

## Fluoride in the Groundwaters of Hard Rock Hirehalla Sub-basin, Karnataka, India

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### Abstract

Hydrogeochemical analysis was carried out in and around parts of Hoovina Hadagali and Harapanahalli taluks, Karnataka, India where increasing fluoride risks were reported. 140 no. of representative water samples were collected for both seasons. Cations such as Ca, Mg, Na and K while anions such as  $CO_3$ ,  $HCO_3$ , Cl,  $SO_4$  and F were analysed along with physical parameters- pH, EC, TDS and H. Analyses were carried out following standard procedure of APHA. Ion selective electrode method was adopted to determine fluoride and compared with different standards such as BIS, ICMR and WHO. F ranged from 0.05 to 5.69 mg/lit. 25.71 % and 20% of water samples in the study area reported to be above allowable limit for both the seasons. Excessive amounts of fluoride ion concentration in drinking water lead to different forms of fluorosis- dental, skeletal and non-skeletal. ArcGIS v10 was used to depict spatial distribution of F samples. Correlation matrix of the study area revealed,  $HCO_3$  and Na showed positive correlation with F, which increases the fluoride content in the water due to associated rock minerals and fertilizers. Thus Hirehalla Sub-basin has alarming fluoride contamination and it's necessary to study and suggest measures for proper management of water resources for drinking purpose and to elucidate fluoride endemic areas.

**Keywords:** Hirehalla Sub-basin, Fluoride, Fluorosis, Drinking water, Correlation matrix.

### Introduction

Water pollution can be defined as the contamination of water resources both surface and underground by harmful contaminants making it unfit for any purpose. Along with quantity, quality of water is very important factor for livelihood depending on agriculture, fishing and animal husbandry. Contamination of groundwater due to excessive concentration of fluoride and arsenic ions has adverse and very serious health hazards.

Of the numerous minerals required for the growth and development of the human health fluoride is one of the essential constituent. The main source of intake of fluoride in human body is through water. But excessive amounts of fluoride intake have very adverse and serious health hazards.

India is one of the 23 nations around the world, which is affected with different kinds of fluorosis- dental, skeletal and non-skeletal due to intake of excessive fluoride concentrated waters i.e. beyond allowable limits (>1.50 mg/lit). The survey estimates to be affecting 62 million people in India covering 16 states<sup>1</sup>.

Therefore in the present study, Hirehalla Sub-basin was selected to study its water quality with special emphasis with respect to fluoride as higher concentrations of fluoride were reported. Further suggest the authorities to keep a check on the water quality at regular intervals and locate fluoride endemic areas so

as to plan and necessitate effective measures to tackle the problem.

**Study Area:** Hirehalla sub-basin is tributary of the river Tungabhadra. Areally, it covers an area of 485 km<sup>2</sup> which includes parts of Hoovina Hadagli and Harapanahalli taluks of Bellary and Davanagere districts respectively, Karnataka, India. Geographically, it falls between 75 45 and 76 15 east longitudes and 14 45 and 15 15 north latitude and is covered in Survey of India (SOI) toposheet numbered 48M/16, 48N/13 and 57B/01. Denudational plateau is the dominant physiographic unit in the study area along with some hills and valleys in some parts. The lowest and highest topographic units are m and m respectively. The sub-basin experiences semi-arid type of climate where April and May months are hottest and December and January cooler. Red sandy and black soils are the main soil

**Geology and Hydrogeology:** Geologically, in the Hirehalla sub-basin, Peninsular Gneissic Complex (PGC) of Archean age is overlain by greywackes with banded iron formations (BIF's), conglomerate and metabasalts and these are intruded by basic dolerite dykes and criss-crossing quartz veins. The rocks are highly weathered and fractured and thus acting as conduit for groundwater reservoir. Hydrogeologically, the study area experiences condition of unconfined aquifer. Thus, the study area forms a hard-rock terrain, typical of most parts of the Peninsular India.

