

Hydrochemistry of groundwater (GW) and surface water (SW) for assessment of fluoride in Chinnaeru river basin, Nalgonda district, (AP) India

G. Machender · Ratnakar Dhakate ·
M. Narsimha Reddy

Received: 29 August 2013 / Accepted: 15 April 2014 / Published online: 15 May 2014
© Springer-Verlag Berlin Heidelberg 2014

Abstract Hydrochemical studies were conducted in Chinnaeru river basin of Nalgonda district, Andhra Pradesh, India, to explore the causes of high fluorides in groundwater and surface water causing a widespread incidence of fluorosis in local population. The concentration of fluoride in groundwater ranges from 0.4 to 2.9 and 0.6 to 3.6 mg/l, stream water ranges from 0.9 to 3.5 and 1.4 to 3.2 mg/l, tank water ranges from 0.4 to 2.8 and 0.9 to 2.3 mg/l, for pre- and post-monsoon periods, respectively. The modified Piper diagram reflects that the water belongs to $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ to $\text{Na}^+\text{-HCO}_3^-$ facies. Negative chloroalkali indices in both the seasons prove that ion exchange between Na^+ and K^+ in aquatic solution took place with Ca^{2+} and Mg^{2+} of host rock. The interpretation of plots for different major ions and molar ratios suggest that weathering of silicate rocks and water–rock interaction is responsible for major ion chemistry of groundwater/surface water. High fluoride content in groundwater was attributed to continuous water–rock interaction during the process of percolation with fluorite bearing country rocks under arid, low precipitation, and high evaporation conditions. The low calcium content in rocks and soils, and the presence of high levels of sodium bicarbonate are important factors favouring high levels of fluoride in waters. The basement rocks provide abundant mineral sources of fluoride in the form of amphibole, biotite, fluorite, mica and apatite.

Keywords Groundwater · Hydrochemical · Fluoride · Water–rock–interaction · Chinnaeru river basin

Introduction

Fluoride in drinking water has become one of the most important geo-environmental and toxicological issues in the world (Arif et al. 2012; Brindha et al. 2011; Hussain et al. 2004, 2010; Singh et al. 2007). Fluoride is considered as physiologically important to man and animals. The major health problems caused by drinking high concentrated fluoride water for a long term are teeth mottling, skeletal fluorosis, thyroxine changes, kidney damage and deformation of bones in children and in adults (Grandjean et al. 1992; Handa 1988; Jain et al. 1999; Kundu et al. 2001; Saxena and Ahmed 2001; Subba Rao 2003; Subba Rao et al. 1998a, b). Fluoride occurrence in groundwater is a natural phenomenon influenced by the local and regional geological setting. It is a unique substance for which there are both lower and upper limits of concentration in drinking water with identified advantages and disadvantages.

High-fluoride in groundwater and surface water has been reported from many parts of the world, particularly in arid and semi-arid areas of India, China, Sri Lanka, Spain, Mexico and many countries in Africa, western USA and South America (Abu Rukah and Alsokhny 2004; Ayoob and Gupta 2006). The serious health risks associated with high fluoride concentrations in drinking water (WHO 2004) warrant investigations of fluoride chemistry encompassing a wide spectrum of hydrochemical and geochemical analyses and appropriate methods of remediation. Granitic rocks contain a relative abundance of fluoride-rich minerals such as micas, apatite and amphiboles, etc. Fluorite (CaF_2) is the principal fluoride mineral, mostly present as an

G. Machender (✉) · M. Narsimha Reddy
Department of Geology, Osmania University,
Hyderabad 500007, AP, India
e-mail: machender_geo@yahoo.co.in

R. Dhakate
CSIR-National Geophysical Research Institute,
Uppal Road, Hyderabad 500007, AP, India

accessory mineral in granites. In granites/gneisses rock types the majority of the fluoride containing minerals are fluorite (0–3.3 %), biotite (0.1–1.7 %), and hornblende (0.1–1.1 %) (Ram Mohan Rao et al. 1993). The world average of fluoride concentration in granitic rocks was found to be 810 mg/l (Wedepohl 1969), while fluoride content of granitic rocks from Nalgonda was found to be in the range of 325–3,200 mg/l, with a mean of 1,440 mg/l (Ram Mohan Rao et al. 1993; Brindha et al. 2011). As groundwater percolates through the weathered rock in the aquifers, it dissolves fluoride bearing minerals hence, releasing fluoride into solution (Cairncross and Feachem 1991; Falvey 1999). Dissolution of such minerals can constitute a major source of fluoride in groundwater (Abu Rukah and Alsokhny 2004; Edmunds and Smedley 2005; Ramesham and Rajagopalan 1985; Reddy et al. 2009, 2010; Shaji et al. 2007).

High concentrations of fluoride in groundwater and surface water also result from evapotranspiration which may trigger calcite precipitation and result in a reduction in the activity of calcium (Ca^{2+}) (Jacks et al. 2005). Several studies have noted an increase in dissolved fluoride concentrations with increasing groundwater residence time (Apambire et al. 1997; Edmunds and Smedley 2005; Genxu and Guodong 2001; Nordstrom and Jenne 1977). Relatively high fluoride concentrations have been found in some deeply circulating groundwater along fault lines (Kim and Jeong 2005; Kundu et al. 2001).

Study of the geochemical process is essential, as fluoride contamination is selective even in similar hydrogeological environments; hence, the unique characteristics of the water that are responsible for higher assimilation of fluoride need to be explored and understood. The groundwater/surface water, not only with similar chemical composition or ionic make up but also within the watershed or sub-basin, has a different degree of fluoride concentration. The reasons for this discreet fluoride absorption could be delineated by attempting a comprehensive study of analytic results, which may open up new ideas for understanding more clearly the water–rock interaction contact chemistry. The geochemistry of groundwater was evaluated in Viapar river basin, Tamil Nadu, by adopting various methods like Gibbs plots, Kelley's index, chloroalkali indices (CAI) and concluded host rock as the main source of dissolved solids in the groundwater (Pandian and Sankar 2007).

Fluorine is the most electronegative element in the periodic table, and the content of fluorine in the lithosphere varies between 100 and 1,500 g/ton. Owing to the universal presence of fluorides in earth's crust, all water contains fluorides in varying concentrations ranging from trace levels to several milligrams per litre (WHO 1994). In surface fresh water such as rivers and lakes, fluoride concentrations are usually low, ranging from 0.01 to 0.3 mg/l (Murray 1986).

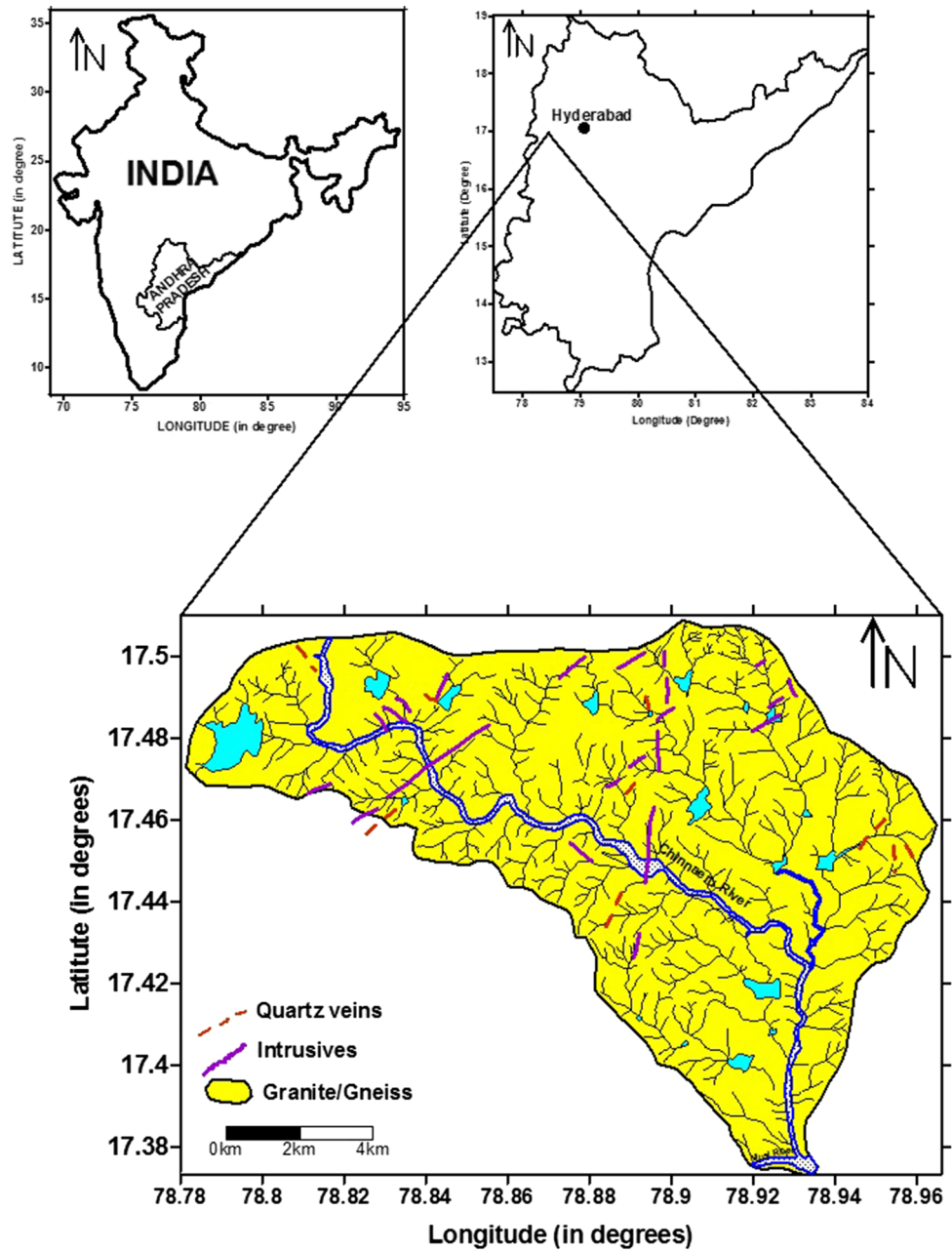
Fluorine occurs in greater abundance than chlorine, copper, or lead. The majority of fluorine found in nature is present in various rocks, soils, waters, plants, slugs, fluxes and other living organisms. Fluoride is essential in small quantities for the prevention of dental caries especially in children. There are several others effects with varying degrees of affliction ranging from body pain, loss of sensation or numbness to brownish yellow staining of teeth. As these symptoms were similar to that of “skeletal and dental fluorosis”, skeletal fluorosis, which has a crippling effect on the individual, which occur due to the deposition of fluoride in the bones. The Nalgonda district in South India is well known for high concentration of fluoride in groundwater (Ram Mohan Rao 1991). Prevalence of fluorosis disease is rampant among a majority of rural habitations of the district where groundwater is the only source for drinking and irrigation requirements. The hazardous characteristics of high fluoride content in groundwater have necessitated the study to explore the reasons for selective enrichment of fluoride in groundwater/surface water to chronicle the various chemical processes that are involved during the evolution of hydro-geochemical facies.

The article outlines the origin of fluoride in groundwater/surface water in a granitic watershed located in Nalgonda district, about 30 km south of Hyderabad, India. Nalgonda district is one of the poorest and most drought-prone districts of Andhra Pradesh in southern India. The area has been associated with high groundwater fluoride concentrations which have been reported to reach up to 10 mg/l (Ram Mohan Rao et al. 1993). Thousands of inhabitants suffer from paralysing bone diseases, deformities of vertebrae, hands and legs, deformed teeth, blindness and other conditions that are common manifestations of this natural hazard in the district. The first fluorosis problem in Nalgonda district was reported (Siddiqui 1968). A better understanding of fluoride geochemistry in the study area is important for evaluating the contamination process more precisely. This study uses a multifarious approach to understand the mechanism responsible for the spatial/temporal distribution and dynamics of fluoride across a small river basin composed of a single bedrock geological unit (granitic and gneiss).

