



Fluoride behaviour analysis in groundwater with reference to hydrogeochemical parameters in basaltic aquifers using remote sensing and GIS technique in parts of Burhner watershed, MP, India

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High fluoride concentration in groundwater leads to health threat to millions of people around the world; therefore, a systematic study is required to understand the behaviour of fluoride in water in terms of the local hydrogeological setting and other hydrogeochemical parameters. The present study is an attempt to assess the hydrogeology of groundwater in the study area to understand the fluoride behaviour in groundwater and to deduce the chemical parameters responsible for the dissolution activity of fluoride. F^- value varies from 0.04 to 14.6 mg/l (mean: 3.15 mg/l) in the study area. It is geologically occupied by basalt rocks where groundwater occurs in the weathered and fractured portions of the rocks and under semi-confined to confined conditions in fractured rocks. High F^- concentration is observed in deeper aquifers compared to shallow aquifers. Physico-chemical conditions like decomposition, dissociation and subsequent dissolution along with long residence time are responsible for leaching of F^- into the groundwater. F^- has +ve or -ve correlation with other parameters of water samples as per their nature. Simple to compound pahoehoe basaltic lava flows are responsible for the fluoride contamination in the confined aquifers (bore wells) of the study area. Overall confined aquifer water quality on the basis of fluoride concentration was found to be unsatisfactory for drinking purposes. About 57.13% of confined aquifers showed higher fluoride than the permissible limit but 100% unconfined aquifers (dug wells) have a low level of fluoride concentration, i.e. below the permissible limit.

Keywords. Fluoride; ground water quality; Deccan basalt.

1. Introduction

About 96% of fluoride in the human body is found in bones and teeth. Fluoride is essential for the mineralisation of bones and the formation of the dental enamel (Park 2011). The area has long been affected with high groundwater fluoride concentration which is reported to reach up to >18.2 mg/l in Mandla district (Chouhan *et al.*

2008) of Madhya Pradesh, India. The main source of fluorine is from drinking water and food such as sea fish, cheese and tea (Passmore *et al.* 1974). Some elements are essential in trace amounts for human beings, while higher concentrations of these elements cause toxic effects, and fluoride (F^-) is one of them (Technical Report, CGWB, Ministry of Water Resources, Govt. of India 1999). Concentration of fluoride between

0.6 and 1.0 mg/l in potable water protects tooth decay and enhances bone development (Kundu *et al.* 2001). Indian drinking water standards have suggested (Standard Methods for the Examination of Water for Drinking Water Specification 2003) a permissible limit of F^- in drinking water at 1.0 mg/l, which is lower than the maximum tolerance limit (1.5 mg/l) of F^- in drinking water specified by WHO guidelines for drinking water quality (WHO 1984). About 85 million tons of fluoride deposits are on the Earth's crust, 12 million tons are found in India (Teotia and Teotia 1984).

The ingestion of water with F^- concentration above 1.5 mg/l results in fluorosis. The first case of fluorosis was detected in India from Andhra Pradesh during early 1930s (Shortt *et al.* 1937). Madhya Pradesh is one of the states affected by endemic fluorosis (Agrawal *et al.* 1997). Endemic fluorosis has been prevalent in India since 1973 (Shortt *et al.* 1937). Endemic fluorosis resulting in high fluoride concentration in groundwater is a public health problem in India (Kotecha *et al.* 2012). The present study is focused on the relationship between fluoride and hydrogeochemical parameters as well as with geomorphology and lithology.

2. Study area

The study area is bounded by latitude $22^{\circ}33'00''$ – $22^{\circ}51'00''$ N and longitude $80^{\circ}31'00''$ – $80^{\circ}41'00''$ E and covers about 325 km² of the geographical area (figure 1). The area has a semi-arid climate with a temperature of 41.3°C and the mean daily minimum is at 24°C. The average annual precipitation is 1182 mm. Sandy loam, loam and clay loam are the main soil types in the study area, which act as a natural filter to screen out many substances that mix with water.

The area is occupied by an undulating dissected plateau, with hills having an elevation of 457–680 m from the mean sea level (msl). River Burhner and its tributary Gurbani and Anari drain the area. The drainage pattern in the study area is sub-dendritic to dendritic. Geologically, the study area is dominated by basaltic lava flows of the Deccan volcanic province. Basaltic lava flows (Upper Cretaceous to Palaeocene) belonging to the Dhuma formations of the Amarkantak group overlie the older formations. The flows are simple 'aa' and compound

'pahoehoe' types (Report: District Resource Map 2003). Alluvium and black cotton soils overlie the basalts belonging to the Quaternary time of the geological era. Rainfall is the main source of groundwater recharge. Groundwater samples were collected under phreatic conditions in the weathered zone, fractured and vesicular basalts (shallow aquifer) and under semi-confined to confined conditions in the fractured zone (deep aquifer). The depth of the water level varies from 1.2 to 8.5 m below the ground level (bgl) in shallow aquifers and from 10.1 to 37.7 m (bgl) in the deeper aquifers. Maximum elevation in the area is 820 m while the minimum elevation is 460 m above msl.

3. Materials and methodology

About 28 water samples were collected from confined aquifers and 14 from unconfined aquifers from different villages (figure 1) for a comparative study. Groundwater sampling and analysis has been carried out during the pre-monsoon of 2009. Fluoride concentration along with other chemical parameters was analysed using the standard chemical analytical techniques (Report: Standard methods for the examination of water and wastewater 1998). Fluoride was analysed by HACH DR 2010, spectrophotometer and TDS, pH and EC have been measured using a hand-held apparatus, and the measured results are presented in table 1. Correlation matrix has been prepared using data from table 1 with the help of Microsoft Office Excel software. The analysed chemical results were used for creating Karl Pearson correlation matrix of the confined aquifers and unconfined aquifers data presented in tables 2 and 3.

IRS P6 LISS-III remote sensing data (figure 2) have been used for preparing geomorphological maps which has been shown in figure 3 along with confined aquifer and unconfined aquifer location on different geomorphic units. Confined aquifer and unconfined aquifer location with Fe^- concentration on different lithological units is shown as figure 4 has been prepared using IRS P6 LISS-III data and the district resource map was published by the Geological Survey of India in Arc GIS software. The analysed fluoride results were created as point shape files in the Arc GIS platform and superimposed on lithological and geomorphic maps for further analysis.

