FLUORIDE GRADATION IN GROUND WATER AND ITS DIVERSE EFFECTS ON RURAL AND URBAN COMMUNITY OF HARYANA (INDIA): A REVIEW

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Abstract
The Potable water is the largest contributor of fluoride in daily uptake. When the fluoride is consumed in permissible limit, it not only improves both bones and tooth strength but also have a positive impact on human body. Whereas the groundwater with fluoride content above the WHO limit of 1.5 ppm may lead to many health ailments such as skeletal and dental fluorosis, increased bone fractures, urolithiasis, decreased birth rate along with lower intelligence in children and impaired thyroid function.

The fluoride concentration in ground water varies area to area depending upon the geochemical behavior of fluoride and the presence of different type of water. The water alkalinity also plays an essential role in activation of fluoride (F⁻) ion mainly from the fluorite (CaF₂). Daily uptake of fluoride is pertaining to the concentration of fluoride, frequency and amount of drinking ground water and the climate of an area. In Haryana state, groundwater act as leading root of water supply and laden with the higher fluoride concentration. All districts are partially or fully affected by fluoride contamination whereas, Bhiwani, Sonepat, Jind, Kaithal, Mahendergarh districts along with some parts of Mewat, Hisar, Palwal and Hodal are most affected by fluoride. The Bhiwani district is found to be with maximum concentration of fluoride approximately 86 mg/L. This review article elaborates the significance of the fluoride (F⁻) ion in ground water and specify the major effects especially on the rural and urban societies. The article provides a fluoride gradation of ground water in Haryana district and related health problem to specific areas.

Key words: Groundwater, Haryana, fluoride, Geochemical, consumption.

Introduction
The amount of daily uptake of minerals in human body affects the individual as well as the society. Groundwater acts as a major source of these minerals including sodium, magnesium, potassium, chloride and especially fluorides (WHO, 2004). In India it has been documented that more than 75% population of rural areas and around 50% of its urban sector water’s requirement are met through groundwater resources. Many places in India was affected with the fluoride contamination leading to deteriorating health effects. The first report of excess fluoride concentration in groundwater was documented in Andhra Pradesh state in the year 1937 (Short et al., 1937). High ground water Fluoride concentration is linked with igneous and metamorphic rocks like gneisses and granite. The same has been stated in West Africa, India, South Africa, Pakistan, Thailand, Sri Lanka and China (WHO, 2006). Contamination of fluoride is present in many countries but in different proportion as shown in fig. 1.

In the crust of Earth, the fluorine is 13th major element found as organic or inorganic fluoride and as a fluoride ion. Major fluoride sources may include minerals such as topaz Al₂SiO₄(F,OH₂), cryolite (Na₃AlF₆), fluorite (CaF₂), amphiboles [A₉₋₁₀B₂₋₃C₇₋₈T₈₋₁₂O₂₂(OH,F,Cl)], sellaite (MgF₂), micas [AB₂₋₃(X, Si)₄O₁₀(O, F, OH)]₂, apatite [Ca₅(PO₄)₃F] (Hem, 1985; Datta et al., 1996; Pickering, 1985; Jadhav et al., 2015). The dissolution of apatite, Fluorite and topaz from local substratum leads to increase the concentration of fluoride in groundwater. It is predicted that India has 14.1% of total fluoride that are deposited on earth’s crust and about 70 million people in 20 states and union territories are under fluorosis risk. The adversely affected areas in India include Andhra Pradesh, Rajasthan, Haryana, Tamil Nadu, Gujarat, Uttar

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There are five major routes of Fluoride exposure in human beings e.g. drinking water, food, drugs, cosmetics and dental products and industrial activities. But drinking water is major contributor i.e. up to 75-90% (Sarala and Rao, 1993). The Fluoride is highly electronegative and does not occur in Free State, it reacts with various elements which may produce ionic compounds like HF and NaF in water and upon dissolution form fluoride ion having negative charge. The standards given by WHO and BIS is given below in the table 1.

Table 1: Guideline Value of Fluoride standards in Drinking water (WHO, 2012; BIS, 2012).

