Plant Archives Volume 20 No. 2, 2020 pp. 3361-3371 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

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

Preeti Gahlot*, Rajesh Dhankhar and Sunil Chhikara

Department of Environmental Science, M.D.U, Rohtak-124001 (Haryana), India

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 (CaF_2). 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 $Al_2SiO_4(F,OH_2)$, cryolite (Na_3AlF_6), fluorite (CaF_2), amphiboles [$A_{0-1}B_2C_5T_8$-O_{22} (OH,F,Cl)], sellaite (MgF_2), micas [$AB_{2-3}(X, Si)_4O_{10}(O, F, OH)_2$], apatite [$Ca_5(Cl,F,OH)(PO_4)_3$ (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

***Author for correspondence :** E-mail: preetivijarnia@gmail.com

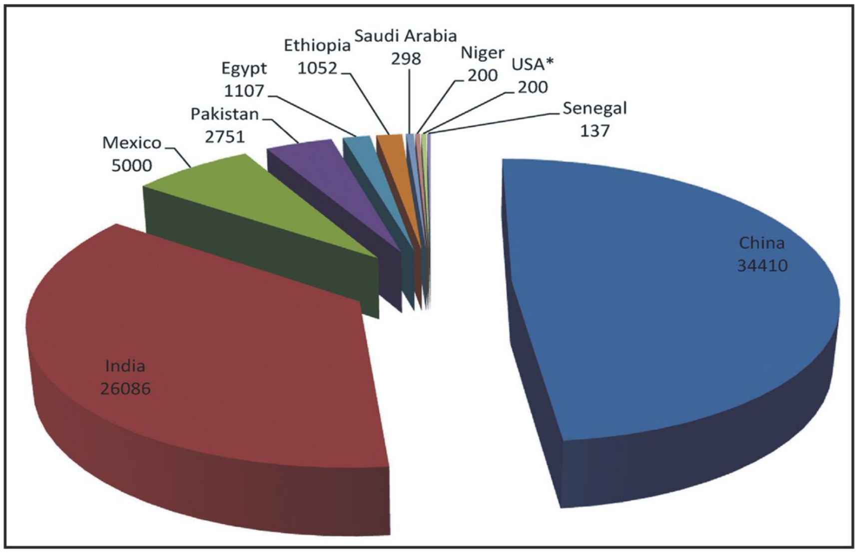

Fig. 1: Predicted Population (in million) exhibit to fluoride ion contamination (CDC, 1993).

Pradesh, Punjab, Madhya Pradesh and Bihar. (Kumaram *et al.*, 1971; Hussain, *et al.*, 2002; Sharma *et al.*, 2007). 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.

Distribution of Fluoride in Haryana

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 upto 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 is occur in the five areas of Hodal block in Faridabad district. The concentration of fluoride ion found 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.

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

Name of Organization	Acceptable limit (in ppm) (desirable limit)	Maximum Permissible Limit (in ppm)
World Health Organization (WHO)	1.0 ppm	1.5 ppm
Bureau of Indian Standards(BIS)	1.0 ppm	1.5 ppm

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 0.27ppm 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 4.21sq.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

Table 2: Fluoride Levels in different cities of Haryana.

S. No.	City/ Town	Number of sampling sites	Fluoride concen-tration (ppm)	References
1	Hisar City	22	0.1-3.4	Kaushik *et al*., (2002)
2	Hisar	126	0.04-16.5	Ravindra and Garg, (2006)
3	Jind	24	0.42-2.0	Mor *et al*., (2003)
4	Jind (Butani)	16	2.1-4.55	Meenakshi *et al*., (2004)
5	Jind (Karkhana)	15	0.88-5.08	Meenakshi *et al*., (2004)
6	Jind (Malar)	16	0.31-6.90	Meenakshi *et al*., (2004)
7	Jind (Rojala)	15	0.84-5.89	Meenakshi *et al*., (2004)
8	Faridabad	78	0.26-8.0	Susheela *et al*., (1993)
9	Faridabad	25	0.04-1.49	Kaushik *et al*., (2004)
10	Jhajjar	101	1.79-2.61	Yadav and Lata, (2003)
11	Beri	99	1.58-2.38	Yadav and Lata, (2003)
12	Bahadurgarh	100	1.56-3.05	Yadav and Lata, (2003)
13	Rohtak	27	0.4-4.8	Kaushik *et al*., (2004)
14	Pataudi		0.95-5.20	Singh *et al*., (2007)
15	Panipat	41	0.24-9.27	Mukul *et al*., (2008)
16	Bhiwani (Tosham)		0.18-9.0	Sudhir *et al*., (2000)

