



Role of Fluoride on Soil, Plant and Human Health: A Review on Its Sources, Toxicity and Mitigation Strategies

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Authors' contributions

The work was carried out in collaboration among all authors. Author GS designed the study, wrote the protocol and wrote the first draft of the manuscript. Authors NC and AGB managed the graphical representation of the study. Author BP managed the literature searches. Author GCH gave the idea about the study. All authors read and approved the final manuscript.

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ABSTRACT

In recent scenario, fluorosis is now going to be a severe problem throughout the globe due to toxic effects of fluoride (F) on both plants, animals and humans. Natural geological sources and increased industrialization have contributed greatly to the increasing incidence of F-induced human and animal health issues. The toxic effects of high doses of F may adversely affect human health by causing skeletal fluorosis, dental fluorosis, bone fractures, the formation of kidney stones, decreased birth rates, weakening of thyroid functionality and impair intelligence, particularly in

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children. High concentrations of F in soil may seriously threaten the life of plants, devastate soil microbial activity, disrupt the soil ecology and causes soil and water pollution. Hydrogen fluorides (HF) in gaseous form accumulated in the leaves of sensitive plants against a concentration gradient and HF mainly damages the plant by entering into its body in the form of gas and affects a variety of plant physiological processes. In this review we discuss about the effect of fluoride toxicity on plant, human and soil health and its mitigation strategies.

Keywords: Fluoride; toxicity; soil; plant; human; ground water.

1. INTRODUCTION

Compared to soil pollution by heavy metals and organic pollutants, soil pollution by fluorides is usually ignored. In fact, fluorine-contaminated soil has an adverse effect on human, animals, plants, and surrounding environment [1]. In 1886, French scientist Henri Moissan discovered that fluoride (F^-) is a uni-negative ion of fluorine (F). The anthropogenic activities like use of phosphatic fertilizer and pesticide, sewage and sludge and depletion of groundwater table have also been indicated to cause an increase in F^- concentration in groundwater [2]. One of the most important toxicological and geo-environmental issues in India is the problem of high fluoride concentration in ground water sources [3]. The fact that the problems associated with the excess fluoride in drinking water is highly endemic and widespread in countries like India prompted many researchers to explore quite a good number of both organic and inorganic materials adopting various processes from coagulation, precipitation through adsorption, ion exchange etc. The element is influential to plants and particularly in animal nutrition because of the harmful effect that it may exert when ingested even in small doses. Compounds with the element fluorine are extensively utilized in almost every biological industry, and pollution by the fluoride ion (F^-) is widespread in the environment. Excessive F intake may adversely affect the health of human, animals, and plants [4]. The high concentration of fluoride ion (F^-) in the environment is toxic for all living organisms. Prolonged contact with F leads to physiological, biochemical, and molecular changes in plants. F toxicity has a deleterious effect on plant metabolic activity, low nutrient uptake, seed germination, growth and productivity, biomass accumulation, photosynthesis, enzymatic activities, protein synthesis, gene expression patterns and reactive oxygen species (ROS) production. It has also been shown to alter the function of various antioxidants, leading to oxidative stress in plants. High F accumulation in plants could also directly or indirectly affect various enzymatic activities,

respiration and photosynthesis without showing any visible symptoms of injury.

Worldwide, more than 200 million people (including 70 million in India and 45 million in China) from 28 tropical countries are suffering from dental, skeletal and/or non-skeletal fluorosis [5]. The widespread prevalence of fluorosis, a disease caused by excess intake of F, in parts of Rajasthan, Tamil Nadu, Uttar Pradesh, Delhi, Andhra Pradesh and Madhya Pradesh suggests that the aspects of excess F intake and their associated harmful effects are more relevant in the context of India compared to most Western countries where fluoridation of water is rather recommended to help prevent dental caries [6,7] of high fluoride-contaminated groundwater is predicted for health-related risks to ~ 200 million people from 29 countries. 20 out of total 29 states of India [8] including West Bengal reported the presence of moderate to high concentration of fluoride in groundwater [9], affecting more than 65 million Indians including 6 million children [10].