<table>
<thead>
<tr>
<th>Name of Organization</th>
<th>Acceptable limit (in ppm) (desirable limit)</th>
<th>Maximum Permissible Limit (in ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>World Health Organization (WHO)</td>
<td>1.0 ppm</td>
<td>1.5 ppm</td>
</tr>
<tr>
<td>Bureau of Indian Standards (BIS)</td>
<td>1.0 ppm</td>
<td>1.5 ppm</td>
</tr>
</tbody>
</table>

In India, Haryana is one of the state having high fluoride concentration ranging from the limit of 15.72 ppm in the Mohana of Sonipat district to highest value of 86 mg/l in Bhiwani district. Approximately 72.5% of water samples were found with less than 1.5 mg/l, whereas 1.0 to 1.5 mg/l fluoride concentration was found in the 8.6% of samples. Fluoride concentration more than 1.5 ppm values were found in the left of 18.9% samples. Excess Fluoride in ground water above 1.5 mg/l are found mostly in parts of Bhiwani, Jhajjar, Mahendergarh, Fatehabad, Gurgaon, Hisar, Jind, Kaithal, Mewat, Rohtak, Palwal, Rewari, Panipat, Sirsa and Sonepat districts and are not appropriate for the purpose of drinking. At most of the places, fluoride more than 1.5 mg/l is detected in areas where agricultural based activities are dominant. The favorable cause due to high fluoride in the ground water are (i) Calcium depleted may be due to exchange or precipitation or exchange phenomenon and (ii) leaching from phosphatic fertilizers where it is present an impurity and to detect the fluoride concentration in distilleries of Haryana different samples were collected and found to contain fluoride up to the extent of 1.95 to 2.32 mg/l. Fluoride content at seven locations were found to be more than permissible limits. In Korawal area, concentration of fluoride is 19.36 mg/L, which is found to be highest in all of them. In Panipat district of Haryana state fluoride concentration falls under the range of 6.6 mg/l to 7.5 mg/l. Fluoride ion concentration in the groundwater of Dabwali town in the Sirsa district fall in between the concentration of 0.90 to 34.50 ppm. The high fluoride ion concentration occur in the five areas of Hodal block in Faridabad district. The concentration of fluoride ion in Hodal blocks are in the extent of 1.0 to 40.0 mg/l. Due to irregular dispersion of rocks that contain fluoride minerals can leads to unequal fluoride distribution in the groundwater of Hisar city.

The fluoride concentration is found to be 0.3-9.0 mg/L in Jhajjar district. Around 60% of the groundwater samples had fluoride ion concentration more than the prescribed limit of 1.5 ppm. In Mewat district, concentration of fluoride is high in ground water. The concentration of fluoride ranges from 0.27 ppm to 1.6 ppm. The spatial distribution of fluoride (Fig. 2) in the study area shows that 1264.81 sq. km area (68.03%) falls under desirable groundwater quality; 365.66 sq. km area (19.67%) area falls under permissible groundwater quality and 4.21 sq. km area (0.23%) falls under non-potable groundwater quality. Hills cover 224.32 sq. km area (12.07%) in the study area. Distribution of fluoride and dental fluorosis was observed in groundwater of different villages of Hisar district of Haryana in India. The fluoride ion concentration is found from 0.5 ppm to 2.98 ppm.

In Baniyani village, almost all places are having fluoride concentration present in permissible limit apart from one sample although there is only one location in Lahli and Masoodpur village that has acceptable range...
of fluoride concentration. In Kalanaur district, two of the regions had concentration of fluoride found within satisfactory range. In rest of the villages nearly 50% sources of water had fluoride volume more than 1 ppm permissible limit. In groundwater, fluoride concentration is an important function for many other factors like velocity of flowing water, solubility and availability of fluoride minerals, pH, temperature, concentration of bicarbonate ions and calcium in water (Khaiwal and Garg, 2006); Meenakshi et al., (2004) had reported the groundwater of various villages in Jind district is contaminated with the fluoride. The outcome displays that more than 50% sources of water had higher fluoride concentrations than the permissible limits. Suitability of ground water with reference to Fluoride in drinking purpose has also been investigating in some other parts of Haryana including Panipat (Bishnoi and Malik, 2008), Hisar (Garg and Khaiwal, 2006, 2007), Jind region (Meenakshi et al., 2004; Mor et al., 2003) Gurgaon region (Singh et al., 2007). Singh et al., (2007) has reported the fluoride content in the ground water of Pataudi block of gurugram district in the range of 0.95 and 5.20 mg/l .Garg et al., (2009) reported up to 86 ppm concentration of fluoride in the ground water of rural habitations of Bhiwani district that is highest fluoride content ever recorded for Haryana state including India. The research done on groundwater inn different district is shown in table 2.