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.

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

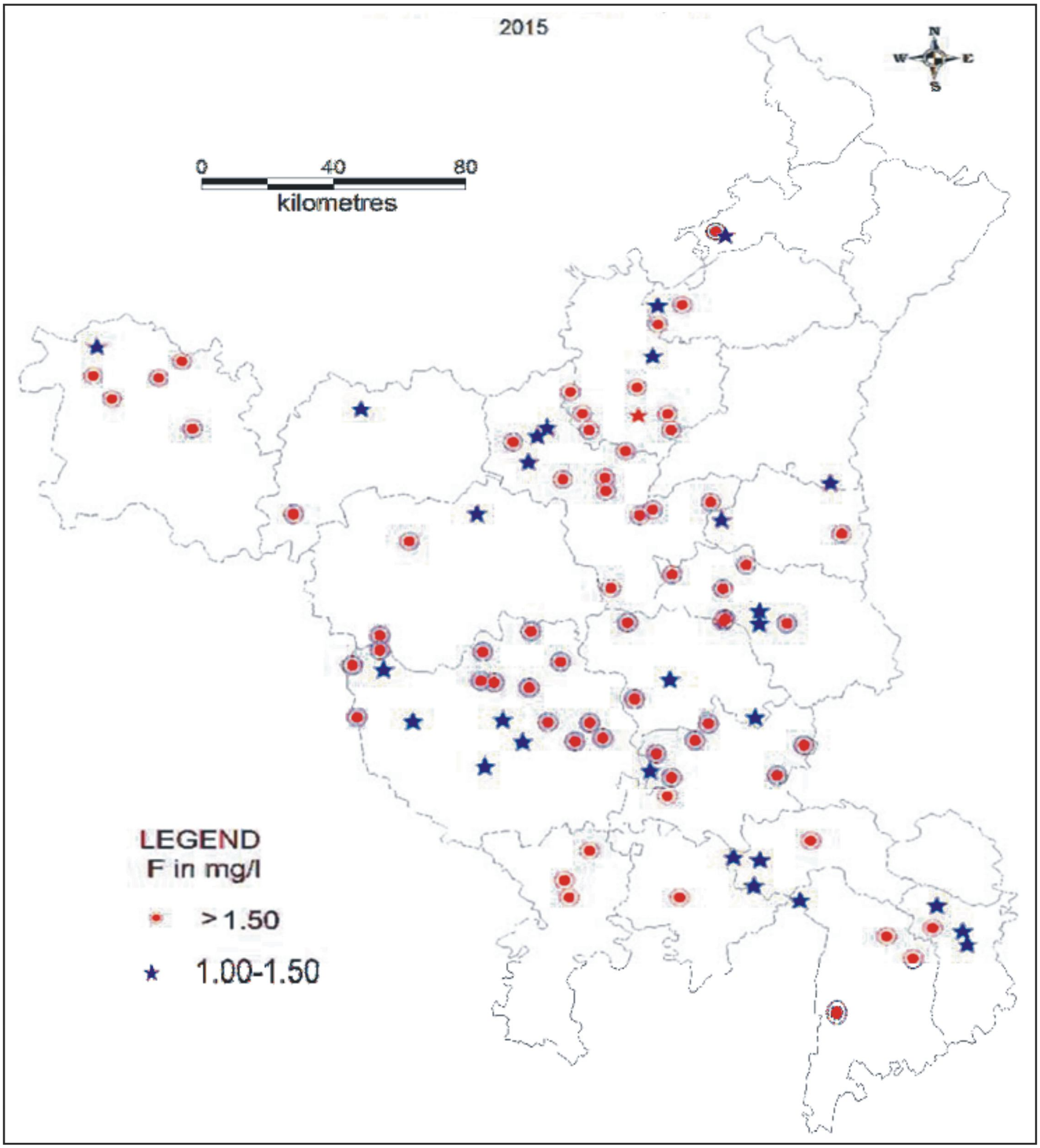

Fig. 2: Distribution of Fluoride in Haryana given by Central Ground water Board (CGWB, Haryana).

Table 3: Distribution of Fluoride district wise in groundwater of Haryana (CGWB, 2015).

S. No.	District Name	Total samples	Concentration range	Fluoride (ppm)
1	Ambala	10	Min	0.14
			Max	0.93
2	Bhiwani	35	Min	0.17
			Max	12
3	Faridabad	6	Min	0.0
			Max	0.92
4	Fatehabad	3	Min	1.37
			Max	2.74
5	Gurugram	17	Min	0.10
			Max	4.26
6	Hisar	21	Min	0.19
			Max	4.04
7	Jhajjar	20	Min	0.37
			Max	6.86
8	Jind	16	Min	0.28
			Max	10
9	Kaithal	16	Min	0.27
			Max	10
10	Karnal	23	Min	0.15
			Max	1.04
11	Kurukshetra	20	Min	0.20
			Max	1.20
12	Mahendergarh	11	Min	0.21
			Max	14
13	Mewat	11	Min	0.28
			Max	2.07
14	Palwal	20	Min	0.21
			Max	2.10
15	Panchkula	18	Min	0.00
			Max	0.73
16	Panipat	12	Min	0.16
			Max	2.23
17	Rewari	7	Min	0.20
			Max	1.85
18	Rohtak	14	Min	0.05
			Max	4.14
