

Occurrence of fluoride in the drinking water sources in and around Bichhiya block, Mandla District, Madhya Pradesh, India

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Abstract

The groundwater in and around Bichhiya block, Mandla District, Madhya Pradesh, India, is reported to have high fluoride content. Therefore, an effort has been made to determine the hydro geochemical factors that are controlling enrichment of F in the underground water resources in this region. The concentration of fluoride ranged from 0 to 6 mg/L in the groundwater samples in the study area. In groundwater, the occurrence of fluoride has both valuable and harmful effects on human health. The granitic terrain consisting of fluoride bearing minerals like biotite, apatite, tourmaline etc. and the basement comprising of Precambrian Gneiss can be considered as a vital source of F in the underground water. The geogenic contamination of F in the aquifers of the study area could be due to the weathering of rocks, leaching from soil and subsequently the circulation of groundwater rich in F between the Precambrian basement and the overlying basalts (rock-water interaction).

Keywords: Geogenic origin, fluorosis, piper's diagram, correlation, zonation maps, GIS, weathering...

Introduction

The most valuable, essential, natural resource on earth is Water. The potability of water depends on its mineral content which in turn signifies the quality of water. The quality of groundwater deteriorates in its due course since it passes through different geological formations under different climatic condition. This deterioration can take place due to "Geogenic contamination" of groundwater which increases the concentration of certain elements naturally in subsurface water causing adverse health effects. This paper, discusses the underground water quality with F as special reference and its geogenic origin. F is imperative in little quantity to supply necessary minerals for the development of bones and tooth enamel¹⁻³. In India, 19 states are found to have high concentration of F in underground water⁴.

In human beings, fluorosis is caused by excessive fluoride⁵, across the world, the major water supply for drinking, is the untreated groundwater. This untreated water has been found to be the chief source of fluoride incorporation and thereby resulting in fluorosis⁶. Although fluorosis can be lessened by food to some extent⁷, it is the utmost prevalent ailment of natural origin particularly in India⁸ and Sri Lanka⁹, and its relation to disproportionate F– in underground water is widely recognized¹⁰.

Fluorosis is a chronic condition which occurs due to excessive intake of fluoride through the water we drink and the food crops irrigated by fluoride contaminated water, marked by mottling of teeth and if severe, calcification of the ligaments. The worst affected is the rural population that uses drinking water supply

from groundwater. Fluorosis can be Dental fluorosis (disturbance of dental enamel during tooth development) or Skeletal fluorosis (bone disease caused by the excessive accumulation of fluoride in the bones). Undernourished children, expecting women, and the underprivileged sections of the country are more susceptible to fluorosis.

Mandla is a tribal district with a glorious history. It is situated in the east central part of Madhya Pradesh and is bestowed with numerous rivers and rich forests. Bichhiya is a tehsil located in the district of Mandla, spreading from 22° 0' to 23° 0' N latitude and 80°15' to 81°50'E longitude (Survey of India, Toposheet No. 64 B/7, 64 B/10, 64 B/11, 64 B/14, 64 B/15) and is severely affected from fluoride contamination. The district has a total area of 13,269Sq.Km. and total area of Bichhiya Tehsil is 2529.74 Sq.km.

The total population of the district was 2, 39,944 Lakh persons as per census of 2011. The granite, gneiss and basalt are well exposed in the study area. During sample collection, pegmatites of different shapes and sizes were also found.

The study area has various geological formation, ranging in age from Archean/Precambrian to Recent. Geological Succession of Mandla Region is as shown in Table-1.

The oldest rock in the area belongs to the Archean that comprises of Granite, Gneisses and Schist of the same age. The granite rocks are generally well jointed and fractured. At places these rock formations are intruded by pegmatites and quartz veins.

