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FLUORIDE TOXICITY IN SOIL AND PLANTS: AN OVERVIEW

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AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration among all authors. Authors AS and AA have conceptualized the topic. Author AS collected the all available literatures and wrote the first draft of the manuscript. Authors CB and IE critically analyzed the study. All authors read and approved the final manuscript.

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Review Article

ABSTRACT

Fluoride, if present in higher concentration for an extended period of time causes diverse toxic effects not only in plants and soil, but also in human beings. These effects on vegetation are mostly through the fluoride contaminated soil, gases, water as well as dust that alter the morphology and physiology of plants. The damages caused by Fluoride in plants may be chronic or acute and their rigidity is dependent on the duration of the fluoride exposure and concentration. Fluoride toxicity in plants results into the continuous accumulation of fluoride into their subcellular structures which then changes towards biochemical activity. Fluoride toxicity negatively influences growth, germination, photosynthesis, mineral nutrition, respiration, reproduction and activity of cellular enzymes. Further this toxicity is well known to prohibit the action of anti-oxidative enzyme systems such as interfere with cell signaling and superoxide dismutase. Fluoride is also noted to obstruct calcium movement which is crucial for germination. Hence, this review highlights the evidences of fluoride toxicity in soil and its damaging effects on the morphology and physiology of the plants.

Keywords: Fluoride; toxicity; ROS; sensitivity; plant stress.

1. INTRODUCTION

Fluoride is potent abiotic atmospheric contaminants. Fluoride toxicity is a reason of concern in many nations mainly where it is present in immoderate amounts in the hydrological areas [1, 2]. Furthermore, fluoride deposition in crops that are irrigated with fluoride-adulterated water is a major problem, especially because of the decline in the rate of photosynthesis and obstructs growth and development in numerous plant varieties [3, 4]. Fluoride risk leads to increased generation of reactive oxygen species (ROS) such as superoxide radicals that can result in deactivation of enzymes; DNA strands breakage and destruct membrane lipids [5-8].

Fluoride toxicity in plants can appear due to immoderate fluoride uptake from diverse native or manmade sources. Fluoride causes phytotoxic effects in many plants [9]. Plants are susceptible to fluoride accumulation and a little accumulation of fluoride can harm the process of their development. Fluoride has

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been identified as a vigorous metabolic barrier [10] and has long been recognized as potent phytotoxic of familiar air pollutants, the phytotoxicity depends upon its atmospheric concentration [11,12]. Only peroxyacetyl nitrate, a component of photochemical smog, can equal this immoderate phytotoxicity [13]. Fluoride causes phytotoxic effects mainly due to its tendency to pileup in plants [14] usually it is accumulated in the foliage. Gaseous fluorides too that penetrate between the stomata are absorbed in a systematic way by the leaves [15]. The gaseous forms of fluoride, such as silicon tetrafluoride (SiF4) or hydrogen fluorides (HFs) have the highest toxicity among all pollutants used in agriculture [16,17]. When fluoride is present inside the leaf, a small amount of fluoride is carried out of the organ by the conducting process.

2. EXISTENCE OF FLUORIDE

Fluoride is the most abundant element on the earth and it is widely dispersed. Fluorine is a pale yellow color gas. At standard temperature and pressure it has an atomic weight of 18.9984 and an atomic number of 9 [18]. In the periodic table, Fluorine is arranged as a halogen present in the Group VII A. In the halide series fluorine is the most electronegative anion [19,20] and chemical and biochemical properties of fluorine are unique because of its reactivity and small size. Though this element is highly toxic yet the mechanisms of fluorine cell signaling is still unknown [21,22].

Fluorine is found everywhere in the atmosphere and an extremely rich element in the earth crust approximately 0.32 g kg^{-1} [23]. The allocation of fluoride in water and soil is changeable depending upon position and place [24]. Fluoride concentration in soil vary from ten to thousands of parts per million (ppm) [25,26] while in natural water origin, the concentrations range from l25 μM to 100 mM (<0.5 to >2,000 ppm; 1 ppm > 55 μM) [27,28]. Groundwater has highest fluoride concentrations as compared to other anions [29,30]. Fluoride toxicity in terrestrial plants has been well determined and studied using experimental methods such as greenhouse, controlled field plot experiments, *etc*. [31]. Fluoride has the ability to activate abnormal morphological symptoms like marginal necrosis, chlorosis. Sensitivity towards fluoride is distinct in various varieties and species of plants [32]. In general, fluoride inhibits the phosphorylation of enzyme activities, other metabolic processes, photosynthetic pigments synthesis and phosphor-proteins in cellular membranes [33,34].

