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Implementing Effective Service Economy Strategies to Reduce Fluoride Uptake in Clover Fodder: Risk Management in Livestock

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Daria Zhdanova[1*], Aleksander Budrin[2], Aleks Krasnov[3], Galina Silkina[4], Daria A. Dinets[5], Angela Bahauovna Mottaeva[6], Ruben Kzaryan[7], Anastasiya Lisenkova[8], Vasilii Buniak[9], Oksana Solodchenkova[10]

1:Graduate School of Service and Trade, Peter the Great St. Petersburg Polytechnic University, 195251 St. Petersburg, Russia.
2:Faculty of Technological Management and Innovations, Saint Petersburg, ITMO, Saint Petersburg, Russia.
3:Graduate School of Service and Trade, Peter the Great St. Petersburg Polytechnic University, 195251 St. Russia.
4:Graduate School of Industrial Management, Institute of Industrial Management, Economics and Trade, St. Petersburg Polytechnic University.
5:Finance and Credit Department, Peoples' Friendship University of Russia.
6:Department of Management and Innovations, Financial University,125167 Moscow, Russia.
7:Department of Technology and Organization of Construction Production, Moscow State University of Civil Engineering, 109377, Russia.
8:Graduate School of Social Sciences, Humanities Institute Peter the Great St. Petersburg Polytechnic University, 195251, Russia.
9:Department of Economics and Finance, Financial University under the Government of the Russian Federation (Moscow) St. Petersburg branch, 197198, St. Petersburg, Russia.
10:Department of Economics and Management, Federal State Budgetary Educational Institution " Financial University under the Government of the Russian Federation", branch, Smolensk;

***Corresponding author:**
Darya Zhdanova – Graduate School of Service and Trade, Peter the Great St. Petersburg Polytechnic University, 195251 St. Petersburg, Russia; digitaltwindm20@gmail.com

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ABSTRACT

Purpose: Fluoride pollution in agricultural environments, particularly from industrial activities such as brick kilns, poses significant risks to crop yield and livestock health. This study investigates the impact of fluoride pollution on clover fodder, a critical feed source for livestock in the Peshawar region of Pakistan, and explores strategies to mitigate fluoride uptake using calcium amendments. Clover, specifically Persian clover (*Trifolium resupinatum* L.), is prone to accumulating high fluoride content, exacerbated by nearby brick kilns emitting hydrogen fluoride (HF). This accumulation poses a risk of fluorosis in livestock consuming the contaminated fodder.

Methodology: A pot experiment was conducted to assess the effectiveness of adding calcium carbonate ($CaCO_3$) at varying concentrations (0, 20, 40, and 60 µg/kg) to reduce fluoride uptake in clover. The study spanned three months, with plants harvested every four weeks to measure fluoride levels.

Results: showed that increasing soil calcium significantly reduced fluoride content in clover leaves. At 60 µg/kg $CaCO_3$, fluoride concentration decreased to 22 µg/kg from an initial 60 µg/kg at 0 µg/kg $CaCO_3$. This reduction was consistent over 12 weeks, demonstrating the potential of calcium amendments to mitigate fluoride uptake. Additionally, a survey of farmers and agricultural extension workers in the affected areas revealed a lack of awareness and mitigation strategies for fluoride pollution.

Conclusion: These findings highlight the need for policy interventions and educational programs to address fluoride pollution in agricultural systems. Implementing effective service economy strategies, such as providing subsidies for calcium amendments and conducting workshops on pollution management, can help reduce fluoride levels in fodder crops and safeguard livestock health. This study underscores the importance of collaborative efforts between government and local communities to develop sustainable solutions for managing fluoride pollution in agriculture.