Table-1: Geological Succession of Mandla Region

Formation	Age	Litho Characteristic					
Alluvium	Recent	Sand, Gravels and Clay					
Laterite	Pleistocene	Compact, ferruginous and weathered product of Deccan Trap					
Deccan Trap	Cretaceous to Eocene	Basaltic lava flows					
Lameta Beds	Lower Cretaceous	Limestone and Sandstone					
Archean	Precambrian	Granite and Gneisses					

The research is intended to analyze the groundwater quality, highlighting the mechanism of ingestion of fluoride in groundwater. The chemical analysis data of groundwater samples, is given in Table-2 for Gneissic aquifer and Table-3 for Basaltic aquifer respectively. It became imperative to compile the data with respect to Fluoride in the study area, due to its direct impact on health especially when the children are affected.

Materials and methods

A large number of groundwater samples, within the study area, from different drinking water sources, were collected and analyzed. For the present paper, only few water samples, with fluoride low or high than the acceptable limits¹¹ are taken into consideration. The analysis is conducted in accordance with the standards of APHA¹². A hand-held Garmin GPS was used to

note the well location of the samples with respect to latitude, longitude and altitude. For the chemical analyses of the water samples Standard methods were adopted. An Orion ion selective electrode (ISE) was used to determine the chloride concentration as well as pH of the water samples. Titration method was used to determine the bicarbonate and carbonate concentration. An Aqua mate UV-VIS spectrophotometer was used to estimate sulphate. Elico Flame Photometer was used to determine the concentration of cations such as Ca, Na and K. The titration method was used to estimate Mg concentration from the total hardness.

On the basis of the chemical analysis result, a correlation analysis was performed between different physico chemical parameters. The value of correlation coefficient 'r' and the correlation results of different parameters with Fluoride is given in Table-4.

The values of correlations are mostly insignificant whether positively or negatively correlated. The only significant correlation is with pH (Figure-1). Other value which is correlated is with K (Figure-2). It seems that fluoride content does not interfere with the bulk chemistry of common elements. pH certainly has a positive significant correlation which could be a determining factor of fluoride content in the present case. In the present case 8.85 pH has highest value of fluoride, indicating higher the alkalinity the greater is the fluoride content if the lithology is the source for the same.

The correlation coefficient 'r' value between F and Ca⁺², F and Mg²⁺ display a weak and negative correlation.

Table-2: Chemical Analysis Data of Groundwater samples from Gneissic Aquifer.

Sample No.	F	Ca	Mg	Na	K	CO ₃	HCO ₃	Cl	SO ₄	TDS	рН	TH
1	1.74	32	12	72	1	6	268	35	31	174	8.09	184
2	1.94	16	9	72	0.6	12	152	26	3	200	8.04	126
3	1.52	18	11	66	1	6	160	65	2	201	7.39	120
4	1.85	16	21	91	1	0	232	64	23	176	7.73	132
5	5.21	28	12	90	0.8	12	240	200	31	747	7.44	294
6	3	16	16	85	0.8	20	190	26	3	199	8.12	120
7	1.19	52	12	68	0.7	12	140	65	31	391	7.98	108
8	0	28	12	62	0.8	12	240	30	12.4	208	7.39	108
9	0	44	9	85	1	16	60	90	6	285	7.7	92
10	0	54	16	88	0.8	10	140	60	31	169	6.6	160

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Table-3: Chemical Analysis Data of Groundwater samples from Basaltic Aquifer.

