Applied Water Science (2020) 10:202
https://doi.org/10.1007/s13201-020-01284-2

ORIGINAL ARTICLE

Monitoring of groundwater quality for drinking purposes using the WQI method and its health implications around inactive mines in Vemula-Vempalli region, Kadapa District, South India

Sudharshan Reddy Yenugu[1] · **Sunitha Vangala**[1] · **Suvarna Badri**[1]

Received: 22 March 2020 / Accepted: 22 July 2020 / Published online: 4 August 2020

Abstract

A study was conducted to evaluate the groundwater quality and health risk assessment for drinking purposes around inactive mining areas in the rural regions of Vemula-Vempalli region using the water quality index (WQI) method. For this study, forty groundwater samples were collected from bore wells and analyzed for physical parameters and major cations and anions followed by standard methods of APHA. From the analytical results, most of the groundwater samples are in alkaline nature; EC, TDS, and TH values are below the permissible limit and major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) & anions (Cl^-, HCO_3, SO_4^{2-}, F^-, NO_3^-) also within the permissible limit except fluoride and nitrate. Fluoride and nitrate in the groundwater range between 0.24–3 and 0.14–269 mg/L, respectively. Magmatic intrusions and water–rock interactions are main responsible for elevated fluoride in groundwater, and agricultural practices and usage of fertilizer are major responsible for higher nitrates in the groundwater. Piper diagram reveals that most of the samples belong to hydrochemical facies Ca^{2+}–Mg^{2+}–HCO_3^- category in this region. A higher concentration of fluoride and nitrate in the groundwater may cause a serious impact on human health. Non-carcinogenic effects of F^- and NO_3^- were computed using total hazard index by adopting USEPA guidelines; THI values in drinking water range from 0.41 to 7.28 (adults), 0.41 to 7.38 (children) and 0.31 to 5.62 (infants); it reveals that children are more prone to the health impact than adults and infants. Overall assessment of WQI values (83.7–186.1 mg/L) shows that 7.5% (excellent), 80% (good), and 12.5% groundwater samples are very poor for drinking purpose in this region.

Keywords Health risk assessment · Fluoride · Nitrate · Inactive mines · Vemula-Vempalli · Kadapa District · A.P. South India

Introduction

Mining activity results in the creation of a lot of inactive/abandoned mine lands (AML). Groundwater quality and public health and safety concerns are the most common environmental issues from inactive mines in several countries with a long history of mining like India (Mhlongo et al. 2013). Due to the groundwater contamination, toxic ions are of a huge health problem noticed in inactive/abandoned mines, especially in India. Toxic elements like fluoride & nitrate are released into groundwater and can be accumulation in crops and may cause significant effect on human health (Davies 1983). Of this, the most common environmental issue related to the inactive/abandoned mines in several countries mainly human health (Sphiwe and Francis 2015). Quality of groundwater is of major concern in deciding the applicability of water quality evolution for drinking purposes, and it must be devoid of harmful elements, living & non-living organisms in groundwater, excessive mineral dissolution which may cause an impact on human health (Muralidhara Reddy et al. 2013). Geogenic and anthropogenic sources from agriculture practices and dissolution of rock and mine water pollution contaminated soil mainly affects on groundwater quality (Guo et al. 2007; Brindha and Elango 2013; Adimalla et al. 2018; Adimalla and Venkatayogi 2018; Li 2016; Wu et al. 2017; Karunaidhi et al. 2019). Freshwater has become a scanty commodity due to overuse, and water is getting contaminated. Groundwater is widely used for drinking, agriculture, and industrial purposes (Adimalla and Wu 2019; Wu and Sun 2016). Over around world

---

✉ Sunitha Vangala
vangalasunitha@gmail.com

[1] Department of Geology, Yogi Vemana University, Kadapa, AP 516 005, India

application of groundwater for drinking and irrigation purpose in the arid and semiarid region is increasing considerably, and 1.5 billion people rely on groundwater for irrigation and drinking purpose (Li and Qian 2018; Adimalla et al. 2019c; Qian and Li 2011; Qian et al. 2012; Adimalla and Qian 2019b; Wu et al. 2014, 2017; Zhang et al. 2018). In India, especially in Andhra Pradesh, numerous studies have been carried out on assessment of groundwater quality for drinking and irrigation purpose, such as (Sunitha and Sudharshan Reddy 2019; Subba Rao et al. 2015, 2016; Adimalla and Wu 2019; Sudharshan Reddy et al. 2018; Muralidhara Reddy et al. 2019) and 90% of the Urban and rural areas depend purely on groundwater for drinking domestic purposes. For this water quality index (WQI), application is the very use full method to assess the suitability of water for various purposes and gives corresponding details on water quality for common people and policymakers to manage water quality. It represents the overall quality of the water in terms of index numbers and provides water quality information in a single value (Aminiyan et al. 2018). The water quality index method classified two different ways such as physicochemical and biological indices. The present attempt has been made to compute WQI based on physicochemical data. WQI is stated as a reflection and rating by the impact of various water quality parameters (Bouderbala 2017; Chaturvedi and Bassin 2010). Most of the researchers use these indices for suitability by human consumption. Hence, to evaluate the groundwater quantity and quality and providing a database are very important for planning and development of water management techniques.

Globally, for two decades, groundwater contamination by fluoride and nitrate is of major public health concern. Because of its importance, these studies have been carried out in arid and semiarid regions worldwide (Adimalla and Qian 2019b; Adimalla 2019; Wu et al. 2015; Ghadepoori et al. 2018; Jafari et al. 2014; Massoudinejad et al. 2016). Groundwater contains a huge amount of dissolved ions exceeding the permissible limit it becomes toxic. Though fluoride is required for normal mineralization of bones and formation of dental enamel in small quantities, when consumed in higher doses (> 1.5 mg/L), it causes dental fluorosis or mottled enamel and higher concentration (> 3.0 mg/L) of fluoride may cause skeletal fluorosis (Sunitha and Sudharshan Reddy 2019). The higher concentration of fluoride is of major health implication in many countries. Higher fluoride concentrations are noted in more than 23 countries in the world, particularly in parts of India, China, Central Africa, and South America (Susheela 1993; Shahriari et al. 2010). So many groundwater quality studies regarding fluoride have been taken up in arid and semiarid regions in the world (Subba Rao 2017, 2018; Adimalla and Li 2019; Adimalla 2020c). Fluoride concentration relies on various factors such as accessibility of circulating water to fluoride-bearing minerals like calcium fluoride (CaF_2), apatite, or rock phosphate [$Ca_3F\ (PO_4)_3$] and cryolite (Hem 1991; Adimalla 2020c; Adimalla et al. 2019b). The content of nitrates in groundwater is increasing in India. Higher nitrate concentrations in drinking water cause a health impact on the human body like methemoglobinemia in infants and stomach cancer in adults (Bulusu and Pande 1990). As such, the United States Environmental Protection Agency (USEPA) has demarcated a maximum contaminant level (MCL) of 10 mg/l NO_3-N (50 mg/l NO_3) (USEPA 2014), and also some research studies show that irrigation activates are the major cause for increasing nitrates in groundwater (Rezaei et al. 2018; Mirzaei et al. 2015; Adimalla et al. 2018). Many parts of states in India like Andhra Pradesh, Bihar, Delhi, Haryana, Himachal Pradesh, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Tamil Nadu, Rajasthan, West Bengal, and Uttar Pradesh contain higher nitrate concentration in groundwater (more than 45 ppm) (CGWB 2013).

Groundwater is primarily used for drinking, agricultural needs in the semiarid region of Kadapa District. Higher concentrations of fluoride and nitrate have been observed in various parts of the Kadapa District (Sunitha and Sudharshan Reddy 2019). The groundwater of this region contains more fluoride and nitrate which is exceeding the W.H.O. permissible limit compare to other ions for drinking purposes. However, comprehensive health risk assessment studies have not yet been studied in this region. However, considering this factor and keeping these views in mind of the importance of public health to understand the status of the groundwater quality in the Vemula-Vempalli region, hence the study was mainly intended to assess groundwater quality for drinking purposes using the WQI method and its health implications around inactive mines in Vemula-Vempalli region, Kadapa District, South India. This study will help in making better suitable groundwater management studies in the Vemula-Vempalli region.

Study area

The study region (408.6 km^2) is located in the southwestern part of Kadapa District, A.P., and situated between latitude 14°18′00″ N; longitude 78°28′ 30″ E falls in Toposheet No. 57J/7(Fig. 1). The whole study area is characterized by quartzite–carbonate shale cycles having an aggregate thickness vary between 6 and 12 km. Barytes and Yellow ochre are important inactive mines noticed in this area; road metal quarries are also observed. Geological study area belongs to Papagni and Chitravati groups of Lower Cuddapah Supergroup (Nagaraja Rao et al. 1987). The rocks have southern dips in the northern portion becoming easterly in the midsection and gradually changing to northeasterly in the south with some local

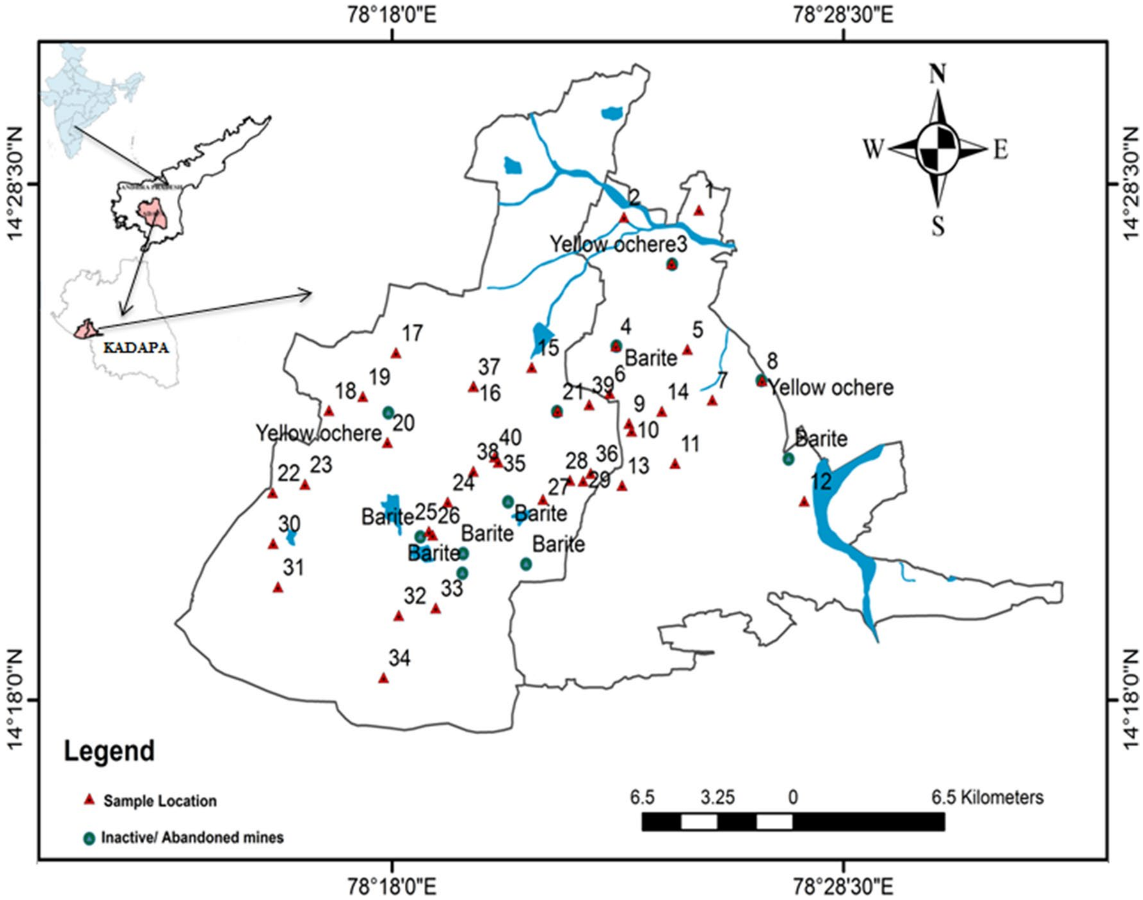


Fig. 1 Location map of study area

variations. The dip of the Papagni series of beds is gently ranging from 8° to 30°. The study area contains basic flows along with igneous rocks remarkably followed by bedding planes like dolerite, quartzite, dolomite, quartzite with conglomerates, and chert. The Pulivendula quartzites occur as comparatively narrow bands separating the Vempalli limestone and shale from the overlying Tadipatri shale (Fig. 2). Important geomorphic units are denudational hills, pediment and pediplain, structural hills. Paddy, groundnut, sunflower, and sweet lime are important crops. Apart from the banana plantation, seasonal fruits (Sweet lime, lemon) are also grown. Drip irrigation is applied in this region particularly for sweet lime. This area experiences arid to semiarid climate. The average annual rainfall is 600–650 mm and also experiences the effect of SW and NE monsoons. Groundwater is the only source for drinking and irrigation purposes (Geological Survey of India 2001). Temperature varies from 43.2 °C (April) to 20.4 °C (December). The depth of water level varies between 10 and 20 m (CGWB 2007, 2013). Groundwater occurs in joints and fractures with weathered zones of Papagni and Chitravathi group of rocks. Massive limestone and gulcheru quartzite formations act as good aquifers. The depth of the water table in the study area ranges from 10 to 30 m.

