Fluoride Contamination in Drinking Water in Rural Habitations of Siddipet, Telangana State, India

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Abstract:
Fluoride rich groundwater is well known in granite aquifers in India and the world. This study examines the fluoride content of well water in different parts of Siddipet area of Medak district, Telangana State. The area is geologically predominantly occupied by granites. Results showed that collected water samples were severely contaminated by the presence of fluoride ion and most of the samples have higher concentration than prescribed WHO standards (1.5 mg L\(^{-1}\)) for drinking water. The quality assessment was made by estimating pH, electrical conductivity, total dissolved solids and hardness besides major cations (Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\)) and anions (HCO\(_3^-\), Cl\(^-\), SO\(_4^{2-}\), F\(^-\), and NO\(_3^-\)). The fluoride concentration ranges between 0.4 and 2.2 mg L\(^{-1}\) with mean 1.1 mg L\(^{-1}\) in this area whereas, distribution pattern showed high concentrations in the vicinity of Siddipet town. The pH of the groundwater samples varied from 6.5 to 9.2 with an average value of 7.5 indicates the alkaline characteristics of the groundwater. The alkaline pH and high bicarbonate are responsible for release of fluoride bearing minerals into groundwater. It was also found that F has a positive correlation with pH and HCO\(_3^-\) whereas negatively correlated with Ca\(^{2+}\), indicating that high fluoride in groundwater is associated with low calcium content. This suggests that the higher pH of water promotes the leaching of fluoride and thus affects the concentration of fluoride in the ground water. The semiarid climate of the region, the granitic rocks and the low freshwater exchange due to periodical drought conditions are the factors responsible for the higher incidence of fluorides in the groundwater resources. The Fluoride incidence in groundwater is mainly a natural phenomenon, influenced by local and regional geological settings and hydrogeological conditions.

Keywords: Drinking water, Groundwater, Fluoride, Fluorosis , Siddipet, Medak district.
Introduction

Fluorine is the 13th most abundant naturally occurring element in the Earth’s crust (0.06 – 0.09%) and is the lightest member of the halogens. It is the most electronegative and reactive of all the elements and as a result, elemental fluorine does not occur in nature, but is found as fluoride mineral complexes. Fluoride ions are essentially required for the healthy growth of bones and teeth of human beings. The fluoride contamination in the groundwater and the resultant disease ‘Fluorosis’ has become a global problem. Fluorine is available in soils and waters due to the weathering of fluoride-bearing minerals predominantly of igneous origin. Apatite [Ca₅(PO₄)₃F] and fluorite [CaF₂] are the most common fluoride-bearing minerals. Biotite [K(Mg,Fe)₃AlSi₃O₁₀(F,OH)₂], hornblende [(Ca,Na)₂₋₃(Mg,Fe,Al)₃(Al,Si)₈O₂₂(OH,F)₂], muscovite, lepidolite, tourmaline, sphene, apophyllite, zinnwaldite, micas and amphiboles (where F⁻ substitutes for OH⁻ within the mineral structures) cryolite (Na₃AlF₆), villiaumite (NaF), topaz (Al₂(SiO₄)F₂) and soils that consist mainly of clay minerals such as vermiculite [(Mg,Fe,Al)₃(Al,Si)₄O₁₀(OH)], kaolinite [Al₂Si₂O₅(OH)₄] and montmorillonite [(Na,Ca)₀.₃₃(Al,Mg)₂(Si₄O₁₀)(OH)₂·nH₂O] are also major sources of Fluoride (Hem 1985; Apambire et al. 1997; Saxena and Ahmed 2003; Edmunds and Smedley 2005; Chae et al., 2007). Endemic fluorosis develops widely in many areas of the world, such as China (Guo et al. 2007), Turkey (Oruc 2003), southeastern Korea (Kim and Jeong 2005), Mexico (Carrillo-Rivera et al. 2002), Africa (Gizaw 1996), Syria, Jordan, Ethiopia, Sudan, Tanzania, Kenya and Uganda (Smith et al. 1953; Ocherse 1953; Grech 1966; Tekle-Haimanot et al. 1987; Fuhong and Shuqin 1988; Kahama 1997; Finkelman et al. 1999; Ando et al. 2001). In the world, around 200 million people from 25 nations have great health risks, with high fluoride in the drinking water (Ayoob and Gupta 2006).