2. BIOCHEMISTRY OF FLUORIDE

In the halides group of the periodic tables (group VII), among all other molecules, fluoride has the great importance due to its smallest size and most electro negativity. Although, the mechanisms of F in biological forms are remains unclear but it has the unique chemical and biochemical properties for the size and reactivity [11-13]. It is 13th most abundant element and distributed widely throughout the earth in soil, water, and food. F, a pale-yellow colored gas, has atomic number 9 and atomic weight of 18.9984 at standard temperature and pressure [14]. It has the tendency to exist in the Free State as diatomic molecules. Due to electro motivity characteristics, these can react with less electromotive elements or chemical groups. Fluoride compounds are formed when the element fluoride combines with other chemical elements. It does not occur in a free state in nature [15]. Fluoride however has many unique chemical properties. These properties had a

great impact on the special biochemical physiological effects. For this reason, F can affect the metabolism and mechanisms of action within the living system. In addition to the chemical properties and isotopic nature of fluorine has had an important impact on our understanding of the metabolism, toxicity, and therapeutic effects of fluoride. ^{19}F is one of the isotopes of F and occurs naturally. This isotope has the extremely short half-life.

3. SOURCES AND SAFETY LIMITS OF FLUORIDE

There are many different sources of F but the main sources are the weathering of rocks, industrial emissions, and atmospheric deposition [16]. The most common sources of F are mineral and geochemical stores and a large proportion of the discharge of F into subsoil water takes place through the degradation of rocks containing fluorine [17]. F is among the more abundant elements in earth crust and is present in various rocks with a range of approximately 100–1000 $\mu\text{g}/\text{mg}$, with 625 $\mu\text{g}/\text{mg}$ being a typical value. High concentrations of F are present in granites, felsic, quartz monzonites, syenites, biotite, and granodiorites. F-containing rocks such as muscovite, pegmatites, amphibolites, and biotite micas supply F to groundwater and soil by different processes such as soil forming and weathering [18]. There are also anthropogenic sources of F such as the emission of hydrogen fluoride (HF) to the air or the addition of fluoride to water with various human activities, e.g., motorization, fluoridation of drinking water supplies, industrialization, and utilization of F containing pesticides [19]. Production of phosphate fertilizers is a major industrial source of F. A substantial amount of fluorine, e.g., 3.5%, is present in fertilizer made from rock phosphate but this percentage is reduced in the manufacturing process [18]. Other anthropogenic sources for the entry of F into the earth include the current utilization of chemicals, such as phosphate manures, calcium fluoride (CaF_2), sodium fluoride (NaF), hydrogen fluoride, sulfur hexafluoride (SF_6), etc. When F is released into the air, it is carried by the wind to the surrounding soil and vegetation and contaminates them. Contamination of soil with F is basically due to utilization of F-containing fertilizers such as phosphorous fertilizers. The F content of soil commonly varies from 150–400 $\mu\text{g}/\text{mg}$ and the value may increase in heavy clay soil up to 1000 mg/kg . The contaminated soil ultimately affects human beings through direct contact, the

inhalation of vaporized soil, and the use of water contaminated with F by its passage through the soil. The use and production of phosphate fertilizers, the ceramic, zinc and steel industries, and energy plants are noteworthy sources of F pollution in the environment [20].

Fluoride is recognized to be physiologically essential nutrient for the normal development and growth of human beings 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. World Health Organization has prescribed the range of fluoride from 0.6 to 1.5 mg L^{-1} in drinking water as suitable for human consumption. Bureau of Indian Standards, 2003 has set a desirable range of 0.6 to 1.2 mg L^{-1} fluoride in drinking water with the maximum permissible limit of 1.5 mg L^{-1} [21]. The fluoride concentration in drinking water should remain below 1.0 mg L^{-1} in areas with warm climate, as well as it may increase up to 1.2 mg L^{-1} in cooler climates [22]. This is due to higher water consumption in warmer climates as a result of higher perspiration. The safe limit of F^- is considered as 0.6–1.2 mg L^{-1} according to environmental and socio-economic conditions of the Indian subcontinent and drinking water intake. But no such specific guideline values for soil, plant and animal systems available.

