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ORIGINAL PAPER

Hydrogeochemistry of fluoride-rich groundwaters in semiarid region of Central India

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Abstract Geochemical and hydrogeochemical studies were conducted to assess the origin and geochemical mechanisms driving the fluoride enrichment in groundwaters of semiarid regions in Central India. The study region is geologically occupied by Precambrian rocks (granites, pegmatites, gneisses, schists, etc.) where groundwater occurs under unconfined condition. Majority of the groundwater locations did not meet the potable water criteria as they contained excess fluoride (>1.5 mg/l). The greater concentrations of fluoride were recorded in the monsoon followed by post-monsoon and pre-monsoon. Ionic composition and hydrogeochemical facies revealed the dominance of carbonate weathering and alkalinity that favors high dissolved fluoride in groundwaters. The values of dissociation constant showed slow weathering of fluorite and fast weathering of calcite in the study area. Rainfall shifted the unsaturated to saturated values of SI_C and SI_F in the monsoon. The factor analysis and saturation indices revealed geogenic origin of fluoride, a condition responsible for perennial fluoride problem in the study region.

Keywords Calcite · Fluoride · Alkalinity · Vindhyan supergroup

Introduction

Occurrence of fluoride in groundwater has drawn worldwide attention due to its considerable impact on human physiology. The assimilation of fluoride by the human body from potable water at the level of 1 mg/l enhances bone development and prevents dental caries (Kundu et al. 2001; Fordyce et al. 2007; Zohoori et al. 2012; Ghosh et al. 2013). The maximum permissible limit of fluoride in drinking water specified by the World Health Organization (WHO 2004) is 1.5 mg/l. Ingestion of water with fluoride concentrations above 1.5 mg/l results in dental fluorosis characterized by opaque white patches, staining, mottling, and pitting of teeth (Kundu et al. 2001). Globally, researchers have reported fluorosis due to intake of fluoride-rich water (Kim and Jeong 2005; Chae et al. 2007; Naseem et al. 2010). More than 200 million people worldwide are thought to be drinking water with fluoride in excess of the WHO guideline value. This includes around 66 million people in India (Majumdar 2011), 45 million people in China (Wuyi et al. 2002), and some 5 million in Mexico (Diaz-Barriga et al. 1997). In India, the problems are most pronounced in the states of Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu, and Uttar Pradesh (Pillai and Stanley 2002).

Many high-fluoride groundwater provinces have been recognized in various parts of the world, particularly northern Argentina, Bangladesh, China, Chile, Ethopia, Jordan, Mexico, Pakistan, Sri Lanka, Syria, Western USA, and many countries in Africa (Haimanot et al. 2006; Farooqi et al. 2007). These studies have confirmed the abundance of fluoride-bearing minerals especially fluorite (CaF_2) in granitic rocks as a generally dominant source of dissolved fluoride in groundwaters (Deshmukh

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et al. 1995; Shah and Danishwar 2003; Tirumalesh et al. 2006; Fordyce et al. 2007; Frengstad et al. 2001; Carrillo-Rivera et al. 2002). Fluoride solubility is controlled by pH and Ca^{2+} content. Fluoride is most soluble at high pH and low calcium levels, because at high levels of calcium, the insoluble mineral CaF_2 (fluorite) is formed (Handa 1975; Gaciri and Davies 1993). Evaporation is another important factor that favors precipitation of Ca^{2+} as $CaCO_3$, resulting in reduction of Ca^{2+} concentration, and consequently, the solubility control of CaF_2 on fluoride enrichment in the aqueous phase become weaker (Datta et al. 1996).

A fluoride-contaminated groundwater is also a serious problem in India at present. Considerable research has been carried out to understand the factors that influence the origin and status of fluoride in groundwaters (Suthar et al. 2008; Srinivasamoorthy et al. 2011; Sharma et al. 2012). However, such studies have not been carried out in Central India (Sidhi district). The pollution indexes >1 revealed prevalence of elevated soil fluoride (Kumar et al. 2015). The high concentrations are found to be associated with geogenic and anthropogenic sources in Sidhi district. In view of this, the present study was carried out to (a) assess the perennial nature of high fluoride concentrations in groundwaters, (b) assess the seasonal variations in geochemical behavior of dissolved fluoride, and (c) regional and global comparison of fluoride affected regions in the world.

Materials and methods

Study area

The Sidhi district is situated on the north-eastern boundary of the Madhya Pradesh State, India, which lies over a transitional area between the Indo-Gangetic plain in the north and the Deccan plateau in the south. It is situated between 22° 47.5′ and 24° 42.10′ north latitude and 81° 18.40′ and 82° 48.30′ east latitude (Fig. 1). The total land covered in the Sidhi district is 10,536 km^2 in which the forest area covers 40 %. The portion of the land used for agricultural purpose is 47 %, but only 17 % of the land used for agricultural purpose has assured supply of irrigation, and the rest of the agricultural land is dependent on rain fed irrigation and produces only one crop a year. The land is largely undulating terrain, which often has steep gradients not ideal for cultivation; the valleys along the major rivers like the Son and the Gopad have fertile soils. Rice, maize, barley, and jute are grown as Kharif crop. In tropical monsoon, the average annual rainfall varies from 1000 to 1200 mm and characterized by natural vegetation comprises support tropical dry deciduous forests. The total population of the area is 11, 26,515 spread with a density of 110/km^2 (Census of India 2011).

Geology

The study region (Sidhi district) in Central India is a part of the Vindhyan-Mahakoshal basin, one of the largest Proterozoic basins in India (Auden 1933; Tondon et al. 1991), and is an important geological domain experiencing semiarid climate. The rocks of both Mahakoshal and Vindhyans are affected by a major east-northeast-west-southwest trending fault/shear zone, sympathetic to Son-Narmada mega-lineament, extending from Tarka in the east to Baharia in the west, in Sidhi district. This zone is marked by linear ridges and low mounds of heterolithic breccias including highly fertile Neoarchaean to Palaeoproterozoic basement-cum-provenance (Chhotanagpur Granitic Gneissic Complex), presence of phyllites/carbon phyllites, episodic mafic and acid magmatism, and basement reactivation. These factors had provided thermal gradient and facilitated hydrothermal solution movements significant for remobilization of geogenic trace elements at suitable locales (Banerjee et al. 2010).