Study area geology and hydrology

Chinnaeru river basin is situated 30 km away from Hyderabad, the capital of Andhra Pradesh State, India (Fig. 1). Geologically, the area consists of granites, gneisses and pegmatite rocks of Archaean age (Fig. 1). The granites are pink and grey in color, hard massive to foliated and jointed. The soil cover is of well developed residual soil of weathered granite. The soil is reddish-brown in

Fig. 1 Key map of the study area showing geology and drainage pattern



color. The soil is fairly permeable and the infiltration rate can absorb most of the rain except for more intensive rains, which can cause considerable surface flow and erosion (GSI 1995; Machender et al. 2013, 2014).

Groundwater occurs in the soil of weathered granite, semi-weathered and fractured hard under the water table and in semi-confined conditions. The average depth of groundwater is about 10–12 m. These rocks possess negligible primary porosity but due to secondary porosity by deep fracturing and weathering, they are rendered with a porosity and permeability, which locally form potential aquifers in study area (CGWB 2007).

Spatial and temporal distribution of fluoride

The high fluoride content was found in the groundwater sample in the basin, but it is well distributed. For pre- and post-monsoon seasons the fluoride concentrations are more than the permissible limit of drinking water standard (WHO 1994) (>1.5 mg/l) which was found in the north-western and south-eastern part of the study area. Similarly, in surface water samples (tank and stream) the high fluoride concentration for pre-monsoon period was found in the north-western, central and southern part of the study area, while for post-monsoon period, the high concentration of

fluoride was found in northern, central and eastern part of the study area. The high fluoride concentration in groundwater samples is found in discharge areas. Fluoride variation in groundwater during pre- and post-monsoon seasons is very wide and uneven. The fluoride also shows contrasting seasonal fluctuation in close proximity. The mixed seasonal trend and uneven spatial distribution could be due to relative abundance of fluoride-bearing minerals and soil texture (Rao 1997). The uneven distribution of fluoride in space and time is primarily due to variation in mineral assemblage of rocks, differential fracture system, and associated hydrochemical processes (Reddy and Rao 2006).

Materials and methods

Groundwater and surface water samples were collected in pre-cleaned and rinsed with acetone and added 1 ml of nitric acid in 1 l polyethylene bottle following (APHA 1995) method from the bore wells, which are used for both drinking and irrigation purposes and from stream channel and tanks for pre- and post-monsoon period, respectively. The location of these samples is shown in Fig. 2. The water samples from the bore wells were collected after pumping out water for about 10 min to remove stagnant water from the well. Forty-seven (28 groundwater, 10 tanks and 9 stream channel) samples during pre-monsoon season and 45 (28 groundwater, 9 tanks and 8 stream channel) samples for post-monsoon were collected for major ion chemistry analysis with in situ measurement of pH and electrical conductivity (EC). The water samples were analyzed in the laboratory of National Geophysical Research Institute, Hyderabad, as per the standard (APHA 1995) procedures. The pH measured using the digital pH meter of EI make, and EC was estimated by the EC analyzer CM 183 model of ELICO make. The classical methods of analysis were applied for the estimation of calcium, magnesium, carbonate, bi-carbonate, and chloride. Sodium and potassium were analyzed by flame photometry method using CL-345 flame photometer of ELICO make. Sulphate was estimated by the turbidity method using the Digital Nephelo-Turbidity meter 132 model of Systronics make. Nitrate was analyzed applying the UV–vis screen method using UV–visible spectrophotometer UV-1201 model of Shimadzu make. Fluoride was analyzed by the ion selective electrode method using Orion 290A+ model of Thermo-electron Corporation. TDS was estimated by calculating summation of cations and anions (epm) method after (Hem 1991). The obtained results were tested for accuracy by calculating the normalized inorganic charge balance (Huh et al. 1998; Mandel and Shiftan 1981). The analytical precision was such that the ion charge balance was within $\pm 5\%$ for all

the samples. Figure 3 shows the graph of total sum of cations versus total sum of anions for pre- and post-monsoon seasons, respectively. The quality of the analysis was ensured by standardization using blank, spike, and duplicate samples.

Results and discussions

The results of chemical analysis for pre- and post-monsoon periods are presented in Tables 1 and 2, respectively. The groundwater is alkaline with the pH value ranging from 7.36 to 10.16, 8.04 to 9.84 and 7.79 to 10.12 in pre-monsoon and 7.1 to 8.0, 7.6 to 9.6 and 7.5 to 8.6 in post-monsoon seasons in groundwater, tank and stream water samples, respectively. EC varies from 204 to 1,946, 190 to 1,709, 224 to 1,315 $\mu\text{S}/\text{cm}$ in pre-monsoon and 548 to 2,472, 330 to 1,303 and 695 to 1,227 $\mu\text{S}/\text{cm}$ in post-monsoon period in groundwater, tank and stream water samples, respectively. TDS varies from 122 to 1,167, 114 to 1,025, 100 to 774 mg/l in pre-monsoon period and 304 to 1,367, 188 to 734, 382 to 1,375 mg/l in post-monsoon period in groundwater, tank and stream, respectively. The concentration of other major constituents like Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^- and NO_3^- showed wide variation. The statistical summary of these constituents are given in Table 3 and the average contents of all ions for pre and post-monsoon period are graphically represented in Fig. 4 for groundwater, tank and stream samples, respectively. Concentration of F^- varies from 0.4 to 2.9, 0.4 to 2.8, 0.9 to 3.5 mg/l in pre-monsoon period and 0.6 to 3.6, 0.9 to 2.3, 1.4 to 3.2 mg/l in post-monsoon period in samples collected from groundwater, tank and stream, respectively. Out of 28 samples collected from groundwater, 11 samples shows high concentration of F^- for both pre- and post-monsoon season, while three samples each collected from tank shows high concentration of F^- for both seasons and eight samples out of nine and seven samples out of eight collected from stream for pre- and post-monsoon period shows high concentration of F^- than permissible limit, respectively.

The concentration of Mg^{2+} is high in groundwater samples containing higher concentration of fluoride; it could be due to the higher solubility of magnesium fluoride than calcium fluoride in water. Apart from F^- , the nitrate concentration is also high in groundwater samples in the basin; about 50 % of the samples have NO_3^- more than permissible limits (45 mg/l) in both pre- and post-monsoon seasons. Improper disposal mechanism of domestic sewerage, organic and animal waste, unlined drainage channels, and leaky septic tanks can be accounted for high nitrate content in groundwater; the NO_3^- is increasing with Cl^- in many samples (Fig. 4), both of which generate from

Fig. 2 Map showing the groundwater, tank and stream sample location

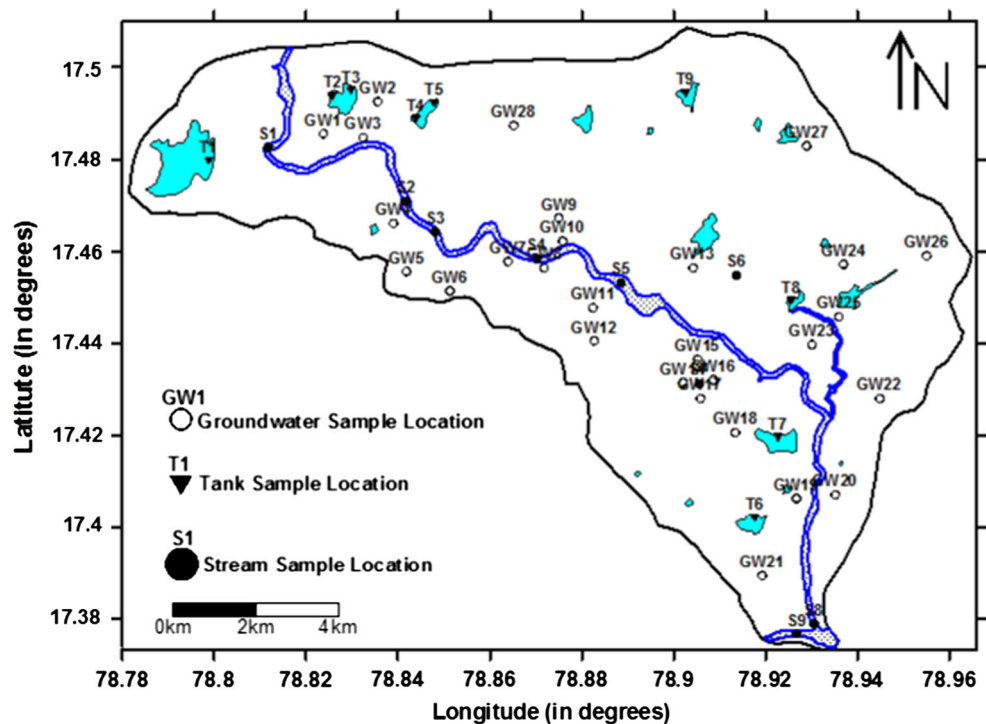
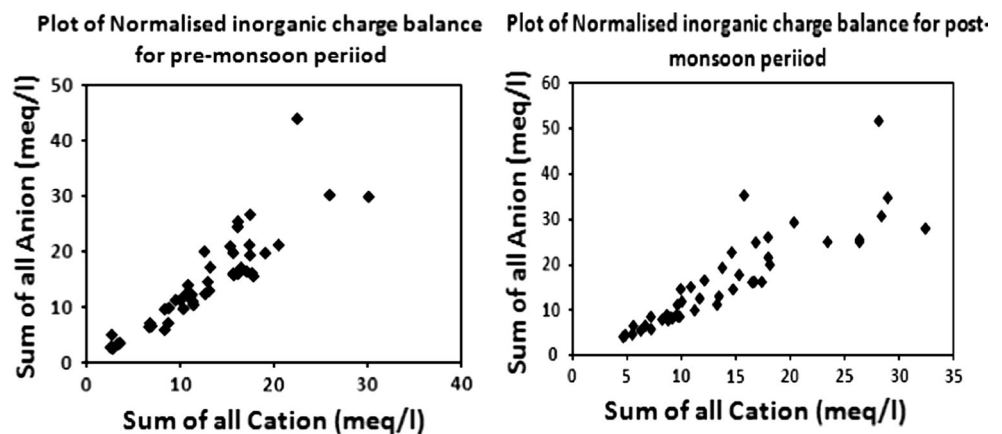


Fig. 3 Graph of total sum of cations and total sum of anions for pre-monsoon and post-monsoon periods



human and animal waste. The high nitrate could also be due to excess application of both organic and inorganic fertilizers, as some samples show scattered distribution for groundwater samples in the NO_3^- versus Cl^- plot (Fig. 5). High fluorides in groundwater are generally associated with high bicarbonate ions and in some cases with high nitrate ions (Handa 1975).