India is confronting the same problem and at present at least 20 states have become endemic to fluorosis (Gupta et al. 2006). Though fluoride enters the body through food, water, industrial exposure, drugs, cosmetics, etc., drinking water is the major contributor (75–90% of daily intake) (Sarala and Rao 1993). The studies carried out by various researchers on groundwater quality with respect to fluoride across India, including Telangana, are reported elsewhere (Shaji et al., 2007; Narsimha and Sudarshan 2013; Asadi et al. 2007; Misra et al. 2006; Sujatha 2003;
Sarala and Rao 1993; Sarma and Rao 1997; Saxena and Ahmed 2001; Narsimha et al., 2012). Fluoride beyond desirable amounts (0.6 to 1.5 mg L\(^{-1}\)) in groundwater is a major problem in many parts of the world. In India too, there has been an increase in incidence of dental and skeletal fluorosis with about 62 million people at risk (Andezhath et al., 1999) due to high fluoride concentration in drinking water. Dental fluorosis is endemic in 14 states and 150,000 villages in India with the problem most pronounced in the states of Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu, and Uttar Pradesh (Pillai and Stanley 2002) and Telangana state one of them. According to the ‘Survey of Status of Drinking Water Supply in Rural Habitation’ conducted by the Rajiv Gandhi National Drinking Water Mission (RGNDRM) in 1993, there are 9,741 villages in India having F content >1.5 mg L\(^{-1}\) in groundwater sources (Susheela 1999). It is generally accepted that groundwaters are enriched in fluoride due to prolonged water–rock interactions (Nordstrom et al. 1989; Frengstad et al. 2001; Carrillo-Rivera et al. 2002). The study area is around Siddipet town in Medak district, which is situated about 105 km north of Hyderabad on Hyderabad–Karimnagar State highway and is bounded by E longitude 78.76942 to 78.90232 and N latitude 18.06768 to 18.24402. The area under investigation falls under semi-arid zone, with a hot, humid climate and predominantly occupied by granite/gneiss of Archaean age. The area experiences a semi-arid climate with an annual mean temperature of 30°C. The mean annual rainfall is recorded as 745 mm, occurring mostly during the southwest monsoon period (June–September). The present investigation was undertaken with the following specific objectives: (i) to assess the spatial variation of fluoride content in the groundwaters of the study area applying GIS technology; (ii) to study the correlation between fluoride and other physico-chemical constituents of groundwater, especially at different levels of fluoride content.

**Material and methods:**

Groundwater samples of 104 habitations located in Siddipet of Medak District were collected in pre-cleaned polythene bottles following standard sampling techniques. The water samples were analyzed for various hydrochemical parameters such as pH, electrical conductivity (EC), total hardness (TH) as CaCO\(_3\), calcium (Ca\(^{2+}\)), sodium (Na\(^+\)), potassium (K\(^+\)), chloride (Cl\(^-\)), sulphate...
(SO₄²⁻), nitrate (NO₃⁻), fluoride (F⁻). Using pH/EC/TDS meter (Hanna HI 9811-5), the EC and pH of water samples were measured in the field immediately after the collection of the samples. Total dissolved solids (TDS) were computed as per Hem (1985) from EC values. Ca²⁺ and Mg²⁺ were determined titrimetrically using standard EDTA. Chloride was estimated by AgNO₃ titration. Na⁺ and K⁺ were measured using flame photometer (Model 130 Systronics Flame Photometer). SO₄²⁻ and NO₃⁻ by colorimetry with an UV-visible spectrophotometer. The fluoride concentration in water was determined electrochemically, using fluoride ion-selective electrode (APHA 1995). This method is applicable to the measurement of fluoride in drinking water in the concentration range of 0.01–1,000 mg L⁻¹. The electrode used was an Orion fluoride electrode, coupled to an Orion electrometer. Standards fluoride solutions (0.1–10 mg L⁻¹) were prepared from a stock solution (100 mg L⁻¹) of sodium fluoride. As per experimental requirement, 2 ml of total ionic strength adjusting buffer grade III (TISAB III) was added in 20 ml of sample. The ion meter was calibrated for a slop of −59.2±2. The composition of TISAB solution was 385.4g ammonium acetate, 17.3g of cyclohexylene diamine tetraacetic acid, and 234 ml of concentrate hydrochloric acid per liter. Exact sampling locations were marked with the help of GPS and the coordinates were plotted on map. A general observation was also conducted with respect to the incidence of dental and skeleton fluorosis.