The physiography is characterized by low hill, extensive plateaus, and river valleys such as Son river valley which is a depository of the Gondwana rocks. Topographically, the district can be divided into three zones, Vindhyan hills or Kaimour range, Gondwana zone, and Archean zone. Sidhi area exposes the oldest rock units of Tonalite-Trondjhemite series formed during proto-continental stage (3.7–2.9 Ga), representing the ancient crust (Roy and Bandyopadhyay 1990). Clay minerals like kaolinite, halloysite, diaspore, gibbsite, nacrite, and dicktite were derived by the localized weathering of arkosic metasediments. Sporadic and some concentrated occurrence of granite veins were reported from the district (Mehrotra et al. 1979). Similarly, some low-grade copper and coal deposits were also recorded in various parts of Sidhi district. Fluoride ions from these minerals leach into the groundwater and contribute to high fluoride concentrations (Karunakaran 1974).

Son catchment having large amount of river deposited sediments slopes from North South and is interrupted by sandy regions and basins. In the study area, the Son-Narmada North Fault (SNNF) marks the tectonic contact between the east-northeast-west-southwest trending volcano-sedimentary sequence of Mahakoshal Group toward the south and Semri Group (Lower Vindhyan) toward the north. A significant aspect of the catchment reflects various depositional surfaces having a succession of overlaying sediments. Highly productive and extensive, unconfined and semiconfined aquifers are found in the Sidhi district. Water level fluctuates with seasonal recharge and discharge and varied from 12.2 to 48.8 m below ground level, showing varying degree of hydraulic conductivity.

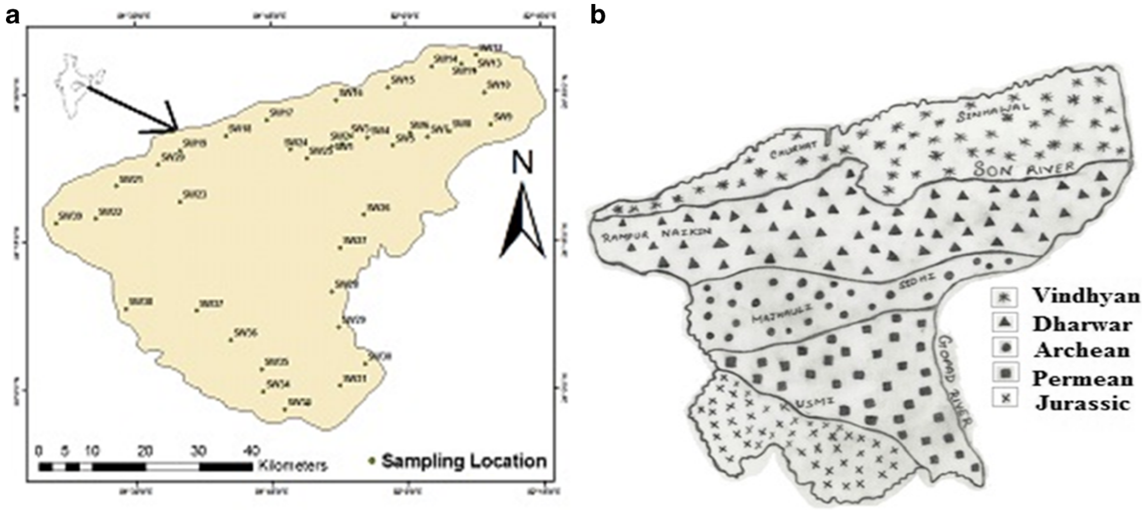

Fig. 1 Map showing **a** sampling locations and **b** geological classification of the Sidhi district

Field sampling and laboratory analysis

To understand the spatial and temporal variation in fluoride enrichment, 39 groundwater samples were collected from hand pumps in such a way that they represent different geological formations and land use patterns at varying topography of the Sidhi district in the pre-monsoon (June 2013) and monsoon (August 2013). The information about the age of hand pumps was collected from local people, and the range varied from less than 1 to 20 years, with an average of 7 years. Similarly, the depth information was collected from users (local people) and it varied from 12.2 to 48.8 m with an average of 25.9 m in the pre-monsoon.

The groundwater samples were collected in clean polypropylene bottles without any air bubbles. Samples from each location were collected for anion and cation analysis. Groundwater samples were filtered by 0.45-μm Millipore filter paper and acidified with 2 N HNO_3 (Ultrapure Merck) for cation analysis, and HBO_3 acid was used as a preservative for nitrate analysis. In situ measurements for temperature, pH, EC, TDS, salinity, and ORP were carried out in the field using multiparameter analysis kit PCSTestr35 (Eutech Oakton). The bottles were properly labeled and brought to laboratory for determining the physicochemical analysis.

Major cation analysis (Na+, K^+, Ca^{2+}, and Mg^{2+}) was carried out by Evans Electro Selenium (EEL) Flame Photometer (APHA 1995). The concentration of HCO_3^- was measured by acid titration, Cl^- by $AgNO_3$ titration, SO_4^{2-} by $Ba(ClO_4)_2$ titration, and NO_3^- by the UV spectrophotometer screening method, and the dissolved silica was determined by the molybdosilicate method, PO_4^{3-} by the ascorbic acid method, and fluoride (F^-) by SPANDS method (APHA 1995). To maintain the purity and quality of the procedures, a known standard was used after every five samples. High purity reagents (Merck) and milli-Q water (Model Milli-Q, Biocel) were used for all the analyses. Analyses were carried out in duplicate to quantify the error. An overall precision was obtained below 5 % for the entire samples. Analytical precision for the measurement of ions was determined by calculating the normalized inorganic charge balance (NICB), which is defined as $[Tz^+ - Tz^- / Tz^+ + Tz^-]$ and represents the fractional difference between the total cations (T_Z^+) and total anions (T_Z^-) (Edmond et al. 1995; Huh et al. 1998). The saturation index of calcite and fluorite was derived using PHREEQC version 2. The partial pressure of the CO_2 at 25 °C was calculated from pH and HCO_3^- content of the groundwater using the equation $\log P_{CO2} = 7.9 + \log aH_2CO_3 - pH$ (Panigrahy and Raymahashay 2005). Saturation of calcite and fluorite was computed with the help of the standard formulas (Hem 1970; Parkhurst and Appelo 1999):

$$CaCO_{3(s)} + H^+ \rightleftarrows Ca^{++} + HCO_3^-$$
$$K_{cal} = a_{Ca}{}^{++} \times a_{HCO3}{}^{-}/a_H{}^{+} = 0.97 \times 10^2$$

$$CaF_{2(s)} \rightleftarrows Ca^{++} + 2\,F^-$$
$$K_{fluor} = a_{Ca}{}^{+} \times 2(a_{F-})^2 = 10^{-10.60}$$

where the prefix “a“ represents the activity of the ion in moles/l.

