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ORIGINAL ARTICLE

Evaluation of groundwater quality, Peddavagu in Central Telangana (PCT), South India: an insight of controlling factors of fluoride enrichment

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Abstract
Groundwater is one of the most valuable natural resources in Peddavagu in Central Telangana (PCT). Most of the PCT region population rely on groundwater for especially drinking purposes. For this reason a thirty-five groundwater samples were collected, analysed various physico-chemical parameters including F^-. The range of fluoride concentration 0.6–3.6 mg/L in Zone-I and 1–3.5 mg/L in Zone-II. pH of groundwater is from 7.1 to 8.4 and 7.3 to 8.3 in Zone-I and Zone-II respectively. Fluoride shows a significant correlation with pH, HCO_3^-, and Na^+, which may leads to enhance the fluoride content in groundwater. Insignificant relationship between F^- and NO_3^- suggests no influence of anthropogenic sources for F^- content in groundwater. The results of the relationship between Na^++K^+ versus total cations (TZ^+), Ca^{2+}+Mg^{2+} versus HCO_3^-+SO_4^{2-} describes silicate weathering is prevails in the groundwater chemistry. The dominance of the water types Na^+-HCO_3^-> Ca^{2+}-Mg^{2+}-HCO_3^-> Ca^{2+}-Mg^{2+}-$SO_4^{2-}$$Cl^-$>$Na^+$-$Cl^-$. Gibbs plot employed to differentiate the controlling mechanisms of hydrochemistry, which showed that rock water interaction is the governing process. Na^+-HCO_3^-, alkaline nature water and rock water interaction can leads to elevate fluoride content into groundwater in the study region. Thereby, most of the region people suffer with fluorosis problem, due to intake of higher fluoride content of drinking water. Therefore, the study region population may avoid such untreated water for drinking and adopt a suitable method to reduce the fluorosis problem in future.

Keywords Groundwater chemistry · Fluoride enrichment · Gibbs · Peddavagu · Telangana

Introduction

As we know that the groundwater is primary resource for drinking, irrigation and other usages in all over the world. Developing countries like India and China groundwater plays crucial role, especially, in arid and semi-arid regions, where inadequate of surface water, most of the region population depends on groundwater for daily needs, particularly drinking purposes. Conversely, contamination of groundwater prevails in such regions by rapid growth of population, usage of huge agricultural fertilizers and pesticides, human unplanned wastages, over exploitation of groundwater, increases industries in rural areas without a suitable plan, emit industries polluted water, and deficiency of seasonal rains (Adimalla and Venkatayogi 2018; Subba Rao et al. 2017). However, there are two ions concentration in drinking water, severely effects on human health and millions of people suffers in all over the world which are fluoride and arsenic. Therefore, it is one of the challenging deal with groundwater scientists and researchers to identify the source of groundwater contamination and protect the groundwater for future generations. However, excess fluoride content in groundwater is one of the main problem that facing the arid and semi-arid regions population. Mineral dissolution with F such as fluorite (CaF_2), muscovite [$(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$], biotite [$K(Mg,Fe)_3AlSi_3O_{10}F_2$], cryolite ($Na_3AlF_6$), and fluorapatite ($Ca_5(PO_4)_3F$), rock water interaction and ion exchange between F^- and OH^-, are the most responsible

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for elevate the high fluoride in groundwater (Todd 1980; Hem 1991; Adimalla and Venkatayogi 2017; Narsimha and Sudarshan 2017b). Especially, arid and semi-arid climatic regions have high evaporation, erratic rainfall and low rate of rainfall, which cause to low rate of groundwater recharges leads to prolonging rock water interaction may cause higher fluoride content in groundwater. Vithanage and Bhattacharya (2015) noticed that high evaporation leads to precipitation of lower solubility minerals (CaCO3), which really reduce the availability of calcium ions in groundwater and stimulate dissolution of fluorite minerals, which leads to enhance the fluoride concentration in groundwater. The occurrence of fluorosis has been reported in 28 countries of the world, including France, Germany, India, China, USA, Holland, Italy, Mexico, Italy, Holland, Spain, Switzerland, Japan, Thailand, Pakistan, Bangladesh, Argentina, Morocco, Middle East countries, Japan, South African Countries, New Zealand, Sri Lanka, West Indies, Spain, North and South American countries, etc., where approximately more than 200 million people suffers with deadly disease "Fluorosis" (Narsimha and Rajitha 2018; Narsimha and Sudarshan 2017a, 2018; Ayoob and Gupta 2006; David 2009; Kim et al. 2012; Li et al. 2014; Narsimha 2018; Karro and Uppin 2013). Amazingly, 45 and 66 million people already under control of with deadly disease of fluorosis in two developing countries like China and India respectively (Narsimha and Sudarshan 2017a). High concentrations of fluoride in groundwater are common in some of the semi-arid areas of Assam, Andhra Pradesh, Bihar, Chhattisgarh, Gujarat, Haryana, Jharkhand, Jammu and Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Telangana, West Bengal, Uttar Pradesh and New Delhi, states in India reported elevated fluoride content in groundwater (Narsimha and Rajitha 2018). Reportedly, all districts are in under high fluoride vulnerable zones in Telangana State (Adimalla and Venkatayogi 2017; Narsimha and Rajitha 2018). The most of the Telangana rural populace rely on groundwater for drinking purposes, without taking any prior treatment, which pushed them into fluorosis problem. However, a limited number of research work has been reported in Telangana, especially on fluoride enrichment in groundwater:

- Adimalla and Venkatayogi (2017) studied and reported elevated fluoride contamination in groundwater in Medak, Siddipet, and Sangareddy districts and found that the major source of F^- in groundwater can be attributed to the weathering and dissolution of fluoride bearing miners.
- Narsimha and Sudarshan (2017a, 2017b) conducted an investigation on contamination of fluoride in groundwater and its effects on human health in Siddipet and Basara, Telangana. They found that the water rock interaction, weathering of rocks, mineral dissolution, and geochemical environment is the main factor influencing the genesis and migration of fluoride content in groundwater.
- Narsimha and Rajitha (2018) carried out extensive study on spatial distribution and seasonal variation in fluoride enrichment in groundwater and human health risk assessment in Telangana, South India, and found high fluoride content in groundwater in post monsoon season due to vast evaporation, rock water interaction and alkaline nature accelerate the fluoride concentration in groundwater.
- Sudarshan et al. (2014, 2016) also found semi-arid climate conditions, erratic seasonal rains, increased water rock interaction leads to dissolution of F^- into groundwater in Karimnagar and Warangal districts in Telanagana.
- Brindha et al. (2011) investigations revealed that the weathering of rocks and leaching of fluoride bearing minerals are the major sources which contributes to elevated concentration of fluoride in groundwater of Nalgonda district, Telangana.
- Reddy et al. (2010) performed a hydrogeochemical characterization fluoride rich groundwater of Wailpalli wastershed in Nalgonda district, Telangana and found that the arid to semi-arid climate, low precipitation factors, high rate of evapotranspiration and F^- rich minerals are instrumental in enrichment of fluoride content in groundwater.
- Sujatha (2003) investigated on fluoride levels in the groundwater of the south-eastern part of Ranga Reddy district, Telangana, who has found that the relative abundance of fluoride bearing minerals, phosphatic fertilizers and the presence of fluor-apatite, which is leached into groundwater and also high fluoride groundwater associated with high HCO_3^- and low Ca^{2+}.