Key-words: hydrogen fluoride, brick kilns, air pollution, sustainable management, environmental impact, agricultural practices, South Asia, Peshawar

INTRODUCTION

Fluoride pollution and toxicity

Fluoride (F) is a concerning problem in agricultural environments, specifically in those areas where there are industrial and economic activities[1] e.g. manufacturing and mining that adds high quantities of fluoride in air, water and soil channels that affects the environment in various ways. These industries mainly include aluminum smelters, cement factories, ceramic factories and brick kiln factories produces high fluoride[2,3]. Since most of the brick kilns are built on/near agricultural lands therefore, agricultural crops are mostly affected directly from fluoride pollution in form of hydrogen fluoride (HF) from these brick kilns that operates around the year[4,5]. In developing countries, there are no specific regulations/laws to govern these brick kilns to regulate its air pollutants[6,7]. These brick kilns also produce, SO_2, NO_x and O_3 apart from HF[5]. Pakistan is an agricultural country and it is facing huge threat from climate change as the country is 6th on climate change vulnerable index (2023) list of countries that are vulnerable to climate change disasters[8]. With country of 224 million population, it faces a daunting task to feed its mass inhabitants in the wake of climate change and environmental pollution[9]. HF is a toxic primary pollutant second to only ozone that is produced from the primary pollutants. HF is generally very toxic to vegetation and can reduce crop yield and quality of different crops[10]. F is naturally accumulated by tea and clover plants without showing any visible foliar injury symptoms[11]. Therefore, tea consumers and animals eating clover fodder are at risk to fluorosis disease[12].

Fluoride uptake by Plants

Plants take fluoride (F) from the atmosphere via leaf stomata or through water and soil by roots[13]. The most common gaseous forms include hydrogen fluoride (HF), sulfur hexafluoride (SF_6), hexafluorosilicic acid (H_2SiF_6), carbon tetrafluoride (CF_4), and silicon tetrafluoride (SiF_4) that enters through leaf matrix via stomata or through leaf surface when in an aqueous solution[13]. In addition, plant can absorb fluoride through roots when it forms various complexes with other elements and becomes bioavailable to the plants in soil. These metal complexes are Al, Ca, Fe and Mg. Xylem translocates these metals complexes to the leaves, where these complexes are broken down and release fluoride[15]. Fluoride is transported either through symplastic or apoplastic pathways inside the leaf in a distal movement into aerial portions in a single direction. Fluoride is predominantly absorbed by passive diffusion mechanisms from the soil-water and is controlled by exclusion at the endodermis barrier[16]. However, energy-dependent active absorption of fluoride allows hyper-accumulator fluoride plants, such as *Camellia sinensis*, to accumulate high levels in their leaves[17].

Various elements like chloride (Cl^-), Ca^{2+}, calmodulin (CaM), and plasma membrane depolarization are involved in the determination of fluoride buildup in plants via membrane transport[18]. However, we are yet to explore the most elusive pathway for fluoride. Fluc protein functions as an F-selective channel, shielding prokaryotes and eukaryotes that resemble yeast from harmful F-accumulation[19,20]. FEX genes that code the fluoride export protein lowers the cytoplasmic fluoride by omission from both plant and animal cells and controls fluoride in eukaryotes[21].

Recent research studies have shown that FEX genes control and regulate the movement of anions including fluoride in plants through tissue specific pathways[18,22]. The regulation of fluoride absorption and accumulation in *Camellia sinensis* involves the regulation of Ca^{2+}, Cl^-, CaM, and plasma membrane potential depolarisation. Exposure to fluoride increased the expression of defense-related genes, such as receptor-like kinases (RLKs), which are involved in the regulation of F^- uptake in plants and the activation of the calcium transporter (Ca^{2+}-ATPase)[17].

Importance of Clover Fodder

Shaftal or Persian clover (*Trifolium resupinannn* L.) is from the Leguminosac family, which is native to South Asian region. It has also been grown as an ornamental plant in Europe for many years. Due to its palatability for domestic animals as a fodder crop its cultivation was boosted in South America, Central Asia, Germany and Australia. Now it is the main fodder crop in Egypt and Iran[23].

In Europe, it was cultivated as an ornamental plant for many years. After its establishment as a fodder crop its cultivation spread to South America, West Germany, Australia, and Central Asia. Now it occupies a significant position as a fodder crop in Africa and Asia. Shaftal was introduced in Pakistan in the early 1900's specifically in Punjab region and then relatively spread to the upper northwestern part of the country to colder place with frequent rainfall[24].

The livestock industry in Pakistan mostly suffers from both low quality and limited quantity of fodder[25]. The yearly livestock feed supplies in the country are met via a mix of crop residues (38%), green forages (51%), grazing (3%) and other concentrates (2%). All together, these animals need an annual total of 90Mt of total digestible nutrients (TDN) and 11Mt of crude protein (CP). However, due to limited resources they only get 7 and 69 Mt of these nutrients, respectively[26].