To evaluate the potential relationship between the various physicochemical parameters, the factor analysis for groundwater samples was carried out by using “Statistical Package for Social Sciences (SPSS), version 16.0.“ The “principal component analysis“ and “Varimax rotation“ were used for extracting and deriving factors, respectively. The map of spatial distribution pattern of dissolved fluoride was produced by using the Arc view (9.3) software for ordinary kriging interpolation

Results and discussion

The statistical parameter (mean, range, standard deviation) of various physicochemical parameters that were analyzed are given in Table 1. The ionic balances were generally within ±5 %. Dominating cations were of the following order: $Ca^{2+}>Mg^{2+}>Na^{+}>K^{+}$, and the dominating anions were of the order $HCO_3^{-}>Cl^{-}>SO_4^{2-}>F^{-}>NO_3^{-}$ in the pre-monsoon and post-monsoon. In monsoon, cations were of the order $Ca^{2+}>Mg^{2+}>Na^{+}>K^{+}$, and the anions were of the order $HCO_3^{-}>SO_4^{2-}>Cl^{-}>NO_3^{-}>F^{-}$, respectively. The concentration (in mg/l) of alkaline earth metal (Ca^{2+} + Mg^{2+}) exceeds that of alkali metals (Na^{+} + K^{+}). The SiO_2 showed significant spatial and seasonal variations and varied from 13.8–62.1, 9.9–75.1, and 7.0–82.5 mg/l in the in the pre-monsoon, monsoon, and post-monsoon, respectively. The pH of ground water was alkaline in the monsoon (7.1–8.5) while acidic to alkaline (6.2–7.8 and 6.8–7.9) in the pre-monsoon and post-monsoon. The concentrations of fluoride found in the ground water locations were higher than the maximum tolerance limit (1.5 mg/l) recommended by World Health Organization (WHO 2004). It ranged from 1.4 to 2.8 mg/l in the pre-monsoon, 2.1 to 3.5 mg/l in the monsoon, and 1.3 to 3.8 mg/l in the post-monsoon.

Seasonal variation in groundwater chemistry

The pH range indicates that the HCO_3^{-} is dominant carbonate species. Strong bases such as SO_4^{2-} and Cl^{-} occurred in low concentrations relative to HCO_3^{-}. An increment in all the ion concentrations in the monsoon indicates rainwater infiltration through soil profile and bedrock leading to desorption of ions in the groundwater system (Rao 2006; Giridharan et al. 2008). The Gibbs' diagram suggests that rock weathering is the dominant mechanism controlling the groundwater chemistry in the study area (Fig. 2). The constituents of TDS are derived from the rock–water interaction, i.e., weathering of carbonate minerals and accessory minerals present in the granite and gneissic rocks in the study area. Piper plot showed that the groundwater is mostly Ca-HCO_3 and Ca-Mg-HCO_3 type (Fig. 3). The effective CO_2 pressure ($\log P_{\mathrm{CO2}}$) is greater than atmospheric value of −3.5 (Raymahashay 1986), especially in the pre-monsoon and

Table 1 Summary of physicochemical parameters of ground water samples collected in the pre-monsoon, monsoon, and post-monsoon

Parameters	Pre-monsoon		Monsoon		Post-monsoon	
	Range	Average	Range	Average	Range	Average
pH	6.2–7.8	–	7.1–8.5	–	6.8–7.9	–
EC (μS/cm)	52–1244	517.8±237.8	60.8–1351.5	578.3±275	92.5–1276	543.7±213.4
ORP (mV)	67–182	147.5±23.9	105–184	138.3±22.1	101–178	140.3±18.1
TDS (mg/l)	175–408	296.8±71.7	229–796	545.2±151.7	302–997	661.7±186.4
Ca^{2+} (mg/l)	9.8–87.8	42.5±19.2	16.8–470	171.2±107.3	20–503.6	166.2±102.1
Mg^{2+} (mg/l)	4.9–67.1	27.1±13.1	6.8–99	43.5±21.5	10.3–119	44.5±23.5
Na^{+} (mg/l)	7.7–27.6	16.8±6.1	8.5–71	18.8±12.5	1.5–51.1	19.9±10.1
K^{+} (mg/l)	1.2–8.8	4±2.1	0.1–22	3.1±4.7	0.14–5.82	1.9±1.5
HCO_3^{-} (mg/l)	38–396	253.6±86.2	96–2000	687.4±359.6	192–2372	722.8±375.1
Cl^{-} (mg/l)	1.3–90	19.1±18.4	8.3–81.8	25.2±18.8	3.3–73.4	15.6±13.8
SO_4^{2-} (mg/l)	10.6–55.6	18.7±9.6	10–55.8	18.5±9.3	4.5–57.8	24.0±11.8
NO_3^{-} (mg/l)	0–7.8	1.4±2.4	0–16.2	3.3±3.4	0–10.4	1.96±2.73
F^{-} (mg/l)	1.4–2.8	2.1±0.3	2.1–3.5	2.8±0.3	1.3–3.8	2.59±0.63
SiO_2 (mg/l)	13.8–62.1	40.2±13.6	9.9–75.1	40.4±15.7	7.0–82.5	31.1±15.81
ΔT_z (%)(μeq/l)	−4.9–5.5	−0.3±2.8	−3.3–2.6	0.39±1.92	−3.3–2.6	0.39±1.92
(meq/l)	9.7–32.9	16.9±5.6	2.1–21.8	8±4.8	1.5–30.8	8.25±5.54
(meq/l)	0.3–1	0.5±0.2	0.1–1.3	0.35±0.23	0.04–1	0.38±0.21
(meq/l)	−18.5–2	−2.8±4.4	−5–1.5	−0.91±1.34	−7.1–1.3	−2.39±1.99
(meq/l)	−0.6–6.2	2.2±1.6	0.4–31.1	9.3±6.2	0.01–1.9	0.35±0.38

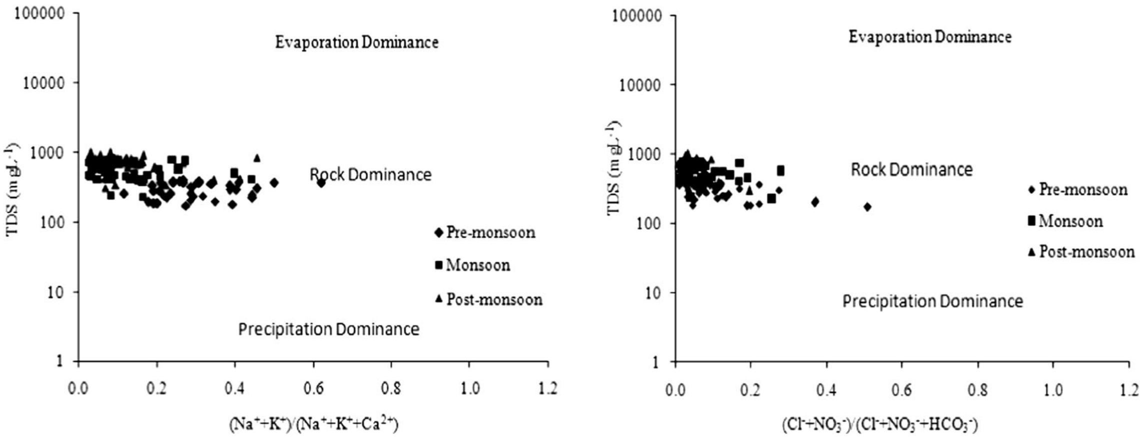

Fig. 2 Gibbs diagram illustrating the mechanisms controlling the chemistry of groundwater samples from Sidhi

