

Appraisal of highly fluoride zones in groundwater of Kurmapalli watershed, Nalgonda district, Andhra Pradesh (India)

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Abstract Fluoride (F) contamination study had been carried out to see its allocation in Kurmapalli watershed, Nalgonda district, Andhra Pradesh, India. The study area is located about 60 km SE of Hyderabad city. The groundwater is the main source of water for their living. The groundwater in villages and its surrounding are affected by fluoride contamination and consequently the majority of the people living in these villages has health hazards and is facing fluorosis. The purpose of this study is to identify the wells with high F, raise awareness in people, study the water chemistry, and also find out the source of F in groundwater. A total of 32 groundwater samples were collected from different wells in both shallow aquifers and deeper fractures zones during October 2004. The chemical analysis of groundwater has been done. Fluoride values vary from 0.7 to 19.0 mg/l. It is noted that the maximum value (19.0 mg/l) is one of the highest values found in groundwater in India and 78% of the total samples show F concentrations that exceeds the permissible limit value (1.5 mg/l). The highest value of F is found at Madanapur bore well which is located at central part of the watershed. The F value of this bore well was monitored from October 2004 to October 2006. During this period the F concentration varies from 17.8 to 21.0 mg/l with mean 19.3 mg/l. There is no correlation of F with chemical parameters except calcium. The Ca has shown inverse proportional with F. Water–rock interaction

studies were also carried out to understand the behavior of F in groundwater at prominent F affected areas. Rock samples were collected and analyzed, and found their enrichment of F. The anthropogenic possibility of F is almost negligible. The rocks of this area are enriched in F from 460 to 1,706 mg/kg. It is indicated that the rock–water interaction is the main source of F in groundwater. The highest values of F are found in middle part of the region and are related to the occurrence of fluoride rich rocks and their chemical kinetic behavior with groundwater.

Keywords Fluoride · Water–rock interaction · Granite rocks · Nalgonda district · India

Introduction

Fluoride helps for the human health as it helps in the normal mineralization of bones and formation of dental enamel (Cao et al. 2000). When the daily intake-dose of F is below 0.5 mg/l (deficiency) some health related problems could occur such as dental caries, lack of formation of dental enamel and deficiency of mineralization of bones, especially among the children. On the contrary, when F daily intake-dose exceeds 1.5 mg/l (poisoning effect), it can cause several health related problems, e.g., fluorosis, which equally affect both young and old (WHO 1984; Kharb and Susheela 1994). The incidence and severity of fluorosis is related to the F content in various components of environment, viz. air, soil, and water. Out of these, water (especially groundwater) is the major contributor to the problem (Agrawal et al. 1997). The problem of excess F concentration in groundwater resources has now become one of the most important toxicological and geo-environmental issues in India as well as several parts of the world

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(Nanyaro et al. 1984; Gaciri and Davies 1993; Gizaw 1996; Andezhath et al. 1999; Wang et al. 1999; Pillai and Stanley 2002; Madhnure et al. 2007). The high concentrations of F have been found in groundwater in China, Syria, Jordan, Ethiopia, Sudan, Tanzania, Kenya and Uganda (Smith et al. 1953; Ocherse 1953; Grech 1966; Latham and Grech 1967; Moller et al. 1970; Lester 1974; Olson 1979; Tekle-Haimanot et al. 1987; Fuhong and Shuqin 1988; Kahama 1997; Finkelman et al. 1999; Ando et al. 2001). The states of Gujarat, Rajasthan, Haryana, Punjab, Uttar Pradesh, West Bengal, Orissa, Madhya Pradesh, Andhra Pradesh, Tamilnadu and Karnataka in India are the most affected with this problem Ramesam and Rajagopalan (1985; Rao et al. 1993; Sisodia 1994; Misra 1997; Garg et al. 1998; Ahmed and Sreedevi 2002; Pillai and Stanley 2002; Jacks et al. 2005). A critical evolution of the occurrence of F in the natural waters of several states and Union territories of India indicates that the permissible limit value (1.5 mg/l) in the groundwater is exceeded as much as in 20 states (Chand Dinesh 2001). According to the 'Survey of Status of Drinking Water Supply in Rural Habitation' conducted by the Rajiv Gandhi National Drinking Water Mission (RGNDRM) in 1993, there are 9,741 villages in India having F content >1.5 mg/l in groundwater sources (Handa 1988; Susheela 1999). It is generally accepted that groundwaters are enriched in fluoride due to prolonged water–rock interactions (Nordstrom et al. 1989; Gizaw 1996; Frengstad et al. 2001; Carrillo-Rivera et al. 2002). The chemical composition of lithology, therefore, is regarded as an important factor determining the F concentration of groundwater. Studies have shown that F is generally enriched in groundwater of the bedrock aquifers of alkali granites and metamorphic rocks (Banks et al. 1998; Dowgiałło 2000; Botha and Van Rooy 2001; Shancker et al. 2003).

As we know that the fluoride incidence in groundwater is mainly a natural phenomenon, influenced basically by the local and regional geological setting and hydro-geological conditions (Handa 1975; Ramesam and Rajagopalan 1985; Tamata 1994; Srinivasa Rao 1997; Ahmed and Sreedevi 2002). The chief sources of F in groundwater are the fluoride-bearing minerals in the rocks and sediments. The important fluoride-bearing minerals are: fluorite (fluorspar), fluorapatite, cryolite, biotite, muscovite, lepidolite, tourmaline, hornblende series minerals, glaucophane-riebeckite, asbestos (chrysotile, actinolite, anthophyllite), sphene, apophyllite, zinnwaldite, etc. These minerals have sufficient amount of fluorine in their composition.

