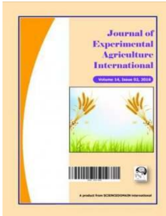

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Immobilization of Fluoride in Soils through Soil Properties - A Review

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

Fluoride (F) is one of the elements that are important in dental and skeletal formation in human beings. If present at optimal levels, it plays a very important role of preventing dental carries. However, its excessive uptake causes dental fluorosis and under extreme cases it causes skeletal fluorosis. F finds its route to human beings mainly through drinking water. However, substantial quantities of F can be taken by human beings through ingestion of food substances that contain elevated quantities of F. For example, tea can accumulate as high as 2965 mg kg^{-1} in their leaves. Therefore F in agricultural soils can be a source of F contamination. Despite the fact that F in crops can be a significant cause of fluorosis, studies on F dynamics in soils and its eventual uptake by crops has received little attention. Therefore this review article presents information on soil properties that enhance or deter F solubility in soils and its eventual bioavailability and the concomitant effects to crop plants. Soil physico-chemical conditions that affect the distribution of different F species and consequently its bioavailability and the uptake by plants have been discussed where pH is the most crucial factor. Cations like Ca and Mg in soils precipitate F thereby rendering it immobile. F in soils can be immobilized by organic amendments. Literature further shows that F is less mobile in heavy textured soils than in light textured soils. Therefore, this article reviews soil properties that can be manipulated so as to attain F immobilisation in soils and deter its uptake. The review has highlighted research gaps on F dynamics, mobilization/immobilization in soils. It is expected that this review will open a call for further research on the identified gaps.

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1. INTRODUCTION

1.1 Occurrence of Fluoride

Fluorine occurs in soils, water, air, vegetations [1]; in beverages like tea leaves [2] and in animals but in small quantities [3]. Fluoride in soils occurs naturally or could originate from industries that use F containing compounds [4, 5]. Phosphatic fertilizers, especially the super phosphates account for a significant anthropogenic source of F in agricultural lands and its elevated concentrations in plants [6]. Fluoride can also be released to the environment through accidental spillage of anhydrous hydrogen fluoride [7]. All these sources lead to elevated quantities of F in the environment thereby posing a threat of contaminating the food web.

Fluoride occurs in many rock forming minerals; hence, its concentration in water and in soils is expected to be high in areas where fluoride forming minerals are abundant. Calcite, fluorite, coal and granite [8] have been reported to cause enrichment of F in underground water resources. Elevated levels of F in the soil and in water have been reported worldwide including in Tanzania [9]. Elevated quantities of F in drinking water [10] and in food materials cause fluorosis. This disorder is characterised by mottling of teeth and under extreme cases, bone deformities [11]. In plants, F can interfere with physiological processes and more effects are observed with the longer exposure [12].

Therefore, the objective of this review was to highlight soil properties that can be manipulated to immobilize F in soils and reduce its plant uptake and come-up with research gaps on soil F immobilization techniques.

1.2 Soil Properties and the Solubility of Fluoride

1.2.1 Soil pH

Soil pH has profound effects on biogeochemistry of F. For example, acidic conditions in soils may increase the bioavailable fraction of F in soils [13] thereby elevating its quantities in food materials. Lower solubility of F occurs at a pH range of from 6 to 6.5 [14] due to the formation of Fe, Al and H complexes, whereas under alkaline conditions, F desorbs from clay minerals. Under alkaline soil conditions, F desorbs as a result of increased OH^- on soil colloids [15] and therefore there is a potential increase in phytoavailability of F. Beans provided with aluminium and fluoride as AlF_3 at pH 4-9, showed an enhanced fluoride uptake and translocation compared to plants given the same concentration of fluoride (as NaF) by itself [16]. This shows that aluminium-F complexes are more bioavailable than is the case for F alone. Soil pH has profound effects on F speciation and consequently its solubility and bioavailability. The enhanced F solubility under these conditions can be attributed to the formation of Al-F complexes at pH around 6. Under neutral to alkaline pH conditions, F solubility can be a result of desorption of free F ion due to repulsion by the negatively charged surfaces [17].