19	Sirsa	11	Min	0.29
			Max	4.52
20	Sonepat	30	Min	0.00
			Max	16
21	Yamunanagar	13	Min	0.14
			Max	0.54

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_2SO_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:

$$CaY^2 + 2\ Na\ (aq) = 2\ NaY + Ca^{2+}\ (aq) \quad (1)$$

Hence Y = 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:

$$CO_2 + H_2O = H_2CO_3 \quad (2)$$

$$H_2CO_3 = HCO^{-3} + H^+ \quad (3)$$

$$HCO^{-3} = CO_2^{-3} + H^+ \quad (4)$$

$$CaCO_3 + H^+\ 2F^- = CaF_2 + HCO^{-3} \quad (5)$$

$$CaF_2 = Ca^{2+} + 2F^- \quad (6)$$

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:

$$CaF_2 + 2HCO^{-3} = CaCO_3 + 2F^- + H_2O + CO_2 \quad (7)$$

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:

$$CaF_2 + 2NaHCO^{-3} \rightarrow CaCO_3 + 2F^- + 2Na + CO_2 + H_2O \quad (8)$$

The CaF2 solubility product is:

$$Ksp19 = [F^-]\ 2[Ca^{2+}] = 4.0 \times 10\text{-}11 \quad (9)$$

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 3: Fluoride ion Concentration and its Adverse Effects.

