Appl Water Sci (2017) 7:2501–2512
DOI 10.1007/s13201-016-0441-0

ORIGINAL ARTICLE

Contamination of fluoride in groundwater and its effect on human health: a case study in hard rock aquifers of Siddipet, Telangana State, India

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Received: 22 July 2015 / Accepted: 14 June 2016 / Published online: 27 June 2016

Abstract Hydrogeochemical investigation has been carried out in the granitic terrain of Siddipet area, Medak district, Telangana State, India with an aim to understand the distribution of fluoride in the groundwater and to understand the relationship of fluoride with other major ions, and also to identify the high fluoride-bearing groundwater zones. 104 groundwater samples were analyzed in the study area for fluoride and other major ions like calcium, magnesium, chloride, carbonate, bicarbonate, sodium, potassium, sulfate, and nitrate in addition to pH and electrical conductivity. The studies revealed that the concentration of fluoride in groundwater is ranging from 0.2 to 2.2 mg L^{-1} with a mean of 1.1 mg L^{-1}. Nearly 22 % of groundwater has more than the permissible limit of fluoride (1.5 mg L^{-1}), which is responsible for the endemic dental fluorosis in the area concerned. Geochemical classification of groundwater shows that Na–HCO_3, Ca–Cl, and Ca–HCO_3–Na are the dominant hydrochemical facies. Gibbs diagram shows rock–water interaction dominance and evaporation dominance, which are responsible for the change in the quality of water in the hard rock aquifer of the study area. The groundwater in villages and its environs are affected by fluoride contamination, and consequently majority of the population living in these villages suffer from dental fluorosis. Hence, they are advised to consume drinking water which has less than 1.5 mg L^{-1} fluoride to avoid further fluorosis risks.

Keywords Hydrochemistry · Groundwater · Fluoride · Siddipet · Telangana · India

Introduction

Fluorine is the lightest halogen and one of the most reactives of all chemical elements (Kaminsky et al. 1990). Fluorine commonly occurs as a negatively charged ion in water, either in trace amounts or as a major ion with high concentrations (Gaciri and Ad Davis 1993; Apambire et al. 1997; Fantong et al. 2009). Fluorosis is a very dangerous and deadly disease affecting millions of people across the world. More than 200 million people from all over the world (among 25 nations) suffer from endemic fluorosis, caused mainly due to excess fluoride in drinking water (Ayoob and Gupta 2006; Hong-jian et al. 2013; Moghaddam and Fijani 2008; Oruc 2008; Fordyce et al. 2007; Ghosh et al. 2013; Mesdaghinia et al. 2010).

In the two largest countries India and China of the world, fluorosis is most severe and well known. High concentration of fluoride, often above 1.5 mg L^{-1}, constitutes a severe problem over a large part of India. About 80 % of the diseases in the world are due to the poor quality of drinking water, and the fluoride contamination in drinking water is responsible for 65 % of endemic fluorosis around the globe (Felsenfeld and Robert 1991). Furthermore, 50 % of the groundwater sources in India have been contaminated by fluoride and more than 90 % of the villages use groundwater for drinking purposes (Subarayan et al. 2012). In fact, more than 40 million people in India are affected due to the prevalence of dental fluorosis (Karthikeyan et al. 2005). In India, the excessive presence of fluorides in groundwater is noticed in nearly 177 districts covering 20 states, affecting more than 65 million

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people, including 6 million children (Gupta et al. 2006). The problem of excessive fluoride in groundwater in India was first reported in 1937 in the state of Andhra Pradesh (Short et al. 1937). Telangana State is one of the fluoride affected states in the country and is considered to be endemic to fluorosis.

The major health problems caused by excessive fluoride are dental fluorosis, skeletal fluorosis, and deformation of bones in children and adults (Susheela et al. 1993). Fluorosis has greatest impact on growing teeth, and children less than 7 years old are particularly vulnerable (Murray 1996). The maximum permissible limit of fluoride in drinking water is prescribed as 1.5 mg L^{-1} by World Health Organization and Indian Council of Medical Research (WHO 2011; ICMR 1975). Fluoride concentration in groundwater is influenced by a number of factors, such as temperature, pH, the presence or absence of complexing or precipitating ions and colloids, solubility of fluorine bearing minerals, anion exchange capacity of aquifer materials (i.e., OH^- for F^-), the size and type of geological formations traversed by water, and the contact time period during which water remains in contact with a particular formation (Apambire et al. 1997). There is also evidence that the adverse health effects of fluoride are enhanced by lack of Ca, vitamins, and protein in the diet (Jacks et al. 1993; Li et al. 1996). Fluorides are released into the groundwater mostly through water–rock interaction by various fluoride-bearing minerals. Fluorite (CaF_2) is the sole principal mineral of fluorine occurring in nature, and is commonly found as an accessory in granitic gneiss (Ozsvath 2006; Saxena and Ahmed 2003). Fluorine is also abundant in other rock-forming minerals like apatite, micas, amphiboles, and clay minerals (Karro and Uppin 2013; Narsimha and Sudarshan 2013; Rafique et al. 2009; Naseem et al. 2010; Jha et al. 2010; Carrillo-Rivera et al. 2002).

The study area is situated about 105 km north of Hyderabad on Hyderabad–Karimnagar State highway, and is bounded by E longitude 78.76942–78.90232 and N latitude 18.06768–18.24402. The area under investigation falls under semi-arid zone, with a hot, humid climate, and predominantly occupied by granite/gneiss of Archean age. The area experiences a semi-arid climate with an annual mean temperature of 30 °C. The mean annual rainfall is recorded as 745 mm, occurring mostly during the southwest monsoon period (June–September). Groundwater is the major drinking water source in the villages of Siddipet area of Medak district of Telangana State, India. Endemic fluorosis as well as its prevalence and severity are poorly known in the study area. The present study was undertaken to assess the fluoride content of groundwater and to statistically correlate the concentrations of fluoride with the other measured parameters, and also identify the wells with high F^- concentration, raise awareness in people and study the water chemistry of groundwater in Siddipet area, Medak district, Telangana, India.

