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Impact of fluoride on agriculture: A review on it's sources, toxicity in plants and mitigation strategies

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Abstract
Fluorine is a very reactive element that does not occur naturally in its state. It is present as fluoride (F) and corresponds to about 0.3 g kg^{-1} of Earth's crust. Generally, it is found in the form of a number of minerals like fluorspar, Cryolite and Fluor-apatite and it is also discharged into the atmosphere through brick production plants, production of phosphate fertilizers (with an average of 3.8%), cement and other industrial processes. Fluoride has both positive and negative effects on plant health. Hydrogen fluorides (HF) in gaseous form accumulated in the leaves of sensitive plants against a concentration gradient and therefore, considered as a most phytotoxic air pollutant, which affects plants at extremely low concentration. HF mainly damages the plant by entering into its body in the form of gas and affects a variety of plant physiological processes. As HF accumulated in the leaves of plants which could endanger the health of humans and animals through the food chain.

Keywords: Fluorine, fluoride, water and soil contamination, human health, plant stress, remediation

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. In the halides group of the periodic table, fluoride (F) has great importance due to its smallest size and most electro negativity. Despite the fact the mechanisms of F in biological forms are still unclear but it has the unique chemical and biochemical properties for the size and reactivity (Jentsch *et al*., 2000; Edwards *et al*, 2010; Zimmermann *et al*., 2011) [24, 12, 58]. The main natural source of inorganic fluorides in soil is the parent rock. Fluoride has both beneficial and harmful effects on tooth enamel. The dominance of dental caries is inversely related to the concentration of fluoride in drinking-water. The low concentrations of fluoride (0.6-1.5mg L^{-1}) provide protection against dental caries, especially in children. In India, because of high consumption of high Fluoride content, approximately 62 million people including 6 million children suffer from fluorosis.

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.

2. Sources of fluoride

Inorganic fluorine compounds are used in industries for different purposes. In industries, fluoride used in aluminium production and as a flux in the steel and glass fibre industries and the waste material discharge in water, soil and environment. They can also be released to the environment during the production of phosphatic fertilizers, bricks, tiles and ceramics manufacturing. Sodium fluoride, fluorosilicic acid and sodium hex fluorosilicate are used in municipal water fluoridation schemes (IARC, 1982; IPCS, 2002) [22, 23].

All these sources of fluoride are contaminating water and soil adversely which affect human health and plants. The major natural source of inorganic fluorides in the soil is parent rock (WHO, 1984). In the environment, fluoride released naturally through the weathering of minerals, volcano emissions and marine aerosols (Symonds *et al*., 1988; ATSDR, 1993) [48, 3]. Some fluoride minerals (e.g., cryolite or Na_3AlF_6) are rapidly broken down during weathering, especially under acidic conditions (Fuge *et al*, 1988) [15]. Other minerals, such as calcium fluoride and fluorapatite ($Ca_5(PO_4)_3F$), are dissolved more slowly (Kabata-Pendias & Pendias, 1984) [26]. In the soil most of the fluoride is insoluble and, for that reason, less available to plants. However, at low pH, clay and organic matter can increase fluoride levels in soil solution and then increasing uptake of fluoride by the plant root. Every year the global release of hydrogen fluoride from volcanic sources through passive degassing and eruptions range from 60 to 6000 kilo tonnes, of this total approximately 10% introduced directly into the stratosphere (Symonds *et al*., 1988) [48].

2.1 Water contamination

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 andthey concluded that "when phosphate fertilization is carried out for many years, very large quantities of highly toxic fluoride are added to the soil" (Hart *et al*., 1934; Science Safeguards, 1935) [20, 43]. They stated that "high concentrations of fluorine are possible in the drainage water from fields because of high use of phosphate fertilizer"(Science Safeguards, 1935) [43]. 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" (Hart *et al*., 1934) [20].

