Fluoride in Agricultral Soil: A Review on its Sources and Toxicity to Plants

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ABSTRACT

Fluorine contents of plants have been investigated for a number of reasons such as assessing its hazard to grazing animals, the diagnosis of plant injury, and for monitoring airborne F pollutants. The average F contents of worldwide soils have been calculated to be 321 mg/kg. The F content of soils is inherited from parent material, but its distribution reflects soil forming processes and soil texture. Relatively close positive relationship between F and clay fraction contents is evident. Fluorides concentrations in topsoil slowly increase where annual inputs through atmospheric pollution and phosphatise fertilisers exceed losses. . Plants are exposed to fluoride through the air, soil, and water. Natural sources include weathering of fluoride minerals (such as cryolite, feldspar, mica, and apatitite), volcanic gases, and marine aerosols. In highly F^{-}polluted soil, as the soil becomes more acidic or alkaline, the risk of zootoxic concentrations of F in shoots of plants would increase. Higher concentrations of F have usually been reported for the aerial parts of plants. Mean F contents of plants grown in uncontaminated areas are very unlikely to exceed 5 mg/kg. The effects of plant F on humans and, particularly, on animals are of the greatest concern. The toxic threshold values of F in forage, is 30 mg/kg. In the present study on toxicity of fluoride in Agricultral soil and sources of fluoride in Agricultural soil.

Keywords: Fluorine, Toxicity, Atmospheric, Uncontaminated, Agricultral.

1. INTRODUCTION

Fluorides are released into the environment naturally through the weathering of minerals, in emissions from volcanoes and in marine aerosols [1, 2]. Estimates of the annual global release of hydrogen fluoride from volcanic sources through passive degassing and eruptions range from 60 to 6000 kilo tonnes, of which approximately 10% may be introduced directly into the stratosphere [1]. Annually, approximately 20 kilo tonnes of fluoride may be released in marine aerosols [1]. The main natural source of inorganic fluorides in soil is the parent rock [3]. During weathering, some fluoride minerals (e.g., cryolite or Na_3AlF_6) are rapidly broken down, especially under acidic conditions [4]. Other minerals, such as fluorapatite (Ca_5 $(PO_4)_3F$) and calcium fluoride, are dissolved more slowly [5]. The mineral fluorophlogopite (mica; $KMg_3(AlSi_3O_{10})F_2$) is stable in alkaline and calcareous soils [6]. However, its solubility is affected by pH. Fluoride in soil is primarily associated with the soil colloid or clay fraction. The clay and organic carbon content as well as the pH of soil are primarily responsible for the retention of fluoride in soils [7]. For all soils, it is the soluble fluoride content that is biologically important to plants and animals. Most of the fluoride in the soil is insoluble and, therefore, less available to plants. However, high soil fluoride concentrations or low pH, clay and/or organic matter can increase fluoride levels in soil solution, increasing uptake via the plant root. If fluoride is taken up through the root, its concentrations are often higher in the root than in the shoot, due to the low mobility of fluoride in the plant. Fluoride is a component of most types of soil, with total fluoride concentrations ranging from 20 to 1000 µg/g in areas without natural phosphate or fluoride deposits and up to several thousand micrograms per gram in mineral soils with deposits of fluoride [8]. The concentration of fluoride in food products is not significantly increased by the addition of superphosphate fertilizers, which contain significant concentrations of fluoride (1–3%) as impurities, to agricultural soil, due to the generally low transfer coefficient from soil to plant material. Fluoride can be taken up from vegetation, soil and drinking-water. Symptoms of fluoride toxicity include emaciation, stiffness of joints and abnormal teeth and bones. Other effects include lowered milk production and detrimental effects on the reproductive capacity of animals. The lowest dietary concentration of fluoride to cause fluorosis in wild deer was 35 mg/kg. Investigations of the effects of fluoride on wildlife have focused on impacts on the structural integrity of teeth and bone. Fluoride has both beneficial and detrimental effects on tooth enamel. The prevalence of dental caries is inversely related to the concentration of fluoride in drinking-water. The prevalence of dental fluorosis is highly associated with the concentration of fluoride, with a positive dose–response relationship. Tolerance levels have been identified for domesticated animals, with the lowest values for dairy cattle at 30 mg/kg feed or 2.5 mg/litre drinking-water. Incidents involving domesticated animals have originated both from natural fluoride sources, such as volcanic eruptions and the underlying geology, and from anthropogenic sources, such as mineral supplements, fluoride-emitting industries and power stations. In view of above, the present study is about toxicity of fluoride in Agricultral soil and sources of fluoride in Agricultural soil. This study may be useful to the farmers for the cultivation purposes.