Groundwater classification

The different groundwater facies proposed were based on the content (meq/l) of selected ions (Soltan 1998). The groundwater of the basin can be classified as normal type, as most of the samples has Cl^- content of >15 meq/l except two samples has Cl^- content >15 meq/l for pre-

monsoon period, while for post-monsoon period it is <15 for all samples (Table 4). A majority of the samples belong to the normal sulphate category, as SO_4^{2-} is <6 meq/l. The TDS of the water is $<1,000$ mg/l in most of the samples, which can be grouped as freshwater type, but 11 and 22 % of the samples for pre- and post-monsoon fall in the brackish category (Table 4). The groundwater can be further classified based on the base-exchange indices (Soltan 1999) determined using the following Eq. 1.

$$r_1 = \text{Na}^+ - \text{Cl}^- - \text{SO}_4^{2-} \text{ meq/l} \tag{1}$$

The groundwater can be grouped as $\text{Na}^+ - \text{HCO}_3^-$ type if r_1 is >1 and $\text{Na}^+ - \text{SO}_4^-$ type for samples having r_1 value of <1 . Fifty percent and 53 % groundwater samples for pre- and post-monsoon seasons belong to $\text{Na}^+ - \text{HCO}_3^-$ type and

Table 1 Major element chemistry of groundwater, stream and tank samples for pre-monsoon period

Sl. no.	pH	EC ($\mu\text{S}/\text{cm}$)	TDS (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Mg^{2+} (mg/l)	Ca^{2+} (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	HCO_3^- (mg/l)	CO_3^- (mg/l)	NO_3^- (mg/l)	F^- (mg/l)
<i>Groundwater samples</i>													
1	7.73	878	526.8	136	2.1	19.6	22	101	30	134.2	15	16.5	2.1
2	7.56	1,438	862.8	188.2	3.1	41.2	115.7	417.8	56.5	146.4	15	51.8	2.7
3	7.82	1,370	490.2	257.2	2.8	39.6	62.5	240.2	72.1	320.25	33	28	2.8
4	8.23	635	381	131	6.6	37.1	85.4	102	49.6	341.6	60	93	1.6
5	7.36	1,158	694.8	90	1.8	82.8	234.6	395.2	119.2	112.85	12	394.5	0.4
6	7.64	619	371.4	75.6	1.8	39.8	34.1	30.7	22.5	192.15	18	15.4	0.9
7	7.59	535	321.4	52.8	1.7	25.4	46.5	11.3	10	301.95	33	14.9	1.4
8	7.59	958	574.8	122.9	6.7	42.5	19.4	95.5	48.3	323.3	42	21.5	1.6
9	7.48	1,775	1,065	168.9	116.5	41.2	48.7	202.6	101.6	213.5	36	188.4	0.4
10	7.4	595	357	125.3	19.7	27.9	61	94.5	40.1	295.85	30	30.3	1.0
11	8.17	630	380	75.9	1.7	40.2	33.5	44.3	34.4	341.6	32	21	1.3
12	7.72	650	390	71.4	2.4	41.6	92.2	121.9	59.1	155.55	18	65.6	0.8
13	7.39	738	442.8	163.1	4	40.4	48.2	181.3	57.6	244	33	51	1.3
14	7.73	1,095	657	101.1	3	47.5	45.7	137.5	101.4	207.4	24	36.7	1.4
15	7.55	939	563.4	72.6	5.2	44.7	111.9	153.7	125.5	164.7	18	140.3	0.6
16	7.54	534	320.4	60.6	4	39.9	69.2	72.5	32	271.45	30	50.1	0.9
17	7.52	811	486.6	160	45.8	64	79.5	145.1	55.2	381.25	57	121.7	2.0
18	8.33	1,227	736.2	254.3	4	35.7	47.5	153.5	78.4	539.85	69	15.4	2.2
19	8.04	1,676	1,005.6	306.5	11.4	49.5	27.2	238.3	95.4	481.9	51	31.2	2.9
20	7.99	1,528	916.8	285.3	8.7	42.7	32.7	205.3	95.3	345.26	48	18.3	2.9
21	7.48	1,409	845.4	476.4	8.9	83.9	45.4	711	125.9	356.85	42	8.3	2.7
22	7.36	998	598.8	166.7	2.6	54.2	113.5	364.9	108.7	97.6	15	171	0.8
23	7.78	1,946	1,167.6	346.8	3.3	45.5	31.3	301	111.6	408.7	48	39.7	2.5
24	7.51	1,283	769.8	288.6	2.8	104.6	94.3	667.4	126.7	189.1	30	71.1	1.4
25	10.16	204	122.4	37	4.7	7.1	6.5	15.3	2.7	118.95	9	33.4	0.8
26	7.58	1,479	887.4	113	3.2	53.8	134.3	150	85.5	283.65	24	186.9	1.3
27	7.58	1,419	851.4	147.3	2.2	46.1	108	261.8	71.2	176.9	18	107.2	1.2
28	7.65	1,191	714.6	128.5	2.8	30.6	52.4	162.6	59.8	231.8	27	53.8	0.8
<i>Stream samples</i>													
1	7.79	541	324.6	129.9	1.3	43.1	43	38.8	8.8	488	66	0	3.5
2	8.29	1,290	774	270.2	4.2	32.2	32.9	269.2	33.3	427	42	0	2.7
3	10.12	640	384	165	4.0	27.3	15.4	111.6	28.4	332.45	27	0.5	2.6
4	9.42	479	287.4	94.4	6.3	18.5	17.7	52.7	27.2	247.05	18	0	1.9
5	9.31	550	330	206.5	6	35.8	20	121.6	24.1	481.9	66	0	3.1
6	9.23	857	514.2	200.8	5.5	34.8	17.9	114.1	23.3	475.8	51	0.	3.0
7	9.19	224	134.4	49	6.9	6.2	9.2	18.2	9.6	134.2	22	0	1.8
8	8.53	1,168	100.8	262.2	6.6	33.5	26.3	210.8	52.5	491.05	48	1.5	3.0
9	8.39	1,315	189	191.1	20.2	33.3	75.1	207.8	67.6	396.5	30	92.9	0.9
<i>Tank samples</i>													
1	9.27	350	210	107.6	4.0	17.3	14.1	55	22.7	259.25	18	0	2.1
2	8.53	245	147	39.3	5.9	8.3	16.4	25.5	11	131.15	15	0.	1.4
3	8.28	251	150.6	44.3	5.9	8.5	14.5	29.7	13.7	146.4	0	0	1.4
4	8.93	190.1	114.06	21.8	4.8	8.1	15.4	11.3	6	140.3	0	0	1.0
5	8.72	224	134.4	25.2	4.7	8.4	14.6	12.7	7	137.25	0	0	1.0
6	8.88	778	466.8	280.3	7.6	41.6	25.2	193.3	79.7	445.3	54	15.4	2.8
7	8.04	195.3	117.18	23.1	6.7	6.7	20.1	12.4	7.1	118.95	6	0.9	0.4

Table 1 continued

Sl. no.	pH	EC ($\mu\text{S/cm}$)	TDS (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Mg^{2+} (mg/l)	Ca^{2+} (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	HCO_3^- (mg/l)	CO_3^- (mg/l)	NO_3^- (mg/l)	F^- (mg/l)
8	9.84	209	125.4	47.6	4.7	3	6	30	16.5	85.4	0	0	1.3
9	8.05	887	532.2	79.2	42.7	27.7	38.9	64.1	14.5	417.85	51	0.	1.4
10	8.47	1,709	1,025.4	217.4	10.6	42	50.3	429	59.3	134.2	12	0	1.6

the remaining 50 and 47 % belong to $\text{Na}^+ - \text{SO}_4^{2-}$ type, 30 and 77 % tank samples for both the seasons belong to $\text{Na}^+ - \text{HCO}_3^-$ type and the remaining 70 and 23 % belong to $\text{Na}^+ - \text{SO}_4^{2-}$ type, while 88 and 87 % stream samples were $\text{Na}^+ - \text{HCO}_3^-$ type and 10 % samples belong to $\text{Na}^+ - \text{SO}_4^{2-}$ type for pre- and post-monsoon seasons (Fig. 6; Table 4). The percentage of samples belonging $\text{Na}^+ - \text{HCO}_3^-$ in tank samples increased significantly in post-monsoon seasons as compared to pre-monsoon seasons due to dissolution of minerals. The groundwater source can be determined based on meteoric genesis index, which was computed by applying (Eq. 2) (Soltan 1999).

$$r_2 = \text{K}^+ + \text{Na}^+ - \text{Cl}^- - \text{SO}_4^{2-} \text{ meq/l} \tag{2}$$

The value of $r_2 < 1$ indicates that the groundwater is of deep meteoric percolation type, and $r_2 > 1$ indicates that the water is of shallow meteoric percolation type. Based on meteoric genesis index, 53 % of groundwater samples from pre- and post-monsoon season show meteoric percolation type, while the remaining show deeper meteoric percolation. Similarly 30 and 88 % samples of tank and stream samples also show meteoric percolation, for pre- and post-monsoon season, respectively (Fig. 7; Table 4). Although continuous drought conditions are prevailing, groundwater over-exploiting is not taking place, and deep meteoric water is not being added to the groundwater repositories. It suggests that F^- is accumulating in the groundwater due to its continuous contact with weathered and fractured aquifer material in the process of recharge and discharge but not from meteoric sources. The effect of monsoon is not so pronounced in the study area, as the area falls in the arid region, where very low annual rainfall is noticed. In monsoon the sufficient quantity of recharge is not taking place in the aquifer regime, and the water in the aquifer is in continuous contact with the fluoride bearing minerals resulting increase of fluoride and other ionic concentrations even after the monsoon season.

Chloroalkali indices (CAI)

The role of aquifer material in the evolution of groundwater chemical composition can be further probed by determining chloroalkali indices (CAI) for cations (CAI-1) and anions (CAI-2). It is imperative to understand the

modifications in water chemistry during its movement and residency time for better evaluation of hydrochemistry of any area, when different geological formation are involved in a watershed or river basin (Johnson 1979; Sastry 1994). CAI-1 [$\text{Cl} - (\text{Na} + \text{K}) / \text{Cl}$] and CAI-2 [$\text{Cl} - (\text{Na} + \text{K}) / (\text{SO}_4 + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3)$] developed by Schoeller (1967) relates the ion-exchange process between groundwater and aquifer material. The CAI-1 and CAI-2 are found to be negative (Fig. 8a, b) in most of the samples, except in eight samples for pre-monsoon (seven samples belong to groundwater and one sample belongs to tank sample) and in six samples for post-monsoon season (five samples belong to groundwater and one sample belongs to tank), indicating that ion-exchange processes are involved between Na^+ and K^+ in water with Ca^{2+} and Mg^{2+} in host rock, and the exchange is indirect during the evolution of sub-surface water chemistry (McIntosh and Walter 2006).

Gibbs plots

The plots in which TDS versus $\text{Na}^+ + \text{K}^+ / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ for cations and TDS versus $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ for anion for pre- and post-monsoon period were plotted to illustrate the groundwater evolution process and the influence of host rock on groundwater chemistry (Gibbs 1970), which indicated that the samples by and large occupied the rock dominance to evaporation dominance fields (Fig. 9a, b) for pre- and post-monsoon seasons. The red colour symbols are for surface water samples (tank and stream samples). The water–rock interaction and aquifer material played major role in evolution of water chemistry, which was further influenced by the evaporation process. Geological location is one of the most important factors affecting groundwater quality (Beck et al. 1985).