1.2.2 Soil texture

Soil texture has a profound effect on F toxicity and bioavailablity in soils [18] with sandy textured soils presenting higher bioavailability than clay textured soils. Therefore, plants grown in heavier textured soils take up less F than plants grown on light textured soils. Germination of plants was found to be inhibited in sandy cultured plants as a result of F toxicity, but germination was not affected by the elevated F concentrations for plants grown on normal soils [19]. This phenomenon is attributed to the fact that particles of clay fraction have a large surface area per unit weight and therefore they have a capability of retaining chemical species of any substance that has an affinity for their surface. Clay textured soils retained 200 to about 500 mg F kg^{-1} while sandy textured ones retained less than 100 mg F kg^{-1} [20] demonstrating that the mobility of F in clay textured soils is lower than that in sandy textured soils. Although soil texture has a profound effect on F solubility, it is difficult to manipulate it under field conditions for the purpose of deterring F mobility.

1.2.3 Soil organic matter

Decomposed organic matter can influence and dominate the properties of soils. The increased organic matter levels may increase the F adsorption capacity of soils [18]. However, [13] reported the depletion of F from top soils and attributed the phenomenon with the low F affinity of organic matter. This elucidates that the mobility of F in soils is not governed by single soil parameters but a joint effects of the properties. This emphasises the importance of studying F mobility under specified soil conditions. F adsorption by organic matter in soils has been reported [21]. This signifies that to halt F solubility in soils it is of prime importance to add organic matter in the F affected soils. These results are crucial in designing F immobilization strategies in F contaminated soils. Therefore, organic matter contents in soils determine the fate of F. However, the study by [21] was a batch experiment carried out in a laboratory. Most F immobilisation studies in soils are still at a laboratory stage. It is therefore very important to carry out field experiments to evaluate the effects of organic amendments in soils on F immobilization. If significant immobilization will be observed under field conditions, it will be a very useful technology especially to developing countries where affordable technologies are required to ameliorate F contaminated soils.

1.2.4 Accumulation of F in food materials

Food materials can be a significant source of F intake by human beings. For example, tea plants have been reported to accumulate F quantities of as high as 2965 mg kg^{-1} dry weight [22]. In the study, the authors showed that soils which had total F contents of 258mg kg^{-1} was found to contain 0.51 mg kg^{-1} soluble F contents, where as soils with total F contents of 463 mg kg^{-1} had water soluble F of 0.25. This shows that only a small fraction of F is soluble. However, tea leaves grown on these soils encountered with such low levels of soluble F had significantly accumulated high F contents, of as high as 574 to 2965. This phenomenon shows that food web can be contaminated by the elevated levels of F in soils if the plants take-up substantial quantities.

In fluoride contaminated soils, the risk of fluoride toxicity may be increased if fluoride contaminated irrigation water is used for irrigation, which is a common practice in many fluoride affected areas. This can significantly elevate the levels of fluoride in soils as well as in crops grown on the soils and may enhance the uptake of F by crops [23] thereby posing a danger of contaminating the food web. A study to compare the accumulation of F in different vegetables particularly the vegetables irrigated with F contaminated water (10 mg F l^{-1}) and those irrigated with clean water was reported [24]. The results revealed that amaranthus grown in F contaminated water accumulated F of up to 20.29 mg F kg^{-1} dry weight compared with 3.88 mg kg^{-1} grown in the control water. Other vegetables such as Cabbage, tomatoes, spinach and okra, had F contents of less than 1.7 mg kg^{-1}. However, the vegetables irrigated with F contaminated waters had higher F contents than those irrigated with tap water. Therefore fluoridated waters should not be used to irrigate F hyper-accumulating plants. It is therefore important to screen crop plants grown on F contaminated areas and avoid those that excessively take-up F.