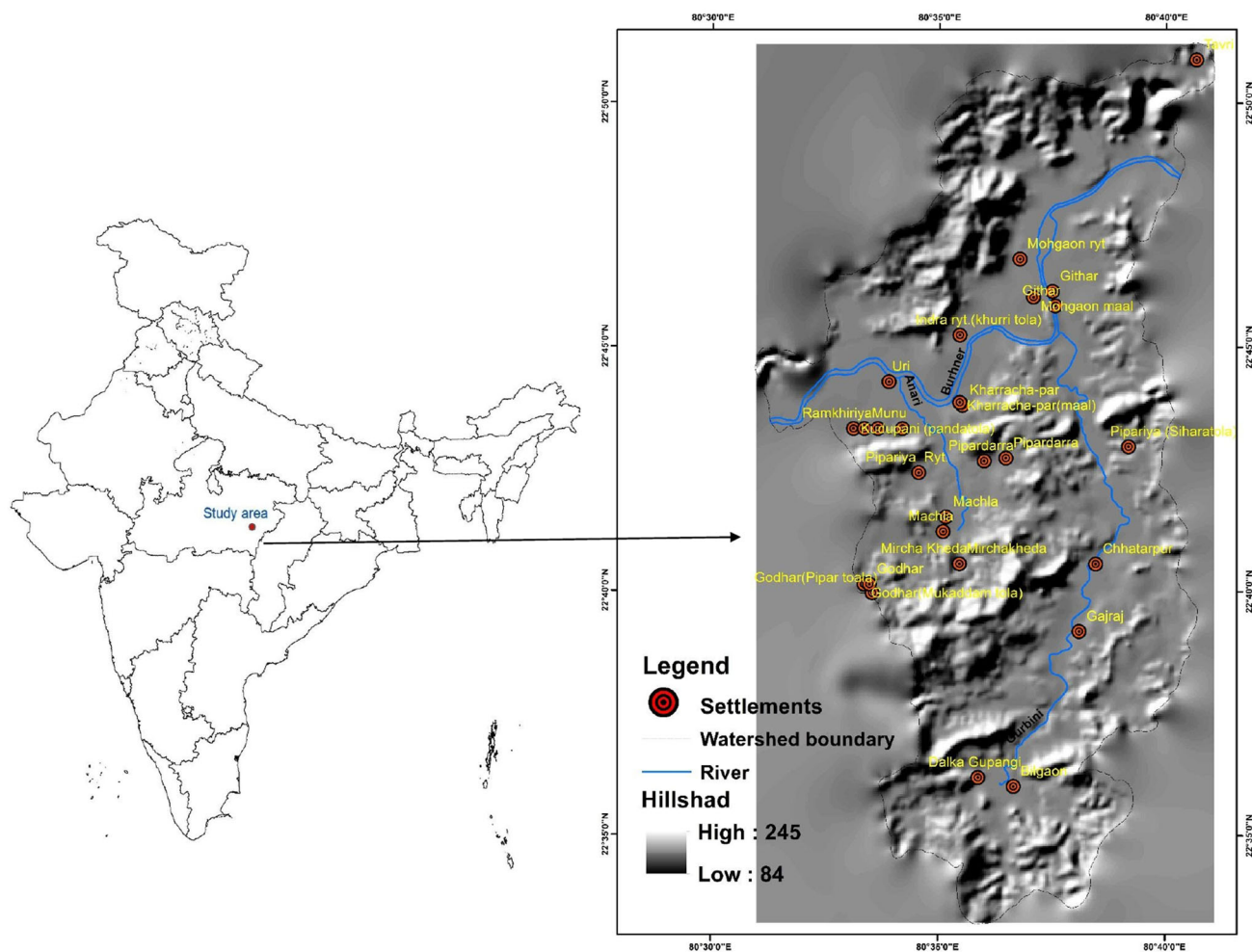


Figure 1. Location map of the study area.

4. Results and discussions

A comparison of the F^- concentration of groundwaters at shallow aquifers <7.5 m bgl and deeper aquifers >7.5 m bgl has indicated that deeper aquifers have higher F^- concentration than shallow aquifers (Standard methods for the examination of water for drinking water specification 2003). The fluoride concentration in 42.87% confined aquifers was under permissible limit (<1.5 ppm) and 57.13% samples showed higher fluoride concentration than the permissible limit. All or 100% of unconfined aquifers showed fluoride concentration below the permissible limit. Similarly, the pH of groundwater from deeper aquifers is high as compared to that of the shallow aquifers.

The geomorphology, hydrogeology and geochemistry of sediments influence the occurrence, origin and mobilisation of arsenic in sedimentary aquifers (Bhattacharya *et al.* 1997; Kinniburgh and

Smedley 2001). Ravenscroft *et al.* (2001) have shown that the occurrence of arsenic has a close relationship with geomorphological units.

The flat terrain of the area with very less slope provides the surface water with these geomorphic features enough time to infiltrate deep into the aquifer, thus providing the pathway for the contaminant to reach the groundwater (Singha *et al.* 2014).

From the analysis of the hydrogeomorphology of the study area, groundwater is being extracted from the unconfined and confined aquifers through dug wells and tube wells, maximum groundwater elevation has taken place in the northern part of the area which is near the river valley (figure 5). As seen in hydrogeological maps, the maximum area falls in the good to the moderate unit and covers 152.59 km² area, maximum water elevation also observed (3.7 and 3.4 m), the second largest unit is moderate to poor covering 134.26 and very good to

Table 1. Results of the chemical analysis of groundwater samples of the study area.