S. No.	Fluoride ion in drinking water (ppm)	Adverse Effect
1.	0.002 ppm in air	Injury to Vegetation
2.	1 ppm in water	Dental caries reduction
3.	50 ppm in water or food	Thyroid change
4.	2 ppm or more in water	Mottled enamel
5.	100 ppm in food and water	Growth retardation
6.	3.1 to 6.0 ppm in water	Osteoporosis
7.	More than 125 ppm in water and food	Kidney change
8.	8 ppm in water	10% osteoporosis
9.	20-80 ppm in water	Crippling skeletal fluorosis
10.	2.5-5.0 gm in actual dose	Death
(Source: Hussain *et al*., 2012)		

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 fluorite 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 ($NaHCO_3$) and bicarbonate chloride ($ClCO_3$), 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 (Ca_{10} $(PO_4)_6(OH)_2$) 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 (Ca_{10} $(PO_4)6F_2$ or Ca_{10} $(PO_4)6OHF$). 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*., 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 spam 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 lapse 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 (noncancerous 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

Alarcon-Herrera, M.T., I.R. Martin-Dominguez and R. Trejo-Vazquez (2001).Well water fluoride, dental fluorosis and bone fractures in the Guandiana Valley of Mexico. *Fluoride*., **34(2):** 139-149.

Aoba, T. (1997). The Effect of Fluoride on Apatite Structure and Growth. *Crit. Rev. Oral Biol. Med*., **8:** 136-153.

Aoba, T. and O. Fejerskov (2002). Dental fluorosis: Chemistry and biology. *Crit. Rev. Oral Biol. Med*., **13:** 155-170.

Bassin, E.B. (2001). Association between Fluoride in Drinking Water during Growth and Development and the Incidence of Osteosarcoma for Children and Adolescents, D.M.S. Thesis, Harvard School of Dental Medicine, Boston, MA, 92-100. Available: http://www.fluoridealert.org/health/cancer/bassin-2001.pdf

Behbahani, M., M.R. Moghaddam and M. Arami (2011). Techno-economical evaluation of fluoride removal by electrocoagulation process: Optimization through response surface methodology. *Desalination*., **271(1):** 209-18.

Bernstein, D.S., N. Sadowsky, D.M. Hegsted, C.D. Guri and P.J. Stare (1966). Prevalence of Osteoporosis in High and Low Fluoride Areas in North Dakota. *J. Amer. Med. Assoc*., **198:** 499-504.

Bhatnagar, A., E. Kumar and M. Sillanpää (2011). Fluoride removal from water by adsorption - A review. *Chem. Eng. J*., **171:** 811-840.

Bishnoi, M. and R. Malik (2009). Ground water quality in environmentally degraded localities of Panipat city. *India J. Environ. Biol*., **29:** 881 886.

Bureau of Indian Standards (2012). Drinking Water Specification (Second Revision), IS 10500.

Cerklewski, F.L. (1997). Fluoride Bioavailability-Nutritional and Clincal Aspects. *Nutr. Res*., **17(5):** 907-929.

CGWB (2010). Ground water quality in shallow aquifers of India.

Chauhan, V. S., P. K. Dwivedi and L. Iyengar (2017). Investigations on activated alumina based domestic defluoridation units. *Journal of Hazardous Materials*., **139:** 103 107.

Cohn, P.D. (1992). A Brief Report on the Association of Drinking Water Fluoridation and the Incidence of Osteosarcoma Among Young Males, New Jersey Depart. Health, November 8, 1992, 17.

Datta, P.S., D.L. Deb and S.K. Tyagi (1996). Stable isotope (18O) investigations on the processes controlling fluoride contamination of groundwater. *J Contam Hydrol*., **24(1)**: 85-96. doi:10.1016/0169-7722(96)00004-6.

Desai, V.K., D.M. Solanki and R.K. Bansalm (1993). Epidemiological Study on Goitre in Endemic Fluorosis District of Gujarat. *Fluoride*., **26(3):** 187-190.

Douglass, C.W. and K. Joshipura (2006). Caution Needed in Fluoride and Osteosarcoma Study. *Cancer Causes Control*., **17:** 481-482.