The above research workers reported that the abundance in fluoride bearing minerals in host rock are the principle source for enrichment of fluoride in groundwater. However, the world Health Organization (WHO) has set 0.5–1.5 mg/L as the minimum and maximum limits for fluoride in drinking water (WHO 2011). Fluoride in small amount is very essential component for normal mineralization of bones and formation of dental enamel, but excessive intake of F^- can cause dental and skeletal fluorosis, especially in arid and semi-arid regions of the world (Adimalla and Venkatayogi 2017; Li et al. 2016; Narsimha and Sudarshan 2013; Sudhakar and Narsimha 2013). Fluorine is the most electronegative element in the periodic table, and the content of fluorine in the lithosphere varies between 100 and 1500 g/ton. The majority of fluorine found in nature is present in various rocks, soils, waters, plants, other living organisms, slags, and fluxes (Reddy et al. 2010). Prevalence of fluorosis disease is rampant among majority of rural habitations of the Siddipet and Karimnagar regions, where groundwater is the only source for drinking purposes. Hence, the present study aims to understand the correlation between fluoride and other chemical indices, hydrogeochemistry of fluoride occurrence and its distribution in the study region. The output of the study give a benchmark to local scholars and decision makers for sustainable groundwater development and protection.

Hydrogeology of the region

The Peddavagu is located in parts of Siddipet and Karimnagar districts, Telangana, South India (Fig. 1). It covers an area of 195 Km^2, falling in the Survey of India toposheet E44H4. The mean seasonal rainfall distribution is 792 mm in southwest monsoon (June–September), 101 mm in northeast monsoon (October–December) (CGWB 2013). The study area experiences semiarid climatic conditions with average temperature of 22 °C in winter to 45 °C in summer. The Peddavagu flows from south to northern side, which suggests southern side is hilly area and northern area is slope region (Fig. 1). The PCT area geologically under hard rock covering area with granite and gneisses are predominant. The occurrence and movement of the groundwater is a consequence of a finite combination of topographical, climatological, hydrological, geological, and structural and pedagogical factors, which together form integrated dynamic system. The Groundwater occurs under unconfined conditions in weathered zone and under semi confined conditions in the fractures and fissures. The shallow aquifers tapping the weathered zone have very limited yields in the non-command areas and limited to moderate yields in the command areas (CGWB 2013).

Materials and methods

Thirty-five groundwater samples were collected in Peddavagu region, Central Telangana (PCT), South India (Fig. 1), in one litre polyethylene bottles and stored at 10 °C. All containers used for sampling were washed with 10% nitric acid solution followed by double distilled water. Immediately after sampling, pH and electrical conductivity (EC) were measured in the field with using pH/EC/TDS meter (Hanna HI9811-5). Total dissolved solids (TDS) were calculated from EC multiplied by 0.64 (Hem 1991). Total hardness (TH) bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}), fluoride (F^-), Nitrate (NO_3^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+) were analysed with using standard methods (APHA 1999) and detailed procedure is presented in Table 1, and flow chart also is depicted in Fig. 2. For analytical accuracy between the concentrations of total cations (TZ^+) and the concentrations of total anions (TZ^-) expressed in milliequivalent per liter (meq/L) of the each sample, ionic balance error ($IBE = \sum TZ^+ - \sum TZ^- \times 100/\sum TZ^+ + \sum TZ^-$) was computed and observed to be within the acceptable limit of $\pm 10\%$ (Domenico and Schwartz 1990).

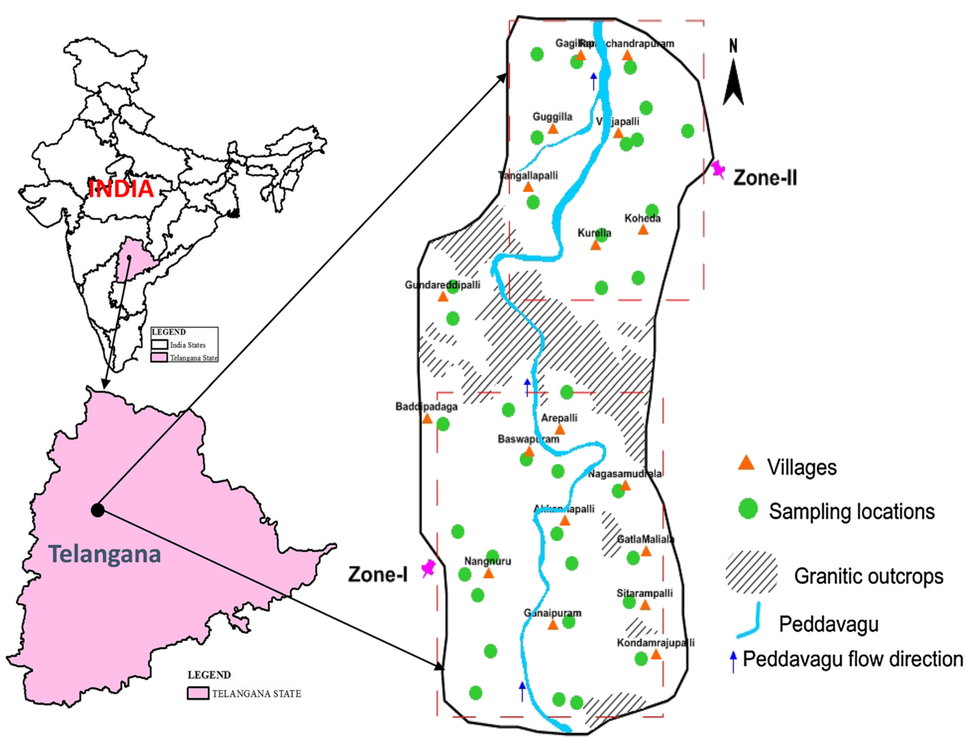

Fig. 1 Location map of groundwater samples in Peddavagu surrounding villages in the Central Telangana (PCT), South India