3. EFFECTS ON SOIL

In soil, most of the fluorine occurs inside the minerals or oxy-hydroxides. About 90 percent of the soil native fluoride content of soil molecules is not penetrable and firmly bound to soil molecules [33, 34]. Mostly soil fluorides related to clay minerals and micas. The fluoride accumulation in soils varies from 20 to 1,000 μg g^{-1} in regions without fluoride deposits or the phosphate accumulation because the natural soil generally has low fluoride concentration [35, 36]. Presence of high levels of the fluoride may also take place at coal-fired power plants, phosphate fertilizers, fluoride releasing industries, and in the proximity of hazardous waste locations [32]. In soil, fluoride is related to its portability in soil and also dependent on the soil adsorption capability, which differs with soil salinity, pH and the types of absorbents present [37]. The pH of soil and natural carbon content is basically important for holding of fluoride inside soils. Fluoride is principally coordinated with calcium or aluminum and clay loam soil; silt soil has more fluoride content than sandy soils [29]. Fluoride forms better bond with Ca, Al, Fe, and varying fluoride is held by soil constituents carrying these elements, including calcium, magnesium and aluminum. Components that form Al and Fe compounds obstruct the mineral surfaces [32]. At low pH, complexes between F and Al are found in soil compounds and called 'free fluoride'. It has also been reported that in some soil types, mainly with high calcium content have high tendency of fixing fluoride [38].

4. EFFECTS ON PLANTS

On a wide variety of plants, numerous examinations were observed about the effects of Fluoride in the form hydrogen fluoride. Campbell [24] prepared a record of the ancient reports regarding the outcomes of fluoride on plants and other living beings. Thomas [39,40] reviewed the damages of gaseous forms of fluoride on various plants. Daines et al. [21] epitomized the effects of fluorine compounds on plants. Fluoride is particularly toxic for the foliage and its concentration can continue over a long period of time [41]. Metabolic processes like photosynthesis and respiration are strongly affected by fluoride. Beside these the transpiration also affected through the movement of fluoride stream from roots to the ~~the~~ stomata, where it is accumulated in leaf margins [42,43]. Damage of fluorine in broadleaf plants causes necrosis of leaf tip and margins while in conifer needles it basically affects the leaf base [40,44]. Salt toxicity or drought stress can have identical signs. Some plants carrying higher concentrations of fluoride and do not show symptoms of toxicity but most plants exhibit symptoms of toxicity at very smaller concentration [45]. Most plants are subtle to fluoride as it is phytotoxic because it changes the sequence and path of the metabolic routes. Hence, it adversely affects growth, germination, respiration, reproduction, assimilation of proteins and amino acids, yield of crops and photosynthesis [46,47]. Fluoride frequently hinders enzymes that need cofactors such as Mg^{2+}, Mn^{2+} and Ca^{2+} ions [48]. Fluoride sensitivity appears to be higher in seeds and seedlings than other parts of plants [45]. A large amount of deposition of fluorides in plants produce leaf damage, fruits damage, and yield (Figs.1 & 2).

Fig. 1. Fluorine exposure causes leaf spots [48] (Neil Bell, 2009; adopted from Kumar et al. [48])

