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ORIGINAL ARTICLE

Assessment of fluoride contamination and distribution: a case study from a rural part of Andhra Pradesh, India

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Abstract

In total, 123 groundwater samples were collected to evaluate the suitability for drinking purpose in a rural part of Andhra Pradesh, India. The groundwater is alkaline in nature and pH varying from 7.18 to 9.32 with a mean value of 8.36. The hydrogeochemical analysis reveals that the fluoride concentration varies from 0.4 to 5.8 mg/L with a mean of 1.98 mg/L. Higher fluoride concentration is found in west-central parts of Markapur region. The villagers have been exposed to the intake of high fluoride-bearing groundwater for the prolonged period and suffering from the deadly disease fluorosis. However, with respect to groundwater chemistry, the fluoride concentration is high in Na^{+}–HCO_3^{-}-type groundwater and low in Ca^{2+}–HCO_3^{-}-type groundwater in the Markapur region. Data plotted in Gibbs diagram show that all groundwater samples fall under rock weathering dominance group with a trend toward the evaporation dominance category. Therefore, rock–water interaction is the primary cause of elevated fluoride in the groundwater of the study region. Furthermore, a significant positive correlation exists between F^{-} and pH, HCO_3^{-} as well as negative correlation exists between F^{-} and Ca^{2+} and NO_3^{-}, which supports that the alkaline nature of water is the main cause for dissolving fluoride-bearing minerals.

Keywords Fluoride contamination · Groundwater · Geochemical behavior · Rural area · Andhra Pradesh · India

Introduction

Groundwater contamination by fluoride is one of the serious problems in the arid and semiarid regions of the world. Particularly in India, a number of people suffer from fluorosis due to intake of high fluoride content through drinking water. Approximately, in India, the excessive fluoride in groundwater is noticed in 177 districts covering 21 states, affecting 62 million people, including 6 million children (Adimalla and Venkatayogi 2018; Ayoob and Gupta 2006).

Nearly 200 million people from 25 nations are affected by the deadly disease of fluorosis (Ali et al. 2016; Adimalla and Venkatayogi 2017). Fluorosis-affected regions are reported from China (Li et al. 2018, 2014; Wu et al. 2015), India (Narsimha and Rajitha 2018; Adimalla et al. 2018a, b, c; Narsimha 2018; Narsimha and Sudarshan 2017a, b, 2018a, b; Rao et al. 2014; Subba Rao et al. 2015), Africa (Gizaw 1996), Korea (Kim and Jeong 2005), Mexico (Diaz-Barriga et al. 1997), Kenya (Gikinju et al. 2002) and Nigeria (Gbadebo 2012). A small amount of fluoride is essential to maintain bones and formation of dental enamel (Adimalla and Venkatayogi 2017; Adimalla and Li 2018). However, prolonged intake of high fluoride in drinking water can surely cause fluorosis (Adimalla and Qian 2019a; Narsimha and Sudarshan 2017a; Li et al. 2018). In general, fluoride is released into groundwater from fluorine-bearing minerals such as fluorite, fluorapatite, biotite, apatite, muscovite, hornblende, villiaumite, tremolite, sellaite, cryolite, topaz, fluocerite, yttrofluorite, gagarinite, bastnasite, microlite, sphene, wohlerite, fluormica, epidote, amphibole,

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lepidolite, montmorillonite, kaolinite, pegmatite, mica, clays, villuanite, phosphorite, and some micas weathered from silicates, igneous, and sedimentary rocks, especially shale (Adimalla et al. 2018a; Ayoob and Gupta 2006; Adimalla 2018; Narsimha and Sudarshan 2017a, 2018a, b), and high rates of evaporation and low precipitation in arid and semiarid areas can also contribute to the fluoride enrichment (Adimalla and Venkatayogi 2017, 2018; Subba Rao et al. 2015). However, fluoride is an important element for human health which has certain limits for intake (Rao et al. 2017; Ali et al. 2016; Narsimha and Sudarshan 2017a, b). World Health Organization (WHO 1984) has fixed a safe limit for fluoride from 0.5 to 1.5 mg/L in drinking water. Moreover, the intake of drinking water with fluoride content less than 0.5 mg/L can cause tooth decay. Larger than 1.5 mg/L fluoride content in drinking water is risky for human consumption which leads to dental fluorosis and skeletal fluorosis when exceeds 3 mg/L (Ayoob and Gupta 2006; Rao et al. 2017; Wu and Sun 2016).

In recent years, a rapid growth of population, industrial development, intense agriculture activity, low rainfall, declining surface water resources, and climate change have caused significant stress on surface/lake water supplies especially in Andhra Pradesh, Telangana states, and other rural parts of the country. Hence, people are forced to depend on groundwater for their daily needs. Eventually, groundwater is becoming more vital water resource primarily for drinking, domestic, and other usages in Markapur provinces. Thus, dental and skeletal health problems are noticed in the Markapur region of Andhra Pradesh. It is reported that the groundwater in areas covering Santhala Moguluru, Guttala madivaram, Vemulapadu, Podili, Kanigiri, Vengayyapalem, Malakonda, Gollapalli, Pasupugallu, Pallamalla, Chandalur and Markapur villages contains fluoride concentration more than the maximum permissible limit of 1.5 mg/L in Prakasam district, Andhra Pradesh (CGWB 2013). Moreover, Prakasam district is not only known for widespread occurrence of fluorosis but also for the occurrence of a high level of fluoride (Rao et al. 2014; Subba Rao et al. 2015), and few efforts have been made to understand the geochemical processes involved in the occurrence of high fluoride concentration in the groundwater of Markapur region. For this reason, a detailed study was undertaken to understand the geochemistry of fluoride in groundwater and to find the relationship of fluoride with other water quality parameters. This study paves the way to provide baseline information on drinking water safety to researchers/scholars and decision makers for investigating local groundwater problems.

Study area

The Markapur province is located in the central-western part of the Prakasam district (Fig. 1). The area geographically lies between the 79°10′~79°22′ north latitudes and 15°35′~15°50′ east longitudes. The vast plains of Markapur and of the adjacent areas are occupied by phyllite/slate (GSI 1993; GSI-NGRI 2006). Slate, when it is siliceous, stands out as a prominent linear ridge. The slate quarries in the study area represent minor ridges formed by siliceous slates. Mining of slate is the major commercial industry in Markapur. Among the carbonates, cherty dolomite is noticed in the south, where it trends E–W and possibly extends into the N–E direction. The carbonate and quartzite are the intercalated sequence in the Cumbum Formations. The main geomorphic units, in the study area, with reference to groundwater, are pediplain shallow, denudational hills, structural hills, and a few linear ridges. Pediplain shallow covers most of the area and is moderate to good in groundwater prospects, mainly because of secondary porosity in the form of cleavage. The groundwater prospects are poor in structural hills, denudational hills, and linear ridges. Hydrogeologically, shales and phyllites of the Markaur region under the Cuddapah Supergroup are considered as hard rocks, lacking in primary porosity. They develop secondary porosity through fracturing and weathering over a long period and become water bearing. Groundwater in shales/phyllites occurs in unconfined conditions in the weathered residuum and under semiconfined to confined conditions in the fissures, joints, bedding planes, and fractures (GSI 1993).

