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Fluoride hazard and assessment of groundwater quality in the semi-arid Upper Panda River basin, Sonbhadra district, Uttar Pradesh, India

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Abstract Around 9000 inhabitants in the Panda River basin, Sonbhadhra District, Uttar Pradesh, India, are vulnerable to a “silent” dental and skeletal fluorosis from groundwater consumption. The fluoride source and seasonal groundwater quality variation were studied by collecting 65 groundwater samples in the Upper Panda River basin. Major rock types are phyllites and granite gneissic rocks. Fluoride concentrations are in the range 0.4–5.6 mg/L in the pre-monsoon season and 0.1–6.7 mg/L in the post-monsoon season. Fluor-apatite and biotite mica in the granite gneissic rock were identified as the main provenance of fluoride in the groundwater through water–rock interactions. Due to precipitation of calcium, soils become alkaline with high contents of sodium; these conditions allow fluoride to accumulate in water. According to risk index calculations, the fluoride-affected villages were shown to fall in the fluoride risk zone (with a risk index of around 1.7). On the basis of mineral stability diagrams, groundwater from the weathered and fractured aquifers appears to be stable within the kaolinite field, suggesting weathering of silicate minerals. The groundwater is chemically potable and suitable for domestic and agricultural purposes, except for a few wells in the southern region that are contaminated with high amounts of fluoride.

Key words fluoride hazard; hydrogeochemistry; chemical relationships; seasonal groundwater quality; irrigation use; Panda River, India

Risques liés au fluor et évaluation de la qualité des eaux souterraines dans le bassin supérieur semi-aride de la rivière Panda, district de Sonbhadra (Uttar Pradesh, Inde)

Résumé Dans le bassin de la rivière Panda, district de Sonbhadhra, Uttar Pradesh, environ 9000 habitants sont exposés à un fluorose dentaire et osseuse ≪ silencieuse ≫ dûe à la consommation des eaux souterraines. La source des fluorures, et la variabilité saisonnière de la qualité des eaux souterraines, ont été étudiées par la collecte de 65 échantillons d’eau souterraine dans le bassin supérieur de la rivière Panda. Les grands types de roches sont des phyllites et des granito-gneiss. Les concentrations en fluorures sont dans la gamme de 0,4 à 5,6 mg/L dans la saison précédant la mousson, et de 0,1 à 6,7 mg/L dans la saison suivant la mousson. Le fluor de l’apatite et le mica des biotites dans le granito-gneiss ont été identifiés comme la principale source des fluorures dans l’eau souterraine par le biais des interactions eau-roche. En raison de la précipitation du calcium, les sols deviennent alcalins avec des teneurs élevées en sodium ; ces conditions permettent aux fluorures de s’accumuler dans l’eau. Selon les calculs de l’indice de risque, les villages exposés au fluor se retrouvent dans la zone à risque (avec un indice de risque d’environ 1,7). Sur la base des diagrammes de stabilité des minéraux, les eaux souterraines des aquifères des zones altérées et fracturées apparaissent stables dans le domaine de la kaolinite, suggérant un altération des minéraux silicatés. L’eau souterraine est chimiquement potable et utilisable à des fins domestiques et agricoles, à l’exception de quelques puits dans la région du Sud qui sont contaminés par de forts taux de fluor.

Mots clefs risque fluor; hydrogéochimie; relations chimiques; qualité saisonnière des eaux souterraines irrigation; fleuve Panda; Inde

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INTRODUCTION

Ever-increasing population and an increased need for agriculture and industries have resulted in water scarcity, and groundwater has become a preferred source of human water supply in many parts of world. It is estimated that approximately one third of the world's population uses groundwater for drinking purposes (UNEP 1999). Due to the natural infiltration capacity of aquifer materials and their long retention time, groundwater is generally considered safe from pathogenic contamination and is believed to require little or no disinfection. This valuable resource is tapped by dugwells and borewells drilled through hard rocks that only store or transmit water when weathered and/or fractured (Raju and Reddy 1998). The hydrogeological factors controlling recharge and hydrogeochemical reactions that result from water–rock interactions, as well as anthropogenic interventions, are important for the chemical constituents to reach the groundwater (Faure 1998, Raju 2007, Raju *et al.* 2009b). Generally, the quality of groundwater depends on the composition of recharge water, the interaction between the water and the soil, the soil-gas, the rock with which it comes into contact in the unsaturated zone, and the residence time and reactions that take place within the aquifer (Fetter 1994, Appelo and Postma 2005). Major ion chemistry analysis of groundwater provides the basis to investigate the weathering reactions in the basin (Jalali 2007, Reddy *et al.* 2010, Raju *et al.* 2011, Raju 2012). By understanding the different geochemical processes that are involved in the evolution of water species, the precise reasons for contamination may be traced, especially in geogenic cases, as the chemical parameters of water indicate the footprints of its chemical contributors and the absorption processes involved in its evolution. The assessment of the suitability of groundwater for domestic water supply requires knowledge of the concentrations of inorganic constituents and their comparison with existing standards (e.g. WHO 1997). Irrigation water quality concerns the kinds and amounts of salts present in irrigation water and their effects on crop growth and development. The appropriate evaluation of water quality prior to its use in irrigation will help to arrest any harmful effects on plant productivity and groundwater recharge.

Fluoride (F^-) contamination is varied even in similar hydrogeological environments; hence, the study of the geochemical processes and unique characteristics of water that might be responsible for the assimilation of F^- ions is essential. Groundwater of similar chemical composition or ionic make-up, and within the same watershed or sub-basin, may have different fluoride concentrations. Reddy *et al.* (2010) evaluated the geochemistry of groundwater in Wailpalli watershed, Andhra Pradesh, India, and concluded that aquifer material plays an important role in the contribution of fluoride to the accompanying groundwater. The excess fluoride content in groundwater, its ill effects on human physiology, and its source and origin in the subsurface have attracted the attention of wide spectrum of researchers (e.g. Handa 1988, Jain *et al.* 1999, Kundu *et al.* 2001, Saxena and Ahmed 2001, Raju *et al.* 2009a). The majority of fluorine found in nature is present in various rocks, soils, waters, plants and other living organisms, slag and fluxes. Fluoride is essential in small quantities for the prevention of dental caries, especially in children. In general, fluoride content in water of 1.5–2 mg/L may lead to dental mottling, found mostly in children up to the age of 12 years, and skeletal fluorosis may occur when fluoride concentrations in drinking water exceed 4–8 mg/L (Apambire *et al.* 1997, Raju *et al.* 2009a). The shortage of water resources of good quality is becoming an important issue in hard-rock and semi-arid zones, and the rapid decline of groundwater supplies is common in many parts of the Indian subcontinent (Raju and Reddy 2007). The net result is that the groundwater regime has been affected detrimentally in terms of quality and quantity. An attempt is made in this paper to deduce both the sources and impact of fluoride, and to evaluate the hydrogeochemical constituents of groundwater with respect to its suitability for domestic and irrigation uses, referring to several aspects of chemical data interpretation in both the pre- and post-monsoon seasons in the Upper Panda River basin, India.

STUDY AREA, GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

The Upper Panda River basin, one of the tributaries of the Son River, is located in the Chopan block of Sonbhadra district and has a drainage area of 216 km^2 (Fig. 1). The study area is bounded between latitude 24°15′–24°30′N and longitude 83°15′–83°30′E, and falls in Survey of India toposheet no. 63P/7 on 1:50 000 scale. The area experiences semi-arid climatic conditions with average annual minimum and maximum temperatures of 10 and 47°C, respectively. The average annual rainfall in the study area is

