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Apprehension of Fluoride Exposure aad its Hazardous Effects on Human and Plant : A Review

Dr Kartick Chandra Pal

1. Introduction

Fluoride (F^-) is a uni-negative ion of the most electronegative element fluorine (F) which is found widely in nature. Fluorine is 13th most abundant element on our planet (Mason and Moore 1982) Fluorine is the lightest halogen in the halogen family (Group 17 in periodic table) and the most chemically reactive non-metal. It has an oxidation state of -1(F^-) and occurs as both organic and inorganic compounds. The small size of fluorine enables it to form strong covalent bonds and to have high coordination numbers in molecular fluorides. Amongst all metal ions, Al^{3+} makes the strongest bonds to F^-, but also beryllium (Be) and calcium(Ca) binds with high affinity (Li, 2003). F^- and OH^- ions have nearly the same size and same negative charge, which means that they have the same ionic potential. Therefore, they can easily replace each other in many rock forming processes (Jones and Atkins, 1999; Saxena and Ahmed, 2001). Fluoride salts is slightly bitter in taste but it does not exhibit any color, taste or smell when dissolved in water in ppm level and therefore is not easy to determine it through physical examination.

Fluoride is recognized to be physiologically essential nutrient for the normal development and growth of human beings (Dhar and Bhatnagar, 2009). Fluoride acts as a double edged sword because, to a certain extent (as per WHO; 0.6 ppm) fluoride ingestion is useful for bone and teeth development, but excessive ingestion causes a disease known as Fluorosis. Fluoride intake through drinking water and food or through the occupational exposure in those engaged in aluminium

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Department of Chemistry, Karimpur Pannadevi College, Nadia, West Bengal

production, magnesium foundries, fluorspar processing, and superphosphate, chronic fluoride intoxication may lead to various health hazards (Hodge and Smith, 1977).

Enhanced fluoride intake through drinking water along with dietary intake significantly substantiates the total fluoride accumulation in body tissue (Pandey and Pandey, 2011). 1 ppm of fluoride in drinking water leads to a reduction in dental caries, with minor side effects such as dental fluorosis (da Cunha and Tomita, 2006; Pizzo et al., 2007). Dental fluorosis is a hypoplasia or hypomineralization of tooth enamel or dentin indicated by barely noticeable whitish striations to confluent pitting and staining produced due to the chronic ingestion of excessive amounts fluoride during the developing period of teeth (Horo-witz, 1986).

Increased bioaccumulation of fluoride in bone causes skeletal fluorosis which leads to severe and permanent bone and joint deformities with pain and stiffness in the joints. WHO (World Health Organisation) (2011) has prescribed the range of fluoride from 0.6 to 1.5 mg/L in drinking water as suitable for human consumption. BIS (Bureau of Indian Standards) (2009) has set a desirable range of 0.6 to 1.2 mg/L fluoride in drinking water with the maximum permissible limit of 1.5 mg/L. But in areas with warm climate, the fluoride concentration in drinking water should remain below 1.0 mg/L, whereas in cooler climates, the recommended limit may increase up to1.2 mg/L (WHO, 1991). This is due to higher water consumption in warmer climates as a result of higher perspiration (Yadav et al., 2009). In tropical countries, the places like Ghana, people consume 3 to 4 liters of water which is higher than the WHO estimate of 2 l/adult/day (Apambire et al., 1997). Therefore fluoride intake and its harmful effects are more relevant in the context of India compared to Western countries, where the fluoridation of water is, instead, recommended to help prevent dental caries (Teotia and Teotia, 1991).

Prolonged fluoride ingestion in human body through highly fluoride contaminated drinking water causes the diseases named fluorosis which is hard to cure. Therefore fluoride contamination in ground is of high concern because constitutes 97% of total global freshwater, and in many regions, groundwater sources constitute the single largest available supply of fresh drinking water (WHO 2004). Again, it is found in many studies that the fluoride concentration increases with the depth to a certain extent. There are basically three types of fluorosis namely, (i) Dental Fluorosis, (ii) Skeletal fluorosis (iii) Non-skeletal fluorosis. Dental fluorosis, a hypoplasia or hypominarilation of tooth enamel or dentin produced due to the chronic ingestion of excessevie amounts fluoride during period when teeth are developing ranges in intensity from barely noticeable whitish striations to confluent pitting and staining (Horowitz, 1986). Skeletal fluorosis leads to severe and permanent bone and joint deformities causing pain and stiffness in the joints and cripples a person. Skeletal fluorosis may occur when fluoride concentrations in drinking water exceed 4–8 mg/L (Teotia and Teotia,1988). Other non-skeletal health disorders that occur due to high fluoride intake through drinking water are muscle fibre degeneration, low haemoglobin levels, deformities in RBCs, excessive thirst, headache, skin rashes, nervousness, depression, urinary tract malfunctioning, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, repeated abortions or still births, male sterility, etc (Meenakshi and Maheshwari, 2006).