### Table 2: Fluoride Levels in different cities of Haryana.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>City/Town</th>
<th>Number of sampling sites</th>
<th>Fluoride concentration (ppm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hisar City</td>
<td>22</td>
<td>0.1-3.4</td>
<td>Kaushik et al., (2002)</td>
</tr>
<tr>
<td>2</td>
<td>Hisar</td>
<td>126</td>
<td>0.04-16.5</td>
<td>Ravindra and Garg, (2006)</td>
</tr>
<tr>
<td>3</td>
<td>Jind</td>
<td>24</td>
<td>0.42-2.0</td>
<td>Mor et al., (2003)</td>
</tr>
<tr>
<td>5</td>
<td>Jind (Karkhana)</td>
<td>15</td>
<td>0.88-5.08</td>
<td>Meenakshi et al., (2004)</td>
</tr>
<tr>
<td>6</td>
<td>Jind (Malar)</td>
<td>16</td>
<td>0.31-6.90</td>
<td>Meenakshi et al., (2004)</td>
</tr>
<tr>
<td>7</td>
<td>Jind (Rojala)</td>
<td>15</td>
<td>0.84-5.89</td>
<td>Meenakshi et al., (2004)</td>
</tr>
<tr>
<td>8</td>
<td>Faridabad</td>
<td>78</td>
<td>0.26-8.0</td>
<td>Susheela et al., (1993)</td>
</tr>
<tr>
<td>9</td>
<td>Faridabad</td>
<td>25</td>
<td>0.04-1.49</td>
<td>Kaushik et al., (2004)</td>
</tr>
<tr>
<td>12</td>
<td>Bahadurgarh</td>
<td>100</td>
<td>1.56-3.05</td>
<td>Yadav and Lata, (2003)</td>
</tr>
<tr>
<td>13</td>
<td>Rohtak</td>
<td>27</td>
<td>0.4-4.8</td>
<td>Kaushik et al., (2004)</td>
</tr>
<tr>
<td>14</td>
<td>Pataudi</td>
<td>25</td>
<td>0.95-5.20</td>
<td>Singh et al., (2007)</td>
</tr>
<tr>
<td>15</td>
<td>Panipat</td>
<td>41</td>
<td>0.24-9.27</td>
<td>Mukul et al., (2008)</td>
</tr>
<tr>
<td>16</td>
<td>Bhiwani (Tosham)</td>
<td>100</td>
<td>0.18-9.0</td>
<td>Sudhir et al., (2000)</td>
</tr>
</tbody>
</table>

### Treatment Methods for Fluoride

Different type of Defluoridation methods have been developed to remove excess fluoride concentration to decrease it to permissible limit i.e. chemical, physical and biological techniques. In today’s world, Defluoridation techniques are used to carry fluoride removal of ground water such as adsorption (Bhatnagar et al., 2011); ion exchange (Chubar, 2011; Gong et al., 2012a), electro coagulation and the coagulation (Behbahani et al., 2011; Gong et al., 2012b) and latest processes include membrane (Richards et al., 2010). Nalgonda technique is developed based on lime and alum precipitation and is widely used technique for fluoride removal. Although membrane method is used to reduce fluoride concentration to acceptable level, surface adsorption is better method for Defluoridation research.

Adsorption is a traditional technique applied for water defluoridation with advantages of being most robust, economic, environment friendly and efficient technique. Progressive methods have been recently developed for cheap and effective removal of fluoride including many economical adsorbents such as activated coconut-shell, soils, alumina, clays, red mud, activated carbon, calcite, activated kaolinites, brick powder, oxides ores, bone char, modified chitosan and various cheap substances (Mohapatra et al., 2009). An easy three step technique is provided through which the fluoride ion adsorption may occur on solid particles: (i) Fluoride ion mass transfer occur on the adsorbent outer surface, (ii) Adsorption of F ion adjacent to the surface’s external particle and (iii) F ions intra-particle diffusion done on the outer surface and desirable interchange with the particles on the pore surface present within the elements (Fan et al., 2003). For the large-scale installations, activated alumina is one of the best solid adsorbents (Chauhan et al., 2007). Alumina is prominent sorbent as it retain its structural resistance without swelling, disintegration and shrinkage in water (Serbezov et al., 2011).