### Materials and Methods

140 representative samples were collected of both surface and groundwater in one litre prewashed polyethylene cans mainly covering Hoovina Hadagali and Harapanahalli taluks. Cans were washed in laboratory before taking to field for sampling using 2:3 ratio of dil HCl and distilled water. Analyses of physio-chemical parameters were carried out following standard guidelines<sup>2</sup>. pH and electrical conductivity (EC) were measured in field using digital meter. TDS was calculated from Ec using  $EC \times 0.65$  (Todd 1980). Volumetric method of analysis was adopted for parameters- Calcium (Ca), hardness (H), carbonate (CO<sub>3</sub>), bicarbonate (HCO<sub>3</sub>), and chloride (Cl). Sulfate (SO<sub>4</sub>) was analysed using colorimeter. Fluoride (F) was analysed using ion selective electrode method. Table 1 shows the results obtained from physic-analyses.

### Results and Discussion

The fluoride (F) concentration in the Hirehalla Sub-basin ranges from 0.05 to 5.69 mg/ltr (Table-1). Comparison studies of water samples with Bureau of Indian Standard<sup>3</sup>, Indian Council of

Medical Research<sup>4</sup> and World Health Organisation<sup>5</sup> revealed that 25.71% of water samples for premonsoon season are above permissible limit while its 20% for postmonsoon season (Table-2). Spatial variation of water samples for fluoride for both seasons is shown in figure 3 and 4. And the effect of intake of varied amounts of fluoride in drinking water on human health is presented in Table-3.

The problems of fluoride were reported in many countries along with India such as China, Spain, Holland, Mexico, Tanzania, Ghana, Kenya, Sri Lanka etc. In India, many researchers, environmentalist and geo-scientists have reported high fluoride ion concentration in waters of hard rock terrain<sup>6-16</sup>. But high fluoride concentrations have also been reported in different regions other than hard rock terrain<sup>17</sup>. Andhra Pradesh, Harayana, Punjab, Rajasthan, Tamil Nadu, Gujarat, Maharashtra, Karnataka, Kerala, Uttar Pradesh, Orissa, Bihar, Assam, West Bengal and Jammu and Kashmir are some of the Indian states where effect of excessive fluoride ion concentration in the water has been reported<sup>1, 18</sup>.