Mostly, water table aquifers occur at shallow depths, whereas semiconfined/confined aquifers at greater depths. Shallow aquifers occur within a depth of 20 mbgl (meters below ground level). The ideal sequence of the strata is weathered, semiweathered, and fractured zones. Nature and thickness of these aquifers depend on the depth of weathering, topography, and recharge conditions of the terrain and hence show wide variations in their water-yielding capacity. Groundwater in deeper aquifers occurs under semiconfined or confined conditions. The tectonic disturbance in the eastern fringe of Cuddapah Supergroup has developed deep-seated fractures in crystalline rocks and such zones form potential aquifers (GSI 1993). The deeper weathered and fractured rock aquifers are being developed by bore wells generally drilled along lineaments and at other favorable locations. The chemical composition and texture of parent rock not only determine the degree to which it can be weathered but also its reactivity and nature of the resultant product. It is observed, in the study area, that weathered clay residuum formed from argillaceous phyllites, shales, and slates generally do not yield more water. On the other hand, weathered residuum containing more quartz yields more water.

The investigated region falls under semiarid climate condition. The average annual temperature varies from 27°C in winter to 45°C in summer. The average annual rainfall is 182.9 mm. Southwest monsoon contributes 61% of the total

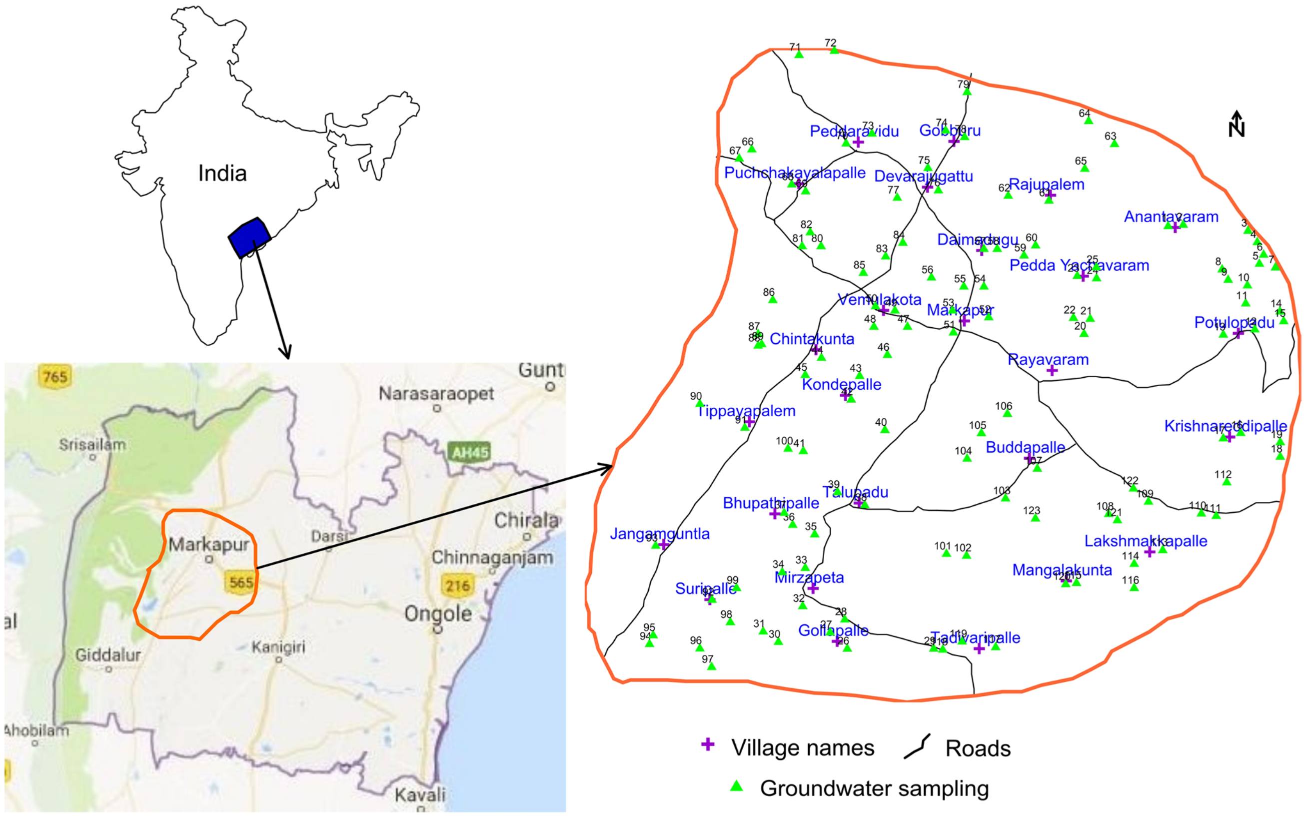

Fig. 1 Location map of the groundwater samples from the Markapur region, India

rainfall. Winds are generally light to moderate, except during the late summer and early southwest monsoon season.

Materials and methods

Groundwater samples were collected from 123 sampling sites in 1-liter clean polyethylene bottles and labeled with sample ID starting from PDM-1 to PDM-123. The samples were analyzed for anionic and cationic constituents using standard methods APHA (1995). The pH, electrical conductivity (EC), and total dissolved solids (TDS) were analyzed on the site using pH/EC/TDS meter (Hanna HI 9811-5; Narsimha and Sudarshan 2017a). Total hardness (TH) was measured by titration method using standard hydrochloric acid and standard EDTA solution. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined titrimetrically using standard EDTA. Sodium (Na^{+}) and potassium (K^{+}) concentrations were determined using Flame photometer (Systronics, 130). Chloride (Cl^{-}) was determined by standard $AgNO_3$ titration. Bicarbonate (HCO_3^{-}) and carbonate (CO_3^{2-}) were determined by titration with HCl. Sulfate (SO_4^{2-}) and nitrate (NO_3^{-}) were determined by using UV–visible spectrophotometer (Spectronic, 21, BAUSCH and LOMB).

The fluoride concentration in groundwater was determined electrochemically, using Thermo Scientific Orion Star A214 Benchtop pH/ISE meter (9609BNWP fluoride ion-selective electrode) using the USEP ion-selective electrode method. This method is applicable to the measurement of fluoride in drinking water in the concentration range of 0.1–1000 mg/L. Standard fluoride solutions (0.1–10 mg/L) were prepared from a stock solution (100 mg/L) of sodium fluoride. As per experimental requirement, 2 mL of total ionic strength adjusting buffer grade III (TISAB III) was added in 20 mL of water sample. The ion meter was calibrated for a slope of -59.2 ± 2. The composition of TISAB solution was as follows: 58 g NaCl, 4 g of CDTA (cyclohexylene diamine tetraacetic acid), and 57 mL of glacial acetic acid per liter.

Eventually, the accuracy of all chemical analyses was verified by calculating ion-charge balance between cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and anions (HCO_3^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-}, and F^{-}) as (cations − anions)/(cations + anions) × 100. All the 123 groundwater samples were within the accepted limit of ± 10% (Domenico and Schwartz 1990).

Results and discussion

Major ion chemistry

The analytical results of pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), bicarbonate (HCO_3^{-}), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), nitrate (NO_3^{-}), and fluoride (F^{-}) concentrations of the groundwater samples are presented in Table 1. The groundwater is mostly alkaline in nature in the Markapur region with pH concentration ranging from 7.18 to 9.32 and with a mean of 8.36 (Tables 1 and 2). The EC concentration varies between 520 and 4400 µS/cm, with a mean of 1451.71 µS/cm. The high mean value for EC emphasizes a wide variation in ionic content among different samples, and also it is a measure of a material's ability to conduct an electric current, and the difference of it indicates a wide variation of salts present in the groundwater. TDS concentration of groundwater is varying between 290 and 2640 mg/L, with a mean of 901.91 mg/L. Further, the TDS is classified as fresh, if it is less than 1000 mg/L; brackish, if it is in between 1000 and 10,000 mg/L; saline, if it varies from 10,000 to 100,000 mg/L; and brine, if it is more than 100,000 mg/L. Accordingly, 67% and 33% of groundwater fell under fresh and brackish category, respectively, in the present study region. The concentration of TH (as $CaCO_3$) shows wide disparity ranging from 80 to 880 mg/L with a mean of 255.68 mg/L (Table 1).