Materials and methods

104 groundwater samples were collected from 39 villages of Siddipet region in the month of July 2014. Samples were collected in plastic containers previously thoroughly cleansed with distilled water and subsequently with sampled groundwater before filling. The fluoride concentration in groundwater was determined electrochemically, using Thermo Scientific Orion Star A214 Benchtop pH/ISE meter, using the USEP ion selective electrode method. As per experimental requirement, 2 ml of total ionic strength adjusting buffer grade III (TISAB III) was added in 20 ml of groundwater sample and determined the fluoride concentration. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined titrimetrically using standard EDTA method. Chloride (Cl^-) was determined by standard $AgNO_3$ titration. Carbonate ($CO_3{}^{2-}$) and bicarbonate ($HCO_3{}^-$) were determined by titration with HCl. Sodium (Na^+) and potassium (K^+) were measured by flame photometry. Sulfate ($SO_4{}^{2-}$) and nitrate ($NO_3{}^-$) were determined using UV–visible spectrophotometer. The EC and pH of water samples were measured in the field immediately after the collection of the samples using pH/EC/TDS meter (Hanna HI 9811-5). Sampling, preservation, and analysis of water samples were carried out following the method recommended by APHA (2005).

Hydrogeochemistry

Results of the hydrochemical parameters and corresponding groups of individual groundwater samples are presented in Table 1, and descriptive statistics for F^- and other parameters are given in Table 2. Table 3 presents the correlation matrix in the analyzed groundwater samples of hard rock aquifers of Siddipet, Telangana State, India. Among the physical parameters, pH ranges from 6.3 to 8.9 with an average of 7.5, indicating the alkaline nature of groundwater. Even though pH has no effect on human health, it is closely related to other chemical constituents of water. According to Keshavarzi et al. (2010), in acidic water, fluoride is adsorbed on a clay surface, while in alkaline water, fluoride is desorbed from solid phases; therefore, alkaline pH is more favorable for fluoride dis-

Table 1 Hydrogeochemical parameters of individual groundwater samples in the hard rock aquifer area with corresponding IV Groups based on F^- concentrations

S. No	Well type	pH	EC	TDS	TH	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	F^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
Group I															
1	BW	7.2	1850	1184	200	Nil	61	391	49	216	0.9	74.148	44.955	65	3
2	BW	7.4	1440	921.6	240	Nil	49	142	84	40	0.7	80.16	48.6	84	4
3	BW	7.2	1840	1177.6	225	Nil	86	96	52	106	0.8	50.1	30.375	77	5
4	BW	7.6	1760	1126.4	300	Nil	61	178	26	57	0.8	44.088	26.73	48	4
5	BW	8.2	3130	2003.2	190	Nil	61	433	87	150	0.9	84.168	51.03	67	6
6	BW	7.3	2210	1414.4	175	21	55	319	67	136	0.7	70.14	42.525	84	34
7	BW	7.8	2180	1395.2	215	Nil	61	202	105	154	0.8	74.148	44.955	77	5
8	BW	7.9	1160	742.4	200	Nil	43	319	46	114	0.7	52.104	31.59	72	1
9	BW	6.9	1900	1216	140	Nil	79	107	37	44	0.7	34.068	20.655	63	1
10	BW	7.1	1900	1216	275	Nil	85	518	42	154	0.8	70.14	42.525	82	8
11	OW	6.8	2490	1593.6	350	Nil	79	263	51	57	0.9	74.148	44.955	74	5
12	BW	7.3	1400	896	280	Nil	61	192	47	123	0.9	36.072	21.87	67	4
13	BW	8.2	1760	1126.4	250	Nil	92	213	108	194	0.7	64.128	38.88	87	61
14	BW	7.3	2250	1440	225	Nil	49	202	89	128	0.7	64.128	38.88	77	3
15	BW	6.8	2170	1388.8	385	Nil	49	305	108	356	0.6	152.304	92.34	89	5
16	BW	7.8	1750	1120	80	12	61	114	52	9	0.6	24.048	14.58	37	4
17	BW	7.9	1550	992	90	6	43	57	93	22	0.5	12.024	7.29	32	3
18	BW	7.6	1910	1222.4	100	6	31	85	33	44	0.5	20.04	12.15	44	4
19	HP	8.2	1100	704	145	Nil	73	121	41	62	0.6	60.12	36.45	71	5
20	BW	7.5	1070	684.8	205	Nil	67	298	54	66	0.7	50.1	30.375	77	5
21	HP	8.4	1710	1094.4	160	Nil	104	284	46	75	0.7	56.112	34.02	72	2
22	HP	7.1	1940	1241.6	180	Nil	61	220	47	62	0.5	52.104	31.59	39	2
23	BW	7.8	1880	1203.2	210	Nil	61	192	58	88	0.8	56.112	34.02	67	4
24	HP	6.8	1120	716.8	225	9	43	121	98	101	0.6	42.084	25.515	55	3
25	BW	7.3	1880	1203.2	180	Nil	55	135	103	185	0.7	48.096	29.16	38	3
26	HP	7.4	1500	960	170	Nil	61	92	33	66	0.7	56.112	34.02	46	3
27	HP	6.8	1070	684.8	185	Nil	73	114	47	101	0.7	56.112	34.02	52	3
28	BW	8.3	1140	729.6	145	Nil	31	192	44	110	0.5	36.072	21.87	43	3
29	HP	6.8	3280	2099.2	230	21	73	596	94	264	0.7	32.064	19.44	117	61
30	HP	6.8	1820	1164.8	250	9	37	185	49	128	0.9	54.108	32.805	66	4
31	BW	7.2	1780	1139.2	140	6	24	227	78	48	0.5	40.08	24.3	69	13
32	HP	6.9	1680	1075.2	190	Nil	61	121	95	145	0.6	66.132	40.095	56	2
33	BW	7.9	2880	1843.2	325	Nil	92	305	49	180	0.9	96.192	58.32	81	4
34	BW	8.3	1530	979.2	65	9	31	50	25	154	0.5	16.032	9.72	36	5
35	BW	7.7	1550	992	70	Nil	43	57	32	48	0.5	10.02	6.075	33	5
36	BW	7.2	2040	1305.6	215	Nil	49	248	47	32	0.8	80.16	48.6	68	4
37	HP	6.9	1150	736	150	12	73	25	96	110	0.7	50.1	30.375	32	4
38	BW	8.2	1820	1164.8	154	Nil	49	64	79	44	0.9	42.084	25.515	31	2
39	HP	7.2	2280	1459.2	200	Nil	79	298	102	88	0.9	70.14	42.525	41	3
40	BW	7.9	3410	2182.4	565	Nil	43	291	59	251	0.8	106.212	64.395	50	4
41	BW	8.2	3740	2393.6	480	Nil	61	289	52	141	0.6	60.12	36.45	92	12
42	BW	7.4	3330	2131.2	375	Nil	73	731	69	123	0.7	56.112	34.02	94	6
43	BW	8.2	2950	1888	355	Nil	49	440	76	44	0.5	130.26	78.975	72	5
44	BW	7.5	3150	2016	280	6	37	973	82	185	0.5	74.148	44.955	105	24
45	BW	7.2	3570	2284.8	350	Nil	61	533	65	361	0.4	126.252	76.545	99	8
46	OW	8.4	1710	1094.4	145	Nil	67	202	29	28	0.8	38.076	23.085	101	22