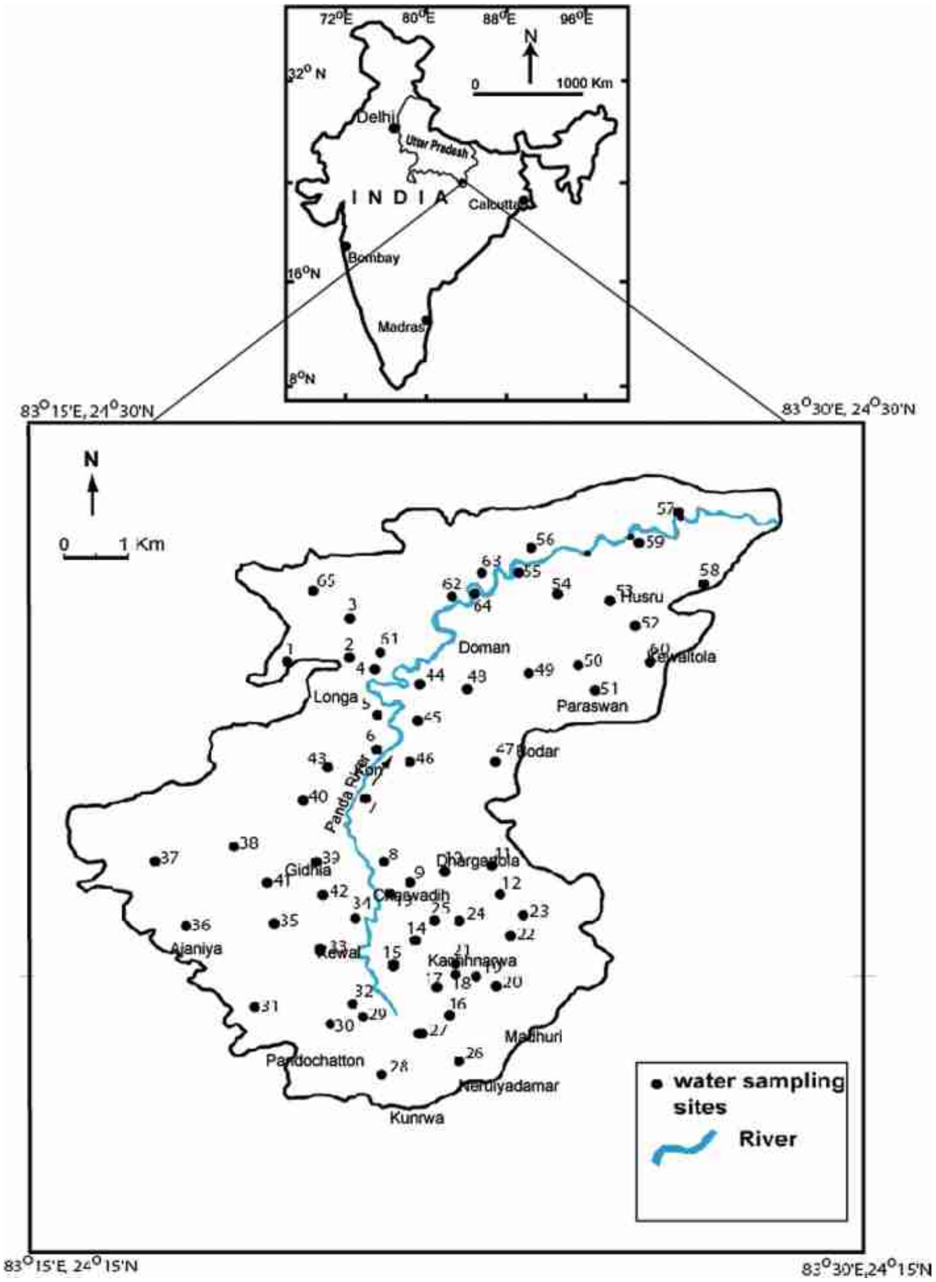

Fig. 1 Physiographic map of the Upper Panda River basin and location of groundwater samples.

850 mm. The elevation ranges from 180 to 413 m a.m.s.l. At several places, low hill ranges of quartzite trending almost east–west break the monotony of the physiography. The main drainage pattern observed is dendritic to sub-dendritic in nature. The Upper Panda River basin is dominated by metasedimentary rock sequences of the Granitoid complex of Palaeo Proterozoic age (Fig. 2). The area is traversed by various generations of quartz veins. A metasedimentary sequence (mainly consisting of phyllites) rests unconformably over the Granitoid complex, which is exposed in the southern part and is overlain by a huge sedimentary pile of Vindhyan sediments, exposed in the northern and northeastern portions. The Granitoid complex comprises granite, granodiorite, gneisses and pegmatite. Major rock types such as conglomerate, sandstone, limestone and porcellanite observed in the northern portion belong to the Meso-Proterozoic age. The northern and southern portions are covered by Early to Late Pleistocene alluvium.

The mode of groundwater occurrence is dependent primarily on the presence and extent of weathered overburden, the saturated thickness of the weathered zone, and the spatial extent and interconnection

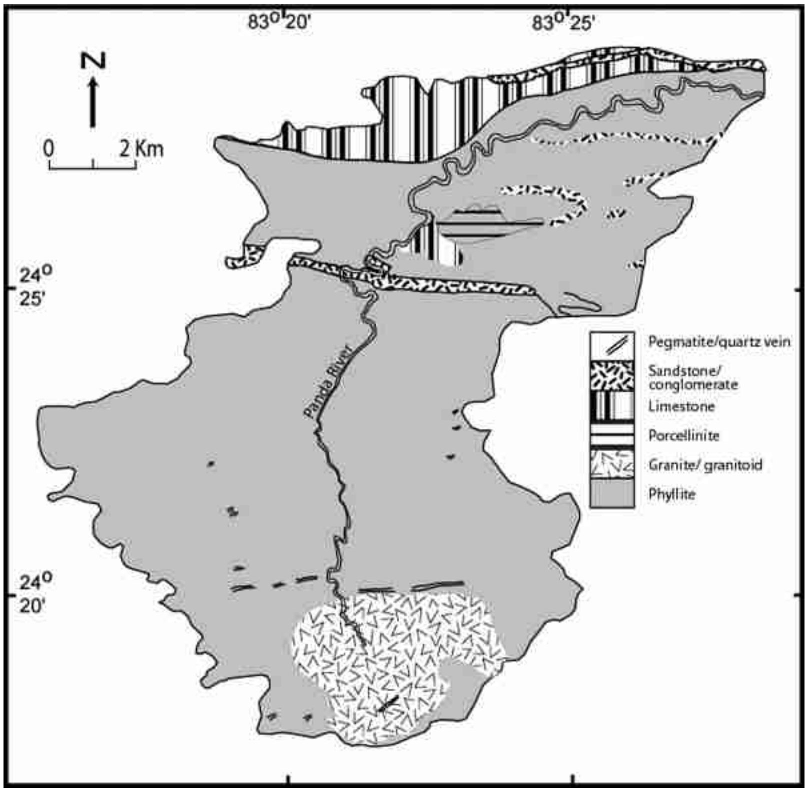

Fig. 2 Geological map of the study area.

of fractures in the underlying bedrock. Recharge to aquifers is predominantly by direct rainfall. Infiltration of recharge water and the subsequent percolation to the groundwater system is made possible only if fractures or joints are interconnected. Phyllite, which comprises the most exposed rocks, has relatively low permeability and serves as a poor aquifer material, but due to the high weathering and presence of numerous fractures, phyllite can contain sufficient water. The groundwater in phyllite is extracted for use by digging open dugwells and borewells. The water table in this zone ranges in depth from 6 to 34.3 m in the pre-monsoon season and from 2.7 to 30 m in the post-monsoon season. The dugwells are mostly circular in shape, varying in diameter from 2 to 7 m. The majority of the dugwells are screened, except in a few places where they pierce through the phyllite. Granite gneiss acts as an aquifuge, i.e. the rock has very low porosity and permeability, but due to high weathering, and the presence of joints and lineaments, the rock acts as an aquitard. Granite gneissic rock is moderately weathered and well-developed fractures make the rock permeable. Significant aquifers have developed within the weathered overburden (i.e. regolith) and fractured bed rock. The depth of the water table varies from 3 to 11.4 m and from 3.2 to 9.8 m in pre- and post-monsoon seasons, respectively. The dugwells in granite gneisses are circular in shape, with a diameter of between 1.9 and 5.6 m, and most of them are screened. The maximum depth of hand tubewells for drinking water use varies from 40 to 60 m b.g.l. Calcretes (lime kankar) deposits are observed at the ground surface in alkaline soils and are also seen in several dugwell sections. Quartz veins and pegmatite that are fractured and brecciated contain a good amount of groundwater. The general flow directions are north–south, SE–NW and SW–NE, which is in accordance with the general slope of the area and also the direction of streamflow.

METHODS AND MATERIALS

A total of 65 groundwater samples were collected from dugwells and borewells during April–May 2006 (pre-monsoon) and October 2006 (post-monsoon) for analysis of major ions using standard procedures (APHA 1995). Groundwater samples were collected in pre-cleaned (acid washed) polythene containers of 1-L capacity for major ion analysis. Samples were filtered using 0.45-μm pore size membrane and stored in polyethylene bottles which were initially washed with 10% HNO_3 and rinsed thoroughly with distilled water. Another set of samples was acidified to $pH < 2$ by adding ultra-pure concentrated HNO_3 for heavy metal measurements. The collected samples were immediately transported to the laboratory where they were stored at 4°C until analysis. The water samples were analysed at the Hydrogeology Laboratory of the Department of Geology, Banaras Hindu University, Varanasi. For all samples, electrical conductivity (EC) and pH values were obtained using EC and pH meters (ELICO). The parameters analysed include the major ions sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), chloride (Cl^-), sulphate (SO_4^{2-}), carbonate (CO_{3-}), bicarbonate (HCO_3^-) and fluoride (Fl^-). Total dissolved solids (TDS) were estimated by summing up all the major cations and anions in the sample. Total alkalinity (TA), CO_3 and HCO_3 were estimated by titrating with HCl. Total hardness (TH) and Ca were analysed titrimetrically using standard EDTA; Mg was computed, taking the difference between TH and Ca values; Na and K were measured by flame photometry (ELICO); Cl was estimated by standard $AgNO_3$ titration; and SO_4 was measured by the turbidimetric method. Fluoride was estimated by using an ion-selective electrode (Orion 96-09 model, Thermo electron Corporation). The total cation and total anion balance (Freeze and Cherry 1979) shows a charge balance error percentage of up to ±5% for all the samples. The quality of the analysis was ensured by standardization using blank and duplicate samples.

RESULTS AND DISCUSSION

Hydrochemistry

Physico-chemical parameters were analysed for 65 groundwater samples collected randomly during the pre- and post-monsoon seasons (Fig. 1). A statistical summary of the hydrochemical parameters determined for each sample is presented in Table 1. The pH values are in the range 6.5–7.7 with a mean of 7.1 in the pre-monsoon and 6.9–8.6 with a mean of 7.4 in the post-monsoon season. The EC ranges are 342–1190 μS/cm (mean: 637 μS/cm) in pre-monsoon and 428–1280 μS/cm (mean: 704 μS/cm) in post-monsoon. In the pre-monsoon season, TDS varies from 206 to724 mg/L (mean: 385 mg/L) and is 140–800 mg/L (mean: 427 mg/L) in post-monsoon. Groundwater samples pre- and post-monsoon contain freshwater, since the TDS values are less than 1000 mg/L (Davis and De Wiest 1966), and all groundwater evaluated is therefore suitable for drinking and irrigation purposes. The low TDS content observed could be either a result of the slow decomposition of most metamorphic and igneous rocks, since the terrain is underlain by mostly phyllite and granite gneissic rocks, or due to the short residence time of the groundwater. Seasonal variation in the TDS, EC and ionic concentrations in the groundwater may be attributed to geochemical processes and anthropogenic activities (Raju *et al.* 2011). Among the cationic concentrations in pre- and post-monsoon seasons: sodium is the dominating ion with means of 55.2 and 62.9 mg/L, respectively, followed by

Table 1 Descriptive statistics of the concentrations of the water quality parameters of the upper Panda River basin.