Biosorption is most advanced technique for biomaterial treatment in water. For the removal of fluoride an economical biosorbents are developed like chitosan and chitin. Beside this, there are many biosorbents such as fungal and algal biomass are also developed for the removal of fluoride. For Defluoridation, materials get from the agricultural waste can be used as economical and eco-friendly option.
Testing of potable water is only option for detection of Fluoride concentration. That’s why a regular check on the Fluoride concentration in groundwater is must for the excellent understanding and management of the fluoride toxicity. Fluoride toxicity is the biggest natural groundwater quality problem that affects the semi-arid and arid parts of India especially in Haryana. Distribution of fluoride in Haryana is given in fig. 2. Similarly distribution of fluoride in terms of its concentration in Haryana is also shown in table 3.

**Fluoride Geochemistry**

The natural guideline follow for the geochemistry of groundwater and surface water mainly rely upon the interaction along with the rocks and may leads to acceptability and widespread health dilemma in different regions of the world. The biggest reason for increasing

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**Fig. 2:** Distribution of Fluoride in Haryana given by Central Ground water Board (CGWB, Haryana).
such health problems is deep bore wells installation for
the water supply in rural area, particularly in tropical
developing countries like India. The outcome of
geochemical fluoride distribution is its impact on the well-
being of humans are mighty visualize in the tropic region
where almost all the people obtain their water and food
directly from their environment resources. The
geochemical route of fluoride may directly affect more
the peoples of the tropics area instead of those who leaves
in the temperate area of more developed countries where
people can obtained water and food from far off places.
Since most of the fluoride ingestion takes place inside
the human body in India is by groundwater water intake
thus for the etiology of fluorosis, a proper understanding
of the fluoride geochemistry in groundwater is required.

The rain water which falls on the planet earth gets
enhanced with CO$_2$ from soil, air and also through the
bacteria’s biochemical reactions with organic matter
while its downward movement. Secondary salts are
leached out, which are available in the soil (mixture of
Na$_2$SO$_4$, NaCl and NaHCO$_3$). If application of phosphate
fertilizers is done than the soil may show different
proportions of fluoride-bearing compounds. At the same
time, a reaction of exchangeable cations goes on with
ion exchange that are exist in the clay complex of soil as:

$$CaY^2+ 2 \text{Na (aq)} = 2 \text{NaY}+ Ca^{2+} (aq)$$

Hence $Y = \text{clay mineral}$.

The hydrogen ion concentration (pH) of groundwater
is enhanced by CO$_2$ dissolution. If the calcareous mineral
(CaCO$_3$) is present, it also gets dissolved as:

$$CO_2+ H_2O = H_2CO_3$$

$$H_2CO_3 = HCO^{3-} + H^+$$

$$\text{HCO}^{3-} + \text{CO}^{3-} + H^+$$

$$\text{CaCO}_3 + H^+ 2F^- = \text{CaF}_2 + \text{HCO}^{3-}$$

$$\text{CaF}_2 = \text{Ca}^{2+} + 2F^-$$

The alkaline water can help in mobilizing fluoride from
weathered rocks, CaF$_2$ and soils can precipitate the
CaCO$_3$ as depicted in the following reaction:

$$\text{CaF}_2 + 2\text{HCO}^{3-} = \text{CaCO}_3 + 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2$$

The fluoride dissolution activity in ground water will
be higher in the presence of excessive sodium bicarbonates and the reaction can be depicted in following
equations:

$$\text{CaF}_2 + 2\text{NaHCO}_3 \rightarrow \text{CaCO}_3 + 2\text{F}^- + 2\text{Na} + \text{CO}_2 + \text{H}_2\text{O}$$

The CaF$_2$ solubility product is:

$$K_{sp19} = [F^-]^2[Ca^{2+}] = 4.0 \times 10^{-11}$$

When the carbonate ions are higher and calcium
content is lower in groundwater than they leads to higher
fluoride concentration in groundwater. It may be noticed
that the groundwater is almost saturated with the fluorite
(sometimes, may be saturated with both fluorite and
calcite).

