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(Review Article)

The Fluorine Footprint of SSP Fertilization: A Comprehensive Review of Its Cascading Effects on Agricultural Landscapes, Ecological Impact and Interconnected Systems

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Abstract

This review provides a clear overview of fluorine, its introduction into the soil, and its cascading effects on the food chain and ecosystem. It focuses on fluorine, the most electronegative element, which has both beneficial and detrimental effects on plants and animals and further focuses on the impact of fluorine from single super phosphate fertilizers on agricultural landscapes, ecology, and interconnected systems. The literature shows that fluorine has adverse effects on plants, such as leaf necrosis and fluorosis, and on animals, such as infertility, dental and skeletal fluorosis, mitochondrial toxicity, and enzyme inhibition. The literature also shows that in low pH soils, fluoride solubility is high, leading to its leaching into the top soil, and in high pH soils, fluoride is precipitated by calcium ions in the form of calcium fluoride compounds. The review highlights a cascading effect of fluorine through the food web. Natural and human-related activities introduce fluorine into the soil, where it is absorbed by plants. The element then bioaccumulates as it moves up the food chain, from plants to herbivores and then to carnivores. Mitigation strategies for fluoride in soils include phytoremediation, fluoride-tolerant plants, fluorine reduction in the SSP manufacturing line, and fluoride sorption using amendments.

Keywords: Ecology, Fluorosis, Fluorine, Phytoremediation, Single super phosphate fertilizers.

1. Introduction

Fluorine is a group 17 element on the periodic table and is classified as a halogen. It has an atomic number of 9 and a mass number of 19. It is the most electronegative element, with an electronegativity value of 3.98[1], [2]. It forms the least stable and most reactive diatomic gas homoatomic bond (Ediss = 158.78kJmol-1) [3]. It is relatively abundant in the earth's crust (525ppm) and is ranked 13th among all elements, existing in chemically bonded forms in different minerals [4]. It is both an essential and harmful element [5]. It is a biogenic element that is essential for human health and biota in natural water [6]. Fluoride ions are termed double-edged swords because of their valuable use in the production of anhydrous hydrogen fluoride, lithium-ion batteries, and bacterial growth inhibition, and also their detrimental effects on both plants and animals, such as lighter leaf color, stunted growth, dental fluorosis, and prolonged larval development[7], [8], [9], [10], [11]. Excessive uptake of fluorine above the prescribed 1.5 mg/l by the World Health Organization causes detrimental effects such as skeletal fluorosis, which occurs when fluoride levels become toxic, leading to osteosclerosis and deformities in the bone, resulting in crippling pain and debility [12], [13], [14]. Current methods used for fluoride treatment include adsorption techniques, chemical treatment, and membrane technology [15]. Other methods employed for fluoride ion removal include biodegradation and electrocoagulation [16]. However, electrocoagulation and membrane technology methods are expensive because of their high energy costs [16].

2. Literature Review

The review was conducted in the following steps: investigating sources of occurrence of fluorine ions, analyzing how fluorine is produced during SSP production, outlining the methods of fluoride detection, investigating fate of fluoride in agricultural landscapes, the fluoride impact on interconnected systems and lastly fluorine mitigation and sustainable management strategies. This was achieved through reviewing literature through online databases such as Springer, Taylor and Francis and Google Scholar. The articles inclusion criteria were: all peer reviewed past articles with relevant information about fluorine, all English peer reviewed articles with necessary information contributing to this review, book chapters with relevant substantial information, and the opposite of the inclusion criteria was the exclusion criteria.

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3. Sources of Occurrence of Fluoride Ions in Nature

There are various sources of fluoride ions in nature, including: geological sources, water sources, and volcanic activity.