Sample No.	F	Ca	Mg	Na	K	CO ₃	HCO ₃	Cl	SO_4	TDS	рН	TH
1	1.94	16	8	78	0.6	20	152	20	38.9	571	6.92	160
2	0.31	32	11	66	1	6	160	20	34.8	139	7.95	180
3	6	32	10	88	1	18	200	110	12.4	209	8.85	120
4	3.2	16	16	75	0.9	18	195	25	12.4	650	8.38	110
5	2.3	18	6	74	0.7	10	159	25	34.8	179	8.18	104
6	0.05	39	6	88	0.8	16	60	0	9	223	7.02	140
7	2	16	8	72	0.6	12	120	30	9	207	8	140
8	5.75	30	10	80	1	20	80	80	12	220	8.36	284
9	4.5	34	5	80	1	15	165	75	6	245	8.18	260
10	3.92	26	11	64	0.7	18	152	125	21.7	215	8.33	48
11	4	16	27	86	0.7	20	110	110	6	311	8.19	268
12	2.29	20	6	74	0.7	14	159	50	27.9	158	8.29	88
13	0.61	72	12	86	0.8	20	190	55	4	217	7.4	44
14	0.64	68	16	64	1	18	220	50	9	195	6.6	152
15	0.22	28	12	78	0.6	10	120	35	31	257	6.9	60
16	3	56	18	67	0.8	20	150	25	12.6	206	8.3	68
17	3.74	32	10	80	1	20	120	50	6.3	143	8.5	88
18	0.09	26	8	88	0.8	16	130	140	25.3	435	7.68	168
19	0.01	38	12	82	0.8	6	180	145	28.5	365	7.95	276
20	0.64	72	12	85	0.8	20	268	75	8.8	378	7.28	260
21	2.45	18	6	78	0.7	20	140	110	41.2	234	7.9	208
22	0	44	9	62	0.7	12	240	120	31.7	513	7.32	440
23	4.7	34	5	85	1	25	200	142	8	153	8.5	156
24	0.93	96	2	75	1	10	384	180	17.7	504	8.13	372
25	0.1	42	11	60	0.9	16	60	65	28.5	188	7.28	188
26	0.14	32	14	88	0.8	12	120	3	9.5	155	7.87	168
27	2.8	26	10	85	0.9	0	195	28	2	152	7.95	160

The ground waters are classified graphically¹³ (Figure-3). In order to understand the chemical characteristics of groundwater, Groundwater Chart Software is used to generate Piper Diagram. The results of the chemical analysis of the groundwater displays the classification of water as various chemical types and

suggests the water quality. The dominant water types in the study area mixed type. The samples are clustered in Ca-Mg-HCO₃ water type, Na-HCO₃ water type, hence mixed facies become dominant in the study area. Dominance of mixed facies suggests that the groundwater is fresh water.

Table-4: Correlation Results.

Parameters	Value of (correlation coefficient 'r')	Correlation Results				
pH and F	0.7338	Positive Correlation				
Ca and F	-0.3444	Negative Correlation				
Mg and F	-0.00401	Negative Correlation				
Na and F	0.138934	Positive Correlation				
K and F	0.252874	Positive Correlation				
CO ₃ and F	0.55975	Positive Correlation				
HCO ₃ and F	-0.05528	Negative Correlation				
Cl and F	0.1849	Positive Correlation				
SO ₄ and F	-0.288	Negative Correlation				
TDS and F	-0.136	Negative Correlation				

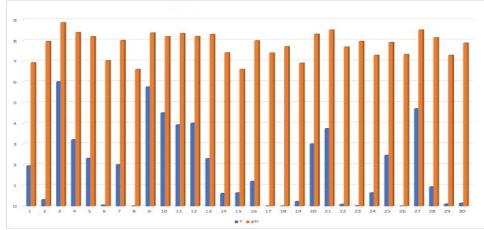


Figure-1: Correlation of pH and F.

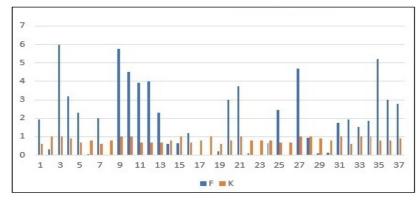


Figure-2: Correlation of K and F.

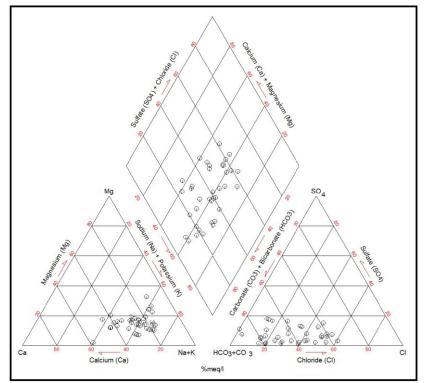


Figure-3: Trilinear Diagram¹³.