Fluoride is absorbed by plant roots (Kamaluddin and Zwiazek, 2003; Pant et al., 2008) and then transported via xylematic flow to the transpiratory organs, mainly leaves, where it can be accumulated with adverse effects. Certain physiological processes are known to be markedly affected by fluoride, including decreased plant growth, chlorosis, leaf tip burn and leaf necrosis (Miller et al., 1999; Elloumi et al., 2005; Mcnulty and Newman, 1961) This fluoride may affect the biochemical ratio of the plant body (Yang and Miller, 1963). The toxic effect of fluoride on pigments like chlorophyll and some secondary metabolites like sugar, ascorbic acid, amino acids and proteins are well documented (Elloumi et al., 2005; Mcnulty and Newman, 1961; Yang and Miller, 1963; Horvath et al., 1978; Verma and Dubey, 2001; Kim et al., 2003; Kundu and Mondal, 2010).

This chapter is designed to provide an overview of the key factors that are accountable for fluoride contamination including the problems caused by such exposure both to human and plant body. This review emphasized on the fluoride pollution scenario in different part of the world and india, the source and occurrence of fluoride in the environment, source of fluoride in human body and its metabolism and accumulation of fluoride and its effect on plants.

2. Fluoride pollution scenario:

2.1 *Fluoride pollution in the world*

Worldwide, more than 200 million people (including 70 million in India and 45 mil-lion in China) from 28 tropical countries are suffering from dental, skeletal and/or non-skeletal fluorosis (Yang et al., 2003). According to UNICEF, fluorosis is endemic in at least 25 countries around the world with the highest prevalence rates in India, China and Africa (Mahapatra, 2007).

2.2Fluoride pollution in India and West Bengal

Endemic fluorosis is prevalent in India since 1937 (Shortt et al., 1937). Of the 85 million tons of fluoride deposits on the earth's crust, the contribution of India is 12 million (Teotia and Teotia, 1994). Naturally, in India fluoride contamination is widespread and intensive. Indians are living in about 200 districts of 20 states in endemic areas of fluorosis and are at risk of developing fluorosis (Susheela, 2005). Over 66 million of the total populations in India are consuming drinking water containing elevated levels of fluoride (FRRDF, 1999). More and more fluoride affected areas are being discovered regularly in different parts of the country. In India, fluoride level in ground water varies substantially in different areas (Dhar and Bhatnagar, 2009). Fluoride concentration as high as 86 mg/L, has been reported from Motipura village of Haryana, India (Garg et al., 2009). 50-100% districts of various states like Andhra Pradesh, Tamil Nadu, Uttar Pradesh, Gujarat and Rajasthan are fluoride affected (RGNDWM, 1993). Some regions in north western and southern India are affected with fluorosis (Agarwal et. al., 1997; Yadav et al., 1999). Evapo-transpiration of groundwater with residual alkalinity raises the fluoride concentration in many parts of India (Jacks et al., 2005). Due to long residence time higher fluoride content was observed in deeper aquifers of Maharashtra than shallow groundwater (Madhnure et al., 2007). The granitic rocks in Nalgonda district of Andhra Pradesh contain average fluoride concentration of 1440 mg/Kg which is much higher than the world average fluoride concentration of 810 mg/Kg (Wedepohl, 1969). The mean fluoride content in Hyderabad granites is 910 mg/Kg (Rao et al., 1993). In West Bengal, excess fluoride in groundwater has been detected so far in 43 blocks spread over seven districts, viz. Purulia, Birbhum, Bankura, Malda, South Dinajpur, North Dinajpur and South 24-Parganas (PHED report, 2009). Fluoride contamination of ground water in the State of West Bengal was first detected during 1996 at Nasipur area of Nalhati-I Block in the district of Birbhum. Basaltic rocks are the source of fluoride in this region (Patra et al., 2010). There after many reports on fluoride contamination came forth from different parts of West Bengal (Gupta et al., 2006; Chatterjee et al., 2008; Kundu and Mandal, 2009 and Ghosh et al., 2010). According to the report of Geological Survey of India (GSI), Precambrian terrain with fractured/shear zones are the possible locale for elevated level of fluoride in ground water in parts of Purulia and Bankura Districts. GSI also reported that the fluoride contamination occurs mostly within tube wells tapping ground water in the basaltic rocks of Rajmahal trap. The dug wells, ponds and tube wells tapping water from alluvium sediments generally contain fluoride beyond 1.50 mg/L.

