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Review

Fluoride Toxicity Limit—Can the Element Exert a Positive Effect on Plants?

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Abstract: The problem of fluoride toxicity to living organisms is the subject of many studies. Its effect, not always toxic, on the human organism has been well documented. However, although the phytotoxicity of the element has been proved, this issue is still being investigated. It seems to be still relevant due to the progressive pollution of the environment and fluoridation of water. Assuming that the source of food for humans is plants, the content of fluoride in fruits and vegetables is important for human health. In the available literature, fluoride has been demonstrated to be phytotoxic at the level of cell transformations, biometric plant parameters, development of resistance, and biochemical processes in plants. However, several studies have provided information on improvement of certain plant parameters, e.g., the length of roots or shoots, caused by low fluoride doses and improvement of respiratory indices. The aim of this study was to analyze changes caused in plants by exposure to fluoride and to determine its beneficial effects based on the latest literature reports. It was based on the latest knowledge from the last 8 years. Attempts were made to compare earlier research results with contemporary items. In conclusion, the analysis has shown that, although some sources provide information on the positive effect of small fluoride doses, the impact of this element requires further investigations, as has not been fully elucidated.

Keywords: environment; fluoride phytotoxicity; biochemical plant changes

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1. Introduction

Fluoride pollution of the environment is a serious problem of the modern world. This element, which is widely distributed in the ecosystem, exerts a considerable impact on all ecosystem components. The interest in fluoride dates back to the 17th century. Although it was not possible to determine its exact properties at that time, it was noticed that a combination of fluorspar with sulfuric acid was able to etch glass. Fluoride was isolated from potassium fluoride in 1886 by chemist Henri Ferdinad Moissan, for which he was awarded the Nobel Prize in 1906. The name of the element refers to its destructive properties. It comes from the Greek word 'phthore', which means 'to destroy' [1]. In turn, as shown by Tressaud [2], the name comes from the Latin word 'fluo', meaning 'flow' and the symbol of fluorine as F appeared in 1814, but until the second half of the 19th century, the symbol Fl was used. The element occurs naturally in water, plants, and soils [3–5]. Additionally, it migrates continuously between individual ecosystems, e.g., from water into soil, where it is consequently taken up by plants. Fluoride is in the 5th place in the hierarchy of environmental poisons [6], and the available literature presents ongoing studies on its beneficial and negative effects on the human organism. It is classified as a halogen and included in group VII A of the periodic table. Fluoride does not occur in the free state in nature. In water, it dissociates into the F^- ion [7]. It has the highest electronegativity of all known elements; it is highly active and can form compounds with all chemical elements except oxygen, nitrogen, and lighter noble gases. The reactions of fluoride with hydrogen and hydrocarbons are usually explosive. In the nomenclature, two names for fluoride can be used interchangeably (fluorine and fluoride): fluorine is the name of the element and fluoride is its ion [8,9].

2. Fluoride Content in the Plant Root Zone

The WHO recommends that optimal dose of fluorine in drinking water as 1.5 mg F/L [10] but no information on the recommended content of fluoride in plants safe for human health was found. Water, soil, and air can be sources of fluoride for plants. However, since the root is the primary organ involved in the uptake of nutrients and undesirable substances by plants and fluoride contained in water reaches the soil during watering, the content of this element in the plant root zone seems to be especially important. There was a double increase in the fluorine content in soils over 50 years [11]. Long-term exposure to fluoride exceeding its limit value (>1.5 mg·L) was found to exert a detrimental effect on plants [12]. Fluoride compounds in soil are located mainly in the humus level, and its content depends mainly on the parent rock, compounds emitted by industrial plants, the use of phosphorus fertilizers and pesticides, or water fluoridation [13–15]. Water fluoridation in some countries has been carried out since 1940 [16]. In soil, the element occurs mainly as fluorapatite ($Ca_5(PO_4)_3F$)), fluorite (CaF_2), cryolite (Na_3AlF_6), topaz ($Al_2(SiO_4)F_2$) [17], and granite biotites [18]. Fluoride is the 13th most abundant element and constitutes approximately 0.06–0.09% in the Earth's crust [19–21]. Its average content in soil has been reported to be in the range from <10 to 1000 $mg{\cdot}kg^{-1}$ [22], 150–400 $mg{\cdot}kg^{-1}$, [23], or 625 $mg{\cdot}kg^{-1}$, with a 1.5% increase in clay soils [13], which contain 1000–3500 $mg{\cdot}kg^{-1}$ [24] or 750–1660 $mg{\cdot}kg^{-1}$ [25] of this element. Sandy soils are usually poor in fluoride, as it leaches into the soil profile [26]. The mobility of fluoride in soil depends on sorption properties, pH, and the content of calcium ions. Higher adsorption is noted in slightly acidic conditions. In acidic soils, it may be even tenfold higher than in alkaline soils [27]. It has been shown in some studies that the percentage of F adsorption increases with an increase in pH to 8 and then declines [28]. Addition of humus to the soil reduces the solubility of fluoride and its uptake by plants [29]. Fluorine ion remediation from the environment can take place in various ways, e.g., as phytoremediation (Figures 1 and 2) [30,31].