Table 1 continued

S. No	Well type	pH	EC	TDS	TH	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	F^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
47	OW	8.4	1870	1196.8	75	Nil	61	78	87	79	0.9	10.02	6.075	63	9
48	BW	7.9	2470	1580.8	250	Nil	49	568	69	348	0.9	186.372	112.995	48	2
49	BW	7.6	2770	1772.8	135	Nil	73	248	64	242	0.7	74.148	44.955	106	3
50	OW	6.9	1180	755.2	180	Nil	61	298	47	119	0.9	62.124	37.665	52	3
Group II															
1	BW	8.1	3850	2464	415	Nil	73	344	86	321	1	100.2	60.75	111	4
2	BW	8.2	2470	1580.8	275	Nil	49	231	45	106	1	66.132	40.095	73	4
3	BW	7.1	1450	928	250	9	104	170	65	172	1	54.108	32.805	71	5
4	HP	7.3	1810	1158.4	185	Nil	91	199	57	141	1	34.068	20.655	56	4
5	BW	7.2	2330	1491.2	285	Nil	79	746	60	114	1	98.196	59.535	86	4
6	BW	8.1	1010	646.4	200	Nil	134	142	127	44	1	40.08	24.3	56	2
7	BW	7.3	1970	1260.8	186	Nil	109	611	65	180	1	66.132	40.095	121	4
8	BW	7.2	2730	1747.2	275	Nil	67	490	83	238	1.1	86.172	52.245	95	2
9	HP	7.4	1770	1132.8	115	Nil	61	71	29	26	1.1	36.072	21.87	33	2
10	HP	6.8	2050	1312	210	Nil	55	124	103	145	1.1	56.112	34.02	93	8
11	BW	7.5	1430	915.2	160	6	73	78	38	62	1.1	32.064	19.44	53	2
12	BW	7.4	1830	1171.2	280	Nil	61	355	56	106	1.2	64.128	38.88	82	9
13	BW	7.5	2350	1504	275	Nil	61	319	64	79	1.2	60.12	36.45	91	3
14	BW	8.1	1540	985.6	260	Nil	61	213	97	136	1.2	58.116	35.235	69	4
15	BW	7.3	1810	1158.4	110	12	37	164	39	75	1.2	36.072	21.87	46	2
16	BW	8.1	2010	1286.4	365	Nil	92	319	52	101	1.2	50.1	30.375	91	11
17	HP	7.5	1850	1184	235	15	61	241	89	304	1.2	60.12	36.45	97	85
18	BW	8.4	1920	1228.8	185	Nil	85	32	78	44	1.2	50.1	30.375	18	1
19	BW	7.8	1160	742.4	75	Nil	43	238	87	114	1.2	26.052	15.795	85	17
20	HP	6.9	1450	928	170	9	61	92	156	66	1.2	56.112	34.02	65	2
21	BW	7.4	1890	1209.6	215	Nil	61	121	74	40	1.3	30.06	18.225	62	3
22	BW	8.5	1430	915.2	235	Nil	61	213	47	194	1.3	62.124	37.665	56	2
23	BW	7.4	1870	1196.8	190	Nil	55	172	49	150	1.3	58.116	35.235	71	2
24	BW	7.2	1170	748.8	235	Nil	61	149	57	70	1.3	56.112	34.02	63	15
25	HP	7.8	1600	1024	225	12	122	142	64	26	1.3	48.096	29.16	66	1
26	BW	7.5	1860	1190.4	125	Nil	85	28	107	20	1.3	26.052	15.795	31	2
27	HP	6.8	1830	1171.2	95	21	31	85	29	22	1.3	30.06	18.225	17	6
28	BW	7.7	1740	1113.6	120	Nil	49	85	25	44	1.4	40.08	24.3	34	4
29	BW	7.6	1910	1222.4	115	Nil	61	85	101	75	1.4	38.076	23.085	60	1
30	BW	8.6	2100	1344	315	Nil	67	284	65	57	1.4	62.124	37.665	59	4
31	BW	7.4	1010	646.4	145	Nil	61	64	92	57	1.4	42.084	25.515	31	2
32	HP	6.9	3310	2118.4	375	Nil	61	568	48	26	1.4	144.288	87.48	82	6
33	BW	6.9	1070	684.8	153	6	43	92	74	88	1.4	40.08	24.3	36	3
Group III															
1	BW	6.9	2490	1593.6	330	Nil	73	284	45	48	1.5	118.236	71.685	61	5
2	BW	8.2	2120	1356.8	240	Nil	61	278	57	141	1.5	64.128	38.88	65	6
3	BW	8.1	1180	755.2	150	Nil	92	57	22	22	1.5	48.096	29.16	38	2
4	BW	6.9	1280	819.2	150	Nil	49	64	31	53	1.6	40.08	24.3	54	3
5	BW	8.3	2410	1542.4	240	Nil	104	341	65	44	1.6	52.104	31.59	98	3
6	BW	8.3	1700	1088	75	Nil	61	85	55	44	1.6	14.028	8.505	46	5
7	BW	7.3	1480	947.2	60	6	31	71	21	194	1.6	40.08	24.3	24	3
8	BW	7.8	1490	953.6	175	Nil	37	128	43	172	1.6	56.112	34.02	40	1