Modified Piper diagram (Chadha diagram)

The groundwater/surface water of the study area has been classified as per modified Chadha’s diagram (Chadha 1999). The diagram is a somewhat modified version of the Piper trilinear diagram. In the Piper trilinear diagram the milliequivalent percentages of the major cations and anions are plotted in two base triangles and the type of

Table 2 Major element chemistry of groundwater, stream and tank samples for post-monsoon period

Sl. no.	pH	EC ($\mu\text{S/cm}$)	TDS (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	CO ₃ ⁻ (mg/l)	NO ₃ ⁻ (mg/l)	F ⁻ (mg/l)
<i>Groundwater samples</i>													
1	7.7	797.6	448	151.7	1.5	15.6	33.9	93.8	27.4	463.6	0	6.7	2.7
2	7.4	1,585	891.3	270.8	7.4	38.8	57	303.2	98	646.6	0	7	2.7
3	7.1	1,399	791.4	129.9	2.8	38.3	115.2	334.4	60.8	317.2	0	97	2.6
4	7.5	1,375	756	228.4	2.8	38.8	42.4	225.8	74.1	427	0	41.4	2.8
5	7.5	815.7	452.6	83.7	2.1	29.6	41.4	38.2	25.1	283.65	24	19.2	1.0
6	7.1	1,513	853.4	70.4	1.8	54.7	163.6	230.6	80.7	402.6	0	288.9	1.0
7	7.6	548.2	304.1	35.8	0.7	14.9	55	13.8	12.8	292.8	0	16.5	0.8
8	7.1	1,083	612.3	91.3	11.1	52.8	70.5	102.7	52.7	414.8	0	82.3	0.8
9	7.4	1,009	565.5	130.3	23.9	24.9	66.9	103.3	42.5	439.2	0	23.3	0.6
10	7.4	1,079	6.5	130.1	99.3	22.6	67.9	97.6	48.3	329.4	24	50.6	0.7
11	7.3	744.9	412	69.7	1.2	33.9	55.9	16.7	21.5	439.2	0	12.6	1.2
12	7.6	906	507.5	76.9	2	49.7	51	55.3	34.9	512.4	0	18.5	2.4
13	7.1	1,577	885.5	160.7	3.6	42.8	125.1	246.8	89.0	512.4	0	109.5	1.4
14	7.3	900	500	69	1.8	39.8	72.1	70.6	74.7	414.8	0	61.6	1.1
15	7.3	753	405.2	38.8	1.5	29.5	60.5	26	15.3	329.4	0	30.5	0.8
16	7.4	2,350	1,325	287.2	113.9	91.9	105	265.4	139.5	305	15	506.7	1.2
17	7.4	2,472	1,367	272	2.3	147	101	403.8	151.3	622.2	0	142.2	1.5
18	7.5	899	510	190	3	23.7	59.7	37.5	35.6	549	0	7.2	2.8
19	8	1,312	735	268.8	15.7	37.4	44.8	154	69.2	506.3	36	22.8	3.3
20	7.5	2,332	1,294	359.8	13.9	73.1	88.1	368.2	103.8	768.6	0	20.2	1.6
21	7.4	1,616	906.4	273.6	3.7	38.8	56	232.7	99.6	488	0	133.6	2.3
22	7.7	1,445	797.5	269.3	1.7	40.5	28.6	250.4	52.9	488	0	1.3	3.3
23	7.3	1,932	1,072	172.9	2.1	45.4	181.8	342.6	107.7	317.2	0	172.6	1.1
24	7.3	1,989	1,114	428	3.6	36.5	35.4	287.8	99.9	634.4	0	63.8	3.6
25	7.4	2,433	1,361	311.3	2.3	84.4	158.6	521.5	129.5	414.8	0	93	1.1
26	7.3	1,037	583.2	91	2.2	37	76.2	81.7	59.2	414.8	0	68.1	1.1
27	7.3	1,049	590.4	139	2	33.2	118.7	199.6	41.8	305	0	44.6	1.9
28	7.4	1,226	678.7	114.4	2.8	31	123.5	199.7	64.9	353.8	0	93.1	0.9
<i>Stream samples</i>													
1	7.9	870.2	493	149.6	1.4	41.8	24.6	44.1	12.8	481.9	39	0.3	3.2
2	8.3	695.2	382.1	112.4	2.7	20.6	42.4	68.8	16.4	301.95	39	0	1.8
3	8.3	718.7	404.9	127.7	2.4	22.8	33.3	72.5	17.5	323.3	36	0	2.2
4	8.4	765.6	422.1	135.2	2.6	25.3	30.2	82.2	22.6	356.75	24	0	2.6
5	8.6	745.9	420.9	141.3	2.1	27.5	24.3	70.1	17.8	344.65	39	0	2.4
6	7.5	2,332	1,294	359.8	13.9	73.1	88.1	368.2	103.8	768.6	34	0	1.6
7	8.4	2,460	1,375	466.8	15.1	86	95	496.2	137.8	616.1	60	2	2.0
8	7.8	1,234	725.6	228.4	15.3	40.8	89.6	256.5	90.4	384.3	42	55.8	1.4
<i>Tank samples</i>													
1	8.3	381	216	44.8	3.8	11.1	37.1	27.4	8.1	204.35	18	0	1.0
2	8.6	476	265	77.3	6.0	14.4	30.7	41.8	11.9	237.9	15	0.2	0.9
3	8.8	680.6	394.4	127.9	3.9	28	20.4	77.6	16.7	332.45	30	0	1.9
4	9.4	330.7	188.5	58.7	2.5	15.5	14.5	28.3	11.4	184	9	0	1.4
5	8.3	444	236	57.1	5.6	15.4	31.3	27.7	8.2	213.5	18	0	0.9
6	9.4	582	310	102.7	4.8	21	17.7	57.7	17.3	213.5	24	0	1.4
7	8.6	761.6	424.6	144.3	3.9	28.3	22.6	100.8	21.5	292.8	33	0.2	2.3
8	9.6	584.6	323.2	115.3	4.2	13.1	9	122.4	11.2	140.3	42	0	1.1
9	7.6	1,303	734	223.8	15.5	44.5	58.5	398.7	59	219.6	16	0	2.0

Table 3 Statistical summary of physico-chemical parameters for groundwater, stream and tank samples

Physico-chemical parameters	Pre-monsoon					Post-monsoon				
	Min.	Max.	Mean	Median	SD	Min.	Max.	Mean	Median	SD
pH	7.36 ^a	10.16	7.76	7.59	0.66	7.1	8.0	7.40	7.4	0.20
	7.79 ^b	10.12	8.92	9.19	0.71	7.6	9.6	8.73	8.3	0.37
	8.04 ^c	9.84	8.70	8.62	0.56	7.5	8.6	8.15	8.6	0.64
EC	204 ^a	1,946	1,061	1,061.36	462.81	548.2	2,472	1,363.48	1,269	557.09
	224 ^b	1,315	784.88	640	392.41	330.7	1,303	615.94	817.9	742.02
	190.1 ^c	1,709	503.84	248	493.04	695.2	2,460	1,227.70	582	292.67
TDS	122.4 ^a	1,167	625	598.8	276.72	6.5	1,367	740.20	718.5	309.85
	100.8 ^b	774	337.6	324.6	207.95	188.5	734	343.52	457.55	413.06
	114.06 ^c	1,025.4	302.30	148.8	295.82	382.1	1,375	689.70	310	166.28
Na ⁺	37.01 ^a	476.39	164.38	136	114.01	35.80	428.02	175.53	145.35	104.23
	48.96 ^b	270.19	174.33	191.1	73.38	44.76	223.78	105.75	145.45	130.26
	21.81 ^c	280.31	88.57	45.95	89.83	112.43	466.85	215.16	102.7	56.03
K ⁺	1.71 ^a	116.48	10.12	3.3	28.35	0.70	113.9	11.88	2.55	27.34
	1.34 ^b	20.19	6.77	6.0	5.32	2.54	15.54	5.59	2.65	6.50
	4 ^c	42.7	9.75	5.9	11.73	1.35	15.32	6.96	4.2	3.86
Mg ²⁺	7.08 ^a	104.55	45.31	41.6	22.22	14.88	147	44.52	38.55	26.93
	6.23 ^b	43.14	29.42	33.3	10.94	11.07	44.47	21.24	34.15	24.55
	3.03 ^c	41.98	17.16	8.45	14.71	20.63	86.02	42.26	15.5	10.72
Ca ²⁺	6.51 ^a	234.64	67.96	52.4	54.21	28.60	181.76	80.56	67.4	41.56
	9.20 ^b	75.13	28.60	20	20.15	9.03	58.46	26.87	37.85	31.58
	6.04 ^c	50.28	21.55	15.9	13.34	24.34	95.04	53.45	22.6	14.81
Cl ⁻	11.27 ^a	710.99	206.36	153.7	188.68	13.81	521.45	189.41	199.65	133.88
	18.19 ^b	269.15	127.20	114.1	86.12	27.36	398.65	98.04	77.35	171.23
	11.32 ^c	428.98	86.30	29.85	132.05	44.11	496.21	182.32	57.7	117.79
SO ₄ ²⁻	2.68 ^a	126.68	70.57	70.58	37.52	12.83	151.28	68.32	62.85	37.63
	8.81 ^b	67.62	30.50	27.2	18.98	8.09	59.03	18.35	20.2	50.06
	5.99 ^c	79.73	23.75	14.1	25.09	12.78	137.8	52.38	11.9	15.87
HCO ₃ ⁻	97.6 ^a	539.85	263.52	263.52	120.21	238.65	768.60	442.58	420.9	122.03
	134.2 ^b	491.05	385.99	427	125.53	140.30	332.45	226.49	370.52	165.67
	85.4 ^c	445.3	201.60	138.77	129.21	301.95	768.60	447.19	213.5	56.85
CO ₃ ⁻	9 ^a	69	31.67	30	96.84	0	36	3.54	0	9.27
	18 ^b	66	41.11	42	18.05	9	42	22.78	39	10.06
	6 ^c	54	26	9	20.58	24	60	39.13	18	10.42
NO ₃ ⁻	8.26 ^a	394.53	74.17	50.1	0.80	0	506.65	79.09	47.6	104.99
	0.5 ^b	92.9	31.65	0	0.81	0	0.22	0.04	0	19.62
	0.92 ^c	15.38	8.15	0	4.84	0	55.75	7.25	0	0.08
F ⁻	0.4 ^a	2.9	1.53	1.4	0.80	0.6	3.6	1.7	1.3	0.92
	0.9 ^b	3.5	2.5	2.7	0.81	0.9	2.3	1.5	2.1	0.58
	0.4 ^c	2.8	1.4	1.4	0.65	1.4	3.2	2.2	1.4	0.51

Min minimum, *Max* maximum, *SD* standard deviation

^a Groundwater samples

^b Stream samples

^c Tank samples

water is determined on the basis of position of the data in the respective cationic and anionic triangular field. The plotting from triangular fields is projected further into the

central diamond field, which represents the overall character of the water. The modified Piper diagram (Chadha 1999), which indicates that most of them are of

Fig. 4 Average content of different chemical constituents for groundwater, tank and stream samples for pre-monsoon and post-monsoon periods

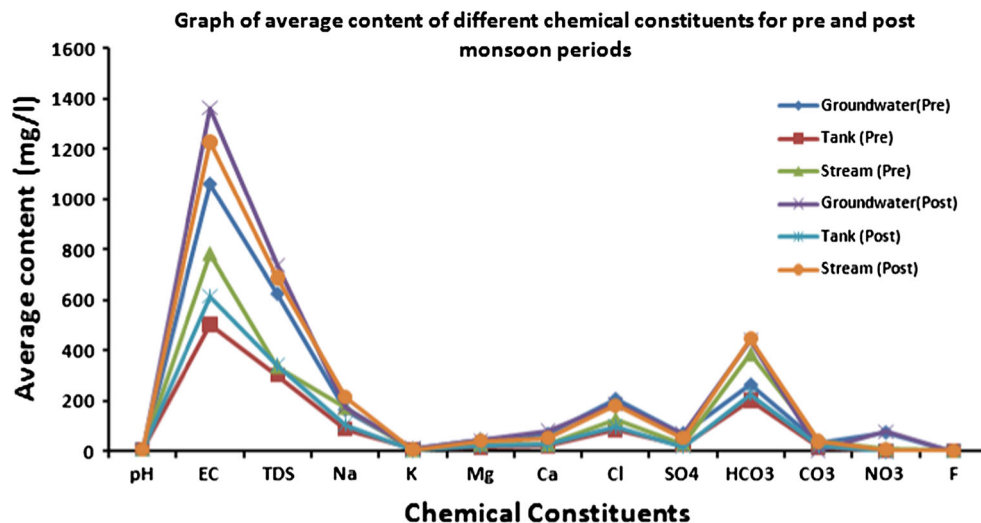
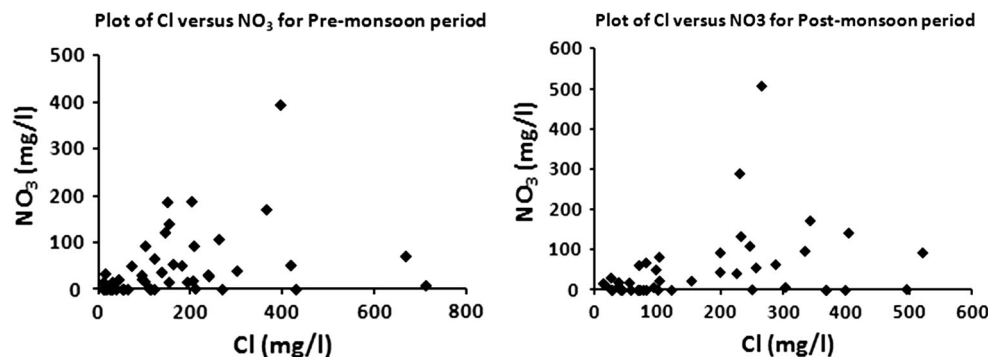