The following are the few thematic maps of different parameters like Fluoride, pH etc. The thematic maps are prepared using GIS tools in ArcGIS 10.3. The maps depict the high fluoride vulnerable zones in the study area (Figure-4). The correlation of pH and Fluoride is also shown through the thematic map (Figure-5).

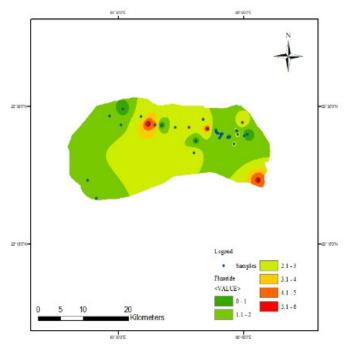


Figure-4: Zonation Map of Fluoride in the study area.

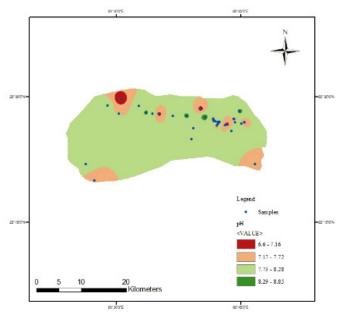


Figure-5: Zonation Map of pH in the study area.

Results and discussion

Fluoride has been classified as an essential parameter in determining the suitability of potable water¹⁴. The groundwater samples collected from the study area contain high percentage of fluoride. The chemical analysis signifies that the groundwater quality in most part of the study area is controlled by the litho-

units present in the study area. Alkaline groundwater's generally tend to solubilize fluoride minerals. There can be various sources of Fluoride in underground water. The weathering of minerals comprising fluoride such as fluorite, apatite or rock phosphate $[Ca_5F(PO_4)_3]$ and mica in underground water is described as the principal source of fluoride ¹⁵. The Apatite mineral contributes the Fluoride concentration in groundwater through the following chemical reaction –

$$Ca_5F(PO_4)_3 + 2H_2CO_3 + 12H_2O \rightarrow 3 Ca (OH)_2 + F^- + 3H_3PO_4 + 2Ca (HCO)_3 + 9H^+$$

Apatite Fluoride

The high content of Fluoride, in the area of study can be the result of leaching from highly weathered Biotite (Mica). The chemical reaction involved in this process is as follows-

K (Mg, Fe)₂(AlSi₃)
$$O_{10}(OH, F)_2 + H_2CO_3 + H_2O \rightarrow 4(Al, Si)_4O_{10}(OH)_8 + H_4SiO_4 + AlHSiO_4 + 5K^+ + 10Fe^{++}$$

Biotite Carbonic Acid Iron $10Mg^{++} + F^-$
Fluoride

The relationship between weathering, dissolution, wall rock contact¹⁶ followed by exchange of ion could be the main mechanism that controls concentration of F in the study area (Figure-6). It is the geological map of the study area that shows the sample location and the litho-unit they belong to. The map has been created using District Resource Map of Mandla District, Madhya Pradesh¹⁷. The primary factor responsible for the excessive F content in underground water is reported to have association with rock types¹⁸.

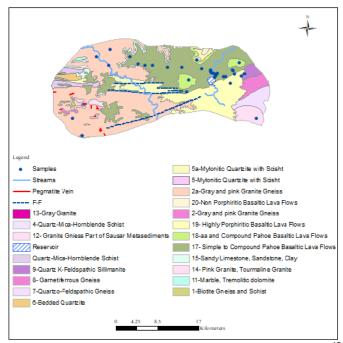


Figure-6: Sample, Litho-Units, Geological Map of Study area¹⁷.