2.2 Chemistry of fluoride in soil system

Fluoride is a unique and naturally occuring element, but not an essential nutrient for plants (Mackowiak *et al*. 2003) [32]. The pH, clay and organic carbon in the soil are mainly responsible for the retention of fluoride in the soil. In soils, fluoride is primarily associated with aluminum or calcium and loam and clay soils have higher fluoride content than sandy soils (Tylenda, 2011; Greenfacts, 2002) [50, 17]. Fluoride forms labile F compoundswith soil components, including clay minerals, Ca,Mg, Fe and Al compounds due to formation of stable bonds (Omueti and Jones 1977) [37]. Elrashidi *et al*. (1998) [14] pointed out that F forms Al and Fe complexes that disturb the mineral surfaces. Barrow and Ellis (1986) [4] subsequently predicted that at low pH, complexes were formed between Al and F in the soil solution and few products were present as F-free. Macintire (1950) [31] also reported that some soils, particularly those with relatively high Ca content, were very effective in fluoride fixing. The electronegative F^- replaces –OH/H_2O groups bound to surficial Al atoms as ligand exchange by losing the Al–OH bonds (Vasudevan *et al*., 2003) [52]. The fluorine occurring in soils comes mostly from minerals or is adsorbed by clays and oxyhydroxides, so that only the latter dissolve less in the soil solution. More than 90 percent of the natural fluoride content of soils is insoluble, or tightly bound to soil particles (Marier and Rose, 1971) [33]. In most soils fluoride is associated with micas and other clay minerals (Tylenda, 2011) [50]. The total fluoride content in soils ranges from 20 to 1,000 $\mu g\ g^{-1}$ in areas without natural phosphate and fluoride deposition, whereas organic soils are generally lower in F content (Davison A, 1983; NAS US, 1971) [10, 51]. 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 (Tylenda, 2011) [50].

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 (Omueti and Jones, 1977) [37]. 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 (Larsen and Widdowson, 1971) [30]. At higher F dose, soil pH changes to alkaline which support to release higher fluoride from soil surface and subsequently plant availability increased (Saxena and Rani, 2012) [42]. 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 (Brewer, 1966a) [6]. Fluoride binds to clay by displacing hydroxide from the surface of the clay (Huang and Jackson, 1965; Bower and Hatcher, 1967; Meeussen *et al*., 1996) [21, 5, 34]. Early studies concluded that F is retained by finer textured soils, particularly those with a significant clay component (Brewer, 1966b) [7]. Later work revealed that the sorption of F also depended strongly on soil pH. The degree of F adsorption is also controlled by soil pH and is greatest in non-calcareous soils, which generally contain higher Al levels (Omueti and Jones, 1977; Barrow and Ellis, 1986) [37, 4]. Adsorption to the soil solid phase is stronger at slightly acidic pH values from 5.5 to 6.5 (WHO, 2002) [53].

2.3 Harmful limits of fluoride to humans and plants

Low concentrations of fluoride provide protection against dental caries, especially in children. The minimum concentration of fluoride in drinking-water required to produce it is approximately 0.5 mg L^{-1}. However, a fluoride concentration in the drinking water of between 0.9 and 1.2 mg L^{-1} has a detrimental effect on tooth enamel and may cause mild dental fluorosis (prevalence: 12 to 33%) (Dean, 1942) [11]. The safe levels have been identified for domesticated animals, with the lowest values for dairycattle at 30 $mgkg^{-1}$ feed or 2.5 mg L^{-1} drinking-water.A large number of the papers published on fluoride toxicity to plants concern glasshouse fumigation with hydrogen fluoride and irrigation with hydrogen fluoride contaminated water. The use of water containing relatively low ($<$3.1mg L^{-1}) levels of fluoride for crop irrigation generally does not increase fluoride concentrations in foodstuffs. However, this is dependent on plant species and fluoride concentrations in soil and water.

3. Detrimental effects of fluoride on plants

The symptoms which are appear in plants due to fluoride toxicity, depends upon many factors such as the concentration, time of exposure, temperature, type of light, intensity, age of plant, composition of the other gases in atmosphere and there rate of circulation. When fluoride has entered into the plants in dissolved form, it is transported *via* the vascular tissue to the leaf edges where it is accumulated (Threshow, 1970) [49]. This accumulation of fluoride can cause minor necrosis on the upper edge of the leaves and progress to the leaf base. In the long term, low HF exposure causes chronic lesions characterized by general chlorosis or chlorosis along the leaf veins. High concentration of F result in acute injury, which characterized by tip and marginal necrosis that progress to leaf bases, or if rapid absorbed, it causes irregular patches of necrosis may occur in the intercostal areas. When fluoride absorbed and translocated to the shoots, causing physiological, biochemical and structural damage and even cell death depending on the concentration in the cell sap (Miller, 1993) [35]. Histochemical studies of fluoride-injured plants have indicated that the damage to leaves first occurs in the spongy mesophyll and lower epidermis followed by distortion and disruption of chloroplast in the palisade cells. The upper epidermis is last to exhibit any distortion or collapse due to F toxicity (Panda, 2015) [38].