Village	Well ID	W/1 (m bgl)	pH	TDS	EC ($\mu\text{S}/\text{cm}$)	F (mg/l)	Ca (mg/l)	Cl (mg/l)	CO ₃ (mg/l)	HCO ₃ (mg/l)	Na (mg/l)	Total depth	WL elevation
<i>Unconfined aquifers</i>													
Pipardarra	DW 1	1.8	7.1	100	140	0.35	22.05	8.99	2	84	2.06	3.8	2
Mirchakheda	DW 2	1.6	6.7	200	260	0.13	48.51	12.99	12	136	4.57	3.6	2
Pipariya	DW 3	1.6	6.9	200	230	0.04	44.1	18.98	8	108	2.06	3.4	1.8
Ramkhiriya	DW 4	1.8	7.1	100	150	0.05	26.46	14.98	0	90	3.53	9	7.2
Uri	DW 5	6.7	6.8	100	200	0.03	20.1	16.56	5	80	23.16	8.2	1.5
Kharrachapar Ryt	DW 6	1.2	6.8	200	330	0.17	35.28	109.89	40	64	9.29	5.3	4.1
Kharrachapar Ryt	DW 7	2.5	6.9	200	240	0.19	40.57	25.97	6	104	6.93	4.5	2
Mohgaon Ryt	DW 8	7.2	6.8	200	320	0.11	25.58	11.99	4	96	7.91	10	2.8
Munu	DW 9	2.9	6.9	400	580	0.01	50.27	95.9	0	100	30.04	4.5	1.6
Bilgaon	DW 10	3.9	7.1	200	270	0.25	27.34	8.99	2	10	4.38	5.5	2.6
Godhar	DW 11	1.2	6.6	100	260	0.06	24.7	11.99	10	170	7.59	3.8	0.8
Gajraj	DW 12	8.5	7.4	300	430	0.03	27.1	7.95	44	190	4.95	2.1	1.1
Dalk Gupangi	DW 13	3	7.3	100	200	0.36	30.8	9.12	5	100	110.7	3.4	1.6
Khajri	DW 14	4.6	7.3	100	220	0.08	14.99	14.98	10	90	10.25	9	4.4
<i>Bore wells</i>													
<i>Confined aquifers</i>													
Githar	BW 1	21.8	9.3	200	330	2.19	5.9	30.3	3	100	65.6	23.8	2
Githar	BW 2	22.8	7.8	200	270	4.6	6.02	25.36	6	110	75.5	24	1.2
Kharracha-par	BW 3	22.8	7.7	200	290	2.7	7.06	31.97	2	122	82.17	24.6	1.8
Kharracha-par (Maal)	BW 4	7.65	8.2	200	330	2.2	8.82	27.97	8	110	73.6	9	1.35
Pipardarra	BW 5	26.7	9.4	200	410	4.2	0.31	2.11	24.3	4	200	28.5	1.8
Pipardarra	BW 6	26	6.9	300	520	10.1	0.14	1.04	130	0	84.82	28	2
Mirchakheda	BW 7	9.8	7.1	200	320	0.23	21.17	26.97	8	112	55.47	11.5	1.7
Machla	BW 8	13	8.4	200	280	10.7	8.82	32.97	4	88	70.78	14.5	1.5
Machla	BW 9	26.8	8.6	100	170	2.1	10.58	7.99	4	104	47.61	28	1.2
Mirchakheda	BW 10	37.7	7.1	300	350	0.11	14.99	25.97	12	128	58.51	38.3	0.6
Pipariya Ryt	BW 11	14.6	8.9	200	320	0.54	10.58	50.95	0	100	17.41	16.5	1.9
Pipariya (Siharatola)	BW 12	18.5	7	200	270	10.1	42.34	31.97	4	92	94.91	20.5	2

Ramkhiriya	BW 13	26	7.7	200	300	1.74	8.82	29.97	0	188	100	28	2
Ramkhiriya (Shikaritola)	BW 14	25	8.2	300	430	14.6	17.64	46.95	0	84	100	26.2	1.2
Uri	BW 15	6.8	7.3	200	320	1.34	15.88	29.97	12	148	84.72	10.5	3.7
Indra Ryt (Khurritola)	BW 16	22	6.7	200	340	0.07	28.22	21.98	8	122	89.31	25.4	3.4
Mohgaon Ryt	BW 17	8.2	6.9	300	380	0.01	35.28	20.97	8	152	8.09	10.5	2.3
Mohgaonmaal	BW 18	15.5	7.6	200	310	1.82	35.28	42.957	0	96	93.28	17.3	1.8
Munu	BW 19	20.5	7.4	200	310	1.22	11.46	26.97	0	188	75.4	22.3	1.8
Kudupani (Pandatola)	BW 20	8.7	6.6	500	610	1.56	59.09	47.95	10	158	57.55	10.8	2.1
Godhar (Mukaddamtola)	BW 21	10.1	6.8	100	200	0.2	40.57	13.99	8	112	5.62	13.2	3.1
Godhar	BW 22	10.2	6.9	100	180	0.2	38.81	13.99	16	84	8.73	13.5	3.3
Godhar (Pipartola)	BW 23	20.2	8.1	200	330	2.5	8.82	43.96	80	22	87.27	22.2	2
Tavri	BW 24	19.3	7	233	343	0.63	32.92	28.63	6	123.33	63.56	21	1.7
Chhatarpur	BW 25	15.8	7.5	100	210	1.18	9.7	13.98	4	158	76.01	17.4	1.6
Gajraj	BW 26	16.1	8.2	200	260	2.7	36.16	97.9	8	92	67.36	17.1	1
Dalka Gupangi	BW 27	16.9	8.4	200	320	7.3	9.72	13.98	4	158	81.05	17.5	0.6
Bilgaon	BW 28	37.1	6.9	400	680	1.46	17.64	14.99	8	112	63.5	39.8	2.7

good as the unit covers 24.77 km² area and the smallest units covered by poor to nil units is 13.38 km² area.

The observation of a 3D model with Arcscene software with regard to the study of the water-level elevation of confined aquifers shows a maximum fluctuation of 3.6 m in bore well (BW) as confined aquifer 15 near the Burhner river valley at 451–505 m elevation from the mean sea level; morphologically, it is in the pediplain units and the lowest elevation of water table is found at 0.6 m. (figure 6), whereas in unconfined aquifers, the maximum elevation of 7 m and minimum of 0.8 m were identified (figure 7).

Groundwater from the unconfined aquifers is slightly acidic to slightly alkaline (pH 6.6–7.4), while that from confined aquifers is slightly acidic to alkaline (pH 6.6–9.4; table 1). The samples have electrical conductivity (EC) values in the range of 140–580 μs/cm in shallow aquifers and 170–680 μs/cm in deeper aquifers. The average calcium (Ca²⁺) concentration from shallow and deep aquifers is in the range 22.05–50.27 and 0.14–59.05 mg/l, respectively. Similarly, sodium (Na⁺) concentration ranges from 2.06 to 110.7 and 5.62 to 200 mg/l in shallow and deep aquifers, respectively. The concentrations of chloride (Cl⁻) in shallow aquifers range from 7.95 to 109.89 mg/l but in deep aquifers, it varies from 1.04 to 97.9 mg/l. The F⁻ concentration ranges from 0.01 to 0.36 mg/l in shallow aquifers (unconfined aquifers) and from 0.01 to 14.6 mg/l in confined aquifers.