Fig. 5 Plot of Cl versus NO_3 for pre-monsoon and post-monsoon periods



Ca^{2+} – Mg^{2+} – HCO_3^- type; some belong to the subgroup of Na^+ – HCO_3^- type and a few fall in the Na^+ – Cl^- type water facies category in a decreasing order. The modified Piper diagrams for pre- and post-monsoon seasons are shown in Fig. 10a, b. The plot for pre- and post-monsoon season indicated scattered distribution with minor variations in their chemical characteristics between two seasons. About eight samples in pre-monsoon deviate from majority facies indicating variations of ionic species within the season, which could be due to local mineralogical differences. The modified Piper plot further strengthens the mineralogy of the aquifer material which played an important role in determining the water chemistry. Na^+ and Ca^{2+} are in a transitional state with Na^+ replacing Ca^{2+} and HCO_3^- replacing Cl^- due to physio-chemical changes in the aquifer and the water–rock interactions (Elango and Kannan 2007).

Hydrogeochemical evaluation

Concentration of different major ions and their interrelationship were studied to understand and illustrate the hydrogeochemical processes that were involved in aquifer

domain during the evolution of different groundwater facies. High sodium content among cations in the groundwater of two seasons (Tables 1, 2) could be due to weathering of silicate rocks such as granite and gneisses, which was further enhanced by evapotranspiration processes as proven in the scatter plot of Na^+/Cl^- versus EC where most of the samples were plotted in a horizontal line parallel to x -axis reflecting evapotranspiration process played crucial role in increasing the concentration of all the species in the water (Fig. 11). Na^+/Cl^- molar ratio will be 1 if halite dissolution is responsible for sodium dominance in groundwater and >1 if Na^+ is released from silicate weathering process (Meybeck 1987). The Na^+/Cl^- molar ratio (Fig. 11; Table 5) is >1 in almost all the samples of both the seasons, indicating that silicate weathering was the primary process responsible for the excess release of Na^+ into the groundwater (Pophare and Dewalkar 2007; Stallard and Edmond 1983). The study of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio (Fig. 12; Table 5) also revealed that the dissolution of dolomite was one of the prime processes involved in enrichment of Ca^{2+} and Mg^{2+} in the groundwater as the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio between 1 and <2 (May and Loucks 1995).

Table 4 Classification of groundwater (Soltan 1998)

	Seasons		Type of water
	Pre-monsoon (% of samples)	Post-monsoon (% of samples)	
Ion concentration			
Cl⁻			
<15 meq/l	96	100	Normal chlorite type
>15 meq/l	4	0	
SO₄²⁻			
<6 meq/l	100	100	Normal sulphate type
>6 meq/l	0	0	
TDS			
<1,000 mg/l	89	82	Fresh
>1,000 mg/l	11	18	
Base-exchange indices			
r₁			
r ₁ < 1	47	36	Na–SO ₄ type
r ₁ > 1	53	64	
r₂			
r ₂ < 1	40	31	Deep meteoric percolation type
r ₂ > 1	60	69	

Almost all the samples in pre-monsoon except one sample in groundwater and one in surface water have <1 Ca²⁺/Mg²⁺ ratio and in post-monsoon season all samples have >1 Ca²⁺/Mg²⁺ ratio. In the plot of Ca²⁺ + Mg²⁺ against HCO₃⁻ + SO₄²⁻ for pre- and post-monsoon seasons (Fig. 13), majority of sample points (85 %) cluster around and below the median line and close to x-axis, indicating that dissolution of calcite is not dominant reaction and ion exchange was responsible for the higher HCO₃⁻ + SO₄²⁻ concentration in groundwater (Cerling et al. 1989; Fisher and Mulican 1997). The Ca²⁺ + Mg²⁺

and Cl⁻ (mmol/l) plot (Fig. 14) further confirm that ion exchange is the dominant process as Ca²⁺ and Mg²⁺ increase with increasing salinity with few exceptions in pre- and post-monsoon samples. The cation contribution to groundwater by silicate weathering can also be assessed by the Na⁺ and K⁺ versus total cation index (Sarin et al. 1989; Stallard and Edmond 1983).

The plot for the pre and post-monsoon seasons (Fig. 15) shows that samples fall along the aquiline, suggesting that the cations in groundwater might have been derived from silicate weathering. The plot of Ca²⁺ + Mg²⁺ versus total cations show that all the points lies above the aquiline (Fig. 15), suggesting the requirement of alkalis to the major ions, which are derived from silicate weathering and alkaline earth silicates. The plot also reveals increasing contribution of Na⁺ and K⁺ with increasing total dissolved solids. The source of Ca²⁺ and Mg²⁺ can be explored by interpreting the Ca²⁺ + Mg²⁺/HCO₃⁻ versus Cl⁻ (mmol/l) ratio plot showing an increase in Ca²⁺, Mg²⁺, and HCO₃⁻ ratio with salinity (Fig. 16). The Ca²⁺, Mg²⁺, and HCO₃⁻ ratio of <1 (Table 5) indicates that Ca²⁺ and Mg²⁺ are added to the solution at a lesser rate than HCO₃⁻, and Ca²⁺-Mg²⁺ originates from the dissolution of carbonate minerals in the aquifer material and from the weathering of accessory and pyroxene and amphibolites minerals as the ratio is about 0.50 (Sami 1992). The low (Na⁺ + K⁺)/Tz⁺ and (Ca²⁺ + Mg²⁺)/Tz⁺ ratio (Table 4) supports that the contribution of cation via silicate weathering but low molar ratio of (Ca²⁺ + Mg²⁺)/(Na⁺ + K⁺) suggest that the major ion contribution by silicate weathering has been less significant. The molar ratio of Ca²⁺/Na⁺, Mg²⁺/Na⁺, and Mg²⁺/HCO₃⁻ (Table 5) suggests that weathering of silicate rocks is responsible for major ion chemistry of the basin.

Ionic dominance pattern

The groundwater samples collected from the study area had high concentrations of Na⁺ constituting 28 and 31 %, and

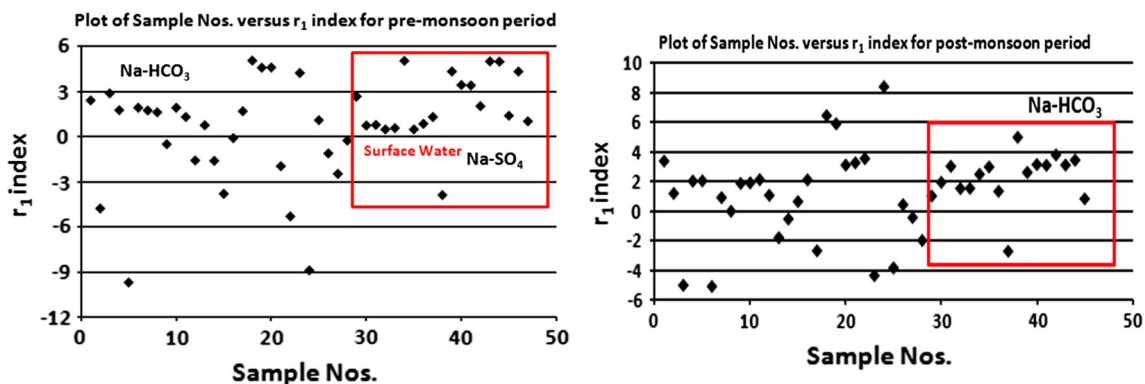


Fig. 6 Base-exchange indices (r₁) plot for pre-monsoon and post-monsoon periods

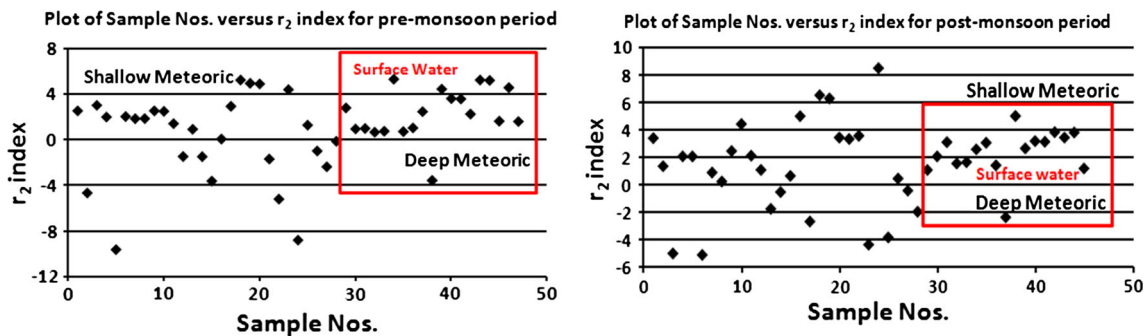
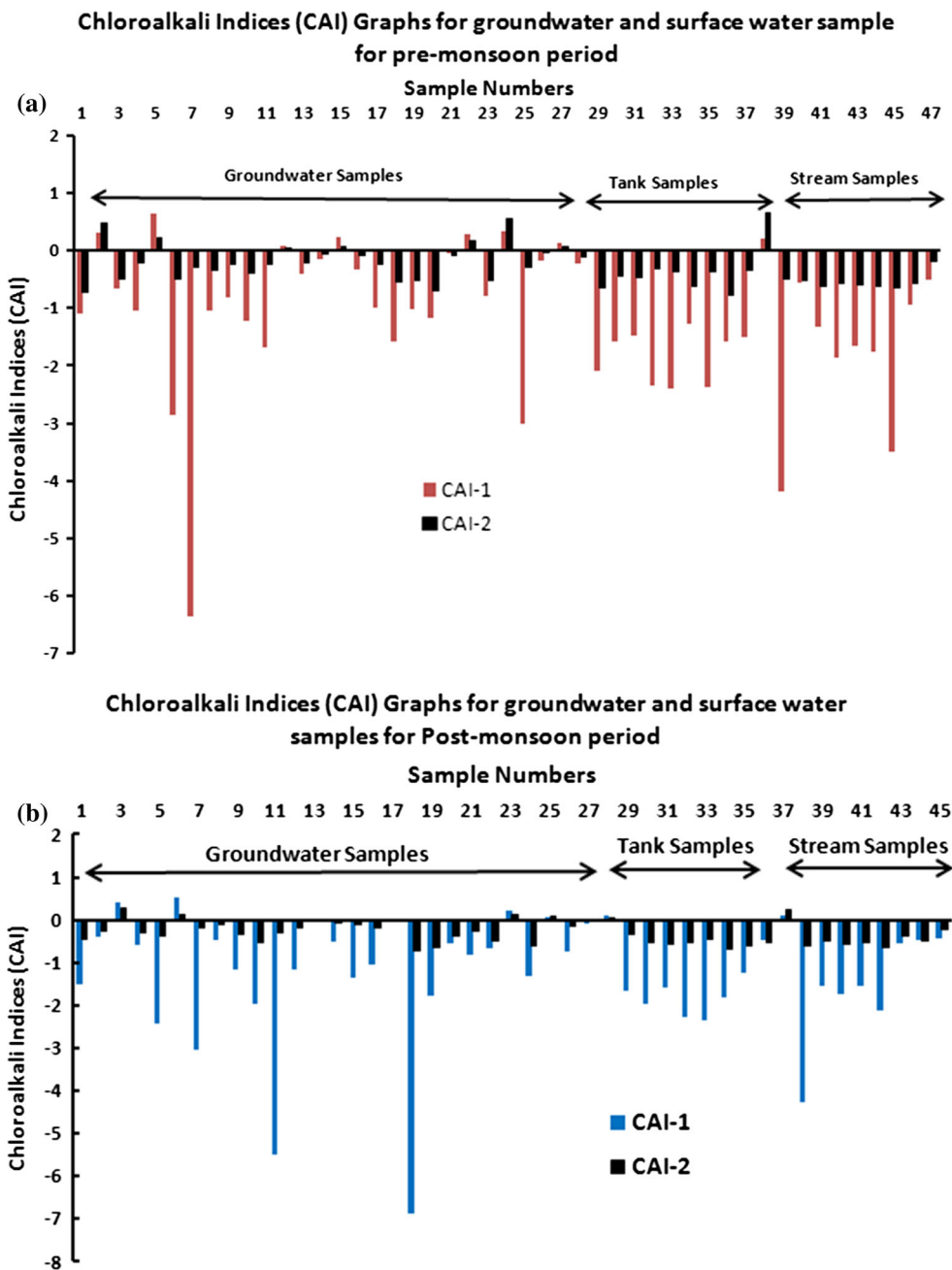