Chemical parameters	Pre-monsoon			Post-monsoon			WHO guidelines (1997)		% of samples exceeding permissible limits	
	Range (mg/L)	Mean	SD	Range (mg/L)	Mean	SD	Desirable	Permissible	Pre	Post
Ca^{2+}	6−69	27.9	11.9	14−78	42.7	12.3	75	200	–	–
Mg^{2+}	10.8−56.8	29.7	11.1	4.02−59.2	23.3	11.5	30	150	–	–
Na^+	10.4−230	55.2	40.8	12.5−256	62.9	42.4	50	200	1.5	1.5
K^+	1.3−3.8	2.2	0.5	1.4−4.2	2.5	0.4	10	12	–	–
HCO_3^-	92−396	211.7	71.1	104−455	202.8	60.9	300	600	–	–
SO_4^{2-}	10−190	97.5	39.4	25−195	111.5	40.7	200	600	–	–
Cl^-	6−66	23.7	13.3	22−96	37.7	13.4	250	600	–	–
F^-	0.4−5.6	0.9	1.0	0.1−6.7	1.2	1.0	0.9	1.5	10.7	18.5
TDS	206−724	385	111.8	140−800	427	108	500	1500	–	–
pH	6.5−7.7	7.1	0.3	6.9−8.6	7.4	0.2	7.0	9.2	–	–
EC	342−1190	637	179	428−1280	704	177	–	–	–	–
TH	94−288	190	40	98−314	199	46	100	500	–	–

calcium (means: 27.9 and 42.7 mg/L), magnesium (means: 29.7 and 23.3 mg/L), and potassium (means: 2.2 and 2.5 mg/L). In this groundwater system, in both the seasons, there is no dominant cation that exceeds the threshold of dominance (i.e. meq/L > 50%). Since no one cation constitutes as much as 50% of totals in the pre- and post-monsoon seasons, the water is recognized as a mixed cation type. The hydrochemistry of cationic dominance pattern is in the order $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ in pre-monsoon samples and $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in post-monsoon samples. In general, weathering, dissolution and base-exchange processes control the levels of cationic concentrations in groundwater.

Among the anionic concentrations in pre- and post-monsoon seasons: bicarbonate is the dominating ion, ranging from 92 to 396 mg/L (mean: 211.7 mg/L) and 104 to 455 mg/L (mean: 202.8 mg/L), respectively; followed by sulphate, 10–190 mg/L (mean: 97.5 mg/L) and 25–195 mg/L (mean: 111.5 mg/L); chloride, 6–66 mg/L (mean: 23.7 mg/L) and 22–96 mg/L (mean: 37.7 mg/L); and fluoride 0.4–5.6 mg/L (mean: 0.9 mg/L) and 0.1–6.7 mg/L (mean: 1.2 mg/L). The anionic dominance pattern is in the order $HCO_3^- > SO_4^{2-} > Cl^- > F^-$ in both the seasons. For most wells, HCO_3^- is the only anion that exceeds the dominance level (meq/L > 50%), whereas SO_4^{2-}, Cl^- and F^- are considerably below the dominance level. Groundwater in the arid to semi-arid regions is generally characterized by high ion concentrations, and the dominant anion species of the water changes systematically from HCO_3^-, to SO_4^{2-} to Cl^- as water flows from the recharge area to the discharge area (Ronit *et al.* 1997).

Hydrochemical facies and solute acquisition processes

The concept of hydrochemical facies offers a mass regional relationship between chemical character, lithology and regional flow pattern. The dominant hydrochemical facies is $Na\text{-}HCO_3$, represented in 60% of all the water samples, since Na is the dominant cation and bicarbonate the dominant anion in both the seasons. Sodium concentration is relatively higher in post-monsoon, which could be attributed to the negative base-exchange index. High sodium concentration may be due to ion-exchange reactions in the groundwater and the re-use of water in irrigation practices. High bicarbonates in the groundwater are derived mainly from the soil zone CO_2, and the weathering of parent minerals. The relatively high concentration of HCO_3^- across the study area indicates that freshly recharged groundwater is present throughout the aquifer. The ionic dominance pattern for groundwater resembles that of leachable ions from the soils, suggesting a lithogenic origin of minerals in the groundwater (Reddy *et al.* 2010, Raju *et al.* 2011). The range and mean chemical compositions of four major hydrochemical facies are shown in Table 2. The $Mg\text{-}HCO_3$, $Ca\text{-}HCO_3$ and $Na\text{-}SO_4$ facies represent 18.5, 15.3 and 6.2%, respectively, of all the pre-monsoon samples analysed, while $Ca\text{-}HCO_3$, $Mg\text{-}SO_4$, $Ca\text{-}SO_4$ and $Na\text{-}SO_4$ represent 35.4, 1.6, 1.5 and 1.4%, respectively, of all the post-monsoon water samples analysed. Sulphate facies are increased in the post-monsoon season because sulphate dissolution is greater during the rainy season due to mixing of infiltrated rainwater. In the pre-monsoon season, evaporation and evapotranspiration bring the SO_4^{2-}- and Cl^--bearing salts into the surface zone, but during the post-monsoon season, these salts are mixed/diluted with rainwater and infiltrate into the groundwater during rainfall events.

Apart from inputs from anthropogenic sources, weathering and ion-exchange processes are major solute acquisition mechanisms that control the concentrations of chemical constituents in groundwater. As described by Gibbs (1970), groundwaters acquire their chemistry mainly from underlying rocks by the natural mechanisms controlling groundwater chemistry. The concentrations of different major ions and their inter-relationships were studied to understand the hydrogeochemical processes that were involved in the aquifer domain during the evolution of different groundwater facies. The relative proportion of various ions in solution depends on their relative abundance in the host rock and on their solubility (Sarin and Krishnaswamy 1984). The dissolution of carbonate rocks proceeds more rapidly than silicate breakdown and is the likely mechanism of solute acquisition in the water system (Raju *et al.* 2011, Raju 2012). The proportion of HCO_3^- and SO_4^{2-} in the water reflects the relative dominance of two major sources of protons during chemical weathering. The importance of two major proton-producing reactions, i.e. carbonation and sulphide oxidation, can be signified on the basis of the C-ratio (Brown *et al.* 1996). The average C-ratio ($HCO_3^-/(HCO_3^- + SO_4^{2-})$) of around 0.6 for both the seasons revealed that coupled reactions of carbonic acid weathering and sulphide oxidation were the major proton producer in these waters (Table 3). Average Na^+/Ca^{2+} ratios

Table 2 Ranges of chemical compositions of major hydrochemical facies.

Facies	Statistical parameter	Chemical parameters (mg/L)																			
		pH		EC (μS/cm)		Ca		Mg		Na		K		HCO_3		SO_4		Cl		F	
		Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
Na-HCO_3	Max.	7.7	8.2	1190	1280	46	59	55.4	48.6	230	256	3.8	4.2	396	455	190	192	66	88	5.6	6.7
	Min.	6.5	6.9	405	428	6	19	10.8	4	29.8	32.1	1.3	1.4	140	120	40	41	10	23	0.4	0.1
	Mean	7.2	7.5	706	751	26.6	37.8	29.4	23.2	73.2	80.2	2.2	2.5	239	219	106	117	26	41	1.3	1.5
	SD	0.3	0.3	188	203	9.6	9.8	11.3	11.4	43.1	45.9	0.5	0.5	70	69.7	40	42.9	13.5	14.4	1.2	1.3
Ca-HCO_3	Max.	7.5	7.9	730	737	69	78	42.2	45	46.3	50.4	3.4	3.4	276	264	100	138	57	96	0.8	1.2
	Min.	6.5	6.9	342	476	26	31	15.6	4.2	10.4	12.5	1.7	2.2	100	132	10	25	9	23	0.4	0.3
	Mean	7.1	7.4	530	610	42.6	50	24.6	22.6	24.1	33.8	2.3	2.5	171	182	73	92	27.5	32.7	0.5	0.7
	SD	0.4	0.3	127	74	13.4	10.4	7.8	10.5	11.3	11	0.6	0.3	54.4	35.3	30.7	30.6	16	16	0.1	0.2
Mg-HCO_3	Max.	7.4	–	750	–	29	–	56.8	–	47.4	–	3.8	–	258	–	125	–	26	–	0.5	–
	Min.	6.5	–	405	–	9	–	27.8	–	12.8	–	1.6	–	128	–	36	–	6	–	0.4	–
	Mean	7.0	–	543	–	19.2	–	39.7	–	25	–	2.2	–	195	–	80.4	–	14.4	–	0.5	–
	SD	0.3	–	92	–	6.5	–	8.6	–	10.6	–	0.6	–	43.8	–	29.7	–	7.2	–	0.0	–
Na-SO_4	Max.	7.2	–	685	–	33	–	35	–	71.9	–	2.4	–	136	–	185	–	20	–	1.1	–
	Min.	6.7	–	444	–	11	–	13	–	38.2	–	1.9	–	92	–	110	–	14	–	0.4	–
	Mean	7.0	–	551	–	23.8	–	23.7	–	49.2	–	2.2	–	112	–	141	–	16.5	–	0.6	–
	SD	0.3	–	99	–	9.2	–	9.5	–	15.3	–	0.2	–	18.2	–	31.3	–	2.6	–	0.3	–

Table 3 Chemical indices derived from hydrogeochemical constituents.