From the correlation matrix (tables 2 and 3), it is found that confined aquifer water samples have a weak positive correlation between pH and F⁻ ($r = 0.239$) which suggests that pH is slightly important in determining F⁻ concentration in the water from confined aquifers. The correlation of F with CO₃⁻ ($r = 0.242$) and Na⁺ ($r = 0.384$) is also a weak positive correlation. A weak negative correlation is seen between fluoride and Ca²⁺ ($r = -0.219$), HCO₃⁻ ($r = -0.386$) in contrast to a significantly very weak positive correlation between fluoride and TDS ($r = 0.135$) and EC ($r = 0.149$) but no clear correlation with Cl⁻ ($r = 0.023$) table 2.

In the case of water from unconfined aquifers, the correlation of F⁻ with TDS ($r = -0.355$), EC ($r = -0.427$), Ca²⁺ ($r = -0.122$), Cl⁻ ($r = -0.173$), CO₃⁻ ($r = -0.168$) and HCO₃⁻ ($r = -0.405$) is weak negative while with pH ($r = 0.271$) and Na⁺ ($r = 0.429$), it is weak positive. The result of the correlation matrix shows that EC, TDS, HCO₃ and

Table 2. Correlation matrix for different water quality parameters of confined aquifers.

	F ⁻ (mg/l)	pH	TDS	EC (μ S/cm)	Ca (mg/l)	Cl (mg/l)	CO ₃ (mg/l)	HCO ₃ (mg/l)	Na (mg/l)
F ⁻ (mg/l)	1								
pH	0.239	1							
TDS	0.135	-0.303	1						
EC (μ S/cm)	0.149	-0.218	0.914	1					
Ca (mg/l)	-0.219	-0.595	0.252	0.057	1				
Cl (mg/l)	0.023	0.145	0.171	-0.031	0.332	1			
CO ₃ (mg/l)	0.242	-0.121	0.148	0.295	-0.262	-0.222	1		
HCO ₃ (mg/l)	-0.386	-0.304	0.056	-0.124	0.232	0.075	-0.661	1	
Na (mg/l)	0.384	0.375	0.064	0.212	-0.408	-0.086	0.150	-0.332	1

Table 3. Correlation matrix for different water quality parameters of unconfined aquifers.

	F ⁻ (mg/l)	pH	TDS (ppm)	EC (μ S/cm)	Ca (mg/l)	Cl (mg/l)	CO ₃ (mg/l)	HCO ₃ (mg/l)	Na (mg/l)
F ⁻ (mg/l)	1								
pH	0.271	1							
TDS (ppm)	-0.355	-0.022	1						
EC (μ S/cm)	-0.427	-0.057	0.924	1					
Ca (mg/l)	-0.122	-0.367	0.653	0.470	1				
Cl (mg/l)	-0.173	-0.278	0.530	0.598	0.466	1			
CO ₃ (mg/l)	-0.168	0.157	0.272	0.333	0.002	0.302	1		
HCO ₃ (mg/l)	-0.405	-0.044	0.159	0.239	0.120	-0.209	0.393	1	
Na (mg/l)	0.429	0.310	-0.132	-0.017	0.032	0.005	-0.158	-0.035	1

The results in tables 2 and 3 are based on Karl Pearson correlation analysis.

CO₃ of confined aquifer water samples have shown a positive correlation which is contrast to that of the unconfined aquifer water samples.

Positive correlation between fluoride with Na and HCO₃ in groundwater shows that the high fluoride content and alkaline sodic characteristics of groundwater result from the dissolution of fluorine-bearing minerals (Chunli *et al.* 2015) and negative correlation of fluoride with Ca²⁺ is as expected due to the low solubility of the fluorides of these ions (Handa 1975; Hem 1991; Hounslow 1995; Smedley *et al.* 2002; Das *et al.* 2003). The preferential removal of Ca²⁺ by several geochemical processes in aquifers, such as calcite precipitation, adsorption and cation exchange, may generate high concentrations of fluoride in groundwater and fluoride hydroxyl exchange/adsorption reaction occurs in the clay minerals with the alkaline water releasing fluoride into the groundwaters, and CaF solubility control and OH-F exchange reactions, F can be enriched in soda water (Chunli *et al.* 2015).

The presence of CaCO₃ favours the dissociation of F⁻ from F⁻ containing minerals (N. Subba Rao 2003).

In general, the aridity of climate is one of the primary reasons for the origin of high F⁻ in groundwater. Several processes, namely the dissolution of F⁻ bearing minerals, ion exchange and evaporative concentration can locally account for high F⁻ concentration in groundwater (Apambire *et al.* 1997; Jacks *et al.* 1993; Agrawal *et al.* 1997; Saxena and Ahmed 2003).

The ions like Cl₂, F, HCO₃, NO₃ and Si show an increasing trend due to the effective leaching from rock matrix along with anthropogenic activities (Srinivasamoorthy *et al.* 2008). Fluoride solubility in groundwater is depend on temperature and pressure (Nordstrom and Jenne 1997).

In the study area, fluoride-bearing minerals are identified as uranyl fluoride, apatite and carbonate fluorapatite (Prasad and Shukla 2014). The main sources of F⁻ in natural water are F⁻ bearing

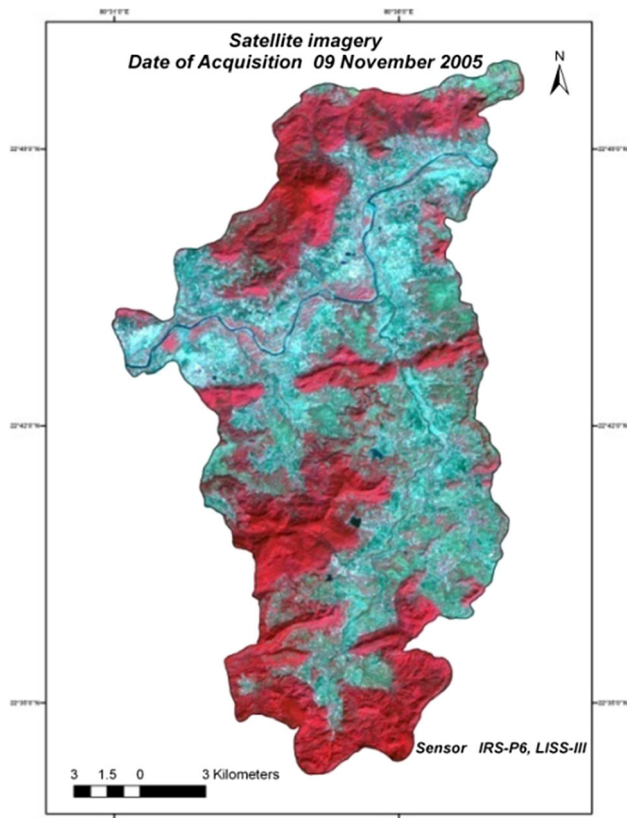


Figure 2. Remote sensing data IRS P6 LISS-III.