3. Sources of fluoride:

3.1 Natural source

Surface rocks, deposits and the oceans are the main sources of fluoride in the biosphere. According to Smith and Hodge (1979), fluoride is the 13th and according to Bell et al. (1970), 17th most abundant element in the earth’s crust in igneous and sedimentary rocks. Its natural concentration is estimated to be 0.06 to 0.09% in the upper layer of lithosphere (Fawell et al., 2006) and the average crustal abundance is 300 mg/Kg (Tebutt, 1983). Hundreds of minerals are known to contain fluoride. The fluoride content in these minerals varies from as high as 73% in the rare mineral griceite (LiF) to many others with less than 0.2% (Weinstein and Davison, 2004). Fluoride occurs in the form of minerals such as biotite, muscovite and hornblende etc. which usually originate from micas, apatite and tourmaline. Fluorite (fluorspar) (CaF2), fluorapatite [$3Ca_3(PO4)_2$ Ca(F,Cl_2)], fluormica (phlogopite) [$KMg_3(Si_3Al)O10(F,OH)_2$], apatite [$CaF_2.3Ca_3(PO_4)$], cryolite [Na_3AlF_6], epidote [$Ca_2Al2(Fe^{3+;}Al)(SiO_4)(Si_2O_7)O(OH)$], sellaite [$MgF_2$], topaz [$Al_2SiO_4(F,OH)_2$], phosphorite [$Ca_3(PO_4)_2$], tremolite[Ca2Mg5Si8O22(OH)2], biotite [$K(Mg,Fe)_3$ $AlSi_3O10(F,OH)_2$], hornblende [$Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$], phosphorite [$Ca_3$ $(PO_4)_2$], certain varieties of mica etc. are the fluoride bearing minerals (Kundu et al., 2001; Mohapatra et al., 2009). Similar occurrence of fluoride both in igneous and sedimentary rocks is reported (Deer et al., 1983).

Soil fluoride is derived from the minerals by weathering and actions of microorganisms, plants and animals. Deposition on the surface from atmosphere by rainfall or by flooding soil fluoride is also derived (Weinstein and Davison, 2004). Fluoride content in soil may vary from under 20 to several thousand mg/Kg (Davison, 1983). Heavier soils tend to have higher concentration of fluoride than sandy soils as most of the fluoride is associated with clay fraction (Weinstein and Davison, 2004). Fluoride content in the soil concentration can vary over a short distance due to variation in underlying parent rocks (Geeson et al, 1998).The fluoride content of soil is dependent mainly on the mineralogical composition of the soil, inorganic fraction, the extent of clay and pH. Mobility of fluoride in soil is influenced mainly by pH and formation of aluminium and calcium complexes (Pickering, 1985). It has been found from most of the researches that in soils with pH< 6 fluoride is mainly bound in complexes with either aluminium or iron (e.g. AlF_2^+, AlF_3, AlF_4^-, FeF_2^+, FeF_3) (Elrashidi and Lindsay, 1985).

Fluoride comes to the aqueous solution due to the weathering process of rocks and minerals through anthropogenic activities and leaching. The fluoride concentration in ground water depends on geology, chemistry, physical characteristics and climate of the area. As evaporative concentration, change in water chemistry and leaching concentrates the fluoride, higher fluoride concentrations tend to occur in arid regions (Weinstein and Davison, 2004). Although the solubility of fluoride bearing minerals are low under normal conditions but the slow kinetics for a long time often enhances leaching and enhancement of fluoride in ground water (Hem, 1989). Dissolution rates of fluorite minerals increase under alkaline condition in the range of specific conductivity between 750 and 1750 µS/cm (Saxena and Ahmed, 2001).

Air borne fluoride arises both from natural and anthropogenic sources. However, a small fraction of the total fluoride exposure arises from air (USNRC, 1993). Fluoride is released into the atmosphere on a large scale due to volcanic ash, dust, industrial production of phosphate fertilizers, coal ash from the burning of coal, smoke in the brick field and volcanic activities. Amongst these aerial fluoride sources, volcanic activities have long been known to be the largest natural source as volcanic rocks are often enriched in fluoride. Magma soluble Hydrogen fluoride gas comes out partially during eruptive activity (D'Alessandro, 2006). During volcanic eruption the aerial emission of fluoride in the form of volcanic ash is deposited on the surface by fall out of particulate fluorides and during rainfall. Due to the high solubility of volcanic ash in rain water the risk of fluoride contamination in groundwater is very high. Percolating rainwater carries this fluoride from the soil surface the groundwater zone. Fluorosis in livestock and humans was identified long ago in 1978 from the Laki eruption (Fridriksson, 1983; Steingrímsson, 1998). Fluoride contaminations in groundwater of Kenya have been found to be caused by volcanic eruption (Gaciri and Davies, 1993). Volcanoes are important source of organo fluorides including some CFCs. These have been shown to contain gaseous fluoride compounds like hydrogen fluoride (HF), ammonium fluoride (NH_4F), silicon tetrafluoride (SiF_4), ammonium fluorosilicate ($(NH_4)_2SiF_6$),sodium fluorosilicate (Na_2SiF_6), potassium fluorosilicate (K_2SiF_6) and potassium fluoroborate (KBF_4) (Weinstein and Davison, 2004). In addition volcanoes erupt some solid fluorides like sodium fluoride (NaF), potassium fluoride (KF), magnesium fluoride (MgF2) and calcium fluoride (CaF2) (Roholam, 1937).