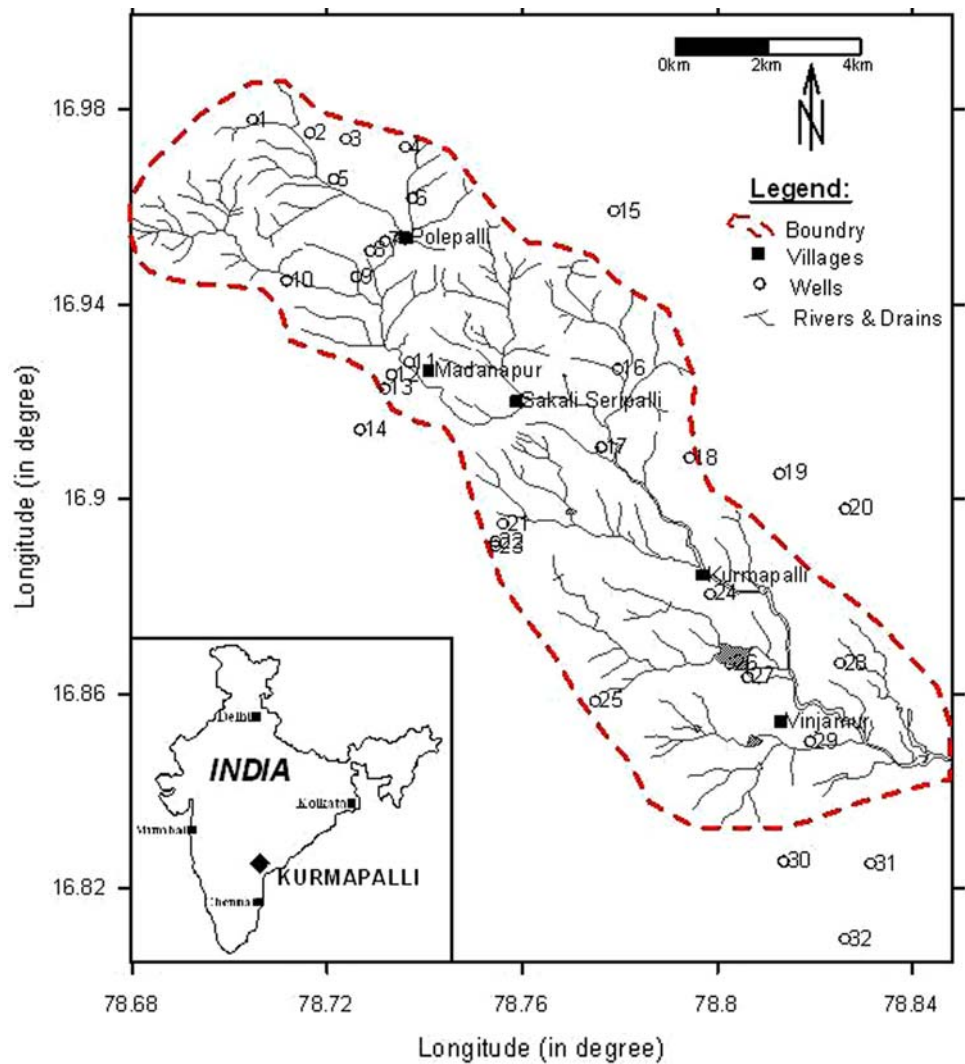
Since rocks are made up of minerals and the soil is derived from parent rocks, F is fairly abundant in rocks and soil. The F content varies in different geological formations i.e. in apatite rocks; amphiboles present in metamorphic

rocks, in the groundwater present in the amphibole formations and weathered formations of pyroxene amphibolites and pegmatites (Sinha 1986; Srinivasa Rao 1997). The weathering and leaching processes, mainly by moving and percolating water, play an important role in the incidence of F in groundwater. The F concentration in groundwater depends upon the following factors like climate, relief, evaporation, precipitation, geology and geomorphology of the area (Liu and Wan Hua 1991). Usually fluorite is leached from rock by water under different pH conditions (Fuhong and Shuqin 1988). Thus pH plays an important role in dissociation and dissolution of F in groundwater (Saxena and Ahmed 2001, 2003). However, the present study area is fairly representative of the granitic aquifers that are affected by the F problems. The area has very high amount of F content in the groundwater and its values are <3.2 mg/l all over the area except the small patches where they are comparatively higher values. The purpose of this paper is to evaluate the quality of groundwater in Kurmapalli in particular intern of F. This study includes the source of F and also their chemical kinetic behaviour with groundwater.