Among the cations, Na^{+} is the most dominant in the Markapur groundwater and its concentration ranged from 30 to 850 mg/L, with a mean of 205.47 mg/L (Table 1). Moreover, one and half times of groundwater samples show higher than the maximum allowable limit of 200 mg/L in the study region. The higher concentration of sodium may be derived from the dissolution of minerals and soil salts as well as the influence of anthropogenic sources (Todd 1980). The concentration of Mg^{2+} in the study area groundwater ranged from 40 to 520 mg/L, with a mean of 170.52 mg/L and about 58% of groundwater samples exceeded the maximum allowable limit of 150 mg/L (Table 1). The concentration of Ca^{2+} ranged between 10 and 360 mg/L, with an average of 85.16 mg/L recorded in the groundwater of study region which shows 1.8 times higher than the maximum allowable limit 200 mg/L for drinking purposes. Ferromagnesian minerals and artificial/human activities are the principal sources for higher content of magnesium and calcium in the groundwater (Hem 1991). The K^{+} content ranged from 0.5 to 88 mg/L, with a mean of 7.23 mg/L in the groundwater of the study region. K^{+} concentration is the least among the major cations in all the sampled groundwater with an estimated percentage mean value of 1.54%. The lower concentration of potassium is generally recorded in groundwater due to its relative greater resistance to weathering, and it is getting out of solution onto clay surfaces leading to its loss (Anim-Gyampo et al. 2018).

A high chloride concentration of groundwater is a result of leaching from the soils and also effect of domestic wastes, domestic effluents, fertilizers, leakages from septic tanks and road salt used to de-ice roads in the winter, and from natural sources such as rainfall, the dissolution of fluid inclusions, and chloride-bearing minerals, which also indicates an index of pollution (Todd 1980; Adimalla and Venkatayogi 2018; Adimalla 2018). In the present study, the concentration of chloride ranges from 25 to 940 mg/L, with a mean of 189.43 mg/L. According to the World Health Organization (WHO 2004) drinking water specifications, the permissible limit in the absence of an alternate source for chloride is 600 mg/L. The results revealed that only 2.4% of groundwater samples show higher than the 600 mg/L in the study region. The maximum allowable limit of sulfate for drinking purpose is 400 mg/L as suggested by the World Health Organization (WHO 2004). The concentration of sulfate is less than the maximum allowable limit of 400 mg/L, which reveals that all the groundwater locations are suitable for drinking purposes in the study region (Table 1). The nitrate concentration varies from 3 to 180 mg/L, with a mean value of 31.28 mg/L in the study area. Thus, the results indicated four times higher than the maximum allowable limit for nitrate in the study region. In the context of Indian scenario, groundwater containing higher than 45 mg/L of nitrate can lead to human health problems (BIS 2012). However, Adimalla et al. (2018c) categorized water based on nitrate concentration in groundwater as being low health risk when nitrate values less the 45 mg/L, high health risk when value range from 45 to 100 mg/L, very high health risk when values more than 100 mg/L. In the current study, 81%, 15%, and 4% of groundwater samples fall in low health risk, high health risk, and very high health risk category, respectively (Fig. 2). Therefore, the high concentration of nitrate in drinking water is toxic and causes blue baby syndrome/methemoglobinemia in children and gastric carcinomas (Adimalla and Qian 2019b; Adimalla 2019; Adimalla and Li 2018).

Fluoride geochemistry

Fluorine is the most electronegative of all elements and occurs primarily as a negatively charged ion in water (Hem 1991; Adimalla et al. 2018a, c). Intake of small concentration is beneficial for human health. However, in the present study area, the concentration of fluoride ranged from 0.4 to 5.8 mg/L with a mean of 1.98 mg/L (Tables 1 and 2), which indicates that the concentration of fluoride is not uniform in the study area. For example, the fluoride

Table 1 Hydrochemical data from a rural part of Andhra Pradesh, India

Sample No.	pH	EC (μS/cm)	TDS (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	CO_3^{2-} (mg/L)	HCO_3^{-} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	F^{-} (mg/L)	NO_3^{-} (mg/L)
PDM-1	8.07	2000	1280	400	120	280	245	49	Nil	430	335	70	4.1	30
PDM-2	8.25	1800	1120	400	120	280	215	3	Nil	310	305	130	3.7	15
PDM-3	8.05	3700	2250	880	360	520	432	4	Nil	380	880	155	1.25	64
PDM-4	8.1	1520	940	340	80	260	185	2	Nil	385	200	66	1.3	23
PDM-5	8.07	3050	1870	400	80	320	490	27	Nil	545	540	120	3.6	110
PDM-6	8.11	2600	1600	620	160	460	245	88	Nil	380	425	140	2.5	180
PDM-7	8.28	1160	715	320	120	200	115	3	Nil	280	142	72	0.8	70
PDM-8	8.43	930	595	180	80	100	122	3	30	330	65	40	1.35	3
PDM-9	8.1	810	525	180	80	100	99	1	Nil	290	42	21	3.8	35
PDM-10	8.44	2000	1250	460	120	340	240	4	30	310	325	180	3.2	55
PDM-11	8.32	1410	860	320	120	200	160	16	15	365	160	47	3.8	67
PDM-12	8.71	1490	925	120	40	80	280	3	55	430	165	65	4.4	12
PDM-13	8.65	1470	910	160	25	135	260	4	55	420	165	60	3.6	11
PDM-14	8.7	1700	1050	180	80	100	300	4	60	480	180	85	4.8	17
PDM-15	8.74	1350	840	120	40	80	245	1	60	400	140	52	3.4	11
PDM-16	8.25	1950	1200	200	40	160	350	4	60	510	235	110	3.6	15
PDM-17	8.523	1230	760	80	10	70	240	1	Nil	390	120	40	5.8	10
PDM-18	8.55	1660	1020	200	40	160	285	3	40	490	185	70	1.45	15
PDM-19	8.7	1430	900	160	40	120	255	3	70	420	155	65	3.6	15
PDM-20	8.7	1810	1120	200	80	120	305	5	60	470	220	75	1.45	20
PDM-21	8.57	1500	935	120	80	40	275	3	40	440	170	35	5.2	15
PDM-22	8.7	1650	1020	160	80	80	295	4	60	330	250	115	1.75	28
PDM-23	8.73	1700	960	200	40	160	285	3	60	380	220	106	1.95	29
PDM-24	7.81	4400	2640	800	320	480	545	15	Nil	490	940	300	1.35	94
PDM-25	8.52	2300	1420	320	80	240	370	2	40	300	440	185	0.7	31
PDM-26	8.67	1620	1000	200	40	160	270	1	50	320	255	74	1.25	40
PDM-27	8.26	1800	1120	240	80	160	300	1	Nil	360	284	90	1.4	42
PDM-28	8.2	4200	2500	680	160	520	550	15	Nil	370	940	285	1.15	97
PDM-29	8.6	1740	1080	200	60	140	300	2	40	320	290	110	1.25	26
PDM-30	8.67	1250	780	200	50	150	190	2	60	330	155	62	1.8	9
PDM-31	8.75	1650	990	240	80	160	265	1	40	365	250	75	1.45	40
PDM-32	8.67	1800	1120	240	40	200	290	3	60	320	295	122	1.4	26
PDM-33	8.6	1490	920	240	80	160	225	2	55	410	170	70	1.4	30
PDM-34	8.53	1600	1000	140	40	100	290	3	40	380	215	87	3.6	8
PDM-35	8.62	1480	930	244	40	204	245	2	30	460	155	44	3.3	20
PDM-36	8.69	1300	820	160	80	80	210	3	40	460	71	51	3.6	37