Table 1 Instrumental, titrimetric and calculation methods were used for chemical analysis of groundwater samples from PCT region, South India

Parameters	Characteristics	Analytical method	Reagents	Unit	References
General	pH	pH/EC/TDS meter	pH 4, 7 and 9.2	–	APHA (1999)
	Electrical conductivity	pH/EC/TDS meter	Potassium chloride	μS/cm	APHA (1999)
	Total dissolved solids (TDS)	Calculation	EC X (0.55–0.75)	mg/L	Hem (1991)
	Total hardness (as $CaCO_3$)	EDTA titrimetric	EDTA, ammonia buffer and Eriochrome Black-T (EBT) indicator	mg/L	APHA (1999)
Major cations	Calcium (as Ca^{2+})	EDTA titrimetric	EDTA, sodium hydroxide and murexide	mg/L	APHA (1999)
	Magnesium (as Mg^{2+})	Calculation	MgH = TH-CaH; Mg = MgH X Eq. Wt of Mg X normality of EDTA	mg/L	APHA (1999)
	Sodium (as Na^{+})	Flame photometric	Sodium chloride (NaCl) and KCl	mg/L	APHA (1999)
	Potassium (as K^{+})	Flame photometric	NaCl and KCl	mg/L	APHA (1999)
Major anions	Bicarbonates (HCO_3^-)	Titrimetric	Hydrosulfuric acid (H_2SO_4) phenolphthalein and methyl orange	mg/L	APHA (1995)
	Chloride (Cl^-)	Titrimetric	Silver nitrate ($AgNO_3$), potassium chromate	mg/L	APHA (1999)
	Sulphates (SO_4^{2-})	UV visible spectrophotometer	HCl, ethyl alcohol, NaCl, barium chloride, sodium sulphate	mg/L	APHA (1999)
	Nitrate (NO_3^-)	UV visible spectrophotometer	Potassium nitrate (KNO_3), Phenol disulponic acid, ammonia	mg/L	APHA (1999)
	Fluoride (F^-)	ISE (Ion selective electrode; Thermo Orion)	TISAB III and NaF	mg/L	APHA (1999)

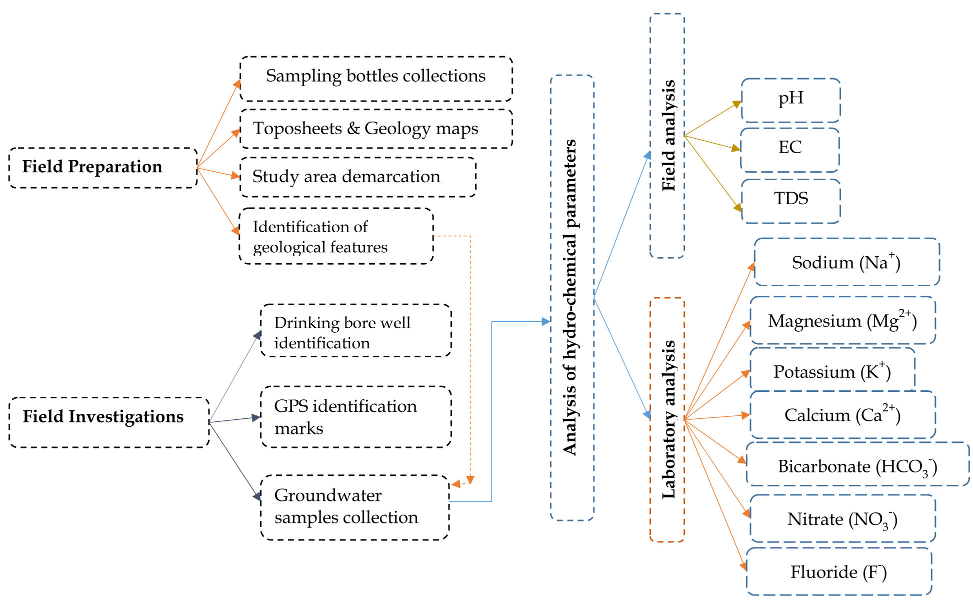

Fig. 2 Flowchart of the adopted methodology to delineate groundwater quality for drinking purposes in the study region

Geo-statistical modeling analysis

One of the Geo-statistical method is called "Geographical Information System" (GIS) is a useful tool to create a different types geochemical maps and also it is very convenient tool to study the spatial distribution of groundwater quality (Sajil Kumar 2017; Seyedmohammadi et al. 2016). Spatial distribution and location maps were created using the kriging method in GIS 9.2 software. Minimum, maximum, mean and standard deviation were calculated using the geo-statistical software "Statistical Package for Social Science".

Results and discussion

General groundwater chemistry

The detailed physico-chemical parameters of analysed groundwater samples and their comparison with the prescribed specification of WHO (2011) are presented in Tables 2 and 3. At Peddavagu in central Telangana (PCT), the pH values of groundwater samples were between 7.1 and 8.4, and 7.3 to 8.3 the mean values were 7.91 and 7.72, in Zone-I and Zone-II respectively (Tables 2, 3), all groundwater samples were within the prescribed limit 6.5 to 8.5 (Table 3), indicating neutral to slightly alkaline water in both zones. It is also noticed that the high fluoride groundwater samples were within the range 7.6–8.4, indicating that the high fluoride groundwater is frequently alkaline water (Fig. 4a). The electrical conductivity (EC) mean values of Zone-I and Zone-II are 914.22 and 1309.84 µS/cm (Tables 2, 3). Total dissolved solids (TDS) varies from 236 to 1942 mg/L and 273 to 3726 mg/L, with mean of 914.22 and 1309.84 mg/L in Zone-I and Zone-II respectively (Tables 2, 3). 8 and 36% of groundwater samples were exceeding maximum permissible limit 1500 mg/L, which are not suitable for drinking purposes (Table 3). However, Freeze and Cherry (1979) categorised water on the basis of TDS concentration into four groups which are represented as fresh (TDS < 1000 mg/L), brackish (> 1000 mg/L), saline (> 10,000 mg/L) and brine (100,000 mg/L). Based on this classification surface water and groundwater fall in fresh category in about 4 and 17 samples only and remaining