Methodology

Experimental methods, sampling, and analysis

Forty groundwater samples were collected from 27 villages around inactive mining areas in September 2018. Depth of bore wells varied between 20 m and 60 m below the ground level. Samples were collected in polyethylene bottles. pH, electrical conductivity (EC), and total dissolved solids (TDS) were analyzed during fieldwork using water analyzer 371 field kit; major cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined by titrimetry, while Na^{+} and K^{+} are determined by flame photometry (Systronic Model No. 128). Major anions like sulfate (SO_4^{2-}) estimated using a flame photometer, chloride (Cl^{-}) determined by titrimetry, fluoride (F^{-}) estimated using

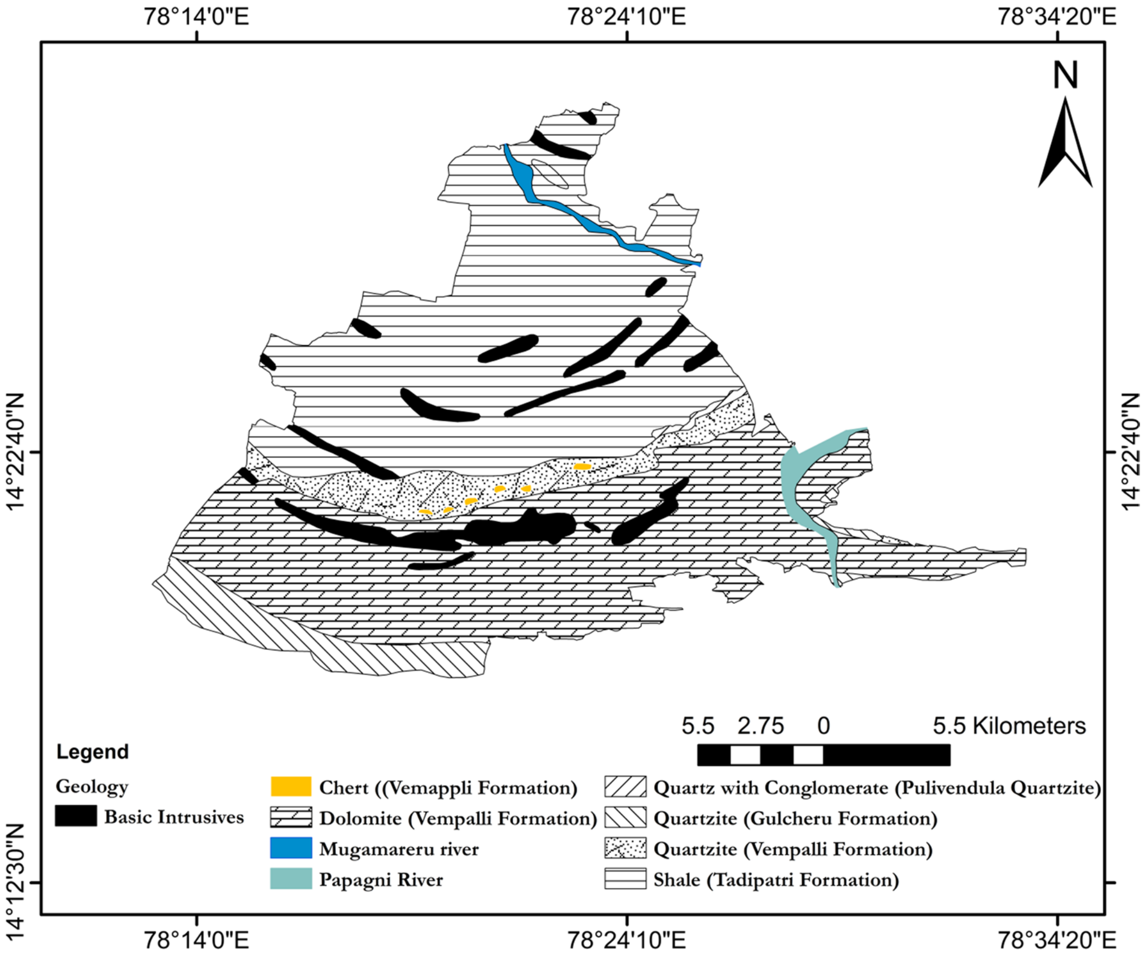


Fig. 2 Geology map of the study area

Orion 4—star ion meter (Model: pH/ISE), and nitrate (NO_3^-) are determined by using spectrophotometer following APHA (2012) standard methods, and suggested precautions were taken to prevent contamination (Hem 1991; Raghunath 1987). A Global Positioning System (GPS) instrument is used for collecting samples. Geographical information system is the very effective tool for analyzing and displaying analytical data and using spatial data for decision-making in several monitoring areas like environmental and engineering fields. Spatial distribution maps were prepared by using the interpolation method in Arc GIS 10.3 software. The inverse distance weight (IDW) method is followed to understand groundwater quality. The spatial distribution of fluoride and nitrate ions in groundwater was demarcated in the maps. WQI was calculated by World Health Organization standards and Indian Standards methods, and Health Risk Assessment has been computed followed by the USEPA guidelines, respectively. The relative weight method was applied for evaluating groundwater quality in the study area (Brown et al. 1970).

Water quality index method

The WQI calculations include three consecutive steps. The first step is "weight assigning," and each of the 14 parameters has been given a weight (wi) based on its relative importance to the overall quality of drinking water as denoted in Table 1. The second step is the "calculation of relative weight" by the equation given below:

$$\mathrm{Wi} = \mathrm{wi} \Big/ \sum_{i=1}^{n} \mathrm{wi} \tag{1}$$

The third step is a "rating of quality (qi)" determined by the given equation

$$\mathrm{qi} = \left(\frac{\mathrm{Ci}}{\mathrm{Si}}\right) \times 100 \tag{2}$$

where Ci is the concentration of each parameter in each water sample and Si is the WHO recommended value for each parameter (Kouadra and Demdoum 2019; Adimalla et al. 2018). Lastly, Wi and qi were used to determine the

Table 1 Relative weights for each parameter

Chemical parameters	Weight (wi)	Relative weight (Wi)	Si	Ci	qi	Sli
pH	4	0.088889	8.5	7.9	92.9	8.2
EC	3	0.066667	1500	970	64.6	4.3
TDS	2	0.044444	500	394	78.8	3.5
TH	2	0.044444	300	270	90	4
Ca^{2+}	3	0.066667	75	18.955	25.2	1.6
Mg^{2+}	3	0.066667	30	24.270	80.9	5.3
K^{+}	3	0.066667	10	0.886	8.8	0.5
Na^{+}	3	0.066667	200	78.027	39	2.6
HCO_3^{-}	4	0.088889	300	195.2	65	5.7
Cl^{-}	3	0.066667	200	46.219	23.1	1.5
NO_3^{-}	5	0.111111	45	28.588	63.5	7.05
SO_4^{2-}	5	0.111111	200	30.843	15.4	1.7
F^{-}	5	0.111111	1.5	0.24	16	1.7
	45	1				48.2

SIi for individual parameters, and hence, WQI can be determined by the equation given below:

$$\mathrm{SIi} = \mathrm{Wi} \times \mathrm{qi} \tag{3}$$

$$\mathrm{WQI} = \sum_{i=1}^{n} \mathrm{SIi} \tag{4}$$

where SIi is the subindex of each parameter. Relative weight method values are presented in Table 2.

Health risk assessment

Health risk assessment consists of four phases like

(I) Identification of risk, (II) Assessment of Dosage, (III) Exposure valuation, and (IV) Hazard characterization are recommended US environmental protection agency (Narsimha and Rajitha 2018; Li and Qian 2018).

In this work F^{-}, NO_3^{-} concentration in groundwater was selected as the parameter for the evolution of human health risk assessment (USEPA 2014). To determine exposure dose ADD through ingestion and potential non-carcinogenic (HQ)

$$\mathrm{ADD} = \frac{\mathrm{CPW} \times \mathrm{IR} \times \mathrm{ED} \times \mathrm{EF}}{\mathrm{ABW} \times \mathrm{AET}} \tag{5}$$

where ADD indicates F^{-}/NO_3^{-} intake (mg/kg/day), CPW indicates specific groundwater pollutant (mg/L), IR denotes the rate of ingestion per year (2.5 L/day adults; 0.78 L/day for children; 0.3 L/day infants) (Narsimha and Rajitha 2018), ED indicates the duration of exposure (Years 64,12 and 0.25 for adults, children, infants, respectively) (Ahada and Suthar 2017), EC indicates the frequency of exposure (days/year, 365 for adults, children, infants), ABW denotes average body weight of the human body in kg [57.5 (adults), 18.7 (Children), and 16.9 (infants)], and AET denotes average exposure time (Days, 23,360 adults, 4380 children's and 365 infants).

Hazard quotient appears if the pollutant exposure dose exceeds the reference dose toxicity effects may appear. This is commonly referred to as the hazard coefficient (HQ). RfD referred to as exposure dosage of F^{-}&NO_3^{-} is 0.4 and 1.6 mg/kg/L, respectively (USEPA 2012). HQ is determined by the following equation.

$$\mathrm{HQ} = \frac{\mathrm{ADD}}{\mathrm{RfD}} \tag{6}$$

Table 2 Health risk related to fluoride ingestion in individuals. *Source*: W.H.O. 1996; Dissanayake 1991)

Classes	F (mg/L)	Effects on human health	Samples	% of samples
Class I	< 0.5	Conductive to dental caries	4	10
Class II	0.5–1.5	Enhances strengthening of bones and teeth	20	50
Class III	1.5–4	Dental fluorosis (mottling of teeth)	16	40
Class IV	4.0–10	Dental and skeletal fluorosis (pain in neck and back bones)	Nil	Nil
Class V	> 10	Crippling fluorosis		

HQ values < 1 indicate that there is no carcinogenic effect, while HQ values > 1 is treated as the unacceptable risk of non-carcinogenic effects on human health (USEPA 2014; Li and Qian 2018).

The non-carcinogenic risk total hazard index (THI) is determined by applying Eq: 3 in which maximum permissible cutoff for non-carcinogenic THI is (USEPA 2014).

$$\mathrm{THI} = \sum_{i=1}^{n} \mathrm{HQi} \tag{7}$$

Analytical accuracy/ion balance

The accuracy of geochemical analysis was assed using the relationship between the concentration of total cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} and the concentration of total anions like CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, and F^- denoted in mill equivalent per liter (meq/L) for each sample, and ionic balance error (IBE) was computed to collaborate the analytical accuracy by the equation shown below:

$$\mathrm{IBE} = \frac{\sum \mathrm{Cations} - \sum \mathrm{Anions}}{\sum \mathrm{Cations} + \sum \mathrm{Anions}} \times 100 \tag{8}$$

The result of ionic balance error (IBE) was within the acceptable limit of ± 3% (Domenico and Schwartz 1990).

Results and discussions

The results of chemical analysis and its statistical data are denoted in Tables 3 and 4. Groundwater samples were analyzed for various ionic and non-ionic parameters to assess the quality. The results are examined in compliance with the Bureau of Indian Standards BIS (2012), and WHO (2012) drinking water standards are presented in Table 4.

Major ion chemistry

pH of groundwater ranges from 7.05 to 8.97, indicating that alkaline nature may be due to precipitation & dissolution process of groundwater (Wagh et al. 2019, 2020). The permissible limit of pH value for drinking water is specified as 6.5–8.5 (WHO 2012). Most of the groundwater is within the permissible limit of pH. Though higher pH could not affect human health, it may affect the taste of drinking water. Electrical conductivity (EC) ranges from 369 to 2590 µS/cm. EC of groundwater can be classified into three categories as (1) class I low salt concentration: EC < 1500 µS/cm, (2) class II average salt concentration: EC 1500–3000 µS/cm, and (3) class III high salt concentration: EC > 3000 µS/cm (Subba Rao et al. 2012). According to this classification of EC, 77.5% of the samples belong to class I (low salt concentration), and 22.5% of samples fall under class II (average salt concentration). Higher EC in groundwater may be due to evaporation and anthropogenic processes. Total dissolved solids (TDS) vary between 188 and 1340 mg/L with a mean of 1232 mg/L. Most of the samples are within the permissible limit of TDS. Generally, higher TDS values in groundwater are due to salt leaching from soils and mining and agricultural activities (Kadam et al. 2019). TH values vary from 100 to 520 mg/L in the study area. The permissible limit of TH for drinking purposes is 500 mg/L (WHO 2012; BIS 2012), and only one sample is exceeding the permissible limit. However, according to Sawyer and McCarthy (1967), TH: < 75 belong to soft category; 75–150 moderately hard; 150–300 hard; and > 300 very hard category. As per this classification 7.5% of the samples belong to the moderately hard category, 67.5% samples are of hard category and 25% of samples belong to the hard categories.