3.2 ***Anthropogenic sources:***

Many types of industrial activities activities result in the emission and deposition of gaseous and particulate fluorides in the environment. Drying, grinding and calcining of fluoride containing minerals, their reactions with acids, smelting and electrochemical reduction of metals using fluoride containing fluxes or electrolytes, firing of brick or ceramic materials, high temperature melting of raw materials in glass manufacture and the use of fluoride containing chemicals for cleaning, electroplating and etching in various process etc. are the basic industrial activities that results in fluoride pollution (Weinstein and Davison, 2004). Aluminium smelting (Haidouti, 1991), cement production and ceramic firing (WHO, 2002), HF alkylation in petroleum refining (Weinstein and Davison, 2004) releases a high amount of fluoride into the environment. Fluorspar [CaF_2], fluorapatite [$Ca_5(PO_4)_2F$] and cryolite [Na_3AlF^6] are the major minerals exploited commercially. Fluorspar is as source of hydrofluoric acid, which is a feed chemical for the production of thousands of organic and inorganic fluorine compounds, including insecticides, pharmaceutical and fabric conditioners. For example, about 80% is used for hydrofluoric acid production and the rest is used as a flux in a variety of industries in USA (Weinstein and Davison, 2004). The deposits of apatite mineral that are contained in the rock phosphates are mined for the production of phosphorus and phosphate fertilizers.

Phosphate containing fertilizers enhances the fluoride content in soil and groundwater (Farooqi et al., 2007). Phosphatic fertilizers contain remarkable amount of fluoride for example superphosphate (2750 mg of F/Kg), potash (10 mg of F /Kg) and NPK (Nitrogen Phosphorous Potassium) (1675 mg of F /Kg) (Srinivasa Rao, 1997). In agricultural areas successive use of these fertilizers results in higher fluoride concentration in groundwater (Young et. al., 2010). If an agriculture field of 1 ha receives 10 cm of irrigation water containing 10 mg/L of fluoride, then the soil can obtain 10 Kg of fluoride (Datta et al. 1996).

Fly ash from the combustion of fossil fuels emits high fluoride in atmosphere. Due to the combustion of coal especially from power plants more than 100 to 150 million tons of fly ash is produced worldwide annually (Prasad and Mondal, 2006). Inappropriate disposal of this fly ash ultimately leaches the fluoride into groundwater. Beside these, the combustion of coal is also a potential source of fluoride emissions in industrial processes (Weinstein and Davison, 2004). Brick kilns which use coal for burning is source of fluoride (Jha et al., 2008), but the amount of pollution depends on the type of coal being burnt as the fluoride content in coal may vary from 40 to 295 mg /Kg (Churchill et al., 1948).

4. Source of fluoride in human body:

4.1 ***Fluoride in Water, Food and vegetables***

As discussed before, water is the main source of daily fluoride ingestion in human body. Permissible upper limit for fluoride in drinking water recommended by WHO (2011) is 1.5 mg/L. Food is the next important source of fluoride in human body. Most food derived from plant or animal, contain fluoride ion at least in minute amounts. Local food habit determines the contribution of food to the total daily intake. Fluoride enters into the food stuffs from soil and water used for irrigation. Some foods concentrate additional fluoride from boiling, processing or contamination. Fluoride levels may vary widely even between samples of the same kind of food. Foodstuffs like vegetables and fruits normally contain fluoride at low concentration (0.1-0.4 mg/Kg). Higher levels (up to 2 mg/Kg) of have been found in barley and rice (WHO, 1986). Diets with high fat level increase deposition of fluoride in bone enhancing the toxicity (USDHHS, 1991). There is a little difference between fluoride contents of leaf or root vegetables and cereals with the exception of spinach which is unusually enriched in fluoride (Gautam et al., 2010). Potato peelings can contain up to 75% of the total fluoride in the whole tuber. The food items carrying high levels of fluorides are rice, wheat, cereal, maize, pulses, cabbage, cucumber, tomato, brinjal, lady's finger, beetroot, potato, onion and sweet potato, banana, grapes, mango, apple, coconut, ground nut, mustard, mutton, beef, pork, fish, egg etc. Food Fluoride concentration in % given in the parentheses are (Mahapatra, 2007): Banana (2.9 - 4.58), Grapes (0.84 - 1.74), Mango (3.7 - 8.18), Apple (5.7 - 5.22), Vegetables (9.0 - 45.0), Cereals (16.0 - 52.0), Pulses (6.0 - 22.0), Mutton (3.0 - 3.5), Fish (1.0 - 6.5), Wheat (5.9), Rice (1.7 - 2.23), Maize (5.6), Cabbage (3.3), Tomato (3.4), Brinjal (1.2), Lady's finger (4.0), Potato (2.8), Onion (3.7).

