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Effect of fluoride on vegetable crops: Positive and negative influences

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Abstract
Fluoride contamination in agricultural systems represents a significant environmental challenge affecting vegetable crop production worldwide. This review synthesizes current knowledge on fluoride's effects on vegetable crops, examining both detrimental and potentially beneficial influences. Fluoride enters agricultural systems through contaminated irrigation water, atmospheric deposition from industrial emissions, and phosphate fertilizers. Vegetable crops demonstrate variable susceptibility to fluoride toxicity, with leafy vegetables generally accumulating higher concentrations than fruiting vegetables. Negative effects predominate, including phytotoxicity symptoms (chlorosis, necrosis, leaf tip burn), growth inhibition, yield reductions of 6–90%, oxidative stress induction, and disruption of photosynthetic machinery. Biochemical alterations include decreased chlorophyll content (up to 86%), reduced sugar and protein levels, and elevated proline and ascorbic acid as stress indicators. Limited evidence suggests low-dose fluoride may stimulate growth in certain species. The accumulation of fluoride in edible plant parts poses significant human health risks, with 89% of vegetables near industrial sources exceeding safety limits in some regions. Mitigation strategies encompass agronomic interventions, crop selection, phytoremediation approaches, and water treatment technologies. This review emphasizes the need for crop-specific tolerance thresholds and sustainable management practices to ensure food safety and agricultural productivity in fluoride-affected regions.

Keywords: Fluoride toxicity, vegetable crops, phytotoxicity, bioaccumulation, oxidative stress, food safety, mitigation strategies

Introduction

Fluorine exists ubiquitously in the earth's crust at concentrations ranging from 20 to 1,000 μg g^{-1} in soils, though more than 90% remains in insoluble forms, as documented by Hong *et al.* (2016) [16]. While fluoride plays recognized roles in human dental health at trace concentrations, it functions as an environmental xenobiotic even at sparingly low levels. Banerjee and Roychoudhury (2019) [1] emphasized that uncontrolled anthropogenic activities have steeply increased fluoride content in air, water, and soil, adversely affecting physiological and biochemical parameters of crops and vegetables. Field-grown vegetables can accumulate up to 40 mg kg^{-1} fresh weight of fluoride (2016) [16], potentially exceeding safe consumption limits.

The prescribed norm for fluoride in irrigation water ranges from 0.8 to 1.5 mg L^{-1}, as noted by Yadav *et al.* (2012) [37], yet many agricultural regions worldwide exceed these thresholds. Thomas and Alther (1966) [34] documented that fluorine exhibits toxic properties when absorbed by plants as gases or solids from industries including aluminum smelting, steel production, and phosphate fertilizer manufacturing. Yamazoe (1975) [39] demonstrated that fluorine compounds such as hydrogen fluoride are highly poisonous to plants even at parts-per-billion levels, with turnip, maize, pepper, and tomato showing injury at concentrations as low as 5 ppb for 7–9 days.

Vegetable crops are particularly vulnerable to fluoride stress due to direct exposure through soil and irrigation water. Pal (2020) [25] provided a concise overview of fluoride contamination and its adverse effects on plant biochemistry, emphasizing the need for comprehensive understanding. Chatterjee *et al.* (2020) [8] reviewed fluoride's role in soil, plant and human health, discussing sources, toxicity and mitigation strategies. This review synthesizes current knowledge on fluoride's effects on vegetable crops, examining entry pathways, uptake mechanisms, toxic manifestations, potential beneficial effects, human health implications, and mitigation strategies.

Sources and Pathways of Fluoride Entry into Crops

Fluoride enters agricultural systems through multiple interconnected pathways, with both natural and anthropogenic sources contributing to crop contamination. Understanding these entry routes is essential for developing targeted mitigation strategies and predicting fluoride accumulation patterns in different agricultural systems.