Fig. 7 Meteoric genesis index (r_2) plot for pre-monsoon and post-monsoon periods

Fig. 8 a, b Chloroalkali indices (CAI) for groundwater and surface water for pre-monsoon and post-monsoon periods



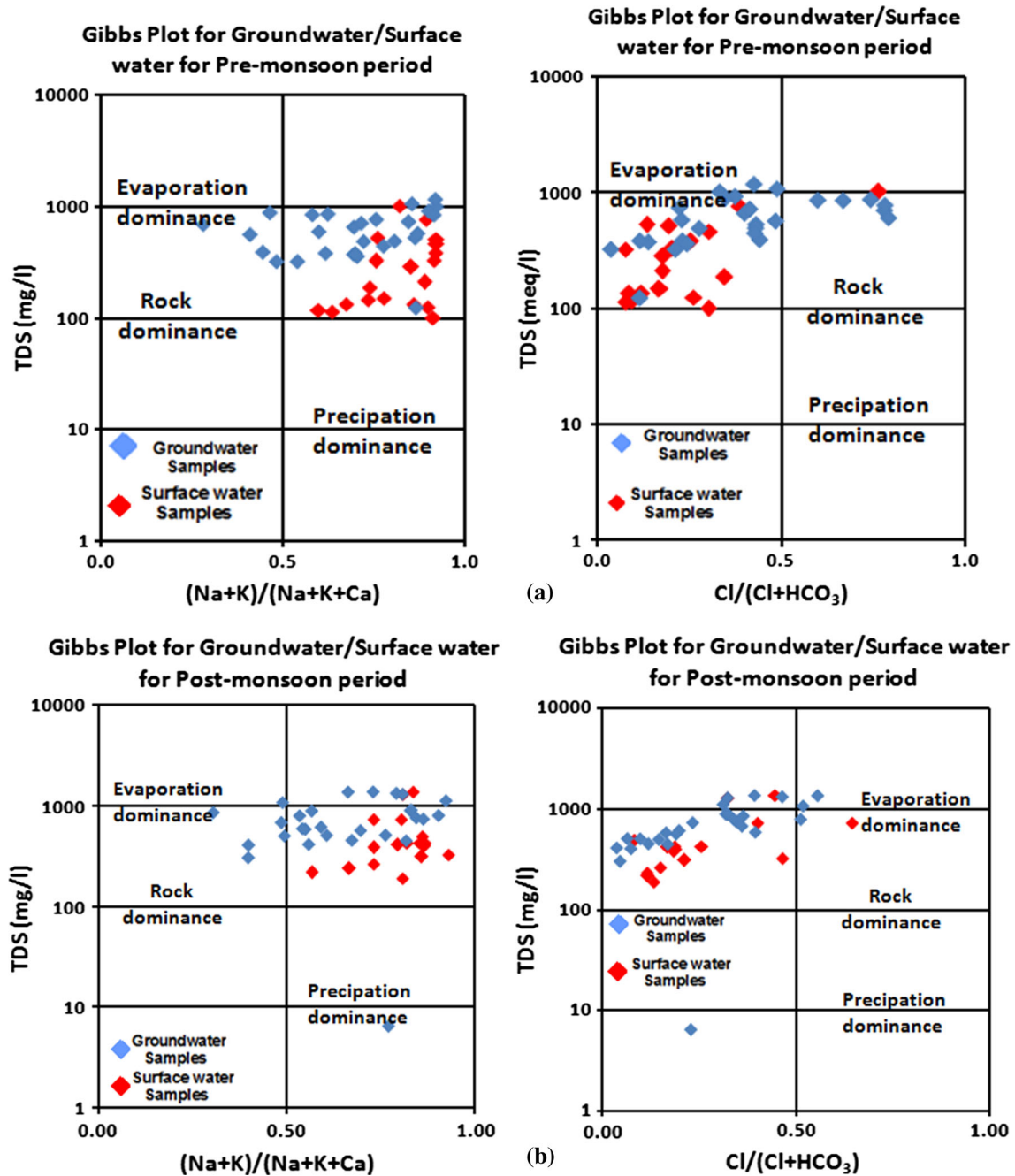


Fig. 9 a, b Gibbs plots for groundwater and surface water for pre-monsoon and post-monsoon periods

concentration of Mg^{2+} constituting 13 and 16 % and K^+ constituting 11 and 20 % among cations for pre- and post-monsoon season, respectively. Among anions Cl^- constituting 17 and 29 %, NO_3^- constituting 100 and 93 % in groundwater samples and no concentration of NO_3^- in surface water except at one sample (post-monsoon season) for pre- and post-monsoon seasons, respectively. The

higher concentration of Na^+ in the groundwater in the study area can be attributed to weathering processes of plagioclase feldspar (albite) and the disassociation of carbonic acid. The nature and amount of dissolved species in natural water is strongly influenced by mineralogy and solubility of rock-forming minerals (Raymahashay 1996). Na^+ concentration increases with fluoride, thereby

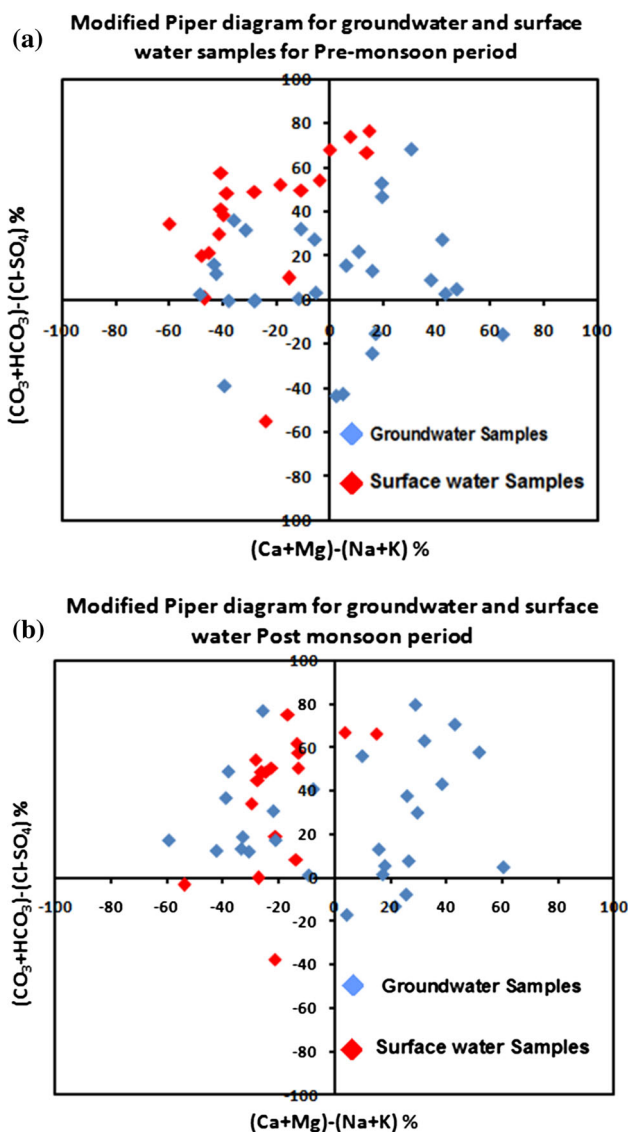
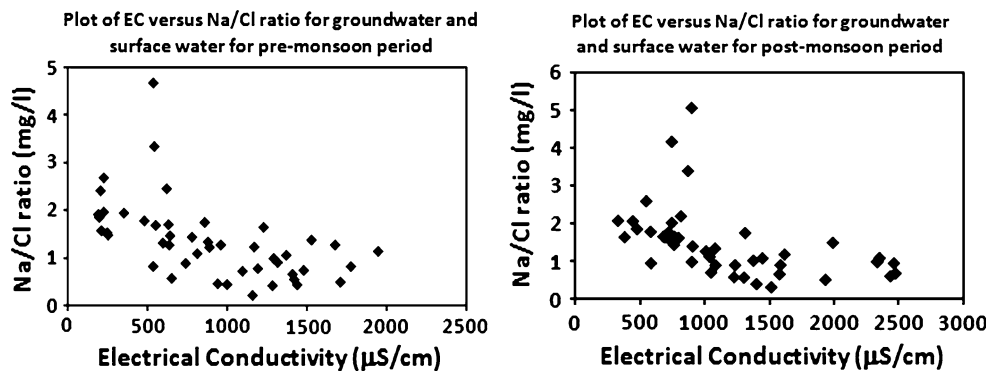


Fig. 10 a, b Modified Piper diagram (Chadha 1999 diagram) for groundwater and surface water for pre-monsoon and post-monsoon periods

increasing the solubility of fluorite in water (Apambire et al. 1997). High concentration of NO_3^- in groundwater is due to excessive use of fertilizers and pesticides.

Fig. 11 Electrical conductivity (EC) versus Na + Cl (meq/l) plot for pre-monsoon and post-monsoon periods



Source of fluoride and its genesis into groundwater

The observed total F^- content of granitic rocks from Nalgonda district ranges from 325 to 3,200 ppm, with a mean of 1,440 ppm, about 1.5 times the mean content of Hyderabad granites (910 ppm) (Ram Mohan Rao et al. 1993). In Nalgonda district, the surface waters have fluoride values as high as 3–7 mg/l in seasonal rivers like Kongal and Halia (Natarajan and Murthy 1974). Porphyritic granite, which contains good amount of fluorite minerals, occurs most prominently in the western part of the area, which forms the source of fluoride to percolating groundwater in this recharge zone. Fluoride content in porphyritic granite, migmatites, and pink granites of the area is varying from nil to 0.54 % and even 1.10 % (Natarajan and Rao 1974). Fluoride-rich rocks located in the recharge area form the source of high fluoride concentration in the surface water as well as groundwaters of the area (IWACO 1992). 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^{2+} by precipitation of calcite (CaCO_3). In the study area the high concentration of F^- in groundwater samples was found in north-western part and in southern part of the basin in pre-monsoon and north-western and south-eastern part of the basin for post-monsoon period, while in surface water it is found in north-western and south-central for pre-monsoon and central and northern part for post-monsoon season, respectively. The occurrence of high fluoride in groundwater is controlled by various factors, including rock chemistry, residence time, well depth, preferential pathways for the upward movement of deep groundwater, and hydrologic condition of the pathways (Kim and Jeong 2005). High fluoride in groundwater occurs as a result of evapotranspiration along the groundwater flow path from recharge areas to local depressions (Jacks 1979). Sodium bicarbonate facies associated with the highest fluoride concentration as observed in the basin are effective in releasing fluoride from the fluorite bearing minerals present in the country rocks.