4.2 ***Fluoride in Beverages***

Tea, coffee, coconut water, beer and wine etc. contain higher levels of fluoride. Tea is enriched with fluoride and about two thirds of the fluoride in leaves is soluble in the beverage (Fung et al., 1999). Each cup of tea may contain 0.3 - 0.5 mg of fluoride. Bottled beverages, have a variable and some have high content of fluoride. Fluoride concentrations in different beverages are (Mahapatra, 2007):

Tea (Dry leaves) 39.8-68.5, Tea infusion 18.13-56.19 (1 gm boiled for 5 min. in 125 ml. water), Tea infusion (1 gm in 125 ml of hot water) 11.13-37.34, Aerated drinks 0.77-1.44, Coconut Water 0.43-0.60.

4.3 ***Fluoride in other sources***

Spices like Almond, Garlic, Ginger, Coriander, Cumin Seeds, Garlic, Turmeric, Black Salt etc contain fluoride. Fluoride concentrations (%) in Coriander, Cumin Seeds, Ginger, Garlic, Turmeric are 2.3, 1.8, 2.0, 5.0 respectively (Mahapatra, 2007). Nuts and oilseeds such as almond, coconut, mustard oil and groundnut also have higher concentration of fluoride. Fluoride concentrations in % in Almond, Coconut, Mustard Seeds, and Groundnut are 4.0, 4.4, 5.7, and 5.1 respectively (Mahapatra, 2007). Significant sources of ingested fluoride are toothpaste in very young children (who tend to swallow most of their toothpaste). The fluoride content in raw material used for the manufacture of toothpaste can be as high as 800-1000 ppm which may range from 1,000 to 4,000 ppm in fluoridated brands (Mahapatra, 2007). Prolonged use of certain drugs leads to chronic adverse effects of fluoride, e.g., sodium fluoride for treatment of osteoporosis, Niflumic acid for the treatment of rheumatoid arthritis, fluoride mouth rinse (Proflo) for the stronger tooth etc. (Kadu et al., 2012).

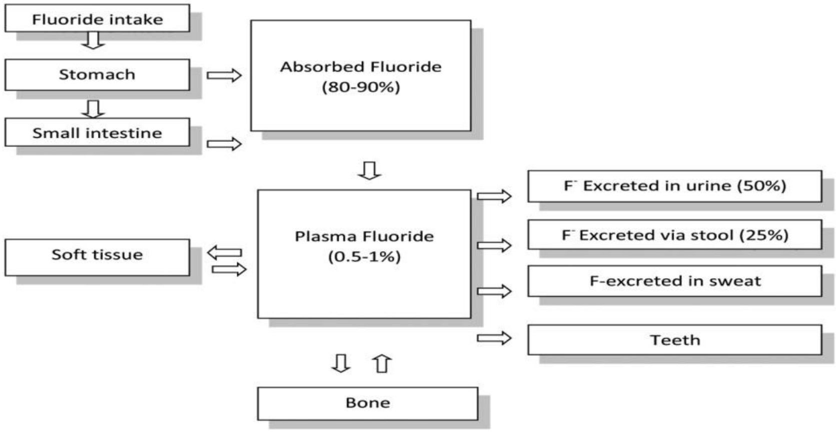
5. Metabolism of Fluoride:

Fluoride can be incorporated in human body through gastrointestinal tract after ingestion, following inhalation, and through the skin. Inhalation and skin absorption are not so important except some occupational exposure situations.

The overall metabolism of fluoride is a three steps process, namely, absorption, distribution, and excretion. In absorption process, the majority of the ingested fluoride is absorbed from the stomach and small intestine into blood stream (Whitford, 1990). This absorption process depends mainly on the solubility of the ingested fluorides, the pH in the digestive system and the presence of compounds in the diet that can complex fluoride (Weinstein and Davison, 2004; Buzalaf and Whitford, 2011). Just after absorption the fluoride levels increase quickly to reach a peak concentration within 20-60 min. as the ions pass the central component, plasma, before being distributed and eliminated (Buzalaf and Whitford, 2011). Usually within 3-6 hours fluoride level decline rapidly due to the uptake of fluoride by hard tissue and efficient removal of fluoride by the kidneys (Whitford, 1994). Fluoride is removed from plasma by urinary excretion or by incorporation into mineralized tissues. The distribution process is understood by Tissue-water to plasma-water ratio (T/P) index. Fluoride intoxication is much effective in case of children as in children less than three years of age only about 50% of total absorbed amount is excreted, where as in adults and children over 3 years about 90% is excreted (Kadu et al., 2012). Fluoride may also pass through the placenta and a minute amount of it is present in saliva, sweat, and milk (Buzalaf and Whitford, 2011).