Table 1 (continued)

Sample No.	pH	EC (µS/cm)	TDS (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	CO_3^{2-} (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	F^- (mg/L)	NO_3^- (mg/L)
PDM-37	8.6	1910	1200	280	80	200	305	3	40	400	310	109	1.4	9
PDM-38	8.4	1030	650	320	160	160	69	18	15	330	64	42	1.3	58
PDM-39	8.62	1130	720	160	80	80	182	2	30	370	71	39	3.7	70
PDM-40	8.5	610	400	220	80	140	35	4	35	230	35	13	0.8	14
PDM-41	8.55	1220	770	200	40	160	184	3	25	380	130	35	3.65	18
PDM-42	8.56	870	560	260	80	180	74	2	25	265	60	42	1.55	36
PDM-43	8.43	1300	820	200	80	120	193	1	20	520	53	20	1.63	52
PDM-44	8.53	850	550	240	80	160	80	0.5	40	310	57	16	1.95	15
PDM-45	8.23	830	510	240	120	120	76	2	Nil	340	42	12	1.45	16
PDM-46	7.95	1230	770	280	140	140	150	1	Nil	215	255	36	0.8	5
PDM-47	7.18	1590	1000	360	120	240	175	32	Nil	360	260	55	1.45	6
PDM-48	8.15	700	450	240	120	120	46	2	Nil	275	32	8	1.15	5
PDM-49	8.3	860	560	220	40	180	90	7	10	350	43	10	1.25	22
PDM-50	8.5	900	580	140	40	100	136	6	30	370	43	6	3.65	13
PDM-51	8.32	890	580	260	60	200	120	13	5	365	35	9	1.45	21
PDM-52	8.52	870	560	240	80	160	83	7	30	350	43	6	1.1	24
PDM-53	8.28	1060	680	240	60	180	124	14	Nil	410	64	13	3.3	20
PDM-54	8.23	1020	650	270	40	230	102	11	Nil	360	78	20	1.4	22
PDM-55	8.25	870	565	240	60	180	76	19	Nil	360	36	6	1.5	22
PDM-56	8.51	860	560	270	40	230	67	9	30	320	57	10	0.85	26
PDM-57	8.42	870	560	240	60	180	77	20	30	340	50	9	1.1	18
PDM-58	8.41	840	520	220	60	160	77	12	20	310	43	8	1.2	19
PDM-59	8.32	890	580	200	40	160	108	5	15	330	57	14	1.8	16
PDM-60	8.32	760	500	170	40	130	92	6	10	290	50	10	1.25	22
PDM-61	8.57	760	470	200	40	160	80	1	40	260	78	10	0.85	15
PDM-62	8.54	520	330	160	60	100	47	1	30	190	28	17	1.25	3
PDM-63	8.26	550	340	200	60	140	30	1	Nil	210	25	12	0.4	22
PDM-64	8.33	890	290	140	80	60	35	3	15	160	28	17	0.5	16
PDM-65	8.19	560	360	160	120	40	53	1	Nil	210	35	13	1.3	11
PDM-66	8.39	840	510	160	40	120	115		25	300	60	18	2	20
PDM-67	8.5	660	430	160	60	100	78	1	40	210	50	15	1.4	22
PDM-68	8.05	930	600	180	40	140	129	1	Nil	395	43	4	1.63	39
PDM-69	8.04	1340	845	240	40	200	120	3	Nil	460	135	12	1.45	4
PDM-70	8.46	900	580	220	40	180	90	24	20	260	115	13	1.1	14
PDM-71	8.07	1020	660	260	80	180	85	3	Nil	310	120	13	1.05	22

Table 1 (continued)

Sample No.	pH	EC (µS/cm)	TDS (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	CO_3^{2-} (mg/L)	HCO_3^{-} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	F^{-} (mg/L)	NO_3^{-} (mg/L)
PDM-72	8.32	740	480	240	40	200	50	8	10	220	78	9	0.8	12
PDM-73	8.23	2900	1780	500	160	340	380	54	Nil	380	480	230	1.35	25
PDM-74	8.7	3100	1900	440	120	320	415	11	50	460	510	190	1.63	125
PDM-75	8.23	2700	1620	440	160	280	340	4	Nil	420	335	235	3.2	138
PDM-76	8.15	2050	1250	360	160	200	300	2	Nil	450	245	200	2.5	54
PDM-77	8.3	1650	1020	280	120	160	245	3	10	420	165	155	2.25	18
PDM-78	8.34	2350	1430	360	120	240	325	4	20	420	305	185	2.1	9
PDM-79	8.44	710	460	180	80	100	75	3	30	250	50	26	0.95	20
PDM-80	8.35	2050	1250	320	120	200	280	4	20	280	300	215	1.9	6
PDM-81	8.37	2250	1370	360	120	240	302	13	20	260	355	210	1.45	19
PDM-82	8.04	2650	1640	240	80	160	485	5	Nil	440	500	145	1.45	76
PDM-83	8.5	2040	1280	160	40	120	390	3	40	525	285	81	1.85	20
PDM-84	8.63	2020	1250	160	60	100	390	3	40	600	230	78	2.25	9
PDM-85	8.35	1880	1180	240	40	200	320	4	15	500	255	65	1.85	24
PDM-86	8.21	1680	1050	240	60	180	267	7	Nil	440	230	65	1.35	10
PDM-87	8.32	2630	1600	200	40	160	505	2	10	680	340	130	2.85	10
PDM-88	8.2	2430	1500	200	40	160	557	3	Nil	600	330	130	4.2	12
PDM-89	8.48	1530	950	260	80	180	225	9	20	320	255	68	1.5	29
PDM-90	8.46	1280	795	200	80	120	195	6	30	380	142	34	1.45	21
PDM-91	8.03	1550	970	420	80	340	237	10	Nil	390	220	62	1.05	20
PDM-92	8.31	1160	730	200	60	140	166	12	10	360	130	32	1.1	9
PDM-93	7.8	1340	840	200	60	140	118	12	Nil	415	140	47	1.05	6
PDM-94	8.6	2450	1520	120	40	80	805	2	40	530	390	118	3.9	5
PDM-95	9.32	1020	655	160	80	80	150	3	10	280	130	29	1.5	20
PDM-96	8.24	660	430	160	80	80	75	3	Nil	240	43	14	1.85	15
PDM-97	8.34	1000	640	200	80	120	130	3	15	260	142	21	1.2	14
PDM-98	8.15	1450	900	280	80	200	195	5	Nil	260	210	80	1.3	18
PDM-99	8.07	1080	700	240	80	160	132	5	Nil	350	114	17	2.25	64
PDM-100	8.06	1630	1020	360	160	200	203	5	Nil	180	340	94	1.5	18
PDM-101	8.51	830	540	200	80	120	95	3	30	300	72	10	4	67
PDM-102	8.44	1110	700	200	80	120	155	6	20	350	106	25	1.5	8
PDM-103	8	1810	1120	480	200	280	178	5	Nil	130	425	95	1.9	85
PDM-104	8.28	1060	660	240	80	160	127	7	Nil	280	135	32	0.9	64
PDM-105	8.25	1060	680	240	120	120	124	4	Nil	330	115	21	1.1	28
PDM-106	8.15	950	610	200	80	120	120	4	Nil	245	130	25	0.85	19