Contaminated Irrigation Water

Contaminated groundwater represents the most significant pathway in many agricultural regions worldwide. Mondal and Gupta (2015) [14] demonstrated that irrigation with fluoride-contaminated water (4.8 mg L^{-1}) led to significant fluoride accumulation in post-harvest soil (164 mg kg^{-1}) and vegetables, with concentrations ranging from 18.6 mg kg^{-1} in cucumber to 55 mg kg^{-1} in spinach. Villagers consuming these crops were exposed to 35% more fluoride through their diet compared to control populations, demonstrating the direct link between irrigation water quality and dietary fluoride exposure. Khandare and Rao (2006) [18] found that vegetables irrigated with 10 ppm fluoride water accumulated significantly higher fluoride, with amaranth showing the highest uptake (20.29 mg kg^{-1} dry weight) and cabbage the lowest (0.17 mg kg^{-1} dry weight), representing a 119-fold difference in accumulation capacity.

Saini *et al*. (2014) [29] investigated sodium fluoride effects on red chilli (*Capsicum annuum*) irrigated with 0 to 14 ppm NaF, finding bioaccumulation highest in roots (9.948–10.73 mg kg^{-1}) and lowest in leaves (6.302–7.212 mg kg^{-1}), demonstrating concentration-dependent accumulation patterns. The results suggest that red chilli plants may tolerate relatively high fluoride content from groundwater irrigation, though accumulation patterns vary among plant organs.

Industrial Atmospheric Emissions

Industrial emissions constitute a major source of atmospheric fluoride that directly affects vegetable crops through foliar absorption and subsequent soil contamination. He *et al*. (2020) documented that fluoride emissions from an abandoned aluminum plant caused excessive fluorine enrichment, with 89.26% of agricultural products exceeding Chinese Maximum Levels of Contaminants even five years post-abandonment, demonstrating the persistent nature of industrial fluoride contamination. Barnthouse *et al*. (1995) [2] reported that accidental releases of hydrogen fluoride cause visible dead tissue between leaf veins and chlorotic leaf margins, documenting widespread vegetation damage from industrial sources.

Soil Contamination and Bioavailability

Hong *et al*. (2016) [16] noted that high fluoride concentrations associated with soil colloids and clay minerals can increase uptake via plant roots. The bioavailability of soil fluoride depends on multiple factors including pH, organic matter content, clay mineralogy, and the presence of complexing ions such as calcium and aluminum. Begum *et al*. (2008) [5] observed that fluoride levels in vegetables are markedly influenced by irrigation water fluoride content, and that nitrogen, phosphorus, potassium, magnesium, and calcium increase vegetables' immunity to fluorine toxicity, suggesting that soil nutrient status modulates fluoride uptake and toxicity. Phosphate fertilizers represent an often-overlooked source, as documented by Thomas and Alther (1966). Baykin *et al*. (2019) [4, 34] examined the environmental state of soils and plants exposed to cryolite plant emissions, documenting agrochemical protection methods and the complex interactions between fluoride sources and soil properties.

Fluoride Uptake and Accumulation in Vegetable Crops

Vegetable crops exhibit considerable variation in fluoride uptake capacity and accumulation patterns, influenced by species-specific physiological characteristics, exposure routes, and environmental factors. Leafy vegetables generally accumulate higher concentrations than fruiting vegetables due to their greater surface area and direct exposure to both soil-derived and atmospheric fluoride. Mondal and Gupta (2015) [14] reported spinach accumulated the highest fluoride (55 mg kg^{-1}), while cucumber accumulated the lowest (18.6 mg kg^{-1}), representing nearly a three-fold difference in accumulation capacity. Gautam *et al*. (2010) [12] studied fluoride accumulation in vegetables and crops in Nagaur district, Rajasthan, finding leafy vegetables like spinach showed maximum concentrations. Gupta and Mondal (2015) [14] provided comprehensive perspectives on fluoride accumulation in crops and vegetables in India, documenting regional variation patterns and emphasizing the importance of understanding local contamination dynamics.