S. no.	EC (µS/cm)		SAR (meq/L)		%Na (meq/L)		C-ratio (meq/L)		CR (mg/L)		CAI 1 (meq/L)		CAI 2 (meq/L)		Na/Ca (meq/L)		Ca+Mg/Na+K (meq/L)	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
1	480	476	0.39	0.7	13.6	22.64	0.61	0.64	0.71	1.07	−0.16	−0.22	−0.02	−0.05	0.39	0.39	6.38	3.41
2	390	542	0.39	0.52	12.54	16.35	0.63	0.39	0.78	2.17	0.28	−0.37	0.07	−0.05	0.4	0.24	5.92	5.11
3	730	665	1.25	1.09	28.96	27.45	0.68	0.68	0.72	1.15	−0.3	−0.1	−0.09	−0.03	0.58	0.42	2.45	2.64
4	353	557	0.41	0.83	15.56	23.64	0.61	0.66	0.84	1.85	0.15	0.37	0.04	0.22	0.35	0.43	5.43	3.23
5	342	489	0.65	0.82	23.1	24.58	0.7	0.77	0.79	0.64	0.15	−0.54	0.04	−0.1	0.55	0.42	3.32	3.06
6	405	647	0.84	1.61	26.28	37.22	0.63	0.49	0.76	1.59	−0.52	−1.47	−0.11	−0.26	1.39	1.12	2.80	1.68
7	650	737	1.00	1.15	24.85	27.54	0.6	0.58	0.89	1.16	−0.26	−0.89	−0.06	−0.15	0.75	0.84	3.02	2.63
8	520	643	1.39	1.44	35.8	34.26	0.68	0.53	0.6	1.7	−1.08	−0.52	−0.25	−0.15	2.0	0.74	1.79	1.92
9	610	705	1.44	1.58	34.21	36.28	0.58	0.58	0.94	1.39	−0.72	−0.77	−0.18	−0.4	1.16	1.02	1.92	1.75
10	540	657	1.96	1.95	45.07	42.77	0.73	0.61	0.52	1.2	−1.69	−0.39	−0.33	−0.3	3.0	2.36	1.21	1.33
11	700	669	2.00	2.37	41.63	50.71	0.73	0.65	0.53	0.98	−1.58	−1.96	−0.33	−0.35	1.55	1.18	1.40	0.97
12	480	505	1.6	3.21	41.01	64.33	0.56	0.63	0.9	1.46	−1.66	−1.39	−0.3	−0.53	1.19	2.18	1.43	0.55
13	550	680	0.85	1.58	23.96	37.01	0.65	0.5	0.68	1.44	−0.4	−1.85	−0.08	−0.27	0.55	0.74	3.17	1.70
14	728	870	2.38	3.02	46.89	51.66	0.67	0.52	0.57	1.39	−3.05	−2.96	−0.4	−0.45	1.68	2.46	1.13	0.93
15	900	941	3.84	3.65	59.14	55.88	0.58	0.39	0.91	1.36	−2.36	−3.23	−0.51	−0.61	3.8	2.87	0.69	0.78
16	1190	1280	10.33	11.25	84.27	85.12	0.64	0.66	0.65	0.81	−6.14	−7.12	−0.85	−0.87	13.4	11.7	0.18	0.17
17	760	896	2.29	3.44	44.19	55.16	0.64	0.54	0.66	1.29	−2.35	−3.17	−0.37	−0.49	1.87	2.5	1.22	0.81
18	820	896	4.64	3.57	66.79	57.69	0.54	0.53	0.95	1.24	−4.09	−3.62	−0.67	−0.53	3.89	2.0	0.49	0.73
19	880	903	4.73	4.62	66.21	65.82	0.6	0.59	0.73	1.08	−4.86	−4.16	−0.66	−0.6	6.05	4.0	0.51	0.52
20	630	664	2.64	3.3	52.05	60.53	0.7	0.71	0.57	0.83	−2.33	−2.58	−0.44	−0.52	1.51	2.26	0.92	0.65
21	640	730	1.34	1.44	31.67	32.89	0.69	0.62	0.64	0.92	−0.73	−1.95	−0.17	−0.25	1.17	0.86	2.15	2.04
22	615	630	0.27	0.3	8.26	8.71	0.61	0.63	0.83	1.17	0.55	0.5	0.12	0.14	0.21	0.21	11.1	10.5
23	930	428	2.76	3.08	47.51	53.52	0.62	0.77	0.62	0.49	−4.56	−4.93	−0.43	−0.57	14.8	1.96	1.10	0.86
24	625	658	1.38	2.63	32.86	50.43	0.52	0.57	0.95	1.18	−1.84	−2.67	−0.24	−0.6	1.75	1.61	2.04	0.98
25	1100	1220	4.39	4.45	59.95	60.13	0.6	0.63	0.82	1.07	−2.53	−2.67	−0.53	−0.65	6.2	5.55	0.66	0.66
26	627	644	1.03	1.06	25.59	26.42	0.46	0.67	1.19	0.82	−1.28	−1.13	−0.17	−0.2	0.88	0.72	2.91	2.78
27	825	1015	2.81	3.23	49.4	50.68	0.64	0.53	0.64	1.81	−3.05	−1.09	−0.42	−0.42	2.94	2.77	1.02	0.97
28	1130	1200	6.03	6.36	70.91	72.49	0.59	0.57	0.71	1.19	−7.42	−4.42	−0.7	−0.96	6.91	5.34	0.41	0.37
29	740	837	3.42	3.14	58.49	54.00	0.49	0.66	0.99	0.87	−6.63	−3.15	−0.57	−0.6	2.65	2.18	0.71	0.85
30	806	825	1.65	1.63	34.35	33.10	0.52	0.59	0.88	0.95	−4.02	−3.29	−0.3	−0.46	2.69	1.65	1.91	2.02

31	450	479	1.36	1.41	37.2	39.03	0.67	0.75	0.54	0.78	−3.05	−1.14	−0.32	−0.27	1.84	0.88	1.68	1.56
32	820	862	2.3	2.13	43.56	40.33	0.55	0.55	0.82	1.2	−4.42	−2.49	−0.39	−0.49	4.08	1.42	1.29	1.47
33	685	707	2.36	2.29	47.61	47.42	0.37	0.51	1.59	1.45	−5.65	−2.56	−0.45	−0.6	2.43	1.38	1.10	1.10
34	520	583	1.2	1.25	32.08	32.13	0.71	0.7	0.46	0.93	−2.18	−0.71	−0.25	−0.18	0.93	1.11	2.11	2.11
35	645	608	1.63	1.76	37.22	42.42	0.68	0.67	0.54	1.1	−2.11	−0.9	−0.29	−0.27	1.78	0.96	1.68	1.35
36	545	568	1.49	1.53	37.4	36.77	0.39	0.7	1.56	0.88	−0.78	−1.1	−0.31	−0.26	1.16	1.34	1.67	1.71
37	930	963	3.05	4.26	49.64	59.4	0.72	0.64	0.4	0.96	−6.74	−3.48	−0.47	−0.71	8.65	3.38	1.01	0.68
38	550	525	0.7	1.08	20.16	30.29	0.47	0.64	1.03	1.07	−2.45	−0.72	−0.16	−0.19	0.97	1.33	3.95	2.30
39	544	532	1.23	0.9	31.92	25.9	0.67	0.66	0.49	0.86	−4.06	−0.48	−0.28	−0.18	1.15	0.79	2.13	2.86
40	405	529	1.14	1.27	35.11	32.96	0.7	0.7	0.45	0.75	−3.45	−1.49	−0.31	−0.27	1.52	0.76	1.07	2.09
41	555	548	1.34	1.55	34.54	37.79	0.55	0.89	0.78	0.36	−3.89	−1.99	−0.31	−0.28	1.3	0.65	1.89	1.64
42	530	548	1.27	1.62	33.2	39.48	0.39	0.63	1.46	1.15	−3.07	−0.6	−0.28	−0.17	3.0	0.73	2.01	1.53
43	480	533	1.09	1.23	30.87	32.26	0.48	0.55	1.03	1.35	−3.18	−1.01	−0.27	−0.27	0.82	0.73	2.23	2.09
44	540	698	0.63	1.29	18.25	29.83	0.64	0.58	0.59	1.12	−1.18	−1.44	−0.11	−0.27	1.25	0.62	4.47	2.35
45	444	848	1.73	2.39	45.41	44.26	0.4	0.48	1.46	2.11	−3.95	−0.76	−0.41	−0.32	1.5	1.25	1.20	1.25
46	620	655	0.63	1.38	17.3	34.66	0.81	0.53	0.09	1.38	−2.09	−1.51	−0.13	−0.36	0.39	0.79	4.70	1.88
47	660	827	1.69	2.22	37.5	43.3	0.71	0.52	0.41	1.36	−4.93	−2.6	−0.33	−0.54	1.06	1.12	1.66	1.31
48	770	832	2.94	2.27	52.39	43.86	0.88	0.59	0.15	1.02	−12.5	−3.18	−0.52	−0.54	3.19	1.23	0.91	1.27
49	408	618	0.82	0.65	26.43	17.85	0.8	0.52	0.3	1.3	−2.12	−0.63	−0.19	−0.13	0.79	0.37	2.78	4.60
50	590	782	0.86	1.35	23.43	29.18	0.6	0.48	0.59	1.69	−6.05	−0.87	−0.22	−0.25	1.29	1.23	3.26	2.42
51	635	672	1.22	1.12	29.98	27.61	0.63	0.49	0.68	1.45	−1.43	−1.6	−0.2	−0.32	0.92	1.1	2.33	2.62
52	520	663	0.59	0.82	17.86	21.47	0.85	0.69	0.18	0.7	−4.41	−1.06	−0.15	−0.15	0.91	0.61	4.59	3.65
53	770	802	1.68	1.70	35.04	36.3	0.76	0.67	0.33	1.26	−5.36	0.6	−0.31	−0.13	2.67	1.49	1.85	1.75
54	485	673	0.47	0.68	15.43	17.67	0.75	0.53	0.33	1.26	−1.92	−0.91	−0.11	−0.12	0.54	0.4	5.47	4.65
55	530	818	1.04	1.47	28.54	30.83	0.72	0.48	0.41	1.81	−3.32	−0.03	−0.24	−0.2	1.23	1.06	2.50	2.24
56	540	575	0.73	0.62	21.34	18.62	0.59	0.52	0.68	1.43	−2.38	−0.22	−0.16	−0.06	0.45	0.53	3.68	4.37
57	667	770	1.5	1.96	34.02	40.92	0.82	0.58	0.25	1.24	−4.5	−1.52	−0.3	−0.39	2.36	1.06	1.93	1.44
58	610	632	1.67	1.31	38.36	32.75	0.7	0.52	0.4	1.31	−7.36	−1.88	−0.36	−0.35	3.52	1.03	1.60	2.05
59	759	606	1.85	1.41	38.46	34.98	0.62	0.8	0.55	0.51	−9.18	−1.79	−0.36	−0.28	1.8	0.87	1.60	1.85
60	510	555	0.59	0.50	16.9	14.95	0.72	0.56	0.39	1.21	−1.87	−0.17	−0.13	−0.04	0.62	0.34	4.58	5.68
61	600	623	1.10	1.16	27.51	29.53	0.7	0.54	0.42	1.22	−3.59	−1.63	−0.23	−0.31	3.67	0.77	2.63	2.38
62	520	565	1.58	1.61	39.49	39.74	0.56	0.46	0.74	1.93	−5.55	−1.2	−0.36	−0.39	0.99	1.36	1.53	1.51
63	518	633	1.81	2.03	43.73	43.55	0.54	0.61	0.81	1.21	−5.76	−1.26	−0.41	−0.35	1.21	0.93	1.28	1.29
64	750	760	1.27	1.38	28.59	29.76	0.6	0.42	0.71	2.22	−1.89	−0.71	−0.21	−0.25	3.49	3.29	2.49	2.48
65	560	606	0.76	0.85	21.21	22.20	0.6	0.47	0.62	1.53	−3.64	−1.11	−0.18	−0.22	0.43	0.64	3.71	3.50