Study area

Kurmapalli watershed (study area) and the sampling points are shown in Fig. 1. It lies between longitude 78.68° and 78.84°E and latitude 16.83° and 16.98°N in Nalgonda District (Andhra Pradesh), India. This area covers about 100 km², which is one of the most drought prone areas of Nalgonda district (Prasad et al. 2007). This basin is characterized by poor land soil scarce vegetation, erratic rainfall, and lack of soil moisture for most part of the year. Recurring drought coupled with increase in groundwater exploitation results in decline of groundwater levels (Rajani et al. 2006). The watershed forms part of semi-arid tract of Deccan plateau. Generally the area is being rained from July to December of the each year. During 2004, rainfall recorded at this watershed is only 400 mm. Out of 400 mm, only 276 mm is recorded during monsoon time i.e. from July to December 2004 and the rest is during summer months when the evaporation rate is quite high and is not useful for agricultural activity. The temperature continuously increases from the end of February to the hottest month (May) to between 35°C and over 46°C. In the coldest month (January), the values recorded ranged between 22 and 26°C. The major rock type in this area is gneissic complex. The slope of the area is 0–1% and having weathered pediplain with alkaline soil extending down the slope from the foot of mountain scarp. In this area 3rd order of stream passing through it and which appeared as good zone of groundwater, but unfortunately this area is highly contaminated with F presumably highest

Fig. 1 Location map of the Kurmapalli watershed, Nalgonda district, India



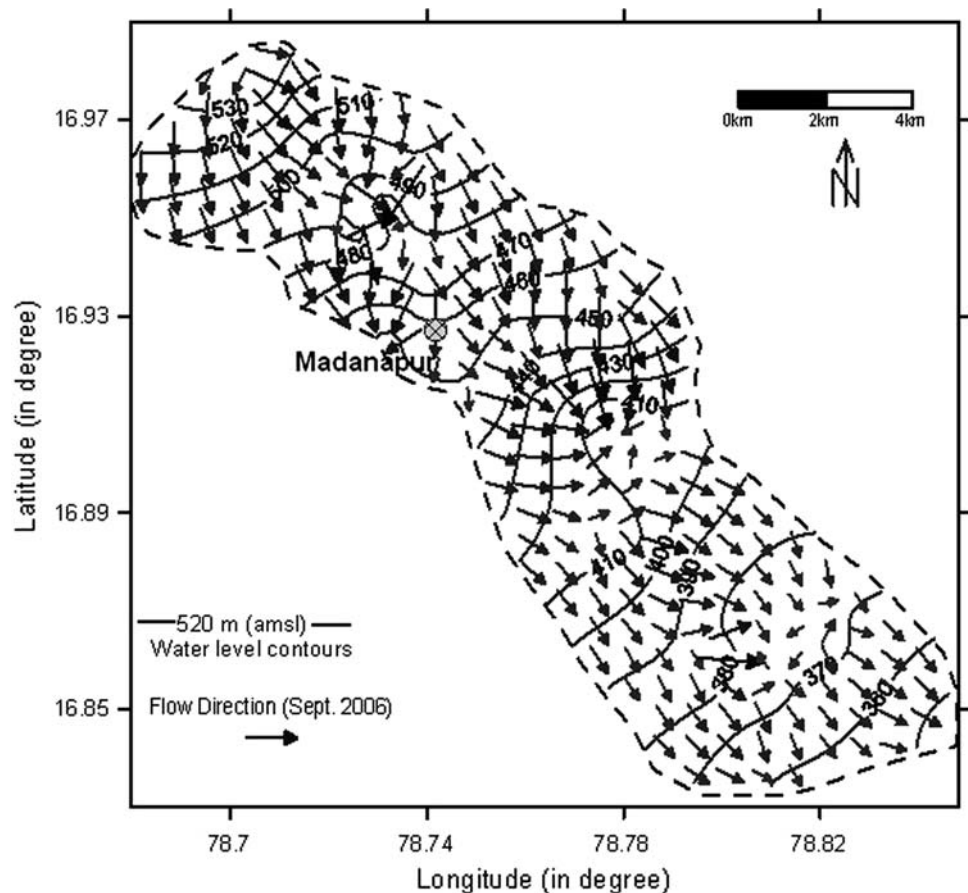
in granitic terrain in India. As a result of this, groundwater has turned into killing water for human race. Madanapur, one village of the study area, lies at 78.7368°E longitude and 16.9281°N latitude has been more affected with F which is considered to be one of the highest F concentrations in India.

Geological and hydrogeological setup

Granite and gneissic cover about 90% of the Kurmapalli watershed and followed by kankar and recent alluvium along the river course. In the northern part of the watershed has massive granite. The older gneisses of the area occupy the high hill ranges and also isolated hillocks, which are mostly of blocky nature and marked by scraps. Gneissic complex covers major part of the area forms the plains and occasionally forms low dome-shaped hillocks. Kankar is found in some patches of southeastern part of the area.

Lineaments are found in all along the study area having NW–SE trend in general and at some places N–S trend has been seen. Drainage pattern is dendritic to sub-dendritic in nature. The dominant lineament directions control drainages at most of the places. The groundwater occurs in weathered portion of aquifer, joints and deep fractures. The groundwater is being exploited through dug wells tapping weathered zone and bore wells tapping from the fractured zones. The general trend of groundwater flow is towards the southeastern direction (Fig. 2). This flow pattern is disturbed at some places of the study area due to over exploitation and local geological settings. The thickness of the weathered zones varies from 5.6 to 20.0 m. The highly weathered part upto 20 m depths in central valley is the potential aquifer. The shallow aquifer gets direct recharge through rainfall and seepage from a number of irrigation tanks and fields. Most of the tanks are either got silted or could not store water due to breach of bunds. This has resulted into a low seepage rate as indirect recharge.