**Result and discussion**

**Quality of chemical data**

The analytical precision of the data was measured using the normalized ionic charge balance (NICB) (Huh et al. 1998), which is defined as

\[
NICB = \frac{\sum Cations - \sum Anions}{\sum (Cations + Anions)} \times 100
\]

Where \(\Sigma\) cations and \(\Sigma\) anions are the sum of me L⁻¹ concentrations of cations and sum of me L⁻¹ concentrations of anions, respectively. It is an important step to ascertain the quality of data. The analysis of major ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, CO₃²⁻, HCO₃⁻, Cl⁻ and SO₄²⁻) is generally enough to give a charge balance because it represents maximum concentration of available dissolved ions in fresh water. The obtained results were tested for accuracy by calculating the normalized inorganic charge balance. Therefore, the analytical precision was such that the ion charge balance was within ±5% for all the samples (Fig. 1) which is generally considered acceptable because it is very...
difficult to analyze all cations and anions (Edmond et al. 1995; Huh et al. 1998).

Fig. 1 Normalized inorganic charge balance

Fig 2. Location and Spatial distribution of fluoride in the study region

<table>
<thead>
<tr>
<th>S. No</th>
<th>Parameters</th>
<th>Range</th>
<th>Mean</th>
<th>WHO (1997)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>6.5-9.3</td>
<td>7.5</td>
<td>7-8.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.5-9.2</td>
</tr>
</tbody>
</table>
Table 1. Groundwater quality in study area and compliance to WHO (1997) drinking water standards

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>EC μS/cm</td>
<td>1010-3850</td>
<td>1910</td>
<td>750</td>
</tr>
<tr>
<td>3</td>
<td>TDS (mg L⁻¹)</td>
<td>646-2464</td>
<td>1223</td>
<td>500</td>
</tr>
<tr>
<td>4</td>
<td>TH (mg L⁻¹)</td>
<td>50-565</td>
<td>207</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>HCO₃⁻ (mg L⁻¹)</td>
<td>18-134</td>
<td>64</td>
<td>200</td>
</tr>
<tr>
<td>6</td>
<td>SO₄²⁻ (mg L⁻¹)</td>
<td>21-156</td>
<td>66</td>
<td>200</td>
</tr>
<tr>
<td>7</td>
<td>Cl⁻ (mg L⁻¹)</td>
<td>25-973</td>
<td>230</td>
<td>250</td>
</tr>
<tr>
<td>8</td>
<td>NO₃⁻ (mg L⁻¹)</td>
<td>9-360</td>
<td>109</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>F⁻ (mg L⁻¹)</td>
<td>0.4-2.2</td>
<td>1.07</td>
<td>0.6-0.9</td>
</tr>
<tr>
<td>10</td>
<td>Ca²⁺ (mg L⁻¹)</td>
<td>10-186</td>
<td>56</td>
<td>75</td>
</tr>
<tr>
<td>11</td>
<td>Na⁺ (mg L⁻¹)</td>
<td>17-134</td>
<td>65</td>
<td>50</td>
</tr>
<tr>
<td>12</td>
<td>Mg²⁺ (mg L⁻¹)</td>
<td>6-112</td>
<td>34</td>
<td>30</td>
</tr>
<tr>
<td>13</td>
<td>K⁺ (mg L⁻¹)</td>
<td>1-85</td>
<td>6.8</td>
<td>100</td>
</tr>
</tbody>
</table>

The analytical results have been evaluated to ascertain the suitability of groundwater in the study area for drinking and domestic purposes based on the World Health Organization (WHO 1997) standards (Table 1). Even though pH has no effect on human health, it is closely related to other chemical constituents of water. pH values for the study area range from 6.5 to 9.2 (with an average of 7.5). The acidic water leads the absorption of fluoride to clay layers; whereas the increase of pH to alkaline nature desorbs the fluoride (Saxena and Ahamed 2001). The possible reaction which shows the alkaline influence on fluoride concentration is given in Eq. (1) (Salve et al. 2008).

\[
CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na + 2F^- + H_2O + CO_2
\]