Table 1 continued

S. No	Well type	pH	EC	TDS	TH	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	F^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
9	BW	7.1	1650	1056	120	Nil	61	57	67	62	1.7	36.072	21.87	23	1
10	BW	7.4	1040	665.6	185	Nil	91	71	98	70	1.7	30.06	18.225	43	4
11	HP	7.6	1890	1209.6	170	Nil	61	199	55	35	1.7	40.08	24.3	56	6
12	BW	6.9	1150	736	175	Nil	43	149	120	123	1.8	44.088	26.73	76	6
13	BW	7.2	1860	1190.4	150	Nil	61	99	62	66	1.8	40.08	24.3	62	1
14	BW	8.3	1830	1171.2	225	Nil	61	511	77	163	1.8	70.14	42.525	94	10
15	BW	7.2	3170	2028.8	250	Nil	73	429	137	84	1.9	68.136	41.31	134	7
Group IV															
1	BW	7.9	1590	1017.6	115	Nil	61	36	49	123	2	36.072	21.87	33	2
2	BW	7.3	1690	1081.6	190	Nil	61	675	97	22	2.1	50.1	30.375	96	3
3	BW	7.8	1540	985.6	200	Nil	99	270	51	13	2	40.08	24.3	102	3
4	BW	7.6	1870	1196.8	225	Nil	92	124	79	62	2	44.088	26.73	82	4
5	HP	8.9	1390	889.6	50	9	18	36	21	9	2.2	10.02	6.075	30	2
6	BW	7.6	1260	806.4	175	Nil	73	57	78	198	2.1	26.052	15.795	59	3

Except pH, EC is expressed as μS cm^{-1}, and all other parameters are expressed as mg L^{-1}

HP hand pump, *BW* bore well, *OW* open well

Table 2 Descriptive statistics for F^- and other physicochemical parameters

Parameters	pH	EC	TDS	TH	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	F^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
Min	6.8[a]	1070	684.8	65	24	25	25	9	0.4	10.02	6.075	31	1
	6.8[b]	1010	646.4	75	31	28	25	20	1	26.052	15.795	17	1
	6.9[c]	1040	665.6	60	31	57	21	22	1.5	14.028	8.505	23	1
	7.3[d]	1260	806.4	50	18	36	21	9	2	10.02	6.175	30	2
Max	8.4[a]	3740	2393.6	565	104	973	108	361	0.9	186.372	112.995	117	61
	8.6[b]	3850	2464	415	134	746	156	321	1.4	144.288	87.48	121	85
	8.3[c]	3170	2028.8	330	104	511	137	194	1.9	118.236	71.685	134	10
	8.9[d]	1870	1196.8	225	99	675	97	198	2.2	50.1	30.375	102	4
Mean	7.5[a]	2020.4	1293.06	218.08	59.62	254.64	63.84	123.6	0.706	61.48	37.28	65.96	7.96
	7.5[b]	1866.06	1194.28	213.76	68.94	220.21	69.94	104.35	1.20	54.78	33.21	65.45	6.85
	7.6[c]	1782.67	1140.91	179.67	63.93	188.20	63.67	88	1.66	50.77	30.78	60.93	4.20
	7.5[d]	1556.67	996.27	159.17	67.33	199.67	62.50	71.13	2.07	34.40	20.86	67.00	2.83
Median	7.4[a]	1860	1190.4	200	61	207.5	56	110	0.7	56.112	34.02	67	4
	7.4[b]	1830	1171.2	210	61	170	65	79.2	1.2	54.108	32.805	65	4
	7.4[c]	1700	1088	175	61	128	57	66	1.6	44.088	26.73	56	4
	7.6[d]	1565	1001.6	182.5	67	90.5	64.5	41.8	2.05	38.076	23.085	70.5	3
SD	0.51[a]	711.94	455.64	101.29	17.32	186.75	24.43	85.20	0.14	34.14	20.70	22.01	12.46
	0.62[b]	580.73	371.67	69.96	20.38	147.35	33.29	55.48	0.12	23.82	14.44	29.80	2.57
	0.62[c]	580.73	371.67	69.96	20.38	147.35	33.29	55.48	0.12	23.82	14.44	29.80	2.57
	0.47[d]	215.93	138.20	64.92	28.84	249.22	27.35	75.57	0.08	14.42	8.74	31.24	0.75

EC is expressed as μS cm^{-1}, and all other parameters are expressed as mg L^{-1}

[a] Group I

[b] Group II

[c] Group III

[d] Group IV

Table 3 Correlation coefficient of analyzed chemical parameters of groundwater in hard rock aquifers of Siddipet, Medak, Telangana, India

	pH	EC	TDS	TH	CO_3^-	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	F^-	Ca^{2+}	Mg^+	Na^+	K^+
pH	1.00													
EC	−0.12	1.00												
TDS	−0.15	0.65	1.00											
TH	0.34	0.64	0.64	1.00										
CO_2^-	−0.13	−0.04	−0.04	−0.23	1.00									
HCO_3^-	−0.09	0.03	0.03	0.20	−0.20	1.00								
Cl^-	0.07	0.61	0.61	0.53	−0.07	0.10	1.00							
SO_4^{2-}	0.17	0.10	0.10	0.12	0.00	0.17	0.12	1.00						
NO_3^-	0.18	0.40	0.40	0.40	0.03	−0.06	0.39	0.22	1.00					
F^-	0.35	−0.31	−0.36	−0.17	−0.12	0.12	−0.15	0.04	−0.23	1.00				
Ca^{2+}	−0.37	0.56	0.56	0.68	−0.22	0.05	0.57	0.13	0.52	−0.22	1.00			
Mg^{2+}	0.34	0.56	0.56	0.65	−0.23	0.05	0.57	0.13	0.52	−0.25	1.00	1.00		
Na^+	−0.02	0.50	0.51	0.53	−0.10	0.29	0.67	0.28	0.37	0.46	0.37	0.37	1.00	
K^+	0.01	0.16	0.16	0.10	0.43	0.02	0.22	0.18	0.33	−0.13	0.01	0.01	0.37	1.00

solution, which is also observed by several other authors (Rafique et al. 2009; Saxena and Ahmed 2003; Rao 2009; Ravindra and Garg 2007; Vikas et al. 2009). In the present case, group III and IV water samples were found alkaline in nature and their pH value varies from 7.3 to 8.9. It is interesting that about 84 % of the samples lie between pH 7.1 and 8.9 (Tables 1, 2), which indicates that the dissolved carbonates are predominantly in the HCO_3^- form (Adams et al. 2001). A positive correlation (Fig. 1a; Table 3) is seen between the pH of groundwater and the fluoride content indicating that the pH, and hence alkalinity, influences the fluoride content in the groundwater. In general, the concentration of nitrate does not exceed 10 mg L^{-1} in water under natural conditions (Cushing et al. 1973). However, nitrate varies from 9 to 361, 20 to 321, 22 to 194, and 9 to 198 mg L^{-1} in group I–IV, respectively (Table 1).