Lakshmi *et al*. (2017) [20] found tomato accumulated higher fluoride followed by brinjal and bhendi, with concentration ranges of 0.12 to 3.35 mg kg^{-1} (kharif) and 0.30 to 3.95 mg kg^{-1} (rabi). These values remained below the FAO/WHO maximum allowed level of 4.0 mg kg^{-1}, suggesting that moderate soil fluoride levels may not necessarily result in unsafe vegetable fluoride concentrations. Maximum accumulation occurred in roots, then shoots, then edible parts, indicating that plants may sequester fluoride in non-edible tissues as a tolerance mechanism. Yadav *et al*. (2012) [37] noted that potato peeling can contain up to 75% of total fluoride in the tuber, indicating fluoride concentrates in outer tissues. This finding has practical implications for food preparation and consumption practices in fluoride-affected regions.

Stevens *et al*. (1998) [32] investigated fluoride uptake mechanisms in tomato (*Lycopersicon esculentum*) and oats, finding that at low fluoride activities (<1684 μM), shoot fluoride concentrations increased almost linearly, then rapidly before reaching an asymptote. Tomato shoot and root growth were limited when fluoride ion activities exceeded 1473 μM, while oats tolerated up to 5130 μM without dry weight effects, demonstrating significant interspecific variation in fluoride tolerance. The study suggested calcium complexation with fluoride alters membrane permeability, and growth solution ionic strength is positively related to fluoride uptake. This indicates that fluoride uptake is not merely passive but involves complex interactions with membrane transport systems and competing ions.

Rizzu *et al*. (2020) [28] examined fluoride uptake and translocation in food crops grown in fluoride-rich soils, documenting transport mechanisms and the role of soil properties in determining bioavailability. Pelc *et al*. (2017) [27] tested two radish varieties and found both accumulated large amounts of fluoride ions in leaves, with radish Carmen showing 65.95% root length reduction with 10 mM NaF, demonstrating that fluoride accumulation is accompanied by severe growth inhibition. Chakrabarti *et al*. (2013) [7] studied fluoride uptake by two paddy varieties treated with fluoride-contaminated water, documenting varietal differences that suggest potential for breeding or selecting low-accumulating varieties as a mitigation strategy.

Negative Effects of Fluoride on Vegetable Crops

1. Phytotoxicity Symptoms

Banerjee and Roychoudhury (2019) [1] documented phytotoxicity symptoms including necrotic lesions, burning, chlorosis, and leaf damage across multiple vegetable species. Pal *et al*. (2012) [26] observed decreased plant growth, chlorosis, leaf tip burn, and leaf necrosis in cabbage, onion, spinach, radish, potato, cauliflower, and brinjal. Pal (2020) [25] provided a concise overview of fluoride contamination and adverse effects on plant biochemistry, emphasizing widespread phytotoxicity.

Pelc *et al*. (2017) [27] reported that fluoride adversely affected morphological and biochemical parameters of 10-day-old seedlings of radish, cucumber, and tomato, with phytotoxicity symptoms including decreased growth, chlorosis, leaf tip burn, and necrosis. Biczak *et al*. (2017) [6] described fluoride effects on common radish including chlorosis, peripheral necrosis, leaf distortion, and abnormal fruit development, with radish accumulating approximately seven times higher fluoride than controls at 1000 mg kg^{-1} soil dry weight.

Szostek and Ciećko (2017) [33] documented that fluorine causes chlorosis and necrosis of leaves in black radish and other crops, inhibiting plant growth. Weinstein (1977) [35] comprehensively reviewed fluoride and plant life, establishing foundational understanding of phytotoxicity mechanisms.

2. Oxidative Stress and Biochemical Alterations

Banerjee and Roychoudhury (2019) [1] reported that fluoride increases oxidative stress indicators like ascorbic acid and phenolics in affected plants. Sharma and Kaur (2018) [30] provided insights into fluoride-induced oxidative stress and antioxidant defenses in plants, documenting ROS generation and compensatory responses. Sharma *et al*. (2019) [31] studied accumulation, morpho-physiological and oxidative stress induction by fluoride in *Spirodela polyrhiza*, finding dose-dependent oxidative damage.