The chemistry of major ions helps to understand the hydrogeochemical process of the groundwater. In the study region, calcium (Ca^{2+}) and magnesium (Mg^{2+}) values in groundwater range from 8.8 to 88.5 and 9.7 to 122 mg/L, respectively. All groundwater samples are within the permissible limit of calcium (> 75 mg/L) and magnesium (> 50 mg/L) (WHO 2012; BIS 2012). Sodium (Na^+) concentration ranges from 24.9 to 429 mg/L. Only two samples are exceeding the permissible limit of Na^+ (> 600 mg/L) (Table 4). The high Na^+ ion may be due to cation exchange and anthropogenic activities. Potassium (K^+) concentration ranges between 0.780 and 12.3 mg/L (Kadam et al. 2019). Only three samples are exceeding the permissible limit of K^+ (> 10 mg/L) (W.H.O 2012; BIS 2012) (Table 4). High potassium content in groundwater naturally occurs from geological sources of potassium or weathering of silicate minerals, and usage of K^+ rich fertilizers (Hem 1985).

Chloride (Cl^-) concentration ranges from 21.3 to 454 mg/L. Bicarbonate (HCO_3^-) concentration ranges between 24.4 and 366 mg/L. All groundwater samples are below the permissible limit of bicarbonate (600 mg/L) and chloride (1000 mg/L) as per WHO 2012 and BIS 2012. Sulfate (SO_4^{2-}) concentration ranges from 10.684 to 224 mg/L. All groundwater samples are within the permissible limit of 400 mg/L suggested by BIS 2012.

Nitrates in groundwater

Agriculture and livestock production accounts for nearly 80% of all the nitrogen added to the environment. Nitrate contamination in groundwater is primarily due to unrestricted usage of N-fertilizer, the unavailability of established soil and water management methods, septic tanks, and inappropriate removal of domestic wastes (Canter 1996; Adimalla 2020b). Nitrate concentration in the study

Table 3 Physicochemical parameters concentrations of the study area

S. no.	Well depth in meters	pH	EC	TDS	TH	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	F^-
1	20	7.9	970	394	270	18.9	24.2	8	78.0	46.2	28.5	30.8	195.2	0.24
2	25	7.9	2245	1150	395	23.3	23.6	1.1	110.8	56.6	39.2	56.1	195.2	0.27
3	35	7.6	2280	1020	415	31.1	122	1.2	140.4	322	269	92.7	244	1.27
4	20	8.5	800	435	210	44.7	65.4	0.7	103.5	71.8	0.4	224.2	195.2	0.62
5	60	8.4	1600	950	310	68.2	43.4	5.6	70.8	34.3	25.2	24.6	195.2	2.06
6	34	8.1	970	450	260	58.6	46.7	2	78.4	51.3	28.4	81.2	195.2	0.73
7	37	8.1	1500	700	310	33.6	41.4	2	39.1	37.8	23.4	11.6	268.4	0.66
8	26	8.4	715	340	160	62.7	62.2	4.8	429.4	43	54.5	24.3	47.3	0.46
9	31	8.5	1145	540	280	44	53.3	11.8	34.3	52.2	30.9	180.2	47.9	0.79
10	35	7.8	1024	520	225	56.2	52.8	8.6	56.4	50.6	26.4	23.4	38.3	0.71
11	42	8.2	782	420	272	69.3	50.3	1.5	24.9	69.9	0.14	52.8	38.8	1.6
12	40	8.6	745	410	254	70.4	56.4	7.8	210.4	51.2	63.4	11.6	40	1.2
13	35	8.1	1175	550	301	32.2	42.2	2.2	40.4	60.8	58.6	10.6	41	2.5
14	60	8.42	823	382	160	24.3	34.2	0.9	98.2	28.4	54.4	30.8	292.8	3
15	27	8.85	390	203	160	8.85	9.7	0.8	125.2	35.5	56.4	40.3	73.2	0.87
16	39	8.1	1450	750	300	48.4	58.3	2.7	78.6	312	35.5	34.5	146	1.6
17	20	8.5	2590	1340	280	16.7	43.7	3.6	92.2	454	45.6	45.2	317.2	0.88
18	36	8.25	369	188	100	40.8	14.5	5.2	47.6	42.6	34.4	42.4	122	0.8
19	52	8.8	1500	800	200	16.4	38.8	1.8	97.3	35.5	56.4	60.2	317.2	2.3
20	45	8.04	2150	1100	280	16.4	58.3	2.5	78.4	78.1	48.6	54.1	292.8	0.87
21	37	8.4	1040	540	200	16.9	38.8	9.2	47.8	142	50.4	34.3	219.6	0.92
22	35	8.07	634	327	180	16.2	19.4	7.6	38.4	135	58.5	48.6	195.2	0.74
23	47	7.05	1070	555	220	40.3	38.8	10.5	78.9	21.3	60.4	60.5	268.4	1.8
24	35	8.39	1430	740	340	24.2	77.7	8.3	85.6	220	43.3	58.3	244	1.19
25	42	8.21	1760	910	140	24.8	20.6	7.5	78.2	135	62.1	43.3	219.6	1.55
26	26	8.67	2170	1120	520	56.3	117	1.6	140.7	369	60.4	48.9	244	0.6
27	28	8.97	1450	750	180	16.3	9.72	1.8	160.4	85.2	57.4	70.3	366	0.92
28	37	8.61	1180	610	140	56.7	24.3	3.4	80.4	56.8	35.5	72.7	317.2	1.8
29	39	7.87	1710	880	280	16.9	43.7	1.5	115.5	234	43.3	64.6	24.4	0.82
30	28	8.51	826	423	200	40.9	24.3	1.5	78.6	71	46.6	68.2	122	0.7
31	25	8.8	1220	630	160	40.6	14.5	4.3	95.6	121	50.4	30.8	268.4	0.4
32	30	8.05	1000	516	260	88.5	38.8	12.3	56.1	106	52.3	42.3	170.8	1.52
33	34	7.95	1150	590	360	40.4	53.4	8.4	48.6	85.2	48.8	54.1	195.2	1.8
34	60	8.1	811	421	200	40.2	29.1	5.3	42.6	49.7	52.5	61.8	195.2	2.2
35	45	8.13	1070	550	240	24.1	43.7	9.2	78.5	99.4	60.4	67.7	47.9	1.2
36	34	7.75	967	500	260	24.3	38.8	5.4	120.8	78.1	58.4	53.6	38.3	0.51
37	38	8.31	792	409	200	40.2	24.3	2.4	68.9	42.6	54.3	46.8	38.8	0.97
38	40	8.43	774	400	200	40.3	29.1	3.4	56.3	35.5	48.6	50.4	40	0.83
39	27	8.2	1170	600	300	32.4	53.4	1.5	98.5	85.2	53.4	58.8	41	1.8
40	55	8.5	1340	715	180	24.5	47.2	2.6	54.2	34.8	42.5	73.6	45	2

*All parameters are expressed in mg/L except pH and EC

region ranges from 0.143 to 269 mg/L. 62.5% of samples are above the permissible of nitrate (> 45 mg/L) (WHO 2012; BIS 2012) (Table 4). Children and young livestock are more prone to nitrate contamination in drinking water. Nitrates in groundwater cause reducing oxygen-carrying capacity in the blood; it can lead to methemoglobinemia (blue-baby syndrome) which is the deadliest effect of nitrate exposure, and there are other serious chronic health impacts like thyroid enlargement, 15 types of cancers, birth defects, hypertension, etc. (Forman et al. 1985; Wagh et al. 2019). In the different processes of the nitrogen cycle, nitrite and nitrates are produced (Ekemen Keskin 2010). NO_3^- is one

Table 4 Statistical data of physicochemical parameters of groundwater

Parameters	Average	Range	W.H.O. (2012)		BIS (2012)		Exceeding permissible limit in % (no of samples)	
			Most desirable	Not permissible	Most desirable	Not permissible	W.H.O. (2012)	BIS (2012)
pH	8.23	7.05–8.97	6.5–8.5	< 6.5 and > 8.5	6.5	8.5	20 (8)	20 (8)
EC	1232	369–2590	< 500	> 1500	500	1500	20 (8)	–
TDS	627	188–1340	< 500	> 1500	500	1500	Nil	Nil
TH	250	100–520	< 100	> 500	300	600	Nil	Nil
Ca^{2+}	38	8.8–88.5	< 75	> 200	75	200	Nil	Nil
Mg^{2+}	44	9.7–122	< 50	> 150	30	100	5 (2)	5(2)
K^+	4.54	0.78–12.3	< 10	> 10	10	–	–	–
Na^+	98	24.9–429	< 200	> 600	200	–	Nil	Nil
Cl^-	110	21.3–454	< 250	> 500	250	1000	Nil	Nil
HCO_3^-	166.5	24.4–366	< 300	> 600	–	–	–	–
NO_3^-	54.51	0.14–269	< 45	> 45	45	–	62.5 (25)	62.5 (25)
SO_4^-	59.0	10.6–224	< 200	> 250	150	400	Nil	Nil
F^-	1.21	0.24–3.0	< 1.5	> 1.5	1	1.5	35 (14)	35 (14)

*All parameters are expressed in mg/L except pH and EC

of the predominant ions in oxygenated water because it had rapid oxidation property. Usually, nitrate found in inorganic fertilizers by this nitrate occurrence in groundwater is very low. If nitrates are found higher concentration in groundwater because the anthropogenic activates the result of leaching agricultural waste & contamination human and animal waste and leakage of septic tank (Adimalla and Qian 2019a; Karunaidhi et al. 2019; Adimalla 2020b), most of the study areas are occupied by gravelly loam and clay soils and cracking clay soils, which possess a low permeable property that makes nitrate infiltration process very slow (CGWB 2016; UDA 2007). Apart from agricultural practices, a higher concentration of nitrates is leached into groundwater in the study area may be due to pollution by inactive/abandoned mine impoundment. In the study area, inactive/abandoned mines are present nearby inhabitant's areas apart from agricultural land areas. Due to this, maximum of the domestic waste and agriculture waste (fertilizer, pesticides, etc.) are dumped into the inactive/abandoned mining areas. Nitrogen and potassium are key elements added as fertilizer in enhancing the yielding capacity of banana and lime crops. In this region, application of nitrate and potassium fertilizers throughout crop period for banana and lime cultivation for every 2–3 weeks is 200 kg/h and 52 kg/h, respectively (Al-Harthi and Al-Yahyal 2009). Due to heavy rainfall in the post-monsoon period, agriculture wastewater will be flown into the inactive mine impoundment. Poultry waste disposal and household/cultivate animal dung fertilizers which were used in agriculture utility are deposited in inactive mine impoundment that reach the groundwater through the infiltration and return flow of irrigation for drinking purposes (Abdesselam et al. 2016; Ako et al. 2014; Raju et al. 2009a, b; Lokesh 2013; Oenema et al. 2005; Adimalla and Taloor 2020). As the majority of the people in this region depend on agricultural practices for their livelihood, the application of fertilizers for crop yields might also be the chief contributing factor for high nitrate concentration. From the spatial distribution map (Fig. 3), it is clear that intensive farming of banana and sweet lime which are located nearby inactive mining areas might have contributed most of the nitrate concentrations in this region. Intensive agricultural practices and human and animal waste disposed of into inactive mine impoundments are the main factors responsible for higher nitrate in the study area.