2. FLUORIDE DISTRIBUTION IN AGRICULTRAL SOIL

The fluorine content of most rocks ranges from 100 to 1,300 mg/kg soil concentrations typically vary between 20 and 500 mg/kg. However, much higher concentrations (1,000 g/kg) can occur in soils that are derived from rocks with high fluorine contents or in soils affected by anthropogenic inputs, such as phosphate fertilizers. Most of the fluorine found in soils occurs within minerals or is adsorbed to clays and oxy-hydroxides, with only a few percent or less dissolved in the soil solution. Fluoride mobility in soil is highly dependent on the soil's sorption capacity, which varies with pH, the types of sorbents present, and soil salinity. Although aluminium smelters, and therefore fluoride emissions, exist in the temperate regions, there is a lack of studies dealing with the effects of addition of fluoride on the chemistry of temperate soils. Moreover the published studies refer to forest soils, whereas the behaviour of managed soils under this circumstance has not been investigated. However, in highly F-polluted soil, as the soil becomes more acidic or alkaline, the risk of zootoxic concentrations of F in shoots of plants would increase. The San Cipri´an Aluminium Smelter-Alumina Refinery Complex, located on the north coast of Galicia, NW Spain, since 1978, emits fluoride to the atmosphere, resulting in increased concentrations of fluorine in soils and vegetation in the immediate surroundings. The soils in the vicinity of the smelter have a high fluoride sorption capacity. The fluoride sorption may bring about changes in the soil composition. Understanding those changes is relevant for the management of the soils close to the smelter. The use of water containing relatively low (<3.1mg/litre) levels of fluoride for crop irrigation generally does not increase fluoride concentrations in foodstuffs. However, this is dependent on plant species and fluoride concentrations in soil and water.

Fluoride content in the bedrock was the most important factor determining fluoride levels in lake waters. Elevated fluoride concentrations were found in acidified areas compared with other regions with similar geology. Similarly, Hirayama et al. (1996) reported increased levels of fluoride (up to 1 mg/litre) in some rivers flowing into Lake Biwa, Japan, because of the local geology. Fluoride in soil is mainly bound in complexes. The maximum adsorption of fluoride to soil was reported to occur at pH 5.5 [9]. In acidic soils with pH below 6, most of the fluoride is in complexes with either aluminium or iron [10, 11, and 6].

Fluoride in alkaline soils at pH 6.5 and above is almost completely fixed in soils as calcium fluoride, if sufficient calcium carbonate is available [12]. Fluoride binds to clay by displacing hydroxide from the surface of the clay [13, 14, and 15]. The adsorption follows Langmuir adsorption equations and is strongly dependent upon pH and fluoride concentration. It is most significant at pH 3–4, and it decreases above pH 6.5. Pickering et al. (1988) [16] determined changes in free fluoride ions and total fluoride levels following equilibration of either poorly soluble fluoride species, such as calcium fluoride and aluminium fluoride, or wastes from aluminium smelters. Fluoride is extremely immobile in soil, as determined by lysimeter experiments. MacIntire et al. (1955) [17] reported that 75.8–99.6% of added fluoride was retained by loam soil for 4 years. Fluoride retention was correlated with the soil aluminium content. The leaching of fluoride occurred simultaneously with the leaching of aluminium, iron and organic material from soil (Polomski et al., 1982) [18]. Soil phosphate may contribute to the mobility of inorganic fluoride [5]. Oelschläger (1971) [19] reported that approximately 0.5– 6.0% of the annual addition of fluoride (atmospheric pollution and artificial fertilizers) to a forest and agricultural areas was leached from the surface to lower soil horizons. Arnesen & Krogstad (1998) [20] found that fluoride (added as sodium fluoride) accumulation was high in the upper 0–10 cm of soil columns, where 50–90% of the accumulated fluoride was found. The B-horizons sorbed considerably more fluoride than the A-horizons, due to higher content of aluminium oxides/ hydroxides. A study by McLaughlin et al. (2001) [21] involving long-term application of phosphate fertilizers has shown a large portion of fluoride applied as impurities in the fertilizer to remain in the 0- to 10-cm depth of the soil profile. In sandy acidic soils, fluoride tends to be present in water-soluble forms [22]. Street & Elwali (1983) [23] determined the activity of the fluoride ion in acid sandy soils that had been limed. Fluorite was shown to be the solid phase controlling fluoride ion activity in soils between pH 5.5 and 7.0. Murray (1984b) [11] reported that low amounts of fluoride were leached from a highly disturbed sandy Pedol soil of no distinct structure. Even at high fluoride application rates (3.2–80 g per soil column of diameter 0.1 m with a depth of 2 m), only 2.6–4.6% of the fluoride applied was leached in the water-soluble form. The pH increased with increasing fluoride application, and this was probably due to adsorption of fluoride, releasing hydroxide ions from the soil metal hydroxides.