EC: electrical conductivity; SAR: sodium adsorption ration; CR: corrosivity ratio; CAI: chloroalkaline indices; %Na: percent sodium.

are greater than unity (i.e. 2.3 and 1.5 in the pre- and post-monsoon seasons, respectively), indicating a deficiency of Ca^{2+} (Table 3). This may be due to a lack of super-saturation and consequent precipitation of $CaCO_3$ and/or ion exchange processes. This is in conformity with field observations that the area is not dominated by limestone rocks. The average $(Ca^{2+}+Mg^{2+})/(Na^{+}+K^{+})$ ratios of 2.4 and 2.1 pre- and post-monsoon, respectively, suggest that the water is largely influenced by silicate weathering along with a small contribution of carbonate weathering (Table 3). A general reaction for the weathering of silicate rocks with carbonic acid can be written as:

$$\begin{aligned}&(Na^{+}, K^{+}, Ca^{2+}, Mg^{2+})\text{silicate} + H_2CO_3\\&\quad = H_4SiO_4 + HCO_3^{-} + Na^{+} + K^{+} + Ca^{2+}\\&\qquad + Mg^{2+} + \text{Solid product}\end{aligned}$$

The role of aquifer material in the evolution of groundwater chemical composition can be further probed by determining chloro-alkaline indices for cations (CAI-1) and anions (CAI-2). It is imperative to understand the alteration in water chemistry that occurs during its movement and residence time for better evaluation of the hydrochemistry of any area, in particular when different geological formations are involved in a watershed or river basin (Johnson 1979, Sastry 1994, Raju 2012). The CAI-1 and CAI-2 indices developed by Schoeller (1967) relate ion-exchange processes between groundwater and aquifer materials. Chloro-alkaline indices (CAI) can be either positive or negative depending on whether exchange is between Na^{+} and K^{+} from water and Mg^{2+} and Ca^{2+} in rocks/soil, or *vice versa*. The average CAI values for pre- and post-monsoon seasons, respectively, are: −3.15 and −1.63 (CAI-1), and −0.29 and −0.33 (CAI-2) (Table 3). The CAI-1 and CAI-2 values of almost all samples are negative, indicating that the ion-exchange processes involved are between $Na^{+}+K^{+}$ of the host rock and $Ca^{2+}+Mg^{2+}$ of water, and the exchange is indirect during the evolution of the subsurface water chemistry (McIntosh and Walter 2006). Therefore, ion exchange is also responsible for the increase of ions in the groundwater. The negative indices indicate the dominance of secondary leaching as a primary source of dissolved salts, followed by the reverse ion-exchange process.

Mineral stability diagram

Mineral stability is an important way in which the approach to equilibrium between clay minerals and natural water can be verified by means of thermodynamic data (Garrels and Christ 1965, Norton 1974). A major application of the mineral stability plots of ion activities is to evaluate the position of water composition in terms of mineral–water equilibrium (Fig. 3). Minerals of the kaolinite group are the main alteration products of weathering of feldspars. As water continues to attack feldspar, pH rises with the increase in cations and silica. Kaolinite forms until the cation and silica content rises so that the formation of montmorillonite is initiated. In Na and Mg-systems, samples fall in the kaolinite stability field indicating dilution of Na^{+} and Mg^{2+} ions. In the Ca-system, samples also cluster in the kaolinite zone, indicating dilution of Ca^{2+} ions; the fact that few of the post-monsoon samples are shifting from kaolinite to Ca-montmorillonite may be due to the dissolution of Ca-rich minerals in the groundwater. In the K-system, most of the groundwaters fall in the kaolinite field of stability and few are shifted towards the amorphous silica zone. They also have dissolved silica contents ranging between quartz and amorphous silica. The presence of excess silica in most waters may be due to the reactions with K mica which can be attributed to the presence of other minerals that equilibrate more rapidly than K feldspar. The data points in all systems fall within the kaolinite stability field, which suggests that infiltrating water enriched by soil CO_2 reacts with silicate minerals contained in the host rocks, particularly plagioclase feldspar, chlorite and biotite. These infiltrating waters will leach out Ca, Mg, Na and HCO_3, resulting in a more silica-rich clay mineral derivative of the silicate minerals contained in the host rock. This implies that the chemistry of the groundwater favours kaolinite formation.

WATER QUALITY ASSESSMENTS

The water quality data obtained by chemical analyses were evaluated in terms of suitability for domestic and irrigation uses.

Suitability of groundwater for drinking and domestic use

The range of hydrochemical parameters of groundwater and their comparison with the prescribed specification of WHO (1997) are summarized

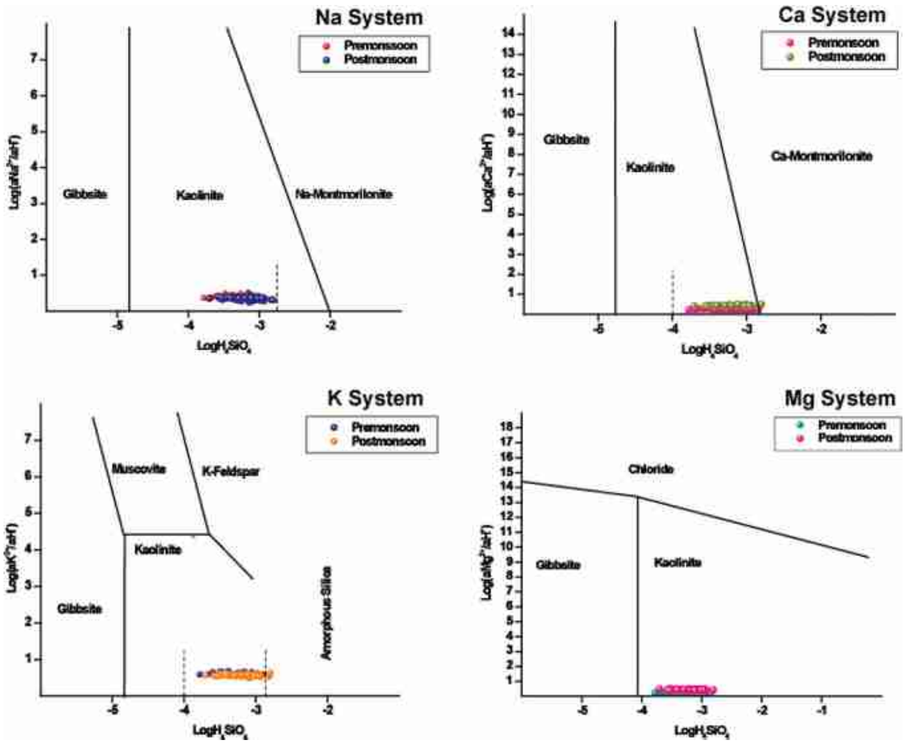

Fig. 3 Stability diagram plots to evaluate the position of water composition in terms of water–rock equilibrium.

in Table 1. Any element which exceeds the permissible limit of WHO is harmful for human consumption. The pH values indicate that the groundwater exhibits slightly alkaline qualities in both the seasons. Based on the classification of TDS content (Fetter 1994), all samples come under the freshwater category (TDS < 1000 mg/L); however, 15% of pre-monsoon and 22% of post-monsoon samples exceed the desirable limit (500 mg/L) of TDS concentration, while all the samples are within the permissible limits of WHO. A higher concentration of TDS may cause gastrointestinal irritation in human beings. The concentrations of calcium and magnesium ions determined for pre- and post-monsoon season samples are lower than the permissible levels set by the WHO guidelines (Table 1).