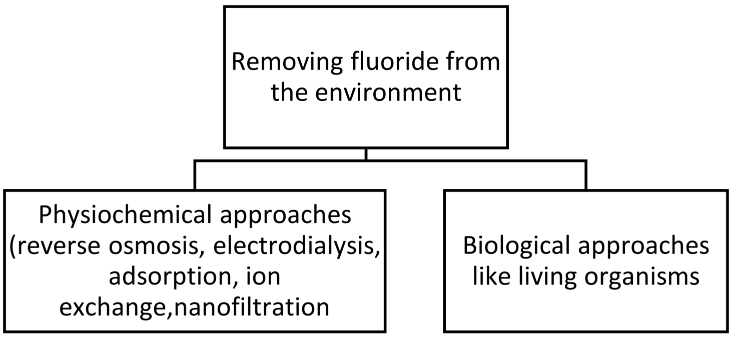

Figure 1. Removing fluoride from the environment [30].

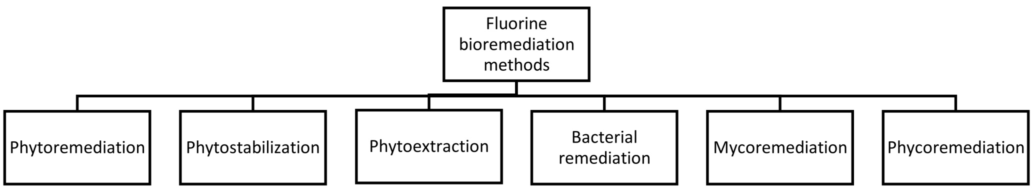

Figure 2. Fluorine bioremediation methods [30,31].

Mitigating the toxic effect of fluoride on the plant is possible through the use of silicon nanoparticles. Nano-Si-priming successfully mitigated the molecular damage and increased the yield of rice grain by reducing the bioaccumulation of fluoride. Stimulated levels of non-enzymatic antioxidants such as anthocyanins, flavonoids, phenolic compounds and glutathione [32]. Biochar is organic material can also decrease the fluoride solubility, fluoride content of plant tissues, oxidative stress and antioxidant enzymes activities [33]. Soil washing could be a viable alternative technology for the remediation of soils contaminated with fluoride. The highest fluoride removal results could obtain using 3 M HCl and HNO_3 [34].