Gilpin & Johnson suggested that fluoride is relatively immobile in soil, since most of the fluoride was not readily soluble or exchangeable [24]. Calcium fluoride was formed in soils irrigated with fluoride solutions. Calcium fluoride is formed when the fluoride adsorption capacity is exceeded and the fluoride and calcium ion activities exceed the ion activity product of calcium fluoride [25]. Breimer et al. (1989) [26] determined the vertical distribution of fluoride in the soil profiles sampled near an industrial region. The adsorption of fluoride from the water phase may be an important transport characteristic in calcareous soils at low flow rates, but this exchange may be rate-limited at high flow rates [27]. Dissolved fluoride concentrations may be high around the root zone in soils with a high fluoride input such as from atmospheric deposition. The high concentrations exist only for a limited time until the fluoride is withdrawn from the solution. The adsorption isotherm was reported to be non-linear between initial concentrations of 10 and 50 mg fluoride/litre. Retention of fluoride in uncontaminated calcareous soil was higher than retention in calcareous soil from areas with fluoride contamination. The adsorption and desorption of fluoride in acidic soil were not related to previous fluoride contamination. Fluoride-containing solutions increased the mobilization and leaching of aluminium from soils. Leaching of aluminium was reported to be greater from soil contaminated from an aluminium smelter than from uncontaminated soil [28]. In the uncontaminated soil, losses of aluminium from the acid soil were higher than those from the calcareous soil.

3. SOURCES OF FLUORIDE IN AGRICULTRAL SOILS:

The fate of inorganic fluorides in the atmosphere is primarily influenced by vaporization, aerosol formation, wet and dry deposition and hydrolysis [29]. Non-volatile inorganic fluoride particulates are removed from the atmosphere via condensation or nucleation processes. Atmospheric fluorides emitted from both natural and anthropogenic sources may be in gaseous or particulate form (Kirk & Lester, 1986). Gaseous forms include hydrogen fluoride, silicon tetra-fluoride (SiF), fluorosilicic acid and sulphur hexafluoride. Particulate forms 4 include sodium aluminium fluoride (cryolite), aluminium fluoride, calcium fluoride, sodium hexa-fluorosilicate, lead fluoride (PbF) and 2 - calcium phosphate fluoride (fluorapatite). Globally, hydrogen fluoride and inorganic fluoride particulates (sodium and calcium fluoride) account for approximately 75% and 25%, respectively, of inorganic fluorides present in the atmosphere [30]. Fluorine and the silicon fluorides are hydrolysed in the atmosphere to form hydrogen fluoride. Hydrogen fluoride may combine with water vapour to produce an aerosol or fog of aqueous hydrofluoric acid. Fluorides adsorbed on particulate matter in the atmosphere are generally stable and are not readily hydrolysed, although they may be degraded by radiation if they persist in the atmosphere (US NAS, 1971). Hydrofluoric acid is approximately 5 orders of magnitude less soluble than hydrochloric acid and will therefore be degassed from marine aerosols more readily than hydrochloric acid. Davison et al. (1973) reported that between 60 and 74% of atmospheric fluoride in urban coal-burning areas in the United Kingdom was in gaseous form. Similarly, approximately 60% of the fluorides in the atmosphere in the Netherlands are in the gaseous state [31]. Atmospheric fluorides may be transported to soils and surface waters through both wet and dry deposition processes (US NAS, 1971).

In water, the transport and transformation of inorganic fluorides are influenced by pH, water hardness and the presence of ion exchange materials such as clays (Environment Canada, 1994). Fluoride is usually transported through the water cycle complexes with aluminium [32]. In areas of extreme acidity and alkalinity, inorganic fluorides may leach from fluoride-containing minerals into surface water or groundwater [33].