High concentrations of Ca and Mg produce encrustation in the water supply. The total hardness (TH) of the analysed samples varies from 94 to 288 mg/L and 98 to 314 mg/L in in pre- and post-monsoon season samples, respectively, indicating that 82 and 18% of the pre-monsoon samples and 86 and 14% of the post-monsoon samples (Table 1) are slightly hard and moderately hard in nature, respectively (Sawyer and McCarty 1967). Increased hardness post-monsoon may be due to excess leaching of Ca and Mg ions into the groundwater. The various combinations of Ca-Mg-Na with HCO_3 water types identified put groundwater in the carbonate hardness category in both the seasons. This type of hardness, according to Driscoll (1989), can be removed by boiling. Hardness has no particularly adverse effect on human health, but it can prevent the formation of lather with soap and increases the boiling point of water. Long-term consumption of very hard water might lead to an increased incidence of urolithiasis, anecephaly, prenatal mortality, some types of cancer and cardio-vascular disorders (Agarwal and Jagetia 1997).

Only one groundwater sample in both the seasons exceeds the permissible limit for sodium (200 mg/L). Higher sodium intake may cause hypertension, congenital heart disease and kidney problems. All samples are within the permissible limit with respect to potassium concentration and all anions (HCO_3, SO_4 and Cl) except fluoride are within the permissible limits recommended by WHO (Table 1). Bicarbonate has no known adverse health effects on humans. Undesirable effects of a high concentration of sulphate in drinking water are associated with respiratory problems (Maiti 1982).

Spatial and temporal distribution of fluoride

Fluoride in water can be a hazard or a blessing depending on its concentration level. It occurs in almost all water from trace to high concentrations (Gaciri and Davies 1993). Fluoride is an essential element for maintaining the normal development of teeth and bones. The fluoride content in the surface waters of the study area is within permissible levels (1.5 mg/L). Fluoride concentration in the groundwater ranges from 0.4 to 5.6 mg/L (mean: 0.9 mg/L) in pre-monsoon, and from 0.1 to 6.7 mg/L (mean: 1.2 mg/L) in post-monsoon samples (Table 1). The lowest values occur in the northern part of the area in the pre-monsoon season and in the north-eastern part in the post-monsoon season; the highest values are identified in the southern region in both seasons (Fig. 4). A low concentration (at least 0.5 mg/L) of fluoride in drinking water is beneficial, since it can help prevent dental caries. However, chronic ingestion of concentrations much greater than the WHO guideline value (1.5 mg/L, WHO 1997) may lead to dental fluorosis (tooth mottling) and, in extreme cases (>3 mg/L), to skeletal fluorosis (bone deformation and painful brittle joints in older people) (Apambire *et al.* 1997, Appelo and Postma 2005, Raju *et al.* 2009a). The severity of fluorosis depends

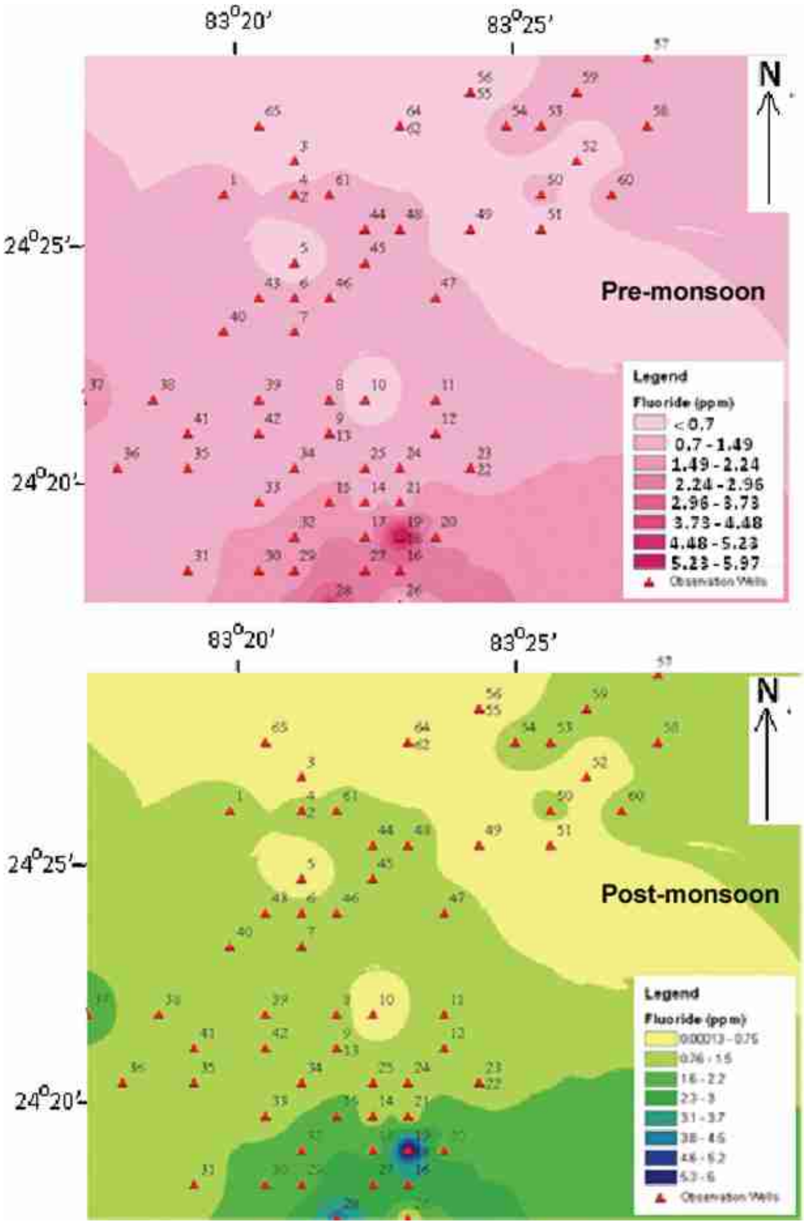

Fig. 4 Spatial distribution of fluoride concentration.

on the concentration of fluoride in drinking water, daily intake, continuity and duration of exposure and climatic conditions. Fluorosis may be present in an individual at sub-clinical, chronic or acute levels of manifestation (Teotia and Teotia 1988).

The spatial distribution of fluoride concentration in the study area (Fig. 4) indicates that seven (10.7%) pre-monsoon and 12 (18.5%) post-monsoon groundwater samples exceed the permissible limit. Most of the high-fluoride (6.7 mg/L) groundwater samples are located in the southern part, where wells are situated on the granite gneissic complex. Most people in the southern part suffer from dental and skeletal fluorosis (Fig. 5) (Raju *et al.* 2009a). In some other granitic complex areas, where fluoride concentration ranges from 1.1 to 1.4 mg/L and from 1.7 to 1.9 mg/L in pre- and post-monsoon samples, respectively, people suffer mainly from dental fluorosis, but skeletal fluorosis may appear in the future due to the prolonged drinking of fluoride-rich water. Phyllite areas are not affected by fluoride disorders, because the fluoride content in the groundwater is within the permissible limit. Of all the samples in the pre- and post-monsoon seasons, 63 and 66.5%, respectively, fall within the recommended range of 0.5–1.5 mg/L for good dental health and bone development, while 26.3 and 15%, respectively, are below the optimum level of 0.5 mg/L; the affected population is prone to dental caries (Apambire *et al.* 1997), and the majority live in the northern and northeastern parts (Fig. 4).

Fluoride variation in the groundwater during the pre- and post-monsoon seasons is very wide and uneven in nature spatially. Fluoride shows contrasting seasonal fluctuations. The mixed seasonal variation and uneven distribution of fluoride in space and time are primarily due to the relative abundance of, and variation in, fluoride-bearing mineral assemblages in the rock formations, the differential fracture system, and associated hydrochemical processes (Reddy and Rao 2006, Raju *et al.* 2009a).

A public health survey was conducted, mainly in the fluoride-affected villages, to help understand the

Fig. 5 Mottling and deformation of ligaments due to the dental and skeletal fluorosis.

Table 4 Detailed village-wise survey on fluoride-affected population.

			Rohinia-damar	Madhuri	Neruiya-damar	Gobardaha	Kunrwa	Tumiya
Children		Observed	9	11	8	27	6	–
		Dental	5	8	6	23	3	–
		Skeletal	4	2	–	2	3	–
Adult	Male	Observed	27	30	16	20	20	19
		Dental	18	24	11	15	14	12
		Skeletal	7	6	2	4	5	–
	Female	Observed	16	21	18	12	12	15
		Dental	9	15	6	10	6	5
		Skeletal	6	6	5	1	4	2
Total		Observed	52	62	42	59	38	34
		Dental	32	47	23	48	23	17
		Skeletal	17	14	7	7	12	2
Percentage (%)		Dental	61.54	75.81	54.76	81.36	60.53	50.00
		Skeletal	32.69	22.58	16.67	11.86	31.58	5.88
F^- (mg/L)		Pre-monsoon	5.49	1.91	2.29	3.33	3.68	1.39
		Post-monsoon	6.1	2.01	3.04	2.52	3.5	1.89
		Average	5.795	1.96	2.665	2.925	3.59	1.64

degree to which the population suffers from dental and skeletal fluorosis (Table 4). The risk was found to increase with an increase in fluoride level in the drinking water. If R is the risk index, the correlation equation is established as follows:

$$I = \frac{1}{n}\sum_{i=1}^{n} C_i$$

$$R = I(0.2k_1 + 0.8k_2)I_0$$

where C_i is the fluoride concentration in the water of each well; I is the average value of F^- concentration in the well water of given area; I_0 is the F^- standard concentration in drinking water; k_1 and k_2 are the correlation coefficients of morbidity of dental fluorosis and skeletal fluorosis, respectively. The constants 0.2 and 0.8 are weighting coefficients that represent harm by dental and skeletal fluorosis, respectively. Skeletal fluorosis is more harmful than dental fluorosis, hence the higher value. The risk intensity of dental and skeletal fluorosis may be divided into different classes (Linthurst *et al.* 1995): $0.5 \leq R \leq 1$ (risk free); $1 \leq R \leq 1.5$ (slight risk); $1.5 \leq R \leq 2.5$ (risk); $2.5 \leq R \leq 3.5$ (high risk); and $R > 3.5$ (very high risk). A risk index of $R > 1.7$ indicates that there is a risk of fluorosis problems in an area. As there is no medicine for the fluorosis problem, there is an urgent need to provide a protected water supply in the fluoride-affected areas.