Generally, the fluoride concentration in groundwater

<table>
<thead>
<tr>
<th>S. No.</th>
<th>District Name</th>
<th>Total samples</th>
<th>Concentration range (ppm)</th>
<th>Fluoride (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ambala</td>
<td>10</td>
<td>Min 0.14</td>
<td>Max 0.93</td>
</tr>
<tr>
<td>2</td>
<td>Bhiwani</td>
<td>35</td>
<td>Min 0.17</td>
<td>Max 12</td>
</tr>
<tr>
<td>3</td>
<td>Faridabad</td>
<td>6</td>
<td>Min 0.0</td>
<td>Max 0.92</td>
</tr>
<tr>
<td>4</td>
<td>Fatehabad</td>
<td>3</td>
<td>Min 1.37</td>
<td>Max 2.74</td>
</tr>
<tr>
<td>5</td>
<td>Gurugram</td>
<td>17</td>
<td>Min 0.10</td>
<td>Max 4.26</td>
</tr>
<tr>
<td>6</td>
<td>Hisar</td>
<td>21</td>
<td>Min 0.19</td>
<td>Max 4.04</td>
</tr>
<tr>
<td>7</td>
<td>Jhajjar</td>
<td>20</td>
<td>Min 0.37</td>
<td>Max 6.86</td>
</tr>
<tr>
<td>8</td>
<td>Jind</td>
<td>16</td>
<td>Min 0.28</td>
<td>Max 10</td>
</tr>
<tr>
<td>9</td>
<td>Kaithal</td>
<td>16</td>
<td>Min 0.27</td>
<td>Max 10</td>
</tr>
<tr>
<td>10</td>
<td>Karnal</td>
<td>23</td>
<td>Min 0.15</td>
<td>Max 1.04</td>
</tr>
<tr>
<td>11</td>
<td>Kurukshetra</td>
<td>20</td>
<td>Min 0.20</td>
<td>Max 1.20</td>
</tr>
<tr>
<td>12</td>
<td>Mahendergarh</td>
<td>11</td>
<td>Min 0.21</td>
<td>Max 14</td>
</tr>
<tr>
<td>13</td>
<td>Mewat</td>
<td>11</td>
<td>Min 0.28</td>
<td>Max 2.07</td>
</tr>
<tr>
<td>14</td>
<td>Palwal</td>
<td>20</td>
<td>Min 0.21</td>
<td>Max 2.10</td>
</tr>
<tr>
<td>15</td>
<td>Panchkula</td>
<td>18</td>
<td>Min 0.00</td>
<td>Max 0.73</td>
</tr>
<tr>
<td>16</td>
<td>Panipat</td>
<td>12</td>
<td>Min 0.16</td>
<td>Max 2.23</td>
</tr>
<tr>
<td>17</td>
<td>Rewari</td>
<td>7</td>
<td>Min 0.20</td>
<td>Max 1.85</td>
</tr>
<tr>
<td>18</td>
<td>Rohtak</td>
<td>14</td>
<td>Min 0.05</td>
<td>Max 4.14</td>
</tr>
<tr>
<td>19</td>
<td>Sirsa</td>
<td>11</td>
<td>Min 0.29</td>
<td>Max 4.52</td>
</tr>
<tr>
<td>20</td>
<td>Sonepat</td>
<td>30</td>
<td>Min 0.00</td>
<td>Max 16</td>
</tr>
<tr>
<td>21</td>
<td>Yamunanagar</td>
<td>13</td>
<td>Min 0.14</td>
<td>Max 0.54</td>
</tr>
</tbody>
</table>
mainly depends on the fluoride concentration in different minerals in different forms of rock and primarily on the dissolution and decomposition activities occurs through the interactions of water and rock. Groundwater with alkaline pH (within the range of 7.6-8.6) and also more concentration of bicarbonate is more favorable for dissolution of fluoride in groundwater which offers that groundwater pH is most important parameter to determine the fluoride concentration in groundwater. In the basic Rocks mineral. Leaching and weathering of minerals that contain fluoride can release fluoride in the solution. The fluoride is the mineral which broadly discover the fluoride concentration in natural water. Hence the solubility product is very less for fluorite (Eq. 9), thus, ground waters has high content of fluoride when groundwater contains very low concentration of calcium. Groundwater present in the form of sodium bicarbonate (NaHCO₃) and bicarbonate chloride (ClCO₃⁻), that means it constantly high content of fluoride. The fluoride which is water-soluble present in sodic surface soil may be treated with the gypsum can be increased with the more exchangeable Na percentage. These type of monitoring along with the exchange mechanism may be suggested in Eq. 1 are important in the text of the account of excess groundwater fluoride because of high soil sodicity present near the south Indian irrigation system that may induce fluorosis amidst the nearby populations.