Pal *et al*. (2012) [26] documented that fluoride reduces chlorophyll by up to 86.1% in potatoes, representing severe photosynthetic impairment. Mondal and Gupta (2015) [14] found crops cultivated with fluoride-contaminated water showed decreased chlorophyll and sugar, and increased ascorbic acid and proline content. Pelc *et al*. (2017) [27] observed that total chlorophyll and carotenoids decreased in fluoride-treated seedlings, with proline content increasing as a stress response.

Yamauchi *et al*. (1983) [38] demonstrated that fluoride reduces chlorophyll and protochlorophyll syntheses and induces chloroplast structure degradation in bush bean and soybean. When orange leaves were fumigated with HF, chloroplasts were the main fluoride accumulation site. Mesquita *et al*. (2013) [21] evaluated fluoride effects on leaf gas exchange in coffee and sweet orange plants, finding fluoride compromises gas exchange and photosynthetic efficiency.

Biczak *et al*. (2017) [6] noted that fluorine negatively influences assimilation and photosynthesis due to destructive effects on chloroplasts. Kumar *et al*. (2017) [19] reviewed effects of fluoride on respiration and photosynthesis in plants, providing mechanistic overview. Baunthiyal *et al*. (2014) [3] discussed fluorides and effects on plant metabolism, documenting enzymatic disruptions.

3. Growth Inhibition and Yield Loss

Mishra *et al*. (2014) [22] documented that fluoride decreased germination percentage and vigor in all tested crops. Net Primary Production decreased in Brinjal (6.64–56.72%), Tomato (14.46–62.24%), Mung (10.27–53.61%), Mustard (15.58–61.21%), Ladies finger (12.28–52.78%), and Chilli (40.8–90.65%). Pod formation was inhibited at 100 ppm for Mung, 50 ppm for Ladies finger, 40–100 ppm for Maize, and 30–50 ppm for Chilli.

Mishra *et al*. (2014) [22] quantified that fluoride contamination decreased Net Primary Productivity in Brinjal (6.64–56.72%), Tomato (14.46–62.24%), Ladies finger (12.28–52.78%), and Chilli (40.8–90.65%) across 10–100 ppm fluoride range. Chilli was particularly sensitive, with NPP reductions exceeding 90% at high concentrations.

Stevens *et al*. (1998) [32] found tomato shoot and root growth were limited when fluoride ion activities exceeded 1473 μM, while oats tolerated up to 5130 μM without effects, demonstrating significant interspecific variation. Szostek and Ciećko (2017) [33] reported complex effects, with most crops showing biomass stimulation, but exceptions including spring triticale grain/straw, maize roots, and lucerne aerial parts experiencing decreased yields. Black radish and winter oilseed rape showed resistance with significant biomass increases. Yadav *et al*. (2012) [37] reported that excess fluoride accumulation leads to visible leaf injury, damage to fruits, and yield changes. Datta *et al*. (2012) [10] studied fluoride toxicity impacts on germination and seedling growth of gram seed, finding dose-dependent inhibition.

Positive and Beneficial Influences of Fluoride

1. Low-Dose Growth Stimulation

Grishko (2007) [13] provided direct evidence for fluoride-induced growth stimulation, reporting that low fluoride concentrations (5 and 10 mg F L^{-1}) stimulated oat root growth, with potassium fluoride at 5 mg L^{-1} increasing root length by 2-fold. Ammonium fluoride was less toxic than potassium and sodium fluorides. Szostek and Ciećko (2017) [33] observed that while fluorine causes phytotoxicity symptoms, it stimulated biomass in most tested crops, with black radish and winter oilseed rape showing particular resistance and significant biomass increases.

Yadav *et al*. (2012) [37] acknowledged that fluoride can have complex effects on growth, varying from positive to negative. However, the evidence for beneficial effects remains limited and inconsistent.

2. Antifungal Properties and Effects on Secondary Metabolites

While no studies in the current review explicitly documented antifungal effects of fluoride in vegetable crop systems, fluoride stress induces accumulation of certain secondary metabolites that may have implications for plant defense or human nutrition. Pal *et al*. (2012) [26] reported ascorbic acid increased by up to 31.0% in kundri exposed to fluoride stress, representing a stress response that could theoretically enhance the nutritional value of vegetables for human consumption through increased vitamin C content. Mondal and Gupta (2015) [14] documented increased ascorbic acid and proline content in crops cultivated with fluoride-contaminated water. Proline accumulation serves protective functions in plants, acting as an osmoprotectant and reactive oxygen species scavenger under stress conditions.