Table 1 (continued)

Sample No.	pH	EC (µS/cm)	TDS (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	CO_3^{2-} (mg/L)	HCO_3^{-} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	F^{-} (mg/L)	NO_3^{-} (mg/L)
PDM-107	8.46	1260	785	240	80	160	173	7	30	380	128	40	0.95	20
PDM-108	8.27	1180	745	200	80	120	175	4	Nil	280	155	52	2.4	36
PDM-109	7.75	1840	1140	400	240	160	220	27	Nil	360	255	94	0.9	42
PDM-110	8.55	1230	760	320	160	160	130	6	40	360	156	26	0.9	124
PDM-111	7.86	1620	1020	330	130	200	220	7	Nil	410	200	85	1.25	10
PDM-112	8.15	1580	980	320	120	200	205	5	Nil	190	341	92	0.9	61
PDM-113	8.32	880	570	200	80	120	106	5	5	280	85	23	2.5	24
PDM-114	8.19	1430	880	280	120	160	184	15	Nil	210	240	82	1.2	12
PDM-115	8.47	920	560	120	80	40	150	1	30	340	43	20	1.45	88
PDM-116	8.56	1020	660	120	60	60	170		40	385	50	18	2	27
PDM-117	8.54	1050	670	160	40	120	163	1	40	390	57	20	2.15	40
PDM-118	8	1090	700	240	100	140	134	3	Nil	380	85	25	3.6	33
PDM-119	8.41	720	450	220	80	140	58	2	20	300	28	4	1.45	31
PDM-120	8.22	780	500	260	100	160	55	2	Nil	320	35	5	1.2	9
PDM-121	8.59	1250	780	200	40	160	184	13	40	450	85	25	2.8	20
PDM-122	8.3	1470	920	200	40	160	242	6	10	250	215	130	1.6	32
PDM-123	8.21	960	620	265	120	145	92	5	Nil	115	141	144	1.45	55

PDM Indicates Prakasam District Markapur Region

Table 2 Groundwater samples from a rural part of Andhra Pradesh, India exceeding the permissible limits prescribed by WHO (2004) and ISI (1993) for drinking purpose

Water quality parameters	Indian Standard (ISI 10500, 1993)		WHO International Standards (2004)		Range in the Markapur region
	Highest desirable	Max. permissible	Most desirable limit	Max. allowable limit	
pH	6.5–8.5	6.5–9.5	6.5	8.5	7.18–9.32
EC	–	–	1400	–	520–4400
TDS	500	2000	500	1500	290–2640
TH	300	600	100	500	80–880
CO_3^{2-}	–	–	–	–	5–70
HCO_3^-	–	–	–	–	115–680
Cl^-	250	1000	200	600	25–940
NO_3^-	–	45	–	45	3–180
F^-	0.6	1.2	0.5	1.5	0.4–5.8
Ca^{2+}	75	200	75	200	10–360
Mg^{2+}	30	100	50	150	40–520
K^+	–	–	–	12	0.5–88
Na^+	–	200	–	200	30–805

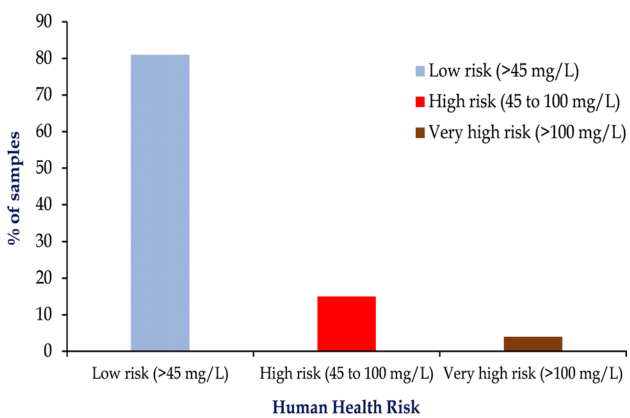

Fig. 2 Distribution of nitrate and its health risk classification in the study area

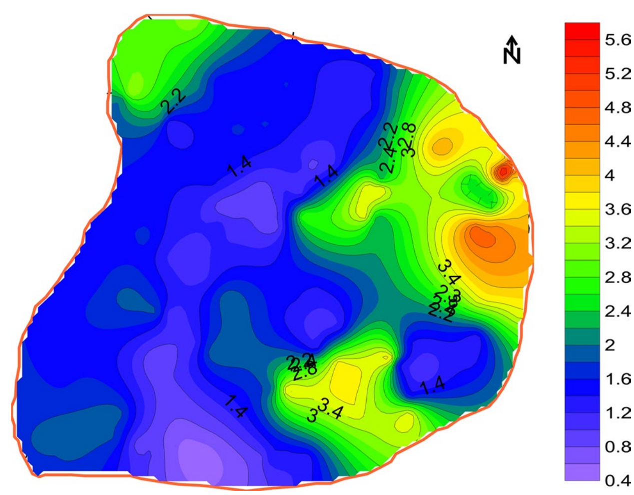

Fig. 3 Distribution of fluoride concentration in the groundwater of the study area

content varies from 0.4 to 1.0 mg/L in 13% of the groundwater samples, 1.1 to 1.5 mg/L in 49% of the groundwater; 1.6 to 2.9 mg/L in 23% of the groundwater; and 3.2 to 5.8 mg/L in 21% of the groundwater samples in the study region (Tables 1 and 2) and it also confirmed from the distribution map of fluoride (Fig. 3). It is clear from the distribution map of fluoride that except for extreme northern and southern parts of the study area, all other areas have excess fluoride (Fig. 3). The highest fluoride concentration is noticed in the west-central part of the area. However, fluoride can gain entry into the human body through different routes, probable transmission routes, and its health effects are shown in Fig. 4. WHO (2004) has prescribed the desirable and maximum allowable limits of fluoride as 1.0 and 1.5 mg/L, respectively, in drinking water. Moreover, United States Public Health Services (US PHS 1987) observed that the recommended limit of fluoride in the drinking water majorly relies on the climatic conditions of the region. Therefore, in the Indian context, the desirable and maximum allowable limit of fluoride in drinking water is fixed as 0.6 to 1.2 mg/L, respectively (BIS 2012). If fluoride concentration less than 0.6 mg/L can cause dental caries, while higher than 1.2 mg/L leads to fluorosis. Based on these limits, it is noticed that the fluoride concentration of groundwater in the study region is 4.83 times higher than the 1.2 mg/L (BIS 2012). However, Dissanayake (1991) categorized drinking water based on fluoride classification as being conducive to dental caries when fluoride concentration is less than 0.5 mg/L, promotes development of strong bones, when the concentration ranged