post-monsoon (Table 2). This is a global trend, indicating that naturally water bodies are commonly out of equilibrium with the atmosphere (Raymahashay 1986). This is due to long-standing water bodies having a significant fraction of high CO_2 groundwater, and the rate of re-equilibration with the atmosphere by releasing excess CO_2 is relatively slow (Stumm and Morgan 1970).

Fluoride geochemistry

The F^- content of groundwaters ranged 1.4–2.8, 2.1–3.5, and 1.3–3.8 ppm in the pre-monsoon, monsoon, and post-monsoon, respectively. The groundwater locations around villages of agricultural and urban areas showed significant seasonal variations in dissolved fluoride. In monsoon, the groundwater

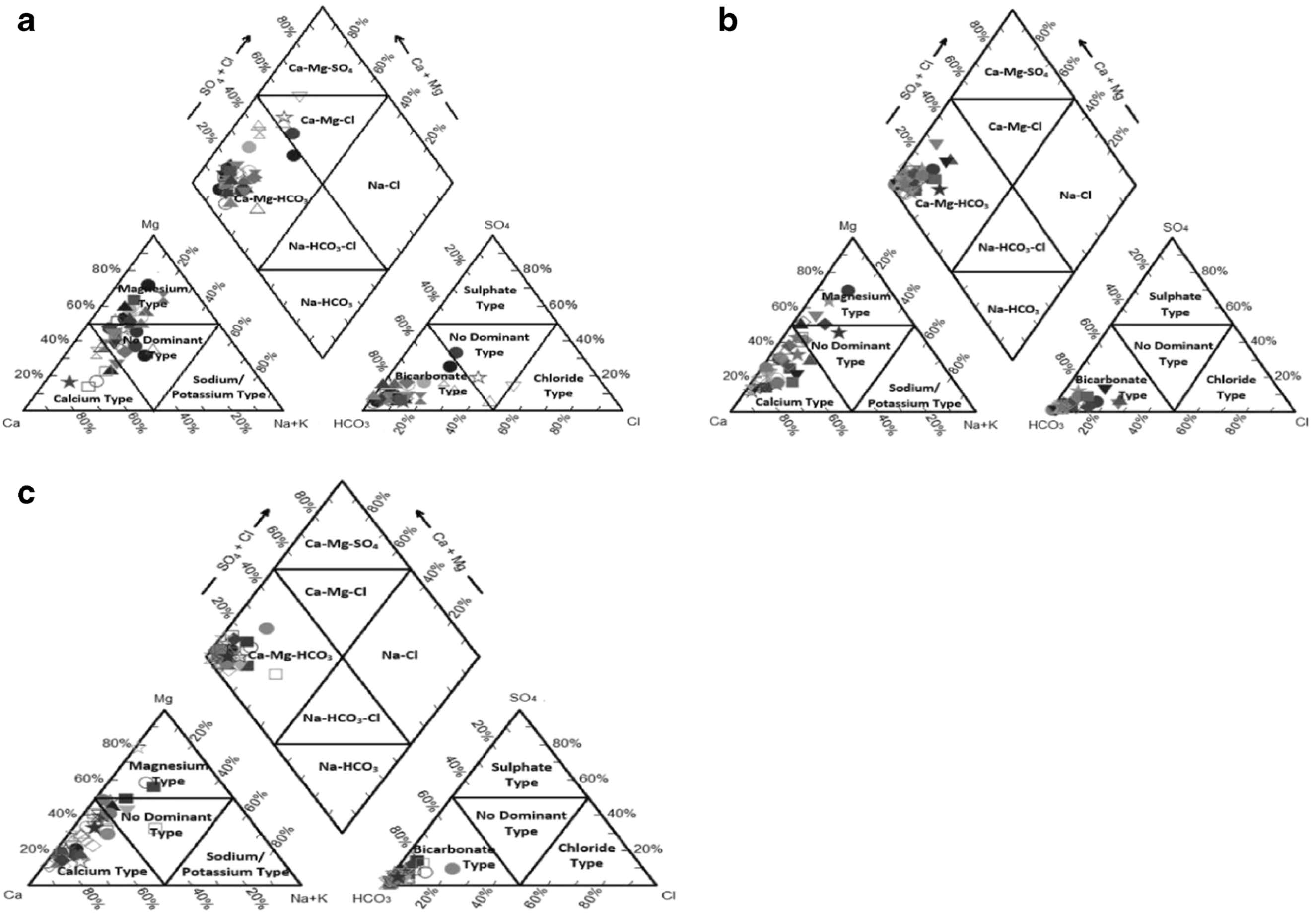

Fig. 3 Piper diagram showing water type in the study area: **a** pre-monsoon, **b** monsoon, and **c** post-monsoon

Table 2 Summary of saturation, dissociation constant, and effective CO_2 pressure