4. FATE AND EFFECT OF FLUORIDE IN SOIL

Soil fluoride is derived from the parent material and therefore its distribution pattern in soil is related to the process of soil formation. The lowest F content are usually present in sandy soil in relatively humid environments, while the higher concentrations of F are found in soil from weathered mafic rocks and in heavy clay soil. Most of the fluorine found in soils is adsorbed to clays and oxy-hydroxides, occurs within minerals, with only a few percent or less dissolved in the soil solution. Fluoride mobility in soil is highly dependent on the soil's sorption capacity, which varies with pH, the types of sorbents present, and soil salinity. In most cases, however, soils act as a sink rather than a source of F^- and water reaching the water table is likely to have low F^- concentration and be dominant by atmospheric concentrations [23]. F enters the soil through different ways such as dry deposition, precipitation, and with contaminated litter where it is absorbed readily. The absorbed F increases

the total soluble F concentration in the soil, influences the pH of soil, and can combine with toxic elements such as aluminum and heavy metals. F can exist as the free fluoride ion (F^-) or form complexes with elements such as iron (Fe), boron (B), calcium (Ca), and aluminum (Al), with the complexes of Al and F being most prevalent.

In most of the soil fluoride is associated with micas and other clay minerals [24]. The total fluoride content in soils ranges from 20 to 1,000 $\mu\text{g g}^{-1}$ in areas without natural phosphate and fluoride deposition, whereas organic soils are generally lower in F content [25,26]. Higher levels of ground fluoride can also occur when phosphate fertilizers are used, where fluoride-releasing industries or coal-fired power plants are located, or in the surrounding area of hazardous waste sites [24]. The release of OH^- in turn might have increased the pH and hence more F leached out in the soil solution due to high alkalinity, which was confirmed by Stevens et al. (1997). In some cases, F retention was greatest near pH 5.5 and decreased at both lower and higher pH levels [27]. At high pH an increasingly unfavorable electrostatic potential decreases retention of F on the soil and increases the F^- concentration in soil solution. It is also due to displacement of adsorbed F^- by the increased concentration of OH^- in soil solution at the higher pH [28]. At higher F dose, soil pH changes to alkaline which support to release higher fluoride from soil surface and subsequently plant availability increased [29]. Fluoride in alkaline soils at pH 6.5 and above is almost completely fixed in soils as calcium fluoride, if sufficient calcium carbonate is available [30]. Fluoride binds to clay by displacing hydroxide from the surface of the clay [27,31,32]. The degree of F adsorption is also controlled by soil pH and is greatest in non-calcareous soils, which generally contain higher Al levels [33,34]. Adsorption to the soil solid phase is stronger at slightly acidic pH values from 5.5 to 6.5 [35]. Fluoride-contaminated water due to continued heavy use of phosphate fertilizers and fluoride-containing industrial waste. In 1943 at the University of Wisconsin, researchers investigated the effect of superphosphate and phosphate rock fertilizers on the amount of fluoride in drainage water and they concluded that "when phosphate fertilization is carried out for many years, very large quantities of highly toxic fluoride are added to the soil" [36,37]. They stated that "high concentrations of fluorine are possible in the drainage water from fields because of high use of

phosphate fertilizer" [37]. Their data, "raise the question of whether our current system of soil fertilization with fluorine-containing phosphates, which could contaminate drinking water, could be hazardous to human health" [36].

5. EFFECT OF FLUORIDE IN PLANTS

Fluorine exists in the environment as gaseous molecules (F_2) and in its reduced form as the ion fluoride (F^-). Under certain circumstances of comparatively lower pH and hardness fluorine occurs as the fluoride ion in water. Plants are exposed to F through different sources such as air, water, and soil. The trace amounts of F available to plants by diffusion in the soil may be absorbed by roots. In plants such as tea, F is naturally accumulated. In some cases, Fluoride unfavorably affects the plant leaves after it intrudes into the leaves because of its high solubility. Fluoride deposition may become relatively slower over time. Fluoride may stop photosynthesis and other essential processes in plants. Fluoride passes from roots to leaves through the process of transpiration or moves through stomata and accumulates in the margins of the leaves. Marginal and tip necrosis is the first symptom of fluorine injury in plant leaves. However, such symptoms may also appear in drought or salinity stress, which can resemble injury caused by Fluoride.

Many investigations have been conducted to find out the effects of F on plants by fumigating plants with high concentration of hydrogen fluoride on a wide variety of plants. In plant foliage fluoride is an accumulative poison it may be gradual over time. Fluoride toxicity suffered plants usually show dead areas on the margins and tips of leaves, which turn yellow or brown and sometimes become dry and brittle. The similar symptoms occur in plants with drought stress or plants suffering from salt toxicity. It usually doesn't kill the plant, but the symptoms can be unattractive [1]. In most plants, fluoride (F^-) is phytotoxic through altering a series of metabolic pathways [38]. Fluoride negatively affects germination, growth, reproduction, yield, respiration, metabolism of amino acids and proteins and photosynthesis by acting on the membranes and the stromal enzymes associated with carbon dioxide fixation and resulting in lowered chlorophyll concentrations [39]. Fluoride often inhibits enzymes that require cofactors like Ca^{2+} , Mg^{2+} , and Mn^{2+} ions [40]. Seeds and

seedlings appear to be potentially more susceptible to fluorides than whole plants. The excess accumulation of fluorides in vegetation leads to visible leaf injury, damage to fruits and reduce yield [41].