Fluoride ion chemistry in groundwater

Fluoride concentration in this region varies from 0.24 to 3.0 mg/L. 60% of samples is exceeding the permissible limit of fluoride (1.5 mg/L). Based on permissible limit, fluoride ion groundwater is classified into four classes: Class I: conductive to dental caries (> 0.5), Class II: enhances strengthening of bones and teeth (1.5); Class III: dental fluorosis (1.5–4), Class IV: dental and skeletal fluorosis (4–10); and Class V: crippling fluorosis (> 10) from this classification; 40% of the samples are fall in class III category in the study region (Table 2) (WHO 2012; BIS 2012). Groundwater is the only reliable source of drinking in this region. The correlation coefficient of fluoride with other parameters was analyzed. Fluoride is showing positive correlation with pH, while the positive correlation of fluoride with Na^+, K^+, HCO_3^- reveals that alkalinity of groundwater with high bicarbonate concentration can increase fluorite solubility in this region

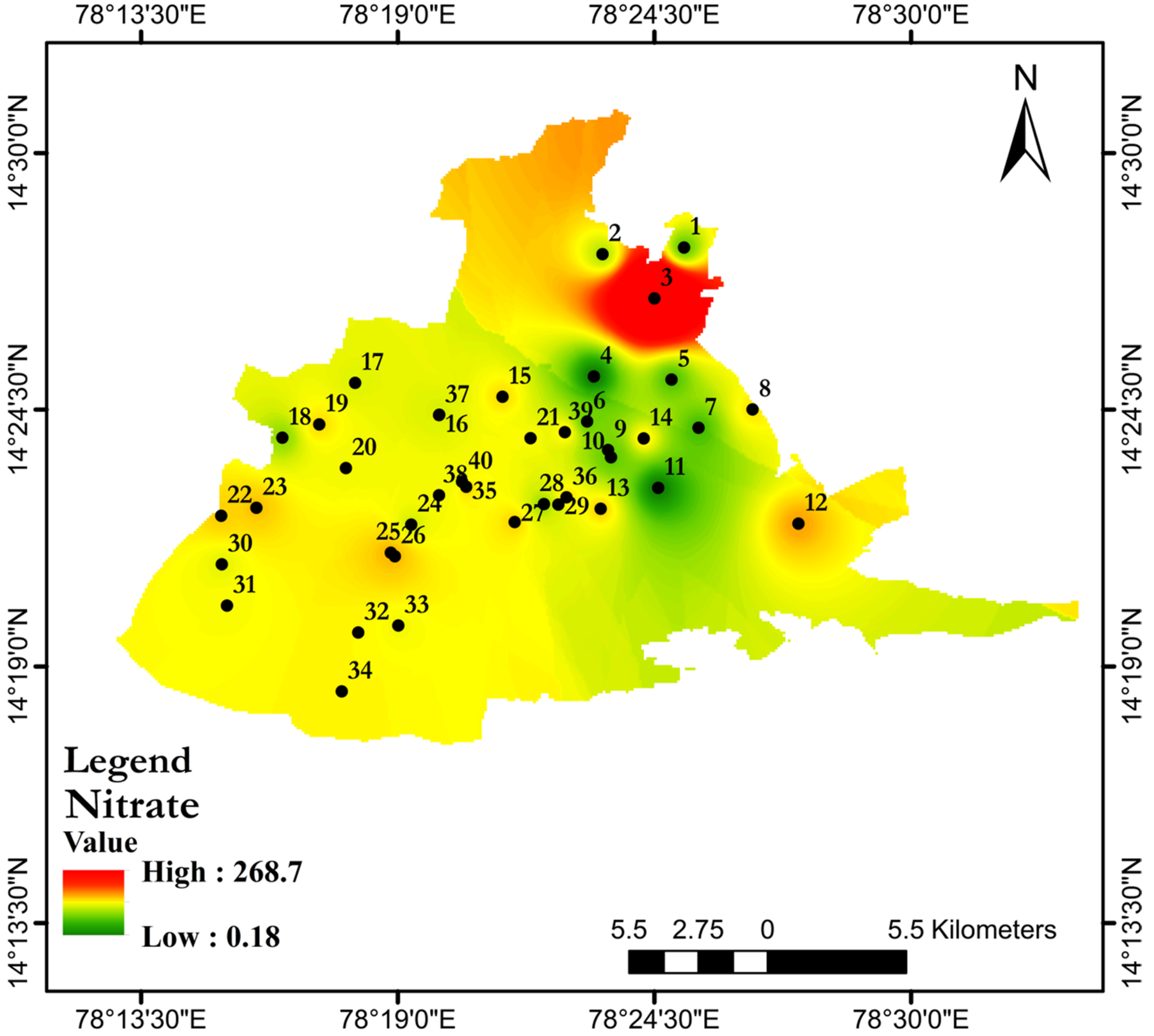


Fig. 3 Spatial distribution map of nitrate contamination areas

(Fig. 4a–e). As the ionic radius of fluoride ion is almost the same as that of hydroxide ion and the two ions commonly substitute one another in the crystal structure, F^- has a similar charge and about a similar range as of the hydroxide particles and form complexes with minerals of low solubility (Hem 1985). According to Brown and Roberson (1977), fluoride ions are easily replaced with OH^- in many rock-forming minerals. Some mineral surfaces may be capable of absorbing anions and if such surface carried fluoride ions, they could perhaps be available for release by substitution of OH^- ions from the water of high pH (alkaline). This indicates that the concentration of fluoride may be more in the waters of high pH (Hem 1985). Therefore, during chemical reaction fluoride can easily replace OH^- ions in many rock-forming minerals. Fluoride solubility in groundwater differs from one rock formation to another. Alkaline pH increases fluoride dissolution activity (Hem 1985; Vikas et al. 2009), whereas in acidic medium fluoride is adsorbed in clays (Saxena and Ahmed 2003; Rizwan and Gurdeep 2013). As most of the samples are alkaline in nature and positive correlation of fluoride with pH may favor the solubility of fluorine-bearing minerals in this region, fluorite, apatite, mica, amphiboles, certain clays, and williamite have the greatest effect on the hydrogeochemistry of fluoride (Raju et al. 2009a, b; Rango et al. 2008). Overall water quality (e.g., pH, alkalinity, hardness, and ionic strength) also plays an important role by influencing mineral solubility, complexation, and sorption/exchange reactions (Apambire et al. 1997; Adimalla and Venkatayogi 2017; Meenakshi et al. 2004; Raju et al. 2009a, b). Higher fluoride in groundwater of this region may due to basic flows along with igneous formation like dolerites and carbonate minerals (Brindha et al. 2011; Brindha and Elango 2013) Hence, geogenic forces are mainly responsible for high fluoride in groundwater because of ion-exchange reaction processes,

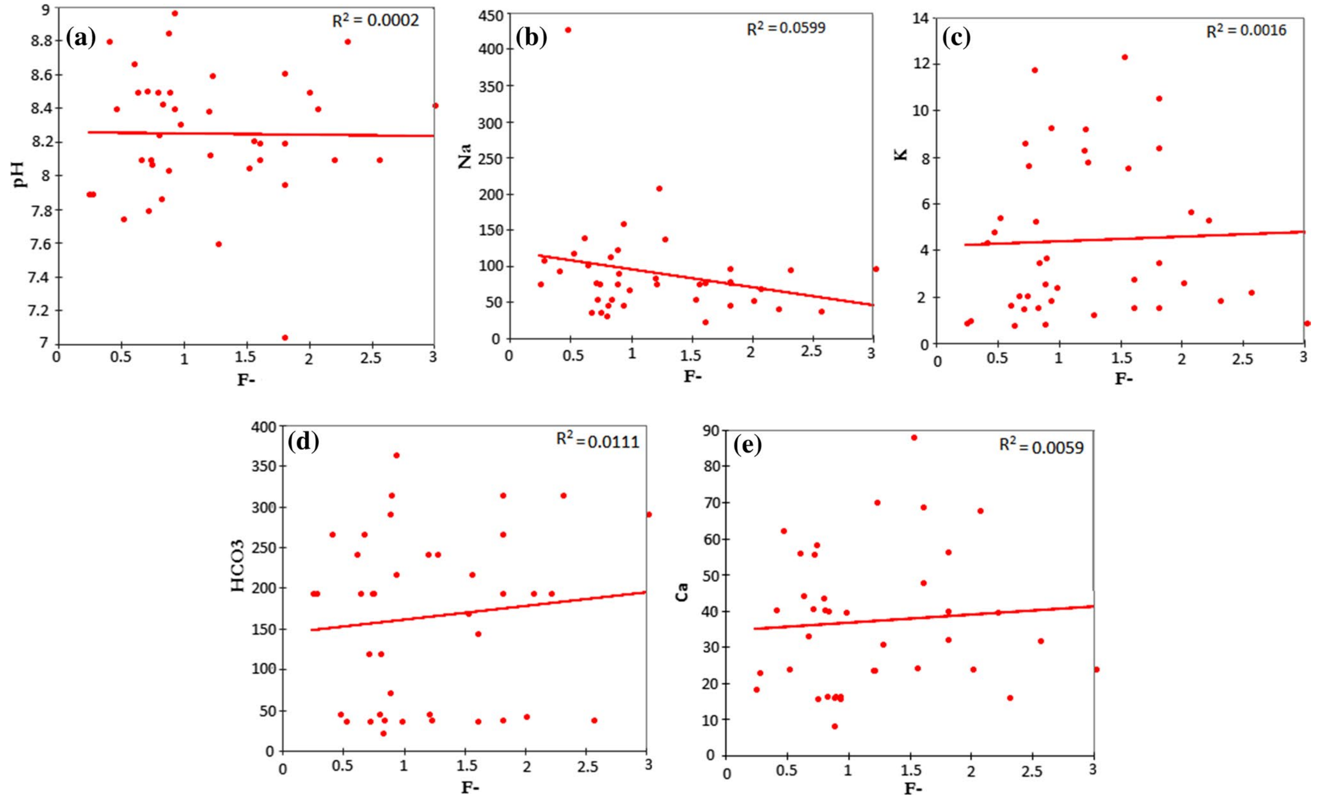


Fig. 4 Fluoride correlation with other physicochemical parameters

water–rock interactions, and influencing mineral solubility factors in the study area. In the chemical weathering process, dissolution of F^- ions is chiefly governed by Ca^{2+} ion driven by thermodynamic principles. Water on reaction with varying carbonate and other minerals plays a significant role in the evolution of groundwater chemistry and hence water–rock interaction that emerges as its characteristic chemistry. Though silicate minerals do not readily interact with groundwater, however, carbonate minerals chiefly occurring in sedimentary rocks, traces in igneous and metamorphic minerals are important in the evolution of most groundwater.

$$CaCO_3 + CO_{2(gass)} + H_2O_{(liquid)} \rightarrow Ca^{2+} + 2HCO_3^- \tag{9}$$

From this, solubility of fluorite can be expressed as (Brown and Roberson 1977)

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \tag{10}$$

$$CaF \leftrightarrow Ca^2 + 2F^- \tag{11}$$

Further reaction between calcite and fluoride ions contact with groundwater media resulted in equilibrium reactions of both solid and solute species. Saturation of groundwater concerning Ca^{2+} and F^- is given below (Prajapati et al. 2017).

$$CaCO_3 + 2F^- + H^+ = CaF_2 + HCO_3^- \tag{12}$$

The above equations reveal that groundwater having a high percentage of fluoride when it was mostly alkaline nature or residual alkalinity nature. Now it is clear that if the pH of the groundwater is constant, fluoride activity is directly proportional to bicarbonate abundance. Presently, groundwater of the study area had mostly alkaline nature; Fig. 3a shows a slightly positive correlation between fluoride and potential hydrogen. It is clear that potential hydrogen is one of the causes to be found higher fluoride in the study area, while some samples in the study may have low fluoride concentrations because the study area under the part of the semiarid environment and solubility process of F^- in groundwater vary from one rock formation to another. If pressure and temperature was under normal conditions, fluoride-bearing minerals have been sparingly soluble in water; under certain physicochemical conditions, dissolution processes are too fast (Prajapati et al. 2017; Adimalla et al. 2019d; Vikas et al. 2009; Adimalla 2020c). In the semiarid region, soil plays a major role in weathering and aqueous leaching processes that determine the amount of F^- in groundwater. Extensive irrigational practices and fertilizer usages are also a cause of higher fluoride concentration in groundwater. Generally, potash fertilizer had higher content of fluoride of 13–77 mg/kg; long-term usage of potash fertilizer (52 kg per hector) throughout the year adds up to fluoride in the groundwater of the study region (Brindha et al. 2011, Brindha and Elango 2013). Groundwater fluctuations and well depth also play an important role in creating a possible environment for the dissolution process below the earth's surface. Figure 5 represents that depth versus fluoride gives a clear idea on fluoride enhancing along with depth which indicates the source of fluoride to be fluoride minerals in the basement (Sunitha and Muralidhara Reddy 2018). From the spatial distribution map (Fig. 6), green color indicates the groundwater samples in villages that are within the standard permissible limit for drinking (< 1.5 mg/L) and red color denotes the groundwater samples in villages exceeding the permissible limits for drinking water (> 1.5 mg/L) according to WHO guidelines. North and middle portions of the study area high fluoride concentration (Fig. 6) indicate the release of fluoride due to water–rock interaction of basic flows and carbonate rocks. According to Dissanayake (1991), as per the health risk related to fluoride ingestion in human beings, 40% of samples belong to class III category (Table 2) are more prone to dental fluorosis.