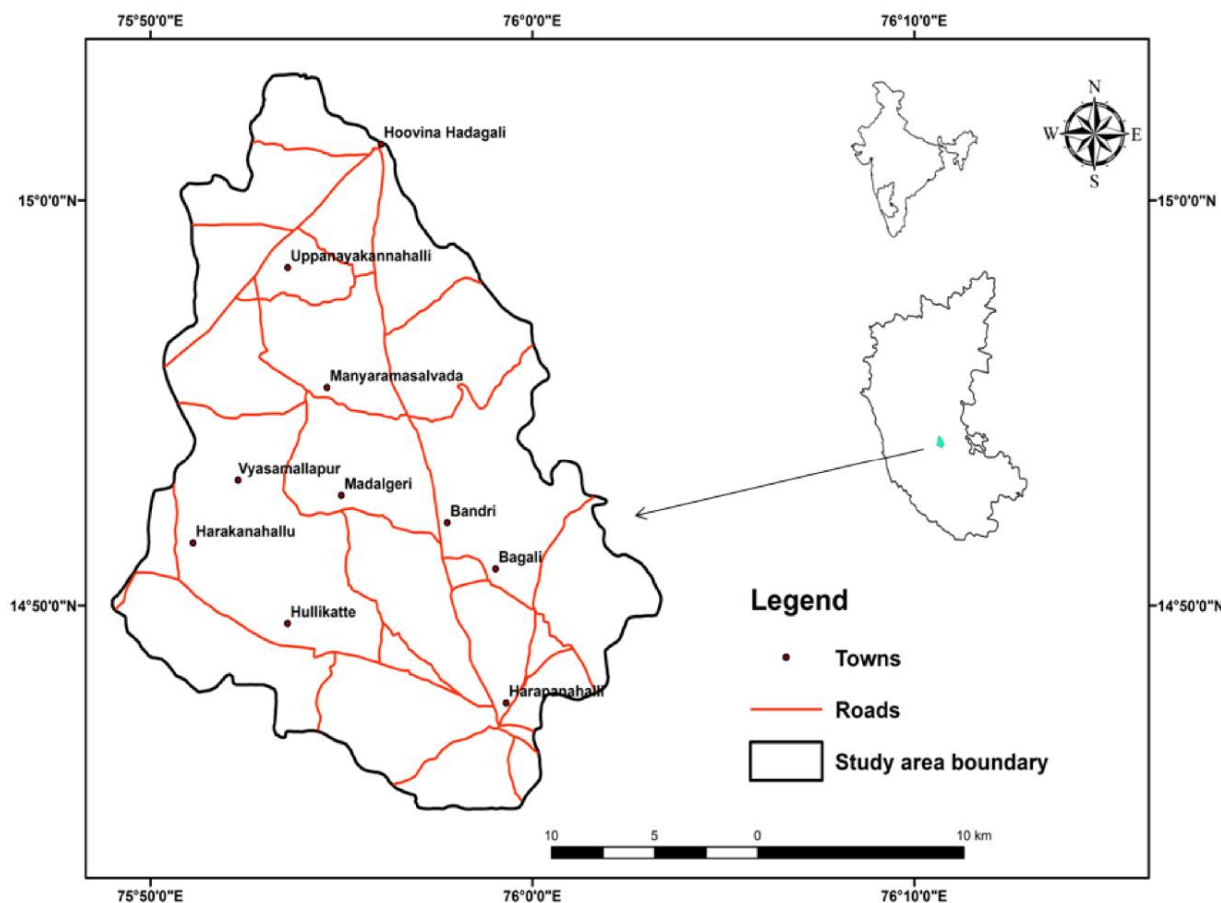
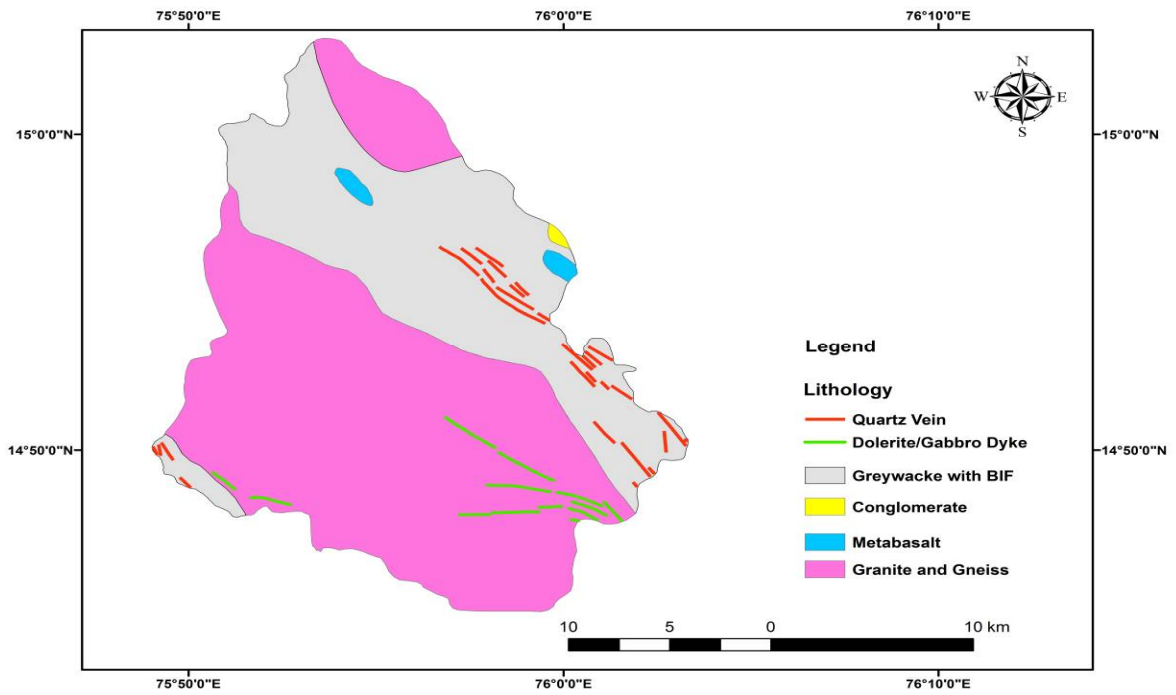
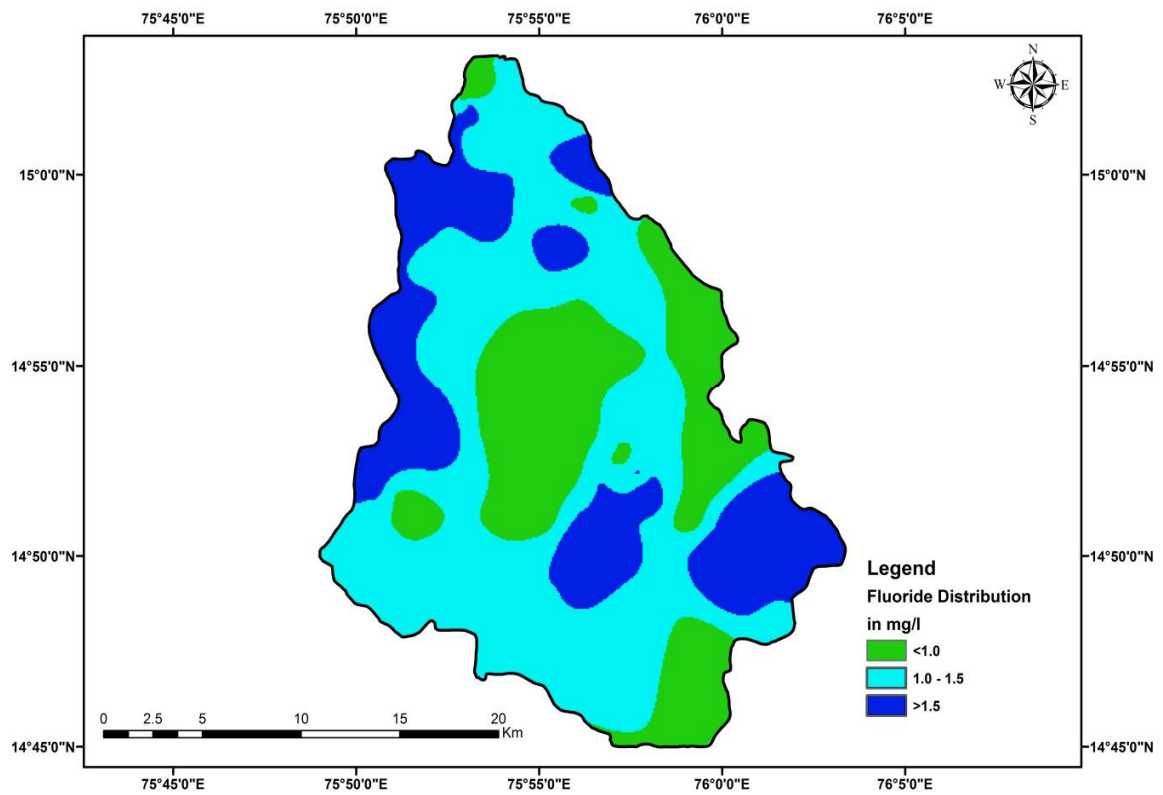