The metabolism of fluoride can be represented as (Mahapatra, 2007):

Fig. 1



Metabolism of fluoride in human body

6. Effect of fluoride on human:

6.1 *Dental fluorosis*

Dental fluorosis, a hypoplasia or hypominarilation of tooth enamel or dentin produced due to the chronic ingestion of excessevie amounts fluoride during period when teeth are developing ranges in intensity from barely noticeable whitish striations to confluent pitting and staining (Horowitz, 1986). The severity of dental fluorosis depends on when and for how long the over exposure of fluoride occurs (Den Besten, 1994).

Teeth are composed of a protein matrix (poly-proline) intimately mixed with an inorganic mineral hydroxy-apatite ($3Ca_3(PO4)_2.Ca(OH)_2$). Fluoride ion (F^-) forms small amounts of fluorapatite through an ion-exchange with the hydroxyl ion (OH^-) in the mineral phase according to the reaction (NHMRC, 1999):

$$3Ca_3(PO_4)_2.Ca(OH)_2 + x\,F \rightleftharpoons 3Ca_3(PO_4)_2.Ca(OH)_{2-x}.CaF_x + xOH^-$$
$(x < 0.1)$

As a result of the substitution of fluoride for hydroxyl ion, the volume of the unit cell decreases due to more efficient ionic packing resulting in denser lattice leading to stronger, acid resistant tooth surface supporting the anti-caries effect of fluoride in drinking water (Aoba, 1997). Disodium monofluorophosphate

(MFP = Na_2FPO_3), the most commonly used fluoride dentifrice, may ion-exchange the FPO_3^{2-} ion with the isostructural phosphate ion (PO_4^{3-}) according to the reaction (NHMRC, 1999):

$$3Ca_3(PO_4)_2.Ca(OH)_2 + yFPO_3^{2-} \rightleftharpoons 3Ca_3(PO4)_{2-y}(FPO_3)y.Ca(OH)_2 + y\,PO4^{3-}$$
$$(y < 0.1)$$

But MFP can also behave as an indirect fluoride source as it is degraded to fluoride ion by oral bacteria utilising general purpose phosphatases present in dental plaque (Whitford, 1990). Both the ion-exchange processes lead to the incorporation of fluoride in teeth, principally in the outer enamel layer.

But at the time of tooth and enamel development, chronic exposure to fluoride causes increased mineralization with the loss of matrix proteins resulting in dose-related disruption of enamel mineralization, excessive retention of enamel proteins, and increased porosity (Aoba and Fejerskov, 2002). Although it is has not yet been confirmed, some researchers have suggested that chronic fluoride exposure causes aged dentin to crack more easily (Doull et al., 2006).

The appearance of white horizontal striations on the tooth surface or opaque patches of chalky white discolorations indicates a mild dental fluorosis (Susheela, 2003; Rao, 2003). The opaque patches can become stained yellow to brown or even black, and increased tooth porosity leads to structural damages, such as pitting or chipping in case of moderate to severe forms of fluorosis (Rao, 2003). Drinking water is the most important factor of dental fluorosis and it has been reported that at least 60 percent of the population are affected where drinking water contains more than 2 mg/L fluoride (Fordyce et al., 2007) reaching upto 100% of the population where fluoride content is 6 mg/L in drinking water. The symptoms of dental fluorosis that appears in different stages are – (i) Dull white or yellow patches and loss of shine; (ii) Yellow white spots turning brown in horizontal streaks; (iii) Brown streak at the tip, in the middle or in the upper part of teeth indicating a child to be exposed to high fluoride in food or water or both up to the age of 2 years, from the age of 2 years up to 4 years and from the age of 4 years up to 6 years and after respectively; (iv) Teeth turning black with pitting and even to be flaked and disfigured (v) Teeth loss at an early age; (vi) Delayed eruption of teeth.

6.2 *Skeletal Fluorosis*

Skeletal fluorosis occurs due to the consumption of drinking-water containing high levels of fluoride. Exposure to additional sources of fluoride such as high-fluoride coal can also be a potential reason for it. Climate, water consumption, nutritional status and diet, additional sources of fluoride and exposure to other substances that modify the absorption of fluoride into the body etc. are the determining factor of skeletal fluorosis. Occupational exposure to higher concentrations of fluoride in the air may also be a cause of skeletal fluorosis. Crippling skeletal fluorosis can result in osteosclerosis, ligamentous and tendinous calcification and extreme bone deformity. Crippling skeletal fluorosis can occur when the drinking water contains more than 10 mg/L of fluoride (Boyle, D. R. and Chagnon, 1995; Reddy and Prasad, 2003).

Skeletal fluorosis is characterized by increase in bone density leading to thickness of long bones and calcification of ligaments. Fluoride accumulated in bone has a biological half-life of several years in this tissue. It is well estabilished that fluoride exposure disrupts the synthesis of collagen and leads to the breakdown of collagen in bone (Susheela and Jha, 1981; Susheela and Mukerjee, 1981; Sharma, 1982). Fluoride stimulates bone growth, although it does not directly stimulate osteoblastic activity, and in vivo, there is a lag time (months to years) before the onset of osteoblastic activity (NHMRC, 1999). The enhanced stability due to replacement of hydroxyl ion by fluoride ion renders the skeletal structures more resistant to osteoblastic resorption, which alters the normal bone remodeling cycle. Because bone remodeling is an integral part of skeletal health, the two properties of fluoride, increased formation of bone and a greater resistance to resorption and remodeling leads to the production of abnormal bone (NHMRC, 1999). In an acute case, fluoride promotes the development of bone cancer (Hrudey et al, 1990; Mahoney, 1991).