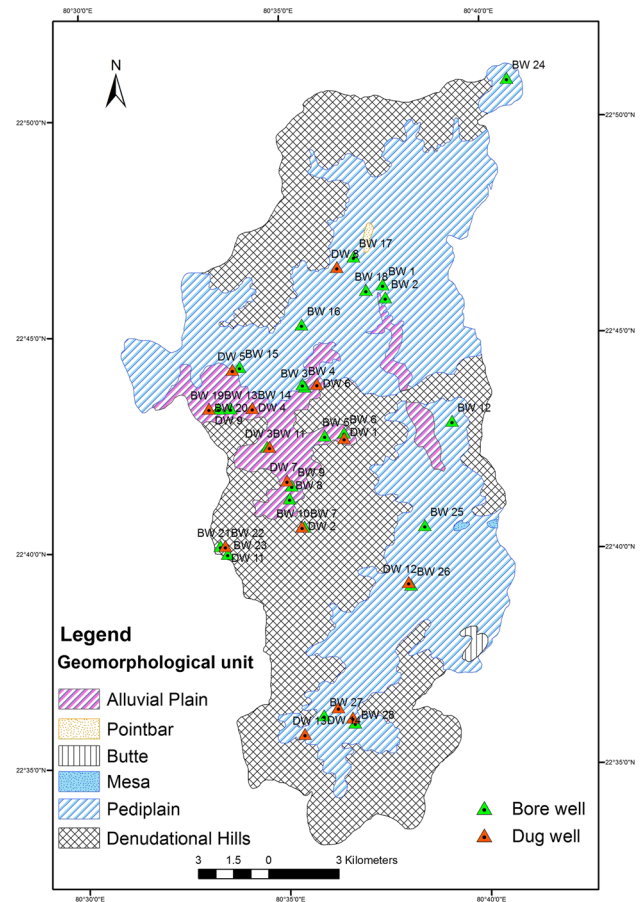


Figure 3. Confined aquifer and unconfined aquifer location on different geomorphic units.

minerals (fluorite, fluorapatite, cryolite and apophyllite) as well as F^- replacing OH^- in the ferromagnesium silicates (amphiboles and micas), and soil consisting of clay minerals (Ramesam and Rajagopalan 1985; Subba Rao *et al.* 1998; Muralidharan *et al.* 2002). According to Saxena and Ahmed (2001), alkaline pH ranging from 7.6 to 8.6 with high and moderate EC are the favourable conditions for CaF_2 dissolution in groundwater. High-fluoride-bearing groundwater is distributed mostly over arid and semi arid areas (Liu and Zhu 1991).

The confined aquifer tapping simple compound ‘pahoehoe’ flows have high concentration of F^- compared to unconfined aquifer tapping simple compound flows. A comparative sluggish movement of groundwater in compound ‘pahoehoe’ flows provided more favourable hydrogeological conditions for dissolution of F^- , as these are more porous and less permeable (Technical Report 2013). The residence times of water with the aquifer materials also significantly regulate the F^- concentrations in the groundwater (Ramamohana Rao *et al.* 1993; Wodeyar and Srinivasan 1996; Saxena and Ahmed 2001). High concentration of F^-

in deeper aquifers compared to shallow aquifers could be due to its high residence time in the aquifer system, thereby having longer contact time for the dissolution of F^- bearing minerals present. The present investigation on groundwater quality with reference to F^- concentration in Burhner watershed indicates that the groundwater is of moderate alkaline to alkaline category and mostly brackish. Weathering and leaching of F^- bearing minerals under an alkaline environment account for the enrichment of F^- in groundwater.

In the study area which has 22 basaltic lava flows and spans a very vast area, F^- bearing minerals are studied and identified, namely (uranyl fluoride (UO_2F_2), apatite [$Ca_5(F,OH,Cl)(PO_4)_3$], carbonate fluorapatite [$Ca_5(PO_4)_3F$]) have been identified by the XRD technique in rock samples from the drilling of selected confined aquifer were collected from different depths which express that the origin of fluoride is geogenic which is responsible for groundwater contamination (Prasad and Shukla 2014). Many researchers have reported that the source of fluoride in the groundwater of the Mandla

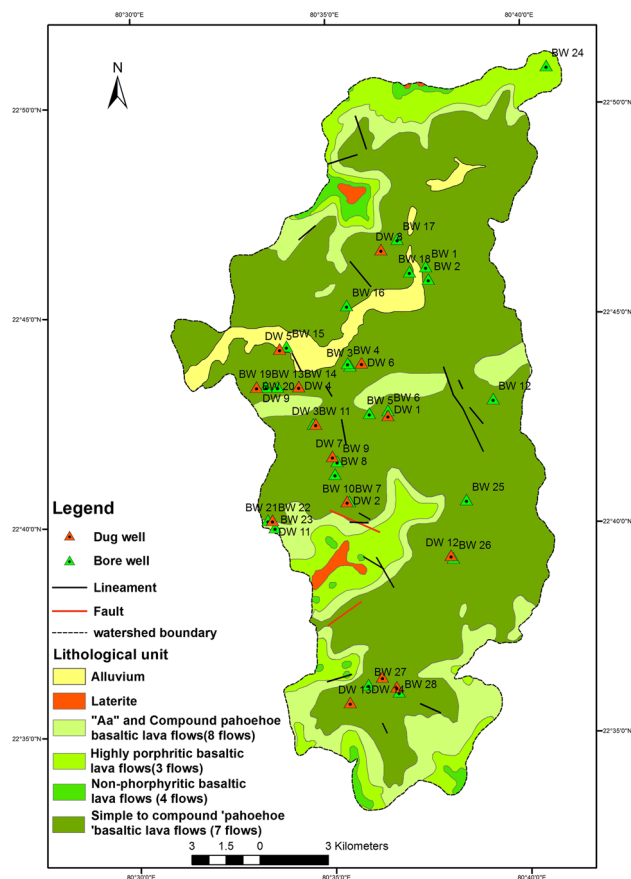


Figure 4. Confined aquifer and unconfined aquifer location with F^- concentration on different lithology.

district is mainly from geological occurrence (i.e., fluoride-bearing minerals, namely, apatite and biotitic mica, fluoride are fluorite, apatite, mica, amphiboles; Purnima 2013).