Fig. 2 Groundwater flow map, Kurmapalli watershed, Nalgonda district, India



Materials and methods

About 32 water samples were collected during October 2004 from bore wells (Fig. 1), which are under use at 0.5 m below the water table, and were pumped more than 5 min. Methods of collection and analysis of water samples followed are essentially the same as given by Brown et al. (1983) and APHA (1985), which is shown in Table 1. These samples were collected in 1-l capacity polythene bottles. Prior to collection the bottles were thoroughly washed with diluted HNO_3 acid, and then with distilled water in the laboratory before filling the bottle with sample. The bottle is rinsed to avoid any possible contamination in bottling and every other pre-cautionary measure has been taken. Fluoride was determined by ion selective electrode method using TISAB (Greenberg et al. 1998). The precise locations of the sampling points were determined in the field using GPS GARMIN-12, Global Positioning System (GPS). Some parameters like pH and electrical conductivity (EC) were measured during the sampling collection using portable kits. The chemical analyses of these groundwater samples were carried out at Geochemistry Laboratory, National Geophysical Research Institute (NGRI), Hyderabad using standard methods (Brown et al. 1983; APHA 1985). Five-rock samples were also collected

Table 1 The instrumental/chemical techniques were used for water analysis

Chemical constituent of groundwater	Instrumental/chemical techniques
EC	Conductivity meter (digital) with selective electrode and sensor
pH	pH meter (digital) with selective electrode
TDS	Gravimetric, total ionic counts
TH	EDTA titro-metric
Na, K	Atomic absorption spectrophotometer
Ca, Mg	EDTA titro-metric and atomic absorption spectrophotometer
Cl	Mohr titrametric and chloride metric
HCO_3	Acidimetric neutralization
SO_4	Spectrophotometer
F	Ion selective electrode method using TISAB

from an exposure close to the highly affected fluoride well (Fig. 6). These rocks were crushed, powdered and milled. Sub-samples were used for chemical analysis at X-Ray Fluorescence Spectrometer (XRF) Laboratory, NGRI, Hyderabad using standard methods (Govil 1985). The analytical precision for the measurements of cations (Ca, Mg, Na, and K) and anions (HCO_3 , Cl, SO_4 , and F),

indicated by the ionic balance error (IBE) was computed on the basis of ions expressed in me/l. The value of IBE was observed to be within a limit of $\pm 5\%$ (Mandel and Shiftan 1980; Domenico and Schwartz 1990).

Results and discussion

Chemistry of groundwater

The results of chemical analysis of groundwater are included in Table 2. The Table 3 gives the minimum, maximum, mean values of chemical constituents and

standard deviation. The analytical results of the samples collected from the area indicate that the groundwater is generally alkaline in nature (pH 7.4–8.5). The EC varies from 490 to 2,000 $\mu\text{S}/\text{cm}$ and total dissolved solids from 310 to 1,280 mg/l. Sodium is dominant ranging from 28 to 252 while Mg varies from 6 to 48 mg/l and Ca from 12 to 180 mg/l. Chloride concentration ranges from 34 to 385 mg/l. Bicarbonate is the next predominant anion, with a concentration varying between 128 and 456 mg/l.

The F concentration varies from 0.7 to 19.0 mg/l and the highest concentrations are observed in the middle part of the watershed. The high fluoride groundwater in

Table 2 Hydrochemical parameters, Kurmapalli watershed, Nalgonda

Well No.	Location	Depth (m)	Discharge (m^3/day)	pH	EC	TDS	TH	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃	F
1	Krishnapalli	54	800	8.2	846	550	233	22	19	125	10	110	60	192	4.4
2	Krishnapalli (main village)	61	700	8.0	1,015	650	252	22	20	154	10	150	65	210	3.2
3	Mall-1	46	300	7.8	490	310	146	12	6	80	5	34	40	128	2.0
4	Mall-2	41	600	7.9	1,015	650	184	32	12	175	10	222	48	140	3.1
5	Godkondla (Rai Bai)	30	200	7.6	740	470	258	42	8	81	5	58	56	208	1.4
6	Godkondla (Marlingam Bai)	46	700	7.9	9,25	590	244	46	18	124	12	120	85	180	3.6
7	Polepalli-1	61	650	7.8	820	525	199	28	15	119	15	112	68	156	9.5
8	Polepalli-2	26	200	8.0	910	580	257	39	21	122	6	136	48	197	1.5
9	Polepalli-3	29	200	7.9	900	570	240	65	23	102	7	136	80	152	1.4
10	Polepalli (Ramnagar)	34	900	8.1	950	615	335	32	18	123	12	68	67	285	4.3
11	Madanapur	52	1000	8.5	770	495	178	19	23	120	10	110	52	136	19.0
12	Madanapur Gate	61	600	8.2	1,070	690	263	32	29	156	12	160	83	202	7.1
13	Kulkulapalli (Madnapur border)	38	200	7.5	1,260	805	379	42	32	170	19	178	53	305	3.8
14	Kulkulapalli	38	300	8.0	1,130	720	381	48	28	125	18	105	80	305	3.1
15	Trigandlapalli	36	500	7.6	1,160	740	355	105	18	110	16	192	62	232	2.7
16	Takkalapalli	37	700	7.9	1,345	860	410	68	22	167	10	185	80	320	2.4
17	Ummapur	58	700	8.0	1,630	1,050	393	56	32	252	22	280	92	305	4.8
18	Saireddigudem	25	300	7.8	1,830	1,170	499	156	38	180	18	288	176	305	1.7
19	Mallepalli	30	200	7.9	1,800	1,155	520	162	36	180	10	256	176	322	1.3
20	Krishrapalli (E)	24	100	7.4	2,000	1,280	530	170	28	206	26	385	128	332	1.5
21	Gollapalli (Samyakya nagar)	21	250	8.1	1,250	800	343	67	24	154	10	176	104	252	2.0
22	Kurmed (Gate)	39	300	8.3	1,175	750	363	60	23	132	22	92	136	280	2.6
23	Gollapalli	27	200	7.7	1,480	945	435	105	38	127	32	232	112	292	1.8
24	Kurmapalli	21	600	7.9	1,530	975	454	120	29	160	10	270	78	305	1.6
25	Annomonpalli	26	200	7.7	1,740	1,110	517	170	22	157	28	293	105	325	1.3
26	Bhadvanegudem-1	34	400	8.3	1,435	915	536	64	40	157	20	44	152	432	3.1
27	Bhadvanegudem-2	31	200	7.6	1,390	885	515	170	40	28	22	245	68	305	1.9
28	Battugudem	55	150	8.1	1600	1,030	556	52	48	177	32	104	152	456	4.2
29	Vinjamoor-1	46	300	8.0	1,400	900	500	100	35	122	23	132	120	365	2.4
30	Vinjamoor-2	43	100	7.9	1,725	1,100	564	176	32	132	22	232	145	356	1.1
31	Varkola	41	500	8.0	1,650	1,050	544	154	23	156	10	205	132	367	1.9
32	Chintapalli	22	150	8.0	1,845	1,180	613	180	31	156	22	232	156	402	0.7