**Health Effect of Fluoride**

- **Beneficial Effect:**

A number of studies shows that the if fluoride is taken in moderate levels then it can decrease the problem of dental caries and, sometimes it can enhancement in the formation of strong bones (Doull *et al.*, 2006; Rao 2003; Edmunds and Smedley 2005). For the formation of bone, mineral Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) is accumulated in and around the collagen fibrils of skeletal tissues. When fluoride is present, it can substitute a column hydroxyl in the hydroxyapatite structure and forms fluorapatite (Ca₁₀(PO₄)₆F₂ or Ca₁₀(PO₄)₆OHF). This substitution causes reduction of crystal volume, an increase in structural stability and a decrease in mineral solubility (Aoba, 1997).

Free fluoride ions in the fluid phase may also serve to increase the driving force for apatite mineral growth (Aoba, 1997). Ever since the beneficial effect of fluoride was recognized during the 1930s, researchers have attempted to identify an optimal fluoride concentration in drinking water to reduce dental caries. This optimal level is obviously dependent upon the amount of water consumed on a daily basis and any additional sources of fluoride in the diet. Most studies in U.S have shown that there is less chances of dental caries when the concentration of fluoride are decline from 0 to nearly between 0.7 and 1.2 mg/l, with small additional benefit when fluoride is increased beyond that range (Heller *et al.*, 1997; Doull *et al.*, 2006). Consequently, the U.S. Centers for Disease Control and Prevention (CDC), with support from the American Dental Association (ADA) and American Dental Hygienist’s Association (ADHA), recommends that communities with public water supplies adjust the fluoride content of their drinking water to a value between 0.7 and 1.2 mg/l, depending on the average maximum daily temperature. Health Canada, a Canadian governmental agency, recommends an optimal drinking water concentration of 0.8 to 1.0 mg/l fluoride. Fluoride play a significant role in the growth of strong bones, some of the doctors have investigated that the ingestion of fluoride may help in the prevention of osteoporosis. A study directed by Bernstein *et al.*, (1966) that the osteoporosis in the part of North Dakota with having of fluoride content of less concentration. Epidemiological study and clinical research have exhibited that the ingestion of fluoride enhanced with suitable dose of Vitamin D and calcium, which can help in bone mineralization (Rich and Ensinck, 1961; Gron *et al.*, 1966; Kleerekoper, 1996; Aoba, 1997; Cerklewski, 1997; Kurttio *et al.*, 1999). Rather it appears that the potential for fluoride to reduce bone fractures follows a U-shaped curve, with the maximum benefits achieved at about 1 mg/l (Kurttio *et al.*, 1999; Hillier *et al.*, 2000; Li *et al.*, 2001; Yiming *et al.*, 2001). When the concentration of fluoride in drinking water may exceed or equal to the 4 ppm may leads to an increase in the incidence of fracture (Sowers *et al.*, 1986; Alarcon-Herrera *et al.*, 2001; Sowers *et al.*, 1991; Sowers *et al.*, 1991).

### Table 3: Fluoride ion Concentration and its Adverse Effects.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Fluoride ion in drinking water (ppm)</th>
<th>Adverse Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.002 ppm in air</td>
<td>Injury to Vegetation</td>
</tr>
<tr>
<td>2.</td>
<td>1 ppm in water</td>
<td>Dental caries reduction</td>
</tr>
<tr>
<td>3.</td>
<td>50 ppm in water or food</td>
<td>Thyroid change</td>
</tr>
<tr>
<td>4.</td>
<td>2 ppm or more in water</td>
<td>Mottled enamel</td>
</tr>
<tr>
<td>5.</td>
<td>100 ppm in food and water</td>
<td>Growth retardation</td>
</tr>
<tr>
<td>6.</td>
<td>3.1 to 6.0 ppm in water</td>
<td>Osteoporosis</td>
</tr>
<tr>
<td>7.</td>
<td>More than 125 ppm in water and food</td>
<td>Kidney change</td>
</tr>
<tr>
<td>8.</td>
<td>8 ppm in water</td>
<td>10% osteoporosis</td>
</tr>
<tr>
<td>9.</td>
<td>20-80 ppm in water</td>
<td>Crippling skeletal fluorosis</td>
</tr>
<tr>
<td>10.</td>
<td>2.5-5.0 gm in actual dose</td>
<td>Death</td>
</tr>
</tbody>
</table>

(Source: Hussain *et al.*, 2012)
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2005). Therefore, although fluoride may hold promise for the treatment of osteoporosis, much remains to be learned about the optimal levels for maximizing the benefits while minimizing the risks (Schnitzier et al., 1997; Aoba, 1997).