Minerals like fluorspar and fluoroapatite are the main sources of fluoride in groundwater (Chouhan *et al.* 2008). The Central Ground Water Board, North Central Region, Bhopal 2013 also reported the geogenic problem of high concentration of fluoride in groundwater of Mandla district.

In the groundwater, major ion chemistry and possibly pH, which are controlled by water–rock interaction processes and the geologic setting in the aquifer, are important in mobilising F (Pujari and Deshpande 2005; Farooqi *et al.* 2007).

The geomorphology, hydrogeology and geochemistry of sediments influence the occurrence, origin and mobilisation of arsenic in sedimentary aquifers (Bhattacharya *et al.* 1997; Kinniburgh and Smedley 2001). Ravenscroft *et al.* (2001) have shown that the occurrence of arsenic has a close relationship with geomorphological units.

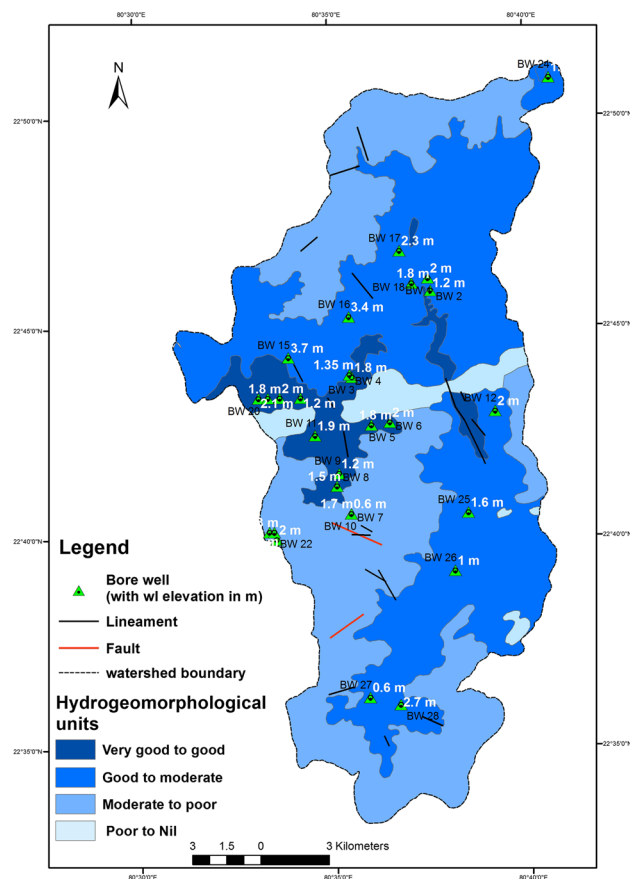


Figure 5. Hydrogeomorphological map.

5. Spatial and temporal distribution of fluoride

The geomorphology, hydrogeology and geochemistry of sediments influence the occurrence, origin and mobilisation, as the geogenic contamination in groundwater is closely related to geomorphology. Confined aquifer and unconfined aquifer location were superimposed on the geomorphological map (figure 3).

Six types of geomorphological units have been identified in the study area, i.e., alluvial and point bar exist as loose and unconsolidated with a flat nature and have 0–5% slope. The largest unit with 46.91% covers a total of 325 km² of geographical area identified as pediplain has moderate to strong with 5–15% slope, the second largest unit is the denudational hill with 15–35% slope, covering 45.00% of the total geographical area, mesa and butte is the smallest unit, covering 1.35% of the total area with >35% very steep slope.

These are the valleys filled with unconsolidated alluvial/fluvial material and form zones of good groundwater prospects. The background is formed

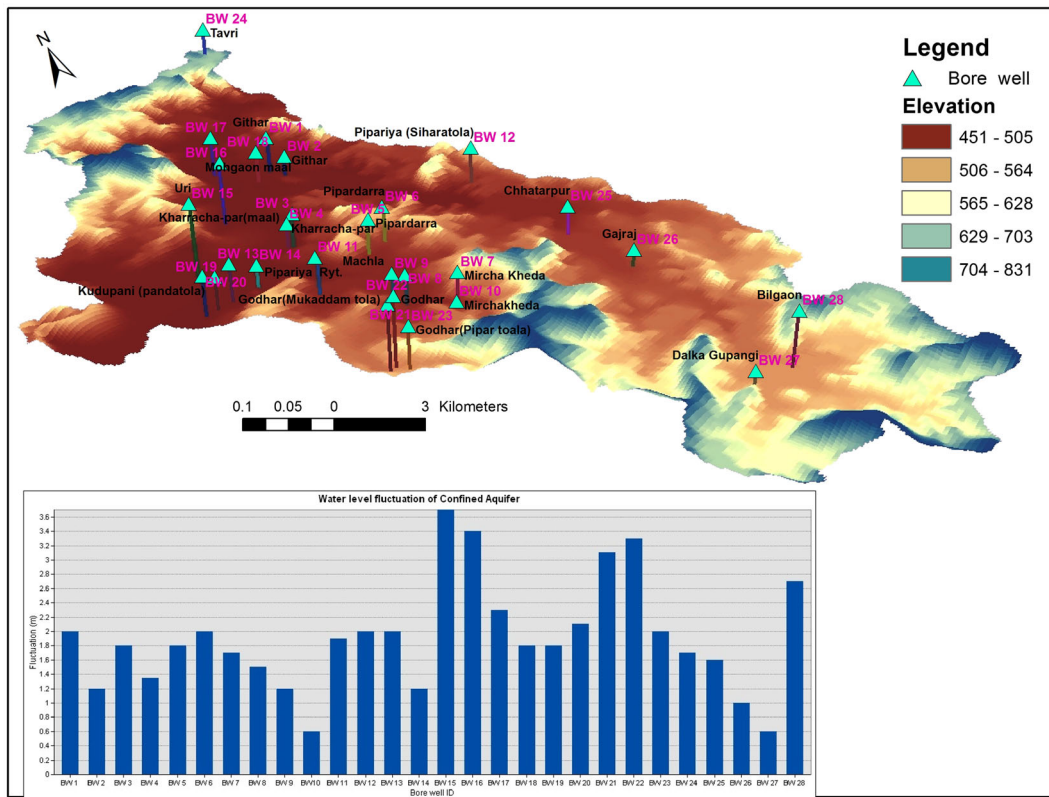


Figure 6. 3D view of water table elevation map and groundwater table of a confined aquifer.