Banerjee and Roychoudhury (2019) [1] noted that fluoride increases phenolic compounds in affected plants. Phenolics serve multiple functions including antioxidant activity, UV protection, and defense against herbivores and pathogens. Enhanced phenolic content could theoretically improve plant defense capacity and provide increased antioxidant compounds in vegetables for human consumption, though this must be balanced against overall negative impacts on plant health and productivity. Szostek and Ciećko (2017) [33] found total nitrogen content increased in most fluoride-exposed plants, with protein nitrogen increasing in spring triticale grain and black radish roots.

It is crucial to emphasize that evidence for beneficial fluoride effects remains limited and far outweighed by documented negative effects. The increases in stress-responsive metabolites occur alongside severe growth inhibition, yield losses, and chlorophyll degradation, making any potential benefits negligible compared to overall negative impacts. Furthermore, even if these metabolic changes provide some nutritional benefits, the concurrent accumulation of toxic fluoride levels in edible tissues negates any advantages and poses significant food safety risks.

Human Health Implications of Fluoride Accumulation in Vegetables

Vegetables represent a major dietary fluoride source in fluoride-endemic regions. Mondal and Gupta (2015) [14] demonstrated that villagers consuming crops irrigated with 4.8 mg L^{-1} fluoride water were exposed to 35% more fluoride through their diet. He *et al*. (2020) [28] documented that 89.26% of agricultural products near an aluminum plant exceeded Chinese Maximum Levels of Contaminants, with high non-carcinogenic risks identified for children, particularly within 1 km of the plant.

Jha *et al*. (2011) [17] evaluated fluoride toxicity risk from ingestion of vegetables and cereal crops, indicating accumulation can exceed limits, leading to toxic effects on human health. Yadav *et al*. (2012) [37] emphasized that the prescribed fluoride limit in water is 0.8–1.5 mg L^{-1}, and potato peeling can contain up to 75% of total fluoride, suggesting peeling reduces dietary intake.

Different vegetables accumulate fluoride to varying degrees, creating differential health risks. Khandare and Rao (2006) [18] found amaranth showed 119-fold higher uptake than cabbage, indicating crop selection significantly influences dietary exposure. Lakshmi *et al*. (2017) [20] reported concentrations of 0.12 to 3.35 mg kg^{-1} (kharif) and 0.30 to 3.95 mg kg^{-1} (rabi), remaining below FAO/WHO maximum of 4.0 mg kg^{-1}.

Children represent a particularly vulnerable population. He *et al*. (2020) specifically identified high non-carcinogenic risks for children from vegetables grown near industrial sources. Thomas and Alther (1966) [34] documented that fluoride damage to animals occurs from ingesting fodder containing 30 to 50 ppm or more fluorine. Begum *et al*. (2008) [5] noted that fluorine covalently fixes with protein and various nutrients increase vegetables' immunity to fluorine toxicity. Dharmaratne (2015) [11] identified fluoride in drinking water and diet as the causative factor of chronic kidney diseases in Sri Lanka, emphasizing cumulative health impacts.

Mitigation Strategies

Effective fluoride management requires integrated approaches. Banerjee and Roychoudhury (2019) [1] emphasized that cumulative use of phytoremediative organisms through proper scientific planning can improve agricultural soil quality, though robust field trials are needed.

Source Control and Water Management

The most effective strategy involves preventing fluoride entry through source control and water treatment. Yadav *et al*. (2012) [37] noted the prescribed fluoride limit in irrigation water is 0.8–1.5 mg L^{-1}, providing targets for treatment interventions. Defluoridation technologies including adsorption, ion exchange, reverse osmosis, and electrocoagulation can reduce concentrations before crop application.