All are bore wells are under unconfined aquifer and located in granitic formation with 0.165 m diameter
 EC in $\mu\text{S}/\text{cm}$, chemical concentration in mg/l, pH $-\text{Log H}^+$, TDS total dissolved solids in mg/l, TH total hardness in mg/l

Table 3 Statistical summary of chemical data, Kurmapalli watershed, Nalgonda

Parameters	Minimum	Maximum	Mean	SD
pH	7.4	8.5	7.9	0.25
EC	490	2,000	1,276	388
TDS	310	1,280	816	248
TH	146	613	381	137
Ca	12	180	82	56
Mg	6	48	26	97
Na	28	252	142	41
K	5	32	16	8
Cl	34	385	173	83
SO ₄	40	176	96	40
HCO ₃	128	456	273	88
F	0.7	19.0	3.3	3.4

pH $-\text{Log H}^+$, EC in $\mu\text{S/cm}$, TDS total dissolved solids, TH total hardness, SD standard deviation

All concentrations are in mg/l

the area is concentrated mostly in and around Madanapur and at Polepalli (shown in Fig. 3). The F concentration exceeded the permissible limit (1.5 mg/l) in 78% of the total samples analyzed. The groundwater flows generally from NW to SE direction. The evaporation rate increases from recharge to discharge areas (Rajani et al. 2006). The dry climate with low rainfall favors salinization of groundwater along the flow direction. An attempt has been made to study the chemical character of the water samples of the area. Figure 4 shows the correlation of Ca and Mg with F content of groundwater and reflects the behavior of Ca and Mg with F in groundwater samples. The highest F (19.0 mg/l in October 2004) is observed in Madanapur bore well where Ca (19 mg/l) is comparatively low. The lowest Ca is more or less related with the calcium precipitation. Highest F likely to be form rock–water interaction where chemical kinetic is well suited and the rock has high value of F. In order to verify the correlation of F concentration with Na, Ca ions present in groundwater are established. These are

Fig. 3 Distribution of fluoride concentrations (mg/l) in Kurmapalli watershed, Nalgonda, India (October 2004)