Doull, J., K. Boekelheide, B.G. Farishian, R.L. Isaacson, J.B. Klotz, J.V. Kumar, H. Limeback, C. Poole, J.E. Puzas, N-M.R. Reed, K.M. Thiessen and T.F. Webster (2006). Fluoride in Drinking Water: A Scientific Review of EPA's Standards, Committee on Fluoride in Drinking Water, Board on Environmental Studies and Toxicology, Division on Earth and Life Sciences, National Research Council of the National Academies, National Academies Press, Washington, DC, 530. (http://www.nap.edu).

Edmunds, W.M. and P.L. Smedley (2005). Fluoride in Natural Waters. In: Selinus O (ed) Essentials of Medical Geology (301-329), Elsevier Academic Press, Burlington, MA.

EPA (2012). Report, Environmental Protection Agency, Ohio. www. epa.state.oh.us/Portals/28/documents/gwqcp/fluoride_ts.pdf. Assessed 30 March, 2016.

Fan, X., D.J. Parker and M.D. Smith (2003). Adsorption kinetics of fluoride on low cost materials. *Wat. Res*., **37:** 4929.

Felsenfeld, A.J. and M.A. Roberts (1991). A Report of Fluorosis in the United States Secondary to Drinking Well Water. *J. Amer. Med. Assoc*., **265(4):** 486-488.

Freni, S.C. and D.W. Gaylor (1992). International Trends in the Incidence of Bone Cancer are not related to Drinking Water Fluoridation. *Cancer*., **70(3):** 611-618.

Garg, V.K., S. Suthar, S. Singh, A. Sheoran and S. Jain (2009). Drinking water quality in villages of southwestern Haryana, India: assessing human health risks associated with hydrochemistry. *Environ Geol*., **58(6):**1329-1340. doi:10.1007/s00254-008-1636-y.

Gelberg, K.H., E.F. Fitzgerald, S.A. Hwang and R. Dubrow (1995). Fluoride Exposure and Childhood Osteosarcoma: A Case-Control Study. *Amer. J. Public Health*., **85(12):** 1678-1683.

Gessner, B.D., M. Beller, J.P. Middaugh and G.M. Whitford (1994). Acute Fluoride Poisoning from a Public Water System. *N. Engl. J. Med*., **330(2):** 95-99.

Gong, W., J. Qu, R. Liu and H.N. Lan (2012). Effect of aluminum fluoride complexation on fluoride removal by coagulation. *Colloids Surf. A*., **395:** 88-93.

Gron, P.H.G. McCann and D. Bernstein (1966). Effect of Fluoride on Human Osteoporotic Bone Mineral. *J. Bone Joint Surg*., **48:** 892-898.

Gupta, S.K., A.K. Seth, A. Gupta and A.G. Gavane (1993). Transplacental Passage of Fluorides. *J. Pediatr*., **123(1):** 139-141.

Heller, K.E. (1997). Dental caries and dental fluorosis at varying water fluoride concentrations. *J. Publ. Health. Dent*., **57:** 136-143.

Hem, J.D. (1985). The Study and Interpretation of the Chemical Characteristics of Natural Water, 3rd Edition, U.S. Geol. Survey Water-Supply Paper 2254.

Hillier, S., C. Coper, S. Kellingray, G. Russell, H. Hughes and D. Coggon (2000). Fluoride in Drinking Water and Risk of Hip Fracture in the UK: a Case-Controlled Study. *Lancet*., **355(9200):** 265-269.

Hussain, I., M. Arif and J. Hussain (2012). Fluoride contamination in drinking water in rural habitations of Central Rajasthan, India. *Environ Monit Assess*., **184(8):** 5151-5158. Doi: 1007/s10661-011-2329-7.

Hussain, I., J. Hussain, K. Sharma and K.G. Ojha (2002). Fluoride in drinking water and health hazardous: Some observations on fluoride distribution Rajasthan. In environmental scenario of 21st Century (355-374). New Delhi: APH.

Jadhav, S.V., E. Bringas, G.D. Yadav, V.K. Rathod, I. Ortiz and K.V. Marathe (2015). Arsenic and fluoride contaminated groundwaters: a review of current technologies for contaminants removal. *J. Environ. Manag*., **162:** 306-325. doi:10.1016/j.jenvman.2015.07. 020.