	Premonsoo					Monsoon					Post-monsoon				
S.N	SI_C	SI_F	$K_{cal\ (10^2)}$	K_{fluor}	Log Pco_2	SI_C	SI_F	$K_{cal\ (10^2)}$	K_{fluor}	Log Pco_2	SI_C	SI_F	$K_{cal\ (10^2)}$	K_{fluor}	Log Pco_2
1	0.36	−0.19	0.20	$10^{-10.44}$	−1.90	1.12	−0.16	1.00	$10^{-10.31}$	−2.05	0.71	−0.17	0.49	$10^{-10.38}$	−1.94
2	−0.73	−0.57	0.15	$10^{-10.82}$	1.40	1.13	−0.17	0.54	$10^{-10.31}$	−1.96	−0.11	−0.57	0.11	$10^{-10.82}$	−1.35
3	0.07	−0.36	0.84	$10^{-10.59}$	−1.63	1.49	−0.10	1.47	$10^{-10.17}$	−1.83	0.46	0.01	0.64	$10^{-10.23}$	−1.45
4	0.07	−0.31	0.95	$10^{-10.56}$	−1.94	1.67	0.30	3.30	$10^{-9.88}$	−2.06	0.53	0.31	1.04	$10^{-9.95}$	−1.58
5	−0.55	−0.58	0.21	$10^{-10.80}$	−1.48	1.33	0.15	2.13	$10^{-10.02}$	−1.64	0.73	0.34	1.42	$10^{-9.86}$	−1.48
6	−0.37	−0.70	0.25	$10^{-10.88}$	−1.51	1.10	−0.18	1.16	$10^{-10.32}$	−2.10	−0.12	−0.84	0.12	$10^{-10.96}$	−1.16
7	−0.67	−1.03	0.26	$10^{-11.01}$	−1.50	1.30	−0.13	1.01	$10^{-10.21}$	−1.73	0.46	−0.09	0.48	$10^{-10.26}$	−1.35
8	−0.81	−0.82	0.10	$10^{-11.01}$	−1.31	1.29	−0.22	0.91	$10^{-10.29}$	−2.05	0.07	−0.22	0.17	$10^{-10.41}$	−1.41
9	−0.76	−0.95	0.12	$10^{-11.15}$	−1.50	0.75	−0.50	0.23	$10^{-10.65}$	−2.72	−0.50	−0.75	0.02	$10^{-10.95}$	−1.60
10	−0.34	−0.76	0.26	$10^{-10.97}$	−1.79	1.80	0.33	0.99	$10^{-9.80}$	−1.57	0.84	0.34	0.38	$10^{-9.82}$	−1.03
11	0.50	−0.41	0.21	$10^{-10.62}$	−2.38	1.57	0.05	1.56	$10^{-10.08}$	−2.11	0.96	0.08	1.27	$10^{-10.13}$	−2.21
12	0.06	−0.51	0.92	$10^{-10.70}$	−1.67	1.50	−0.15	1.55	$10^{-10.21}$	−1.94	0.51	−0.06	0.56	$10^{-10.25}$	−1.60
13	0.01	−0.49	0.83	$10^{-10.68}$	−1.80	1.97	0.36	0.78	$10^{-9.78}$	−1.83	0.90	0.40	0.26	$10^{-9.82}$	−1.47
14	−0.78	−0.69	0.13	$10^{-10.91}$	−1.17	1.59	−0.01	1.79	$10^{-10.09}$	−2.23	0.35	−0.07	0.34	$10^{-10.27}$	−1.41
15	0.28	−0.23	1.41	$10^{-10.47}$	−1.89	1.33	−0.11	0.93	$10^{-10.22}$	−2.10	0.56	1.12	0.49	$10^{-10.19}$	−1.77
16	−0.91	−1.04	0.15	$10^{-11.27}$	−2.31	−0.43	−0.89	0.02	$10^{-11.07}$	−2.03	0.07	−0.26	0.22	$10^{-10.49}$	−2.24
17	−1.42	−0.91	0.05	$10^{-11.13}$	−1.19	0.16	−0.56	0.06	$10^{-10.69}$	−1.70	−0.68	−0.84	0.04	$10^{-11.07}$	−1.53
18	−0.22	−0.48	0.51	$10^{-10.69}$	−1.70	1.42	−0.21	1.21	$10^{-10.29}$	−2.30	0.06	−0.18	0.25	$10^{-10.40}$	−1.60
19	0.37	−0.30	0.21	$10^{-10.52}$	−2.39	1.00	−0.09	0.49	$10^{-10.25}$	−1.98	0.69	0.24	0.79	$10^{-9.99}$	−2.18
20	−0.35	−0.61	0.33	$10^{-10.82}$	−1.62	1.51	0.25	2.38	$10^{-9.90}$	−1.67	0.47	0.21	0.81	$10^{-10.04}$	−1.31
21	−0.12	−0.57	0.45	$10^{-10.77}$	−1.82	1.75	0.11	2.67	$10^{-10.00}$	−2.21	0.45	0.16	0.42	$10^{-10.08}$	−1.48
22	−0.04	−0.42	0.55	$10^{-10.64}$	−1.71	1.40	0.14	1.16	$10^{-10.02}$	−1.99	0.47	0.12	0.31	$10^{-10.12}$	−1.57
23	−0.12	−0.63	0.53	$10^{-10.83}$	−1.91	1.51	0.08	1.71	$10^{-10.06}$	−2.00	0.70	0.20	0.64	$10^{-10.05}$	−1.81
24	0.05	−0.41	0.86	$10^{-10.63}$	−1.84	2.19	0.36	1.21	$10^{-9.75}$	−2.17	0.77	0.34	1.45	$10^{-9.9}$	−1.38
25	−0.18	−0.72	0.55	$10^{-10.78}$	−1.63	1.99	0.16	0.58	$10^{-9.92}$	−2.16	0.76	0.20	1.11	$10^{-10.02}$	−1.49
26	−0.31	−0.51	0.40	$10^{-10.74}$	−2.05	2.11	0.47	1.31	$10^{-9.70}$	−2.48	0.68	0.59	1.62	$10^{-9.67}$	−1.62
27	−0.50	−0.66	0.24	$10^{-10.86}$	−1.67	2.13	0.42	1.41	$10^{-9.73}$	−2.47	0.55	0.24	1.06	$10^{-9.98}$	−1.42
28	−0.15	−0.55	0.48	$10^{-10.76}$	−1.87	2.06	0.44	1.20	$10^{-9.73}$	−2.20	0.63	0.32	1.27	$10^{-9.9}$	−1.36
29	−0.92	−0.66	0.10	$10^{-10.90}$	−1.79	1.43	0.30	0.31	$10^{-9.91}$	−1.91	0.05	0.05	0.36	$10^{-10.19}$	−1.26
30	−1.12	−0.81	0.06	$10^{-11.05}$	−1.69	1.07	−1.00	0.59	$10^{-10.27}$	−2.26	−0.60	−0.47	0.10	$10^{-10.71}$	−1.21
31	−0.27	−0.78	0.40	$10^{-10.98}$	−2.08	1.74	0.02	2.36	$10^{-10.07}$	−2.52	0.48	0.39	1.51	$10^{-9.84}$	−1.83
32	−0.36	−0.52	0.32	$10^{-10.74}$	−1.58	1.39	−0.18	1.15	$10^{-10.25}$	−2.30	0.07	−0.31	0.27	$10^{-10.48}$	−1.15
33	−1.09	−0.91	0.04	$10^{-11.19}$	−2.94	−0.48	−0.49	0.02	$10^{-10.77}$	−2.36	0.09	0.10	0.37	$10^{-10.14}$	−2.15
34	−1.35	−0.88	0.16	$10^{-11.16}$	−2.43	0.93	−0.05	0.55	$10^{-10.26}$	−2.14	−0.02	0.21	0.32	$10^{-10.07}$	−2.14