Forage deficits may result from a range of factors including land scarcity, soil nutrient imbalance, water deficiency, poorly adapted germplasm and extreme weather events[27]. A lack of farmer knowledge of forage production, utilization and conservation techniques may also contribute to the problem3. Smallholder farmers perceive that these feed gaps could be filled by increasing forage production per unit area, through the use of improved varieties, appropriate agronomic practices and timely availability of required inputs. Forage production is also often constrained by the availability of quality seed[28]. Consequently, farmers often have to produce their own seed, even if it is inferior.

Shaftal is considered an economic valued fodder crop for sustainable agricultural production because of its cost effective inputs and high restorative natur5. It has a dual benefit of getting forage and seed production[28]. There are several varieties of clover crops that depend on the genotype and harvesting management to get better crop yield[26]. The latest information is limited about its genotypes and its accumulation of fluoride in its leaves as farmers get several cutting of the crops in a single season. Therefore, information about the dry matter accumulation in addition to fluoride over several weeks/months in clover crop is important and that can determine the harvesting and reducing fluoride accumulation strategy.

Clover is one of the main multi-cut fodder crops in Pakistan as it belongs to the Miscawi crown branching type that is able to produce 5 to 6 cuts per season[26]. The seed yield is obtained after the last harvest of the season. Smallholder farmers are mostly dependent on the information of the new variety which can result in adoption of these new varieties. If the varieties are high yielding and require less water and are resistant to diseases, then farmers will quickly adapt them. However, if they came to know about the fluorosis connection with clover fodders then they will be very worried about their livestock, which are their main source of earning. It is therefore imperative to select that kind of clover varieties that are resistant to fluoride accumulation in its leaves to reduce the impacts of fluoride on livestock animals. In addition, the participatory research approach is demand driven and has benefits associated to the adoption of new improved varieties[26]. The researcher and farmer then collaborate to evaluate the selected cultivar at the farm level.

Clover is now the number one choice of farmers in Khyber Pakhtunkhwa province as its growing season lasts from early winter that stretched deep to summer giving valuable feed source to livestock farmers. However, most of these clover fodder crops are grown in the vicinity of brick kilns near Peshawar[29]. Clover is known for accumulating high fluoride content naturally. There is a concern that brick kilns that produce HF can further accentuate the fluoride concentration in clover crops. This can enhance the chances of fluorosis disease in livestock that feeds upon them.

According to Ahmad et al[5], there are over 400 brick kilns just outside Peshawar mostly on agricultural lands. These brick kiln factories are not regulated properly by the local government due to which they are using low quality fuel e.g. used engine oil, low grade coal and domestic wastes that are causing huge pollution in the city. These toxic pollutants are not only affect the environment but are directly affecting crop yield and quality. They also reported that fruit orchards of plum and apricot were affected significantly by HF due to which Farmers were reluctant to grow more orchard trees and were opting for alternative crops that are resistant to HF. Another study[29] reported the F level in three different clover varieties, from 38 to 50 ppm, in the same area near brick kiln outside Peshawar (Figure 1). They also revealed high fluoride content in tomato and wheat varieties.