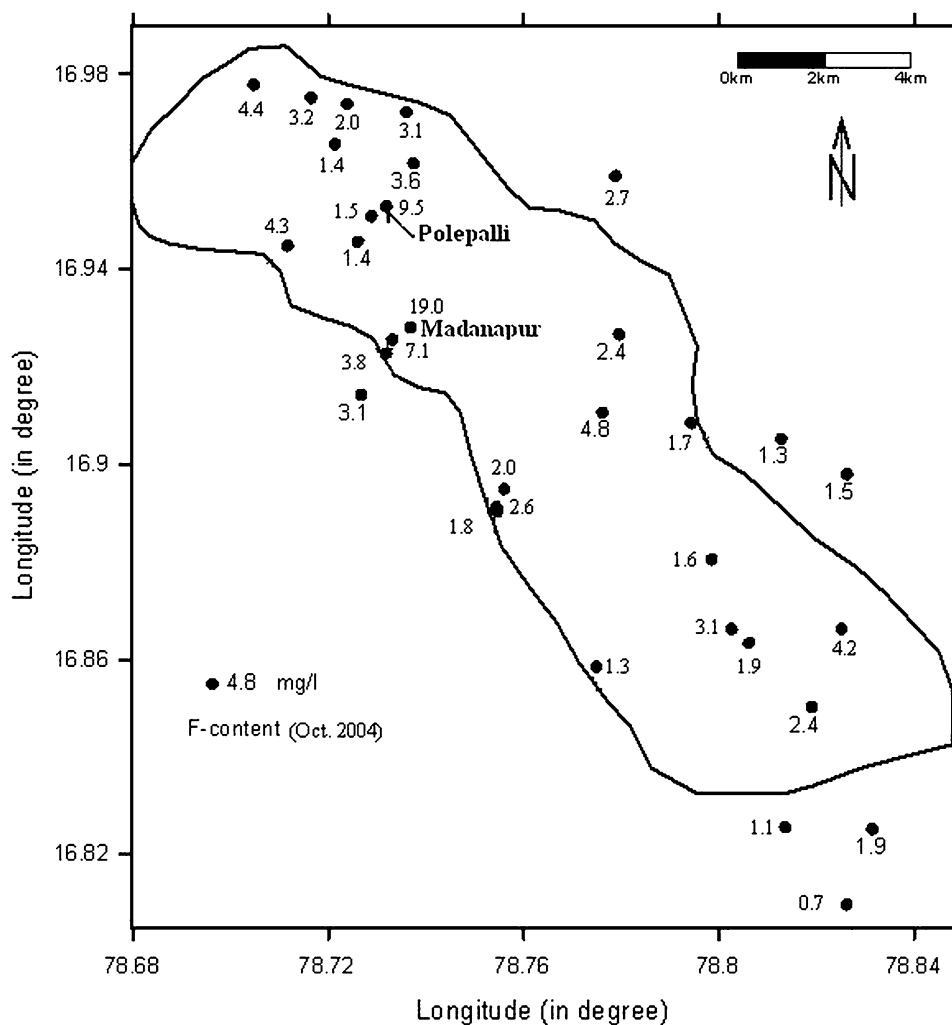


Fig. 4 Correlation of fluoride with Ca and Mg

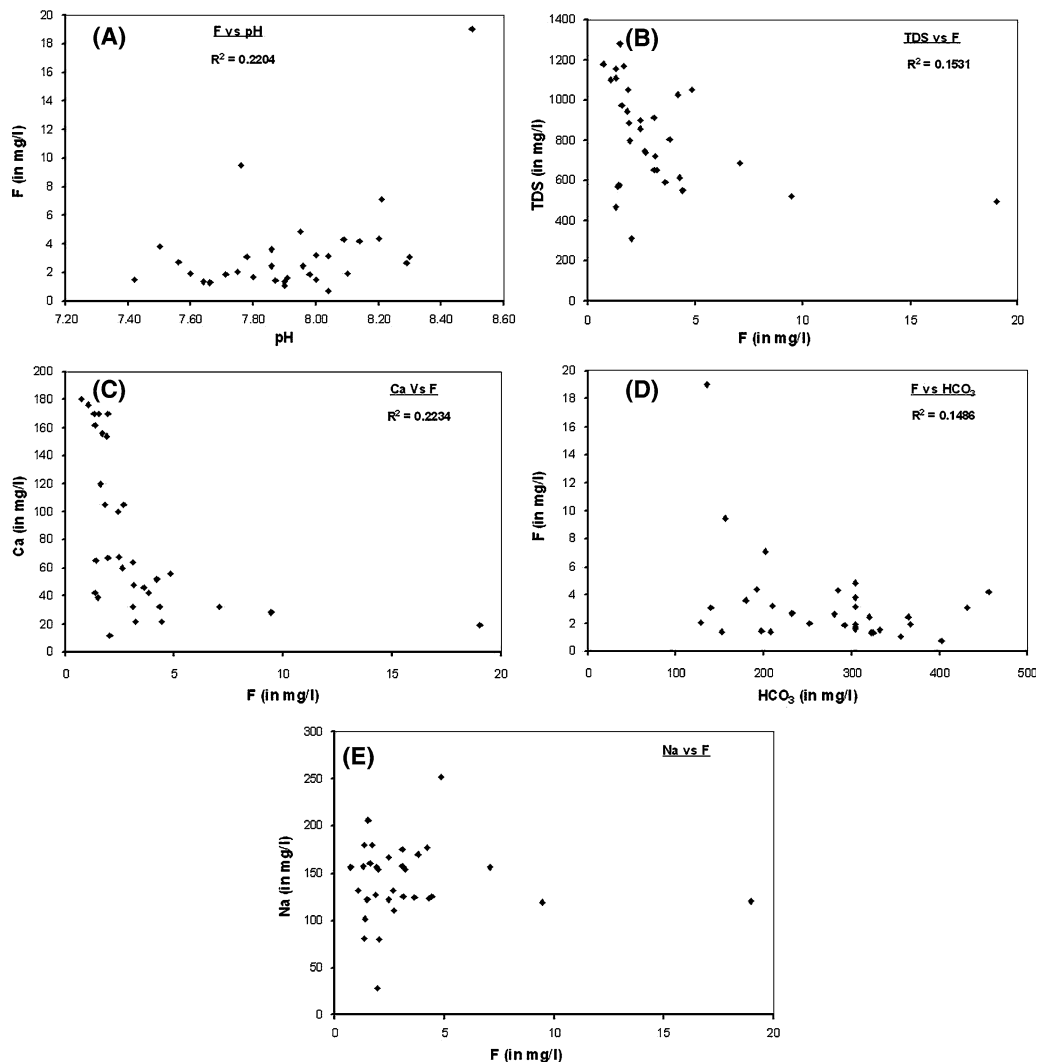
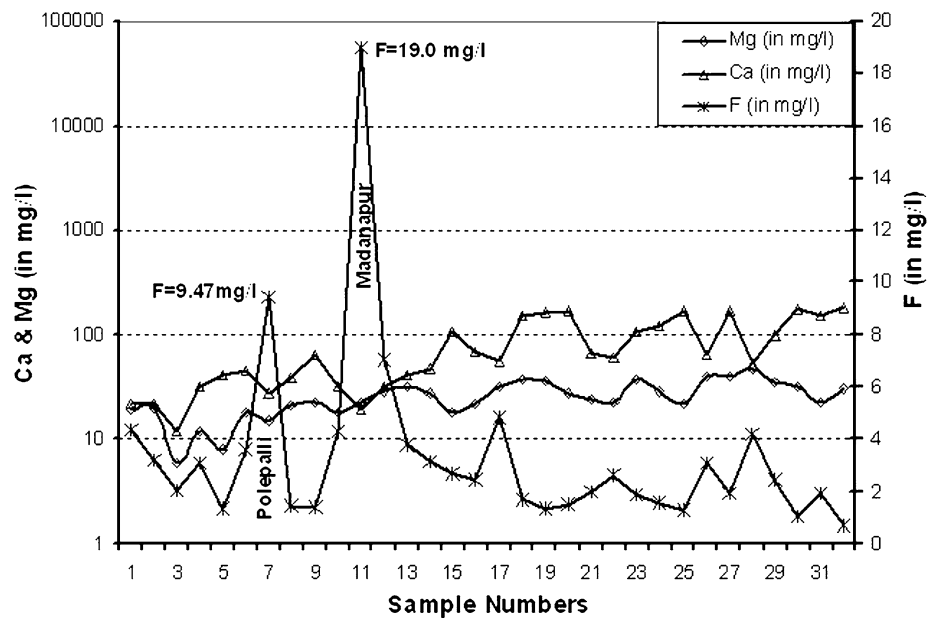