Table 2 (continued)

	Premonsoo					Monsoon					Post-monsoon				
S.N	SI_C	SI_F	K_{cal} (10^2)	K_{fluor}	Log Pco_2	SI_C	SI_F	K_{cal} (10^2)	K_{fluor}	Log Pco_2	SI_C	SI_F	K_{cal} (10^2)	K_{fluor}	Log Pco_2
35	−1.47	−1.77	0.01	$10^{-11.55}$	−2.03	0.25	−0.19	0.13	$10^{-10.45}$	−2.32	−0.96	−1.22	0.01	$10^{-11.40}$	−1.57
36	−0.74	−1.02	0.24	$10^{-10.97}$	−2.61	0.85	−0.16	0.29	$10^{-10.38}$	−2.75	0.27	−0.22	0.09	$10^{-10.45}$	−2.54
37	−0.49	−1.24	0.78	$10^{-10.79}$	−2.06	2.09	0.05	0.72	$10^{-9.96}$	−2.66	0.67	0.08	0.68	$10^{-10.10}$	−1.62
38	−0.72	−1.22	0.18	$10^{-10.97}$	−1.90	2.03	0.13	0.58	$10^{-9.93}$	−2.47	0.64	0.15	0.57	$10^{-10.05}$	−1.51
39	−0.16	−0.71	0.39	$10^{-10.95}$	−2.12	1.90	0.15	1.00	$10^{-9.95}$	−2.52	0.62	0.12	0.49	$10^{-10.10}$	−1.84

locations in Vindhyan region showed significant enrichment of dissolved fluoride compared to pre-monsoon. The 77 % groundwater locations had >2.5 mg/l dissolved fluoride compared to pre-monsoon (3 %) and post-monsoon (52 %). Moreover, 26 % groundwater locations showed >3 mg/l dissolved fluoride in monsoon compared to post-monsoon (16 %) especially in the Archean region. Karunakaran (1974) reported sporadic and some concentrated occurrence of granite veins in the study area. Kumar et al. (2015) reported high concentrations of fluoride in agricultural soils of Sidhi district. Fluoride-bearing minerals occupy the joints, fractures, faults, and vertical openings in the gneissic and granitic formations which are the oldest geological formations in Sidhi and have undergone maximum weathering (Suma Latha et al. 1999). Fluoroapatite and micas in the granites were identified as the main provenance of fluoride in the groundwater through water–rock interactions in an alkaline medium (Fantong et al. 2010). While reacting with granitic rocks for a prolonged period, the F^- concentrations of groundwater are continuously enriched even after the groundwater reaches an equilibrium state with respect to fluorite (CaF_2) due to removal of Ca by precipitation of calcite (Handa 1975; Saxena and Ahmed 2003), as shown in the following equation:

$$CaF_2 + 2HCO_3^- = CaCO_3 + 2F^- + H_2O + CO_2$$

The saturation index of calcite (SI_C) and fluorite (SI_F) for all three seasons is given in Fig. 4. In pre-monsoon, the SI_C of 59 % groundwater locations are in equilibrium and remaining 41 % are undersaturated; in the monsoon, 90 % groundwater locations are oversaturated and remaining 10 % are in equilibrium with calcite; and in the post-monsoon, 41 % are in equilibrium or approaching to equilibrium, 51 % oversaturated, and remaining 8 % groundwater locations are undersaturated. Seventy percent

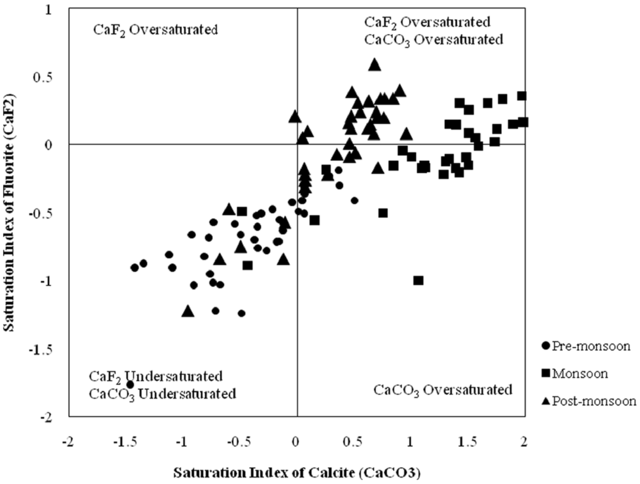

Fig. 4 Plot of calcite saturation index (SI_C) versus fluorite saturation index (SI_F)

groundwater locations are undersaturated and remaining 25 % are found in equilibrium with respect to SI_F in the pre-monsoon; in the monsoon, 90 % locations are oversaturated; and in the post-monsoon, 85 % are in equilibrium, 8 % undersaturated, and only 3 % groundwater location is oversaturated. In nutshell, the rainfall trigger shift in the unsaturated to saturated values of SI_C in the monsoon and post-monsoon (Table 2). When groundwater equilibrated with respect to fluorite, the activities of Ca^{2+} and F^- shift toward fluorite saturation; consequently, high fluoride concentrations are dependent upon mechanisms that decrease Ca^{2+} in the pre-monsoon and monsoon.

The equilibrium constant of calcite (K_{cal}) varied from 0.01×10^2 to 1.41×10^2 in the pre-monsoon, 0.02×10^2 to 3.30×10^2 in the monsoon, and 0.01×10^2 to 1.62×10^2 in the post-monsoon (Table 2). In the pre-monsoon, the K_{cal} values is less than 0.97×10^2 (Hem 1970), indicating significant calcite weathering due to sufficient hydrogen ion concentration (a strong weathering agent). The equilibrium constant of fluorite (K_{fluor}) is greater than $10^{-10.6}$ except five locations in the monsoon and seven locations in the post-monsoon (Parkhurst and Appelo 1999), indicating that the dissociation of fluorite is very slow in groundwater system. These spatial and seasonal variations in the solubility of calcite and fluorite might be due to the following: (a) differences in local geological settings, (b) effective CO_2 pressure ($\mathrm{Log}P_{CO2}$), and (c) experiencing seasonal fluctuations in groundwater level in the groundwater system.