Fluoride toxicity causes reduction in root length and shoot length due to unbalanced nutrient uptake by seedlings [42]. [43] studied that shoot length decreased gradually with increasing the F concentration and maximum reduction of root biomass occurred up to 82.5% @ 95 mg NaF kg⁻¹ soil. Similar result was demonstrated by [44] for wheat (*Triticum aestivum*), Bengal gram (*Cicer arietinum* L.), mustard (*Brassica juncea*) and tomato (*Lycopersicon esculentum*). [45] reported that there were the necrosis and chlorosis in the plant, reduction in growth of shoot and root and ultimately reduced the yield of *Triticum aestivum* due to this high concentration of fluoride. Leaf spots in various crops are also found due to fluoride toxicity (Fig. 1).

Total soluble sugar and proline content in leaves initially decreased but both are increased with increasing fluoride concentration because there was gradual accumulation of proline during the germination period, with increasing fluoride concentration due to synthesis of proline rich proteins during stress. The increase in the level of sugar and proline content might be enhancing the tolerance capacity of plant under stress condition [46,47]. [48] reported that total soluble sugars of mung bean (*Vigna radiata*) seedlings and, particularly, reducing sugars, decreased with increase in F concentration. [38] reported that the chlorophyll, Ca, Mg, starch and sugar content of the leaves showed a significant decrease. The protein content in leaves of seedlings showed gradual decrease with increasing fluoride concentration due to stress [49].

5.1 Effects of Fluoride on Photosynthesis

Among the pollutants, F⁻ stands out because of its electro motivity, electronegativity, and high phytotoxic potential. Above all these factors, it has the capacity to preferentially enter through the stomata [60]. F accumulation caused the leaves ultrastructural and structural damages occur in cells and tissues, respectively. After the impairment of cells and tissues, it will be very drastic effects on stomatal conductance and gas exchange of plants [51]. Fluoride accumulation also hampered the photosynthesis. F affects photosynthesis is mainly by reducing the synthesis of chlorophyll, degradation of chloroplasts, and inhibition of Hills reaction. The chlorophyll content is also decreased and the photosynthetic system of plants is impaired. Ultimately, these caused to decrease the CO₂ assimilation and production [52,53]. In plants thylakoid membranes, photosynthetic electron transport chain has been studied after the F exposure. It was found that, accumulation of F inhibits the photosystem-II (PSII) electron transport rate followed by a subsequent increase in the photosystem-I (PS-I) electron transport rate. This result indicated that state transitions being a mechanism for F toxicity. According to the study of Ballantyne [54], it was reported that F treatment with 190 ppm on plants reduces the photosynthetic pigments. It was also found, in the study of Reddy and Kaur [55]. Plants grown on F contaminated soil has the reduced in photosynthetic capacity, chlorophyll-a (Chl-a) and chlorophyll-b (Chl-b) concentrations, total chlorophyll, carotenoids, and leaf area [56,57]. The reduction of chlorophyll contents in the plants may be due to F reduced the chlorophyll biosynthesis [58]. Probably, quantity and activity chlorophyll degrading enzyme chlorophyllase goes to higher after the F accumulation [57]. At the semi-arid region, where plants grow on F contaminated soil showed the same effects [59].