Table 5 Minimum, maximum, mean and median seasonal values for different indices

Indices seasons	Pre-monsoon (meq/l)				Post-monsoon (meq/l)			
	Min.	Max.	Mean	Median	Min.	Max.	Mean	Median
Na^+/Cl^-	0.4	7.2	2.1	9.1	0.5	7.8	2.2	1.9
$\text{Ca}^{2+}/\text{Mg}^{2+}$	0.6	18.5	5.5	11.3	1.5	17.1	6.5	5.4
$\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^-$	0.4	10.0	1.6	2.3	0.4	2.6	1.0	0.8
$\text{Na}^+ + \text{K}^+/\{\text{Tz}^+\}$	0.2	0.8	0.5	1.6	0.2	0.8	0.5	0.6
$\text{Ca}^{2+} + \text{Mg}^{2+}/\{\text{Tz}^+\}$	0.2	0.8	0.5	1.4	0.2	0.8	0.5	0.4
$\text{Ca}^{2+} + \text{Mg}^{2+}/\text{Na}^+ + \text{Cl}^-$	0.2	1.7	0.6	1.3	0.2	2.2	0.7	0.6
$\text{Ca}^{2+}/\text{Na}^+$	0.1	3.0	0.5	1.2	0.1	2.7	0.6	0.4
$\text{Mg}^{2+}/\text{Na}^+$	0.1	1.7	0.5	1.4	0.2	1.5	0.5	0.4
$\text{Mg}^{2+}/\text{HCO}_3^-$	0.2	3.7	0.8	0.5	0.2	1.5	0.5	0.4

Min minimum, Max maximum, Med median

Fig. 12 Plot of sample nos. versus Ca/Mg ratio for groundwater and surface water samples for pre-monsoon and post-monsoon periods

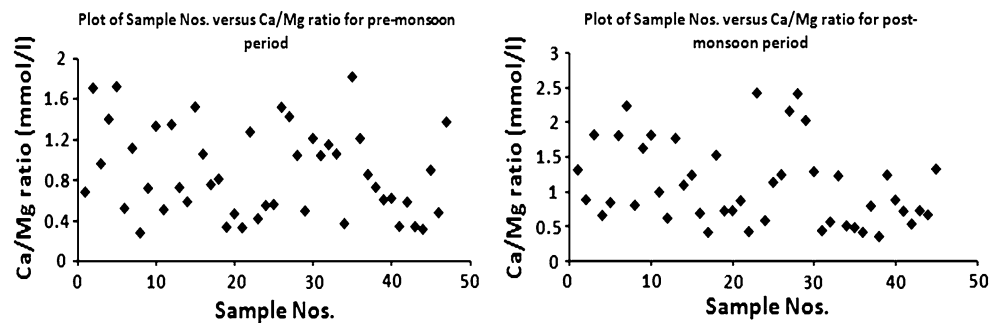


Fig. 13 Plot of Ca + Mg (meq/l) ratio versus $\text{SO}_4 + \text{HCO}_3$ (meq/l) for groundwater and surface water samples for pre-monsoon and post-monsoon periods

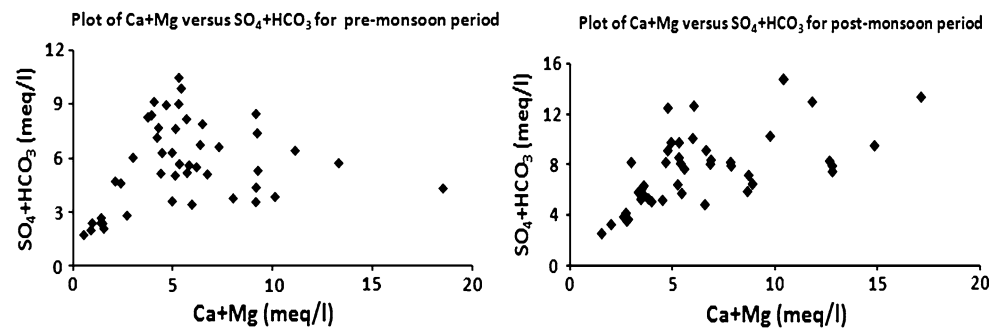
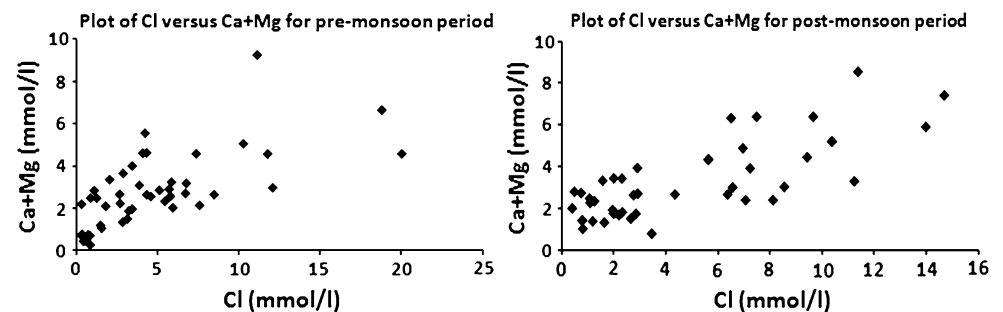


Fig. 14 Plot of Cl (mmol/l) versus Ca + Mg (mmol/l) for groundwater and surface water samples for pre-monsoon and post-monsoon periods



Datta et al. (1996, 1999) studied the fluoride concentration in groundwater using $\delta^{18}\text{O}$ isotopes to integrate with recharge characteristics and fluoride concentration in a Pushkar Valley, Rajasthan. They concluded in their study

the processes controlling the leaching of fluoride ions from soil and rock into the aquifer system. They concluded that the $\delta^{18}\text{O}$ isotopic composition can be approachable for the characterization of the contamination process under

Fig. 15 Plot of Ca + Mg (meq/l) versus sum of cation (meq/l) for groundwater and surface water samples for pre-monsoon and post-monsoon periods

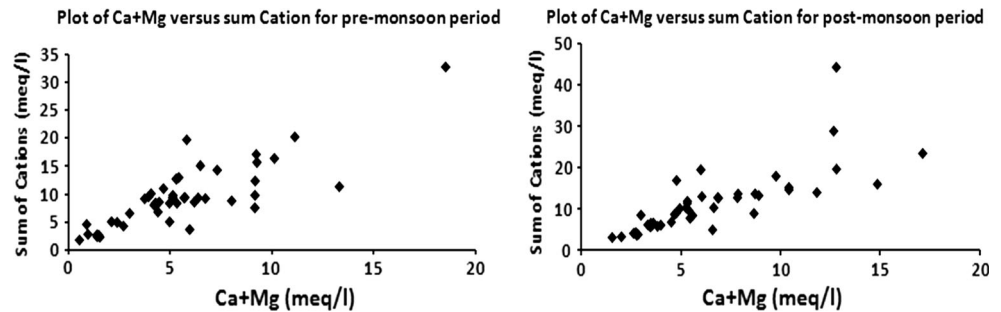
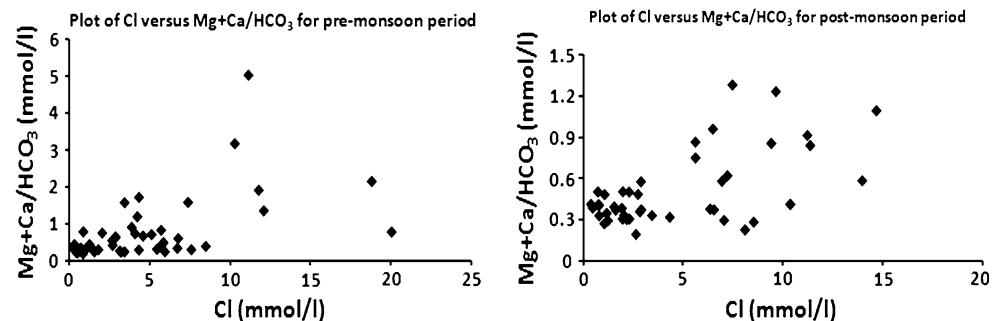


Fig. 16 Plot of Cl (mmol/l) versus Mg + Ca/HCO₃ (mmol/l) for groundwater and surface water samples for pre-monsoon and post-monsoon periods



different hydro-metrological conditions in arid and semi-arid region. Further, they conclude that the indiscriminate disposal of anthropogenic and animal waste is likely the cause for deterioration of the water quality in the area.

Conclusions

The F⁻ concentration varies from 0.4 to 2.9 and 0.6 to 3.6 for pre- and post-monsoon period, respectively. Fifty-three percent samples for pre- and post-monsoon shows shallow meteoric percolation, while 47 % shows deep meteoric percolation; 50 % of the samples show Na⁺-HCO₃⁻ type and Na⁺-SO₄²⁻ type for pre- and post-monsoon periods. Modified Piper diagram reveals that most of the samples show the Ca²⁺-Mg²⁺-HCO₃⁻ type and Na⁺-HCO₃⁻ type and few are Na⁺-Cl⁻ type. Chloroalkali index (CIA) is found to be negative for most of the samples for pre- and post-monsoon period, respectively. Evaluation of hydrogeochemical features reflects that weathering of silicate rocks is responsible for major ion chemistry of groundwater in Chinnaeru river basin. Water-rock interaction and evapotranspiration, which were further influenced by arid to semi-arid climate and low precipitation factors of the area, played crucial role in the modification of concentration of species in groundwater especially the fluoride. Influence of aquifer material and availability of F⁻ rich minerals are instrumental in enrichment of F⁻ in groundwater rather than the inherent chemical characteristics of water. The dry climate with little rain and high evaporation

rate increase the ion concentration in water, which gradually becomes higher than the solubility products for different minerals following precipitation of soil carbonates. Due to precipitation of calcium, soils become alkaline with high contents of sodium; these conditions allow fluoride to accumulate in water. The structural disturbances and intense weathering processes together with fractured semi-confined aquifer system have accentuated the release of fluoride from rocks and soils to groundwater under the alkaline environment. Isotope studies like δ¹⁸O can also be useful in identifying the sources of fluoride in groundwater and the processes involved in increasing the fluoride concentration in groundwater resources.

Acknowledgments The authors are also thankful to the honourable reviewer for his valuable, scientific comments and suggestions for the improvement of the scientific content of the manuscript. The authors are grateful to the Editor-in-Chief and handling Editor for their encouragement and support.

