Monitoring of Fluoride Concentration in Groundwater of Tosham Block, Bhiwani District, NW, India: Correlation with Physico-Chemical Parameters

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Abstract

Hydrogeochemical investigations were carried out in the eight villages of Tosham Block, district Bhiwani, Haryana to recognize the mechanism and sources of enrichment of fluoride in the groundwater. The results specify that concentrations of fluoride attain up to 1.9 mg/l in groundwater samples. In the soils, the overall fluorine contents vary between 1.1 and 2.7 mg/kg, which could have sufficient potential to released fluorine into the groundwater. In groundwater, the fluoride enrichment is primarily controlled by solubility of fluorite, intensity of evapotranspiration, residence time and the processes of weathering prevailing in Tosham area. Moreover, various other water quality parameters such as pH, electrical conductivity, total hardness, and total alkalinity as well as calcium, magnesium, carbonate, bicarbonate and chloride concentrations were also calculated. A logical calculation of correlation coefficients between different physico-chemical parameters was done. The 67% of groundwater samples do not comply with WHO standards of fluoride for drinking purposes. The excessive fluoride concentration in the groundwater of villages under study causes dental fluorosis among people especially the children. Except few of villages, without any prior treatment, the overall quality of water was found unacceptable for drinking purposes.

Keywords

Fluoride, Fluorosis, Groundwater, Hydrochemistry, Tosham

1. Introduction

An adequate supply of safe water for household consumption is one of the ut-
most challenges of the twenty-first century. Constantly, the demand for water is on rise. The water resources are unevenly distributed over the earth’s surface. Moreover, the excellence of the water resources, which are disproportionately scattered over the surface of earth, is fading due to the anthropogenic and natural activities. In the near future, the countries even having gigantic water resources could experience water scarcity. The properties of groundwater have also been changing simultaneously corresponding to heavy use of fertilizers, dumping of industrial and municipal waste. Hence, to study the variation in quality parameters, the analysis of groundwater is essential. The groundwater quality could be rated for various uses, like industrial, drinking agriculture on the basis of the physico-chemical parameters. The groundwater pollution also governed by the geology of the area where widespread cavern systems are beneath the water table [1]. The changes in groundwater quality respond to the deviation in chemical, physical, and genetic environments through which it passes [2]. Fluoride with an optimum concentration within a narrow range between toxic exposure and beneficial ingestion is essential for human beings [3] [4] [5]. Due to long term intake of waterborne fluoride over the permissible limit of 1.5 mg/l set by the World Health Organization (WHO) and 1.0 mg/l by China, endemic fluorosis has been extensively reported in numerous areas such as Mexico, China, India and Africa [6]-[12]. The low concentrations of Ca\(^{2+}\), cation exchange, high pH, sometimes high concentrations of Na\(^+\) and HCO\(^{-}\), evapotranspiration, hydrolysis of silicate minerals are the most common factors behind the fluoride enrichment in groundwater [13]. The correlation between fluoride and other physical parameters has done in this study. A positive correlation coefficient of sodium with fluoride in ground water has reported in groundwater samples of study area. In the present investigation, the analysis of ground water samples of eight villages of Tosham block of Bhiwani District is presented. The correlation analysis of the physicochemical parameters, pH, EC, TH, Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), CO\(_3\)^{2-}, F\(^-\) and HCO\(_3\)^{-} measured in 19 samples collected from eight villages. The results obtained are presented and discussed in this paper. The purpose of this study is to elucidate the fluoride distribution in area under study and to establish a correlation between fluoride concentration and physico-chemical parameters of groundwater of Tosham block, Bhiwani district, NW, India. The present paper also tries to find the role of local geology in fluoride contamination in area under study.