Fig. 1. Leaf spots due to fluoride toxicity

5.2 Effects of Fluoride on Respiration

The hazards of fluoride to plant tissues are widely recognized, so injury of vegetation in certain industrialized areas has been attributed to fluoride accumulation [60]. One of the manifestations of fluoride accumulation is alteration of respiration rates [61,62]. Decrease of tissue respiration by fluoride is probably in large part due to inhibition of respiratory enzymes. For example, succinic, malic, and NADH dehydrogenases; enolase; phosphoglucomutase, hexokinase and ascorbic acid oxidase; and ATPase are all known which are inhibited by fluoride except ATPase [63-67]. [68] demonstrated that fluoride treatment on plants resulted in increased use of the pentose phosphate pathway. This was evident with fluoride-stimulated respiration and fluoride-inhibited respiration. The increased use of the pentose phosphate pathway may have been due to inhibition of the glycolytic enzyme enolase. In another study, Lee, et al. [69], later showed increased activities of glucose-6-phosphate dehydrogenase, cytochrome oxidase, peroxidase, and catalase in fluoride-injured tissues. In one study of, Lords and McNulty [63], reported that a correlation between high ATP levels and fluoride-stimulated respiration in leaf tissue has been found. The phase of stimulated tissue respiration may be in part due to fluoride enhanced mitochondrial ATPase activity. On the other hand, ADP levels are believed to be a controlling factor in respiration [70]. It appears that fluoride treatment induces a number of physiological and biochemical changes in plant tissue that may contribute to increased tissue respiration. The observations of Lee, et al. [66], also stated that glucose-6-phosphate dehydrogenase, catalase, peroxidase, and cytochrome oxidase activities are increased with fluoride treatment.

6. EFFECT OF FLUORIDE IN ANIMAL AND HUMAN BODY

6.1 Toxicity of F in Humans

The research has shown repeatedly that the consumption of F can extremely be harmful and in some cases deadly. In terms of acute toxicity, F is slightly less toxic than arsenic and more toxic than lead. High concentrations of F can lead to serious poisoning incidents with death. Water-soluble fluorides are rapidly and almost completely absorbed in the gastrointestinal tract

after oral intake. Absorbed fluoride is transported via blood; with prolonged intake of fluoride from drinking-water, concentrations in the blood are the same as those in drinking-water, a relationship that remains valid up to a concentration in drinking-water of 10 mg L^{-1} . There is virtually no storage in soft tissues because fluoride is incorporated into teeth and bones. After cessation of exposure, mobilization from these tissues takes place because incorporation into teeth and skeletal tissues is reversible. The concentration of fluoride in environmental matrices is of particular interest because of its toxic effect. In the prevention of caries, daily intake of milligrams per day of fluoride has been found to be beneficial; long-term exposure to higher quantities may have deleterious effects on enamel and bone, and single gram dose cause acute toxic effect or may even be lethal. Fluoride, which is a very toxic element causes adverse health effects on humans and animals due to environmental and occupational exposure. It has been classified as a priority pollutant by the United States Environmental Protection Agency and the German Research Council. The toxicological and physiological behavior of fluoride depends on its oxidation state. Elemental fluoride is more toxic than its salts. Hence, its determination is very important because of its implications in health as well as in pharmaceutical formulations. Metabolism of F in the human body is given in Fig. 2.

Acute toxicity can result from the accidental ingestion of excessive amount of fluoride. The manifestations of acute fluoride toxicity are usually limited to nausea and vomiting. High level of fluoride exposure may adversely affect neurodevelopment in children. Fluorosis is endemic in several regions of the world, with skeletal fluorosis being the most reported worldwide. Dental fluorosis, a hypoplasia or hypo mineralization of tooth enamel or dentin, produced the chronic ingestion of excessive amounts fluoride during a period when teeth are developing in a range of intensity from barely noticeable whitish striations to confluent pitting and staining (Fig. 3).

Fluoride's actions on bone appear to be mediated at several levels. Fluoride can also directly interact with the bone mineral matrix physiochemically and delays the mineralization process and is capable of altering bone crystal structure (Fig. 4).

Fluoride induced nephrotoxicity is kidney injury due to toxic levels of serum fluoride, commonly due to release of fluoride from fluorine-containing drug. The kidney injury is characterized by failure to concentrate urine, leading to polyuria, and subsequent dehydration and hypernatremia and hyperosmolarity. Fluoride also stimulate intrarenal vasodilatation leading to increased medullary blood flow, which interferes with the counter current mechanism in

the kidney required for concentration of urine. The effects of fluoride on female and male fertility are now considered to be a factor causing infertility problems. The available research indicates that high F exposure is associated with the increased level of follicle stimulating hormone (FSH) and luteinizing hormone (LH) decreased testosterone levels and changes in its conversion into its potent metabolites.