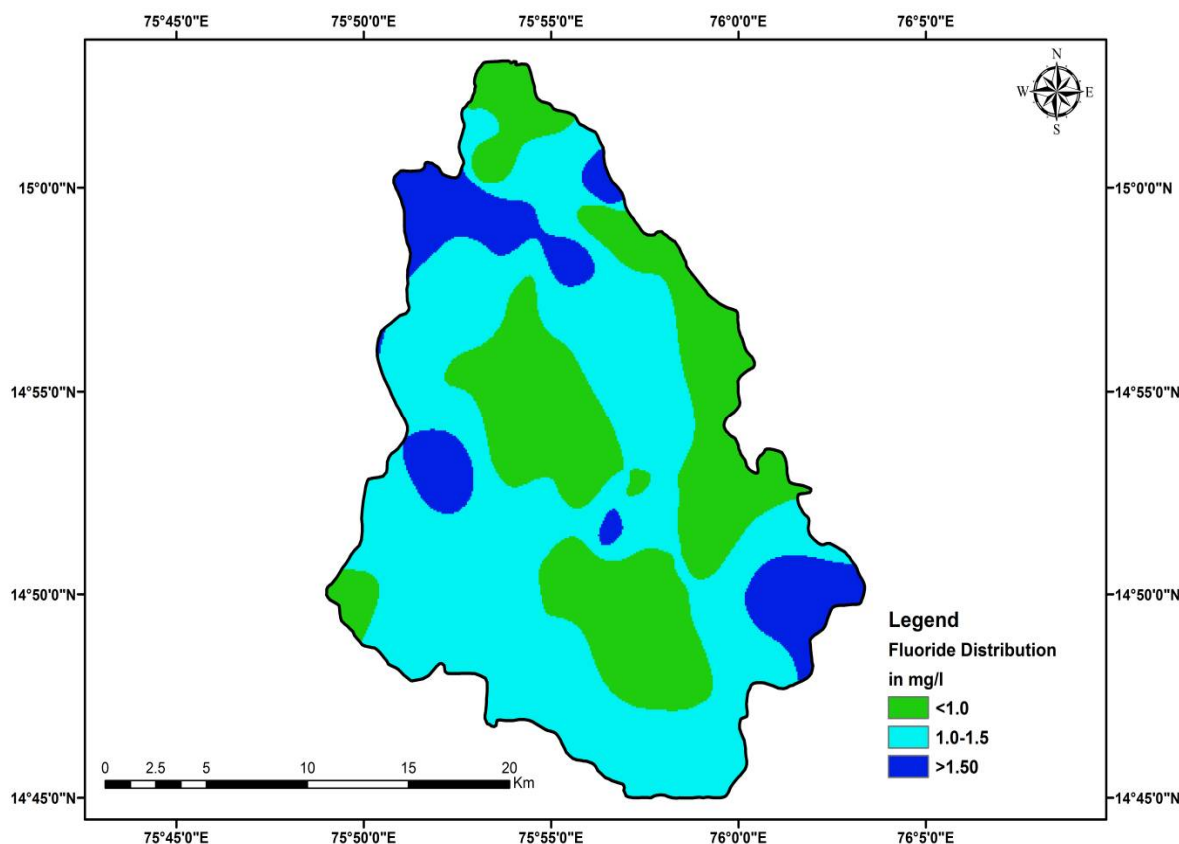
Figure-1  
 Location of Hirehalla Sub-basin