Table 2 Hydrogeochemical parameters of individual groundwater samples in PCT region, South India

Sample ID	X	Y	pH	EC	TDS	TH	Ca^{+2}	Mg^{+2}	Na^{+}	K^{+}	HCO3	Cl^{-}	NO_3^{-}	SO_4^{-2}	F^{-}
PVZW-1	79.0856	18.0892	7.36	1886	1207	90	150	11	89	16	310	178	98	214	0.75
PVZW-2	79.0473	18.1148	7.50	1525	976	243	130	22	92	15	354	130	87	180	0.84
PVZW-3	79.0535	18.0992	7.93	2952	1889	258	50	39	150	24	220	126	74	52	1.8
PVZW-4	79.0645	18.0954	7.98	599	383	138	60	15	50	4	220	47	45	89	2
PVZW-5	79.0643	18.0757	7.96	369	236	115	120	12	12	5	268	14	56	110	1.1
PVZW-6	79.0294	18.0765	7.80	1510	966	160	75	45	60	5	214	28	35	220	1.9
PVZW-7	79.0319	18.0627	8.10	1440	922	560	55	65	235	5	610	192	65	241	3.6
PVZW-8	79.0416	18.0684	7.80	1700	1088	225	28	50	120	7	214	160	45	273	2.4
PVZW-9	79.0362	18.0563	8.20	1530	979	155	95	34	140	7	275	185	120	143	2.8
PVZW-10	79.0907	18.0679	8.10	1380	883	170	55	23	200	5	450	28	75	178	3.1
PVZW-11	79.0694	18.0662	7.10	860	550	253	120	35	65	5	232	53	28	229	0.6
PVZW-12	79.0896	18.0541	8.20	1160	742	210	60	35	120	4	214	323	74	170	2.8
PVZW-13	79.0937	18.0360	8.40	430	275	120	45	24	190	12	530	302	110	173	3.1
PVZW-14	79.0683	18.0479	7.90	1500	960	160	130	25	95	4	183	263	50	230	1.6
PVZW-15	79.0710	18.0222	8.12	1640	1050	280	100	35	56	3	214	188	25	150	1.9
PVZW-16	79.0648	18.0233	7.81	1340	858	270	75	28	120	3	195	128	35	120	2.1
PVZW-17	79.0408	18.0386	8.20	1350	864	240	120	85	160	7	317	71	28	138	2.5
PVZW-18	79.0355	18.0253	8.10	1070	685	160	35	45	210	4	580	46	44	185	3.5
PVZW-19	79.0675	18.1205	7.60	3034	1942	268	81	16	149	8	430	267	99	87	2
PVZW-20	79.0241	18.1104	8.00	1780	1139	210	65	27	180	4	530	337	53	210	3.1
PVZW-21	79.0277	18.1540	8.03	943	604	185	18	34	178	7	531	59	24	140	3.2
PVZ-22	79.0886	18.1991	7.35	1304	834	153	95	18	89	4	150	112	28	34	1.4
PVZ23	79.0899	18.2233	7.30	426	273	85	120	12	37	3	146	37	17	26	1.5
PVZ-24	79.0710	18.2250	7.31	1402	897	270	130	30	65	8	210	153	37	71	1.1
PVZ-25	79.0572	18.2274	7.90	2030	1299	175	42	55	100	1	244	53	75	170	1.9
PVZ-26	79.0797	18.1534	8.10	1070	685	120	56	28	120	7	195	21	45	280	2.1
PVZ-27	79.0926	18.1567	7.89	2280	1459	111	55	32	121	5	305	85	25	246	2.5
PVZ-28	79.1100	18.2031	8.30	1100	704	312	35	25	210	3	647	25	55	170	3.5
PVZ-29	79.0953	18.2105	7.70	2624	1679	175	80	38	120	5	200	357	110	98	1.5
PVZ-30	79.0975	18.1777	7.75	582	373	135	147	18	41	9	287	71	76	150	1
PVZ-31	79.0923	18.2004	7.64	5822	3726	298	70	24	180	9	665	150	110	142	2.7
PVZ-32	79.0572	18.2012	7.63	2952	1889	375	80	16	107	6	336	270	48	132	1.9
PVZ-33	79.0559	18.1807	7.63	3034	1942	218	95	41	118	10	262	380	52	185	1.3
PVZ-34	79.0799	18.1702	7.44	2624	1679	205	110	25	129	7	403	265	24	112	1.4
PVZ-35	79.0278	18.1437	7.98	1402	897	305	60	43	150	5	397	96	84	120	2.1

PVZW Peddavagu Zone-I groundwater samples, *PVZ* Peddavagu Zone-II groundwater samples

Table 3 Statistical analysis of the hydrochemical characteristics of groundwater samples obtained from the PCT, South India

Parameters	pH	EC µS/cm	TDS mg/L	TH mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^{+} mg/L	K^{+} mg/L	HCO_3^- mg/L	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	F^- mg/L
Minimum	7.1[a]	369	236	90	18	11	12	3	183	14.2	24	52	0.6
	7.3[b]	426	273	85	35	12	37	1	146	21	17	26	1
Maximum	8.4[a]	3034	1942	560	150	85	235	24	610	337	120	273	3.6
	8.3[b]	5822	3726	375	147	55	210	10	665	380	110	280	3.5
Mean	7.91[a]	1428.47	914.22	212.76	79.39	33.55	127.19	7.33	337.64	148.74	60.48	168.19	2.22
	7.72[b]	2046.63	1309.84	209.68	83.93	28.96	113.36	9.36	317.56	148.16	56.14	136.15	1.85
STDEV	0.32[a]	1380.40	883.45	88.97	33.85	11.98	35.55	14.48	157.08	121.66	30.67	75.36	0.74
	0.31[b]	669.54	428.51	97.46	37.64	17.80	49.27	5.27	137.77	103.66	29.26	57.26	0.91
MDL	6.5[a]	–	500	100	75	50	–	–	–	200	–	200	0.6
MPL	8.5[b]	–	1500	500	200	150	200	12	–	600	45	400	1.5
% SEMPL	–[a]	–	8	4	–	–	13	4	–	–	50	–	67
	–[b]	–	36	–	–	–	7	–	–	–	43	–	50

STDEV Standard deviation, *MDL* maximum desirable limit, *MPL* maximum permissible limit, *%SEMPL* percentage of samples exceeds the maximum permissible limit

[a]Zone-I

[b]Zone-II

are in brackish category (Fetter 1990; Table 4). About 69% and 50% of groundwater samples from the Zone-I and Zone-II are within < 1000 mg/L (fresh) water and remaining groundwater are above > 1000 mg/L, which are considered as brackish water (Table 4). The TH in Zone-I and Zone-II groundwater ranges from 90 to 560 mg/L and 85 to 375 mg/L, with mean of 212.76 and 209.84 mg/L respectively (Tables 2, 3). Only one groundwater sample are exceeding maximum permissible limit 500 mg/L, prescribed by WHO (2011) (Tables 2, 3).