3. Fluoride in Plants–Uptake

Fluoride uptake from soil by plants proceeds via diffusion and is linearly correlated with the total activity of the fluoride anion in the soil solution. Plants usually do not take up the element in excessive amounts, as it is often present in soil in unavailable forms. However, soils contaminated with this element pose a problem [29]. Fluoride is absorbed by plant roots, transported via xylematic flow to transpiratory organs, and stored in leaves [35,36]. Saturation of cell walls with calcium ions has an impact on F ion filtering and limits the uptake of the element by the plant. Fluoride ions can also be absorbed through chloride channels [37]. Fluoride is found in the apoplast and sometimes a small amount is also found in plasmalemma or tonoplasts. Fluoride levels are low in shoots because the endoderm acts as an effective barrier. Fluoride reaches the vascular system through a non-selective route, bypassing the endoderm [38]. The uptake rate is influenced by the type of compounds of F^- with other elements. HF compounds are taken up at the fastest rate, faster than compounds with aluminum or the fluoride anion. It has also been shown that the presence of aluminum in soil increases fluoride uptake [39]. As reported by Das et al. [40], at neutral pH, fluoride is easily bound in soil and is not available to plants. As mentioned above, the availability of calcium ions in soil is associated with formation of CaF_2: fluoride is bound and is thus unavailable for plants [24]. Plant affinity for fluoride adsorption is a species-specific trait, which depends on the plant growth stage. The content of fluoride in plants ranges from 0.6 to 1 mg·100 g dry weight [41] or 1–10 μg/g dry weight [37]. Some plants are able to secrete fluoride in the form of fluoroacetate and vinyl fluoride [41]. Such plants as tea, spinach, cabbage, lettuce, and kale are fluoride hyperaccumulators. The fluoride content in leafy and root vegetables usually does not differ from that in cereals, except for spinach and onions [40]. The content of fluoride was estimated at 25.7 μg/g in spinach and 22.2 μg/g in onion [42]. Leafy vegetables tend to accumulate larger amounts of this element than root vegetables [43]. Agarval and Chauhan [44] reported an increase in the accumulation of fluoride in barley leaves in comparison with grains. Tea absorbs up to 20–30-fold greater amounts of fluoride from soil than other plants. The content of fluoride in tea can be as high as 100–200 $mg{\cdot}kg^{-1}$, with 98% of this amount accumulated especially in older leaves [45,46]. The accumulation of fluoride in tea leaves is correlated with the presence of Al in soils where tea is grown (acidic soils). This may be associated with Ca^{2+} and CaM ions involved in the aluminum ion pretreatment, which contribute to enhancement of accumulation of fluoride in tea leaves [47]. Considering the high concentration of fluoride in tea and its popularity, it is a source of fluoride for humans. Consumption tea can deliver fluoride exposure dose from 0.03 $mg{\cdot}kg^{-1}$ d^{-1} to 0.14 $mg{\cdot}kg^{-1}$ d^{-1} to the children and 0.01 $mg{\cdot}kg^{-1}$ d^{-1} to 0.06 $mg{\cdot}kg^{-1}$ d^{-1} to adults [46]. The adequate intake (AI) for F from all sources is set at 0.05 mg/day/kg body weight for all ages over 6 months [48]. Studies show regular tea consumption (5 cups a day) can represent up to 173% of the AI (for an adult weighing 70 kg) [49]. According to research. Esfehani et al. [50] the differences in fluoride content depending on the type of tea are presented in Table 1. However, Mochammad [51] marked fluoride contents of tea after 5 min ranged from 0.95 to 4.73 mg/L for black teas, from 0.70 to 1.00 mg/L for green teas.

Table 1. Fluoride concentration in all three types of tea (in mg/L) average time of brewing 5 and 15 min [50].

Kind of Tea	mg F/L
White	1.37
Black	1.84
Green	0.23

The content of calcium in vegetables may increase fluoride accumulation due to the affinity of calcium ions for phosphorus. The amaranth, which is characterized by high content of calcium, was found to accumulate high concentrations of fluoride [52]. Antagonistic reactions between F and Cu concentrations in lettuce plants were reported by Senkondo et al. [53]. Roots of beet plants were reported to have a fluoride level of 3.41 at the soil content of 176 mg·dm^{-3} [54]. An almost 10-fold higher level of this element, i.e., 29.04 mg·kg^{-1}, was reported in other studies [55]. A comparison of the content of fluoride in wheat, tomato, and potato plants cultivated in different parts of India showed the highest levels of this element in wheat (8.77 µg·g^{-1} vs. 2.85 µg·g^{-1} in tomatoes and 2.07 µg·g^{-1} in potatoes) [56]. In chamomile plants, the content of fluoride compounds was estimated at 0.03 mg F·dm^{-3} by Emekli-Alturfan et al. [57] and 3.19 mg F·kg^{-1} by Telesiński et al. [58], who analyzed various varieties of chamomile. Interesting research was reported by analyzing the content of fluoride in citrus and non-citrus fruits. The fluoride concentration in citrus fruits and non-citrus fruits was similar and ranged 0.04 ppm (Orange) to 0.18 ppm Guava [59]. Jaudenes et al. [60] and Zohoori et al. [61] in Table 2 summarizes the average levels of fluoride in selected fruits and vegetables. With a soil content of 20 mg F·kg, in the roots, leaves, shoots, pods, grains soybean, respectively, were recorded 1.90, 2.35, 1.32, 1.38, 1.03 (mg F·kg) [62].

Table 2. Fluoride content in selected species of vegetables and fruits.