**Figure-2**  
Geology of Hirehalla Sub-basin



**Figure-3**  
Spatial distribution of fluoride samples for premonsoon



**Figure-4**  
**Spatial distribution of fluoride samples for postmonsoon**

Naturally, groundwater contains mineral ions. These ions slowly dissolve from soil particles, sediments, and rocks as the water travels along mineral surfaces in the pores or fractures of the unsaturated zone and the aquifer<sup>10,19</sup>. Fluorite, apatite, rock phosphate and topaz are some of the most common and important fluorine bearing minerals which constitute natural source for fluoride in drinking water. According to Teotia et al.<sup>20</sup>, fluoride ion concentration increases in water samples having low calcium and magnesium hardness and high alkalinity.

The fluoride incidence in the groundwaters depends on its chemical composition which depends on sub-surface lithology, surface topography and climatic conditions. The content of fluoride is related to the depth of the source. In areas where there is no industry or any human activity that can cause anthropogenic contamination of groundwater, there the high levels of fluoride ions are due to geogenic sources<sup>21</sup>. The variation of fluoride is dependent on a variety of factors such as amount of soluble and insoluble fluoride in source rocks, the duration of contact of water with rocks and soil temperature, rainfall, oxidation- reduction process<sup>14</sup>.

Also correlation matrix studies of the Hirehalla Sub-basin for both seasons revealed, HCO<sub>3</sub> and Na are positively correlated with F (Table-3 and Table-4). This implies that excessive fluoride ion concentrations in the waters can be attributed to fluorine bearing minerals associated with the source rocks and application of fertilizers and pesticides.

The Hirehalla Sub-basin is of typical semi-arid climate with hard granite and gneiss as predominant rock types wherein fluoride and associated minerals are most likely to be found in excess in the joints, fractures, faults, vertical openings<sup>22</sup>. Thus from the study it is observed and justified, the fluoride incidence in the groundwaters can be attributed mainly due to hydrogeochemical sources.

Some of the methods to reduce the high concentration of fluoride ions in groundwater are by constructing artificial recharge structures and by rain water harvesting techniques wherein fluoride concentration in groundwater is directly diluted. Another method include by installing defluoridation tank wherein fluoride is adsorbed by adsorbents. Some of the well known adsorbents include alum, lime, bleaching powder, charcoal, activated alumina, fly ash, brick etc<sup>23, 24, 25</sup>.