3.1 Geological sources: These are mainly minerals and rocks, such as fluorite (CaF2), cryolite (Na3AlF6), and fluorapatite (Ca5(PO4)3F) [13], [17]. Fluorapatite is an igneous rock used in the fertilizer manufacture. It contains approximately 2 – 4% fluorine [18], [19]. Weathering of fluoride ore and marine aerosols releases fluoride ions into the soil [20]. Marine aerosols contribute approximately 0.4 – 1Mt of fluorine to the atmosphere annually [21].Approximately 1 – 4% of fluoride ions are released into the soil through fertilizers. Fumigants and insecticides containing fluoride ion-containing compounds, such as sodium silicofluoride, sulfuryl fluoride, barium fluorosilicate, and fluralin, also contribute to fluoride accumulation in soils [22].

3.2 Water sources: This is a result of industrial effluent discharges from coal, which has 295 mg/L fluorine [23], fertilizer, and paint industries as well as from communal discharge. The following are some of the factors responsible for fluoride contamination in water sources: chemical properties of water, nature of rocks, leakage of shallow water, and others [13], [24].

3.3 Volcanic activity: Volcanic eruptions release fluoride ions in the form of hydrogen fluoride through volcanic degassing, which is deposited on the earth's crust and, with time, leaches into the soil and eventually reaches the water table [25].

4. Fluorine from Single Super Phosphate (SSP) Fertilizer

Single superphosphate is a fertilizer produced from phosphate rock, mainly fluorapatite, which is an igneous rock. The rock contains 2 – 4% fluorine [18], [19]. During SSP manufacturing, a series of reactions occur in which fluoride ions are removed from the process, but at the end of the process. [26] reported that 1 – 1.5% of fluoride ions remained in the fertilizer. Figure 1 shows the fate of fluorine during SSP production by [27].

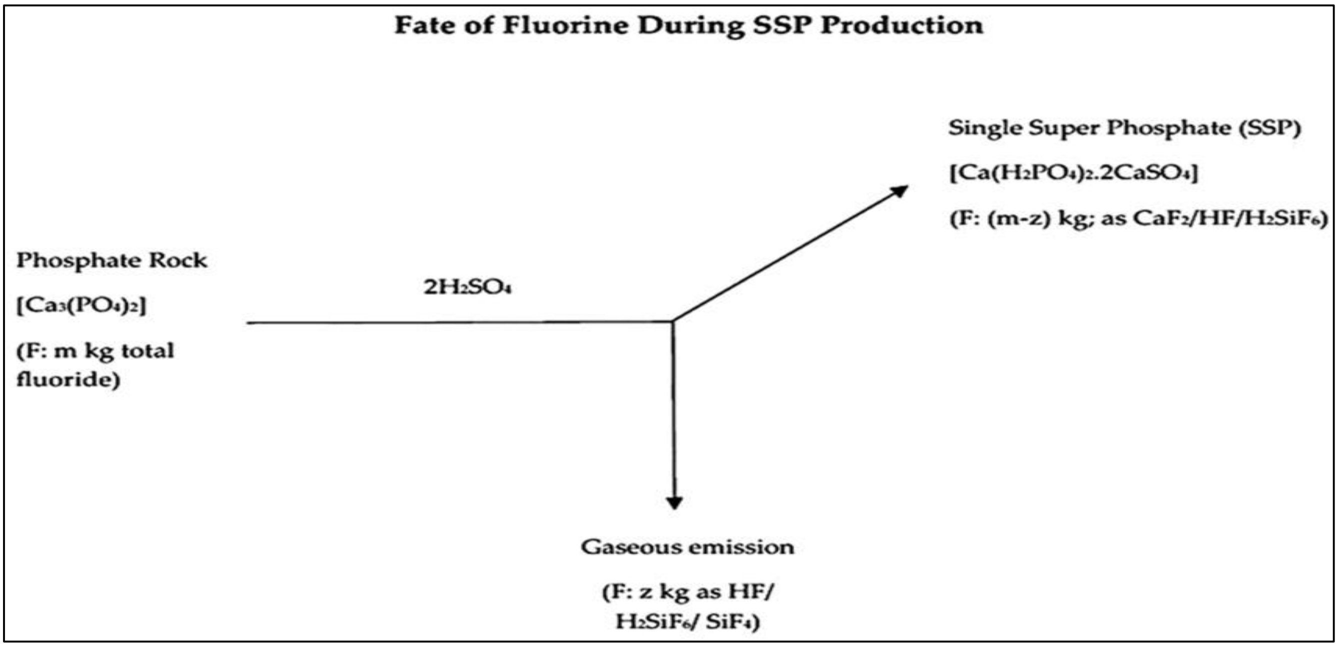

Figure 1. Fate of fluorine during SSP production [27]