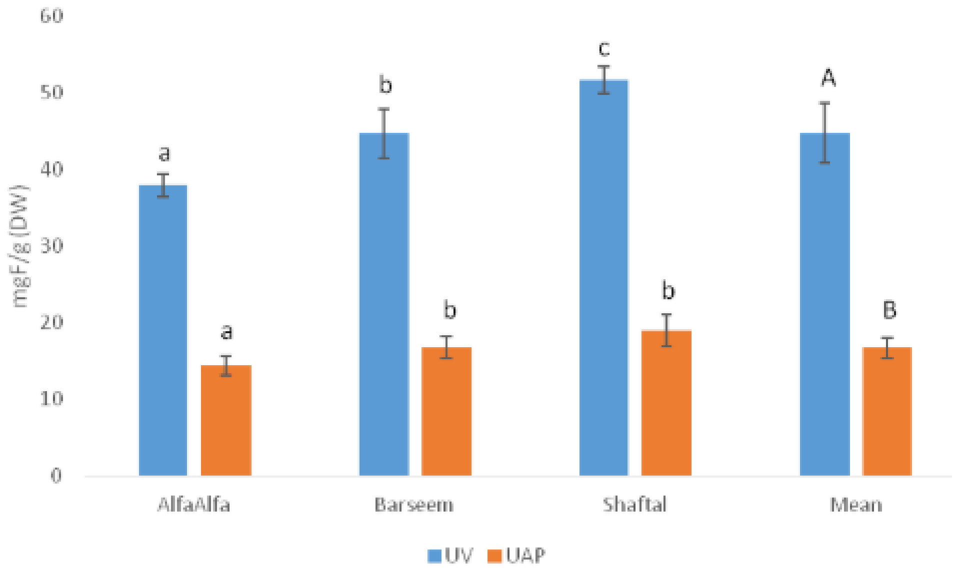

Figure 1: The F concentration in clover leaves varieties were significantly higher at brick kiln areas compared to control areas. The mean values are based on 4 replicates with error bars showing standard error between the means.

Calcium for Plants growth

Most of the crops need calcium in their soil to grow better[30]. Ca is needed for the cell walls and cell membrane development inside the plant[31]. In addition, Ca doesn't leach into the water table or runoff from the soil, enhances the permeability of water molecules and lowers the soil pH.

The current study was designed to carry out pot experiment for clover fodder (Shaftal) crop that have the high fluoride accumulation[29] in brick kiln area of Peshawar to regulate the fluoride content in clover by adding $CaCO_3$ in different concentrations to avoid possible fluorosis in local livestock and its milk products, and to devise service economy strategies for policy interventions to reduce fluoride in fodder crops.

METHODOLOGY

Experimental Setup

The pot experiment was conducted at the university of Agriculture, Peshawar. Different concentrations (0, 20, 40 and 60 µg/kg) of lime was added to 15x30 diameter pots having soil. Each treatment had 3 replicates. 5 seeds of Shaftal clover were sown in each pot, and were irrigated with deionized waster. After the emergence on day 7, plants were thinned down to 3 plants in each pot. The plants were watered every day except on rainy days. The experiment ran from January to April (3 months). The plants were harvested after every 4 weeks. Three cuts in 3 months were taken to assess the impact of lime on fluoride uptake.

Fluoride content in Soil and plant

F chemical analysis: The measurement of the total F content of the plant leaves were carried out by the method explained previously by Ahmad et al.[5] One gram of the dried material (80ºC) was ignited overnight at 500°C in nickel crucibles in a furnace. The ash was fused with 1 g sodium hydroxide using a Bunsen burner. After cooling, the fusion product was dissolved with a few milliliters of distilled water and was transferred into a 50 mL PE flask. 12.5 mL aqueous citric acid solution (340g L-1) and 5 mL hydrochloric acid (conc. hydrochloric acid:distilled water, 1:1, v/v) were added and then the solution was adjusted to pH 6.2 using sodium hydroxide, making up a final volume of 50 mL. Twenty-five mL of this solution was mixed with 25mL of a total ionic strength adjustment buffer (TISAB for the F determination, WTW Wilhelm, Germany). The F content of the samples was measured using a F-sensitive electrode (ISE F 800 DIN, WTW Wilhelm, Germany) coupled to an ion meter (Inolab pH/Ion 735 WTW Wilhelm, Germany). The calibration was made using five NaF standard solutions according to the following equation:

$$CF = 10(E–K) S$$

Where, CF = the F concentration
E = the electrode potential
K = the intercept
S = the slope of the function

Calcium content in soil

The procedure includes the extraction of calcium ions from soil samples having one mol/L of ammonium acetate ($CH_3CO_2NH_4$), and then measuring the calcium ion concentration via LAQUA twin calcium ion B-751 meter by the method of Petrou et al[32]. One gram of soil samples was accurately weighted and placed in glass beaker (100mL). 20 mL of 1mol/L $CH_3CO_2NH_4$ was added to the beaker. After shaking for one hour at amplitude of 40m/min @250 speed rpm, the Ca^{2+} was extracted from the soil by reciprocating shaker. The liquid was then filtered through Whatman's No.6 filter paper. LAQUA twin B-751 meter was calibrated with the help of standard solutions (150 and 2000mg/L Ca^{2+}) that contain the same amount of $CH_3CO_2NH_4$ as in the filtered samples. The filtered solution in small amount was placed on LAQUA twin Ca^{2+} sensor and was measured.