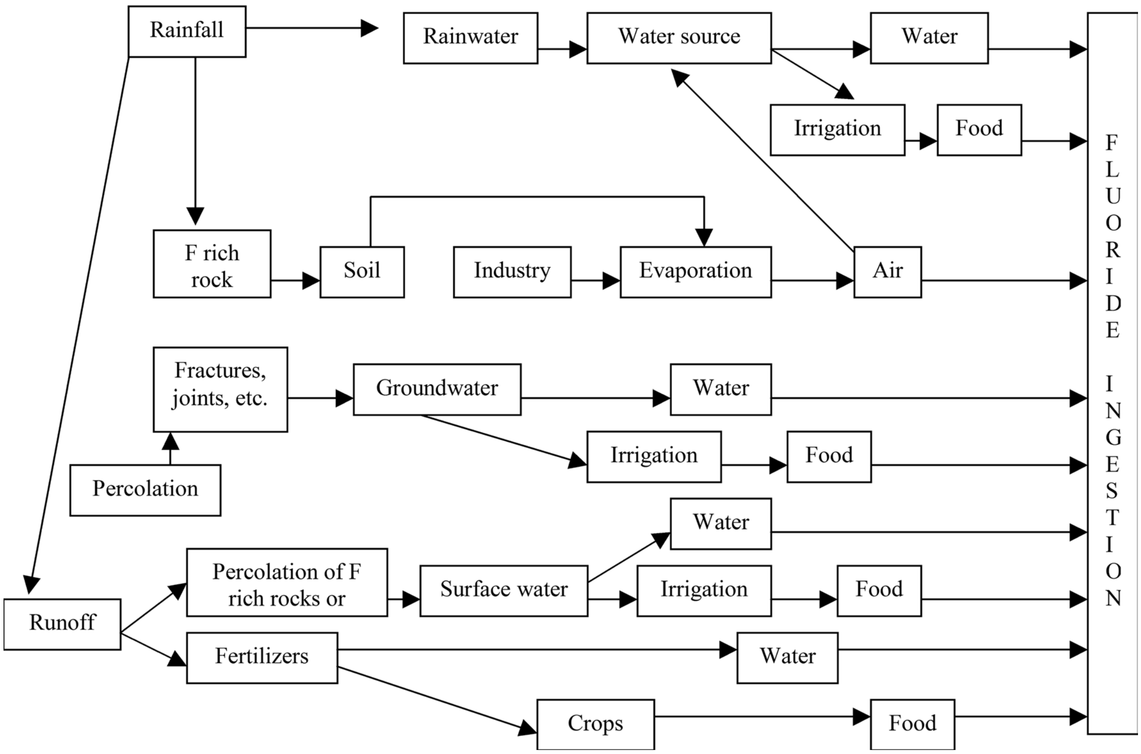

Fig. 4 Probable transmission routes of fluoride ingestion

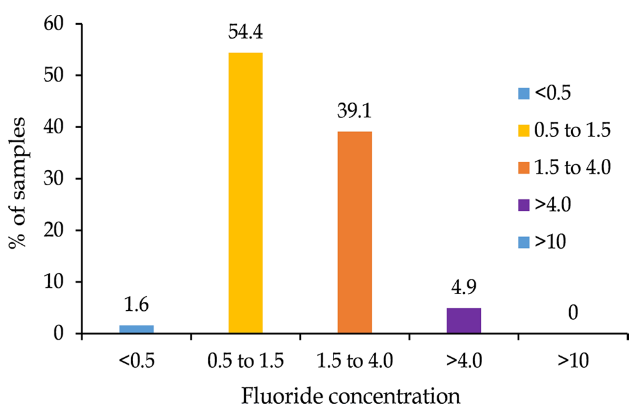

Fig. 5 Fluoride classification in the groundwater of Markapur region, India

between 0.5 and 1.5 mg/L, promotes dental fluorosis in children, when fluoride concentration ranged from 1.5 to 4.0 mg/L, and promotes dental and skeletal fluorosis when its concentration is greater than 4.0 mg/L, respectively. As shown in Fig. 5, fluoride classification, 1.6% and 54.4% of groundwater samples are conducive to dental caries and promote the development of strong bones and teeth category, respectively, while 39.1% and 4.9% of groundwater samples promote dental fluorosis in children and promote dental and skeletal fluorosis category, respectively (Fig. 5, Table 3).

Table 3 Effects of fluoride ingestion on human health Dissanayake (1991)

Fluoride concentration (mg/L)	Effect on human health
< 0.5	Conducive to dental caries
0.5 to 1.5	Promotes development of strong bones and teeth
1.5 to 4.0	Promotes dental fluorosis in children
> 4.0	Promotes dental and skeletal fluorosis
> 10	Crippling skeletal fluorosis, possibly cancer

Correlation of fluoride with other parameters

For understanding the relation between fluoride and other chemical parameters, correlation plots provide significant geochemical information and also help to know the controlling factors and its mechanism of fluoride enrichment in the groundwater (Adimalla et al. 2018a; Wu et al. 2019). A moderate positive correlation is observed between fluoride and pH (Fig. 6a) which indicates that the higher alkaline nature of water accelerates the enrichment of fluoride concentration and thus typically affects the concentration of fluoride in the groundwater (Narsimha and Sudarshan 2017a, b, 2018a, b; Narsimha and Rajitha 2018). A significant positive correlation is noticed between fluoride with bicarbonate (Fig. 6b) and also fluoride with sodium (Fig. 6c), which declares that