Groundwater major ion chemistry

The general dominance of cations were in the order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, while dominance of anions were in order of $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > F^-$ in Zone-I and Zone-II respectively. The dominant cation Na^+ concentration in the groundwater of the study area ranges from 12 to 235 mg/L, with mean of 127.19 mg/L, 37 to 210 mg/L, with mean of 113.36 mg/L, in Zone-I and Zone-II respectively (Tables 2, 3). However, 13 and 7% of groundwater samples above the prescribed limits 200 mg/L (Table 3). Ca^{2+} and Mg^{2+} are within the prescribed limits 200 and 150 mg/L, respectively in the study region (Table 3). The concentration of potassium in Zone-I ranges from 3 to 24 mg/L, while in Zone-II 1 to 10 mg/L (Tables 2, 3). The mean concentration of HCO_3^- 337.64 mg/L in Zone-I and 317.56 mg/L in Zone-II in the study region (Table 2). However, HCO_3^- was the dominant anion over Cl^-, SO_4^{2-}, NO_3^- and F^-. Cl^- and SO_4^{2-} concentrations were with the prescribed limits 600 and 400 mg/L respectively (Table 3). Nitrate enters in the water system either by surface runoff or by leaching through soil surface via percolating water, animal wastes, and anthropogenically as a by-product of agriculture and human wastes (Narsimha and Sudarshan 2013; Garwood and Ryden 1986; Saravanan et al. 2018; Wagh et al. 2017). Elevated nitrate concentrations in drinking water may be harmful to human health, especially for infant babies causing ''blue baby syndrome" known as methemoglobinemia (Coinly 1945). NO_3^- concentration in groundwater in the study region ranges from 24 to 120 mg/L and 17 to 110 mg/L, with mean of 60.48 mg/L and 56.14 mg/L in Zone-I and Zone-II respectively (Tables 2, 3). 2.6 times in Zone-I and 2.4 times in Zone-II higher than the WHO maximum recommended limit of 45 mg/L (Table 3), therefore which is unsafe for drinking purposes.

Distribution of fluoride and its mobilization processes

A limit of fluoride concentration in drinking water is very essential element for human health (0.5–1.5 mg/L; WHO 2011), but it exceeds the limit, it become a very dangerous to health. The fluoride concentration in the study region groundwater was found in Zone-II higher than the Zone-I; ranges from 0.6 to 3.6 mg/L, 0.8 to 3.5 mg/L, with mean of 2.22 and 1.81 mg/L respectively (Tables 2, 3). However, 81 and 50% of the groundwater samples were found to exceed the world health organization (WHO 2011) prescribed limit of 1.5 mg/L in Zone-II and I respectively (Table 3), which may cause fluorosis in the study region. Overall, 2.4 times higher than the maximum acceptable limit (1.5 mg/L) of fluoride content in the PCT groundwater. Moreover, to understand the spatial variation of fluoride concentration in groundwater sources, sampling sites with the corresponding fluoride concentrations (represented with different colours for two concentration groups; <1.5 and > 1.5 mg/L) were mapped using GIS 9.2 software (Fig. 3). The spatial patterns of fluoride distribution is depicted in Fig. 3, and comparison of fluoride concentration in the groundwater samples from paired close and away from the Peddavagu (PV). The fluoride concentration increased with the distance from PV and reached its maximum level 3.6 mg/L. It is clearly understood that the near the PV (shallow) groundwater samples contained low content of fluoride than the away the PV (deep) groundwater.

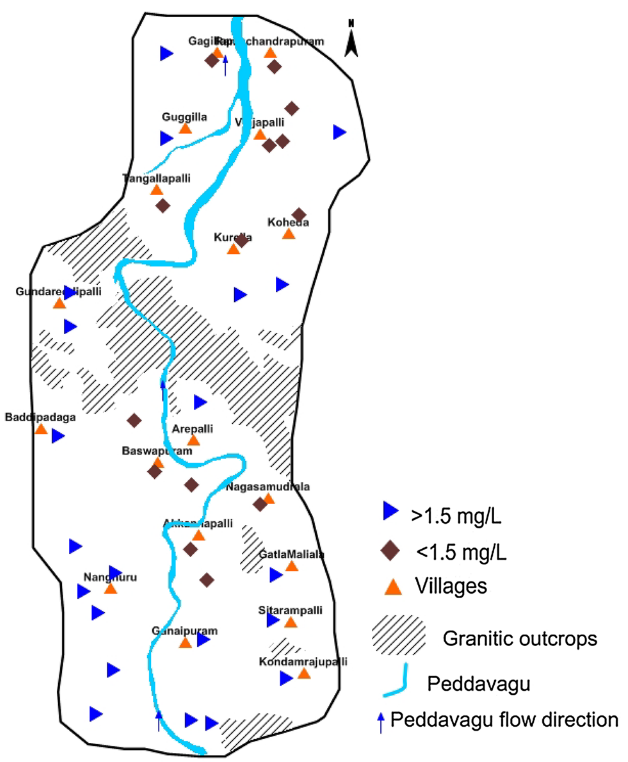

Fig. 3 Distribution of fluoride concentration in the Peddavagu surrounding villages in Central Telangana, South India