Conversation survey for service economy and mitigation strategies in agriculture

Conversation survey was carried out in brick kiln area from farmers and agricultural extension workers. The following questions were asked about the status of service economy and mitigation strategies. What is the status of fluoride pollution in the area? Do you know anything about fluoride pollution and its impact on the clover fodder? What are the causes of fluorosis and how it can be treated/controlled in livestock? Are there any adaptation/mitigation strategies? Has there been any mitigation program from the government/NGOs?

Statistical Analysis

The analysis was carried out via SPSS 19.0 software. LSD and One-way ANOVA test were conducted to determine the significance of difference at ($P < 0.05$). Results are presented as means ± standard error (SE) were based on 3 replicated.

RESULTS AND DISCUSSION

The leaf fluoride concentration significantly decreased with the increase in CaO content in the soil after four weeks of plant emergence as shown in Figure 2. At 0 µg/kg CaO treatment, the fluoride leaves concentration was 60 µg/kg which increased above 60 µg/kg in 20 µg/kg CaO soil concentration. By further enhancing the CaO concentration in soil by 40 and 60 µg/kg, the fluoride leaf concentration further decreased 38 µg/kg at 40 and 22 µg/kg at 60 µg/kg, respectively in 40 and 60 µg/kg treatments (Figure 2).

After 8 weeks in to the experiment, the fluoride concentration had increased to 75 µg/kg at 0 CaO concentration in soil as shown in Figure 3. The fluoride concentration decreased significantly by 61 µg/kg in 20 µg/kg CaO treatment. The fluoride concentration in clover leaves further decreased in 40 and 60 µg/kg to below 50 and 30 µg/kg, respectively (Figure 3).

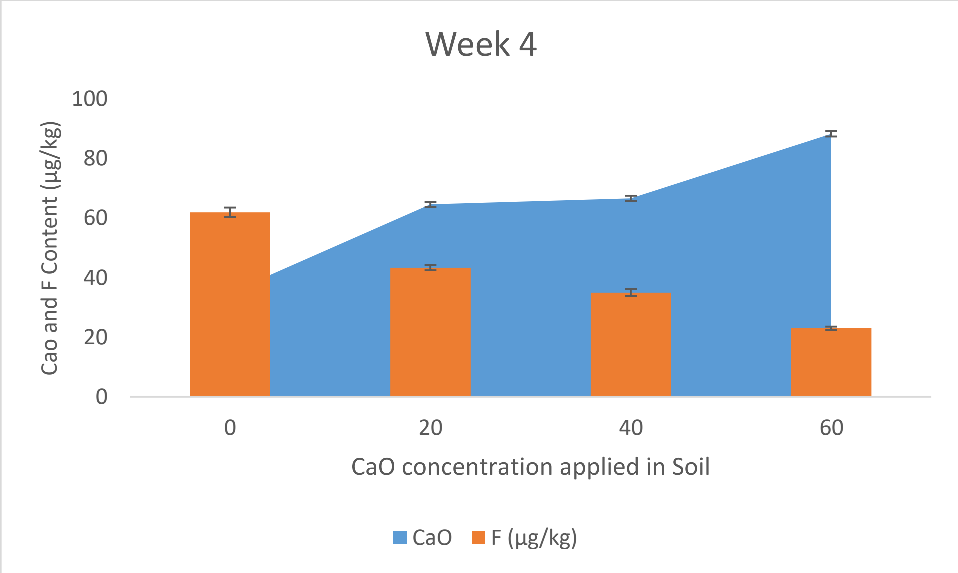

Figure 2: showing the effects of soil CaO concentration on the fluoride content of clover leaves after 4 weeks of plant emergence. Values are the means of 3 replicates with error bars showing standard error between the means.