A plethora of literature exists on methods to remove F from drinking water. Studies on ways of immobilising F in soils and deter its uptake by crops and studies on remediating soils contaminated with F have received little attention. Information on the concentrations of F in soils is scant in literature. Therefore there are no globally developed critical levels of F in soils above which the soils are considered F contaminated [20]. In parts of Europe for example, the maximum permissible soil water soluble F concentration is 45 µg g^{-1}. These values are higher than the total F concentrations in natural soils. It is therefore of utmost importance to carry further studies on F dynamics in soils so as to finally come up with critical levels of F in soils under specific conditions above which a soil is considered contaminated.

2. FLUORIDE SPECIES IN SOIL SOLUTION AND UPTAKE BY PLANTS

Different plant species have different tolerance levels to F. A group of F susceptible plants can be seriously affected by low foliar F concentrations whereas highly tolerant plant species may not show toxicity symptoms even at elevated F concentrations. F hyper-accumulating, tolerant plants are more dangerous because if consumed by animals or by human beings, a significant quantity of F will be ingested. Therefore, in F contaminated soils it is important to screen all the food crops for human consumption. Furthermore, pastures that are used to feed herbivores should be screened as well so as to avoid the potential F contamination of the food web. In developing countries, such information is missing in literature and further research is called for. The need to have such information from less F researched countries stems from the fact that the F availability in soils and its eventual uptake is mainly dependent on joint effects of soil properties. To a great extent, soil types and their respective physico-chemical properties differ from one location to another and hence limiting the transfer of F bioavailability information from one location to another.

As presented earlier, soil physical and chemical properties play a major role in F solubility and its concomitant bioavailability. The total F concentrations in soils that exceed 500 mg F kg^{-1} usually shows the presence of fluoride-rich minerals. In mineral soils, fluoride is bound to aluminium, calcium and silicate. This leads to low F solubility and low leaching rates [25]. However, in tilled soils, vertical migration of F has been reported [26].

Therefore depending on the type of F species present in soils, which are mainly controlled by soil physico-chemical properties, F uptake can be attenuated or enhanced. Researching on soil conditions that favour the presence of each species will significantly improve F immobilisation techniques in soils.

It is a well known fact that the contaminants adsorbed and sequestered onto solid phase components may not be bioavailable and therefore not toxic to organisms [27]. The most bioavailable fraction of F in soils is the water soluble fraction. In soils where the total F content was measured to be 154 and 204 mg kg^{-1}, the corresponding water soluble fraction was only 0.129 and 6.2 mg kg^{-1}, respectively. This testifies that the total F contents in soils may not be a good indicator of its bioavailability. The total F contents in soils therefore can just be used to alert on the contamination levels but the potential bioavailability should be estimated using the available fractions. However, the actual bioavailability should be estimated using uptake studies using specific plants. This argument is rooted from the fact that soil physico-chemical properties dictate F bioavailability. Plant species in question as well determines whether F is taken up excessively or the uptake is deterred. It is important that the bioavailability studies involve uptake studies instead of ending up in measuring the different chemical species and conclude on bioavailability status of F in a particular soil. The deposition of fluoride on soil will only have a significant effect on plant uptake if the concentration gets higher than about 500 mg kg^{-1} [25].

3. BIOAVAILABILITY OF FLUORIDE TO PLANTS IN RELATION TO SOIL PROPERTIES

Although the main route of F uptake by plants is through soils, substantial quantities can be taken from the air if the air is contaminated by F. The air F uptake is mainly through stomata which it then undergoes translocation to the tips and to the leaf margins [28].