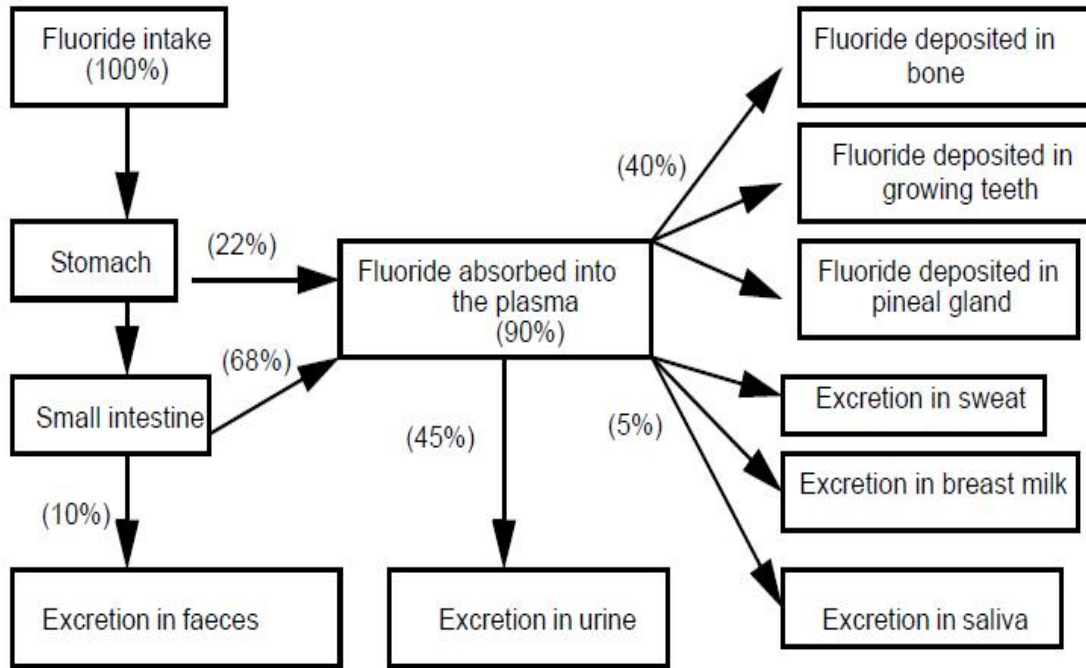


Fig. 2. Metabolism of F in the human body [65-68]



Fig. 3. Effect of fluoride on dental fluorosis



Fig. 4. Effect of Fluoride on bones

6.2 Toxicity of F in Birds and Animals

Although all animals are susceptible to high doses of F, the tolerance level changes from one species to another. The metabolism of F in animals is similar to that of humans (Fig. 5) [75]. Among the terrestrial vertebrates, herbivores are more susceptible than carnivores and other animals. Domestic and wild herbivores are more exposed to environmental F contamination because they are nonselective.

eaters and can consume contaminated feed, water and forage. Cattle and sheep have attracted more attention from researchers worldwide, perhaps due to their large populations and their greater economic importance. However, other animals, including water buffaloes, horses, goats, pigs, and wild cervids, can also suffer from F-toxicity naturally [75]. Skeletal, non-skeletal, and dental fluorosis have been studied in buffaloes, camels, donkeys, horses, and cattle [76].