Grup	Species	Concentration (mg·kg)
vegetables	onion	0.01 [60]
	lettuce	0.08 [60]; 0.05 [61]
	potato	0.99 [60]
	tomatoe	0.96 [60]; 0.01 [61]
	carrots	0.04 [60]
	celery	0.01 [60]
	cucumber	0.01 [60]
fruits	bananas	1.72 [60]
	plums	<0.005 [61]
	berries	0.008 [60]
	kiwi	0.010 [60]
	oranges	0.023 [61]
	grapes	0.028 [61]
	cherries	0.010 [61]

The literature provides information on the use of various plant species as bioindicators of fluoride pollution of the environment, i.e., such indicator plants as *Gladiolus*, *Tulipa*, *Crocus*, *Freesia hybrida*, *Hypericum perforatum*, *Larix*, or *Pinus* [63]. An increase in fluoride concentrations in the air leads to emergence of necrotic lesions in the leaves of these plants. Fluoride is absorbed from the air through stomata, or fluoride dissolved in water enters the leaf interior through the epidermis. In the cell, fluoride is mainly present in cell walls and lower amounts are accumulated in chloroplasts, mitochondria, and ribosomes [41].

4. Effects of Fluoride on Plants

There is abundant information in the available literature on the toxic effects of fluoride on human and animal organisms. Plants are regarded as a source of food and, due to their content of fluoride compounds, a source of this element for humans. Fluoride uptake by plants is regarded as a marginal and non-hazardous process in the natural environment. Nevertheless, it is becoming an increasingly important concern in industrialized areas (fluoride emission into the air) or in areas watered with fluoridated water. Excessive exposure to fluoride compounds may cause irreversible biochemical and morphological changes in plants [56].

4.1. Visual Signs of Fluoride Phytotoxicity in Plants

The rate of emergence of signs of phytotoxic effects of fluoride in plants depends, e.g., on the intensity, exposure time, temperature, and type of light [64]. Plant exposure to excessive fluoride concentrations is first manifested by chlorosis and drying of lamina margins, which is followed by shedding of leaves. Necrosis causes plasmolysis and loss of palisade and spongy parenchyma cells. Fluorides also induce degradation of photosynthetic pigments, thereby inhibiting photosynthesis. HF leads to replacement of the magnesium atom with two hydrogen atoms in chlorophyll molecules [41,65]. A characteristic sign is tip burn as well as a visible sharp and dark line separating dead from living tissue. In *Hypericum perforatum* plants, NaF was initially found to cause wilting and produce a reddish-brown color of lamina margins, which consequently led to leaf death. Changes in the structure of chloroplasts and increased production of anthocyanins were detected as well [66]. The chloroplast structure degradation and the decrease in the chlorophyll content have been confirmed by other studies [38,67]. In another research in *Cicer arietinum* noted that carotenoid and chlorophyll a and b were stimulated at 1.0 and 2.5 mM NaF [64], however, opposite results were found in melon studies where fluoride levels reduced chlorophyll and carotenoids [68]. This thesis was also confirmed in other studies [69]. *Riccinus communis* is tolerant to a concentration of 1.5 and 3.0 mg $KF \cdot dm^{-3}$, visual signs of toxicity such as chlorosis and necrosis and changes in parenchyma tissues, cell collapse and phenolic compound at 4.5 mg $KF \cdot dm^{-3}$ [70].

Ornamental coniferous and deciduous trees and shrubs react to excessive levels of fluoride as well. The changes can be especially observed on trees in urban areas. In conifers, the natural level of fluoride in needles is $2 \div 12$ mg/kg. Differences in the content of the element in needles are associated with their age (higher content in older needles). The phytotoxicity of fluoride manifests itself in brown discoloration of the leaf blade. In conifers, the spots are darker with brown-red to black color. It is assumed that coniferous trees are more sensitive to the effects of toxic compounds, e.g., fluoride, than deciduous trees [41,71].

4.2. Biochemical Changes in Plants

The content of fluoride in plant leaves induces changes in the activity of antioxidant enzymes and the content of flavonols, phenols, and ascorbic acid [63]. *Hydrilla verticilata* plants were immersed in solutions containing various concentrations of fluoride in the range of 0–40 $mg \cdot dm^{-3}$. The exposure of the plants to the concentration of 10 $mg \cdot dm^{-3}$ resulted in an increase in the content of chlorophyll, protein, and carbohydrates, in comparison with the control. In turn, an excess amount of fluoride (20 $mg \cdot dm^{-3}$) reduced the level of these parameters but increased the activity of guaiacol peroxidase and superoxide dismutase SOD and the amount of ascorbic acid (AsA) and glutathione (GSH) [72]. Fluoride-induced stress may result in conversion of glucose, fructose, and mannose in plant tissues into sucrose and raffinose. This process may represent a mechanism adopted by plants to reduce F toxicity [73]. A decline in germination rates, inhibition of root growth, and inhibition of catalase activity in the embryo and roots of winter wheat were induced by increasing concentrations of NaF in the medium [35]. F affects photosynthesis mainly by reducing chlorophyll synthesis, degrading chloroplasts and inhibiting the Hills reaction. The chlorophyll content is also reduced and the photosynthetic system of plants is weakened. 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 [38].