The possible sources of nitrates are poultry farms, animal wastages and septic tank leakages, and agricultural activities, which are noticed in the study area. These results suggest that groundwater has an elevated level of nitrate, greater than the drinking water guideline value of 45 mg L^{-1} (WHO 2011). The presence of high nitrate concentration in the drinking water increases the incidence of gastric cancer and other potential hazards to infants and pregnant women (Nagireddi Srinivasa Rao 2006) birth malformations, and hypertension (Majumdar and Gupta 2000). Chloride occurs naturally in all types of water. The concentration of chloride content in the water samples was recorded from 25 to 973, 28 to 746, 57 to 511, and 36 to 675 mg L^{-1} (Table 1). The majority of groundwater shows concentration of chloride above the WHO (2011) suggested maximum permissible limit of 250 mg L^{-1}. The bicarbonate concentration in the groundwater ranges from 24 to 104, 31 to 134, 31 to 104, and 18 to 99 mg L^{-1} in group I–IV, respectively (Table 1). The high concentration of bicarbonate when compared to carbonate in the water is the result of the reactions of soil CO_2 with dissolution of silicate minerals. TDS include inorganic salts, such as calcium, magnesium, potassium, and organic matter that are dissolved in water. As per the TDS classification (Fetters 1990) 72, 70, 60, and 40 % from group I, II, III, and IV belongs to brackish type (TDS >1000 mg L^{-1}). Electrical conductivity ranges from 1070 to 3740, 1010 to 3850, 1040 to 3170, and 1260 to 1870 µS/cm from groups I, II, III, and IV, respectively (Table 1). According to a report of International Water Management Institute (IWMI), the TDS did not play direct role in health risks, but prolonged consumption of high salt containing water (TDS above 500 mg L^{-1}) can cause kidney stone, a phenomenon widely reported from many parts of the country. The sodium concentration in groundwater ranges from 31 to 117, 17 to 121, 23 to 134, and 30 to 102 mg L^{-1}, in group I–IV, respectively (Tables 1, 2). The high concentration of sodium ions among the cationic concentrations reflects rock weathering and/or dissolution of soil salts stored by the influence of evaporation (Stallard and Edmond 1983). The permissible limit of Na^+, in potable water is 200 mg L^{-1}, and none of the samples exceed the limit. The concentration of calcium ranges from 10 to 186, 26 to 144, 14 to 144, and 10 to 50 mg L^{-1} and magnesium 6 to 112, 15 to 87, 6 to 71 and 6 to 30 mg L^{-1}, respectively (Table 1). The calcium and magnesium ions present in the groundwater are possibly derived from leaching of calcium and magnesium-bearing rock-forming silicates. The permissible limit for calcium and magnesium

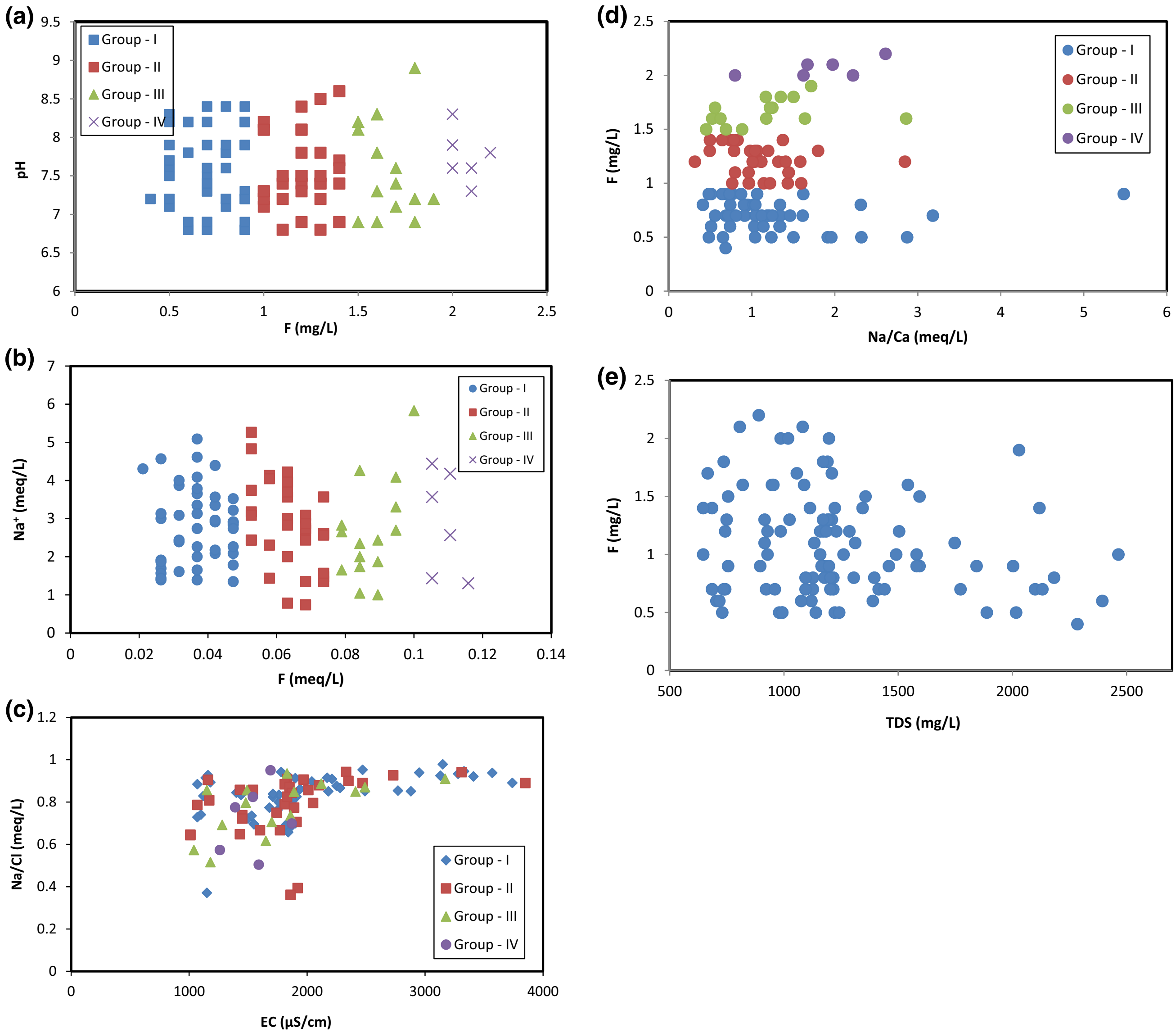

Fig. 1 Relationship among fluoride and other elements in the groundwater of hard rock aquifers of Siddipet, Telangana State, India