4. FLUORINE TOXICITY IN PLANTS

Fluorine (F) occurs in the atmosphere as gaseous molecules (F_2) and in reduced form as particulate fluoride (F). In water, inorganic fluorides usually remain in solution (as fluoride ions) - under conditions of relatively low pH and hardness. Plants are exposed to fluoride through the air, soil, and water. Natural sources include weathering of fluoride minerals (such as cryolite, feldspar, mica, and apatitite), volcanic gases, and marine aerosols. Aluminium smelting, brick, glass and ceramic manufacturing, and high phosphate fertilizers can also be important sources. Many municipal water sources inject fluorine (at 1 ppm) as an additive to prevent tooth decay. Use of this water for irrigation can result in toxicity symptoms on sensitive plants. In general, soil fluoride is not available to plants. Roots take up small amounts of soil fluoride diffusion, which results in a low background concentration in the plant foliage. There are exceptions such as tea plants that are natural accumulators of fluoride. Gaseous uptake of fluoride by leaves is rapid due to its high solubility. Fluoride is an accumulative poison in plant foliage. Accumulation may be gradual over time. Fluoride strongly inhibits photosynthesis and other processes. It will move in the transpiration stream from roots or through stomata and accumulate in leaf margins. Typical fluorine injury symptoms on broadleaf plants include marginal and tip necrosis that spread inward. Conifer needles exhibit tip necrosis that spreads to the base. Drought stress or salt toxicity can have similar symptoms. A wide variety of plants are sensitive e to fluoride toxicity. Typical indoor foliage plainclude Dracaena, Tahitian Bridal Veil (*Gibasis pellucida*), and the spider plant (*Chlorophytcomosum*). Both Dracaena deremensis and D. fragrans (corn plant) are very sensitive e to fluoride toxicity. Fruits such as apricot, blueberry , grape, peach, and plums are also sensitive conifers that are sensitive e include Douglas- fir, western larch, most pines, and blue spruce. Sensitive e flowering plants include gladiolus, lily , tulip, and yucca. Avoiding fluorine toxicity starts with knowing which plants are sensitive. Avoid fluoridated water, high phosphate fertilizers, and low soil pH. An exception would be low pH- loving plant like blueberry. High calcium levels in the soil or rooting medium, such as use of dolomite, can help tie up fluoride and prevent injury

5. CONCENTRATIONS IN PLANTS

Fluorine contents of plants have been investigated for a number of reasons such as assessing its hazard to grazing animals, the diagnosis of plant injury, and for monitoring airborne F pollutants. Higher concentrations of F have usually been reported for the aerial parts of plants. Mean F contents of plants grown in uncontaminated areas are very unlikely to exceed 5 mg/kg. However, in some vegetables, for example, spinach leaves, its concentration may reach up to 28 mg/kg. According to general opinion, plant F seems to be positively correlated with the concentration of F in rainwater. Davison et al discussed a method of the prediction of F concentrations in pasture using multiple regression techniques and including data on aerial deposition of F and rainfall. Several plants, especially forage vegetation, when growing in polluted areas are reported to contain large amounts of F. Most of the F pollution is likely to be deposited on the leaf surface, which was shown by findings of Fuge and Andrews. They reported that F in unwashed grasses from an area of china clay industry ranges from 756 to 3240 mg/kg, whereas F ranged from 330 to 1410 mg/kg in grasses from the same area, but washed in distilled water. Results of the pot experiment clearly indicate that soil F is not an important source of this element to red maple and orchard grass. Pine needles are common and good indicators for the F pollution. Pine needles from the vicinity of an aluminium smelter contain F above 1000 mg/kg, while the background value for F in pine needles in Poland is below 20 mg/kg. Geebelen et al. (2005) used transplanted lichens as bio monitors for atmospheric F pollution and observed the F accumulation up to 243 mg/kg near the F point source. Some parts of plants, growing in acid soils, accumulate increasing amounts of F with time, such as in the case of old tea leaves, which contain up to 300 times more of this element than young leaves (Siemin´ski, 2001).

6. CONCLUSION

The investigation supports the hypothesis that fluoride has a toxic effect on soil microorganisms. There was a negative correlation between high concentrations of fluoride and the activity of phosphatise enzymes, which is indicative of a reduced microbial activity and thereby reduced soil health. Finally the applied fluoride was largely retained in the soil, which shows that accumulation of fluoride is possible and long-term pollution effects likely. Deposition of fluoride have followed volcanic eruptions and based on the results in this experiment, it seems likely that retained enzymatic activity due to fluoride pollution from such eruptions can have a negative effect on soil fertility and health .The F concentrations in the shoots exceeded the recommended limit for F contents in pasture grass only in ryegrass grown in the most polluted soil. Concentrations of F in clover on the other hand, were much higher and exceeded this limit even in moderately polluted soil. Liming of soil reduced the availability of soil F, but even in unlimed soil the root uptake was relatively low compared with possible uptake from air around the Al smelters. Although F accumulation increases the soil solution and soluble and labile pools of F in soils, due to its strong adsorption, these comprise only a minor fraction of total soil F. Hence, the effect of F accumulation in soils does not appear to pose a threat to groundwater supplies. A combination of the strong adsorption of F in soils and its low rate of uptake by most plants means that normal pastoral plants are not likely to be greatly affected by increasing soil F concentrations. At high pH (>6.5), desorption of non-specifically adsorbed F may also result in higher plant F uptake. The activity of soil micro-organisms is likely to be negatively affected as soil F concentrations rise. Data on the critical soil F concentration affecting soil microbial activity is scarce and inconclusive. Although soil F is not likely to be passed on to grazing animals via pasture, it can be directly taken up by soil ingestion during grazing. Only once this additional information is obtained can adequate recommendations be made for mitigating the risks of increasing F levels in our pastoral systems, and developing practices that are sustainable in the future.

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