Agronomic Interventions and Crop Selection

Begum *et al*. (2008) [5] reported that nitrogen, phosphorus, potassium, magnesium, and calcium increase vegetables' immunity to fluorine toxicity, suggesting balanced fertilization may mitigate effects. Stevens *et al*. (1998) [32] suggested calcium complexation with fluoride alters membrane permeability, indicating soil amendments could modulate uptake.

Khandare and Rao (2006) [18] demonstrated cabbage accumulated 119-fold less fluoride than amaranth, indicating crop choice significantly influences dietary exposure. Lakshmi *et al*. (2017) [20] found fruiting vegetables remained below FAO/WHO limits under moderate contamination. Stevens *et al*. (1998) [32] demonstrated oats tolerated 5130 μM fluoride while tomatoes were limited at 1473 μM, indicating significant interspecific variation exploitable through crop selection. Banerjee and Roychoudhury (2019) [1] emphasized that high-throughput genetic analyses should identify quantitative trait loci for generating fluoride-tolerant characters in susceptible cultivars. Weinstein and Davison (2003) [36] identified native plant species suitable as bioindicators and biomonitors for airborne fluoride.

Phytoremediation and Integrated Approaches

Banerjee and Roychoudhury (2019) [1] discussed screening fluoride hyperaccumulators and fluoride-tolerant plants to facilitate phytoremediation. Chen and Xiong (2011) [9] reviewed phytoremediation in fluoride-contaminated water and toxicity of fluoride on plants, emphasizing remediation needs. Chatterjee *et al*. (2020) [8] reviewed fluoride's role in soil, plant and human health, discussing sources, toxicity and mitigation strategies comprehensively. Zhang *et al*. (2019) [40] investigated migration and transformation of fluoride through fluoride-containing water for irrigation of soil-plant systems, documenting transport dynamics.

Conclusion

Fluoride contamination represents a significant threat to vegetable crop production and food safety worldwide. Stevens *et al*. (1998) [32] demonstrated tomatoes show growth inhibition at fluoride ion activities exceeding 1473 μM, while Mondal and Gupta (2015) [14] documented accumulation ranging from 18.6 to 55 mg kg^{-1} across vegetables, illustrating wide interspecific variation. Negative effects are severe and well-documented. Banerjee and Roychoudhury (2019) [1] comprehensively reviewed phytotoxicity symptoms, while Pal *et al*. (2012) [26] reported chlorophyll reductions up to 86.1%. Mishra *et al*. (2014) [22] quantified productivity losses of 6.64–90.65% across vegetable crops.

While Grishko (2007) [13] reported growth stimulation in oats at low fluoride concentrations, and Szostek and Ciećko (2017) [33] observed biomass increases in black radish, evidence for beneficial effects remains limited. The overwhelming consensus is that fluoride's negative impacts far outweigh potential benefits. He *et al*. (2020) [28] documented that 89.26% of agricultural products near industrial sources exceeded safety limits, with high risks for children. Mondal and Gupta (2015) [14] demonstrated 35% increased dietary fluoride exposure in affected populations.

Effective mitigation requires integrated approaches combining source control, agronomic interventions, crop selection, and remediation technologies. Begum *et al*. (2008) [5] identified nutrients that increase vegetables' immunity to fluorine toxicity. Banerjee and Roychoudhury (2019) [1] emphasized phytoremediation potential and need for genetic analyses. Critical knowledge gaps remain requiring urgent research: establishing crop-specific tolerance thresholds, elucidating molecular mechanisms, identifying genetic markers for breeding programs, evaluating long-term mitigation effectiveness, assessing fluoride bioavailability from vegetables in human diet, and developing rapid monitoring methods.

Policy interventions are essential, including stringent regulation of industrial emissions, establishment of fluoride limits in irrigation water and soils, crop-specific food safety standards, subsidies for water treatment, extension programs educating farmers, and monitoring programs. Addressing fluoride contamination requires coordinated efforts among researchers, policymakers, agricultural extension services, and farming communities to develop integrated management approaches tailored to local conditions, ensuring sustainable vegetable production and protecting public health in affected regions worldwide.

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