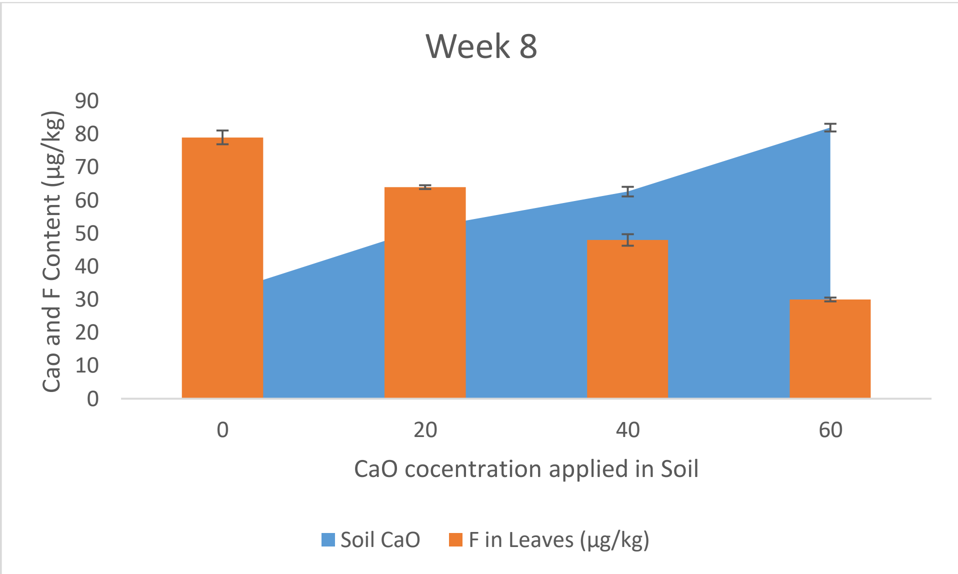

Figure 3: showing the effects of soil CaO concentration on the fluoride content of clover leaves after 8 weeks of plant emergence. Values are the means of 3 replicates with error bars showing standard error between the means.

The fluoride concentration in clover leaves was increased 91 µg/kg in week 12 of the experiment in 0 soil CaO treatment as shown in Figure 4. However, the fluoride concentration in clover leaves decreased significantly in 20, 40 and 60 µg/kg. The fluoride concentration in clover leaves was 63 µg/kg in clover leaves in 20 µg/kg CaO soil treatment, 50 µg/kg fluoride in clover leaves at 40 µg/kg and came down below 40 µg/kg in clover leaves in 60 CaO soil treatment after 12 weeks of plant emergence (Figure 4).

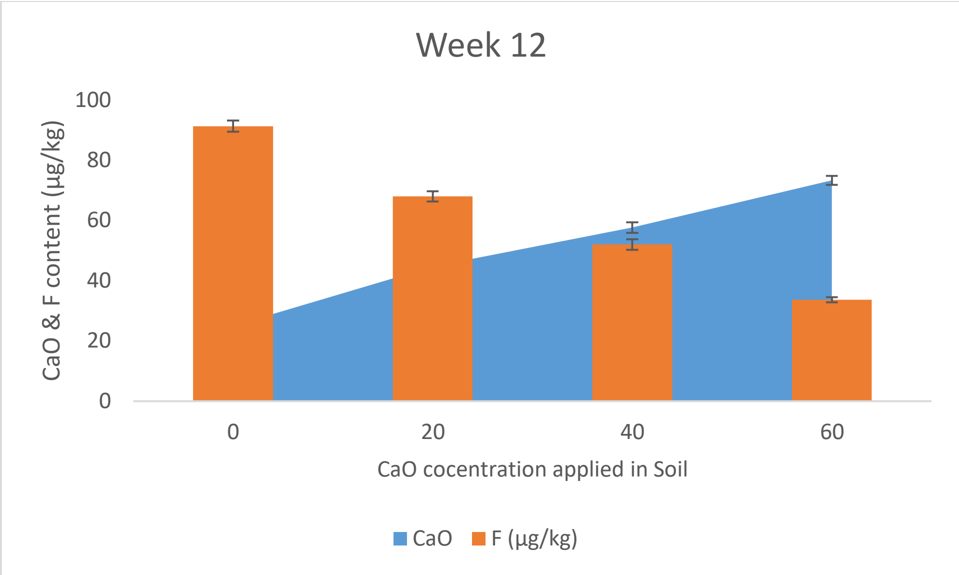

Figure 4: showing the effects of soil CaO concentration on the fluoride content of clover leaves after 12 weeks of plant emergence. Values are the means of 3 replicates with error bars showing standard error between the means.