2. Geology Setting of the Study Area

Malani Igneous Suite (MIS) representatives are well exposed in the Bhiwani district (at Tosham area) of Haryana, Jodhpur, Jhunjhunu, Barmer, Pali, (at Siwana, Kundal and Nakora areas) Jaisalmer Jalore, districts of Rajasthan and are also reported from Nagar Parkar, Kirana hills (Pakistan). Tosham Ring Complex (Survey of India topography sheet No. 44P/13; Scale 1:50,000); (28°46’N - 28°55’N; 75°50’E - 75°58’E) is located 160 KM WNW of Delhi which is a part of Malani
Igneous Suite. Malani Igneous Suite (MIS) is one of the most important alkaline anorogenic magmatism in the Indian subcontinent which represents the Pan-African thermotectonic episode [14]. Tosham is a town situated on the foot of Tosham hill range in district Bhiwani, Haryana. As of 2011 India census, Tosham had a population of 11,271. Females constitute 47% and 53% of the population are males. There is a well-known temple of Mugipa and are numerous holy ponds on Tosham Hill inside the caves, namely Surya Kund, Pandu Teerth-Kund, Kukkar, Vyaskund, A small tank like reservoir also found on the summit of the hill to conserve rain water. The geology of Tosham is described by many researchers [15] [16]. The main rock types of Tosham are granites (hypersolvus and subsolvus), rhyolites, dacites, trachytes, andesites, basalts, gabbros and dolerites. They occur in the form of ring dykes, ring structures, scattered hummocks, inselbergs and residual hills where the exposures are covered by sand dunes. Granites from Tosham and adjoining areas are generally pink, grey and green color and medium grained leucocratic with biotite or hornblende granites. Quartzite is also noticed at some locality. Granites exposed at Khanak, Nigana, Dulheri, Riwasa and Nigana are leucocratic to melanocratic, medium to coarse grained and porphyritic nature. Granitoids from Khanak are grey to pinkish with medium to coarse grained nature. They are composed of quartz, alkali feldspar, plagioclase and biotite. Granite porphyry and quartz porphyry from Khanak occur in pockets and are reported to be of marginal phase of differentiation [17].

3. Sampling and Analytical Methods

Nineteen groundwater and nineteen soil samples were collected from eight villages of Tosham area (Figure 1). All of the groundwater samples were collected from boreholes and dugwells after filtration through 0.45 μm PVDF branes (Milipore) and sealed on the spot. Samples for the determination of major cations (Na+, Ca2+, Mg2+ and K+) were stock up in polyethylene bottles that had been soaked in 5% HCl and before collection three times rinsed by distilled water. Then, 1% (v/v) concentrated redistilled HNO3 was added to stabilize the samples to pH < 2. Samples for major anions (Cl−, F−, \( \text{NO}_3^- \), and \( \text{SO}_4^{2-} \)) were stored in polyethylene bottles without chemical agents added. Major elements and trace elements were analyzed within 2 weeks after sampling. Eh, pH, temperature, and EC (electrical conductance) were measured in situ during sampling and alkalinity (\( \text{HCO}_3^- \)) by Gran titration on site. To minimize the contact of sample with air, the unfiltered sample water was used to measure pH and Eh. The concentrations of most trace elements and major ions were determined by inductively coupled plasma emission. The ion chromatography is used for determination of major anions. The titration was employed to measured alkalinity. Most measurements exhibited errors of approximately 5% or less. All samples were measured at the Central Soil Salinity Research Institute, Karnal. The soil samples were collected surface soil from 25 to 50 cm at Villages of Tosham which were
air-dried without the sunlight in naturally. The water soluble fluoride and total fluoride contents of soil samples were tested.

4. Results

The result of analysis of physico-chemical parameter and fluoride in groundwater is summarized in Table 1. The desirable limit and permissible limit of fluoride (in the absence of an alternate source), as per WHO Standard are 1.0 mg/l and 1.5 mg/l respectively. It results in fluorosis sickness if exceeding 1.5 mg/l. In the present analysis, fluoride concentration varies in range of 0 to 1.9 mg/l (Table 1). The highest concentration of fluoride is shown by groundwater sample of Panjokhera village. Out of all samples, 67% of samples are found within prescribed desirable limit. The 17% of samples cross the permissible limits and remaining 16% sample have fluoride concentration higher than desirable but within the permissible limits (Figure 2). The concentration of fluoride in soil samples of eight villages are shown in Figure 3. The positive correlation between fluoride concentration of soil \( F(s) \) and groundwater samples \( F(w) \) is exhibited by Figure 4. The most of samples peak overlapping each other establishing that both soil as well as the groundwater sample show the similar trend of variation of fluoride concentration. The concentration of fluoride in water is directly
Table 1. Result of groundwater analysis (all values are in mg/l except pH and EC).