**Table-1**  
**Physico-chemical analyses results**

Parameter	Unit	Minimum		Maximum		Std. Deviation	
		Pre	Post	Pre	Post	Pre	Post
Ca	mg/ltr	8.01	17.63	113.83	81.76	19	13.99
Mg	mg/ltr	1.84	1.94	127.37	191.78	31	33
Na	mg/ltr	15.45	20.74	323.87	323.87	71	74
K	mg/ltr	0.02	0.001	2.79	3.21	0.509	0.671
CO <sub>3</sub>	mg/ltr	0	0	65	0	9	0
HCO <sub>3</sub>	mg/ltr	30	30	220	170	38	30
Cl	mg/ltr	31.24	41.18	592.14	570.84	122	112
SO <sub>4</sub>	mg/ltr	22	58	350	380	63	81
<b>F</b>	mg/ltr	<b>0.05</b>	<b>0.25</b>	<b>5.69</b>	<b>2.9</b>	<b>0.73</b>	<b>0.52</b>
Hardness	mg/ltr	80	92	772	780	128	115
pH	-	7.67	7.44	8.92	8.98	0.212	0.373
EC	µs/cm	323	338	2646	2554	568	647
TDS	-	210	220	1720	1660	366	417

**Table-2**  
**Comparison of water samples with different standards**

Standard	Desirable Limit	Permissible Limit	Samples exceeding permissible limit	
			Premonsoon	Postmonsoon
BIS (2003)	1.0	1.5	18	14
ICMR (1975)	1.0	1.5	18	14
WHO (2005)	-	1.5	18	14

**Table-3**  
**Various effect of fluoride intake on human body**

Sl. No.	Fluoride Concentration (mg/lit)	Effect
1	0.0	Limited growth and fertility
2	<0.5	Dental caries
3	0.5 – 1.5	Promote dental health and prevent tooth decay
4	1.5 – 4.0	Dental fluorosis
5	4.0 – 10.0	Skeletal fluorosis
6	>10.0	Crippling fluorosis

**Table-3**  
**Correlation matrix of groundwaters during premonsoon**

pH	EC	H	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	F
1										
0.270	1									
-0.030	0.608	1								
-0.167	-0.234	-0.010	1							
0.059	0.585	0.821	-0.332	1						
0.012	0.544	0.263	-0.245	0.259	1					
-0.139	0.162	0.050	0.345	-0.254	-0.056	1				
0.305	0.312	0.035	-0.531	0.182	0.287	-0.022	1			
0.095	0.827	0.671	-0.145	0.617	0.615	0.094	0.060	1		
0.062	0.479	0.409	0.283	0.313	0.402	0.147	0.129	0.371	1	
0.458	0.120	-0.277	-0.198	-0.200	0.212	-0.116	0.320	0.068	0.103	1

**Table-4**  
**Correlation matrix of groundwaters during postmonsoon**

pH	EC	H	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	F
1										
0.200	1									
0.366	0.538	1								
0.037	-0.237	-0.063	1							
0.165	0.658	0.898	-0.284	1						
0.093	0.867	0.336	-0.357	0.520	1					
-0.022	0.148	0.010	-0.063	0.061	0.184	1				
0.388	0.517	0.311	-0.207	0.312	0.570	0.003	1			
0.166	0.856	0.666	-0.102	0.801	0.744	0.193	0.390	1		
0.128	0.757	0.454	-0.094	0.515	0.677	-0.010	0.332	0.606	1	
-0.068	0.072	-0.153	-0.125	-0.133	0.301	-0.068	0.329	0.042	0.010	1

**Conclusion**

Physico-chemical analyses of Hirehalla Sub-basin were carried out for both pre- and post- monsoon. 140 units of water samples

were analysed and compared with different standards viz BIS, ICMR and WHO. Special preference was given to fluoride as the analyses revealed high risks of fluoride in both seasons. 25.71% and 20% of water samples were reported to be above



permissible limits for premonsoon and postmonsoon respectively. Dental and skeletal fluorosis was reported. Major lithounits are granites and gneiss as basement rock which are overlain with greywacke with BIF and metabasalt. The excessive fluoride presence in the groundwaters is mainly due to hydrogeochemical origin. Further, it is suggested to map in detail and monitor at regular intervals the quality of water and in particular fluoride endemic areas so as to further plan for mitigation and management of water quality to prevent further deterioration of groundwater quality. Furthermore advised to construct recharge structures and install defluoridation tanks at suitable sites.

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