**Adverse Effects**

Long time susceptibility to the immense fluoride concentration bring into the deleterious effect on bones, tooth and other organs. (Perumal et al., 2013). Fluoride is considered to be beneficial for health of living organisms if it is taken in prescribed amount i.e. 0.5 to 1.5 ppm. High Fluoride ion concentration is causing the hefty health hazards (as shown in Table 3) in various regions of the earth. Health disturbances which are caused due to chronic exposure to high concentration of fluoride concentration are referred as fluorosis (Hussain et al., 2012). It is also known to cause dental and skeletal fluorosis, thyroid, osteosclerosis, kidney changes and if the concentration of fluoride ion in drinking water is beyond the 1.5 mg/l, it may leads to the gastrointestinal, cardiovascular, neurological, endocrine, reproductive, molecular level and immunity effects (WHO, 1997).

**Dental Fluorosis**

It is mainly occur in human beings who consumes fluoride rich groundwater having concentration more than 1.5 mg/l especially in children’s of eight years. If fluoride intake is more, lustre is lost from the enamel. If it shows the slight form, then it distinguished by opaque and white areas on the surface of tooth and while its extreme form, tooth are noticeable as blackish yellow or brown and also shows rigorous pitting on the teeth (Meenakshi and Maheshwari, 2006).

Exposure of Fluoride ion may leads to a disruption of dose-related enamel mineralization results in excessive retention of enamel proteins, anomalously large gaps in its crystalline structure and increased porosity (Aoba and Fejerskov, 2002). Dentin is accumulated in the fluoride (Vieira et al., 2004; Kato et al., 1997), the mineralized tissue present beneath the tooth enamel, few of the investigations had suggested that the exposure of chronic fluoride concentration caused crack in the aged dentin instinctively (Doull et al., 2006).

In the three blocks of Haryana i.e. Bahadurgarh, Jhajjar and Matanhail, 2nd stage fluorosis were reported in most of the children. At the same time, in the blocks of Sahlawas and Jhajjar, 1st stage dental fluorosis was popular amongst the children. The dental fluorosis was observed in all the blocks of Jhajjar except Matanhail. The maximum number of children affected by the dental fluorosis were present in the Dhakla village of Sahlawas Block around 94.85%.

**Skeletal Fluorosis**

The fluoride threshold level required for causing skeletal fluorosis mainly depend on water quality intake and various other factor associated with diet (Raja Reddy et al., 1985). Doull et al., (2006) studied skeletal fluorosis in eight cases that has been recorded in the U.S., six of them were taking medication for renal problem in a Clinic (Johnson et al., 1979). The rest of two cases having a lady who takes drinking water from the well which contains fluoride concentration of 7.3-8.1 ppm for a time span of 7 years (Roberts and Felsenfeld, 1991) and the other lady who had drinking instant tea for about 10 years, which is made of fluoride (2.8 ppm) contaminated water in large volumes (Whyte et al., 2005).

Continues drinking of water having fluoride more than 8 mg/l leads to Skeletal Fluorosis (Singh et al., 2011). Fluoride ion gets accumulated in the joints of pelvic, neck, knee and shoulder bones and causes problem while moving and walking. The signs of skeletal fluorosis are burning sensation, pain in sporadic, back stiffness, tingling and prickling in the limbs, chronic fatigue, weakness in muscles, abnormally Ca deposited in ligament as well as bones (Meenakshi and Maheshwari, 2006). Fluoride concentration more than 4 ppm in ground water may leads to a problem of brittle and dense bones (osteoporosis). It may affect a large population worldwide and is responsible for fractures in the peoples of having 45 years age. It is investigated that around 20% of the people who suffered from the hip osteoporosis associated fractures may die in almost 6 months. Men are facing osteoporosis at higher risk in comparison of females (Hussain et al., 2012).

**Other health challenges**

Excessive drinking of fluoride rich water may cause to muscle fiber degeneration, red blood cells deformities, low hemoglobin levels, excessive thirst, rashes on skin, headache, perturbation, neurological, depression, gastrointestinal, nausea, malfunctioning in urinary tract, abdominal pain, reduced immunity, male sterility, tingling sensation in toes and fingers, repeated abortions or still births other than dental and skeletal fluorosis. It may also culpable for the change in their working mechanisms of digestive system, liver, kidney, respiratory, central nervous system, excretory and as well as reproductive system (Singh et al., 2011; Meenakshi et al., 2006).