| VILLAGES     | pH  | EC      | TDS  | Na     | Cl     | K     | Ca     | Mg     | NO3   | CO3   | HCO3  | F    |
|--------------|-----|---------|------|--------|--------|-------|--------|--------|-------|-------|-------|------|-----|
| KHANAK       | 7.0 | 24,400.0| 15,616.0| 4548.0 | 6948.2 | 24.06 | 1442.88| 206.55 | 0     | 0     | 1855.01| 1.6  |
| KHANAK       | 7.5 | 4400.0  | 2816.0| 309.9  | 1290.4 | 17.14 | 1042.08| 230.85 | 0     | 0     | 512.57| 0.0  |
| DADAM        | 7.9 | 1300.0  | 832.0 | 113.0  | 241.1  | 0.50  | 641.28 | 170.1  | 0     | 0     | 268.49| 0.0  |
| DADAM        | 8.0 | 2180.0  | 1395.2| 267.9  | 482.1  | 0.80  | 340.68 | 72.9   | 0     | 0     | 488.16| 0.0  |
| PANJOKHERA   | 8.0 | 1670.0  | 1068.8| 327.9  | 205.6  | 0.10  | 240.48 | 24.3   | 0     | 0     | 634.61| 1.9  |
| PANJOKHERA   | 8.2 | 2000.0  | 1280.0| 419.8  | 531.8  | 0.40  | 320.64 | 72.9   | 0     | 0     | 329.51| 1.1  |
| SARAL        | 8.0 | 1544.0  | 988.2 | 218.9  | 368.7  | 6.22  | 380.76 | 109.35 | 0     | 0     | 183.06| 1.4  |
| SARAL        | 7.2 | 950.0   | 610.6 | 174.9  | 205.6  | 2.41  | 240.48 | 24.3   | 1.3   | 0     | 732.24| 0.0  |
| TOSHAM       | 8.0 | 1931.0  | 1235.8| 424.8  | 312.0  | 2.71  | 280.56 | 60.75  | 0     | 0     | 305.10| 0.7  |
| TOSHAM       | 8.6 | 3170.0  | 2028.8| 549.8  | 879.2  | 5.41  | 240.48 | 48.6   | 0     | 24    | 366.12| 0.0  |
| DULHERI      | 7.8 | 5000.0  | 3200.0| 839.6  | 1446.4 | 2.71  | 1382.76| 218.7  | 0     | 0     | 305.10| 0.0  |
| DULHERI      | 7.9 | 1017.0  | 650.9 | 185.9  | 156.0  | 0.20  | 220.44 | 36.45  | 0     | 0     | 268.84| 0.3  |
| NIGANA       | 7.6 | 10,580.0| 6771.2| 1809.2 | 2141.2 | 5.81  | 681.36 | 85.05  | 0     | 0     | 414.94| 0.6  |
| NIGANA       | 7.5 | 3520.0  | 2252.8| 489.8  | 950.1  | 0.80  | 460.92 | 109.35 | 0     | 0     | 329.51| 0.4  |
| RIWASA       | 7.8 | 1271.0  | 813.4 | 219.9  | 255.2  | 2.61  | 260.52 | 72.9   | 0     | 0     | 427.14| 0.6  |
| RIWASA       | 8.0 | 2630.0  | 1683.2| 475.8  | 694.8  | 2.81  | 240.48 | 60.75  | 0     | 0     | 231.88| 1.8  |
| DHARAN       | 8.6 | 896.0   | 573.4 | 183.9  | 184.3  | 0.20  | 180.36 | 36.45  | 0     | 0     | 219.67| 1.4  |
| DHARAN       | 8.1 | 742.0   | 474.9 | 144.9  | 129.3  | 0.80  | 140.28 | 12.15  | 0     | 0     | 244.08| 0.9  |
| PWD GUEST    | 6.9 | 2130.0  | 1363.2| 150.9  | 553.0  | 10.93 | 460.92 | 97.2   | 5.1   | 0     | 244.08| 0.7  |

proportional to concentration of fluoride in soil and thus establishing positive correlation. Khanak and Panjokhera are two villages that have highest concentration of fluoride both in soil and groundwater samples. Twenty percent of fluoride affected villages in the world are in India [18].