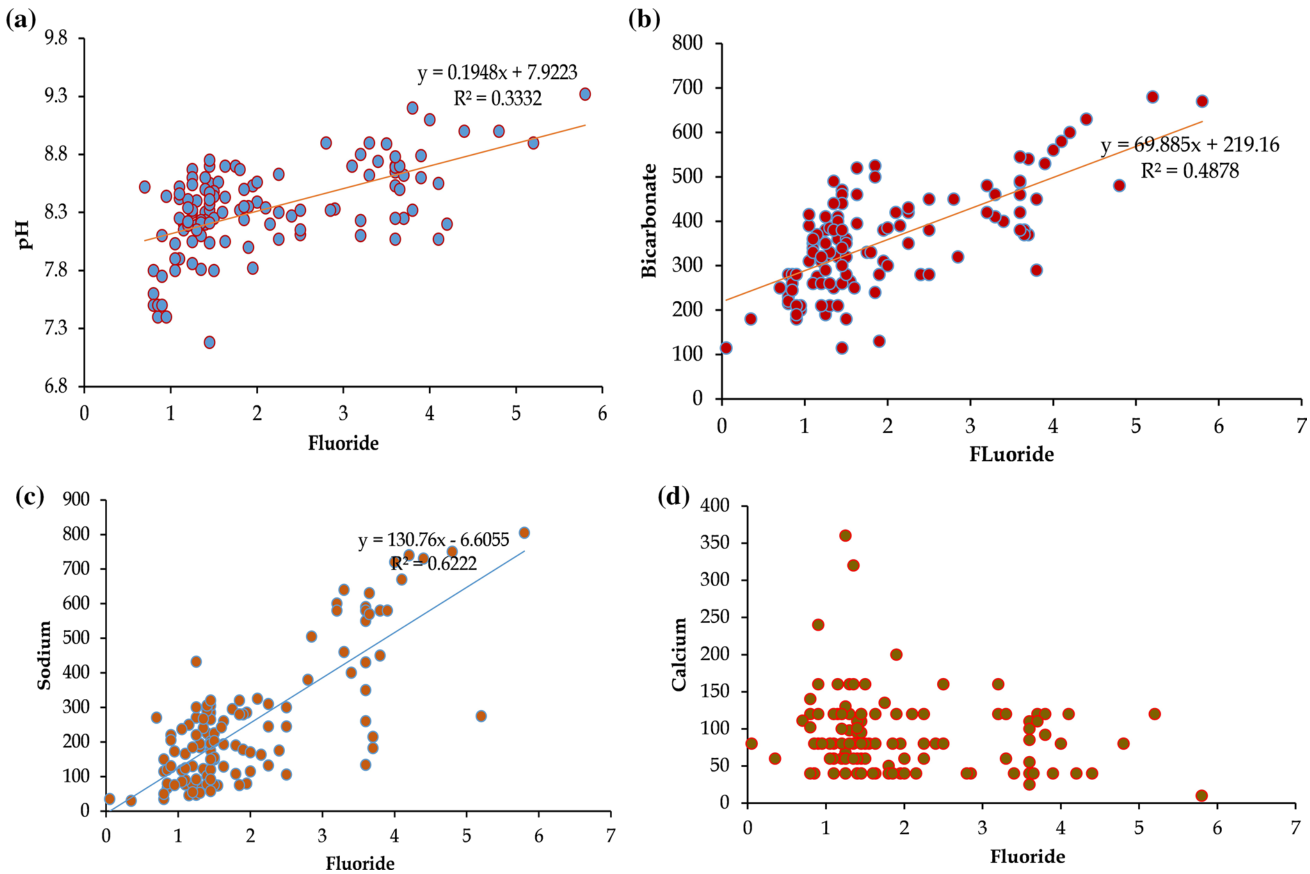

Fig. 6 Correlation between **a** fluoride and pH, **b** fluoride and bicarbonate, **c** fluoride and sodium, and **d** fluoride and calcium in the groundwater of Markapur, India

the alkaline environment is the dominant controlling chemical mechanism for leaching of fluoride from the fluoride-bearing minerals in the groundwater of the study region (Adimalla et al. 2018a; Li et al. 2018; Subbarao et al. 2017; Ayoob and Gupta 2006). Moreover, as shown in Fig. 6d, the correlation of fluoride and calcium, this clearly indicates that the presence of high calcium content favored low fluoride concentration in the groundwater. It is observed that the major role of precipitation process that is a vital mechanism for enhancement of fluoride occurrence in groundwater (Adimalla et al. 2018a; Narsimha and Sudarshan 2017b, 2018a, b; Li et al. 2018) and negative relations of fluoride with magnesium (Supplementary Fig. 1) is an agreement as established by Reddy et al. 2016. A number of studies have demonstrated that the positive correlations between fluoride and both pH, bicarbonate and sodium typically accelerate the fluoride concentration in groundwater as well as an inverse relationship between fluoride and calcium, which reveals the concentration in fluorite saturated groundwater (Adimalla and Venkatayogi 2017; Adimalla et al. 2018a, b; Ayoob and Gupta 2006; Narsimha and Sudarshan 2017a, b; Narsimha and Rajitha 2018). However, Fig. 7a, b reveals that the high concentration of EC and TDS is always linked with greater fluoride concentration and the similar observations noticed in different regions (Adimalla et al. 2018a; Subba rao et al. 2015; Adimalla and Venkatayogi 2018, 2017; Narsimha 2018; Narsimha and Sudarshan 2013). Moreover, EC and TDS correlation with fluoride is not as high as pH, bicarbonate, and sodium in the study area, which divulges that a higher affinity of fluoride with pH and bicarbonate rather than EC and TDS. However, there is no significant relationship existed between fluoride and SO_4^{2-}, Cl^-, and K^+ (Supplementary Fig 1), which revealed that the ionic concentrations added into groundwater is not from similar sources. Furthermore, it is indicated that no considerable relation exists between F^- and NO_3^- (Fig. 8) as these elements are added to groundwater from dissimilar sources, F^- from geogenic and NO_3^- from anthropogenic sources.

Groundwater types

Piper Trilinear diagram (Piper 1953) is one of the most widely applied methods for characterizing groundwater type. Therefore, analysis data were plotted on Piper (Piper

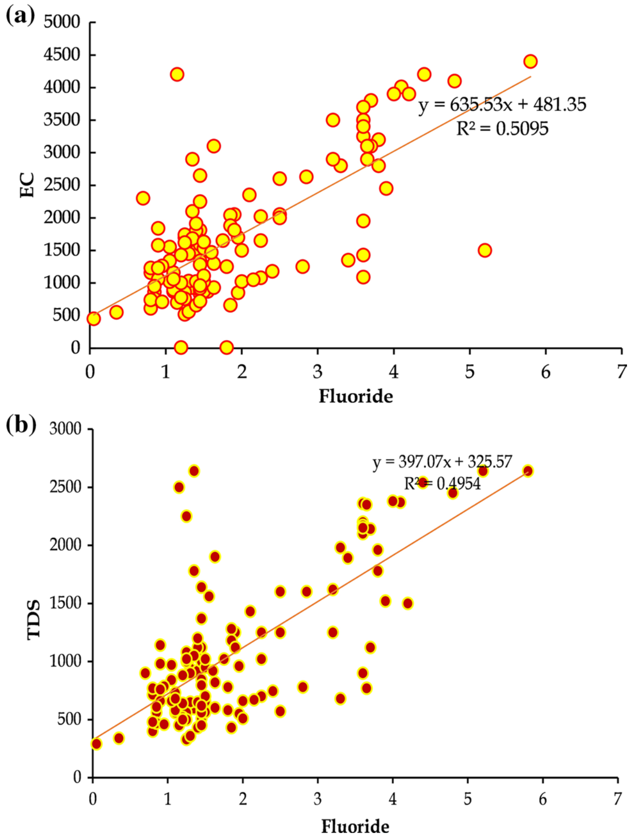

Fig. 7 Correlation between **a** fluoride and EC, and **b** fluoride and TDS in the groundwater of Markapur, India

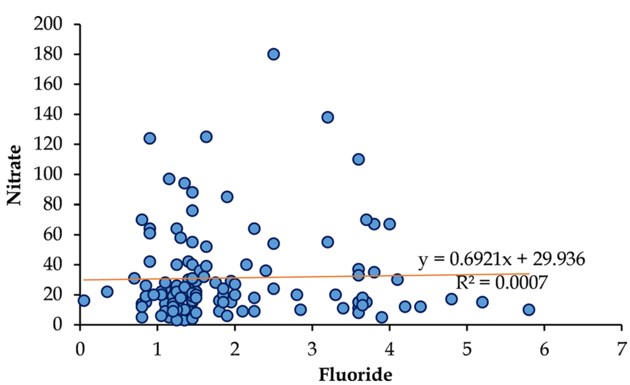

Fig. 8 Correlation between fluoride and nitrate in the groundwater of Markapur, India

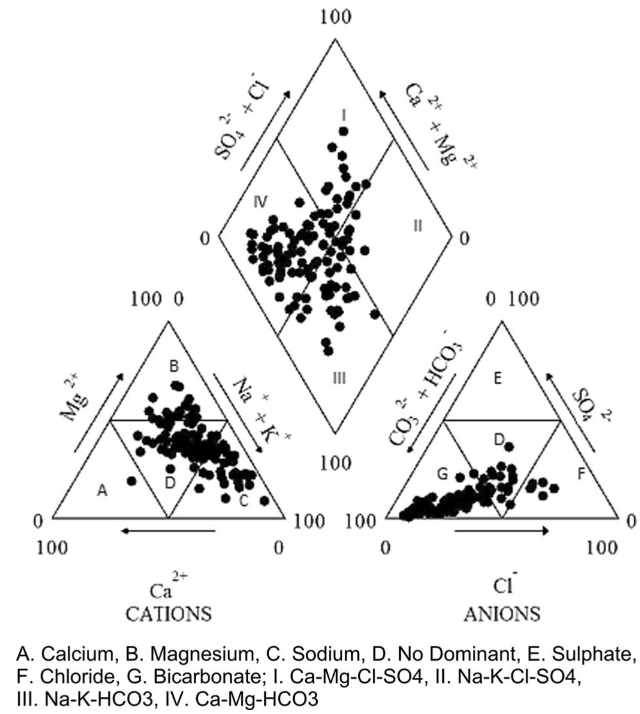

Fig. 9 Hydrogeochemical classification of the groundwater samples from the Markapur region, Prakasam district, Andhra Pradesh, India