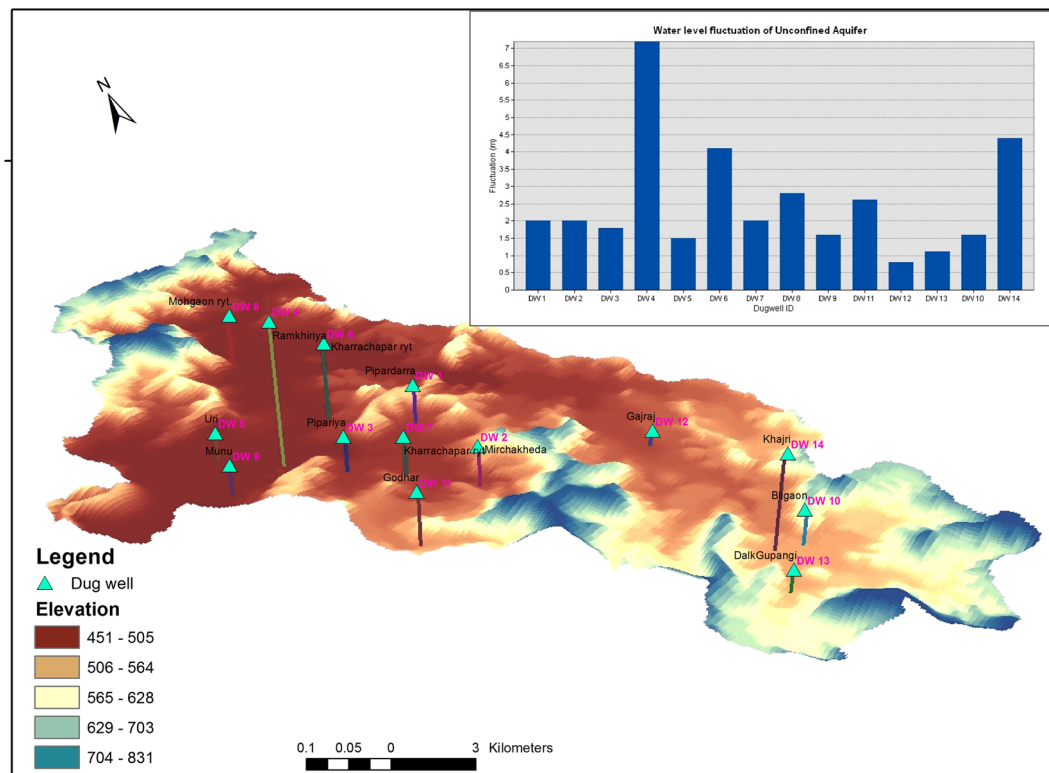


Figure 7. 3D view of water table elevation map and groundwater table of an unconfined aquifer.

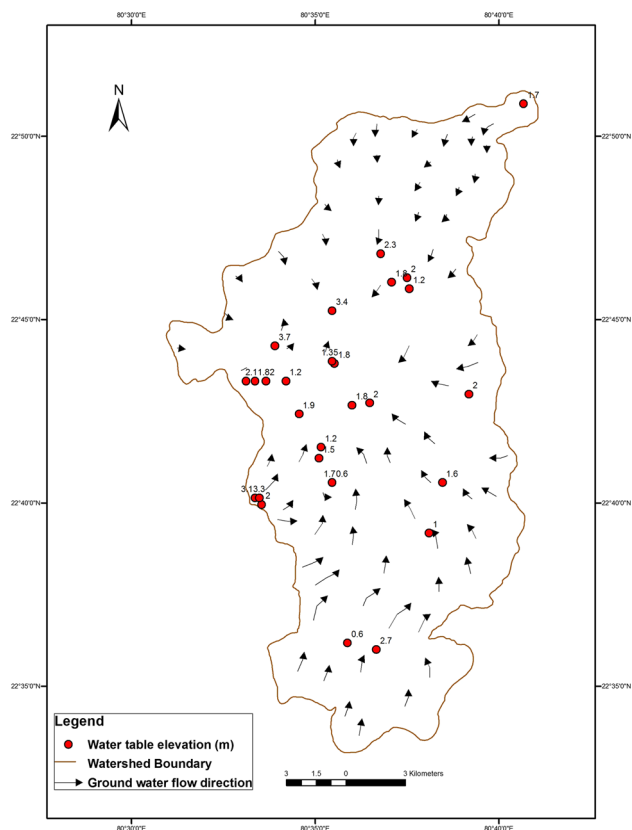


Figure 8. Water table elevation map and groundwater flow of a confined aquifer.

of pediplains made up of granitic gneisses of the Chota Nagpur gneissic complex.

In the groundwater studies, fluoride distribution plays an important role, especially in the demarcation of hydrogeomorphic units and associated groundwater characteristics (Manual for National Geomorphological and Lineament Mapping 2010).

The groundwater flows towards the western direction, and the water table follows to the general topography of the area (figure 8). The fluoride concentration in the study area seems to be controlled by geomorphic units due to the selective capability of different geomorphic units to allow the percolation of water below the ground. In the denudational hill unit, fluoride concentration in the confined aquifer ranges from 0.01 to 10.1 mg/l. In alluvial plains, it varies from 0.54 to 14.64 mg/l and in the pediplain geomorphic unit ranges between 0.11 and 2.5 mg/l. Majority of the samples show more fluoride concentration in drinking water than the permissible limit (1.5 mg/l) in the confined aquifer which falls in the alluvial terrain including a coned aquifer having the highest concentration (14.6 mg/l) located at the Ramkhiriya Shikaritola village, which is located in the western part of the

Table 4. Saturation index values of fluorite and calcite ($CaCO_3$).