Fig. 5 a Cross plots in between F and pH, b TDS and F, c Ca and F, d F and HCO₃, e Na and F

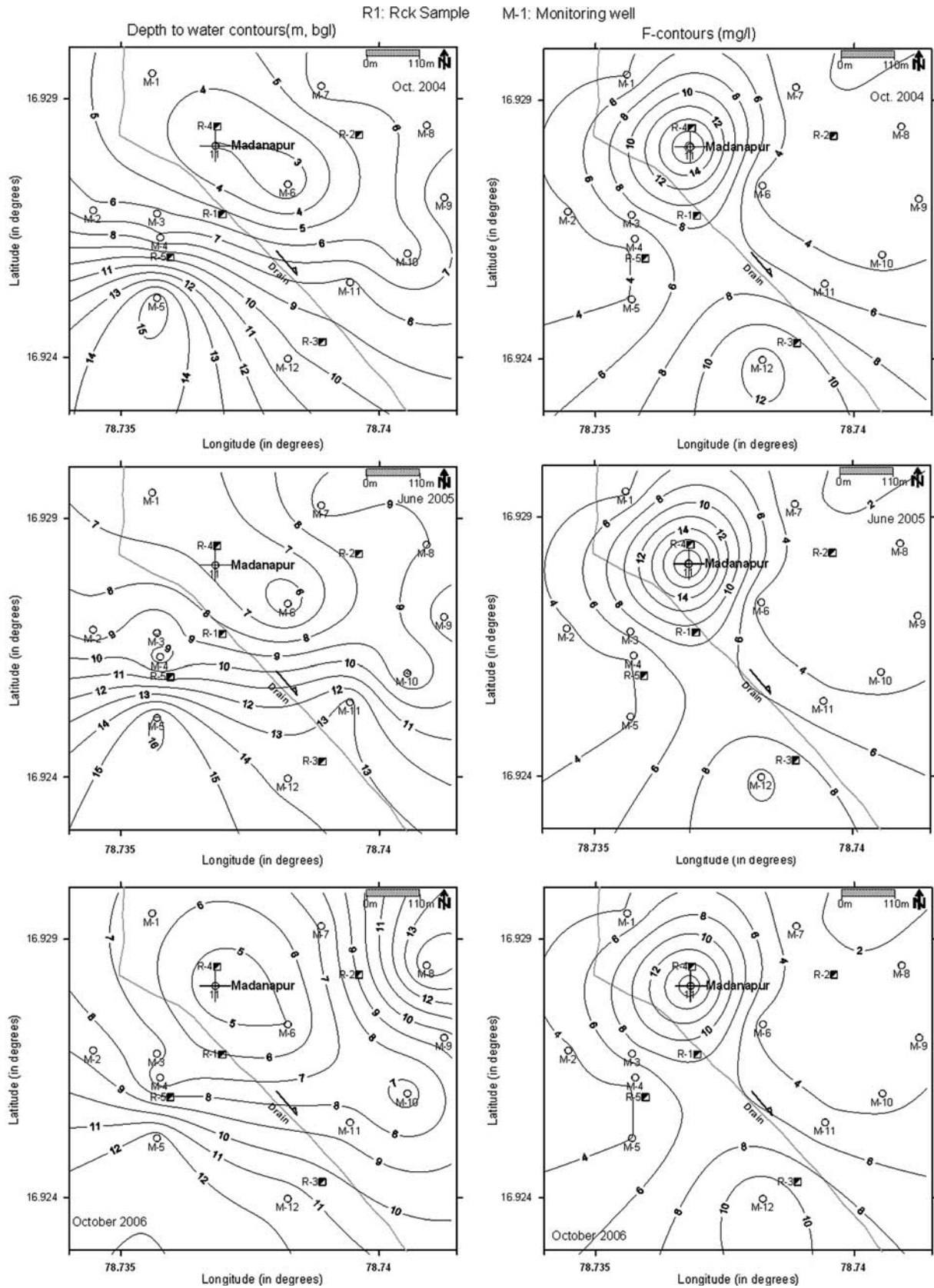


Fig. 6 Status of F and depth to water level at Madanapur village, Nalgonda

clearly indicates the negative relation of F with Ca. However no other correlation existed can give any conclusion.