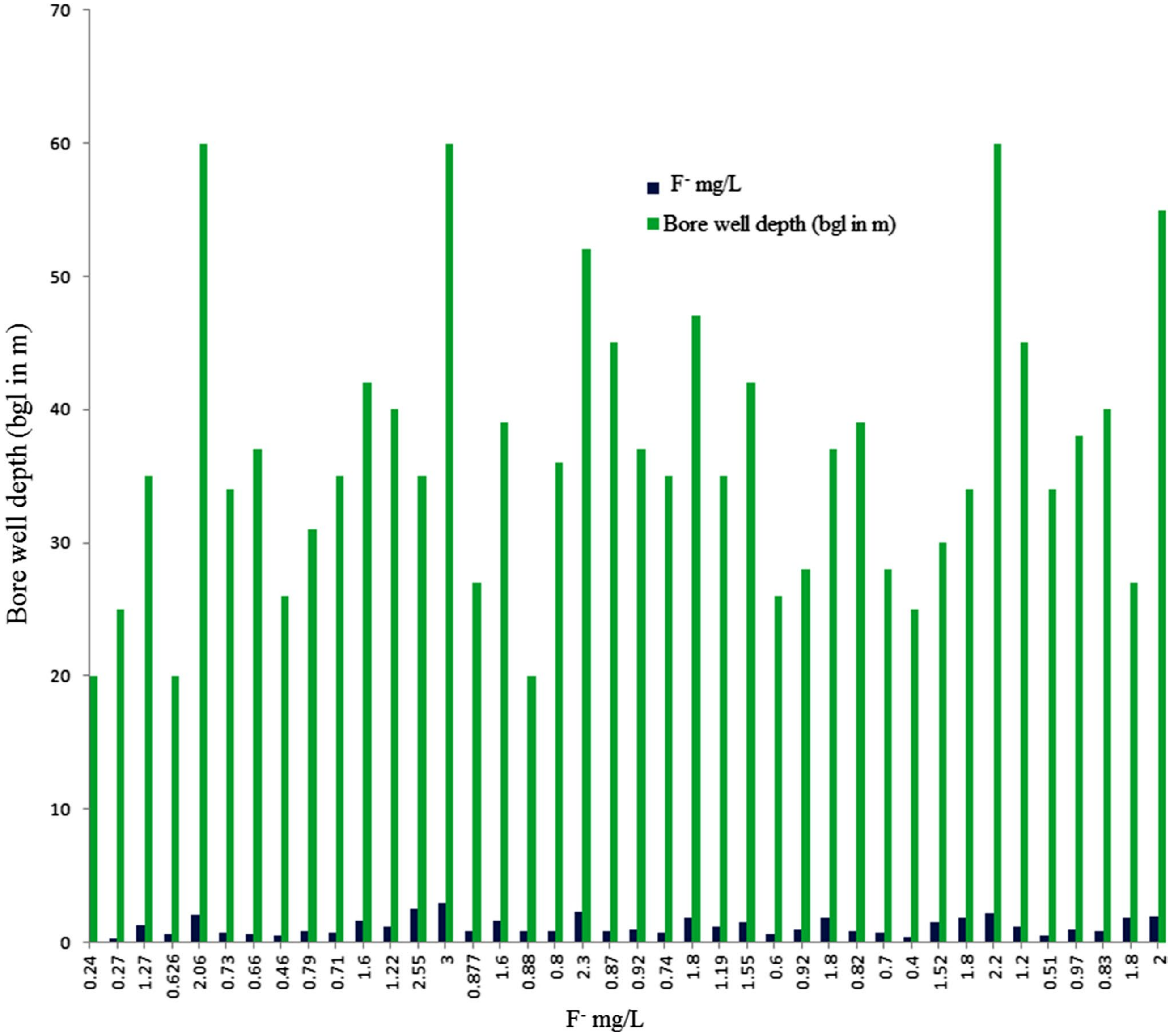


Fig. 5 Bar chart of F^- versus depth

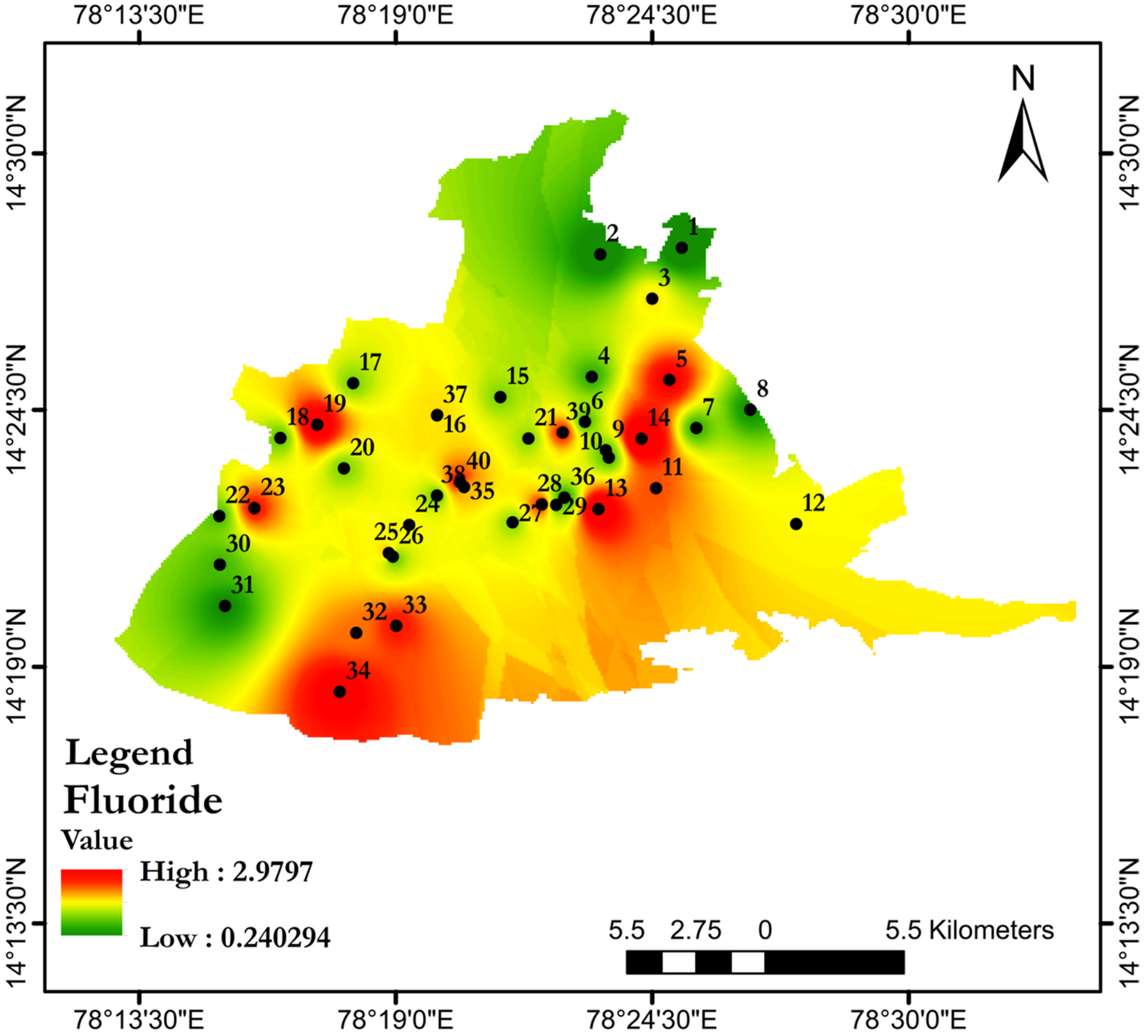


Fig. 6 Spatial distribution map of F⁻ contamination areas

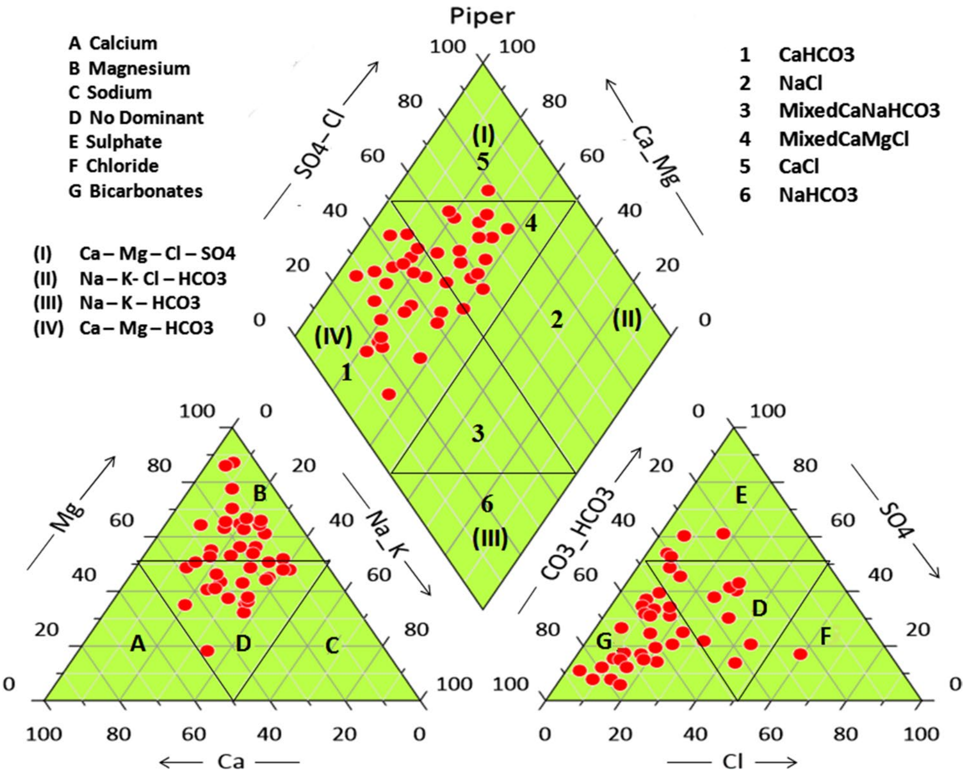
Hydrogeochemical facies

Piper diagram (1944) was a very effective tool to determine the hydrogeochemical facies of groundwater. It denotes the classification of water type, identification of hydrogeochemical facies, and mixing of two samples. Piper diagram includes two triangles and one diamond-shaped area. In this, one of them shows cations and another shows anion and remaining diamond-shaped area shows both anions and cations. According to this piper diagram, groundwater of this study group is six types. (I) Ca^{2+}–HCO_3^-, (II) Na^+–Cl^-, (III) mixed Ca^{2+}–Na^+–HCO_3^-,(IV) mixed Ca^{2+}–Mg^{2+}–Cl^-, (V) Ca^{2+}–Cl^-, and (VI) Na^+–HCO_3^- (Adimalla et al. 2019d). From the diamond-shaped triangular diagram, 57% of the samples belong to Ca–Mg–HCO_3 type and remaining 42% of the samples belong to mixed Ca–Mg–Cl type reveals that carbonate rock dissolution processes dominate in the groundwater of this region, and from cation triangle zone it is clear that 50% of the sample falls in no dominant zone; another 50% samples fall in magnesium dominant zone; from triangle anionic zone, 65% of the samples fall in bicarbonate zone and 25% samples fall in no dominance zone remaining samples fall in sulfate zone (Fig. 7).

Mechanisms of groundwater chemistry

The mechanism of groundwater chemistry was prepared by Gibbs (1970) for analyzing mechanisms of groundwater chemistry. It reveals the chemical reaction between the composition of water and the controlling mechanism of the natural water chemistry variations using graphical plots. TDS versus $Cl^-/Cl^-+HCO_3^-$ and TDS versus $(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$ were divided into three zones: precipitation, rock dominance zone, and evaporation dominance zones. Most of the groundwater samples fall in rock dominant zone, and it reveals that water–rock interaction or

Fig. 7 Piper diagram



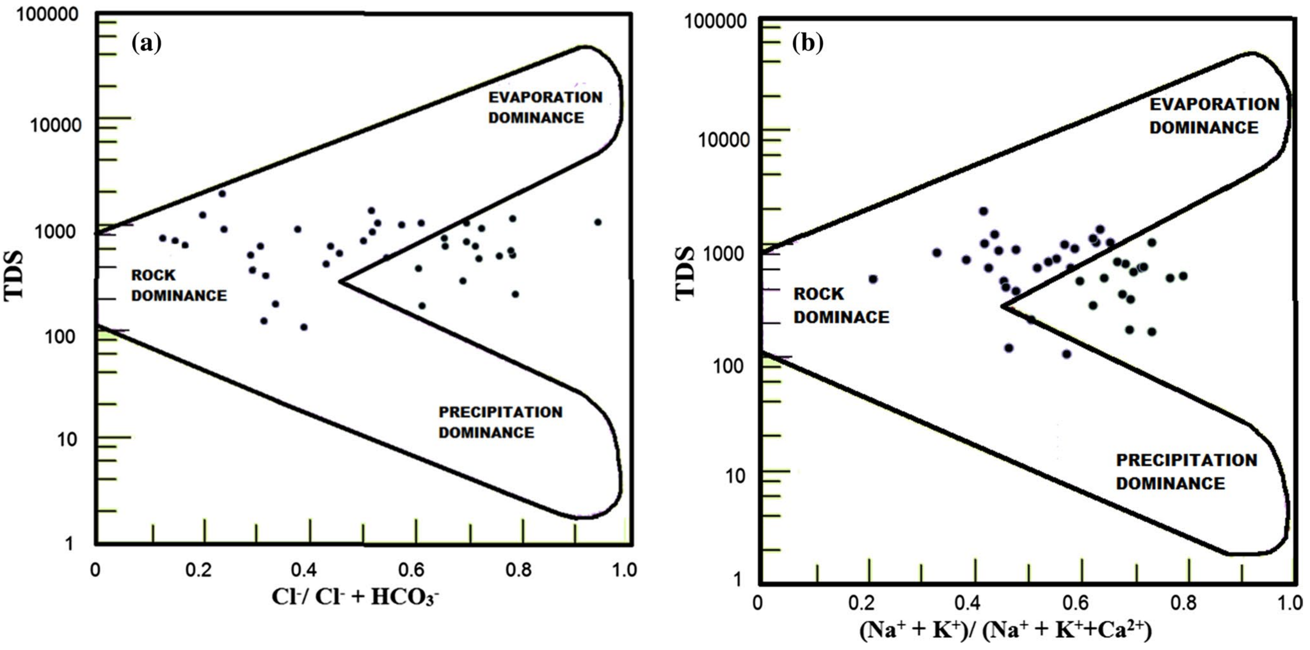


Fig. 8 Mechanism controlling of groundwater chemistry plots (Gibbs 1970) **a** $Cl^-/Cl^- + HCO_3^-$ **b** $(Na^+ + K^+)/(N^+ + K^+ + Ca^{2+})$

weathering of rock-forming minerals and also host rock weathering mechanisms predominate in this region (Fig. 8). These mechanisms are mainly responsible for high fluoride in groundwater of the study region (Adimalla 2020c; Adimalla and Venkatayogi 2017).