Although the mechanism that leads to skeletal fluorosis are little understood, the stages of development are well-documented (Hileman 1988; Rao 2003; Susheela 2003; Edmunds and Smedley 2005). In early stages, the symptoms include pain and stiffness in the backbone, hip region, and joints, along with increased bone density (osteosclerosis). With progress of this condition, various ligaments of the spine can also become calcified and ossified and in advanced stages, fluorosis produces neurological defects, muscle wasting, paralysis, crippling deformities of the spine and major joints, and compression of the spinal cord (Ozsvath, 2009). Severe pain and stiffness in the backbone, stiffness in joints, rigidity in the hip region, increased thickening and density of bone, besides calcification of ligaments, constriction of vertebral canal and inter-vertebral foramen pressure on nerves, deformities in limbs, hunch back, paralysis, muscular wasting and premature aging are the symptoms of skeletal fluorosis.

6.3 ***Non-skeletal Fluorosis***

Other non-skeletal health disorders that occur due to high fluoride intake through drinking water are muscle fibre degeneration, low haemoglobin levels, deformities in RBCs, excessive thirst, headache, skin rashes, nervousness, depression, urinary tract malfunctioning, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, repeated abortions or still births, male sterility, etc (Meenakshi and Maheshwari, 2006).

As fluoride is excreted in urine through the kidneys, it may affect the functioning of kidneys. A few studies reported that chronic ingestion of fluoride can have non-carcinogenic effects on the kidney with the incidence of kidney stones (Doull et al., 2006).

Several researchers studied the effects of fluoride on the endocrine system found a relation between endemic goiter and fluoride exposure in human populations (e.g., Steyn, 1948; Desai et al., 1993; Jooste et al., 1999) although the exact causal mechanism for effect of fluoride on the thyroid has not yet been established (Doull et al., 2006). A number of studies conducted in China have suggested that dietary fluoride ingestion has an adverse effect on the intelligence of children (e.g., Zhao et al., 1996; Xiang et al., 2003; Wang et al., 2007). Trivedi et al. (2007) found a statistically significant inverse relationship between the intelligence quotient (IQ) and urinary fluoride levels of school-aged children. Although the actual mechanism occuring in human brain is not known but, according to the suggestion of Guan et al. (1999), changes in the membrane lipids may be the cause of alteration of phospholipids and ubiquinone in the brain of rats due to chronic fluoride ingestion. Several other studies also comply with this fact (Trivedi et al., 2007; Ge et al., 2010).

Fluorides are known to cause chromosome damage and mutations and are therefore considered possible carcinogens. Several studies have found evidence for a relationship between fluoride exposure and specific cancers prevalence, for example, uterine cancer (Tohyama 1996; Yang et al. 2000) and colon cancer (Yang et al. 2000; Takahashi et al. 2001). According to the study of Freni (1994), there is a association between increasing fluoride concentra-tions and decreasing birth rates in human being. The results of other studies suggest that high fluoride ingestion on males have an effect on the morphology and mobility of sperm (Chinoy and Narayana, 1994), or the levels of testosterone, follicle-stimulating hormones and inhibin-B (Susheela and Jethanandani, 1996; Ortiz-Perez et al., 2003).
In cases of acute fluoride toxicity, a variety of gastrointestinal effects, including nau-sea, vomiting, diarrhea and abdominal pain have been reported (Penman et al. 1997; Sidhu and Kimmer 2002). Studies involving animal reveal that fluoride can stimulate the secretion of stomach acid, reduce blood flow away from the stomach lining, and even cause the death of gastrointestinal tract epithelium cells (Doull et al., 2006). Adverse gastrointestinal symptoms are common in areas of endemic fluorosis with poor nutrition (Gupta et al., 1992; Susheela et al., 1993).

7. Accumulation of fluoride and its effect on plants:

7.1 *Accumulation*

The fluoride concentration in plant leaves varies from <1 to several thousand mg/Kg (Weinstein and Davison, 2004). Plants usually have from <2 to about 20mg/Kg fluoride in the leaves growing in soils containing about 600 to 800 mg/Kg fluoride (Weinstein, 1977). Leaf concentration may reach several thousand mg/ Kg where the soil fluoride content is much higher such as in fluospar mine waste. Cooke et al. (1976) reported concentrations from 280 to over 4000 mg/Kg in arrange of grass and legume species.