A positive correlation between pH and F^- ($r^2 = 5987$) was seen in this study and shown in Fig. 4a, reveals alkaline nature water more favourable for enhance the F^- in groundwater. It is also found that the F^- is an increase trend with Na^+ ($r^2 = 6772$) and HCO_3^- ($r^2 = 5715$; Fig. 4b, c), indicates the major influential factor is alkaline nature of water is one of the source of enrichment of F^- in groundwater. Consequently, alkaline nature water is favourable for F^- dissolution (Narsimha and Sudarshan 2017a), and Li et al. (2016) obtained similar results in and around Hua County, China. A number of researcher have been reported similar conclusions or results by Adimalla and Venkatayogi (2017), Narsimha and Sudarshan (2017a, 2017b, 2018), Narsimha and Rajitha (2018). In general low concentration of Ca^{2+} also a significant source of the F^- concentration in groundwater (Table 2; Narsimha and Sudarshan 2017b). There is no significant correlation between NO_3^- and F^-, which instigates that no involvement of anthropogenic source has been occurred in enrichment of F^- in the study region (Fig. 4d). Moreover, to identify the source of the contribution of primary rock forming minerals like silicate and carbonates weathering process more influence the groundwater quality. If TZ^+ (total cations) and $HCO_3^- + SO_4^{2-}$ dominants than $Na^+ + K^+$ and $Ca^{2+} + Mg^{2+}$ respectively, that indicates silicate weathering is dominant or predominant process in the groundwater (Narsimha and Sudarshan 2017a, b; Stallard and Edmond 1983; Narsimha and Rajitha 2018). As shown in Fig. 5a, b, $Ca^{2+} + Mg^{2+}$ versus $HCO^{3-} + SO_4^{2-}$ and $Na^+ + K^+$ versus TZ^+, indicates that the major number of groundwater samples plunge below the equiline 1:1 ($y = x$), which divulges of silicate weathering is the major geochemical process in the study region. However, a few points (Fig. 5a) plot above the equiline and some of the along the equiline, which suggests both silicate and carbonate weathering is in prevail in the geochemical process. Moreover, $Na^+ + K^+$ shows a

Table 4 TDS classification in groundwater in PCT, South India

Water type	TDS concentration (mg/L)	% Of groundwater in Zone-I	% Of groundwater in Zone-II	References
Fresh	< 1000	69	50	Freeze and Cherry (1979)
Brackish	> 1000	21	50	
Saline	> 10,000	–	–	
Brine	100,000	–	–	
Desirable for drinking	< 500	14	14	Davis and De Wiest (1966)
Permissible for drinking	500–1000	36	57	
Useful for irrigation	1000–3000	43	29	
Unfit for drinking and irrigation	> 3000	7	–	

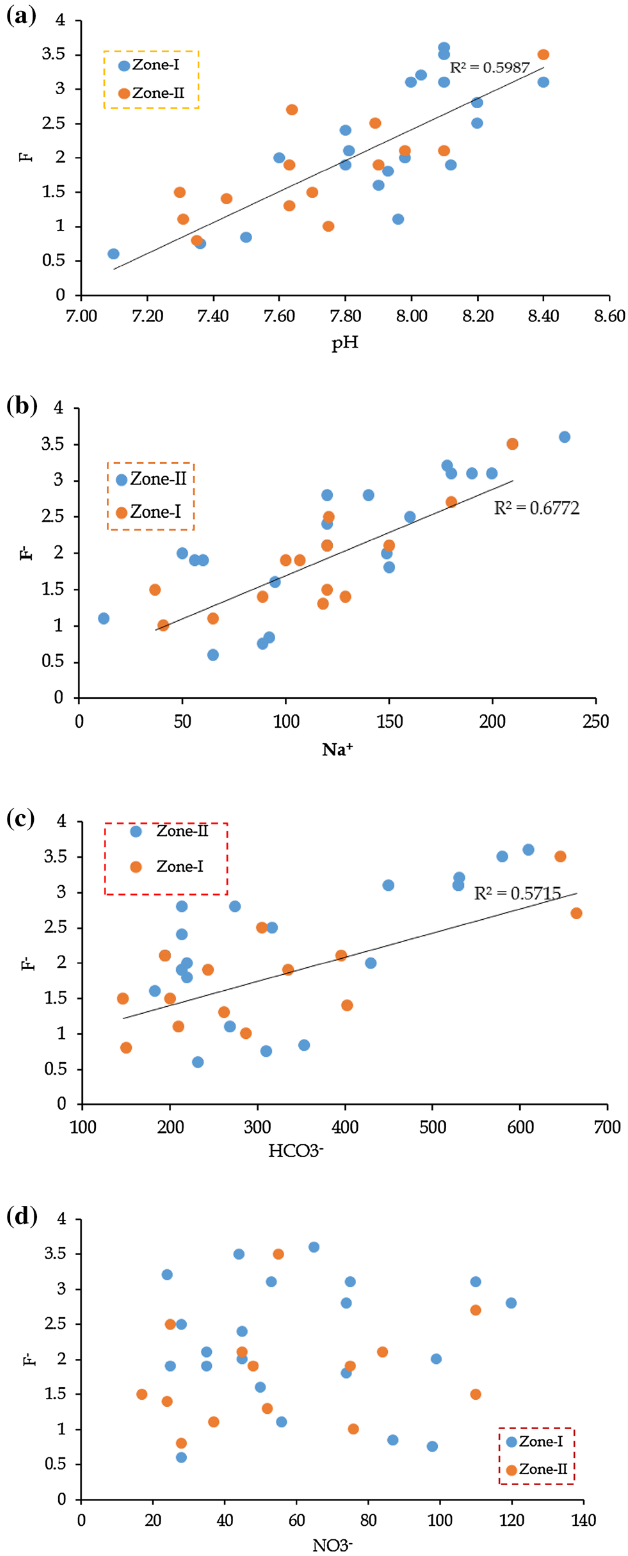

Fig. 4 Relationships between major elements **a** F^- versus pH, **b** F^- versus Na^+, **c** F^- versus HCO_3^- and **d** F^- versus NO_3