Water Quality Index in groundwater (WQI)

The estimation of groundwater suitability for drinking purposes in the Vemula-Vempalli region is achieved using the relative weight water quality index method. The selection of the physicochemical parameters for calculating the index depends on several factors such as the importance of the parameter and purpose of the index method presented in Table 1 (Drinking or Irrigation) (Aminiyan et al. 2018). The systematic computation of the WQI values varies from 83.7 to 186.1 mg/L (Table 5), and it was categorized as Class I: Good, Class II: Poor, Class III: Very poor, and Class IV: Unsuitable for drinking purposes. Water quality index classification as shown in Table 6, according to this classification, 7.5% of samples are excellent, 85% good, 12.5% poor for drinking purposes (Table 6). Higher WQI in the study area may be due to extensive irrigational practices and extensive groundwater exploitation, and geogenic forces like rock weathering mineral dissolution and also anthropogenic practices are responsible for founding high WQI values in this region. The spatial distribution map of the water quality index is shown in Fig. 9; it depicts that most of the study areas fall into the good category as denoted in green color, and some eastern parts show poor water quality shown in red color in this part may cause extensive irrigational practices and extensive groundwater exploitation main responsible factors (Ewaid and Abed 2017; Abdelkader 2017).

Human Health Risk Assessment (HHRA) of F$^-$ and NO$_3$$^-$

An innovative method developed by USEPA (United Environment Protection Agency) has designed as a modern method to assess human health risk assessment has vide applicability (Adimalla 2020a, b; Adimalla et al. 2019a). The evolution of non-carcinogenic risks due to fluoride and nitrate in groundwater is of greater concern in many countries (Narsimha and Rajitha 2018; Nadia et al. 2015). Continuous consumption of contaminated drinking water affects human health. Fluoride and nitrate contamination in drinking water is of greater public health concern in many regions of the world. These ions are regarded as a non-carcinogenic risk to human health for adults, children, and infants. Eventually, excessive concentration of F$^-$ and NO$_3$$^-$ in drinking water in the study region poses adverse impact on human health, for which health risk assessment has been employed in the study area. Hence, this study aims in the assessment of human health risk considering drinking water as the main passage. To identify this problem, hazard quotient (HQ) is an essential tool to determine non-carcinogenic health risk by computing-related hazard index (HI) as depicted in Table 7. The higher concentration of fluoride and nitrate ions is observed in Vemula-Vempalli region. HQ values of fluoride in this region range between 0.15 and 1.92 (adults), 0.16 and 1.95 (children), and 0.12 and 1.49 (infants) with an average values of 0.78, 0.79, and 0.60, respectively (Table 7). From the USEPA 2014 guidelines, 30%, 30%, 12.5% of the groundwater are > 1 (Table 8) and may cause adverse health impacts on adults, children, and infants, respectively. HQ values of nitrates in the study area range from 0.003 to 6.46 (adults), 0.003 to 6.55 (children), and 0.003 to 4.99 (infants) with the average value of 1.31, 1.32, and 1.01, respectively (Table 7). 70%, 70%, and 37.5% of the groundwater samples

Table 5 WQI at individual sampling station

S. no.	WQI	Water quality status
1	48.2	Excellent
2	68.4	Good
3	167.5	Poor
4	67.1	Good
5	80.5	Good
6	64.6	Good
7	61.3	Good
8	74.8	Good
9	74.3	Good
10	60.9	Good
11	57.2	Good
12	186.1	Poor
13	75.2	Good
14	78.8	Good
15	48.7	Excellent
16	84.9	Good
17	97.9	Good
18	47.1	Excellent
19	85.3	Good
20	83.3	Good
21	71.4	Good
22	61.8	Good
23	82.8	Good
24	91.1	Good
25	80.8	Good
26	114.5	Poor
27	73.6	Good
28	74.5	Good
29	72.6	Good
30	58.4	Good
31	64.5	Good
32	82.8	Good
33	83.6	Good
34	73.9	Good
35	74.5	Good
36	63.8	Good
37	57.4	Good
38	56.2	Good
39	76.4	Good
40	74.4	Good
	47.1	
	186.1	
	79.3	

Table 6 Water quality classification based on WQI value

Class	WQI value	% of samples	Water quality status
A	< 50	7.5	Excellent
B	51–100	85	Good
C	101–200	12.5	Poor water
D	201–300	Nil	Very poor water
E	> 300	Nil	Water un suitable for drinking

are above the acceptable limit > 1 (Table 8) and may cause a health risk of adults, children, and infants, respectively. According to the USEPA 2014 guidelines, THI values must not be above > 1. If the THI values are above > 1, that shows non-carcinogenic effects on human beings. From the results, it is clear that THI values in this region range from 0.41 to 7.28 (adults), 0.41 to 7.38 (children), and 0.31 to 5.62 (infants) with the average values of 2.06, 2.09, and 1.59, respectively (Table 8). Figure 10 denotes comparison of THI in the studied groups as denoted, the THI in each of the three groups was greater than 1, which has to be taken care of and proper precautionary measures.

Conclusions

Groundwater is the prime source for drinking and irrigation in the Vemula-Vempalli region, Kadapa District, South India. The study mainly focused on exploring the groundwater quality in the view of drinking purposes.

- Groundwater is alkaline and hard. Most of the parameters are below the permissible limit of BIS and W.H.O. limits except fluoride and nitrate. Groundwater is not potable in terms of nitrate and fluoride. Based on the WQI classification for drinking purposes, 12.5% of

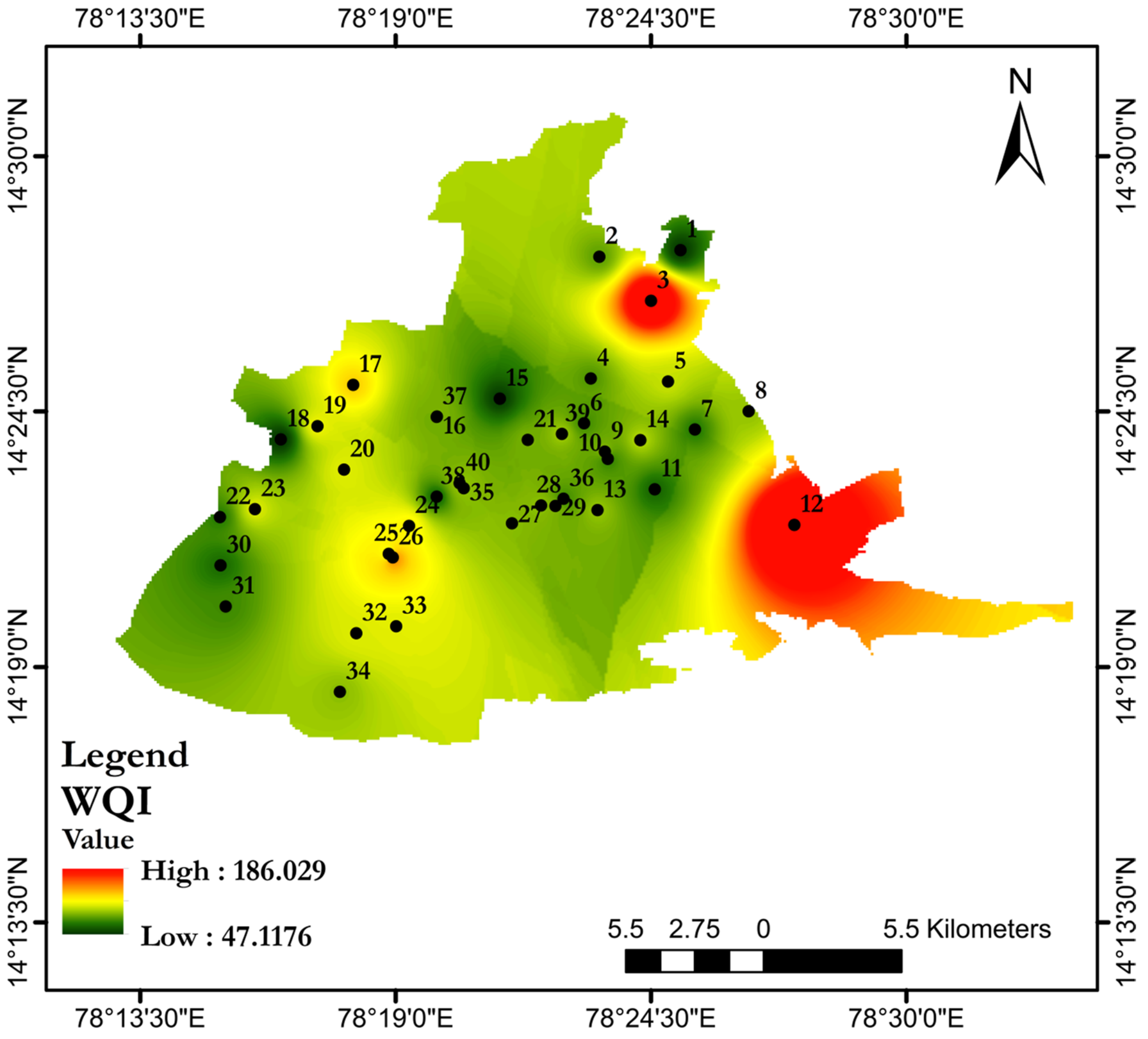


Fig. 9 Spatial distribution map of water quality Index

Table 7 Computation of hazard quotient for adults, children, and infants

S. no.	Adults			Children			Infants		
	HQF	HQN	HQT	HQF	HQN	HQT	HQ	HQN	HQT
1	0.15	0.68	0.84	0.16	0.69	0.85	0.12	0.53	0.64
2	0.17	0.94	1.11	0.18	0.95	1.13	0.13	0.72	0.86
3	0.81	6.46	7.28	0.83	6.55	7.38	0.63	4.99	5.62
4	0.40	0.01	0.41	0.41	0.01	0.41	0.31	0.009	0.31
5	1.32	0.60	1.92	1.34	0.61	1.95	1.02	0.46	1.48
6	0.47	0.68	1.15	0.47	0.69	1.16	0.36	0.52	0.88
7	0.42	0.56	0.98	0.43	0.57	0.99	0.33	0.43	0.76
8	0.29	1.31	1.60	0.30	1.33	1.62	0.23	1.01	1.24
9	0.51	0.74	1.24	0.51	0.75	1.26	0.39	0.57	0.96
10	0.46	0.63	1.09	0.46	0.64	1.10	0.35	0.49	0.84
11	1.03	0.003	1.02	1.04	0.003	1.04	0.79	0.003	0.79
12	0.78	1.52	2.30	0.79	1.54	2.33	0.60	1.17	1.78
13	1.63	1.41	3.04	1.66	1.42	3.08	1.26	1.08	2.35
14	1.92	1.30	3.23	1.95	1.32	3.27	1.49	1.01	2.49
15	0.56	1.35	1.91	0.57	1.37	1.94	0.43	1.04	1.48
16	1.03	0.85	1.88	1.04	0.86	1.90	0.79	0.66	1.45
17	0.56	1.09	1.66	0.57	1.11	1.68	0.44	0.84	1.28
18	0.51	0.82	1.34	0.52	0.84	1.35	0.40	0.63	1.03
19	1.47	1.35	2.83	1.50	1.37	2.87	1.14	1.04	2.18
20	0.56	1.17	1.72	0.57	1.18	1.75	0.43	0.90	1.33
21	0.59	1.21	1.80	0.60	1.23	1.82	0.46	0.93	1.39
22	0.47	1.40	1.88	0.48	1.42	1.90	0.37	1.08	1.45
23	1.15	1.45	2.60	1.17	1.47	2.64	0.89	1.12	2.01
24	0.76	1.04	1.80	0.77	1.05	1.82	0.59	0.80	1.39
25	0.99	1.49	2.48	1.01	1.51	2.52	0.77	1.15	1.92
26	0.38	1.45	1.83	0.39	1.47	1.86	0.30	1.12	1.41
27	0.59	1.38	1.97	0.60	1.40	1.99	0.46	1.06	1.52
28	1.15	0.85	2.00	1.17	0.86	2.03	0.89	0.66	1.55
29	0.53	1.04	1.56	0.53	1.05	1.58	0.41	0.80	1.21
30	0.45	1.12	1.57	0.46	1.13	1.59	0.35	0.86	1.21
31	0.26	1.21	1.46	0.26	1.22	1.48	0.20	0.93	1.13
32	0.97	1.25	2.23	0.99	1.27	2.26	0.75	0.97	1.72
33	1.15	1.17	2.32	1.17	1.19	2.36	0.89	0.90	1.79
34	1.41	1.26	2.67	1.43	1.28	2.71	1.09	0.97	2.06
35	0.77	1.45	2.22	0.78	1.47	2.25	0.59	1.12	1.71
36	0.33	1.40	1.73	0.33	1.42	1.75	0.25	1.08	1.33
37	0.62	1.30	1.92	0.63	1.32	1.95	0.48	1.00	1.48
38	0.53	1.16	1.70	0.54	1.18	1.72	0.41	0.90	1.31
39	1.15	1.28	2.43	1.17	1.30	2.47	0.89	0.99	1.88
40	1.28	1.02	2.30	1.30	1.03	2.33	0.99	0.78	1.77
	0.15	0.003	0.41	0.16	0.003	0.41	0.12	0.003	0.31
	1.92	6.46	7.28	1.95	6.55	7.38	1.49	4.99	5.62
	0.78	1.31	2.06	0.79	1.32	2.09	0.60	1.01	1.59

samples are of poor quality for drinking purposes and unhealthy for the domestic purpose in this region. It may be due to a higher amount of hardness and extensive agricultural practices in this region.