The controlling influence of concentration of fluoride in the soil solution has been established by growing plants in aqueous culture media. When groundwater is used in irrigation, the vegetables grown also incorporate fluoride. Fluoride is absorbed by plant roots (Kamaluddin and Zwiazek, 2003) and then transported via xylematic flow to the transpiratory organs, mainly leaves, where it can be accumulated with adverse effects. The fluoride content of the leaves increases approximately in proportion to the concentration bathing the roots in aqueous culture media (Cooke et al. 1978). The concentration of fluoride in plant increases with time and is highest in the roots and is progressively lower in younger leaves that are more distant from the root (Weinstein and Davison, 2004).The concentrations differ from species to species.

Plant may also uptake fluoride from air when gases containing fluoride (mainly HF) deposited on leaf surfaces. Cuticular uptake of plant leaves is important in the case of plants in dry habitats (Areas et al., 1980). Boundary layers, nature of the surfaces and stomatal apertures of plant leaves determines the uptake of fluoride by plant. The quantitative relationship between exposure to HF and the fluoride content of vegetation were examined by Hitchcock et al. (1971). The simplified dose rate equation (NAS, 1971; Weinstein, 1977) is:

$$\Delta F = KCT$$

Where is the change in fluoride concentration (mg/Kg), K= accumulation coefficient, C= the concentration of hydrogen fluoride (μg/m3) and T= duration of exposure (days). The hydrophilic pores of cuticles through which low molecular weight solutes in water solutions permeate are lined with fixed negative charges, and therefore cations can permeate but not the anions like fluoride (F-) (Marschner, 1995). But probably after weathering or insect damage fluoride penetrate cuticles (Davison, 1982). Spray of

NaF solution applied to leaves can cause necrosis identical to that caused by HF. Heavy particulate deposits on wet leaf surface may also cause visible injury (McCune et al., 1965).

7.2 ***Effect***

Certain physiological processes are known to be markedly affected by fluoride, including decreased plant growth, chlorosis, leaf tip burn and leaf necrosis (Miller et al., 1999; Elloumi et al., 2005; Mcnulty and Newman, 1961) This fluoride may affect the biochemical ratio of the plant body (Yang and Miller, 1963). The toxic effect of fluoride on pigments like chlorophyll and some secondary metabolites like sugar, ascorbic acid, amino acids and proteins are well documented (Elloumi et al., 2005; Mcnulty and Newman, 1961; Yang and Miller, 1963; Horvath et al., 1978;
Verma and Dubey, 2001; Kim et al., 2003; Kundu and Mondal, 2010). Fluoride causes reduction in photosynthetic pigment concentration (Lal and Ambasht, 1981), inhibition of photosynthesis (Darral, 1989) and changes in carbohydrate metabolism (Asthir et al., 1998). The symptoms of fluoride injury is manifested by an initial chlorosis of the leaves (Hitchcock et al.,1962) which is characterized by a yellow to brown bleaching of the tips and upper margins of plant leaves, with subsequent tissue collapse, cupping, and other distortions (Hitchcock et al.,1962). Although the precise mechanisms by which fluorides induce injury in plants is not known but the affects concerning the alteration of plant cell ultrastructure and physiological processes by fluoride is well studied (Wei and Miller, 1972; Thomas and Alther, 1966). Effects of fluoride on photosynthesis, respiration, RNA structure, and on cellular metabolites involved in the reactions of certain enzymes are well documented (Brandt and Heck, 1968; Lee et al., 1965; Chang, 1968; Yang and Miller, 1963).

8. Summery

Worldwide fluoride pollution is of severe concern alongwith our country, India. Excessive ingestion of fluoride in human body for a long period causes dental fluorosis, skeletal fluorosis, and non-

skeletal fluorosis like gastrointestinal, neurological, and urinary problems. The distribution of fluoride in the environment is uneven and largely is believed to derive from geogenic causes. The natural sources of fluoride are the minerals like fluorite, fluorapatite, and cryolite; whereas anthropogenic sources include coal burning, oil refining, steel production, brick-making industries, and phosphatic fertilizer plants, among others. The fluoride compounds that occur naturally in drinking water are almost totally bioavailable (90%) and are completely absorbed from the gastrointestinal tract. As a result, drinking water is considered to be the potential source of fluoride that causes fluorosis. Because the bioavailability of fluoride is generally reduced in humans when consumed with milk or a calciumrich diet, it is highly recommended that the inhabitants of fluoride-contaminated areas should incorporate calcium-rich foods
in their routine diet. Fluoride can also be accumulated in plants when the soil, fertiliger or irrigational water contains excessive amount of fluoride. The accumulation occurs via xylematic flow which in turn shows a toxic effect on chlorophyll and some secondary metabolites like sugar, ascorbic acid, amino acids and proteins. The effect of fluoride on plant may be visible due to some yellow to brown bleaching of the tips with subsequent tissue collapse, cupping, and other distortions.

Therefore some remedial measures like supply of fluoride free drinking water and awareness of people residing in fluoride prone region is required.

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