In the study area, the deeper crystalline rocks are well exposed. The primary porosity in these rocks is low, and the groundwater occurs in cracks and fissures. In these zones, flow of underground water is slow which results in the increase of the residence time of groundwater thereby, increasing the concentration of fluoride. Hence, it can be inferred that the excessive concentration of Fluoride in the underground water is owed to its geogenic origin.

The unhealthy effects of fluorosis can be prevented by discontinuance/capping of existing borewells which are fluoride affected. In such areas, shallow dug wells should be used for tapping drinking water reserves.

Fluoride is essential for the growth of teeth and bones, therefore, children particularly below the age of 7 are more vulnerable. Hence, in primary schools, a survey of oral hygiene must be undertaken periodically.

Some inexpensive methods like Nalgonda technique could be practiced in the study area to remove/control excessive fluoride.

Even though few inexpensive removal techniques are suggested, few simple dietary habits can also be inculcated to reduce the damaging effect of fluorosis. The important aggravating factors are found to be calcium and vitamin C deficiencies. Hence, in fluoride prevalent areas, diet rich in Vitamin C and calcium must be augmented. Therefore, to diminish fluorosis, the effective way is to change the dietary habits of susceptible people. This little step can definitely help in reducing the menace of "Crippling giant" to some extent.

Conclusion

In the area of study, there are two domains of higher concentration of fluoride. On the basis of their distribution with two different age terrains with different altitudinal positions most simple model that can thought of is of two sources.

Therefore, there may be two distinct sources of fluoride water: i. The basement of Gneissic migmatite rocks, ii. The Simple and Compound Basaltic terrain in which aquifer depth is much above the basement rock/terrain.

Yet there is a serious incompatibility with the two-source conclusion as the high concentrations in the basaltic terrain are not uniformly distributed whereas almost all the samples from the basement have fluoride values on higher side of the desired normal concentrations. If the areal pattern of high concentration is incorporated in the reason of decipherment as given below.

The high fluoride content samples fall on a line, which may be called as high fluoride lineament. The reason to call it HFL (High Fluoride Lineament) is that, it follows other prominent lineaments south of Basaltic terrain, partially bounding the basalt in the central part of the study area. This striking

parallelism is good reason to assign it a status of High Fluoride Lineament.

Other important point is that there are three to four variations in the basalt, but HFL passes though the Simple and Compound Basaltic terrain, 'Pahoehoe' basalt, and is not associated with Non-porphyritic Basalt or other Basalt of 'Aa' type.

Thus, the conclusion that the basement being the source candidate holds strong possibility as supported by spatially linear nature of High Fluoride concentrations in Basaltic terrain and deep circulations are facilitated by the fault is trending nearly east-west.

The position of the base of the aquifer in basaltic terrain is quite higher and cannot be seemingly ascribed to have any contact with basement gneissic terrain, yet for the linear distribution of high fluoride water samples which bears parallel relation with the two southern fault system it may be surmised that deep circulations of groundwater have led enrichment of fluoride content as derived from the basement.

The excessive Fluoride in the study area has led to severe harmful effects on the health of the people. It has resulted in both Dental as well as Skeletal Fluorosis in various age groups residing in the study area (Figure-7).



Figure-7: Real time impact of fluorosis in the study area.

In the study area, from the chemical analyses results of groundwater, it is evident that the quality of groundwater in most part of the study area is controlled by the lithology present in the study area. The natural sources of Fluoride in groundwater of the study area can be the natural mineral sources like Apatite, Biotite, Hornblende and Tourmaline. The presence of crystalline basement rocks and its weathering (Disintegration, Dissociation and Dissolution) could be the contributing factor to excessive Fluoride content in the study area. Hence it can be inferred that, in the study area the excessive fluoride is probably of geogenic origin. In order to maintain the health of the people with respect to water quality it is essential that the authorities

should take immediate step. Water quality needs to be continuously monitored in the study area. The zonation maps can help in delineating the most vulnerable zones. The people should be educated by organizing awareness program.

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