- Around 60% of the groundwater is above the permissible limit (1.5 mg/L) of fluoride in groundwater of the study area. Geogenic forces like water–rock interaction of carbonate rocks and basic flows (Dolerites), mineral

Table 8 Assessment of non-carcinogenic risk of adult, children, and infants based on total hazard index

	HQ fluoride		HQ nitrate		THI	
	Safe	Risk	Safe	Risk	Safe	Risk
NCA	NS < 1 (PS)	NS > 1 (PS)	NS < 1 (PS)	NS > 1 (PS)	NS < 1 (PS)	NS > 1 (PS)
Adults	28(70%)	12 (30%)	12 (30%)	28(70%)	3 (7.5%)	37 (92.5%)
Children	28 (70%)	12 (30%)	12 (30%)	28 (70%)	3 (7.5%)	37 (92.5%)
Infants	35 (87.5%)	5 (12.5)	25 (62.5%)	15 (37.5%)	8 (20%)	32(80%)

NCA non-carcinogenic risk, *HQ* hazard quotient, THI total hazard index, *NS* number of samples, *PS* percentage of samples

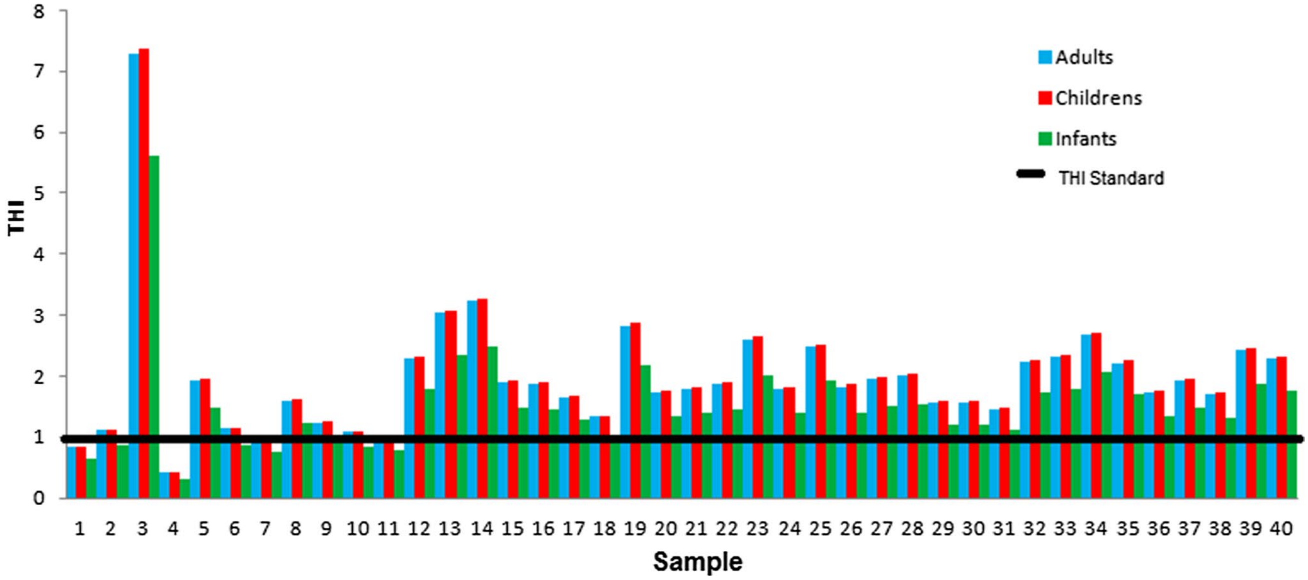


Fig. 10 Comparison of THI in the studied groups with THI Standard

dissolution from carbonate rocks, extensive usages of fertilizers, and alkalinity of groundwater may cause higher fluoride concentration in this region, and it has Ca^{2+}–Mg^{2+}–HCO_3^- water type and rock dominance was favoring the dissolution of fluoride in groundwater and suitable defluoridation techniques are needed to purify this water. Higher nitrate concentrations may be due to extensive irrigation practices runoff from agricultural fields to inactive mine impoundments, and the usage of intensive potash-type fertilizers causes higher nitrate in groundwater. Hence, the source of fluoride and nitrate is geogenic and anthropogenic sources, respectively.

- Total hazard index values reveals that children are more prone to the risk of fluoride and nitrate than adults.
- This study will help the policy-makers to adopt proper remedial management techniques like defluoridation, nitrate removal setup (reverse osmosis process and ion exchange), and rainwater harvesting in the study area.

Acknowledgements This research has been financed by the Department of Science and Technology (DST-INSPIRE), Government of India; INSPIRE fellowship under AORC, sanctioned to the first author which is gratefully acknowledged. The authors are grateful to the editor and anonymous reviewers for suggestions and comments which improved the manuscript significantly.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Abdesselam S, Halitim A, Jan A (2016) Anthropogenic contamination of groundwater with nitrate in arid region: case study of southern Hodna (Algeria). Environ Earth Sci 70:2129–2141

Abdelkader B (2017) Assessment of water quality index for the groundwater in the upper cheliff plain, Algeria. J Geol Soc India 90:347–356. https://doi.org/10.1007/s12594-017-0723-7

Adimalla N (2019) Groundwater quality for drinking and irrigation purposes and potential health risks assessment: a case study from semi-arid Region of South India. Exposure Health 11(2):109–123. https://doi.org/10.1007/s12403-018-0288-8

Adimalla N (2020a) Controlling factors and mechanism of groundwater quality variation in semiarid region of South India: an approach of water quality index (WQI) and health risk assessment (HRA). Environ Geochem Health 42(6):1725–1752. https://doi.org/10.1007/s10653-019-00374-8

Adimalla N (2020b) Spatial distribution, exposure, and potential health risk assessment from nitrate in drinking water from semi-arid region of South India. Hum Ecol Risk Assess Int J 26(2):310–334. https://doi.org/10.1080/10807039.2018.1508329

Adimalla N (2020c) Assessment and mechanism of fluoride enrichment in groundwater from the hard rock terrain: a multivariate statistical approach. Geochem Int 58(4):456–471. https://doi.org/10.1134/S0016702920040060

Adimalla N, Li P (2019) Occurrence, health risks, and geochemical mechanisms of fluoride and nitrate in groundwater of the rock-dominant semi-arid region, Telangana State, India. Hum Ecol Risk Assess Int J 25(1–2):81–103

Adimalla N, Qian H (2019a) Groundwater quality evaluation using water quality index (WQI) for drinking purposes and human health risk (HHR) assessment in an agricultural region of Nanganur, south India. Ecotox Environ Safe 176:153–161

Adimalla N, Qian H (2019b) Spatial distribution and health risk assessment of fluoride contamination in groundwater of Telangana: a state-of-the-art. Geochemistry. https://doi.org/10.1016/j.chemer.2019.125548

Adimalla N, Taloor AK (2020) Hydrogeochemical investigation of groundwater quality in the hard rock terrain of South India using Geographic Information System (GIS) and groundwater quality index (GWQI) techniques. Groundw Sustain Dev. https://doi.org/10.1016/j.gsd.2019.100288

Adimalla N, Venkatayogi S (2017) Mechanism of fluoride enrichment in groundwater of hard rock aquifers in Medak, Telangana State, South India. Environ Earth Sci 76:45. https://doi.org/10.1007/s12665-016-6362-2

Adimalla N, Venkatayogi S (2018) Geochemical characterization and evaluation of groundwater suitability for domestic and agricultural utility in semi-arid region of Basara, Telangana State, South India. Appl Water Sci 8:44. https://doi.org/10.1007/s13201-018-0682-1

Adimalla N, Wu J (2019) Groundwater quality and associated health risks in a semi-arid region of south India: implication to sustainable groundwater management. Hum Ecol Risk Assess 25(1–2):191–216. https://doi.org/10.1080/10807039.2018.1546550

Adimalla N, Li P, Venkatayogi S (2018) Hydrogeochemical evaluation of groundwater quality for drinking and irrigation purposes and integrated interpretation with water quality index studies. Environ Process 5(2):363–383. https://doi.org/10.1007/s40710-018-0297-4

Adimalla N, Li P, Qian H (2019a) Evaluation of groundwater contamination for fluoride and nitrate in semi-arid region of Nirmal Province, South India: a special emphasis on human health risk assessment (HHRA). Hum Ecol Risk Assess Int J 25(5):1107–1124

Adimalla N, Marsetty SK, Xu P (2019b) Assessing groundwater quality and health risks of fluoride pollution in the Shasler Vagu (SV) watershed of Nalgonda, India. Hum Ecol Risk Assess. https://doi.org/10.1080/10807039.2019.1594154

Adimalla N, Qian H, Li P (2019c) Entropy water quality index and probabilistic health risk assessment from geochemistry of groundwaters in hard rock terrain of Nanganur County. Geochemistry, South India. https://doi.org/10.1016/j.chemer.2019.125544

Adimalla N, Venkatayogi S, Das SVG (2019d) Assessment of fluoride contamination and distribution: a case study from a rural part of Andhra Pradesh, India. Appl Water Sci 9:94. https://doi.org/10.1007/s13201-019-0968-y

Ahada CPS, Suthar S (2017) Assessment of human health risk associated with high ground water fluoride intake in southern districts of Punjab, India. Exposer Health. https://doi.org/10.1007/s12403-017-0268-4

Ako AA, Eyong GET, Shimada J (2014) Nitrate contamination of groundwater in two areas of the Cameroon Volcanic Line (Banana Plain and Mount Cameroon area). Appl Water Sci 4:99–113

Al-Harthi K, Al-Yahyal R (2009) Effect of NPK fertilizer on growth and yield of banana in northern Oman. J Hortic For 1(8):160–167

Aminiyan MM, Aitkenhead-Peterson J, Aminiyan FM (2018) Evaluation of multiple water quality indices for drinking and irrigation purposes for the Karoon river, Iran. Environ Geochem Health. https://doi.org/10.1007/s10653-018-0135-7

Apambire WB, Boyle DR, Michel FA (1997) Geochemistry, genesis and health implications of fluoriferous groundwater in the upper regions of Ghana. Environ Geol 33:13–24. https://doi.org/10.1007/s002540050221

APHA (2012) Standard methods for the examination of water and wastewater, 22nd edn. American Public Health Association, New York

BIS (2012) Indian standards specification for drinking water, BIS: 10500: 2012. http://www.cgwb.gov.in/Documents/WQ-standards.pdf

Bouderbala A (2017) Assessment of water quality index for the groundwater in the Upper Cheliff Plain, Algeria. J Geol Soc India 90:347–356. https://doi.org/10.1007/s12594-017-0723-7

Brindha K, Elango L (2013) Geochemistry of fluoride rich groundwater in a weathered granitic rock region, Southern India. Water Qual Expo Health 5:127–138. https://doi.org/10.1007/s12403-013-0096-0

Brindha K, Rajesh R, Murugan R, Elango L (2011) Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India. Water Qual Expo Health 172:481–492. https://doi.org/10.1007/s10661-010-1348-0

Brown DW, Roberson CE (1977) Solubility of natural fluorite at 25_C. USGS J Res 5(4):509–517

Brown RM, Mc Clelland NI, Deininger RA, Tozer RG (1970) A water quality index: do we dare? Water Sew Work 117:339–343

Bulusu KR, Pande SP (1990) Nitrates a serious threat to groundwater pollution. Bhu-Jal News 5:39–43