Although fluoride is essential for formation of dental enamel and normal mineralization of bones and is one of the important life elements to individual health with presence in small amount, however at a higher concentration might cause detrimental effects on individual health. The largest contributor to the daily intake of fluoride is drinking water. The food when derived from plants grown in the contaminated soil also becomes another source of fluoride intake when they are used as food. The prolonged experience to elevated concentration of fluoride is poisonous to bones, teeth and other organs. If present in high concentration in drinking water, it is also known to cause thyroid [19], neurological, kidney changes, gastrointestinal and endocrine problems. In its harsh form, dental fluorosis is characterized by yellowish brown to black stains, severe pitting and opaque areas on the tooth surface. It has been estimated that 20% of those who bear osteoporosis linked hip fractures die within six months. In comparison to males, females are at four times greater threat of osteoporosis. In bottle fed infants, intake higher than 50 mg/l are identified to have been linked with
Figure 2. Fluoride distribution in groundwater samples of Tosham area.

Figure 3. Fluoride distribution in soil samples of Tosham area.

Figure 4. Positive correlation of fluoride distribution in soil and groundwater samples of Tosham area.
methaemoglobinaemia. The fluoride concentration and associated risk are given in Table 2.

5. Discussion

Geochemical Processes Influencing Fluoride Concentrations

The key hydrochemical types are Na-Cl and Ca-HCO₃ in the area under study. The groundwater samples having high concentration of TDS belong to Na-Mg-HCO₃-SO₄ and Na-Mg-Cltypes, possibly due to dissolution [20]. Thus the variation in chemistry of groundwater advocate that in the host rocks of the TRC, there are tough geochemical reactions that occur, where hydrolysis reactions of silicate playing a leading role, e.g.,

\[
2\text{CaAl}_2\text{Si}_2\text{O}_8 + 6\text{H}_2\text{O} = \text{Al}_2\text{Si}_{10}\text{O}_{22} (\text{OH})_4 + 2\text{Ca}^{2+} + 4(\text{OH})^{-}
\]

\[
2\text{NaAlSi}_3\text{O}_8 + 2\text{H}_2\text{CO}_3 + 9\text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_5 (\text{OH})_4 + 2\text{Na}^{+} + 2\text{HCO}_3^{-} + 4\text{H}_2\text{SiO}_3^{-}
\]

During the processes of weathering, dissolution, hydrolysis and dissociation could take place at the same time. Kaolinite, calcite, plagioclase, K-feldspar, albite and silicate in these practices consume a huge amount of protons. That is perhaps why some groundwater samples exhibit high HCO₃⁻ and pH values. Due to the release of Na⁺ and Ca²⁺, the groundwater in the area under study is altered into Ca-Na-HCO₃ and Ca-HCO₃. Previous studies have indicated that even after the groundwater reaches an equilibrium state with respect to fluorite (CaF₂), the high concentration of groundwater fluoride continuously augment due to the decrease in the Ca²⁺ concentration by the precipitation of calcite (CaCO₃). The slightly decrease in calcium concentration facilitates the fluoride enrichment [21]. The higher concentration of fluoride in groundwater is caused by presence of fluorine bearing minerals [22]. The dissolution of CaF₂, is promoted by high alkalinity, liberate fluoride into groundwater because precipitation of dolomite and calcite can diminish the Ca²⁺ concentration in groundwater (hydrolysis reaction) e.g.