Changes associated with fluoride phytotoxicity result in lower resistance and higher susceptibility of plants to infections and pathogens [74]. When air-borne fluoride is the source of pollution, its bioaccumulation in plants rises with the distance from the soil surface, with the highest accumulation recorded at a height of several meters. Hence, trees and shrubs are more vulnerable than shorter plants. *Taxus baccata* and *Robinia pseudoacacia* are regarded as pollution-resistant species. In some studies, HF was found to have a stimulating effect on the plant respiration process (fluoride concentration in the air of approx. 2 mg·m^3) and to increase enzyme activity [41]. However, other studies have found this in ATP-forming organelles such as chloroplasts, mitochondria, and the plasma membrane, ATP synthase enzymes were found to be inhibited by accumulated F [38].

4.3. Ontogenetic Changes

Excess concentrations of fluoride have been reported to reduce the mass of plant roots and the length of roots and shoots. A study conducted by Pant et al. [75] reported inhibition of root growth and reduction of shoot length caused by 0.001, 0.01, and 0.02 M of sodium fluoride (NaF) in wheat (*Triticum aestivum* L.), Bengal gram (*Cicer arietinum* L.), mustard (*Brassica juncea* L.), and tomato (*Lycopersicon esculentum* L). This tendency was first observed after the application of 0.01 m NaF. Noteworthy, the application of the dose of 0.001 M resulted in an increase in the length of roots in the wheat, Bengal gram, and tomato, compared to the control, and an increase in the length of shoots in all species except wheat. The effect of watering with water contaminated with fluorine compounds on plant growth traits was observed in an experiment with rice (*Oryza sativa* L.). The plants exhibited higher accumulation of fluoride in roots than shoots, lower germination rates, and increased catalase activity [76]. Treatment of chickpea and barley seeds with different levels of NaF (1.0, 2.5, 5.0, and 10.0 mM) resulted in a clear percentage reduction in the germination rate, seedling emergence rate, and seed vigor index [77].

5. Changes in the Chemical Composition of Plants Induced by Fluoride

Cultivation of plants in soils contaminated with fluoride compounds exerts an impact on their chemical composition. Increased phosphorus content in black radish, air-dried yellow lupine mass, and spring triticale roots was observed after application of higher fluoride doses into the soil. Inverse relationships were noted in the case of maize roots [78]. The correlation between the presence of fluoride in soil and phosphorus uptake by plants was confirmed by Fung and Wong [79]. Negative correlations were found by Nagaraju et al. between fluoride and zinc in *Arachis hypogaea* stems, fluoride and lead in *Phaseolus vulgaris* leaves, and fluoride and zinc in *Lycopersicon esculantum* stems [80]. *Solanum tuberosum* is regarded to be highly resistant to increased fluoride concentrations in soil, which has been confirmed in some investigations. No signs of fluoride phytotoxicity were detected in potato plants growing in the presence of 0–190 mg NaF·kg^{-1} of the element in the soil. Nevertheless, the fresh mass of roots, shoots, and leaves was reduced [40]. The phytotoxicity threshold in the onion shoot was estimated at 55 mg NaF·kg^{-1}, i.e., a value that resulted in a 50% biomass reduction. Concurrently, greater accumulation of fluoride was noted in onion roots and shoots than in bulbs [81]. *Erodium glaucophyllum* in response to fluoride stress shortens its vegetation period and *Rantherium suaveolens* stores fluoride in dead tissues. The stress reaction of these plants was also higher accumulation of calcium in the leaves [82].

6. Conclusions

Fluoride is toxic to plants. Its excessive accumulation in the environment, especially in the root zone, induces irreversible changes in various horticultural and agricultural species. Plants exposed to fluoride compounds exhibit alterations in their appearance, metabolism, chemical composition, and physiology. Fluoride phytotoxicity manifests itself in changes in the activity of enzymes, has an adverse effect on the photosynthesis process, and leads to inhibition of plant growth and biomass gain. However, the recent literature provides little information about fluoride concentrations in the medium that constitute toxicity threshold values. The thesis that low amounts of fluoride may have a stimulating effect on some plant parameters requires verification and further research. Nevertheless, the hypothesis of the very thin and not fully understood boundary between the toxic and neutral or stimulating effect of fluoride on plants depending on the plant species seems to be supported.

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