Fluoride geochemistry

Porphyritic granite gneissic rocks, which contain considerable amounts of fluorite minerals, especially fluor-apatite and biotite mica, form the source of fluoride ions to the percolating groundwater. Fluorite (CaF_2) has been generally considered as a dominant source of groundwater fluoride, especially in granitic terrains (Deshmukh and Chakravarti 1995). However, its dissolution in freshwater is low and, furthermore, its dissolution rate is remarkably slow (Nordstrom and Jenne 1977). When groundwater reacts with granite gneissic rocks for a prolonged period, the fluoride concentrations are continuously enriched, even after the groundwater reaches an equilibrium state with respect to fluorite (CaF_2) due to the removal of Ca^{2+} by precipitation of calcite ($CaCO_3$). Sodium carbonate type water ($Na\text{-}HCO_3$) in weathered rock formations allows precipitation of calcite from Ca^{2+} and $CO_3{}^{2-}$ ions and accelerates the dissolution of CaF_2, thereby releasing fluoride into the groundwater (Saxena and Ahmed 2003):

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2$$

The occurrence of calcium carbonate gravels (lime kankar) in the soil and weathered layers confirms the precipitation of calcite. The occurrence of high-fluoride groundwater is controlled by various factors, including rock chemistry, residence time, well depth, preferential pathways for the upward movement of deep groundwater, and the hydrological condition of the pathways (Kim and Jeong 2005). High fluoride in the 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 are effective in releasing fluoride from fluorite-bearing minerals present in the rock.

Petrography studies are imperative to reveal the presence of minerals in a rock specimen, since fluorite, apatite, biotite and various other minerals take part in rock–water interaction to release fluoride ions to the groundwater system. Microscopic analysis of granite gneissic rock shows the presence of quartz, microcline, biotite, apatite, sphene and minor chlorite, in which apatite and biotite are fluoride-bearing minerals (Fig. 6). Normally, biotite in granite gneissic rocks may contain as much as 0.91% fluorine; hornblende contains 0.17% fluorine; and fluor-apatite has a fluorine concentration of 3.72% (Deer *et al.* 1985). The petrographic investigations show the presence of F-containing minerals of: 20–25% biotite and 5–10% fluor-apatite. Some researchers have suggested that high fluoride concentrations in groundwater may be a result of the dissolution of biotite, which may contain significant fluorine at OH^- sites of the octahedral sheets (Nordstrom *et al.* 1989, Li *et al.* 2003). Apatite grains are euhedral to subhedral with variable grain size and closely associated with biotite and chlorite. Using XRD analysis, rock powder samples were indexed using major known peak profiles of mineral apatite, which are comparable with the value of lattice parameters available for fluor-apatite (Raju *et al.* 2009a). Fluor-apatite along with biotite mica releases fluoride ions; hence it indicates the geogenic origin of fluoride in groundwater.

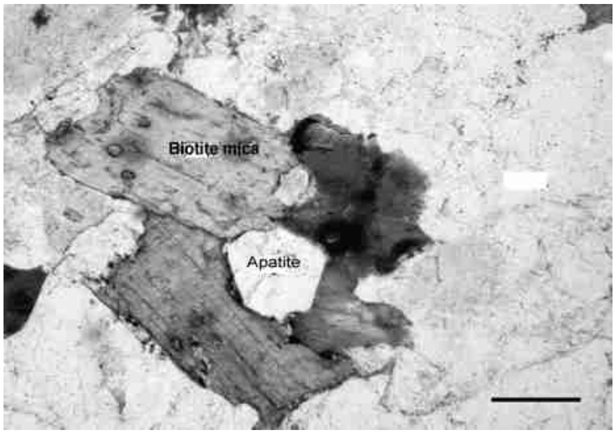

Fig. 6 Petrography analysis of granite gneissic rock.

During the process of chemical weathering, the dissolution of fluoride species in natural water is controlled by calcium and governed by thermodynamic principles. The fluoride concentration in groundwater is controlled by mineral fluorite according to Brown and Roberson (1977):

$$\mathrm{CaF_2} = \mathrm{C}a^{2+} + 2\mathrm{F}^-$$

$$K_{\mathrm{CaF_2}} = a(\mathrm{Ca}^{2+})$$

$$a(\mathrm{F}^-)^2 = 10^{-10.58} \text{ at } 25^\circ\mathrm{C}$$

where K represents the solubility product constant and a denotes the activities of the corresponding ions. Thus the activities of calcium and fluoride are negatively correlated. Minerals rich in calcite ($CaCO_3$) also favour the dissolution of fluoride from fluoride-rich minerals. Decreasing Ca concentrations are observed under alkaline conditions with a corresponding rise in Na noticed in highly fluoride-affected areas. Therefore, fluoride can accumulate in water if the groundwater is low in calcium ions. In the present study, a broad negative correlation between calcium and fluoride has been observed, with a regression coefficient of −0.131 and −0.219 in pre- and post-monsoon season samples, respectively, and a positive correlation between sodium and fluoride (regression coefficient of 0.686 and 0.602, respectively) (Fig. 7).

The negative relationship between fluoride and Ca+Mg (Kundu *et al.* 2001, Reddy *et al.* 2010) may be due to prior precipitation of $CaCO_3$ from water and only limited incorporation of F^- in the $CaCO_3$ structure, so that there is always a net balance of F^- in solution. Semi-arid climatic conditions and low rainfall facilitate evapotranspiration, which leads to an increase in alkalinity of soil and groundwater. In an acidic medium (low pH), fluoride is adsorbed in clays; however, in an alkaline medium, it is desorbed and thus alkaline pH is more favourable for fluoride dissolution (Saxena and Ahmed 2003). It is clear that, if the pH is constant, the activity of fluoride is directly proportional to the amount of HCO_3^-. This relationship is independent of Ca because of the low solubility product CaF_2. A positive correlation is observed between HCO_3^- and fluoride with regression coefficients of 0.357 and 0.442 in pre- and post-monsoon groundwater samples, respectively (Fig. 7). Groundwater in contact with calcite and fluorite solid phases develops equilibrium reactions. The saturation

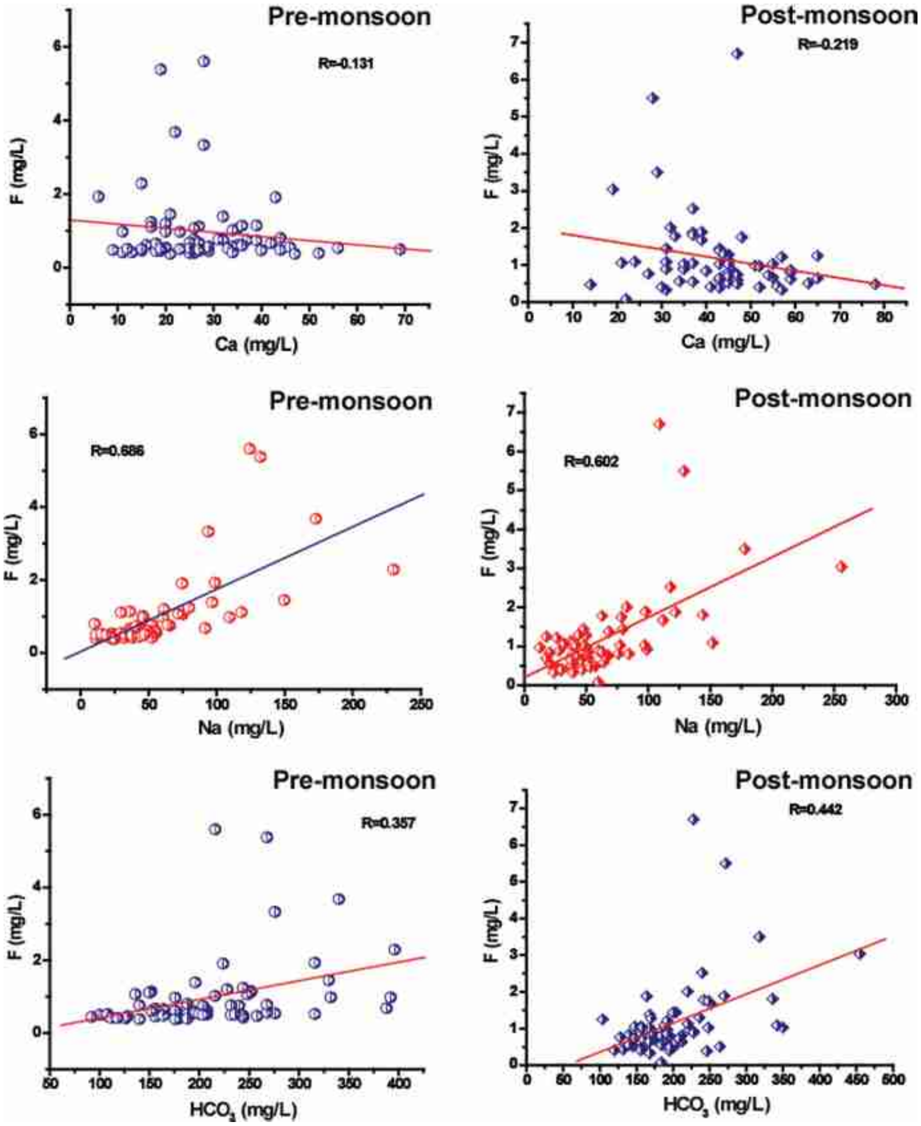

Fig. 7 Scatter diagrams for fluoride *vs* calcium, sodium and bicarbonate ions.