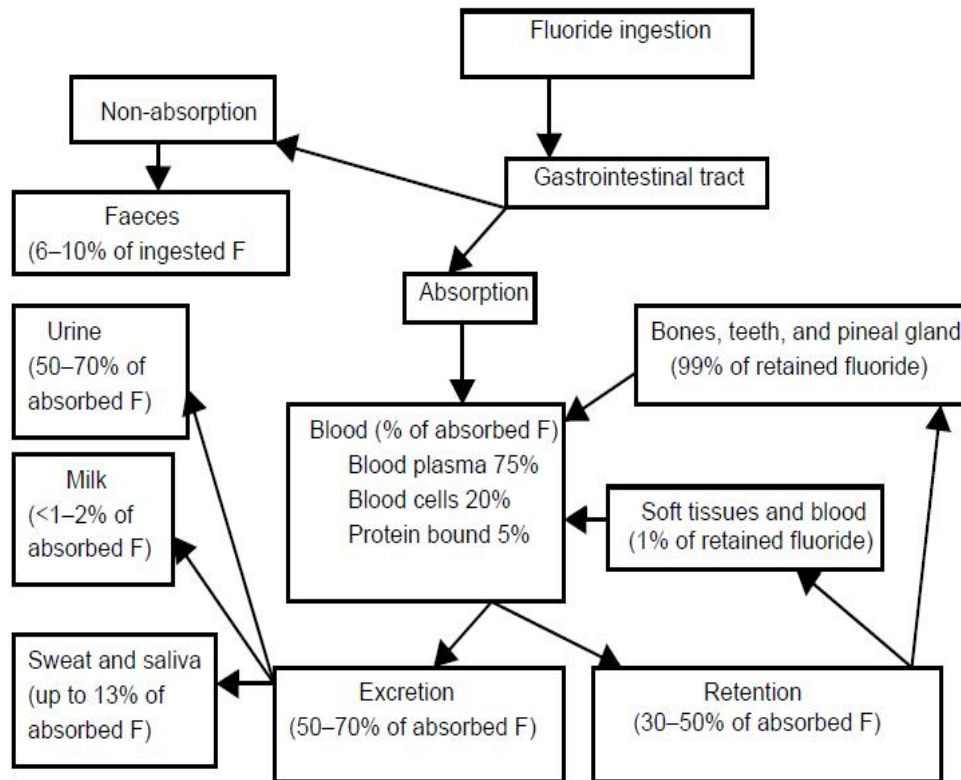


Fig. 5. Fluoride metabolism in the animal body after its oral ingestion [75]

7. MITIGATION STRATEGIES OF FLUORIDE TOXICITY

Fluoride has various adverse effects on human being and plants thus its monitoring and mitigation are necessary. There are various physical and chemical method for defluorination of drinking water. Apart from these physical and chemical methods, biological processes are also reported for phytoremediation and defluorination from the soil, water or air using bio-sorbent prepared from plant material and bioremediation through microbes.

7.1 Physical and Chemical Method of Defluorination

7.1.1 Adsorption

Absorbent provides active sites for F^- ions adsorption. Use of activated alumina for domestic defluorination plant was launched in 1991 by UNICEF in rural India [76]. However, its application needs a specific range and also not economic. Besides, alumina, bone char, brick piece column, mud pot, etc. are reported to be used for removal of F^- . In spite of bone char being economical, however, it is culturally sensitive leading to general reluctance in its acceptability. Mud pot with alumina content is economical and readily acceptable by rural people.

7.1.2 Ion exchange

Ion exchange employs synthetic chemicals anionic exchange resin like Deaceodite FFIP, Tulsion A-27, Ambalite TRA400, Polyanion (NCL), Lewatit MIH59 and cationic exchanger resins like Wasoresin IR, Polystyrene resin, sulfonated saw-dust carbon [78] for removal of F^- ions present in water. Carbon used as cation exchange resin has better durability [79]. According to [78] sulfonated saw-dust impregnated with 2% alum solution and sulfonated coal using aluminum solution are reported to be used for F^- ion removal from water. Fluoride can be removed by applying anion exchange resin by substituting with Cl^- that can be backwashed with supersaturated sodium salt-containing water.

7.1.3 Precipitation

Fluoride gets precipitated in insoluble form like fluorapatite thus get separated from aqueous

phase. Few well-known techniques that use the precipitation methods are as follows:

1) **Nalgonda Technique:** Nalgonda is a district in Andhra Pradesh where it was used for the first time for defluorination of drinking water at community level developed by CSIR-National Environmental Engineering Research Institute, Pune [80]. It consists of different units including mixing of aluminum salt and lime, flocculation, sedimentation, filtration, and finally disinfection using bleaching powder. The settled sludge is eventually removed. pH range for best F^- removal efficiency is obtained in the range 5.5-7.5. Lime is also applied to form bigger and denser flocs. The advantages of this technique are i) readily available chemical, ii) economical, acceptability, simple design and handling, iii) simultaneous, removal of other water pollutants like colour, odour, turbidity, bacteria and organic contaminant.

2) **Contact precipitation:** Calcium and phosphate are used to precipitate the F^- followed by filtration using bone char that has been pre-saturated with F^- . The presence of saturated bone charcoal medium acts as a catalyst for the precipitation of F^- either as CaF_2 , and/or fluorapatite [81].

3) **IISc Method (developed by Indian Institute of Science (IISc), Bangalore):** It is applied at Kolar, Karnataka to treat 15 L of F^- contaminated water by using MgO , $Ca(OH)_2$ and $NaHSO_4$. In this method, F^- ion gets removed as insoluble MgF_2 .

