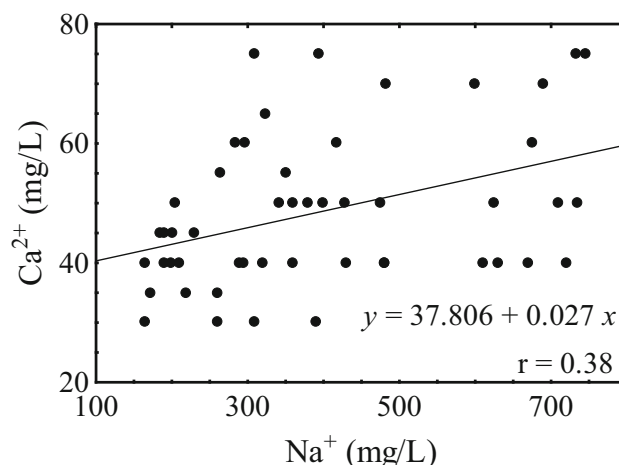


Fig. 11 Correlation between Na^+ and Ca^{2+}

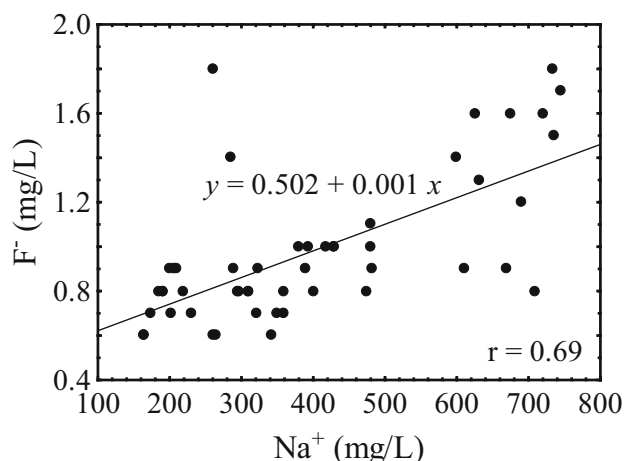
Table 3 Saturation index

Particulars	Saturation index	Remarks
CaCO ₃	3.12	Precipitation
CaF ₂	-2.13	Dissolution

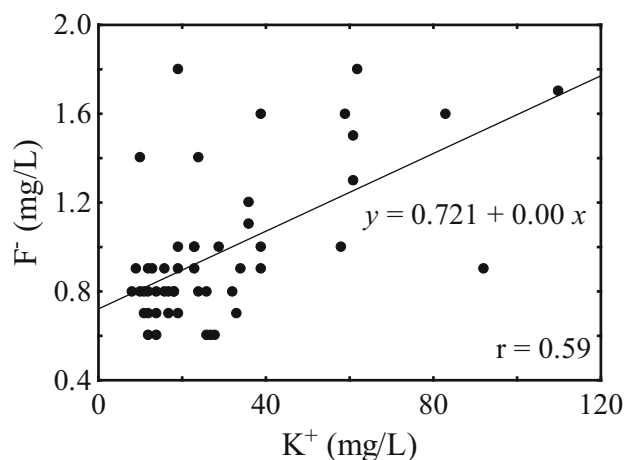
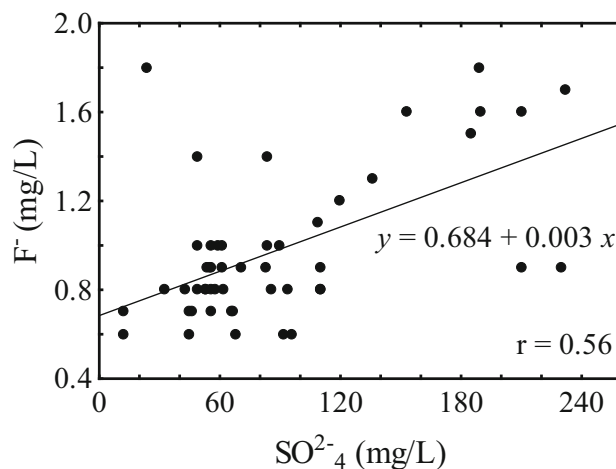
content. As a result, it favours a higher dissolution of CaF₂ from the source material to compensate for requirement of Ca²⁺ ions in the chemical equilibria (Freeze and Cherry 1979). Thus, it shows an under saturation with respect to CaF₂, causing a higher F⁻ content in the groundwater and thereby the Na⁺ shows a good positive correlation with F⁻ ($r = 0.69$; Fig. 12) and a poor positive relation with Ca²⁺ ($r = 0.38$; Fig. 11), as also discussed earlier in the review literature from other regions. Further, the poor relation between Na⁺ and Ca²⁺ is a result of the concurrent increase or decrease in the cations, depending upon the dissolution, precipitation, concentration effects and ion exchange (Admas et al. 2001).