The mean fluoride concentration of clover leaves was 77.3 µg/kg in 0 CaO soil treatment after 12 weeks of germination as shown in Figure 5. The mean fluoride concentration of 20 µg/kg was noted in 20 CaO soil treatment. While 45 and 28 µg/kg mean fluoride concentrations were found in 40 and 60 µg/kg CaO soil treatments, respectively. This suggests that calcium application of soil has significantly reduced the fluoride content in clover leaves. The fluoride content in clover leaves has significantly reduced with the passage of time. There has been more than two-fold reduction in fluoride concentration in clover leaves within 4 weeks by applying CaO in soil.

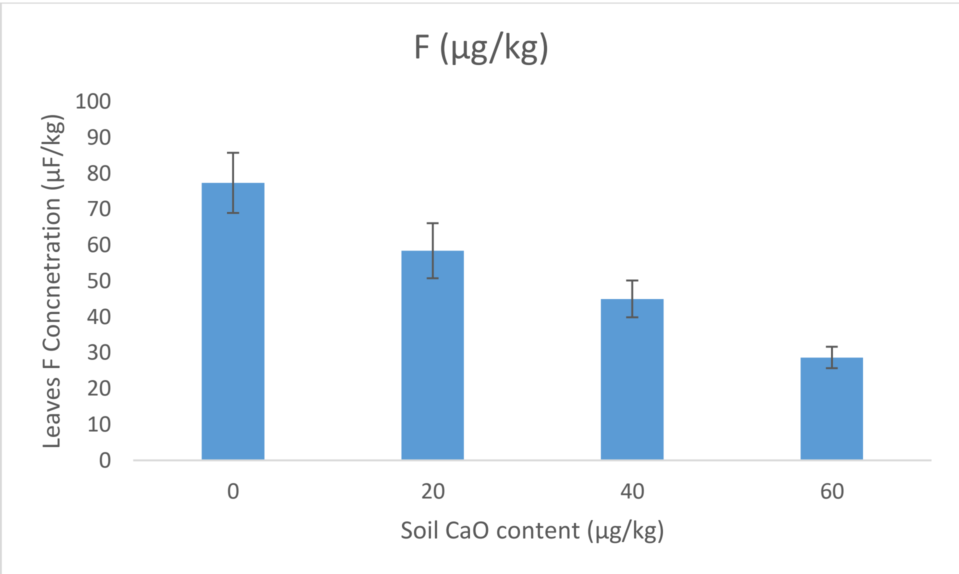

Figure 2: showing the mean effects of soil CaO concentration on the fluoride content of clover leaves. Values are the means of 3 replicates with error bars showing standard error between the means.

The previous literature suggests that soil fluoride is a mobile element. This mobility in soil plays an important role in releasing fluoride into the groundwater, which is primarily affected by soil texture, organic matter, pH and other ions concentrations[33,34,35]. The soil fluoride content ranges from 100-400 mg/L. Fluoride is mainly attached to the fractions of clay of soil colloids that mostly depends on soil pH and alkalinity for its mobility[35,36]. e.g. the bioavailability of fluoride increases in acidic medium but fluoride solubility lowers with the increase in soil pH between the range of 6.0-6.5[37,38]. Fluoride mostly attaches to aluminum and calcium in the soil to form complexes that are higher in clay and silt compared to sandy soils[38]. High salinity affects the mobility of fluoride as other ions also compete for absorption sites[39]. In addition, evaporation from soil can also affects the concentration of soil fluoride and salinity. The immobility of fluoride is because it is not exchangeable and readily soluble. However, soluble fluoride (organic) is imperative for the growth of animals and plants[33].

The current study is in line with the above studies that found that increased calcium concentration in soil was been taken up by clover plants and significantly reduced the fluoride concentration in clover leaves. Ruan et al[17] worked on fluoride uptake by tea plant and its response to soil pH and calcium content. They reported that leaf fluoride content reduced significantly with the increase in calcium concentration in the soil that raised the soil pH from 4.3 to 4.9, 5.4, 5.8 and finally to 6.5. Water soluble fluoride was also increased by liming of the soil. This increased the Ca bioavailability significantly that decreased the fluoride content of tea leaves. The reduction in fluoride uptake by clover plant might be related to the restricting the passage of fluoride from the soil to it translocation in the leaves as the cell wall permeability was changed significantly by the addition of calcium in the soil. This inhibition of calcium from root to shoot is because Ca increases the fluoride retention and limits the speed of fluoride transport inside the transpiration stream that has also been reported by Stevens et al[40].