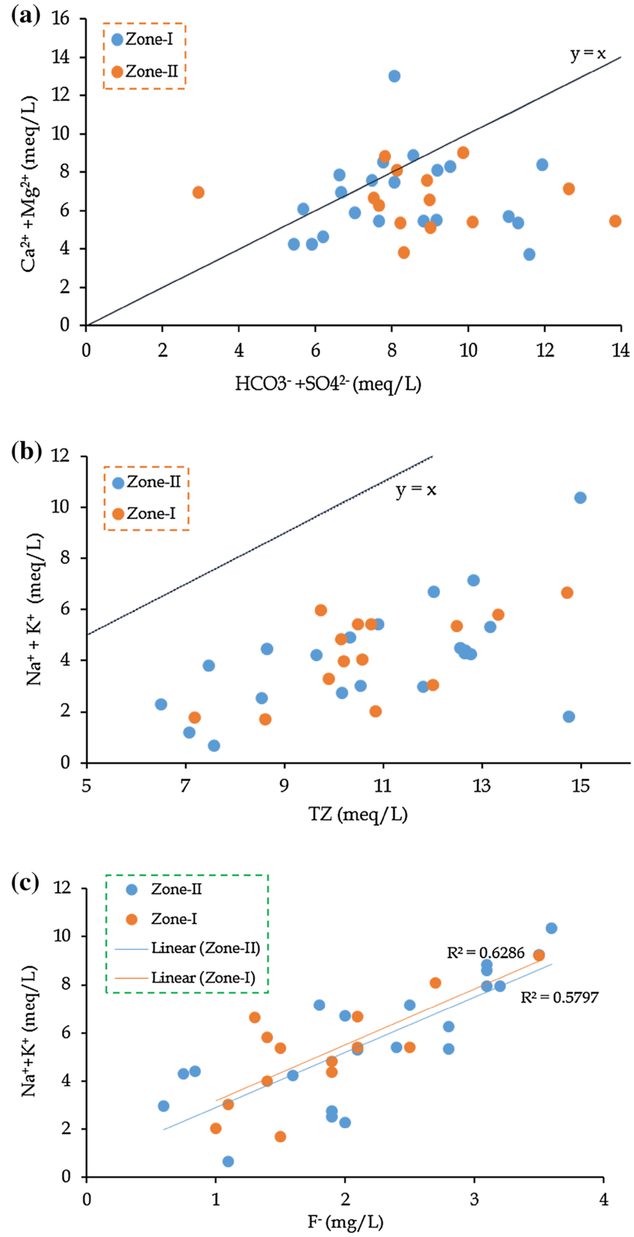

Fig. 5 Scatters plots of **a** $Ca^{2+}+Mg^{2+}$ versus $HCO_3^-+SO_4^{2-}$ concentrations, **b** Na^++K^+ versus TZ^+ (total cation) concentrations, and **c** Na^++K^+ versus F^-

significant correlation with F^- ($r^2=6286$; Fig. 5c), reveals that the ion exchange process accelerate in fluoride bearing minerals, which may cause to elevate F^- content in groundwater and explained in Eqs. (2, 3).

Rock dominance (RD) mechanism in the groundwater

In order to evaluate the source of dissolved chemical constituents, such as precipitation dominance (PD), rock dominance

(RD) and evaporation dominance (ED), Gibbs diagrams were performed in the study region (Gibbs 1970). The Gibbs used two ratios to estimate the PD, RD and ED, which are $Cl^-/(Cl^-+HCO_3^-)$ and $Na^++K^+/(Na^++Ca^{2+}+K^+)$ as a function of TDS in all groundwater samples were plotted and depicted in Fig. 6a, b. Figure 6a, b, indicates that all groundwater samples were in the rock dominance (RD) zone, suggests that the weathering of rock and its accessory minerals dissolution which are presented in the host rock is the main controlling factor of groundwater chemistry, leads to enhance of fluoride and other chemical constituents in the groundwater. It was culminated that the Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, Cl^- and TDS ions in groundwater are derived from the rock water interaction, i.e., weathering of minerals and accessory minerals present in the parent rocks in the study region. However, Adimalla and Venkatayogi 2017 found weathering of rocks (rock dominance) is the main cause to higher F^- content in the groundwater of Medak, Telangana, India. Narsimha and Sudarshan 2017a have identified rock dominance is the principal cause for elevated F^- content in the groundwater in the Siddipet, Telangana State, India. Moreover, rock-water interaction or weathering of rocks (RD) generally govern the groundwater chemistry (Narsimha and Sudarshan 2017b; Adimalla and Venkatayogi 2018; Ehteshami et al. 2016; Narsimha and Rajitha 2018). Faten et al. (2016) also noticed that the weathering rocks or (RD) is the principal mechanism of controlling the groundwater chemistry in Northeastern, Tunisia. Thomas et al. (2016) conducted a groundwater quality study in Ghana and found rock water interaction process includes the chemical weathering of rocks are majorly influence the groundwater chemistry.

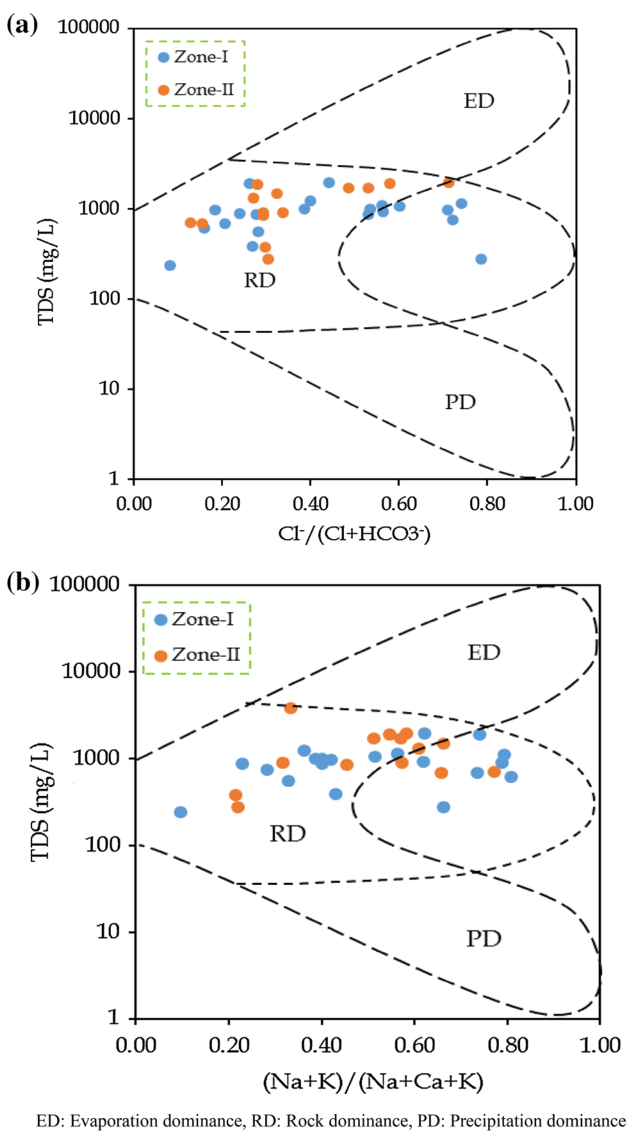

Fig. 6 Gibbs plots **a, b** showing that rock dominance (rock–water interaction) controls the hydrochemistry of groundwater in PCT region, South India