Canter LW (1996) Nitrates in groundwater. CRC Press, Boca Raton. ISBN 0873715691

Central Ground Water Board (CGWB) (2007) Ground water information. CGWB, Kadapa District

Central Ground Water Board (2013) Ministry of water resources Government of India Ground Water Brochure YSR District (Kadapa), Andhra Pradesh

Central Ground Water Board (2016) Ministry OF WATER RESOUrces Government of India Ground Water Brochure YSR District (Kadapa), Andhra Pradesh

Chaturvedi MK, Bassin JK (2010) Assessing the water quality index of water treatment plant and bore wells, in Delhi, India. Environ Monit Assess 163:449–453. https://doi.org/10.1007/s10661-009-0848-2

Davies BE (1983) Heavy metal contamination from base metal mining smelting: Implication of man and his environment. In: Applied environmental geochemistry (ed) 1st Thorton, Academic Press, London, pp 425–462

Dissanayake CB (1991) The fluoride problem in the groundwater of Sri Lanka-environmental management and health. Int J Environ Stud 38:137–156

Domenico PA, Schwartz FW (1990) Physical and chemical hydrogeology. Wiley, New York, p 824

Ekemen Keskin T (2010) Nitrate and heavy metal pollution resulting from agricultural activity: a case study from Eskipazar (Karabuk, Turkey). Environ Earth Sci 61:703–721. https://doi.org/10.1007/s12665-009-0385-x

Ewaid SH, Abed SA (2017) Water quality index for Al-Gharraf River, southern Iraq. Egypt J Aquat Res 43:117–122. https://doi.org/10.1016/j.ejar.2017.03.001

Forman D, Al-Dabbagh S, Doll R (1985) Nitrates, nitrites and gastric cancer in Great Britain. Nature 313:620–625

Geological Survey of India (GSI) (2001) District resource map. Cuddapah District, Andhra, Pradesh

Ghadepoori M et al (2018) Heavy metal analysis and quality assessment in drinking water Khorra mabad city, Iran. Data Brief 16:685–692. https://doi.org/10.1080/15569543.2017.1370601

Gibbs RJ (1970) Mechanisms controlling world water chemistry. Science 170:1081–1090

Guo F, Jiang G, Yuan D (2007) Major ions in typical subterranean rivers and their anthropogenic impacts in southwest karst areas, China. Environ Geol 53:533–541

Hem JD (1985) Study and interpretation of the chemical characteristics of natural water L: US Geological Survey water-supply paper 2254. US Geological Survey, Alexandria

Hem JD (1991) Study and interpretation of the chemical characteristics of natural water, 3rd edn. Scientific Publishers, Jodhpur

Jafari A et al (2014) Process optimization for fluoride removes from water by *Moringa oleifera* seed extract. Fluoride 47:152–160

Kadam A, Wagh Vasant, Umrikar B, Sankhua R (2019) An implication of boron and fluoride contamination and its exposure risk in groundwater resources in semi-arid region. Environment Development and Sustainability, Western India. https://doi.org/10.1007/s10668-019-00527-w

Karunaidhi D, Aravinthaswamy P, Subramani T, Wu J, Srinivasamoorthy K (2019) Potential health risk assessment for fluoride and nitrate contamination in hard rock aquifers of Shanmuganadhi River basin, South India. Hum Health Risk Assess Int J. https://doi.org/10.1080/10807039.2019.1568859

Kouadra R, Demdoum A (2019) Hydro geochemical characteristics of groundwater and quality assessment for the purposes of drinking and irrigation in Bougaa area. Acta Geochim, Northeastern Algeria. https://doi.org/10.1007/s11631-019-00393-3

Li P (2016) Groundwater quality in western China: challenges and paths forward for groundwater quality research in western China. Expo Health 8:305–310

Li P, Qian H (2018) Water resources research to support a sustainable China. Int J Water Res Dev 34(3):327–336. https://doi.org/10.1080/07900627.2018.1452723

Lokesh L (2013) A study of nitrate contamination in groundwater of Delhi, India. Asian J Water Environ Pollut 10:91–94

Massoudinejad M et al (2016) Adsorption of fluoride over a metal organic frame work uio-66 functionalized with amine group and optimization with response surface methodology. J Mol Liq 221:279–286

Meenakshi Garg VKM, Kavita R, Malik A (2004) Groundwater quality in some villages of Haryana, India: focus on fluoride and fluorosis. J Hazard Mater 106:85–97. https://doi.org/10.1016/j.jhazmat.2003.09.007

Mhlongo SE, Dacosta FA, Mphephu NF (2013) In search of appropriate rehabilitation strategies for Abandoned Nyala magnesite mine, Limpopo Province of South Africa. Int J Eng Appl Sci 2:58–70

Mirzaei R et al (2015) Nitrate contamination of drinking and agricultural groundwater resources in Shahrood and Damghan, Iran. J Mazandaran Univ Med Sci 25:117–127

Muralidhara Reddy B, Sunitha V, Prasad M, Sudharshan Reddy Y, Ramakrishna Reddy M (2019) Evaluation of groundwater suitability for domestic and agricultural utility in semi-arid region of Anantapur, Andhra Pradesh State, South India. Groundw Sustain Dev. https://doi.org/10.1016/j.gsd.2019.100262

Nadia EH, Kenneth PC, Nuria M et al (2015) Nitrate in drinking water and bladder cancer risk in Spain. Environ Res 137:299–307

Nagaraja Rao BK, Rajurkar ST, Ramalingaswamy G, Ravindra Babu B (1987) Stratigraphy structure and evolution of the Cuddapah Basin. Geol Soc India 6:33–86

Narsimha A, Rajitha S (2018) Spatial distribution and seasonal variation in fluoride enrichment in groundwater and its associated human health risk assessment in Telangana State, South India. Hum Ecol Risk Assess Int J 24(8):2119–2132

Oenema O, van Liere L, Schoumans O (2005) Effects of lowering nitrogen and phosphorus surpluses in agriculture on the quality of groundwater and surface water in the Netherlands. J Hydrol 304:289–301. https://doi.org/10.1016/j.jhydrol.2004.07.044

Piper AM (1944) A graphical interpretation of water analysis. Trans Am Geophys Union 25:914–928

Prajapati M, Jariwala N, Agnihotri P (2017) Spatial distribution of groundwater quality with special emphasis on fluoride of Mandvi Taluka, Surat, Gujarat, India. Appl Water Sci 7:4735–4742. https://doi.org/10.1007/s13201-017-0636-z

Qian H, Li P (2011) Hydrochemical characteristics of groundwater in Yinchuan plain and their control factor. Asian J Chem 23(7):2927–2938

Qian H, Li P, Howard KWF (2012) Assessment of groundwater vulnerability in the Yinchuan plain, Northwest China using OREADIC. Environ Monit Assess 184(6):3613–3628. https://doi.org/10.1007/s10661-011-2211-7

Raghunath HM (1987) Groundwater, 2nd edn. Wiley Eastern Limited, New Delhi, p 563

Raju N, Dey S, Das K (2009a) Fluoride contamination in ground waters of Sonbhadra District, Uttar Pradesh, India. Curr Sci 96(7):979–985

Raju NJ, Ram P, Dey S (2009b) Groundwater quality in the lower Varuna river basin, Varanasi district, Uttar Pradesh. J Geol Soc India 73:178

Rango T, Bianchini G, Beccaluva L, Ayenew T, Colombani N (2008) Hydrogeochemical study in the Main Ethiopian Rift: new insights to the source and enrichment mechanism of fluoride. Environ Geol 58:109–118

Rezaei H, Jafari A, Kamarehie B, Fakhri Y et al (2018) Health risk assessment realted to the fluoride, nitrate, and nitrate in the drinking water in the Sanandaj. Human and Ecological Risk Assessment, Kuristan County. https://doi.org/10.1080/10807039.2018.1463510

Rizwan R, Gurdeep S (2013) Ground water quality status with respect to fluoride concentration in industrial area of Angul District Orissa, India. Indian J Sci Res Technol 1:54–61

Sawyer GN, McCarthy DL (1967) Chemistry of sanitary engineers, 2nd edn. McGraw Hill, New York, p 518

Saxena VK, Ahmed S (2003) Inferring the chemical parameters for the dissolution of fluoride in groundwater. Environ Geol 43:731–736. https://doi.org/10.1007/s00254-002-0672-2

Shahriari T et al (2010) Evaluation of fluorine concentration in drinking-water sources in South Khorasan 2008–2009. J Birjand Univ Med Sci 17:33–41

Sphiwe EM, Francis AD (2015) A review of problems and solution of abandoned mines in South Africa. Int J Min Reclam Environ. https://doi.org/10.1080/17480930.2015.1044046

Subba Rao N (2017) Controlling factors of fluoride in groundwater in a part of South India. Arab J Geosci 10:524

Subba Rao N (2018) Groundwater quality from a part of Prakasam District, Andhra Pradesh, India. Appl Water Sci 8:30

Subba Rao N, Surya Rao P, Venkat Ramireddy G (2012) Chemical Characteristics of groundwater and assessment of groundwater quality in Varaha River Basin, Visakhapatnam District, Andhra Pradesh, India. Environ Monit Assess 184(5):189–214

Subba Rao N, Rao PS, Dinakar A et al (2015) Fluoride occurrence in the groundwater in a coastal region of Andhra Pradesh, India. Appl Water Sci 7:1467–1478

Subba Rao N, Dinakar A, Surya Rao P et al (2016) Geochemical process controlling fluoride bearing groundwater in the granitic aquifer of a semi arid region. J Geol Soc India 88:350–356

Sudharshan Reddy Y, Sunitha V, Suvarna B, Prasad M (2018) Assessment of Groundwater quality with special reference to Fluoride in groundwater surrounding abandoned mine sites at Vemula, Y.S.R. District, A.P. JETIR 5(11):769–777

Sunitha V, Muralidhara Reddy B (2018) Defluoridation of water using menthe longifolia (Mint) as Bioadsorbent. J Geophys Union 22(2):207–211

Sunitha V, Sudharshan Reddy Y (2019) Hydrogeochemical evaluation of groundwater in and around Lakkireddipalli and Ramapuram, Y.S.R District, Andhra Pradesh, India. Hydroresearch. https://doi.org/10.1016/j.hydres.2019.11.008

Susheela AK (1993) Prevention and control of fluorosis in India. Rajiv Gandhi National Drinking Water Mission, Ministry of Rural Development, New Delhi. Health Aspect 1:20–22

United States Department of Agriculture (UDA) (2007) Hydrology national engineering handbook. Natural resources conservation service title 210-VI-NEH part 360, Washinton, DC. http://directives.sc.egov.usda.gov/technical/handbook/

USEPA (2014) Human Health Evaluation Manual, Supplemental Guidance: Update of Standard Default Exposure Factors, OSWER Directive 9200.1-120. United States Environmental Protection Agency, Washington, DC

Vikas C, Kushwaha RK, Pandit MK (2009) Hydro chemical status of groundwater in District Ajmer (NW India) with reference to fluoride distribution. J Geol Soc India 73:773–784

Wagh VM, Panaskar DB, Shrikant VM, Manesh LA, Uday L (2019) Nitrate associated health risks from groundwater of Kadava River Basin Nashik, Maharashtra, India. Hum Ecol Risk Assess Int J. https://doi.org/10.1080/10807039.2018.1528861

Wagh V, Shrikant M, Aniket M, Ajaykumar K, Dipak P, Varade Abhay (2020) Study of groundwater contamination and drinking suitability in basaltic terrain of Maharashtra, India through PIG and multivariate statistical techniques. J Water Supply Res Technol AQUA. https://doi.org/10.2166/aqua.2020.108/651699/jws2020108

WHO (1996) Guidelines to drinking water quality, vol 2. World Health Organisation, Geneva, p 989

WHO (2012) Guidelines for drinking water quality, 4th edn. WHO Press, Geneva

Wu J, Sun Z (2016) Evaluation of shallow groundwater contamination and associated human health risk in an alluvial plain imported by agriculture and industrial activities, mid-west China. Expo Health 8(3):311–329. https://doi.org/10.1007/s12403-015-0170-x

Wu J, Li P, Qian H (2014) Assessment of soil salinization based on allow cast method and its influencing factors in a semi arid agriculture area, northwest China. Environ Earth Sci 71(8):3465–3475. https://doi.org/10.1007/s12665-013-2736-x

Wu J, Li P, Quan H (2015) Hydrochemical characterization of drinking groundwater with special reference to fluoride in an arid area of China and the control of aquifer leakage on its concentration. Environ Earth Sci 73(2):8575–8588. https://doi.org/10.1007/s12665-015-4018-2

Wu J, Wang L, Wang S (2017) Spatiotemporal variation of groundwater quality in an arid area experiencing long term paper waste water irrigation, northwest china. Environ Earth Sci 76(13):460. https://doi.org/10.1007/s/2665-017-6787-2

Zhang Y, Wu J, Xu B (2018) Human health risk assessment of groundwater nitrogen pollution in Jinghui canal irrigation area of the loess region, northwest China. Environ Earth Sci 77(7):273. https://doi.org/10.1007/s12665-018-7456-9