The fluoride may affect the early stages or pigment synthesis anddegradation of chloroplast structure (Kumar *et al*., 2013) [28]. The concentrations F at the leaf tips can thus reach quite high concentrations why the first signs of fluoride toxicity are often observed at the leaf edges (Threshow, 1970) [49]. Fluoride strongly inhibits photosynthesis and other physiological processes. Some of the visible evidences of toxic effects of fluorides to plants are necrosis and chlorosis (Landis *et al*., 2011) [29]. Both necrosis and chlorosis eventually lead to plant death. Kumar *et al*. (2013) [28] studied that the concentration of 'F' ions in 200 mg kg^{-1} reduced chlorophyll content in green leaves of wheat which caused chlorosis and necrosis.

Many investigations have been conducted to find out the effects of F on plantsby 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. Photosynthesis and other processes inhibited strongly by fluoride. The movement of fluoride in plants occurs with transpiration stream from roots or through stomata and accumulates in leaf margins. Usually fluorine injuries symptoms appear on broadleaf plants include marginal and tip necrosis that spread inward. 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.

Fig 1: Leaf spots due to fluorine toxicity (Neil Bell, 2009)

In most plants, fluoride (F) is phytotoxic through altering a series of metabolic pathways (Elloumi *et al*., 2005) [13]. 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 (Garrec *et al*., 1981) [16]. Fluoride often inhibits enzymes that require cofactors like Ca^{2+}, Mg^{2+}, and Mn^{2+} ions (Panda, 2015) [38]. 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 andreduce yield (Ando, 1998) [2].

The fluoride toxicity symptoms in plants are necrotic regions, especially at the tips and along margins of leaves. Some crops have long cropping times and therefore will be irrigated with fluorinated water by growers for months which increase the risk of developing fluoride toxicity (Wollaeger, 2015; Krupa, 2001) [55, 27]. Photosynthesis was reduced by the extent of the injured areas, but the green portions of the leaf remained fully functional. Recovery from this inhibition of photosynthesis was relatively slow. The exact mechanism of injury to plants by fluorides is unknown.

Fluoride toxicity causes reduction in root length and shoot length due to unbalanced nutrient uptake by seedlings (Sabal *et al*., 2006) [40]. Mondal and George (2015) [36] studied that shoot length decreased gradually with increasing the F concentration and that maximum reduction of root biomass upto to 82.5% at the fluoride dose @ 95 mg NaF kg^{-1} soil. Similar result was demonstrated by Pant *et al*. (2008) [39] for wheat (*Triticum aestivum*), Bengal gram (*Cicer arietinum* L.), mustard (*Brassica juncea*) and tomato (*Lycopersicon esculentum*). Saini *et al*. (2008) also reported that both root and shoot growth decreased with increasing accumulation of NaF for *Prosopisjuliflora*. Agarwal and Chauhan (2014) [1] 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.

Fresh weight, dry weight and percent of seedlings decreased monotonically with increasing fluoride concentration due to reduction of metabolic activity in presence of fluoride (Gupta *et al*., 2009) [19]. Maize and chilli are more sensitive to fluoride contamination than other crops such as tomato, mung, mustard, ladies finger. Bustingorri *et al*. (2015) [8] reported that yield loss of soybean reached 30% at F levels 375 mg kg^{-1} or greater. Singh *et al*. (1979) [45] studied that increasing F above 50 mg L^{-1} decreased the yield of rice. Among crops, vegetables and fruits normally contain fluoride though at low concentration between 0.1 and 0.4 mg kg^{-1} while higher levels up to 2 mg kg^{-1} of fluoride have been found in cereals (Jolly *et al*., 1974) [25].