Conversation survey for service economy and mitigation strategies in agriculture

The results of the conversation survey give a clear picture regarding the fluoride pollution and its impact on crops and livestock at brick kiln area. According to the farmers that did not know much about the fluoride pollution emitting from brick kilns, although they are quite concerned about its impact on their health as these brick kilns produced visible black carbon emissions. According to the farmers they depend a lot on the clover as their main fodder for their livestock. They did not know about fluorosis disease in animals. There are also no mitigation strategies conducted by either the government or NGO to tackle this issue. Apart from farmers the agricultural extension workers were also ignorant about the issue and took a keen interest on how to address the fluoride pollution and its impact on agriculture.

The farmers and agriculture extension workers suggested that there should be workshops and training on service economy and mitigation strategies for agriculture in the affected areas. They also suggested subsidy and tax wavier on agricultural inputs. They also asked about what are the alternatives to reduce the effects of fluoride pollution on crops and livestock?

Fluoride pollution in agricultural systems is an important concern, mostly in areas like Peshawar city where industries, like manufacturing and mining are responsible for adding significant amount of fluoride quantitates in to the air soil and water. Fodder like clover is mainly used for livestock feeding and is naturally vulnerable to fluoride uptake, resulting in significant effects on animal health. Livestock eating fluoride-polluted silage can develop fluorosis having symptoms like lameness, decreased productivity and mottled teeth. This research explores service economy strategies to mitigate fluoride uptake, focusing on sustainable agricultural practices, technological innovations, and policy interventions.

Therefore, the current study was about out to mitigate the fluoride levels by applying CaO in soil.

The strategy was successful as it reduced the fluoride concentration in clover leaves by more than half in three months. This is because calcium is retained by the soil and limits the uptake of fluoride into the leaves casing tis concentration to recede. This mitigation strategy is beneficial to areas where there is high fluoride toxicity like the brick kiln areas where crops fruits and fodders are exposed to harmful gases from brick kilns around the year.

For the improvement of service economy regarding local agriculture, there is a need to arrange awareness projects that includes training and workshops for farmers and technical persons of the local government to enhance agricultural practice and outcomes to reduce the environmental pollution effects on crops and fodders. To date, there has been no survey on the status of fluorosis and other livestock diseases in the area. The government should devise a strategy to enhance collaboration between researchers, agronomists, farmers and policy advisors to develop and disseminate quick information regarding best practices and livestock diseases to management risks related to agriculture like fluoride pollution and its contamination.

Other service economy strategies, like amendments of soil, water management, and introducing resistant fluoride varieties can also reduce the fluoride toxicity in plants that can ultimately save animals from fluorosis. In addition, the integration of advanced techniques through modern technology e.g. remote sensing and precision agriculture will also have positive impact on these strategies.

The current study highlights many challenges in applying the service economy strategies effectively. The main concern was the limited awareness of the local farmers about the fluoride pollution and its impacts on the environment. They also have limited financial resources and regulation of the current laws regarding the environment. However, opportunities exist in leveraging technological advancements, enhancing stakeholder collaboration, and developing supportive policies to address these challenges.

Policy recommendations include establishing guidelines for safe fluoride levels in agricultural environments, promoting research and development of fluoride-resistant crops, and providing financial and technical support to farmers for adopting best practices. Additionally, policies should encourage industrial accountability and the reduction of fluoride emissions. The limitation of the study was that the data is collected from the field and it was difficult to control all the parameters like soil pH. Therefore, an *in vitro* study in pots with selected HF fumigation should be conducted.

CONCLUSIONS AND RECOMMENDATIONS

It was concluded from the current study that Ca in form of lime can reduce fluoride content of clover leaves in the long run. However, by implementing effective service economy strategies to reduce fluoride uptake in clover fodder requires a multi-faceted approach involving technological innovations, stakeholder collaboration, and supportive policies. By addressing the challenges and leveraging opportunities, the agricultural sector can enhance livestock health, productivity, and sustainability. Future research should focus on refining mitigation techniques, expanding stakeholder engagement, and monitoring the long-term impacts of implemented strategies.

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