Principal component analysis

The factor analysis of dissolved F^- along with physicochemical parameters indicates five factors (Table 3). The total variability accounted for five factors was 75.09, 82.90, and 80.22 % in the pre-monsoon, monsoon, and post-monsoon, respectively. The first factor (F1) contributes 21.88 % of the total variance in the pre-monsoon and was strongly loaded on EC, Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, and Cl^- indicating dominance of carbonate weathering and leaching of salts in the groundwater system. Similar loading is observed in the monsoon and post-monsoon. The F2 (accounts for 16.44, 20.72, and 20.01 % of the total variance in the pre-monsoon, monsoon, and post-monsoon) is mainly associated with high loadings of pH, TDS, and F^- indicating geogenic origin of the fluoride in the study area. This factor also shows that the geogenic parameters determine the alkalinity of the groundwater that favours substitution of fluoride for hydroxyl ion on clay surfaces at high pH (Karunakaran 1974; Apambire et al. 1997). Weak or negative loading on SiO_2 and Na^+ support lack of silicate origin of fluoride. Hence, it appears that the carbonate weathering and alkalinity favors the dissolution of fluorite (CaF_2) as a plausible source of fluoride ion in groundwater: $CaF_{2(s)} \leftrightarrow Ca^{2+} + 2\,F^-$.

Regional and global comparison of fluoride

Vikas et al. (2009) reported 1.44 mg/l mean fluoride in alkaline and saline groundwaters of Northwest India. Geologically, this region is occupied by Precambrian rocks

Table 3 Factor analysis of the physicochemical parameters

Parameters	F1	F2	F3	F4	F5
pH	−0.65, 0.22, −0.71	0.60, 0.86, 0.28	0.17, 0.35, 0.35	0.04, −0.09, 0.42	−0.02, −0.14, 0.38
EC	0.83, 0.91, 0.77	0.39, −0.17, 0.45	−0.09, 0.03, 0.32	0.03, −0.02, 0.08	0.06, −0.11, 0.01
ORP	−0.07, −0.29, 0.15	−0.04, −0.36, −0.41	0.33, 0.50, −0.40	0.84, 0.28, 0.60	0.12, 0.46, 0.23
TDS	−0.35, 0.17, 0.55	0.62, −0.73, 0.64	−0.29, 0.53, 0.27	−0.14, −0.06, 0.30	−0.06, 0.11, 0.10
Ca^{2+}	0.51, 0.24, 0.27	0.19, 0.60, 0.74	0.62, 0.44, −0.57	0.04, 0.49, 0.06	−0.34, 0.31, −0.24
Mg^{2+}	0.50, 0.66, 0.51	0.33, 0.07, 0.46	−0.23, 0.38, −0.24	0.12, 0.03, 0.09	0.71, −0.30, 0.51
Na^+	0.59, 0.74, 0.60	0.45, −0.15, 0.37	0.05, −0.01, 0.50	−0.20, −0.32, 0.05	−0.33, 0.15, −0.02
K^+	0.32, 0.30, 0.40	−0.10, 0.30, −0.28	0.66, 0.48, 0.05	−0.33, 0.51, 0.44	0.09, 0.38, 0.60
HCO_3^-	0.54, 0.40, 0.11	0.63, 0.5, 0.83	0.37, −0.57, −0.53	0.06, 0.39, 0.03	0.19, 0.13, 0.06
Cl^-	0.63, 0.69, 0.80	−0.35, −0.38, 0.10	−0.01, 0.24, 0.20	−0.23, 0.15, 0.33	0.08, 0.36, 0.16
SO_4^{2-}	0.50, 0.68, 0.62	0.27, −0.07, 0.02	−0.49, 0.40, −0.12	−0.04, 0.18, 0.39	0.03, 0.30, 0.47
NO_3^-	0.46, 0.59, 0.64	−0.40, −0.49, −0.19	−0.05, 0.01, −0.14	0.54, 0.05, 0.34	−0.08, −0.41, 0.07
F^-	−0.61, 0.14, 0.76	0.66, 0.86, 0.33	0.23, 0.43, 0.22	0.12, −0.10, 0.44	0.10, −0.04, −0.03
SiO_2	0.31, 0.50, 0.29	0.37, 0.02, 0.26	−0.39, −0.09, 0.42	0.34, −0.61, −0.47	−0.51, 0.32, −0.22
Eigenvalue	3.06, 3.29, 2.90	2.30, 2.90, 2.80	2.01, 2.03, 2.30	1.71, 1.97, 1.85	1.43, 1.41, 1.39
% of variation	21.88, 23.50, 20.72	16.44, 20.72, 20.01	14.34, 14.50, 16.40	12.23, 14.09, 13.20	10.20, 10.10, 9.90
% cumulative variation	21.88, 23.50, 20.72	38.32, 44.22, 40.73	52.66, 58.72, 57.12	64.89, 72.81, 70.32	75.09, 82.90, 80.22

Note: pre-monsoon, monsoon, post-monsoon

Table 4 Regional and global comparison of fluoride

S.N	Location	Mean(F) (mg/l)	Remarks	Description			References
				Geology	Water-type	Nature	
1.	Northwest India (*n*=66)	1.44	Hand pumps, dug cum bore wells, and tube wells	Alluvial formations and Precambrian rocks (granites, gneisses, and schists)	HCO_3-Cl, Na-K	Alkaline, medium to high saline waters	Vikas et al. 2009
2.	Western India (*n*=118)	2.82	Hand pumps	Bedrock of gneisses and schists		Saline	Suthar et al. 2008
3.	Northeastern India (*n*=40)	0.68	Hand pump	Archaean gneissic Complex, Gondwana supergroup, Upper piedmont, Lower piedmont	Ca-HCO_3	Alkaline	Sharma et al. 2012
4.	Eastern India	1.04* 0.73**	Tube wells and dug wells	Archaean weathered and crystalline rocks	Ca-HCO_3	Alkaline	Routroy et al. 2013
5.	Central India (*n*=27)	1.1	Shallow hand pumps, dug wells, and tube wells	Bundelkhand granite, Bijawar group, Vindhyan supergroup, alluvium	Ca-HCO_3, Mg-HCO_3, Na-HCO_3	Alkaline	Avtar et al. 2013
6.	Southern India	0.8* 1.4**	Dug/bore wells	Charnockites, peninsular gneiss, and calc gneiss of metasedimentary group, peninsular gneiss, charnockites, and calc gneiss	Mg-Ca-Cl-HCO_3, Na-Mg-HCO_3-Cl, Na-Mg-Cl-HCO_3, and Na-Cl-HCO_3	Alkaline	Srinivasamoorthy et al. 2012
7.	Southern India (eastern coastal region) (*n*=18)	0.9	Bore well	Sedimentary formations	Na-HCO_3-Cl, Na-Cl-HCO_3	Saline	Srinivasamoorthy et al. 2011
8.	Southern peninsular India (*n*=15)	3.9	Dug wells and boreholes	Granites and accessory minerals present in association with pegmatitic rocks	Na-HCO_3	Alkaline	Padhi and Muralidharan 2012
9.	Pakistan (*n*=32)	3.33	Dug wells	Metamorphic rocks, igneous rocks, granitic rocks	Na-HCO_3	Alkaline	Naseem et al. 2010
10.	North China (*n*=61)		Yuncheng basin	–	SO4–Na, SO4–Cl–Na–Mg, and SO4–Cl–Na	Saline	Gao et al. 2007
11.	Central Japan Sub-basin I (*n*=23) Sub-basin II (*n*=22)	5.48 8.96	Boreholes	Sedimentary rocks, granitic rocks	Na–(Ca)–HCO_3	Highly saline	Abdelgawad et al. 2009
12.	Africa (*n*=37)	14.3	Tap, river, borehole, storage tank, lake	Granitic rocks			Wambu and Muthakia 2011
13.	South Korea (*n*=377)	5.7	Deep thermal groundwater	Metamorphic and sedimentary rocks	Na-HCO_3, Ca-HCO_3	Alkaline water	Chae et al. 2007
14.	North Jordan (*n*=22)	0.02	Wells	Chert, limestone, dolomite, jointed, and fractured	Ca-HCO_3 type	Alkaline	Rukah and Alsokhny 2004