Table 2. Fluoride concentration and its harmful effects.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Fluoride in drinking water (mg/l)</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 mg/l in water</td>
<td>Dental caries reduction</td>
</tr>
<tr>
<td>2</td>
<td>2 mg/l in water</td>
<td>Mottled enamel</td>
</tr>
<tr>
<td>3</td>
<td>0.002 in air</td>
<td>Injury to vegetation</td>
</tr>
<tr>
<td>4</td>
<td>50 mg/l in food or water</td>
<td>Change in thyroid harmone</td>
</tr>
<tr>
<td>5</td>
<td>20 - 80 mg/day or more</td>
<td>Crippling skeletal fluorosis</td>
</tr>
<tr>
<td>6</td>
<td>8 mg/l in water</td>
<td>10% osteoporosis</td>
</tr>
<tr>
<td>7</td>
<td>More than 125 mg/l</td>
<td>Kidney change</td>
</tr>
<tr>
<td>8</td>
<td>100 mg/l in water or food</td>
<td>Retardation in growth</td>
</tr>
<tr>
<td>9</td>
<td>3.1 - 6 mg/l in water</td>
<td>Osteoporosis</td>
</tr>
<tr>
<td>10</td>
<td>2.5 - 5.0 gm in actual dose</td>
<td>Death</td>
</tr>
</tbody>
</table>
Consequently, with groundwater flow the continuous dissolution of silicate can direct the slight increase in the Na\(^+\) concentration and decrease in the Ca\(^{2+}\) concentration. The enrichment of Na in groundwater may be contributed by Na-Ca ion exchange [23]. The clay minerals and sediments can release Na\(^+\) into the groundwater and take up Ca\(^{2+}\) from groundwater, therefore change the value of [Na]/[Ca]. From Figure 5, we undoubtedly see that F concentration increase with the value of [Na]/[Ca].

Dissolution of high heat producing granite and acid volcanic in TRC leads to the increase in Na\(^+\) concentrations and anorthite weathering contributes to genesis of Na-HCO\(_3\) type water in Tosham area. Moreover, the fluoride exhibits the positive correlation with bicarbonate and negative correlation with calcium. This can be explained on the basis of the chemical thermodynamics as shown in the following equation:

\[
\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-
\]  

(1)

By applying the law of chemical equilibrium constant \(K_1\) can be expressed as,

\[
K_1 = \left[ \text{Ca}^{2+} \right] \left[ \text{HCO}_3^- \right] / \left[ \text{H}^+ \right]
\]  

(2)

Equilibrium constant \(K_2\) in dissolution of CaF\(_2\) dissolved in water is given by

\[
K_2 = \left[ \text{Ca}^{2+} \right] \left[ \text{F}^- \right]
\]  

(3)

Using Equations (2) and (3),

\[
K_1/K_2 = \left[ \text{HCO}_3^- \right] / \left[ \text{H}^+ \right] \left[ \text{F}^- \right]
\]  

(4)

![Figure 5](image_url)  

**Figure 5.** The plot of F\(^-\) concentration vs Na/Ca.
The Equation (4) shows the relationship between bicarbonate, hydrogen ion and fluoride and interpret that if the pH (hydrogen ion activity) of water is constant an increase in fluoride ion would be accompanied increases in bicarbonate ions while in Equation (2) shows that increase in the fluoride is accompanied by corresponding decrease in calcium ions and thus shows negative correlation. The interionic relationship of F vs pH, \( \text{Ca}^+ \), \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) in the groundwater samples of area under study is depicting in Figures 6-9.

6. Conclusions

Fluoride concentration in most of the groundwater samples of Tosham area, Bhiwani, NW, India found to be higher than BIS standards. This study reveals that the fluoride bearing minerals are the foremost sources for fluoride in

![Figure 6. Scatter plot of F$^-$ vs pH of groundwater samples of Tosham area.](image)

![Figure 7. Scatter plot of F$^-$ vs CO$_3^{2-}$ of groundwater samples of Tosham area.](image)
groundwater in villages of Tosham area. Due to removal of Ca$^{2+}$ by the precipitation of calcite, the fluoride enrichment may still continue even when fluorite (CaF$_2$) reaches an equilibrium state. The prolonged rock-water interactions facilitate the enrichment of groundwater fluoride. Though precipitation may perhaps cause dilution effects, weathering, ion exchange, dissolution of high heat producing granites are complimentary for fluoride fortification in groundwater of area under study. Fluoride distribution is related with pH, chloride, calcium and magnesium. In present study, the parameters like EC, pH, chloride, Total Hardness, magnesium and calcium show the positive correlation with fluoride. Moreover, the parameters like bicarbonate, total alkalinity and carbonate exhibit the negative correlations with fluoride.
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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References