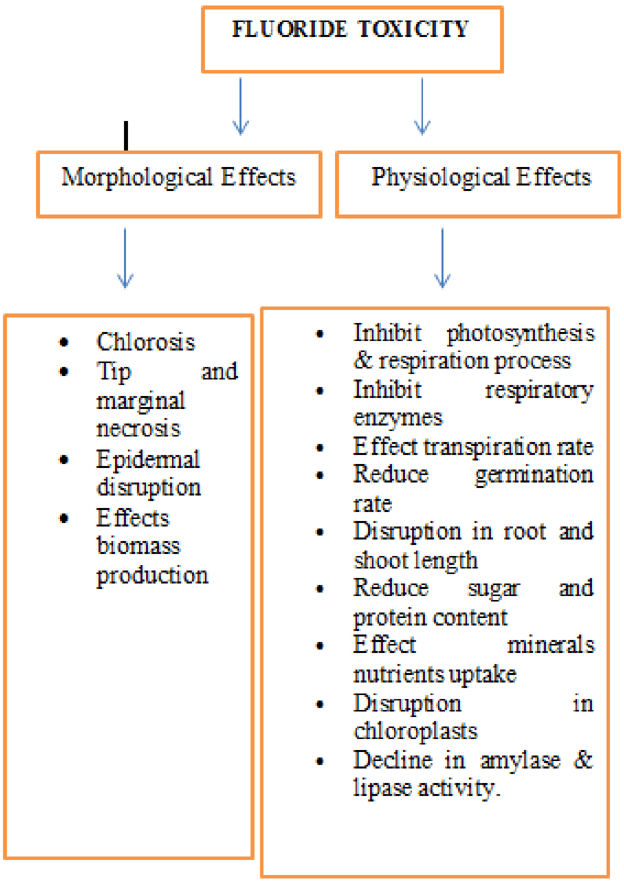

Fig. 2. Changes morphological and physiological attributes due fluoride toxicity

4.1 Effects on Anabolic Process

Fluorides influence the rate of photosynthesis primarily by bringing down chlorophyll composition or by degeneration of the chloroplasts, especially by obstruction of the Hill reaction [49,50]. The chloroplasts are the primary acquirer of fluoride. Many reports have underlined that fluorides give rise to dangerous effects on photosynthetic pigments such as anthocyanin, chlorophylls-a, b and carotenoids [51]. Fluoride was seen to decrease the accessibility of Fe^{2+} ions which are important for chlorophyll production [43]. Additionally, fluoride stimulated interference in the electron transport system, specifically at the photosystem II. It has also been investigated that oxygen is constantly built throughout the photolysis of water [52]. By the exchange of fluoride with Cl^- ions of the photosystem II, it obstructs the photo-oxidation of water and results in the production of new free radicals in the proteins, which is inefficient in balancing the system of photolysis [53]. It has been investigated that the inhibited synthesis may be the outcome of the loss of granulation of the chloroplasts, subcellular organization and short stomatal conductance linked to a less CO_2 uptake [54,55]. Moreover, in the chloroplasts, Fluorides also appear to influence the process of sucrose synthase, RUBISCO (ribulose 1, 5-bisphosphate carboxylase) and the enzymes related with CO_2 fixation. Its deposition was shown to be best in the roots with gradual lower levels in the shoots, leaves and seeds [45, 56].

4.2 Effects on Catabolic Process

Cellular respiration gives the energy for production of new biomass, ion uptake transfer of photosynthates, absorption of components, including protein movement, nitrogen as well as prevention of ion gradients [11, 57]. Low accumulation related to low fluoride is accustomed to prompt O_2 intake, whereas exposure at higher concentration or for longer time obstructs respiration [58]. In comparison, two studies investigated that the respiratory process was rather susceptible to fluoride and in others it was restricted [35]. The concentration of fluoride is dependent on the tissue of the plant, its age, time of accumulation in tissues, location and fluoride accumulation in the distinct parts of plants [41]. The shift from glycolysis to the pentose phosphate channel which occurs over a lengthy time span of tissue may show a link between inhibition and tissue span or through high susceptibility of few glycolytic enzymes to fluoride [14, 59]. Fluorides obstruct tissue respiration by the obstruction of respiratory enzyme activities like peroxidase, ascorbic acid, malate dehydrogenase and polyphenol oxidase succinate [40, 60]. However, the cause for fluoride-stimulated respiration is less evident. When plants are exposed to fluoride many species of plants demonstrate a significant use of the pentose phosphate pathways [61]. In fluoride damaged tissues, the activities of cytochromes oxidase, peroxidase, catalase and glucose-6-phosphate dehydrogenase were elevated [62].

4.3 Effects on Seed Germination and Seedling Growth

Phytin is fragmented by the enzyme phytase during germination to provide mineral phosphate to the young seedlings [63]. Fluoride has been shown to delay germination and seedling root growth by inhibiting the dephosphorylation of phytin components in tissues by suppressing phytase enzymes. Phytin produces inorganic phosphates which are the sources of orthophosphates that are important for the metabolism of RNA during the germination process [64, 65]. One of the elements that can hinder the growth rate of fluoride- treated seedlings is a limited amount of phytin derived orthophosphate. The amount of phytin derived orthophosphates possibly the reason which obstructs the germination rate of fluoride-treated seedlings [15, 66].

4.4 Uptake and Accumulation of Fluoride by Plants

Significant constant deposition of fluoride into the subcellular parts of the plants causes toxic responses in the plants [67, 68]. Fluoride initially deposited in leaves and moves through the water and soil into the roots by a passive diffusion system [50, 69]. Though, researchers examine that the uptake of fluorides from the atmospheric air is more important than from the soil [70]. Accordingly, fluoride is transferred through xylem tissues through the symplastic and apoplastic pathways into the shoots. Fluoride is also transferred by biological lamina through non-ionic dispersion of hydrogen fluoride (HF) [71, 72]. The minute neutral particles of HF go across the cell membranes seven times quicker than the fluoride ion. Moreover, at the present time, the exact system of fluoride absorption into the cells has not been fully investigated [25, 73]. The toxicant of fluoride in the distinct plant portions differ and depend upon its movement from the soil to the roots [11].