The following equations (1 and 2) show the reaction steps responsible for fluoride ion removal in the SSP manufacturing process [19].

$$CaF_2.3Ca_3(PO_4)_2 + 7H_2SO_4 \rightarrow 3Ca(H_2PO_4)_2 + 7CaSO_4 + HF\uparrow \quad (1)$$

$$Ca_5(PO_4)_3F + 5H_2SO_4 \rightarrow 3H_3PO_4 + 5CaSO_4\downarrow + HF\uparrow \quad (2)$$

The produced hydrogen fluoride reacts with the added silica (SiO2) to produce hydrofluorosilicic acid, and silicon tetrafluoride, and water, as shown in Equations 3 and 4:

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O \quad (3)$$

$$4HF + SiO_2 \leftrightarrow SiF_4 + 2H_2O \quad (4)$$

5. Methods of Fluoride Detection

Fluoride detection is mainly performed using analytical methods. According to [13], mass spectrometry, ion selective electrode, and ion chromatography are the methods used. Fluoride concentration is detected using chromogenic and fluorogenic sensors in analytical methods.

5.1 Mass spectrometry: An analytical technique that uses the measurement of the mass-to-charge ratio of ions [28]. The first step is the production of ions of the compound in the gas phase, typically by electron ionization [29]. Detection of fluoride ions using standard mass spectrometry can be difficult because of its low ionization efficiency and isobaric interferences [30]. Therefore, gas chromatography – mass spectrometry (GC-MS) [31], inductively coupled plasma mass spectrometry (ICP – MS) [32], tandem mass spectroscopy (ICP – MS/MS), and combustion ion chromatography coupled with mass spectrometry (CIC – MS) [32] are specialized methods that have been developed for mass spectrometry.

5.2 Ion selective electrode: This electrochemical method that uses the direct potentiometry principle, where ta potential difference is generated across a selective membrane that is directly proportional to the log of F- activity in the solution[33]. The most common single crystal membrane used is lanthanide fluoride (LaF3), where an electrical potential is created by the passage of only F- from the membrane and then measured against a reference electrode [34].

5.3 Ion chromatography: An analysis technique used to analyze ions by separating them based on their affinity for the mobile phase (an eluent) and stationary phase (an ion-exchange resin) [35]. A fluoride sample is introduced into an ion chromatograph system, and the separation of F- from other ions, such as Cl-, Br-, and SO42-, occurs as the sample passes through the ion – exchange column [36]. Eluents, such as sodium carbonate/bicarbonate solutions, are used in this process. The F- concentration was quantified using the peaks generated by the calibration curve.

6. Fate of Fluorine in Agricultural Landscapes

SSP fertilizers are applied to soils for plant growth. The fluorine content in SSP fertilizer from ZIMPHOS, Msasa, Zimbabwe is in the range of 1 – 2%, and when applied to soils, fluorine leaches into the soil, water system, and is taken up by plants, resulting in dangerous effects to both plants and animals.

6.1 Soil accumulation: Fluorine applied to the soil through SSP fertilizer accumulates in the top soil [37]. Fluorine in soil is in the range of 150 – 400ppm but for contaminated soils, the figure rises to 1000 – 1500ppm [38]. Clay minerals, aluminium and iron hydroxides, and oxides contribute to the strong sorption of F- into the top soil. The continuous application of SSP with high fluorine content eventually leads to the further accumulation of F- to alarming levels [37]. Fluorine mobility is influenced by factors such as soil pH, clay composition, and the presence of calcium carbonate (CaCO3) [39]. At low pH values, the potential for its leaching is higher due to the formation of soluble complexes with iron or aluminium and at high pH values, it reacts with calcium ions and precipitates as calcium fluoride (CaF2) [39].