Hydrogeochemical facies and evaluation

The Piper diagram has mostly been used for to identify the groundwater types and its influential factors that involve in the groundwater chemistry (Piper 1944). Piper diagram consists of three distinct fields including right one is cation (Ca^{2+}, Mg^{2+}, Na^+, K^+) triangular, left one is anions (Cl^-, SO_4^{2-}, HCO_3^-, Cl^-) triangular and top one is a diamond shaped field (Fig. 7). Two triangular diagrams explicate the dominance of cation and anions individual percentage, and each point projected into the diamond shaped field, along a line parallel to upper margin of the field, where elucidates overall characteristic of the groundwater chemistry. Moreover, diamond field classified into four class, which are Ca^{2+}-Mg^{2+}-HCO_3^-, Ca^{2+}-Mg^{2+}-SO_4^{2-}-Cl^-, Na^+-Cl^- and

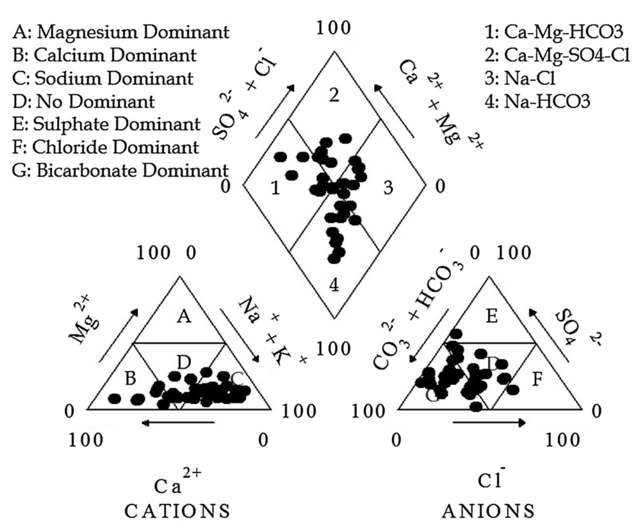

Fig. 7 Chemical facies of the groundwater of the PCT region, South India (after Piper 1944)

Na^+-HCO_3^- (Fig. 7). 38 and 23% of groundwater samples were in field of Na^+-HCO_3^- and Ca^{2+}-Mg^{2+}-HCO_3^- water types respectively. The order of the water types Na^+-HCO_3^-> Ca^{2+}-Mg^{2+}-HCO_3^-> Ca^{2+}-Mg^{2+}-$SO_4^{2-}$$Cl^-$>$Na^+$-$Cl^-$, which were dominated hydrochemical facies in the study region. Sodium bicarbonate type of groundwater is found to favour fluoride dissolution (Handa 1975). Similar results were found in the Siddipet, Basara and Medak regions in Telangana, India, where fluoride high with sodium bicarbonate water (Adimalla and Venkatayogi 2017, 2018; Narsimha and Sudarshan 2017a, b). In addition, fluoride was positive correlations with Na^{2+} and HCO_3^-, which was described above and that was the one of main reason for higher F^- content in the groundwater (Fig. 4b, c). The fluoride concentration increases through groundwater interaction with granitic rocks and its accessary minerals dissolution, resulting in Na^+-HCO_3^- water types. However, it is an exceptional result that fluoride concentration are high in granitic rocks groundwater with chemical compositions affected by mineral dissolution.

Occurrence of fluoride in groundwater

It has been noticed in the world average fluoride concentration in granitic rocks as 810 mg/kg, 1440 and 910 mg/kg in Nalgonda and Hyderabad granitic rocks respectively Telangana State, and also in China it is found 1043.28 mg/kg (Adimalla and Venkatayogi 2017; He et al. 2013; Wedepohl 1969). Geochemical data analysis of the granitic rocks of the area (Chin et al. 1995) has revealed that the granitic rocks were genetically related to the fluorite mineralization and the contents of fluorine in the fluorite-related granitic rocks ranged between 400 and 1800 mg/kg. However, the presence of apatite and biotite has been reported in the study area (Adimalla and Venkatayogi 2017). Precambrian rocks such as granite, granite gneisses, biotite rich grey granites were occupied in the study region. It is believed that granitic rocks contain a relative abundance of F^- rich minerals such fluorite, apatite, amphibole, muscovite, biotite, which may leaching into groundwater through weathering and mineral dissolution processes and rock water interaction, can constitute a major source of F^- in groundwater. The possible chemical reactions shown below:

$$CaF_2 + 2HCO_3^- = CaCO_3 + 2F^- + H_2O + CO_2 \quad (1)$$

For the Eq. (1) shows dissolution of fluorite in groundwater with high HCO_3^- content.

Muscovite:

$$KAl_2\left[AlSi_3O_{10}\right]F_2 + 2OH^- = KAl_2\left[AlSi_3O_{10}\right][OH]_2 + 2F^- \quad (2)$$

Biotite:

$$KMg_3\left[AlSi_3O_{10}\right]F_2 + 2OH^- = KMg\left[AlSi_3O_{10}\right][OH]_2 + 2F^- \quad (3)$$

The study region groundwater is in alkaline nature (Table 2) with high HCO_3^- and Na^+ shows a significant correlation with F^- (Fig. 4b, c), this may cause for ion exchange (OH^- can replace the exchangeable F^-) of fluoride bearing minerals: muscovite Eq. (2) and biotite Eq. (3), thereby increasing the F^- content in groundwater.

Conclusions

In the study region majorly occupied by hard rocks terrain and the chemical composition of the groundwater in the PCT region is dominantly Na^+-HCO_3^- and Ca^{2+}-Mg^{2+}-HCO_3^-. According to TDS above 50% of groundwater under fresh water category and TH about 99% of groundwater samples were within the prescribed limits. Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} ions were within the WHO limits for drinking purposes, while Na^+ and NO_3^- concentration were 13 and 50% of groundwater samples exceeds the prescribed limits 200 and 45 mg/L respectively. pH of groundwater is in slightly increased in alkaline nature. The alkaline nature water triggered fluoride enrichment in the groundwater, it is basically depend upon local geology and hydrogeochemical environment and climate conditions. The higher fluoride content in groundwater are mostly weathering of host rocks and its mineral dissolutions, in particularly dissolution of fluoride bearing minerals like apatite, biotate and muscovite. Further, silicate weathering also accelerate the fluoride bearing minerals dissolutions, lead to elevated fluoride content in groundwater. It is interesting to note that the spatial distribution of fluoride concentration in the study area, along the Peddavgu water contain low fluoride concentrations, while away from the Peddavagu water contain higher fluoride concentration in the groundwater.

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