To establish the relationship of F with other water quality parameters, correlation analysis was performed. Acidity/alkalinity of the groundwater is a factor that controls the leaching of F from the fluoride bearing minerals. The correlation study made and the scatter plots brought out a positive correlation ($r = 0.47$) between the pH and F concentration, indicating that higher-alkalinity of the water promote the leaching of F and thus affect the concentration of F in groundwaters (Fig. 5a). There is a negative correlation with TDS in groundwater as shown in Fig. 5b. Groundwater with high F generally contains low levels of calcium. The calcium ion activity in the natural environment is controlled mainly by carbonate ion, which forms insoluble calcite. Thus the activities of calcium and F are negatively correlated with correlation coefficient ($r = -0.47$). Hence if rocks/soils and groundwater are low in calcium, the water can be enriched in F. The negative correlation between Ca and F is shown in Fig. 5c. The

negative correlation coefficients was also observed between F and HCO_3 ($r = -0.39$), and whereas no correlation observed between F and Na, which indicate the HCO_3 and Na solubility may not favor the higher value of F in the study area (Fig. 5d, e).

Water–rock interaction studies

Geology of the study area is mainly granite and gneisses covered with black clayey soil. To study the influence of rock for F contamination, five-rock samples were collected from an exposure close to the elevated fluoride well (as shown in Fig. 6). Results of the chemical study are presented in Table 4. The chemical composition of rocks collected near to the F enriched area showed that the F concentrations ranged from 460 to 1,706 mg/kg. However the F value in sample no. R-2 is not traceable (Krishna et al. 2007). The variation of F in rock is well reflected in groundwater. It is indicated the possibility of F in groundwater is more where the rock is consistent with high in F. Hence a fairly good chemical kinetic condition in

Table 4 Results of chemical analysis of rock samples, Kurmapalli watershed, Nalgonda

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	F
R-1	39.64	6.25	0.88	0.02	5.76	41.14	0.79	2.17	0.15	0.05	892
R-2	32.57	4.72	0.07	0.01	0.66	54.72	0.18	1.6	0.07	0.08	ND
R-3	69.88	14.87	3.78	0.05	1.25	1.77	1.44	4.4	0.72	0.1	586
R-4	68.55	13.28	3.89	0.04	1.08	2.43	2.57	5.42	0.61	0.35	1706
R-5	53.88	13.25	12.86	0.16	4.75	9.36	2.19	1.32	0.81	0.23	460

All oxides are in wt%, F in mg/kg, ND not detected

Table 5 Results of fluoride values and depth to water level in and around F enriched Madanapur village, Kurmapalli watershed, Nalgonda

Monitoring wells at Madanapur Village	Depth to water level (m, bgl)			Fluoride value (in mg/l)		
	October 2004	June 2005	October 2006	October 2004	June 2005	October 2006
M-3	6.26	10.23	7.50	7.1	6.6	7.2
11	2.97	6.75	4.23	19.0	21.0	17.8
M-6	2.10	5.26	5.00	2.9	2.8	3.0
M-11	8.23	13.26	8.54	5.2	4.5	4.5
M-9	7.89	10.64	9.52	3.2	3.6	3.8
M-12	10.25	13.59	11.54	13.	10.5	11.8
M-4	7.19	8.23	6.12	4.2	4.2	4.2
M-2	6.24	8.41	8.63	3.8	3.7	3.8
M-5	15.63	16.21	12.59	4.1	3.8	4.0
M-1	4.58	6.25	6.50	3.9	3.6	4.1
M-10	5.46	7.86	6.50	3.3	3.3	3.3
M-8	6.24	8.96	14.86	2.6	2.6	2.3
M-7	6.48	9.35	7.12	2.4	2.4	2.4

particular significant period in between mineral and groundwater exists in the study area. Deeper aquifer with good discharged found to be more in enriched in fluoride (as it is also observed in sample numbers 11, 7, 12 and 17 in Table 2). The dark mineral fraction of gneisses (separated in a high intensity magnetic field) contains high concentrations of F. This in combination with the relative stability of fluorapatite during the weathering process indicates that the main source of F^- in groundwater is from granite and gneisses rocks. Fluorine is lost during weathering at approximately the same rate as other elements from the mineral phase (Handa 1975; Nordstrom et al. 1989; Ahmed and Sreedevi 2002; Saxena and Ahmed 2003).

The seasonal depths to water level and F values were collected from the elevated F affected area (around Madanapur village). It is presented in Table 5. This table indicates the depth to water level varies from 5.26 to 16.21 m below groundwater level (bgl) corresponding to F values vary from 2.4 to 21.0 mg/l in June 2005 in and around Madanapur village. The trends of these parameters are also shown in Fig. 6. This indicates, F is approximately proportional to the water column of aquifer. It means that when the depth to water level below ground level is decreasing then F value is increasing trend in the study area.

Conclusions

- Fluoride (21.0 mg/l) is found in groundwater at Madanapur village, Kurmapalli watershed, Nalgonda district, Andhra Pradesh, which is one of the highest F in groundwater of granite terrain in India.
- Concentration of F in rock samples varies from 460 to 1,706 mg/kg. This indicates that rock is enriched in F.
- The lack of Ca in groundwater may decrease the possibility of creating precipitation of CaF_2 ; fluoride is inversely proportional to calcium; and also the formation of NaF, which has a high solubility, could enhance the high concentration of fluoride. This indicates that source of fluoride in groundwater is due to rock-water interaction.
- Middle part of the study area is more affected by F contamination in groundwater as well as deeper aquifers are enriched in F.

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