6.2 Water contamination: After SSP is applied to soil, fluorine can be leached into groundwater and further transported via surface runoff due to high rainfall, low buffering capacity, or certain pH conditions [40]. Fluorine leached into groundwater (GW) (>1.5 mg/L concentration) is a cause for concern if GW is a drinking water source, as it poses a significant public health and environmental threat [41], [42].

7. Ecological Impact of Fluorine

High levels of fluorine from SSP fertilizers have detrimental ecological impacts on soil microorganisms and nutrient cycling, phototoxicity, plant uptake, and livestock and wildlife.

7.1 Effects on soil microorganisms and nutrient cycling: High levels of fluorine are toxic to microorganisms, affecting the microbial structure, resulting in the disruption of biogeochemical processes such as organic matter decomposition, phosphorus solubilization, and nitrogen fixation. Microorganisms assist in transferring and recycling nutrients among several reservoirs during the mineralization process [38]. Fluorine alters the microbial communities of soil by enzyme inhibition, acting as phosphate analogs, and inhibiting the glycolytic cycle [38], [43].

7.2 Phytotoxicity and plant uptake: Fluorine is taken up by plants through the roots, and its influence on plants alters their chemical composition and leads to plant deterioration [44]. Fluorine intrudes and affects plant leaves because of its high solubility and may stop photosynthesis in plants [44]. When fluoride ions are taken up by other roots, they move up the plant through transpiration and enter the leaves through the stomata, where they cause marginal and tip necrosis and fluorosis [45]. Excessive fluoride levels lead to fruit spoilage [46].

7.3 Impact on livestock and wildlife: A study by [47] involved two horses that drank water with high fluorine concentrations, and they suffered multiple joint and dental defects. Microscopic analyses revealed cement necrosis and hypercementosis in horses. The chief sources of fluorine in animals are vegetation in fluoride-contaminated soils, water contaminated with fluoride, and feed supplements with excess fluoride [48]. Excess fluoride alters the architecture and physiology of animal organs. The liver, which detoxifies toxic substances, is affected by excess fluoride ions in the body [48]. Acute intoxication of cattle by excess fluorine causes constipation, ruminal statis, and gastroenteritis, which are due to the formation of hydrofluoric acid in the stomach [49]. The nervous system of cattle also affected by excess fluorine, resulting in weakness, muscle tremors, hyperesthesia, pupillary dilatation, and constant chewing [49]. Post-calving anestrous and decline in fertility when 8 – 12ppm of fluorine diet is fed to cattle, overshooting the normal 0.2 mg fluorine per deciliter concentration in cattle shows a reproductive defect due to excess fluorine [49].

8. Fluorine Impact in Interconnected Systems

The fluorine footprint in fertilizer extends into the food chain, where plants affected by fluorine are eaten by herbivores/grazers and omnivores, which are eaten by carnivores, leading to biomagnification and bioaccumulation in the food web. In humans, fluoride interacts:

- Enzymes inhibit their activity in the millimolar range and stimulate cell proliferation in the micromolar range [50].
- Cells by superoxide anion generation, mitochondrial toxicity, and modification of the release of neurotransmitters acetylcholine [51], [52].
- Teeth and bones causing dental and skeletal fluorosis. Ingestion of over 8 mg/L of fluoride affects the skeletal system [23]. Dental fluorosis ends at eight years in humans due to the complete maturation of the enamel [50].
- The reproductive system causing infertility in men when they drink water with a high fluoride concentration of approximately 35 mg/L [50].
- Excessive fluoride affects the brain, disrupts the secretion of thyroxin hormones, increasing density and bone mass and affects the nervous system [23].
- Excessive fluoride can cause DNA damage by inducing oxidative stress which leads to generation of reactive oxygen species (ROS) [53] and also cause liver apoptosis [54]
- Excessive fluoride also cause epigenetic alterations in humans, which alters gene expression without alteration of DNA sequence [55]