set by WHO are 200 and 150 mg L^{-1}, respectively; samples from all the locations/groups have calcium and magnesium concentrations well below this limit (Table 1). The total hardness is varying from 65 to 565, 75 to 415, 60 to 330, and 50 to 225 mg L^{-1}. Groundwater of the entire study area lies within the maximum permissible limit of 600 mg L^{-1} prescribed by WHO (2011). Sawyer and McCarthy (1967) classified groundwater, based on TH, as groundwater with TH <75, 75–150, 150–300 and >300 mg L^{-1}, designated as soft, moderately hard, hard, and very hard, respectively. The analytical result indicates the water in the study area is moderately hard to very hard. The hardness of the water is due to the presence of alkaline earths such as calcium and magnesium. High concentration of TH in water may cause kidney stone and heart disease in human.

Discussion

To understand the chemical characteristics of groundwater in the hard rock aquifers of Siddipet, groundwater samples were plotted in Piper trilinear diagram (Piper 1944; Fig. 2). The groundwater has been classified into different hydro-

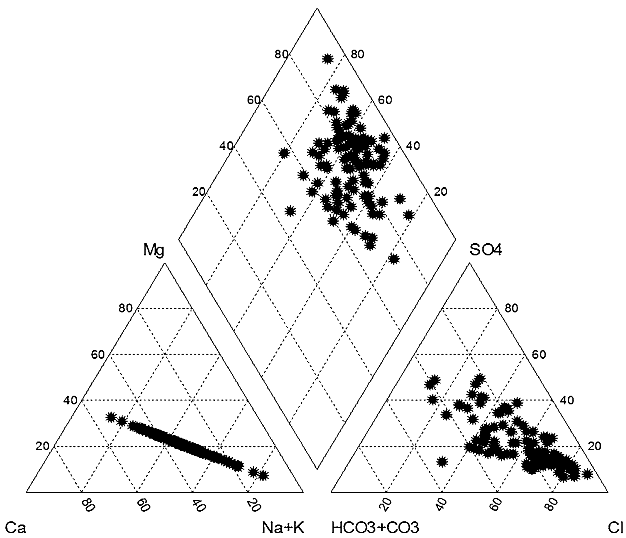

Fig. 2 Piper trilinear diagram for representing the analyses of groundwater in hard rock aquifers of Siddipet, Telangana State, India

chemical types, and the concentration of fluoride is found high in sodium bicarbonate (Na–HCO_3), calcium chloride (CaCl), sodium bicarbonate chloride (Na–HCO_3–Cl), calcium bicarbonate chloride (Ca–HCO_3–Cl), and waters. Groundwater in the sodium bicarbonate (Na–HCO_3) type always has very high fluorine contents. It is also suggested that silicate weathering domination and rock–water interaction are the primary factors in increasing the major ion concentration in the groundwater. The high Na^+ concentration in groundwater may be related to the cation exchange mechanism in the aquifers (Kangjoo Kim and Seong-Taekyun 2005). The deficiency of calcium ion concentration in the groundwater favors fluorite dissolution leading to excess of fluoride concentration (Table 1).

Gibbs diagram represents the ratio of $Na^+/(Na^+{+}Ca^{2+})$ and $Cl^-/(Cl^-{+}HCO_3^-)$ as a function of TDS, which is widely used to assess the functional sources of dissolved chemical constituents, such as precipitation dominance, rock dominance, and evaporation dominance (Gibbs 1970; Fig. 3a, b). The groundwater of groups III and IV are influenced largely by water–rock interaction when compared to the groundwater of groups I and II. The water–rock interaction and aquifer material played major role in evolution of water chemistry, which was further influenced by the evaporation process. Geological location is one of the most important factors affecting groundwater quality. The concentration of F^- in the groundwater is found to increase with an increase in Na^+ (Table 1). A significant positive correlation occurs between F^- and lithogenic Na^+ (Fig. 1b; Table 3). Thus, the lithogenic Na^+ can be used as an index of weathering of minerals (Ramesam and Rajagopalan 1985). The weathering caused by alternative wet and dry conditions of the arid, and semi-arid climate is responsible for the leaching of F^- from the minerals in the soils and rocks (Subba 2003; Wodeyar and Sreenivasan 1996; Subba et al. 1998a, b; Saxena and Ahmed 2001). Evaporation process is a common phenomenon in groundwater system. Evaporation will increase the

