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### Review Article

## Effects of Fluoride on Respiration and Photosynthesis in Plants: An Overview

### Abstract

Among all the halides, Fluoride (F) caused most severe adverse effects on plants through air, soil, and water, exposure. Besides the nutritional importance of this element, after its desirable limits in the plants, it caused adverse effects on plants through interfering with various physico-biochemical parameters; with or without any visible symptoms of injury. Due to higher level of fluorides in plants, it also causes less development of plants through affecting several pathways associated with photosynthesis, respiration, protein synthesis, carbohydrate metabolism, and nucleotide synthesis. Photosynthesis and respiration are the most important process in the plants to acquire the basic energy and their utilization. Fluoride has great effective importance on these to pathways. On this view, the present review critically discusses the toxic effects on respiration and photosynthesis of agricultural crops and trees.

### Introduction

Fluoride is the most important member of halides group. In halide group effect of Chloride and Iodide on organism have been well studied [1-3], but less is understood about the biological importance of fluoride. The fluoride is smallest and most electronegative anion in the halide series. Fluoride has its unique chemical and biochemical properties for the size and reactivity, but the mechanisms of cell signaling for the fluoride are incompletely characterized. Fluoride is ubiquitously present in the environment that means it is found in soil, water and air [4]. It is a highly abundant element in the earth crust approx 0.32 g/kg [5, 6]. The distribution of fluoride in soil and water is variable depending on location. In soil, range of fluoride concentrations are from ten to thousands of parts per million (ppm) [6]. In natural water sources, the concentrations range from 125 µM to 100 mM (<0.5 to >2,000 ppm; 1 ppm > 55 µM) depending if the water is in contact with high levels of fluoride-containing minerals [7,8]. In groundwater, fluoride concentrations is highest among the any anion [4], fluoride is one of the most important phytotoxic air pollutants. Fluoride (F) toxicity on terrestrial plants has been studied and has been clearly demonstrated in the entire scientific manner like laboratory, greenhouse and controlled field plot experiments [9]. Injury to vegetation due to high concentration fluoride, commonly gradual accumulation of in the plant tissue over a period of time [10]. It has the capability to induce the abnormal morphological symptoms like chlorosis, tip and marginal necrosis etc [11]. Sensitivity will be different in various species and varieties to fluoride are reported. Fluoride interferes with phosphorylation of phosphoproteins in cellular membranes

[12], enzyme activities [11,13], and photosynthetic pigments synthesis and other metabolic process [14,15]. The present review, critically discussed the toxic effects on respiration and photosynthesis of agricultural crops and trees of exposure to fluoride.

### Basics of Fluoride

Fluoride is the 13<sup>th</sup> most abundant element and distributed widely throughout the earth [16]. F is a pale yellow colored gas. It has the atomic number of 9 and atomic weight of 18.9984 at standard temperature and pressure. Fluorine is classified as a halogen, present in the Group VII A of the Periodic Table of Elements (Figure 1; source 17). The halogens consist of fluorine, chlorine, bromine, iodine, and astatine. These all are electromotive elements. They have the nature to exist in the free state as diatomic molecules. Having been electromotivity,

Fluoride (F)	
Discovery Year: 1885 Discoverer: Henri Moissan	
Basic Elemental, Atomic and Material Properties	Thermodynamic and Nuclear Properties
Block: p, Group: 17, Period: 2	Boiling point (°C): -188.12
Electron shell configuration: 2-7	Melting Point (°C): -219.6
Gas atomic multiplicities: 2	Phase: Gas
Atomic Radius (pm): 42	Heat of fusion (KJ/mol): 0.26
Covalent radius (pm): 71	Specific heat (J/kg*K): 824
Van der waals radius (pm): 147	Vaporization heat (KJ/mol): 3.27
Mass: 18.9984032	Radioactive: False
Electronegativity: 3.98	Half life (S): Infinity
Valence: 1	Lifetime (S): Infinity
Electron affinity (kJ/mol): 328	Neutron cross section (Barns): 0.0096

Figure 1: Basic properties of Fluoride [Source: 17].

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 [18]. Assumption on the biochemical properties of fluorides might be similar to those of other halogenated compounds. This assumption may be partially correct. Like other halogen member, inorganic fluorides dissociate in aqueous solution and release to monovalent fluoride anion ( $F^-$ ), along with its associated cation. Fluoride however has many unique chemical properties. These properties had a great impact on the special biochemical physiological properties to the fluorides. For these reason, F can affect the metabolism and mechanisms of action within the living system [18]. 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 an extremely short half-life [19,20].

### Fluoride Source, Uptake, Translocation and Accumulation by Plants

At higher level of F, it has the great phototoxic effects on vegetation. It released into the environment from a number of industrial sources, use of phosphate fertilizers in agriculture, and weathering of volcanic ashes etc. [21,22]. Some type of soils has high levels of natural fluorides. It could be transferred from soil to roots, and then to above ground parts, or absorbed by leaves from the air. Toxic level of F are found in tree leaves [23,24]. Uptake of F by roots is made through the mechanism like passive diffusion process. Most of the absorbed F is remains exchangeable and readily extractable from the root by mild washing procedures [25,26]. Experimentally, it was found that, mainly F found in the apoplast and some times, little amount also found in the plasmalemma or tonoplast. Levels of F are found low in the shoot as the endodermis acts as an effective barrier. Fluoride reaches the vascular system by a non-selective route that bypasses the endodermis [27]. Uptake of F from air is higher than from the soil. It was found that the level of fluoride in roots is lower than the leaves [28,29]. According to the result of Sloof et al. [30], it was found that the main route of uptake of F by plants is from aerial deposition on the plant surface. From all these studies it could be assumed the pathways of fluoride absorption in the plants. Some experimental works has been highlighted on the F accumulation capacity of plants. Plant uptake and accumulation capacity mainly depends on the plant's species and the ionic strength of the surrounding environment where it is growing. If the environment has the high concentration of F, then simultaneously F concentration will be higher [10,31,32]. Type of soil has the influence on the F accumulation in plants. Higher concentrations of Ca in soil inhibit the F accumulation in plants from soil [33].