9. Mitigation and Sustainable Management Strategies

To address the impact of the fluorine footprint from SSP fertilizer sustainable mitigation and management practices and policies that protect the environment and its ecosystem must be outlined. According to [39], fluoride mitigation strategies can be in-situ or ex-situ treatment method. In-situ method proved key in reducing fluoride concentration in Anantapur district in India by use of artificial recharge. The following are also fluoride mitigation methods:

9.1 Fluorine reduction during SSP manufacturing: It is crucial to reduce the fluorine content in the final product during the production. Most of the fluorine is removed during phosphate rock pretreatment through flocculation and during the acidulation stage, where fluorine leaves as HF and CaF2. If it is stoichiometrically impossible to remove more fluorine during these processes, another unit operation, such as a calcination or leaching unit, must be added to reduce fluorine to approximately 0.1% in the final SSP product.

9.2 Soil remediation and management: As fluorine precipitates at high pH levels, increasing the soil pH can immobilize fluoride ions and precipitate them as CaF2 [39]. The sorption of fluoride using amendments such as red mud, fly ash, or biochar, can reduce its bioavailability [56]. There is a need to apply a circular economy approach to avoid secondary contamination where fluorine is removed from the soil to the amendments. Phytoremediation techniques using plants with high fluorine accumulation or tolerance to extract fluorine from soil can be used [57]. This method can be slow and requires close attention to the resultant biomass. Plants such as tea, spinach, and potatoes are known to have high fluorine tolerance [45], [58]. A study by [59], which was done in Southeast of Tunisia, showed that there was 37 – 360mg/kg accumulation of fluoride by plants. Additionally, planting crops that are less susceptible to fluoride uptake can minimize the risk of food contamination [60].

Table 1. Comparison of the mitigation strategies

Fluorine reduction during SSP manufacturing	Fluorine reduction through soil remediation and management
It is a proactive approach removing fluorine at the source	Addresses the fluoride in soil issue at hand
Significant reduction of fluorine accumulation in the soil.	Has diverse options for removal and reduces bioavailability of F^-
There is direct control through quality control in the process	Relatively cheap and a green approach that uses natural bioprocesses
Technically challenging and resource intensive	Does not remove the fluorine in the but immobilizes
Does not address fluorine contamination from other sources	The sorption amendments may cause secondary contamination for example fly ash might contain heavy metals
Capital intensive and high operational costs	It is a slow process and time consuming

10. Conclusion & Future Research

The comprehensive review of the fluorine footprint from SSP underscores its pervasion and detrimental effects across agricultural landscapes, ecology, and interconnected systems. Continuous accumulation of fluorine in soils leads to surface runoff contaminating water systems that extend to vegetation, plants, animals, and humans, thereby furthering bioaccumulation and biomagnification through the food web. Further research is needed to investigate the stability and remobilization of CaF2 precipitated under dynamic environmental conditions. There is also a need to develop models for predicting fluorine behavior in soils which would assist in identifying potential contamination hotspots, conducting future risk assessments and appetite and evaluating the effectiveness of proposed long-term mitigation strategies. Silent impacts, such as neurotoxicity and bone fluorosis due to chronic low-level fluoride in both plants and animals, need to be investigated. There is also need to develop rapid, cost effective and in-situ monitoring tools for fluoride. It is therefore recommended to:

- Develop a more benign and atom economical methods for incorporating fluorine into organic molecules.
- Designing more sophisticated fluorinated nanoparticles and polymers for targeted drug delivery targeting the brain or tumors
- Synthesizing fluorinated probes for bioimaging

Nomenclature

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DNA – deoxyribonucleic acid

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The authors declare that there are no relevant financial or non-financial competing interests to be reported.

Data Availability Statement

Data sharing not applicable to this article as no datasets were generated or analyzed during the current study.

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