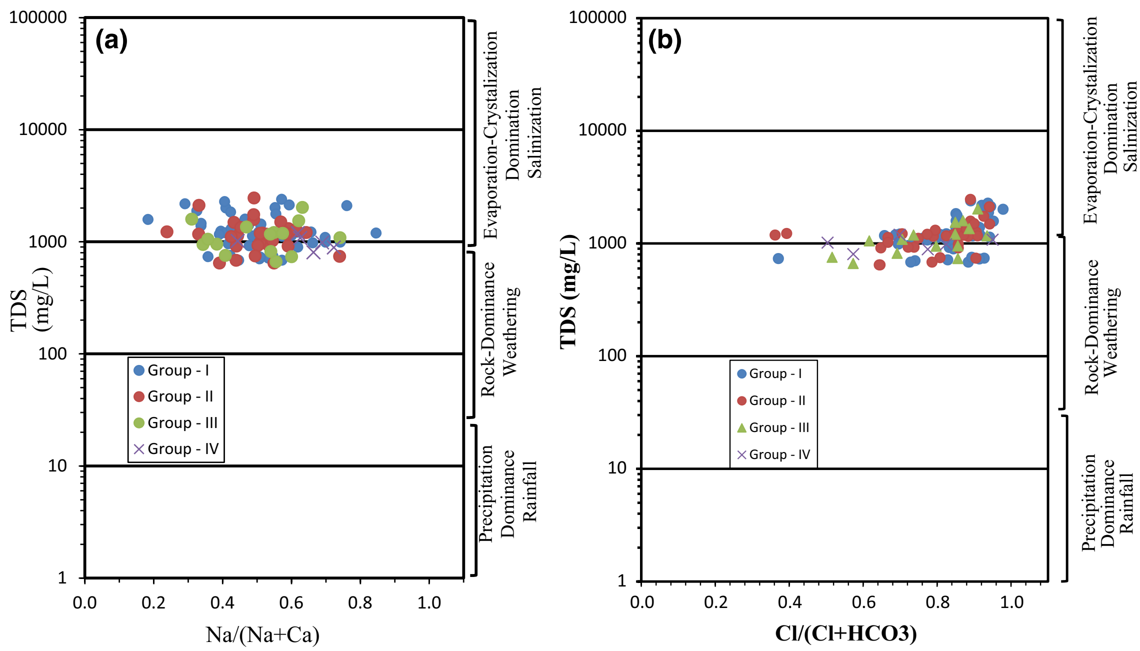

Fig. 3 Gibbs (1970) diagram illustrating the mechanisms controlling the chemistry of groundwater samples of the hard rock aquifer area, plot of Na/Na+Ca vs TDS and Cl/(Cl + HCO_3) vs TDS

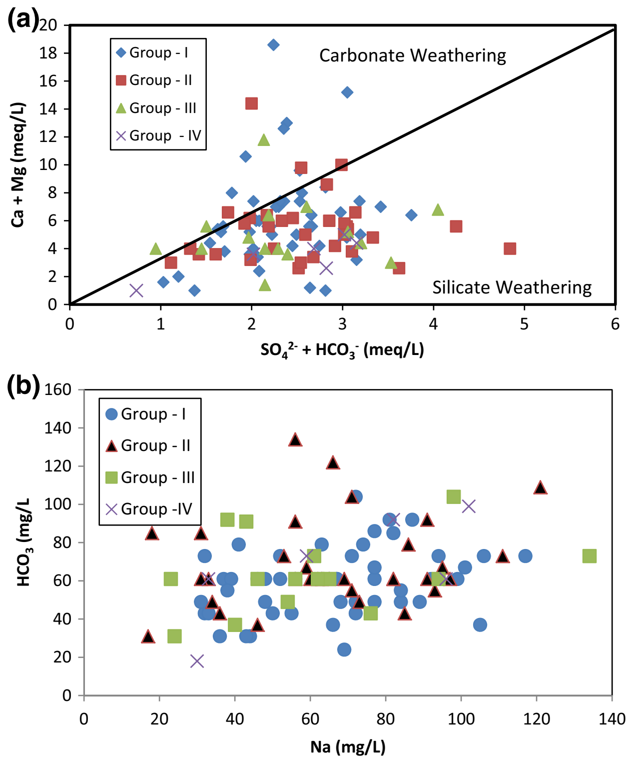

Fig. 4 Scatter diagram for carbonate weathering vs silicate weathering processes dissolution of rock salts and weathering of sodium bearing minerals

concentration of total dissolved solids in groundwater, and the Na^{+}/Cl^{-} ratio remains the same, and it is one of the good indicative factors of evaporation (Fig. 1c). This observation indicates that evaporation may not be the major geochemical process controlling the chemistry of groundwater in this study region or ion exchange reaction dominating over evaporation. It is also observed that the ratio of Na^{+}/Ca^{+} is increased with reference to the increase in fluoride concentration (Fig. 1d) in all groups. A negative correlation between TDS and F^{-} is observed which suggests the influence of rock–water interaction (Fig. 1e; Table 3). Na^{+}/Cl^{-} ratio is found greater than one in all groups indicating that the Na is released from silicate weathering reactions (Meybeck 1987). Evidences for silicate weathering are shown by the relationships of Na^{+} vs HCO_3^{-} and $(Ca^{+}+Mg^{+})$ vs $(SO_4^{2-}+HCO_3^{-})$ (Fig. 4a, b). The F^{-}-bearing water was found to have a negative relationship with Ca^{2+}, which indicates that high F^{-} in groundwater is associated with low Ca^{2+} content (Table 1; Fig. 5a); this is in agreement with the previous finding (Handa 1975). Fluorite, the main mineral that controls the geochemistry of F^{-} in most environments is found in significant amount in granite, granite gneisses, and pegmatite (Deshmukh et al. 1995). F^{-} concentration in study area ranges from 0.2 to 2.26 mg L^{-1} with a mean of 1.1 mg L^{-1} (Tables 1, 2). Concentration of F^{-} marginally exceeds the permissible limit of drinking water (1.5 mg L^{-1}) in about 22 % of the groundwater samples. The present investigation indicated that the high F^{-} concentration more than 1.5 mg L^{-1} are observed in Nanchrpalli, Ponnala, Silanagar, Ganpur, Venkatapuram, Irkod, Rampur, Appannapalli, Pullur, Ankampet, Raghapuram, Randampalli, Narsapur, Mittapalli, Boggolonibanda, and Nancharpalli villages. Distribution of F^{-} in groundwater of the Siddipet area is presented in Fig. 5b, and high F^{-} concentration has been noticed in southern part of investigated area. Variations in the concentration of F^{-} in groundwater from the study area suggest preferential dissolution of F^{-} bearing minerals due to variation in the control parameters. Finally, bedrock containing fluorine minerals is responsible for the high F^{-} in the groundwater of the study area.