Many researches show that there is a positive correlation within the concentration of fluoride ion calculated in umbilical cord and maternal blood plasma, which help the placenta to transmit the fluoride passive diffusion from the mom to the featus (Malhotra et al., 1993; Gupta et al., 1993).
A study was carried out in Jhajjar (Haryana) suggests a meaningful positive correlation exist between the urine, fluoride(F) ion concentration in groundwater and serum present in the children who are suffering from fluorosis. A maximal number of children (94.63%) suffered with fluorosis were reported from the village of Dadanbad. The research disclosed that the amount of fluoride in serum as well as in urine was much higher than the universal accepted amount of fluoride. Similar study is also conducted in Gurgaon (Haryana) by Singh et al which showed that the concentration of fluoride in serum and urine was very high.

Singh et al., (2001) conducted a study and tested beyond 18,700 people who lives in different part of our country India and the amount of fluoride (F) ion in the potable water extents from the 3.5 to 4.9 ppm and result shows that the patients are suffering from skeletal fluorosis, which enhance the chances of kidney stone by 4.6 times. However, because of this study it is clear that the formation of kidney stone is at greater risk due of malnutrition, it is problematic to come to a decision. A study carried in China shows that the ingestion of fluoride in diet causes an consequence on the intellectuality of children (Li et al., 1995; Wang et al., 2007; Lu et al., 2000). Children who takes high (2mg/l) level fluoride can scored poor intelligence test than the children who takes lower (>1 mg/l) fluoride.

Doull et al., (2006) reported that the research may conclude the main impact of fluoride ion on endocrine system result in minimization of thyroid function and impaired glucose tolerance (Type II diabetes), increased parathyroid activity and calcitonin activity and secondary hyperparathyroidism,. However, they shows different effect in different individuals and some characterized as the subclinical, means causing no detrimental health effects. The good pattern of the complication intricate to understand the fluoride outcome on the endocrine system bring into being by many researchers within exposure of fluoride and endemic goiter in the human society (Steyn, 1948; Obel, 1982; Desai et al., 1993;Jooste et al., 1999).

A diversity in the gastrointestinal effects, may include abdominal pain, diarrhea, nausea, vomiting, all had been stated in study of receptive fluoride toxicity (Sidhu and Kimmer, 2002; Gessner et al., 1994; Penman et al., 1997). Most of the studies carried on animal’s shows that fluoride can reduce blood flow and provoke the stomach acid secretion far away from stomach lining and also enhance in lase of epithelium cells present in gastrointestinal tract (Doull et al., 2006).

Fluoride is mainly accumulated in the body mainly in skeleton and may leads to cancer in bone. Most of the researches on the animals shows osteoma (nontcancerous bone tumors) and also leads to increased osteosarcoma (bone cancer), but there is no particular study found on human beings (Doull et al., 2006). Research on human beings shows combined results, but they may suggest a positive relationship between the osteosarcoma and ingestion of fluoride (Cohn, 1992; Takahashi et al., 2001; Bassin, 2001), some of them show no association. (Mahoney et al., 1991; Freni and Gaylor, 1992; Gelberg et al., 1995) and even few of them shows negative associations (Gelberg et al., 1995; McGuire et al., 1991). Advance researches shows that some of the groups of boys having age between 6-8 can be more prone to the carcinogenic effects due to ingestion of fluoride than the other groups of peoples (Bassin et al., 2006), beside that further studies will be required to authenticate these type of studies (Joshipura and Douglass, 2006).

**Conclusion**

The present review disclosed that the Haryana groundwater which is polluted with the fluoride and the peoples of the Haryana state was in contact with the higher levels of fluoride that was taken up in the form of drinking water. Major population of Haryana state is relying on groundwater for their irrigation as well as domestic purposes, which is not applicable for use. As per WHO guidelines, groundwater on almost all the parts of Haryana is not appropriate for the purpose of drinking as shown in the present review.

The Fluoride (F) study of groundwater in Haryana state exhibited that water in many areas heavily contaminated with fluoride and not suitable for human consumption and it is mainly influenced by the rock minerals and waste disposal from industries. This review declared states that fluoride value of almost all district are above the permissible limits given by WHO/BIS. The water quality degradation is mainly due to industrial growth and to achieve the demand and supply according to the growth of population. Hence, an awareness in the form of education is necessary and avoid the discharge of industries waste to water bodies.

**References**


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