4.5 Effect of Fluoride Toxicity on Mineral Nutrition

Different levels of phosphorus, nitrogen and calcium nutrition are well known to affect the sensitivity of the plants variously [74]. Average level of phosphorus, nitrogen and calcium promote absorption and transfer of fluorine in adequate amounts which give rise to notable leaf damage. Less phosphorus appears to have the minimal restraint effect [38, 70]. Calcium has a propensity to bring fluorine in the structure of insoluble elements inside or through the roots causing decrease in the damage to the plant foliage. Signs of critical fluorine toxicity on the leaves were always related with the excessive fluorine foliage content [21].

4.6 Effects on Growth of Vascular Plants

Decrease plant growth rate and vigor indicate accumulation of fluorides. Portions of green stems as well as leaves can accumulate greater concentrations of fluoride from the environment apart from bare portions because of large surface area and abundant stomata. Fluoride accumulated in the margins of dicotyledonous leaves and in the tips of monocotyledonous leaves where it causes chlorosis or necrosis [46,75]. Depletion in root and shoot growth is associated with subjection to airborne fluorides; these effects on growth appear to lead to noticeable damage in the plant foliage [4,72]. Hydrogen fluoride fumigation at anthesis and booting decreases the irrigation of crops because of lesser and smaller spikes. In the kernel of plants, fluoride accumulation hardly expands because the fumigation shows that the fluorides neither transfer from the leaves to the mature seeds [74-76]. It is also mentioned that hydrogen fluoride affects fruiting and leaf injury separately. Subjection of crops to fluoride through anthesis intensely decreases yield, expressing an unfavorable effect on the fertilization procedure [76].

5. STRATEGIES TO COMBAT THE FLUORIDE TOXICITY

Ahmad et al. [77] experimentally studied that silicon addition reduce NaCl toxicity in Mung bean through the changes in physio-biochemical and antioxidant enzymes. Mung bean treated with different NaCl concentration show decrease in length and dry weight of root and shoot. Silicon addition to salt stress plant leads to decrease salt effect on growth and biomass. Silicon increases antioxidant enzymes in NaCl stressed plant.

Dresler et al. [78] experimentally studied silicon effect on maize growth under the stress of cadmium. Cadmium stressed plant show depressed plant growth whereas silicon addition leads to reduce the accumulation of cadmium in maize roots. Hence silicon prevents the uptake of cadmium and shows the positive influence on growth of maize seedlings.

Zhu et al. [79] experimentally studied that silicon reduce salt stress effect and enhance antioxidant enzyme activities in cucumber leaves. Addition of silicon in salt stress plant leads to enhance antioxidant enzymatic activity and reduce LPO and H_2O_2 concentration. An increase in the antioxidant enzyme concluded that silicon may be associated with metabolic activity in salt stress cucumber. Kanchan et al. [80] also highlighted the utility of silicon application in the mitigation of fluoride present in arid soils.

Collivignarelli [81] reported the mitigation of fluoride in ground water by the use of palm residues. Chaudhary et al. [82] highlighted the importance of microbes in the remediation of fluoride toxicity. Recently GAO et al. [83] had done experiment related to the treatment of toxic concentration of fluoride in the shallow ground water bodies and their findings are promising.

Another approach would depend on the identification of tolerant relatives of major crops and their incorporation in the breeding programmes to develop the desired crop varieties.

6. CONCLUSION

Fluoride toxicity in soil and plants is a global issue due to its negative impacts on the soil, plants and human beings also. Many researches have shown these negative impacts on soil and plants, though the unavoidable uptake of soil bound fluorides and its gaseous form by roots and leaves, respectively. The toxicity of fluoride is not only toxic to the higher plants but also it negatively interacts with the soil micro-flora and hence damaging the micro and macro environment in many parts of the world. To combat with this one has to understand the molecular, physiological and biochemical basis of agricultural fluoride tolerance, consequently, there is a desperate need of more research on the effects of fluoride toxicity stress on various plants to find out few tolerant species and reclamation programmes that can be helpful in making future strategies. In this review an overview has been presented which would be helpful for the researchers that are engage in this particular aspect.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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