of groundwater with respect to calcite and fluorite is explained by (Handa 1975):

$$CaCO_3 + 2F^- + H^+ = CaF_2 + HCO_3^-$$

The ion activity product (IAP) and saturation index (SI) of fluorite and calcite in the analysed groundwater samples were calculated using the geochemical program WATEQ4F (Garrels and Christ 1965). The SI values of all but two pre-monsoon season groundwater samples were under-saturated with respect to fluorite and calcite, which suggests that Ca^{2+} concentration is not above the limit of fluorite saturation and is therefore not responsible for suppressing the dissolution of fluorite. Of the post-monsoon season samples, 14 were super-saturated with respect to calcite and one was supersaturated with respect to fluorite, which indicates that calcite precipitation is the driving force for fluorite dissolution, even though fluorite solubility is low.

Suitability for irrigation use

Salinity and sodicity are the principal water quality concerns in irrigated areas of arid and semi-arid regions. Salts may harm plant growth physically by limiting the uptake of water through modification of the osmotic processes, or chemically by metabolic reactions such as those caused by toxic constituents (Todd 1980). The effects of salts on soils include changes in soil structure, permeability and aeration, which indirectly affect plant growth. The parameters such as sodium adsorption ratio (SAR), percent sodium (%Na), residual sodium carbonate (RSC), corrosivity ratio (CR) and electrical conductance (EC), are important for the classification of water for irrigation use. Salinitization of irrigated lands is a major cause of the loss of production and also has adverse environmental impacts. On the basis of EC values (USSL 1954), 75% of pre-monsoon samples and 69% of post-monsoon samples are in the "good" category and 25 and 31%, respectively, are the "medium" category (Table 5).

High concentrations of sodium are undesirable in water because sodium absorbs into the soil via cation exchange sites, causing soil aggregates to disperse, thus reducing its permeability (Hem 1991). In natural water, %Na is used to evaluate its suitability for agricultural purposes (Wilcox 1948). The percentage of sodium in the study samples ranges from 8.26 to 84.27 and from 8.71 to 85.12 in in pre- and post-monsoon seasons, respectively (Table 3). The %Na classification of water indicates that only one groundwater sample in both the seasons is unsuitable for irrigation (Table 5), and agricultural yields are generally low in areas irrigated with these waters. This is probably due to the presence of excess salts, which cause osmotic effects on the soil–plant system. Hem (1991) stated that the combination of EC and SAR can be used to determine the suitability of water for irrigation, and indicated that EC near 2000 μS/cm and SAR $>$ 10 would represent a high sodium hazard. Edet and Okereke (2005) mentioned that groundwater of low salinity (EC $<$ 200 μS/cm) and low sodium hazard (SAR $<$ 1.5) is excellent for irrigation of almost all soils. The SAR values ranges from 0.27 to 6.03 and from 0.3 to 6.36 in in pre- and post-monsoon seasons, respectively (Table 3). All samples are in the "excellent" category, except for one sample in each season that is in the "good" category (Table 5). The relationship of SAR and EC values suggests that two major irrigation water types exist in the area, i.e. "medium salinity and low sodicity" and "high salinity and low sodicity" waters. These types of water can be used for irrigation in almost all soils with little danger of Na^+ development. Plants with moderate tolerance can be grown in the medium salinity and low sodicity irrigation water. Only one post-monsoon season sample has high salinity and high sodium content, which is not suitable for plant growth. Adjusted SAR, adj.SAR, is a value corrected to account for the removal of Ca^{2+} and Mg^{2+} by their precipitation with HCO_3^- and CO_3^- added to the water and is defined as:

$$\text{adj.SAR} = \mathrm{Na}^+ / \sqrt{\frac{(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})}{2\,[1 + 8.4\mathrm{PH}_c]}}$$

$$\mathrm{PH}_c = (p_{k_2} - p_{k_c}) + p(\mathrm{HCO}_3^- + \mathrm{CO}_3^{2-}) + p(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})$$

where p refers to the negative logarithm; $(pk_2 - pk_c)$ is the summation of Ca^{2+}, Mg^{2+} and Na^+. The calculated adj.SAR values (2.7–10.9 and 3.3–11.9 in in pre- and post-monsoon seasons, respectively) are higher than the sodium adsorption ratio. This indicates that the concentration of HCO_3^- in water samples may be high and this causes precipitation of Ca^{2+} as calcium carbonate, resulting in higher SAR or high sodium hazard in the water. Based on the adj.SAR values, the majority of the groundwater samples were found satisfactory for irrigation use, since the adj.SAR values do not exceed 8 (Jalali 2007).

Table 5 Irrigation classification of groundwater using different methods.

Water class	Range	Pre-monsoon	Post-monsoon
Sodium percent (Na%) classification			
Excellent	0−20	10	6
Good	20−40	34	34
Permissible	40−60	17	19
Doubtful	60−80	3	5
Unsuitable	>80	1	1
Electrical conductivity (EC) classification			
Excellent	<250	–	–
Good	250−750	49	45
Fair/Medium	750−2250	16	20
Poor/Bad	2250−5000	–	–
Sodium Adsorption Ratio (SAR) classification			
Excellent	0−10	64	64
Good	10−18	1	1
Fair	18−26	–	–
Poor	>26	–	–
Residual Sodium Carbonate (RSC) classification			
Good	<1.25	61	62
Medium	1.25−2.5	2	2
Bad	>2.5	2	1
Corrosivity Ratio (CR) classification			
Safe	0−1	58	48
Unsafe	>1	7	17

Just as the SAR is an index reflecting the hazard of sodium ions to plant and soil health, the residual sodium carbonate (RSC) is an index used to determine the HCO_3^- hazard (McLean *et al.* 2000). High bicarbonate levels in groundwater can stunt plant growth and lead to calcite precipitation, decreased soil permeability, lowered infiltration capacity and an increase in erosion (McLean *et al.* 2000). The classification of water quality for irrigation use according to the US Salinity Laboratory (1954), indicates that, in pre- and post-monsoon seasons, respectively, 92 and 95% of the samples fall below the RSC value of 1.25 (suitable for irrigation), 5 and 3% are in the range 1.25–2.5 (marginal for irrigation), and the remaining 3 and 2% have values >2.5 (not suitable for irrigation) (Table 5). A high value of RSC in water leads to an increase in adsorption of sodium in the soil system (Eaton 1950). In the post-monsoon season, the water table level is shallow and, therefore, infiltrated water dilutes the groundwater and thus reduces the effect of RSC.

The corrosivity ratio (CR) denotes susceptibility of groundwater to corrosion and is expressed as the ratio of alkaline earths to saline salts in groundwater. The effects of corrosion are losses in the hydraulic capacity of pipes. The corrosivity ratio ranges from 0.18 to 1.59 and from 0.36 to 2.22 for for pre- and post-monsoon season samples, respectively (Table 3). Analysis of groundwater samples indicates that 89.2% of the pre-monsoon samples are safe (CR < 1) and 10.8% are unsafe (CR > 1), whereas 73.8% of post-monsoon samples are safe and 26.2% are unsafe (Table 5). Hence the majority of the water is safe for long-distance transportation through metallic pipe lines, but in the "unsafe" areas, PVC pipes should be used for water supply instead.

CONCLUSIONS

The evaluation of hydrogeochemical features reflects that the weathering of silicate rocks is responsible for the major ion chemistry of groundwater in the Upper Panda River basin. The ionic dominance pattern among cations is in the order: Na > Mg > Ca > K in pre-monsoon groundwater samples, and Na > Ca > Mg > K in post-monsoon samples and that of the anions is $HCO_3 > SO_4 > Cl > F$ in both the seasons. The majority of samples with fluoride content <1.5 mg/L show Ca-HCO_3 signatures, while those with fluoride >1.5 mg/L show a tendency towards Na-HCO_3 type of waters. The molar ratios of groundwater chemistry evolve by silicate weathering reactions, although most of the pre-monsoon season groundwaster samples and the majority of the post-monsoon season samples have not reached equilibrium with carbonate minerals. The ion activities of cation systems fall within the kaolinite stability field, suggesting that the contribution of major ion chemistry is from the weathering of silicate rocks. Hydrochemical studies reveal that the majority of groundwaters in the study area are suitable for domestic and irrigation use, except in the southern part where the groundwater is affected by high fluoride concentration. The occurrence of high fluoride concentration (pre-monsoon: 5.6 mg/L, post-monsoon: 6.7 mg/L) in some of the wells is attributed to the dissolution of fluor-apatite and biotite, minerals that are associated with the Granitoid complexes. The availability of fluoride-rich minerals and the influence of aquifer materials, rather than the inherent chemical characteristics of water in the granite gneissic rock complex, are instrumental in the fluoride enrichment of the groundwater. Water–rock interaction is responsible for the major ion chemistry of the groundwater, and evapotranspiration and low rainfall played crucial roles in changing the concentration of species in the groundwater, including fluoride ions. An environmental awareness programme is recommended, in which the health implications of fluoride are emphasized through education of the public and community participation in this under-developed region of Sonbhadra district, Uttar Pradesh.

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