Fluorine is the most electronegative element and it combines directly with most elements, forming fluorides that are among stable chemical Compounds [29] with low solubility. Most of the inorganic fluoride in the soil exists in insoluble forms; therefore, the possibility of being taken up by plants and leaching may be low. The uptake of fluoride by a plant from the soil depends on the plant species in question [30] and, to some extent, the ionic species of fluoride present in soil solution [31]. The solubility of F in soil is controlled mainly through F adsorption by inorganic constituents of the soil and soil pH [30]. Cations like Ca and Mg in soils precipitate F [32] culminating in the arresting of calcium transport and detoxification of fluoride. There is a strong positive correlation between the total contents of F in soils with Ca, as well as Cd, and phosphorus [7].

Fluoride compounds in soils are sparingly soluble in water and hence their bioavailability is low [33]. Therefore, it is only the soluble part of F that can be taken up by plants [30]. Calcium reduced F uptake by tea plants not only because of the formation of CaF_2 precipitates, but also because of the effect of Ca on the properties of cell wall or membrane permeability and of the alteration of F speciation and their quantities in soil solutions [34]. F uptake increases with an increase in ionic strength [32]. This shows that the ions can adsorb F in soils thereby lowering F solubility. In so doing the F uptake by crops can be attenuated.

Calcium and Aluminium hydroxide and iron III hydroxides can precipitate F in soils and reduce F activity [18]. Aluminium in soil solution may complex F resulting to an enhanced uptake of both elements [35]. However, other studies have revealed that F in soils may precipitate aluminium especially under low pH conditions because fluoride is a powerful ligand for aluminium and may form aluminium-fluoride immobile complexes [13]. This may lead to the attenuation of the rhizotoxic effects of aluminium such as inhibited growth.

High Ca contents in soils deterred the bioavailability of F to alfalfa and rye grass [17]. The deterred uptake was attributed to the formation of CaF_2 around root surfaces culminating in the precipitation of F around the roots. This shows that Ca has high affinity for F [7]. This explains a significant positive correlation between Ca and F observed in most soils.

4. FLUORIDE CONTENTS IN FOOD MATERIALS

It is now well documented that food substances grown in fluoridated areas can be a very important source of fluoride intake [36]. This is because plants can take up substantial quantities of F through soils [37] or through leaves where gaseous F emitted from industries enters through stomata [1]. Fluoride can be taken up by plants through airborne gases, particulates, and rain water [19]. Plants take up F from soils therefore if the plants are irrigated with F contaminated water, elevated levels of F can be encountered in the plants in question. Despite this fact, there is no clear cut F concentration in irrigation water that has been designated [19]. F in irrigation water enhanced the availability of F to Raddish leaves (*Raphanus sativus*), Spinach leaves (*Spinacea oleoracea*) and mustard leaves (*Brassica compestris*) [38].

The maximum permissible limits of F in drinking water are 1.5 mg l^{-1} [15]. However, there is no strict critical limit of F in soil above which the F concentration may be regarded as detrimental [1]. There is no globally accepted F concentration in plants above which a plant material is considered toxic [20]. When F is taken by plants, it may exert biochemical effects especially on fluoride sensitive enzymes [39]. There is an urgent need to carryout research on the critical concentration of F levels that is allowed in irrigation waters in fluoride contaminated soils. Different plant species have different capacity to extract F in soils even if such plant species have been grown on the same soils with the same soil properties and F contents [40].

4.1 Detrimental Effects of Fluoride to Plants

The F tolerance of crop plants to F have been investigated [1]. The authors found that different plant species have different capacities of tolerating F in different plant parts. Just as it is for animals and human beings, elevated levels of F in plants may cause physiological, biochemical and structural damage. Symptoms like necrosis and even cell death can be developed depending on F concentration in the cell sap. In tea, older leaves had accumulated elevated F contents than the young leaves. Onions can tolerate high levels of F up to 200 mg F kg^{-1} without showing toxicity symptoms. However, at 400 mg F kg^{-1}, toxicity signs such as decrease in biomass and leaf tip burning may be evident. However, the concentrations of F in bulbs in a treatment that received 200 mg F kg^{-1} did not differ significantly from the concentrations of F in control treatments. In the study the roots had higher F concentrations than was the case with bulbs. This phenomenon can be attributed to low permeability of F through the endodermis.