1953) and depicted in Fig. 9. It categorized the groundwater into four types which are (1) Ca^{2+}–mg^{2+}–HCO_3^-, (2) Na^+–K^+–HCO_3^-, (3) Ca^{2+}–mg^{2+}–Cl^-–SO_4^{2-}, and (4) Na^+–K^+–Cl^-–SO_4^{2-} (Li et al. 2016a, b). Results are shown in Fig. 9 and observed that most of the groundwater samples fall in the area Ca^{2+}–mg^{2+}–HCO_3^- (54%), Na^+–K^+–HCO_3^- (34%), and Ca^{2+}–mg^{2+}–Cl^-–SO_4^{2-} (15%) which are the major water types, and few groundwater samples are plotted in Na^+–K^+–Cl^-–SO_4^{2-} (7%). However, as discussed above, fluoride is shown significant correlations with bicarbonate and sodium (Fig. 6b, c). Based on this observation, fluoride concentration is quite high in Na^+–HCO_3^- type of water compared with Ca^{2+}–HCO_3^- or mixed (Ca^{2+}–mg^{2+}–HCO_3^-)-type water (Fig. 9). Moreover, 34% of groundwater samples are found under Na^+–HCO_3^- or mixed type (Na^+–K^+–HCO_3^-) and cause favor to fluoride dissolution in the study region. A number of previous studies suggested that the Na^+–HCO_3^- water type, decreasing calcium concentration, increasing sodium concentration, and neutral-to-alkaline pH nature of water are more favorable for fluoride dissolution process, thereby accelerating the fluoride concentration in groundwater (Rao et al. 2017; Ali et al. 2016; Adimalla et al. 2018a, b; Narsimha and Sudarshan 2017b). Moreover, Na^+–HCO_3^- water type, mainly deeper groundwater, is influenced by the ion exchange process (Saxena and Ahmed 2003).

$$CaF_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \tag{1}$$

Therefore, the possible above ion exchange processes can accelerate and influence the fluoride solubility in the groundwater, which chiefly reveals that the presence of excessive Na^+–HCO_3^- in groundwater leads to dissociation activity of fluoride and can be higher in a high alkaline condition

(Saxena and Ahmed 2003; Adimalla and Venkatayogi 2017; Adimalla et al. 2018a; Li et al. 2014).

Mechanism of rock dominance

Gibbs (1970) proposed a diagram to understand the relationship of chemical components of waters from their respective aquifer lithologies. The chemical data of groundwater samples from Markapur, South India, were plotted in the Gibbs (1970) diagram (Fig. 10), using Eqs. 2 and 3, where all ionic concentrations are in meq/L.

$$\text{Gibbs ratio-I (for anions)} = \frac{Cl^-}{(Cl^- + HCO_3^-)} \quad (2)$$

$$\text{Gibbs ratio-II (for cations)} = \frac{Na^+}{(Na^+ + Ca^{2+})} \quad (3)$$

Gibbs diagram (Fig. 10) revealed that the most of the groundwater samples fall under the rock dominance, which typically originates from the weathering of the bedrocks which is a vital process to accelerate the fluoride concentration in groundwater (Li et al. 2016a, b; Adimalla and Wu 2019) and also (Fig. 10) groundwater samples end up with evaporation process of water chemistry, and finally, none of the sampling points lie in the precipitation dominance (Fig. 10). It mostly comes from igneous and sedimentary rocks in different aquifers, where fluoride-bearing minerals occur. These are the source of fluoride especially in India where longer water–rock interaction with aquifer materials and alkaline water activates leaching process in fractured zones and fluctuation zone (Kumar et al. 2014; Narsimha and Sudarshan 2013, 2017a, b, 2018a, b). Similar investigations using the Gibbs diagram such as Adimalla et al. (2018a) have found that elevated concentrations of fluoride are associated with groundwater that plots in the "rock dominance" field in a Gibbs diagram. Similarly, observations were noticed in Kolar and Tumkur Districts of Karnataka (Mamatha and Rao 2010), Chirala and Ongole of Andhra Pradesh (Subba Rao et al. 2015; Rao et al. 2017), and Chimakurthy pluton, Prakasam District, Andhra Pradesh (Reddy et al. 2016). However, it is also supported by the existing negative correlation between fluoride and nitrate (Fig. 8), which indicates that the elevated fluoride comes through the water–rock interaction, not by the anthropogenic sources.

Conclusions

Geochemical behavior and controlling factors of fluoride in groundwater of Markapur area, Andhra Pradesh, are studied and assessed. The following conclusions were drawn:

- The fluoride concentrations varied from 0.4 to 5.8 mg/L, and it is clear that the level of fluoride is higher in 54 groundwater locations than that of recommended upper limit by WHO and by Bureau of Indian Standards.
- Evaluation of the hydrogeochemical facies in the groundwater revealed that 54% and 34% of samples belong to

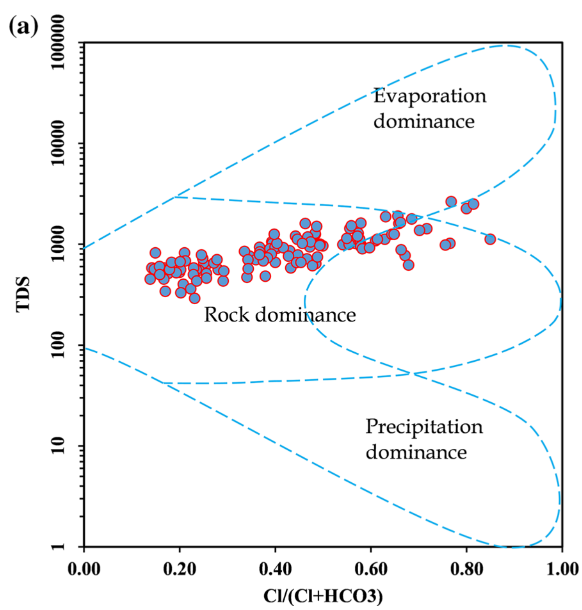

Fig. 10 Gibbs diagram, illustrating the mechanisms controlling the chemistry of groundwater samples from Markapur, Prakasam district, Andhra Pradesh, India

the Ca^{2+}–HCO_3^- or mixed Ca^{2+}–Mg^{2+}–HCO_3^-, Na^+–HCO_3^- water types, whereas high fluoride concentration belongs to majorly Na^+–HCO_3^- water type and relatively low concentrations in Na^+–K^+–Cl^-–SO_4^{2-} water type in Markapur region.

- Furthermore, rock–water interaction, mixing process of aquifer, and dissolution of minerals have affected the hydrogeochemical characteristics. Therefore, the reason of high fluoride in the study region is due to rock–water interactions, deficiency of calcium, and alkaline nature of water.
- Most of the people in the area depend on groundwater for their daily needs, without any primary treatment and actually they do not know much about the quality of groundwater and hence, people suffer from the dental and bone fluorosis in their lifetime.
- It is recommended to avoid high fluoride groundwater and depend on alternate sources. It is suggested that rainwater harvesting is one of the ways to dilute the fluoride concentrations in groundwater and helps to avoid excessive fluoride intake in the present study region.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interests regarding the publication of this paper.

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