Confined aquifer		
Village	SI (fluoride)	SI (calcite)
Githar	-2.41	-0.47
Githar	-2.48	-0.95
Kharrachapar	-2.2	-0.9
Kharrachapar (Maal)	-2.29	-0.35
Pipardarra	-1.09	-0.61
Pipardarra	-1.75	-4.6
Mirchakheda	-2.9	-0.36
Machla	-3.59	-0.26
Machla	-2.45	0.11
Mirchakheda	-1.6	-1.2
Pipariya Ryt	-1.1	0.36
Pipariya (Siharatola)	-2.3	-0.95
Ramkhiriya	-2.6	-0.66
Ramkhiriya (Shikaritola)	-0.67	-0.22
Uri	-2.05	0.86
Indra Ryt (Khurritola)	-0.16	-1.3
Mohgaon Ryt	-1.5	-0.92
Mohgaonmaal	-2.8	-0.45
Munu	-2.73	-0.82
Kudupani (Pandatola)	1.96	-1.1
Godhar (Mukaddamtola)	-0.78	-1
Godhar	-1.03	-1.1
Godhar (Pipartoala)	-2.52	-1.2
Tavri	-1.88	-0.97
Chhatarpur	-2.06	-0.8
Gajraj	-3.04	0.16
Dalka Gupangi	-3.61	0.58
Bilgaon	-2.53	-1.6
Unconfined aquifer		
Village	SI (fluoride)	SI (saturation)
Pipardarra	-1.28	-1.1
Mirchakheda	0.79	-1
Pipariya	-0.27	-0.95
Ramkhiriya	-0.38	-1
Uri	0.64	-1.5
Kharrachapar Ryt	-0.84	-1.4
Kharrachapar Ryt	-0.35	-1
Mohgaon Ryt	0.98	-1.4
Munu	-1.23	-1
Bilgaon	-1.67	-2
Godhar	-0.88	-1.3
Gajraj	-0.22	-0.49
Dalk Gupangi	-0.14	-0.71
Khajri	1.31	-1.1

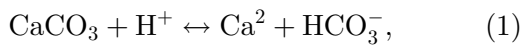
watershed, whereas in the case of the unconfined aquifer, the denudation hill has 0.03–0.36 mg/l and the pediplain has 0.06–0.13 mg/l and 0.01–0.35 mg/l in the alluvial plain (figure 3).

Correlation analysis of lithology of the area and the confined aquifer fluoride concentration reveals that the highest value of fluoride (14.6 mg/l) is found in simple to compound pahoehoe basaltic lava flows and other higher concentration is also found in the same type of lava flow which indicates that this unit contains fluoride-bearing minerals major lineament in the middle of the study area (figure 4).

To evaluate which particular minerals, of the mentioned minerals, might be contributing to the fluoride levels in the groundwater of this area, the use of the geochemical model PHREEQC 3.4.0 was made. The model helps to speciate the quantitative chemical analysis results. Simulations done over the raw quantitative data lead to results presenting phases (major minerals) predicted to be present in the water and saturation index (SI) of these phases.

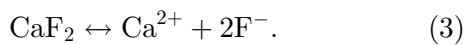
The SI values obtained from PHREEQC simulations carried out on two sets of data for confined aquifer and unconfined aquifer water samples, one where highest value of fluoride has been recorded and another where the lowest value of fluoride has been recorded, are presented in table 4.

Fluoride ion takes a relatively long time to leach out into groundwater due to its low solubility. Under such conditions, its occurrence is predominantly controlled by free calcium ions (Ca^{2+}) sourced into groundwater majorly from the common mineral, calcite (CaCO_3) (Jacks *et al.* 2005). The dissociation reactions and solubility products of fluorite (equations 1 and 3) and calcite (equations 2 and 4) can be demonstrated by the following equations (Handa 1975):



where the equilibrium constant is

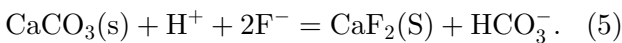
$$K_{\text{calcite}(\text{CaCO}_3)}(K1) = [\text{Ca}^{2+}][\text{HCO}_3^-]/[\text{H}^+], \quad (2)$$



Equilibrium constant is

$$K_{\text{fluorite}}(K) = [\text{Ca}^{2+}][\text{F}_2^-]. \quad (4)$$

On coupling the above equations, Handa (1975) formulated equation (5) as follows:



Equilibrium constant is

$$K_{\text{calcite-fluoride}}(K1/K2) = [\text{HCO}_3^-]/[\text{H}^+][\text{F}^-]^2. \quad (6)$$

From the above formulations, it can be interpreted that at a homogeneous pH range (defined by the H^+

ion concentration), where water is of the bicarbonate type, fluoride concentration in water tends to rise with a dip in the calcium concentration.

The SI of a chemical compound is calculated using the formula as given below:

$\text{SI} = \text{Log}_{10} Q/K$. The SI values are explained based on the standard given by Sreedevi *et al.* (2006), Al-Amry (2009) and Dey *et al.* (2011).

6. Source of fluoride and recommendations

The uneven distribution of fluoride in space and time is primarily due to the variation in mineral assemblage of rocks, differential fracture system and associated hydrochemical processes (Reddy and Rao 2006).

In basaltic rocks, in general, the source of fluoride is basically apatite (Wedepohl 1972; Nanyaro *et al.* 1984). The uranyl, fluoride apatite and carbonate fluorapatite (Prasad and Shukla 2014) were identified as fluoride-bearing minerals in the Burhner watershed. In groundwater, it occurs as a result of evapotranspiration along the groundwater flow path from replenished areas to local depressions (High fluoride groundwater in Southern India 1979). We suggest that the drinking water source from the affected area may be met from a shallow unconfined aquifer. Confined aquifer water may be used for other domestic purposes. Local users of water should be educated about the hazards of the consumption of high F^- rich water and the use of simple methods of defluoridation. Some important defluoridation techniques (Nalgonda, activated alumina and ion exchange) should be adopted in the area.

7. Conclusions

Hydrogeochemistry interconnected to the weathering of rocks is responsible for major ion chemistry of groundwater in the Burhner watershed. Water-rock interaction and evapotranspiration, which were further influenced by arid to semi-arid climatic factors of the area, play a key role in the modification of the concentration of species in groundwater, especially, fluoride. The structural variation and intense weathering processes together with a fractured confined aquifer system have forced the release of fluoride from rocks to groundwater in an alkaline environment. If the calcium concentration is high in groundwater in any area, there is a

possibility of a high concentration of fluoride, whereas it is a direct contrast in the case of sodium. According to SI values, most of the water samples of (confined aquifers and unconfined aquifers) the study area are under-saturated with respect to fluorite and supersaturated with respect to calcite (CaCO_3).

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