### Effects of fluoride on photosynthesis

Multiple metabolic pathways and mechanisms, and consequently, the productivity of agricultural crops might be impairing through the several air pollutants [34]. The response of plants to pollution depends on the toxicity of the chemical element, duration of plant exposure and the species sensitivity [35].

Among the pollutants,  $F^-$  stands out because of its electromotivity, electronegativity, and high phytotoxic potential. Above all these factors, it has the capacity to preferentially enter through the stomata [36]. 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 [37].

One experiment conducted by Mesquita et al. [38], reported that damage to the epidermis and stomata of leaves from young plants of coffee and orange when these are exposed to hydrogen fluoride (HF) in a semi-open mist chamber. It has the possibility of the loss of regulation in mechanisms of stomatal aperture and closure. In the chloroplasts, F affects enzymes, such as ATP synthase, ribulose biphosphate carboxylase-oxygenase and sucrose synthase, which have their activity reduced [39].

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  $CO_2$  assimilation and production [40,41].

In plants thylakoid membranes, photosynthetic electron transport chain has been studied after the F exposure. It was found that, accumulation of F inhibit the photosystem-II (PS-II) 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 [42], 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 [43].

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 [44, 45]. The reduction of chlorophyll contents in the plants may be due to F reduced the chlorophyll biosynthesis [46]. Probably, quantity and activity chlorophyll degrading enzyme chlorophyllase goes to higher after the F accumulation [45]. At the semi-arid region, where plants grow on F contaminated soil showed the same effects [47].

### 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 [48]. One of the manifestations of fluoride accumulation is alteration of respiration rates [49,50]. Either inhibition or stimulation may occur depending on a number of factors such as the species and age of plant, the length of exposure, and the fluoride concentration. Many investigators have reported fluoride inhibition of respiration in a number of plant species [51]. Others have found that lower concentrations may result in a stimulation of respiration [51].

It was demonstrated by Yu and Miller [50] that fluoride treatment of soybean leaf tissue at both high and low concentrations resulted in an initial stimulation followed by inhibition. 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 [52-55].

Inhibition of phosphoglucomutase, the enzyme that participating in sucrose biosynthesis, in higher plants could account for the inhibition of sucrose synthesis in F-fumigated plants [56]. In higher plants, energy metabolic pathways also stunned due to the toxic effects of F. It was found that in ATP forming organelles like chloroplasts, mitochondria, and plasma membrane, ATP synthase enzymes was inhibited by accumulated F. However, at the time of environmental stress condition, plasma membrane associated ATPase (P-ATPase) and tonoplast associated ATPase (V-ATPase) are the main enzymes those has shown the first alteration of their structure. F accumulation also hampered their structure as well as function [57]. From this incident it was demonstrated that these two enzymes are the main initial defensive enzymes against the F injury. On the other hand, Enolase was found to be the most important enzyme of carbohydrate metabolism inhibited by F. Fluoride competition with  $Mg^{+2}$  resulted in a slow decrease of enzyme activity and subsequently, in a complete loss of enzyme activity. In one of the recent findings on six planktonic algae, enolase was inhibited by F [58,59]. The reasons for respiratory stimulation or maintenance of high respiratory rates with fluoride-treated plant tissues are less obvious.

Ross, et al. [60], 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. [61], 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 [51], 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 [62].

A possible explanation is that fluoride may be affecting the mitochondrial membrane, as mitochondrial ATPase activity is believed to be accelerated by destruction of membrane integrity [55]. Some other studies [63,64] have suggested that swelling of mitochondria may be related to loss of membrane integrity. It was found that, the membrane is the main site of fluoride action in plants [65,66]. The observed increase in extractable mitochondria may be responsible for part of the fluoride stimulation of tissue respiration as was suggested for pathogen-

enhanced respiration in sweet potato tissue [67]. 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. [54], also stated that glucose-6-phosphate dehydrogenase, catalase, peroxidase, and cytochrome oxidase activities are increased with fluoride treatment. They demonstrated that this phenomenon happened due to the general F injury, and might be exception of glucose-6-phosphate dehydrogenase activity.

## Conclusion

In this overview, we reviewed on showing the adverse effects of fluoride compounds on the cellular function of plant biological systems. Several studies demonstrated that fluoride can interact with the cellular processes of photosynthesis and respiration. Although many enzymes involved in these alterations of the photosynthesis and cellular respiration machinery have been identified, however many of the targets and the exact mechanisms/pathways taking part in these events are still unknown. The complexity of fluoride's effects on these processes are closely related to its dose and concentration. However, in the environment, fluoride is frequently remains with other elements in different forms, which does not necessarily lead to more pronounced toxicity. In some cases, antagonistic effects have been reported. Hence, due to the data scarcity on toxic effects of fluoride in combination with other metalloids or metals on the photosynthesis and respiration, it has the necessary to conduct such studies in the field level as well as molecular level also.

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