(granites, pegmatites, gneisses, schists, etc.), where groundwater occurs under unconfined condition. In Western India, the average fluoride concentration was recorded to be 2.82 mg/l in saline groundwaters located in peninsular block and mainly composed of quartzite, sandstone, mica schist, phyllites, etc. (Suthar et al. 2008). In Northeast India, Sharma et al. (2012) reported 0.68 mg/l mean fluoride in the alkaline aquifers adjoining exposure of rocks of igneous origin appears to be the result of leaching out from the residual weathered boulders of original igneous rock mass of the Bhutan foothills. Routroy et al. (2013) studied the spatial and seasonal variations of fluoride concentrations in groundwaters in Nayagarh district, Odisha. Lithologically, the garnet-sillimanite gneiss is the predominant rock type, which is highly altered. The major fluoride rich minerals are plagioclase, orthoclase, biotite, hornblende, hypersthenes, and quartz. The analytical results indicate that the alkaline surface water of the Nayagarh is a unique example of the compound impact of weathering, hydrologic, and anthropogenic processes. In Central India, Avtar et al. (2013) reported 1.1 mg/l mean geogenic fluoride in alkaline groundwaters located in Bundelkhand granites overlain by the Bijawar group of rocks (Bhattacharya and Bhattacharyya 1976). Srinivasamoorthy et al. (2012) studied the spatial and seasonal variations in fluoride concentration in crystalline bedrock aquifers in Southern India. The major litho units were charnockites, peninsular gneiss, and calc gneiss of metasedimentary group. Higher degree of weathering, easy accessibility of circulating water to the weathered rocks due to intensive, and long time irrigation are responsible for the leaching fluoride from their parent minerals present in soil and rocks (Srinivasamoorthy et al. 2011). Further high concentration has been brought about due to semiarid climate of the region and long residence time of groundwater in the aquifer (Wodeyar and Sreenivasan 1996). Padhi and Muralidharan (2012) reported chronic regions with excess fluoride in geoenvironment of semiarid granite watershed in southern peninsular India. The average concentration was recorded to be 3.9 mg/l in alkaline groundwaters. The saturation indices indicated that majority of groundwater in the study area is oversaturated with respect to calcite and is saturated with fluorite.

Global and regional comparison (Table 4) reveals that the high groundwater fluoride concentrations in Pakistan, China, Japan, Africa, Korea, Jordan, etc. is associated with igneous and metamorphic rocks such as granites and gneisses. Fluoride concentrations up to 7.85 mg/l has been reported in fluoriferrous groundwater originates from granite rocks of Proterozoic to late Proterozoic age type in association with hornblende diorite and microgabbros in Thar Desert of Pakistan (Naseem et al. 2010). Chae et al. (2007) found high fluoride concentration in Na-HCO_3 type and lowest in Ca-HCO_3 type groundwaters in South Korea. Fluoride concentration was positively related to the Na concentration and negatively related to that of Ca^{2+}. This implies that the geochemical behavior of fluoride in groundwater is related to geochemical process releasing Na^+ and removing Ca^{2+} ions. Gao et al. (2007) studied the fluoride in the groundwater of Yuncheng basin of North China and reported two important reasons for fluoride enrichment: (a) high fluoride in the salt water and (b) dissolution of fluoride-bearing minerals. The simulation result indicates that the major hydrogeochemical reaction is the precipitation of calcite and the dissolution of dolomite, gypsum, and fluoride during the mixing. Abdelgawad et al. (2009) studied sedimentary and granitic rocks of Mizunami area, Japan. The highly saline groundwater chemistry in the sedimentary rocks of Central Japan generally changes from Na-Ca-HCO_3 water type in the shallow zone to Na-HCO_3 water type in the deep zone. Groundwater in granitic rock is classified as Na-(Ca)-Cl water type, and it is possibly controlled by mixing processes occurring between low salinity groundwater (Na-(Ca)-HCO_3 water type) in the sedimentary rocks and higher salinity groundwater (Na-(Ca)-Cl water-type) (Abdelgawad et al. 2009). Wambu and Muthakia (2011) reported 6.57 mg/l in borehole water around Gilgil area of Nakuru, Kenya. The high concentration was attributed to extensive evaporation resulting in precipitation of dissolved salts rich in fluoride. In subsequent monsoon, rainwater percolates through the soil profile and enriches the groundwater with dissolved salts containing fluoride. The concentrations of fluoride in groundwater of North Jordan range from 0.009 to 0.055 mg/l and undersaturated with respect to calcite and fluorite (Rukah and Alsokhny 2004).

Chae et al. (2007) reported descending order of fluoride concentrations in groundwaters with respect to geology is as follows: metamorphic rocks≥granitoids≥complex rock≫volcanic rocks≥sedimentary rocks. This infers that the geological source of fluoride in groundwater is related to the mineral composition of metamorphic rocks and granitoids.

Conclusion

The present study reveals significant spatial and temporal variations in the total dissolved solids and major ions as a result of evapotranspiration during the pre-monsoon and percolation of rainwater through soil profile and bedrock in the monsoon. Weathering of carbonate minerals mainly the dissolution and precipitation of calcite in neutral to alkaline conditions control the enrichment of ions in groundwaters. Groundwater locations in the Archean and Vindhyan region showed relatively significant enrichment of fluoride in the monsoon. The saturation indices of calcite and fluorite suggests calcite precipitation is the driving force for the fluoride ion buildup in the groundwater and the possibility of further increase in fluoride concentration due to dissolution of fluorite. The excess fluoride concentration in groundwater of the study region implies urgent need to implement suitable remedial measures, and defluoridation of the pumped water seems to be a viable option for long-term relief measures.

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