The increase of Na⁺:Cl⁻ ratio from 0.83 to 1.47 (Table 2) indicates modification of NaCO₃ water (Na⁺:Cl⁻ >1.0) by dissolution or mixing of NaCl (Na⁺:Cl⁻ <1.0; Dhiman and Keshari 2006; Gao et al. 2007, 2013), while the ratio of HCO₃⁻:Ca²⁺ increases from 2.28 to 3.38, which signifies an increase of HCO₃⁻ (Saxena and Ahmed 2003). The concentration of F⁻ (0.77–1.53 mg/L) also follows a similar trend of Na⁺:Cl⁻ and HCO₃⁻:Ca²⁺ ratios. These infer that the Na⁺ and HCO₃⁻ favour the chemical condition for dissolution of F⁻ and, therefore, a good positive correlation of F⁻ with HCO₃⁻ ($r = 0.64$) and Na⁺ ($r = 0.69$) is observed from the study area (Figs. 8, 12), as also reported similar observations (discussed in review literature) from other regions. This is also supported by the hydrogeochemical facies.

A positive correlation of F⁻ with K⁺ ($r = 0.59$), SO₄²⁻ ($r = 0.56$) and NO₃⁻ ($r = 0.64$) is observed from the study

**Fig. 12** Correlation between Na⁺ and F⁻

area (Figs. 13, 14, 15), as also discussed similar results from other regions (in review literature). This indicates the influences of uncontrolled usage of agro-chemicals (nitrogen, phosphate and potash fertilisers) and soil amendments (gypsum) for higher crop yields, because the nitrogen variety promotes over-grass shoot growth, phosphate type supports strong root growth, potash variety helps gross withstand stress, drought or disease and gypsum aids to alter the physical or chemical properties of the soils (Todd 1980; Fekri and Kasmaei 2013; Subba Rao 2014). Therefore, these chemicals are responsible for the concentrations of F⁻, K⁺, SO₄²⁻ and NO₃⁻ in the groundwater. In addition to this, domestic wastes and leakage of septic tanks contribute K⁺ and NO₃⁻ to the groundwater system (Bhosle et al. 2001; Ayoob and Gupta 2006; Subba Rao 2014; Subba Rao et al. 2014a, b). Thus, the anthropogenic activities appear as a supplementary source of F⁻ to its further elevation in the groundwater.