The presence of high F^{-} (with low EC) zones in the investigated region, namely Boggulonibanda (2.2 mg L^{-1},1390 µS cm^{-1}), Ponnala (2.1 mg L^{-1}, 1690 µS cm^{-1}), Silanagar (2 mg L^{-1}, 1870 µS cm^{-1}), Ganpur (1.7 mg L^{-1}, 1040 µS cm^{-1}), Irrkod (1.6 mg L^{-1}, 1490 µS cm^{-1}), Rampur (1.8 mg L^{-1}, 1860 µS cm^{-1}), Appannapalli (1.8 mg L^{-1}, 1860 µS cm^{-1}), Pullur (1.8 mg L^{-1}, 1830 µS cm^{-1}), and Ankampet (1.7 mg L^{-1}, 1890 µS cm^{-1}) suggests preferential dissolution of F^{-} bearing minerals. The study area is predominantly occupied by granite/granitic gneiss. It is likely that these rocks could be providing higher F^{-} to groundwater during weathering. Koritnig (1951) suggested that F^{-} is leached in the initial stages of weathering of granite massifs. 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. It is generally accepted that groundwater is enriched in F^{-} due to prolonged water–rock interactions (Saxena and Ahmed 2001; Gizaw 1996; Frengstad et al. 2001; Carrillo-Rivera et al. 2002). The present study area represents granitic aquifers affected by very high amount of fluoride content with a maximum of 2.2 mg L^{-1}. The problem is further aggravated due to lack of alternate source of drinking water, many a times the entire village depends upon a single source for cooking and drinking purposes. Therefore, it is suggested that the government authorities take serious steps to supply drinking water with low fluoride to the identified fluoride endemic villages in hard rock aquifers of Siddipet, Telangana State, South India.

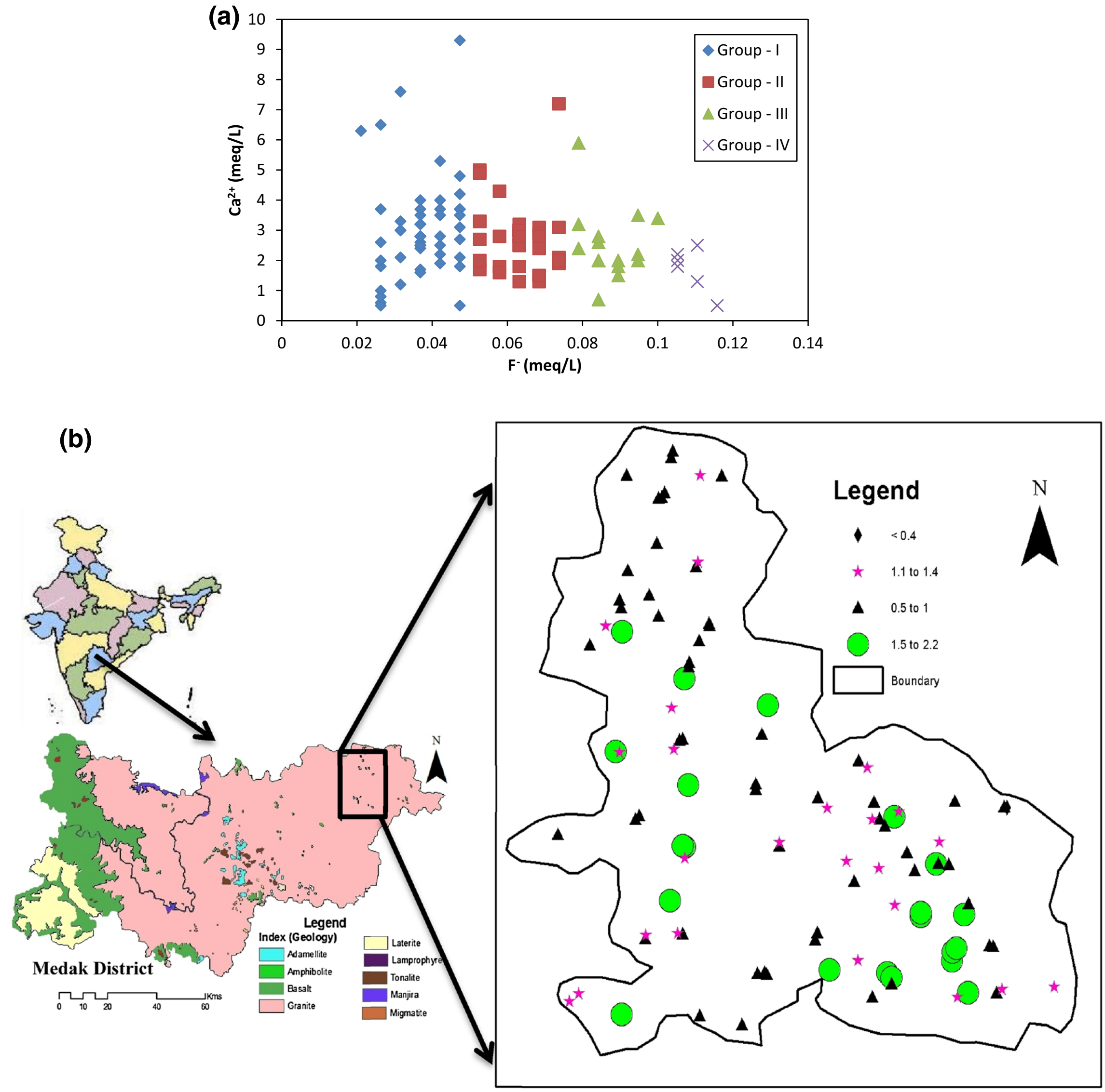

Fig. 5 (**a**) Correlation fluoride vs calcium. (**b**) Study area showing location of wells sampled for groundwater analysis fluoride distribution in the Siddipet area

Conclusion

Hydrogeochemical investigation carried out in the siddipet area of Telangana State revealed that the concentration of F^- in groundwater is ranging from 0.2 to 2.2 mg L^{-1}. 22 % of groundwater samples in the villages of Nanchrpalli, Ponnala, Silanagar, Ganpur, Venkatapuram, Irkod, Rampur, Appannapalli, Pullur, Ankampet, Raghapuram, Randampalli, Narsapur, Mittapalli, Boggolonibanda, and Nancharpalli exceed the drinking water standard of 1.5 mg L^{-1} set by WHO, which is responsible for the endemic dental fluorosis in these areas. The area is occupied by granitic/-granitic genesis of the Archean age. The F^--bearing minerals apatite, muscovite, and biotite are present in these rocks are responsible for the higher concentration of F^- in the groundwater due to rock–water interaction.

Acknowledgments The authors sincerely thank the anonymous reviewers for their very keen observations and helpful suggestions which had enhanced the quality of the paper. Financial support of the A. Narsimha by the Department of Science and Technology (DST)—Science and Engineering Research Board (SERB) Government of India, New Delhi under the Start-Up Research Grant (Young Scientists) project (SR/FTP/ES-13/2013) is gratefully acknowledged.

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