References

- Abu Rukah Y, Alsokhny K (2004) Geochemical assessment of groundwater contamination with special emphasis on fluoride concentration in North Jordan. *Chemie der Erde* 64:171–181
- Apambire WM, Boyle DR, Michel FA (1997) Genesis and health implications of fluori-ferrous groundwater in the upper regions of Ghana. *Environ Geol* 35(1):13–24
- APHA (1995) Standard methods for the examination of water and waste water. American Public Health Association, Washington
- Arif M, Hussain I, Hussain J, Sharma S, Kumar S (2012) Potential fluoride contamination in the drinking water of Nagaur Tehsil of

- Nagaur district, Rajasthan, India. *Bull Environ Contam Toxicol*. doi:10.1007/s00128-012-0572-4
- Ayoob S, Gupta AK (2006) Fluoride in drinking water: a review on the status and stress effects. *Crit Rev Environ Sci Technol* 36(6):433–437
- Beck BF, Asmussen L, Leonard R (1985) Relationship of geology, physiography, agriculture land use and ground-water quality in Southern Georgia. *Groundw GRWAAP* 23(5):627–634
- Brindha K, Rajesh R, Murugan R, Elango L (2011) Fluoride contamination in groundwater in parts of Nalgonda district, Andhra Pradesh, India. *Environ Monit Assess* 172:481–492
- Cairncross S, Feachem RG (1991) *Environmental Health Engineering in the tropics: an introductory text*. Scotland, pp 20–28
- Cerling TE, Pederson BL, Damn KLV (1989) Sodium–calcium ion exchange in the weathering of shales implication for global weathering budgets. *Geology* 17:552–554
- CGWB (2007) Central Ground Water Board. Ground Water Information, Nalgonda district, Andhra Pradesh, pp 1–41
- Chadha DK (1999) A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrol J* 7:431–439
- Datta PS, Deb DL, Tyagi SK (1996) Stable isotope (^{18}O) investigations on the processes controlling fluoride contamination of groundwater. *J Contam Hydrol* 24(1):85–96
- Datta PS, Tyagi SK, Mookerjee P, Bhattacharya SK, Gupta N, Bhatnagar PD (1999) Groundwater NO_3 and F contamination process in Pushkar Valley, Rajasthan as reflected from ^{18}O isotopic signature and ^3H recharge studies. *Environ Monit Assess* 56:209–219
- Edmunds WM, Smedley PL (2005) Fluoride in natural waters. In: Selinus O (ed) *Essentials of medical geology*. Elsevier Academic Press, London, pp 301–329
- Elango L, Kannan R (2007) Rock–water interaction and its control on chemical composition of groundwater. In: *Developments in environmental science*, vol 5, Chap 11. Elsevier, Amsterdam, pp 22–243
- Falvey DA (1999) Groundwater geochemistry. *Earthwise* (British Geological Survey Magazine) issue no. 13
- Fisher RS, Mulican WF (1997) Hydrogeochemical evolution of sodium-sulphate and sodium-chloride groundwater beneath the Northern Chihvahan desert, Trans-Pecos, Texas USA. *Hydrogeol J* 10(4):455–474
- Genxu W, Guodong C (2001) Fluoride distribution in water and the governing factors of environment in arid north-west China. *J Arid Environ* 49:601–614
- Gibbs RJ (1970) Mechanisms controlling World's water chemistry. *Science* 170:1088–1090
- Grandjean P, Olsen JH, Jensen OM, Juel KJ (1992) Cancer incidents and mortality in workers exposed to fluoride. *Natl Cancer Inst (Bethesda)* 84:1903–1909
- GSI (1995) Geological Survey of India's geology and minerals map of Nalgonda district, Andhra Pradesh, India
- Handa BK (1975) Geochemistry and genesis of fluoride containing groundwaters in India. *Ground Water* 13(3):275–281
- Handa BK (1988) Fluoride occurrence in natural waters in India and its significance. *Bhu-Jal News* 3(2):31–37
- Hem JD (1991) Study and interpretation of the chemical characteristics of natural water, 3rd edn. US Geol Surv Water Supply Paper-2254:264. Scientific Publ., Jodhpur
- Huh Y, Tsoi MY, Zaitiser A, Edward JN (1998) The fluvial geochemistry of the river of Eastern Siberia-1 tributaries of Lena river drainage the sedimentation platform of the Siberia Craton. *Geochim Cosmochim Acta* 62:1657–1676
- Hussain J, Sharma KC, Hussain I (2004) Fluoride in drinking water and its ill affect on Human Health: a review. *J Tissue Res* 4(2):263–273
- Hussain J, Hussain J, Sharma KC (2010) Fluoride and health hazards: community perception in a fluorotic area of Central Rajasthan (India) an arid environment. *Environ Monit Assess* 162:1–14
- IWACO (1992) Water resources study AP-III vol. II main report. Rural Water Supply, AP, India Director-General of International Coop, The Netherlands, pp 29, 40
- Jacks (1979) High fluoride groundwater in Southern India. Central Groundwater Board, Coimbatore
- Jacks G, Bhattacharya P, Choudhary V, Singh KP (2005) Controls on the genesis of some high fluoride ground waters in India. *Appl Geochem* 20:221–228
- Jain CK, Ali I, Sharma MK (1999) Fluoride contamination in groundwater Indian scenario. *Indian J Environ Prot* 19:260–266
- Johnson CC (1979) Land application of water-an accident waiting to happen. *Ground Water* 17(1):69–72
- Kim K, Jeong GY (2005) Factors influencing natural occurrence of fluoride-rich ground-waters: a case study in the southeastern part of the Korean Peninsula. *Chemosphere* 58:1399–1408
- Kundu N, Panigrahi MK, Triparthy S, Munshi S, Powell MA, Hart BR (2001) Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh district of Orissa, India. *Environ Geol* 41:451–460
- Machender G, Dhakate R, Tamma Rao G, Loukya G, Reddy MN (2013) Assessment of trace element contamination in soils around Chinnaeru river basin, Nalgonda district, India. *Environ Earth Sci* 70:1021–1037
- Machender G, Dhakate R, Reddy MN, Panduranga Reddy I (2014) Hydrogeochemical characteristics of surface water (SW) and groundwater (GW) of the Chinnaeru river basin, northern part of Nalgonda district, Andhra Pradesh, India. *Environ Earth Sci* 71(6):2885–2910
- Mandel S, Shiftan ZL (1981) Groundwater resources investigation and development. Academic, New York
- May AL, Loucks MD (1995) Solute and isotope geochemistry and groundwater flow in the Central Wasatch Range, Utah. *J Hydrobiol* 170:795–840
- McIntosh JC, Walter LM (2006) Paleowater in Silurian–Devonian carbonate aquifers: geochemical evolution of groundwater in the Great Lakes region since Late Pleistocene. *Geochim Cosmochim Acta* 70:2454–2479
- Meybeck M (1987) Global chemical weathering of surficial rocks estimated from river-dissolved leads. *Am J Sci* 287:401–428
- Murray JJ (1986) *Appropriate use of fluorides for human health*. World Health Organisation, Geneva
- Natarajan V, Murthy SRN (1974) Fluorite bearing granites in Shivannagudem area, Nalgonda district, AP. In: *Proceedings of National Symposium on Fluorosis, India: Indian Academy of Geoscience, Hyderabad*
- Natarajan V, Rao MVR (1974) Hydrochemical investigation for fluoride bearing minerals in Kangal and Hallia river basin, Nalgonda district, AP. In: *Proceedings of National Symposium on Fluorosis, India: Indian Academy of Geoscience, Hyderabad*
- Nordstrom DK, Jenne EA (1977) Fluorite solubility equilibria in selected geothermal waters. *Geochimica Cosmochimica Acta* 41:175–188
- Pandian K, Sankar K (2007) Hydrogeochemistry and groundwater quality in the Vaippar River Basin, Tamil Nadu. *J Geol Soc* 69:970–982
- Pophare MA, Dewalkar SM (2007) Groundwater quality in eastern and south eastern parts of Rajura Tehsil, Chendrapur district, Maharashtra. *Gondwana Geol Mag Special* 11:119–129
- Ram Mohan Rao NV (1991) Hydro-geochemistry and fluoride in Nalgonda district of Andhra Pradesh, India. In: *International symposium on applied geochemistry, Osmania Univ, Hyderabad*, pp 255–261

- Ram Mohan Rao NV, Surya Prakasa Rao K, Schvilg RD (1993) Fluorine distribution in waters of Nalgonda district, Andhra Pradesh, India. *Environ Geol* 21:84–89
- Ramesham V, Rajagopalan K (1985) Fluoride ingestion into the natural waters of hardrock areas, Peninsular India. *J Geol Soc India* 26:125–132
- Rao S (1997) The occurrence and behaviour of fluoride in groundwater of the Lower Vamsadhara River Basin, India. *Hg. Sci J* 42(6):877–892
- Raymahashay BC (1996) *Geochemistry for hydrologists*. Allied Publishers, New Delhi
- Reddy AGS, Rao PN (2006) Occurrence, behaviour and genesis of fluoride in groundwater of Wailpalli watershed in Nalgonda district, Andhra Pradesh, India. *J Appl Geochem* 8(2A):618–630
- Reddy DV, Nagabhushanam P, Sukhija BS, Reddy AGS (2009) Understanding hydrological processes in a highly stressed granitic aquifer in southern India. *Hydrol Process* 23:1282–1294
- Reddy DV, Nagabhushanam P, Sukhija BS, Reddy AGS, Smedley PL (2010) Fluoride dynamics in the granitic aquifer of the Wailpally watershed, Nalgonda district, India. *Chem Geol* 269(3–4):278–289
- Sami K (1992) Recharge mechanism and geochemical processes in a semi arid sedimentary basin, South Africa. *J Hydrol* 139:27–48
- Sarin MM, Krishnaswamy S, Dilli K, Somayajulu BLK, Moore WS (1989) Major ion chemistry of the Ganga–Brahmaputra river system: weathering processes and fluxes to the Bay of Bengal. *Geochim Cosmochim Acta* 53:997–1009
- Sastry JCV (1994) Groundwater chemical quality in river basins, hydrogeochemical facies and hydrogeochemical modeling. Lecture notes-refresher course conducted by school of Earth Sciences, Bharathidasan University, Thiruchirappalli
- Saxena VK, Ahmed S (2001) Dissolution of fluoride in groundwater: a water–rock interaction study. *Environ Geol* 40:1084–1087
- Schoeller H (1967) Qualitative evaluation of groundwater resources. In: *Methods and techniques of groundwater investigation and development, water research, series-33*. UNESCO, pp 44–52
- Shaji E, Bindu J, Viju Thambi DS (2007) High fluoride in groundwater of Palghat district, Kerala. *Curr Sci* 92:240–245
- Siddiqui AH (1968) Fluorosis in Nalgonda district Hyderabad, India. *Fluoride* 1–2:76–85
- Singh B, Gaur S, Garg VK (2007) Fluoride in drinking water and human urine in Southern Haryana, India. *J Hazard Mater* 144:147–151
- Soltan ME (1998) Characterization, classification and evaluation of some groundwater samples in Upper Egypt. *Chemosphere* 37:735–747
- Soltan ME (1999) Evaluation of groundwater quality in Dakhla Oasis (Egyptian Western Desert). *Environ Monit Assess* 57:157–168
- Stallard RF, Edmond JM (1983) Geochemistry of the Amazon, the influence of geology and weathering environment on the dissolved load. *J Geophys Res* 88:9671–9688
- Subba Rao N (2003) Groundwater quality: focus on fluoride concentration in rural parts of Guntur district, AP, India. *Hg. Sci J* 48(5):835–847
- Subba Rao N, Krishna Rao G, John Devdas D (1998a) Variation of fluoride in groundwaters of crystalline terrain. *J Environ Hydrol* 6:1–5
- Subba Rao N, Prakasa Rao J, Nagamalleswar Rao B, Babu N, Madhusudhan Reddy P, John Devdas D (1998b) A preliminary report on fluoride content in groundwater of Guntur area, AP, India. *Curr Sci* 75:887–888
- Wedepohl KH (ed) (1969) *Handbook of geochemistry* (vol II-1). Springer, Berlin
- WHO (1994) Fluorides and oral health, (Technical report series no. 846). World Health Organisation, Geneva
- WHO (2004) *Guidelines for drinking-water quality*, 3rd edn. World Health Organization, Geneva, p 212