The EC in the study region is varied from 1010 to 3850 μS/cm with an average of 1910 μS/cm (n = 104). The TDS ranged from 646 to 2464 mg L⁻¹ with a mean value of 122 mg L⁻¹. According to the TDS classification, 30% of the groundwater samples belong to the freshwater type (TDS < 1,000 mg L⁻¹), and the remaining comes under brackish category (TDS > 1,000 mg L⁻¹; Freeze and Cherry 1979). The WHO drinking water and domestic limit for TDS is 500 mg L⁻¹, and all the groundwaters in the study area are all above this limit (Table 1). Hardness is an important criterion for determining the usability of water for domestic, drinking, and many industrial supplies. Hardness of the water is attributable to the presence of alkaline earths, i.e., Ca and Mg. Hardness has no known adverse effect on health, but it is mainly an esthetic concern because of the unpleasant taste. Hardness can be classified as temporary due to carbonate and bicarbonates or...
permanent due to sulfate and chlorides of calcium and magnesium. Total hardness varies between 50 and 565 mg L$^{-1}$ with an average of 207 mg L$^{-1}$. The groundwater with total hardness (TH) value less than 75 mg L$^{-1}$ is considered as soft. Hardness is a very important property of water for domestic purposes. Elevated NO$_3^-$ and Cl$^-$ contents are indicative of anthropogenic impact on groundwater quality. Naturally, NO$_3^-$ concentration in crystalline rocks is very low, and therefore, high concentrations of NO$_3^-$ in some groundwater within the study area indicates that human activity is increasingly impacting the water quality. High levels of nitrate accompanied with high content of chloride are suspected to come from human and animal waste effluent. In this study, a very strong positive correlation between NO$_3^-$ and Cl$^-$ ($r^2 = 0.15$; Fig. 3) exists and is a diagnostic indicator of anthropogenic activity on groundwater quality. Nitrates have undesirable effects when present in drinking water and also high concentrations of nitrates can cause methaemoglobinaemia, gastric cancer, goiter, birth malformations, and hypertension (Majumdar and Gupta 2000).

Fig. 3 Scatter plot of Cl$^-$ versus NO$_3^-$ in groundwater of the Siddipet

<table>
<thead>
<tr>
<th>S. No</th>
<th>Possible combinations</th>
<th>Ratio values (range, average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HCO$_3$/Cl</td>
<td>0.04-3.04 (0.50)</td>
</tr>
<tr>
<td>2</td>
<td>Na/Cl</td>
<td>0.08-1.28 (0.40)</td>
</tr>
<tr>
<td>3</td>
<td>Na/Ca</td>
<td>0.26-6.29 (1.39)</td>
</tr>
<tr>
<td>4</td>
<td>HCO$_3$/Ca</td>
<td>0.26-6.09 (1.44)</td>
</tr>
<tr>
<td>5</td>
<td>NO$_3$/Cl</td>
<td>0.03-4.40 (0.69)</td>
</tr>
</tbody>
</table>

Table 2. Ratio and correlation values of different water quality variables
R² = 0.040

(a) F (mg L⁻¹) vs Ca (mg L⁻¹)

(b) F (mg L⁻¹) vs Mg (mg L⁻¹)

(c) F (mg L⁻¹) vs HCO₃ (mg L⁻¹)

(d) F vs (HCO₃+CO₃)/(Ca+mg)
Guideline value & F mg L$^{-1}$ water & Possible health effects

<table>
<thead>
<tr>
<th>Recommended minimum</th>
<th>0.5</th>
<th>Dental cavities may occur at lower concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimal range</td>
<td>0.5-1.5</td>
<td>No adverse health effects, cavities decrease</td>
</tr>
<tr>
<td>Recommended maximum</td>
<td>1.5</td>
<td>Mottling of teeth and dental fluorosis may occur at higher concentrations. Association with skeletal fluorosis at &gt;3 mg l$^{-1}$ concentrations</td>
</tr>
</tbody>
</table>

Table 3 International guidelines for fluoride concentrations in drinking water and possible health effects (from WHO, 1997)

Nitrate concentrations of groundwaters are in the range 9–360 mg L$^{-1}$ with a mean of 111 mg L$^{-1}$. All most all locations of the waters have nitrate concentrations greater than 10 mg L$^{-1}$, the potable water nitrate concentration limit (WHO 2004). Chloride concentrations of groundwaters are in the range 25–973 mg L$^{-1}$ with a mean of 236 mg L$^{-1}$. The permissible limit of Cl in potable water is 250 mg L$^{-1}$. Sulfate ion concentrations in the study area vary between 21 and 156 mg L$^{-1}$ with a mean of 66 mg L$^{-1}$; thus, SO$_4^{2-}$ ions are in compliance with WHO limits (WHO 2004). Concentrations of SO$_4$ above 250 mg L$^{-1}$ are objectionable for domestic water uses.