Johnson, W.J., D.R. Taves and J. Jowsey (1979). Fluoridation and Bone Disease. In: Johansen, E, Taves, DR and Olsen, TO (eds) Continuing Evaluation of the Use of Fluorides, AAAS Selected Symposium. 275-293, Westview Press, Boulder, CO.

Jooste, P.L., M.J. Weight, J.A. Kriek and A.J. Louw (1999). Endemic Goitre in the Absence of Iodine Deficiency in Schoolchildren of the Northern Cape Province of South Africa. Eur. *J. Clin. Nutr*., **53(1):** 8-12.

Kato, S., Ç. Nakagaki, Õ. Toyama, Ô. Kanayama, Ì. Arai, Á. Togari, S. Matsumoto, M. Strong and C. Robinson (1997). Fluoride Profiles in the Cementum and Root Dentine of Human Permanent Anterior Teeth Extracted from Adult Residents in a Naturally Fluoridated and a Non-Fluoridated Area. *Gerodont*., **14(1):** 1-8.

Khaiwal, R. and V. K. Garg (2007). Hydro-chemical survey of groundwater of Hisar City and assessment of defluoridation methods used in India. *Environmental Monitoring and Assessment*., **132(1-3):** 33-43. doi:10.1007/ s10661-006-9500-6.

Kleerekoper, M. (1996). Fluoride and the Skeleton, *Crit. Rev. Clin. Lab. Sci*., **33:** 139-61.

Kleerekoper, M. and D.B. Mendlovic (1993). Sodium Fluoride Therapy of Postmenopausal Osteoporosis. *Endocr. Rev*., **14(3):** 312-323.

Kumaran, P., G.N. Bhargava and T.S. Bhakuni (1971). Fluorides in groundwater and endemic fluorosis in Rajasthan. *Indian J. Enviro. Health*., **13:** 316-324.

Kurttio, P., N. Gustavsson, T. Vartiainen and J. Pekkanen (1999). Exposure to Natural Fluoride and Hip Fracture: A Cohort Analysis in Finland. Amer. *J. Epid*., **150(8):** 817-824.

Kaushik, A., K. Kumar, Kanchan, Taruna and H. R. Sharma (2002). Water quality index and suitability assessment of urban groundwater of Hisar and Panipat in Haryana. *Journal of Environmental Biology*., **23:** 325-333.

Kaushik, A., K. Kumar, I.S. Sharma and H.R. Sharma (2004). Groundwater quality assessment in different landuse areas of Faridabad and Rohtak cities of Haryana using deviation Index. *Journal of Environmental Biology.*, **25**: 173-180.

Li, X.S., J.L. Zhi and R.O.G ao (1995). Effect of Fluoride Exposure on Intelligence in Children. *Fluoride*., **28(4):** 189-192.

Li, Y., C. Liang, C.W. Slemenda, R. Ji, S. Sun, J. Cao, C.L. Emsley, F. Ma, Y. Wu, P. Ying, Y. Zhang, S. Gao, W. Zhang, B.P. Katz, S. Niu, S. Cao and C.C. Jr. Johnston (2001). Effects of Long-Term Exposure to Fluoride in Drinking Water on Risks of Bone Fractures. *J. Bone Miner. Res*., **16(5):** 932-939.

Lu, Y., Z.R. Sun, L.N. Wu, X.Wang, W. Lu and S.S. Liu (2000). Effect of high-fluoride water on intelligence in children. *Fluoride*., **33(2):** 74-78.

Mahoney, M.C., P.C. Nasca, W.S. Burnett and J.M. Melius (1991). Bone Cancer Incidence Rates in New York State: Time trends and Fluoridated Drinking Water. *Amer. J. Public Health*., **81(4):** 475-479.