**Fig. 13** Correlation between K⁺ and F⁻**Fig. 14** Correlation between SO₄²⁻ and F⁻

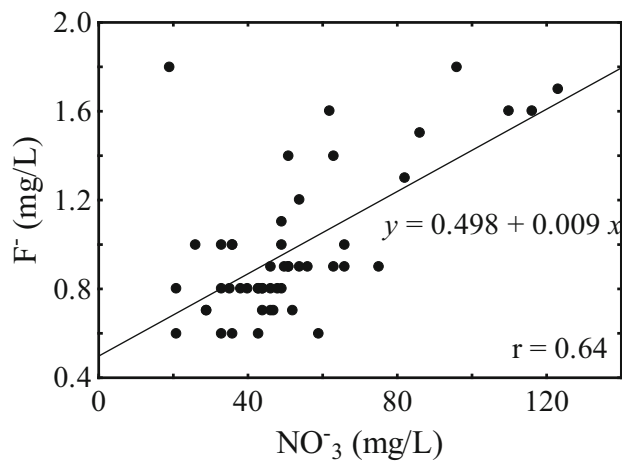


Fig. 15 Correlation between NO_3^- and F^-

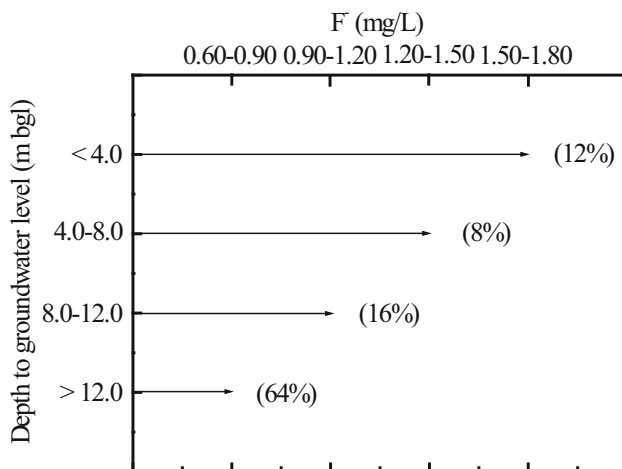


Fig. 16 Fluoride content with depth to groundwater level. Value in bracket denotes percentage of wells

Figure 16 shows that the concentration of F^- increases with the decrease of the depth. It suggests that the factors that control the F^- content in the groundwater are prevalent in the shallow depth rather than those in the deeper level. It is a result of higher rate of solubility, dissolution and leaching of salts present in soil and/or weathered zone, and ion exchange and evaporation in the shallow depth. This is also supported by the above discussion explained for understanding the causative factors that control the F^- content in the groundwater.

Remedial measures

- (a) The study area receives 94 % (846 mm) of the total rainfall during monsoon. It can be possible to reduce the F^- content in the groundwater, if a number of

rainwater harvesting structures are constructed, as reported in other regions (Narasimha and Pradeep 1997; Bhagavan and Raghu 2005). This is a simple low-cost alternative to the existing high-cost approaches (Nalgonda technique, activated alumina, red mud, montmorillonite, magnesia, etc.).

- (b) Calcium food is essential to control the F^- content in the human body.
- (c) Application of CaSO_4 and CaCl_2 can also reduce the F^- content in the groundwater (Fekri and Kasmaei 2013).
- (d) Public awareness on causes of high concentration F^- in drinking water and its health implications is necessary for success of groundwater quality management measures.
- (e) The study helps the planning authorities to mitigate the F^- content in the drinking water.

Conclusions

Fluoride varies from 0.60 to 1.80 mg/L in the coastal region, which exceeds the threshold limit of 1.20 mg/L in 20 % of the total groundwater samples. The occurrence of F^- -bearing minerals in the country rocks are the main geogenic source of F^- in the groundwater. Alkalinity (pH and HCO_3^-) plays a significant role in dissolution and leaching of F^- . As a result, a positive correlation of F^- with pH and HCO_3^- is observed. The clays lead to a longer contact of water with aquifer material for active solubility and dissolution of F^- -bearing minerals, and are also responsible for anion exchange between F^- and OH^- . The influences of saline water, ion exchange between Na^+ and Ca^{2+} , and the precipitation of CaCO_3 due to evaporation reduce the Ca^{2+} content, which favour to dissolve CaF_2 to maintain the chemical equilibria. Thus, there is a positive correlation between Na^+ and F^- . Anthropogenic activities act as supplementary factor for further elevation of F^- in the groundwater. This is supported by positive correlation of F^- with K^+ , SO_4^{2-} and NO_3^- . These factors are dominant in shallow depth so that the groundwater shows higher content of F^- in the shallow depth than that in the deeper depth. Hydrogeochemical facies also support this hypothesis. Appropriate management measures are suggested to reduce the F^- in the groundwater.

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