Total soluble sugar and proline content in leaves initially decreased but both are increased with increasing fluoride concentration because there was gradual accumulation ofproline 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 (Yang and Miller, 1963; Greenway and Munns, 1980) [56, 18]. Yu (1996) [57] reported that total soluble sugars of mung bean (*Vigna radiata*) seedlings and, particularly, reducing sugars, decreased with increase in F concentration. Elloumi *et al*. (2005) [13] 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 (Singh *et al*., 1985) [46].

4. Methodology for fluoride removal

Some technologies are available for fluoride removal which may help to reduce fluoride toxicity from water and soil.

i. **Nalgonda Technique:** In the Nalgonda technique, two chemicals (Dahi *et al*., 1996), alum (aluminum sulphate or potassium and aluminum sulphate) and lime (calcium oxide) are added and rapidly mixed with the fluoride contaminated water. Flakes develop (aluminum hydroxides) by subsequent gentle stirring and are removed by simple sedimentation. By combining sorption and ion exchange with some of the hydroxide groups produced, the main contents of the fluoride is removed along with the flocs.
ii. **Bone Char:** Bone char is simply ground animal bones charred to remove all organics. It consists mainly of tricalcium phosphate and carbon. It has been described by Scott *et al*. (1937) [44] and Sorg and. al. (1978) [47] in defluoridation plants. This material, which was developed to bleach tube syrup, is initially more economical than bone.
iii. **Synthetic tri-calcium phosphate:** The product is prepared by reacting phosphoric acid with lime. With 1% NaOH solution followed by gentle acid rinse, the medium is regenerated. 700 mg of fluoride / L can be eliminated.
iv. **Florex:** A mixture of tri-calcium phosphate and Hydroxy -apatite, commercially known as Florex, had the ability to remove fluoride from 600 mg of fluoride per liter and was regenerated with a 1.5% solution of sodium hydroxide.
v. **Activated Carbon & Lime:** Different types of activated carbon have been described as having a high fluoride removal capacity. After a routine review of raw and treated municipal waste, it was (Scott *et al*. 1937) [44] reported that reduction in fluoride concentration compared to the fluoride in the raw water in the effluents from lime softening plants.
vi. **Lime stone, special soils and clay etc.:** Recently limestone and heat-treated soil were tried for fluoride removal. Limestone has been used to reduce fluoride concentrations in wastewater below the maximum contamination level (MCL) of 4 mg / l. On the basis of experimental data, a mechanism of fluoride sorption by clay minerals is proposed. The study examined the removal of fluoride by adsorption on inexpensive materials such as kaolinite, bentonite, coals and lignite seeds.
vii. **Fly Ash and natural minerals:** The removal of fluoride was attempted using natural materials such as red soil, charcoal, brick, and fly-ash. The study shows that red soil has good fluoride removal capacity followed by brick, fly ash and charcoal.
viii. **Electrokinetic remediation:** Electrokinetic (EK) decontamination is an effective method of treating soils, sludges and sediments contaminated by organic and inorganic pollutants. The EK technique is based on the application of a direct electrical potential to the contaminated soil by means of a series of electrodes. In the direct current electrical field, a variety of reactions and transport processes in the contaminated soil leads to the mobilization of contaminants to the electrodes. In this technology, an electric field is used to promote the movement of contaminants towards the electrode. However, other native compounds present in the soil can also be mobilized. However, there was limited research evaluating the soil fertility after electro kinetic treatment.

However, the effectiveness of these fluoride removal techniques is not very high. The Nalgonda process, Bone charcoal and Calcined clay are low costs methods for domestic use. At the community level, the Nalgonda process is also a cost-effective method. If a high fluoride removal is necessary then electro kinetic remediation is preferred.

5. Conclusions

High intake of fluoride, via ingestion or inhalation from different sources cause toxicity in humans and plants. The problems of fluoride contamination in groundwater is a major concern. Plants species susceptibility to fluoride pollution may be severely damaged. Considering all these issues, fluoride toxicity and its mitigation mechanisms became a noticeable complication to the agricultural scientists for getting stable yield under the influence of fluoride stress. It is only possible when the additional information becomes available that appropriate recommendations can be made to mitigate the risks of increasing F levels in our pastoral systems and to develop sustainable practices in the future.

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