Malhotra, A., A. Tewari, H.S. Chawla, K. Gauba and K. Dhall (1993). Placental Transfer of Fluoride in Pregnant Women Consuming Optimum Fluoride in Drinking Water. *J. Indian Soc. Pedod. Prev. Dent*., **11(1):** 1-3:

McGuire, S.M., E.D. Vanable, M.H. McGuire, J.A. Buckwalter and C.W. Douglass (1991). Is There a Link Between Fluoridated Water and Osteosarcoma. *J. Amer. Dent. Assoc*., **122(4):** 38-45.

Meenakshi, V.K. Garg, Kavita, Renuka and A. Malik (2004). Groundwater quality in some villages of Haryana, India: focus on ûuoride and ûuorosis. *J. Hazard. Mater*., **106B:** 85-97.

Meenakshi, R.C. and Maheshwari (2006). Fluoride in drinking water and its removal. *J. Hazardous Mater* ., **137:** 456-463.

Mohapatra, M., S. Anand, B. K. Mishra, D. E. Giles and P. Singh (2009). Review of fluoride removal from drinking water. *Journal of Environmental Management*., **91:** 67-77. https://doi.org/10.1016/j.jenvman.2009.08.015.

Mor, S., M. Bishnoi and N.R. Bishnoi (2003). Assessment of groundwater quality of jind City. *Indian Journal of Environmental Protection*., **23:** 673-679.

Obel, A.O. (1982). Goitre and Fluorosis in Kenya. *E. Afr. Med. J*., **59(6):** 363-365.

Pickering, W.F. (1985). The Mobility of Soluble Fluoride in Soils. *Environ. Pollut* ., **9(44):** 281-308.

Raja reddy, D., K. Lahiri, N.V. Ram Mohan Rao, H.S. Vedanayakam, L. N. Ebenezer and R.M. Suguna (1985). Trial of magnesium compounds in the prevention of skeletal fluorosis-an experimental study. *Fluoride* ., **18:** 135-140.

Rao, N.C.R. (2003). Fluoride and environment-A review. In Proceedings of the third international conference on environment and Health, Chennai, India, ed. J. martin, V. Bunch, m. Suresh and T. Vasantha Kumaran, 386-399. Madras, India: Department of Geography, Universityof madras and Faculty of Environmental Studies, York University.

Ravindra, K. and V. K. Garg (2006). Distribution of fluoride in groundwater and its suitability assessment for drinking purpose. *International Journal of Environmental Health Research*., **16:** 163-166. Doi: 10.1080/09603120500538283.

Rich, C. and J. Ensinck (1961). Effect of Sodium Fluoride on Calcium Metabolism of Human Beings. *Nature*., **191:** 184-5.

Sarala, K. D. and P.R. Rama Krishna (1993). Endemic fluorosis in the village Ralla Anantpuram in Andhra Pradesh: An epidemiological study. *Fluoride.*, **26:** 177-180.

Schnitzier, C.M., J.R. Wing, F.J. Rall, M.T. Vander Merwe, J.M.

Mesvita, K.A. Gear, H.J. Robson and R. Shires (1997). Fewer Bone Histomorphometric Abnormalities with Intermittent than with Continuous Slow Release Sodium Fluoride Therapy. *Osteopor. Internat*., **7(4):** 376-89.

Sharma, K.C., M. Arif, I. Hussain and J. Hussain (2007). Observation on fluoride Contamination in groundwater of district Bhilwara, Rajasthan and a proposal for a low Cost defluoridation technique. In The XXVIITH conference of the international Society for fluoride research (ISFR XXVII), 9-12 October, 2007. Beijing, China.

Short, H.E., T.W. A.S.Bernard and A.S. Mannadinayer (1937). Endemic fluorosis in Madras presidency. *Indian J. Med. Res*., **25:** 553-561.

Sidhu, K.S. and R.O. Kimmer (2002). Fluoride Overfeed at a Well Site Near an Elementary School in Michigan. *J. Environ. Health*., **65(3):** 16-21.