Lower concentrations of F in the bulbs are attributed to higher biomass leading to biological dilution. This is a testimony that bulbs are more protected than leaves against excessive uptake of F. High levels of fluoride concentrations in soils can inhibit germination of seeds. For example [30] reported germination failure of up to 52 % of *Oryza sativa* L. var. *Swarno* at a concentration of 50 mg F l^{-1}. Seed germination, growth and biomass of cluster bean were reduced with increased F concentrations and at 30 µM mortality of seeds occurred [35].

F toxicity symptoms such as necrosis and drop as well as a significant reduction in dry weight by olive leaves which were subjected to 80 mM NaF were observed [28]. Accumulation of higher quantities of F in germinated seeds of rice than in mature plants has been reported [30]. Soybean showed toxicity when the concentrations of F in irrigation water reached 25 mg L^{-1} [41].

Some plants have demonstrated the ability of restricting the transfer of F from soils to roots in soils with high concentrations of F [40]. However, different crops have different capacities to accumulate F [42]. Crops that accumulate elevated levels of F without showing toxicity signs pose higher risks of contaminating the food web than crops that are sensitive to F toxicity. Humans who grow and consume F tolerant crops may be consuming elevated quantities of F unnoticed through the crops. It is important to screen all crops growing in F contaminated soils for F accumulations. Those crops which accumulate elevated quantities of F should be restricted. Alternatively, research on immobilization of F in soils can be carried out to explore the possibility of reducing mobility and uptake of F by hyper-accumulator plants, using soil amendments or manipulating some soil properties. F^- activities exceeding 1473 µM in a dilute nutrient solution inhibited shoot and root growth of tomatoes [32]. However, F^- activities of up to 5130 µm did not have an effect on shoot or root dry weights of oats, suggesting that different plants have different tolerance to F^- toxicity.

The total F contents in soils may not be a good indicator of F content that may be taken-up by plants because the plant available species is a free form of F [17]. This is because contaminants may have been tightly bound to soil colloids and rendered immobile. Therefore, water soluble F is a good indicator of bioavailable F in soils [7]. Therefore, this fraction should be used to infer the potential F bioavailability. Soluble F contents in soils were positively correlated to F contents in rice plants. However, the total F contents in soils were not correlated to F contents in rice. It was further reported that the solubility of freshly added F due to anthropogenic activities especially the spillage of hydrofluoric acid decreased with time in a process called aging thereby rendering F less bioavailable. Therefore, studies that use F spiked soils may exaggerate the risks associated with the mobility and bioavailability of F in soils. The F mobility in long-term F contaminated soils may completely be different from the mobility of F in recently contaminated soils, especially as a result of spillage. Therefore, the methodologies for risk assessment in the two types of F contaminated soils should take into consideration the aging factor. It is suggested that water soluble F fraction should be used as an indicator for F mobility in soils because it is this F fraction that is in fact bioavailable. Some plant species tolerate elevated levels of F in soil solutions and in plant tissues. Several mechanisms have been proposed to explain the tolerance. Restricted F uptake by plants can be attributed to fluoride exclusion at the root level or fluoride detoxification at a cell level [1].

5. CONCLUDING REMARKS AND PROPOSAL FOR FUTURE RESEARCH

The bioavailability of F is paradoxical. High to low bioavailability have all been reported, elucidating that the F bioavailability is soil or plant specific. This makes F mobility studies in F contaminated areas justifiable. Most studies reported immobilization of Fluoride in laboratory studies. More research now ought to be directed to field environments. Future studies should explore the dynamics of F in soils and uptake by crops grown on F affected soils and irrigated with F contaminated waters. Because it is a common practice for farmers in F contaminated areas to use F contaminated water for irrigation and for spraying. Manipulation of soil properties such as increased soil pH and soil amendments like organic residues and calcium containing compounds can immobilise F in soils thereby deterring its bioavailability.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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