7.2 Defluorination Using Biological Agents

7.2.1 Bio sorbent

Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. Compared to the use of chemical sorbent, techniques using bio sorbent are widely advocated for F^- removal from water due to its easy availability, eco-friendly and efficiency. It can be prepared abundantly from easily available agricultural byproducts like sugarcane charcoal [82], activated rice husk [83], neem and Kikar leaves [84], water hyacinth [85], activated carbon prepared from *Musa paradisiaca* peel and *Coffea arabica* husk [86] and produces lesser sludge. Bio sorbent provides a solid support having

active group/site to adsorb contamination from soil, air or water [87]. The efficiency of adsorption fungal biomass has been reported to enhance when treated with calcium and alkali that are responsible for binding with F^- . Treatment with cation ions suppresses the negative charges of cell surface and provide the site for the adsorption of anions [88]. Sorption and removal of F^- depends upon pH of sites, the presence of cation and anions in environment and sorbent surface, allied species etc. It is generally found that increase in pH decreases the defluorination. [88] observed 24% of F^- removal by *Fusarium moniliforme* at pH 5.0 while only 11% at pH 8.0. At high pH, defluorination might be decreased due to competition between F^- and OH^- while at low pH amine group gets protonated which facilitate binding of F^- .

7.2.2 Phytoremediation

Phytoremediation basically refers to the use of plants and associated soil microbes to reduce the concentrations or toxic effects of contaminants in the environment. Phytoremediation is being considered as effective and low-cost remediation technique to decontaminate the soils from pollutants [89]. According to [90] the maximum bioaccumulation of F^- i.e., 9.948mg kg^{-1} was observed in leaves of *Hordeum vulgare* variety RD 2052 while minimum, i.e., 6.302 mg kg^{-1} in its grains in the presence of 18 mg Kg^{-1} NaF. [91] studied the accumulation of F^- in the aerial part of native plants in the surrounding soils of the coastal superphosphate industries in the Gulf of Gabes (Southeast of Tunisia) and found accumulation in the range of 37-360 mg Kg^{-1} . They recommended three native potential perennials, i.e. *Rhanterium suaveolens*, *Atractylis serratuloides* and *Erodium glaucophyllum* for an in-situ phytoremediation on arid F^- polluted sites. A study conducted by [92] showed that *P. stratiotes*, *Eichhornia crassipes* and *Spirodela polyrhiza* could remove 12.71% to 19.87% of F^- from 3mg $F^- L^{-1}$ contaminated water.

7.2.3 Bioremediation

Bioremediation is a process used to treat contaminated media, including water, soil and subsurface material, by altering environmental conditions to stimulate growth of microorganisms and degrade the target pollutants. Fluoride resistant bacteria play a major role in bioremediation and biotransformation of anions to convert them as less available and less

dangerous form [93] and effectively reduce the F^- by binding them with ionophores. Low concentration of NaF was found significant to *C. pyrenoidosa* in increasing oxygen consumption and total phosphorylated nucleotides in the respiration [94]. According to [95], *Oscillatoria limnetica*, *Ankistrodesmus braunii*, *Scenedesmus quadricauda*, *Cyclotella meneghiniana* and *Stephanodiscus minutes* showed tolerance or no significant effect up to 50 mg L^{-1} . Fluoride export protein (FEX) present in fungal cell coded by FEX gene causes rapid expulsion of cytoplasmic F^- and thus reduces F^- toxicity.

8. CONCLUSION

Through this review, it is summarized that having the electronegativity, fluoride is ubiquitously present in the environments. In some countries it is within the range, whereas most of the countries which have been reviewed showed more than the permissible level as per guideline recommended by WHO. High intake of fluoride, via ingestion or inhalation from different sources cause toxicity in humans and plants. Plants species susceptibility to fluoride pollution may be severely damaged. The problems of fluoride contamination in groundwater is a major concern. Among different sources, water is the important source of fluoride exposure. Hence, water purification techniques should be developed for safe and economic method for portable water. High fluoride exposure affects human beings and animals' health through oxidative stress, immune suppression, apoptosis, and affecting nutrient utilization. Hence, ameliorative measures are important to prevent their endemicity and disease progress. Meanwhile, plant bioactive molecules, several synthetic molecules, and pineal gland secretions have shown protective effect against fluoride toxicity. However, more extensive studies are required for wide application of these molecules as therapeutics agents.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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