Singh, P.P., M.K. Barjatiya, S. Dhing, R. Bhatnagar, S. Kothari and V. Dhar (2001). Evidence Suggesting That High Intake of Fluoride Provokes Nephrolithiasis in Tribal Populations. *Urol. Res*., **29(4):** 238-244.

Singh, P., B. Rani, U. Singh and R. Maheshwari (2011). Fluoride contamination in Ground water of Rajasthan and its mitigation strategies. *Journal of pharmaceutical and bio-medical sciences*., **6(6):** 1-12.

Singh, B., S. Gaur and V.K. Garg (2007). Fluoride in Drinking Water and Human Urine in Southern Haryana, India. *J. Hazard. Mater*., **144:** 147-151.

Sowers, M.F.R., G.M. Whitford, M.K. Clark and M.L. Jannausch (2005). Elevated Serum Fluoride Concentrations in Women Are Not Related to Fractures and Bone Mineral Density. *J. Nutr*., **135(9):** 2247-2252.

Sowers, M.F.R., M.K. Clark, M.L. Jannausch and R.B. Wallace (1991). A Prospective Study of Bone Mineral Content and Fracture in Communities with Differential Fluoride Exposure. *Amer. J. Epidemiol*., **133(7):** 649-660.

Sowers, M.F.R., R.B. Wallace and J.H. Lemke (1986). The Relationship of Bone Mass and Fracture History to Fluoride and Calcium Intake: A Study of Three Communities. *Amer. J. Clin. Nutr*., **44(6):** 889-898.

Steyn, D.G. (1948). Fluorine and Endemic Goitre. *S. Afr. Med. J*., **22(16):** 525-526.

Stormer, J.C. and I.S.E.Carmichael (1970). Villiaumite and the Occurrence of Fluoride Minerals in Igneous Rocks, *Amer. Miner*., **55:** 126-134.

Susheela , A.K., A. Kumar, M. Bhatnagar and R. Bahadur (1993). Prevalence of endemic fluorosis with gastrointestinal manifestations in people living in some North-indian villages. *Fluoride*., **26:** 97-104.

Takahashi, K., K. Akiniwa and K. Narita (2001). Regression Analysis of Cancer Incidence Rates and Water Fluoride in the U.S.A. Based on IACR/IARC (WHO) Data (1978-1992). *J. Epidemiol*., **11(4):** 170-179.

Torra, M., M. Rodamilans and J. Corbella (1998). Serum and urine ionic ûuoride. *Biol. Trace. Elem. Res*., **63:** 67-72.

Vieira, A.P., R. Hancock, H. Limeback, R. Maia and M.D. Grynpas (2004). Is Fluoride Concentration in Dentin and Enamel a Good Indicator of Dental Fluorosis. *J. Dent. Res*., **83(1):** 76-80.

Wang, S.X., Z.H. Wang, X.T. Cheng, Li, J., Sang, Z.P. Zhang, X.D. Han, L.L. Qiao, S.Y. Wu, Z.M. and Z.Q. Wang (2007). Arsenic and Fluoride Exposure in Drinking Water: Children's IQ and Growth in Shanyin County, Shanxi Province, China. *Environ. Health Perspec*., **115(4):** 643-647.

Whyte, M.P., K.Essmyer, F.H. Gannon and W.R. Reinus (2005). Skeletal Fluorosis and Instant Tea. *Amer. J. Medicine*., **118(1):** 78-82.

World Health Organization (2004). *Guidelines for drinking-water quality*, 3rd ed., vol. 1, Recommendations . Geneva, Switzerland: World Health Organisation.

World Health Organization (2006). *Fluoride in drinking water.* London, UK: World Health Organization, IWA Publishing.

Yadav, J.P. and S. Lata (2003). Urinary fluoride levels and prevalence of dental fluorosis in children of Jhajjar District, Haryana. *Indian J. Med. Sci*., **57:** 394-399.