A spatial variation map of fluoride concentration and location of the study was plotted in Fig. 2. A high concentration was observed in the southern and SW part of the study area. The high concentration can be attributed to release of fluoride from the hard rocks. Mutual relationships between F$^-$ and other major ions are presented to illustrate geochemical behaviour of F$^-$ (Fig. 4). An international guideline for fluoride concentrations in drinking water and possible health effects was presented (Table 3). Calcium exhibits

Fig. 4. Mutual relationships between F$^-$ and other major ions.
antipathetic association with $F^-$, reflecting precipitation of $\text{CaF}_2$, due to high solubility product (Gizaw 1996). Majority of the plots (Fig. 4a) are confined towards the low concentration zone of Ca. The availability of Ca ions in the study area is lacking. Probably the plagioclase feldspars provide source of Ca ions in the groundwater. The manner of Mg versus $F^-$ is quite similar to Ca except a few variations (Fig. 4b). The plot of $F^-$ versus $\text{HCO}_3^-$ (Fig. 4c) is nearly linear showing good relationship between them. Results of the linear regression analysis on the dependence of $F^-$ and $\text{HCO}_3^-$ (total alkalinity) indicate a positive correlation, which might be due to the release of hydroxyl and bicarbonate ions simultaneously during the leaching and dissolution process of fluoride bearing minerals into the groundwater. The higher rate of weathering and leaching of minerals increases the fluoride ion concentrations with higher levels of alkalinity as well. The high bicarbonate bearing water has alkaline nature, which favours the stability and mobility of $F^-$ ions in the groundwater. This is also supported by the various studies in the different part of the world, where positive correlation exists between $F^-$ and $\text{HCO}_3^-$ ions (Gizaw 1996). High fluoride levels are also associated with the higher concentrations of Na$^+$ ions. This also favours that groundwater with high $\text{HCO}_3^-$ and Na$^+$ content are usually alkaline and have relatively high OH$^-$ content, so the OH$^-$ can replace the exchangeable $F^-$ of fluoride bearing minerals, increasing the $F^-$ content in groundwater. The relation of ($\text{HCO}_3^- + \text{CO}_3^-$) and ($\text{Ca} + \text{Mg}$) with $F$ is be explained in Fig. 4d. As the ($\text{HCO}_3^- + \text{CO}_3^-$)/($\text{Ca} + \text{Mg}$) ratio increases, there is a subsequent increase in fluoride concentration was observed. The relation between Na, Ca and $F$ can be better explained by a plot between Na/Ca versus $F$ (Fig. 4e). This ratio between Na and Ca was found in the range of 0.26–6.29 with average of 1.39, is greatly influenced by the cation exchange and increase the ratio value may be due to the lowering of calcium activity whereby high sodium activates the dissolution (Shaji et al. 2007). The ratio of $\text{HCO}_3^-/\text{Cl}$ was found in the range of 0.04–3.04 with a average of 0.50 (Table 2). The average ratio value of 0.50 indicates dominance chloride ion is prevalent in the region. The Na/Cl ratio was observed in the range of 0.08–1.28 (Table 2). The decrease in ratio indicates modification of sodium carbonate water by dissolution or mixing with sodium chloride, whereas increase in chloride may be due to local recharge (Dhiman and Kesari 2006). The $\text{HCO}_3^-/\text{Ca}$ ratio was in
the range of 0.26–6.09 (1.44). It was observed that in 65% of the samples, the HCO₃/Ca ratio was above 1, indicating favorable chemical conditions during the fluoride dissolution process (Saxena and Ahmed 2003). Thus high concentration of fluoride is geogenic in origin, i.e. local hydro-geological conditions in the area are responsible for its higher concentration in groundwater.

Conclusions:
The study of groundwater quality with emphasis on fluoride concentration in Siddipet indicated that the groundwater is alkaline in nature. The presence of high HCO₃⁻, Na⁺ and pH favours the release of F⁻ from aquifer matrix into groundwater. The alkaline nature of the groundwater favours the solubility of fluoride bearing minerals. In an alkaline environment the fluoride ions are desorbed thus supplementing the dissolution of fluoride bearing minerals. It is also found that a high concentration of sodium favours dissolution of fluoride bearing minerals at higher pH. Geochemical behaviour of groundwater from the study area suggests that high fluoride groundwater contain low levels of Ca and high alkalinity. The groundwater in the area is brackish and highly contaminated by fluoride. The granitic rocks contain abundant fluoride bearing minerals, which upon weathering are leached out and dissolve in groundwater. The higher ratio of Na/Ca indicates dissolution of fluoride minerals at higher pH and the HCO₃/Ca ratio indicate the chemical condition favouring dissolution of fluoride ions. Regular intake of fluoride rich waters seems to be the main cause for high incidence of fluorosis in the region. Use of GIS technology to assess the spatial variation of groundwater fluoride concentration has enabled to identify low-fluoride areas located in the north part and high-fluoride areas in the southern and south-western parts. It is recommended that residents be encouraged to use rainwater harvesting for their water consumption needs to alleviate this fluoride problem.

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