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REVIEW ARTICLE

Fluoride in soil and plant

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Abstract

Fluorine is unique chemical element which occurs naturally, but is not an essential nutrient for plants. Fluoride toxicity can arise due to excessive fluoride intake from a variety of natural or manmade sources. Fluoride is phytotoxic to most plants. Plants which are sensitive for fluorine exposure even low concentrations of fluorine can cause leave damage and a decline in growth. All vegetation contains some fluoride absorbed from soil and water. The highest levels of F in field-grown vegetables are found up to 40 mg kg^{-1} fresh weight although fluoride is relatively immobile and is not easily leached in soil because most of the fluoride was not readily soluble or exchangeable. Also, high concentrations of fluoride primarily associated with the soil colloid or clay fraction can increase fluoride levels in soil solution, increasing uptake via the plant root. In soils more than 90 percent of the natural fluoride ranging from 20 to 1,000 $\mu g\ g^{-1}$ is insoluble, or tightly bound to soil particles. The excess accumulation of fluorides in vegetation leads to visible leaf injury, damage to fruits, changes in the yield. The amount of fluoride taken up by plants depending on the type of plant, the nature of the soil, and the amount and form of fluoride in the soil should be controlled. Conclusively, fluoride is possible and long-term pollution effects on plant growth through accumulation of the fluoride retained in the soil.

Keywords: fluoride, phytotoxicity, plant, soil

Introduction

Fluorine, discovered as an element in other compounds in the early 1500s by the German physician Georgius Agricola, does not occur in the elemental state in nature because of its high reactivity and fluoride is the negative of element fluorine. Fluorine is the most reactive of all elements and no chemical substance is capable of freeing fluorine from any of its compounds. For this reason, fluorine does not occur free in nature and was extremely difficult for scientists to isolate. Fluorine in the form of fluorides in a number of minerals, of which fluorspar, cryolite and fluorapatite are the most common is the 13th most abundant element in the Earth's crust: 950 ppm are contained in it. Annual world production of the mineral fluorite in around 4 million tons, and are around 120 million tons of mineral reserves. Soils contain approximatively 330 ppm of fluorine, ranging from 150 to 400 ppm. Some soils can have as much as 1,000 ppm and contaminated soils have been found with 3,500 ppm (Information and Science, 2013).

Fluorine and fluoride are widely used in industry. They are used in aluminum production and as a flux in the steel and glass fiber industries. One very useful fluorine-containing product is polytetrafluoroethylene (PTFE), a fluorinated plastic sold under a well-known trade name and used domestically on cooking utensils because of its heat resistance and non-stick properties. Fluorine and fluoride are also used in the production of pesticides, such as sulfuryl fluoride, and in an intermediate step in the enrichment of uranium for nuclear reactors. They can also be released to the environment during the production of phosphate fertilizers, bricks, tiles and ceramics. Fluorosilicic acid, sodium hexafluorosilicate and sodium fluoride are used in municipal water fluoridation schemes (IARC, 1982; IPCS, 2002). Although sodium fluoride is soluble in water (IARC, 1982), aluminum, calcium and magnesium fluorides are only sparingly so (US EPA, 1985).

Fluoride may be an essential element for animals and humans. For humans, however, the essentiality has not been demonstrated unequivocally, and no data indicating the minimum nutritional requirement are available. Small amounts of fluorine are naturally present in water, air, plants and animals. As a result, humans are exposed to fluorine through food and drinking water and by breathing air. Fluorine can be found in any kind of food in relatively small quantities. Large quantities of fluorine can be found in tea and shellfish. Fluorine is essential for the maintenance of solidity of our bones (Lenntech, 2016). Although elemental fluorine is highly toxic due to its reactivity, fluorides are generally less so. Nevertheless, ingestion of soluble metal fluorides in other than very small amounts can have serious toxic effects and for this reason, toothpaste and mouthwash should not be swallowed. The acute effects of fluoride ingestion include damage to the brain and kidneys and effects on the heart. According to the U.S. Department of Agriculture, the Dietary Reference Intakes, which is the "highest level of daily nutrient intake that is likely to pose no risk of adverse health effects" specify 10 mg day for most people, corresponding to 10 L of fluoridated water with no risk.

Virtually all foodstuffs contain at least traces of fluorine. All vegetation contains some fluoride, which is absorbed from soil and water. The highest levels in field-grown vegetables are found in curly kale (up to 40 mg kg^{-1} fresh weight) and endive (0.3 - 2.8 mg kg^{-1} fresh weight) (Slooff et al., 1988). Other foods containing high levels include fish (0.1 - 30 mg kg^{-1}) and tea (US EPA, 1985; Slooff et al., 1988). High concentrations in tea can be caused by high natural concentrations in tea plants or by the use of additives during growth or fermentation. Levels in dry tea can be 3 - 300 mg kg^{-1} (average 100 mg kg^{-1}), so 2 - 3 cups of tea contain approximately 0.4 - 0.8 mg (IPCS, 1984; Slooff et al., 1988). In areas where water with a high fluoride content is used to prepare tea, the intake via tea can be several times greater (Janssen et al., 1988). With plants that are sensitive for fluorine exposure, even low concentrations of fluorine can cause leave damage and a decline in growth. Too much fluoride, whether taken in form the soil by roots, or absorbed from the atmosphere by the leaves, retards the growth of plants and reduces crop yields. Those more affected are corns and apricots. Animals that eat fluorine-containing plants may accumulate large amounts of fluorine in their bodies. Fluorine primarily accumulates in bones. Consequently, animals that are exposed to high concentrations of fluorine suffer from dental decay and bone degradation. Finally, it can cause low birth-weights (Lenntech, 2016).

Fluorides are released into the air in wind-blown soil. Hydrogen fluorides can be released into air through combustion processes in the industry. Fluorides found in air will eventually drop onto land or into water. When fluorine is attached to very small particles it can remain in the air for a long period of time. In the atmosphere 0.6 ppb of fluorine are present as salt spray and organic chloride compounds. Up to 50 ppb has been recorded in city environments. When fluorine from the air ends up in water it will settle into the sediment. When it ends up in soils, fluorine will become strongly attached to soil particles. In the environment fluorine cannot be destroyed; it can only change form. Fluorine that is located in soils may accumulate in plants. The amount of uptake by plants depends upon the type of plant and the type of soil and the amount and type of fluorine found in the soil.

Thus, fluorine and fluoride as the negative form of fluorine are essential element for animals and humans while the fluoride through gaseous uptake by leaves is an accumulative poison in plant foliage as well as a toxic effect on soil microorganisms. Therefore, the fluoride which is largely retained in the soil is possible and long-term pollution effects likely. In this review we compile the information currently known about fluoride and identify what we should understand and investigate the fluoride in soils and plants from many fields of research, including geochemistry, soil science, and plant science.

1. What are fluorides and fluorine?

Fluorine

Fluorine is unique chemical element which occurs naturally, but is not an essential nutrient for plants (Mackowiak et al., 2003). Fluorine that naturally occurs only in very low concentrations in the environment in the absence of anthropogenic source is a chemical element with symbol F and atomic number 9. Fluorine is an univalent poisonous gaseous halogen which includes chlorine, bromine, and iodine and is pale yellow-green, irritating gaseous element with a sharp odor.

Fluorine atoms have nine electrons, one fewer than neon, and electron configuration $1s^2 2s^2 2p^5$: two electrons in a filled inner shell and seven in an outer shell requiring one more to be filled. The outer electrons are ineffective at nuclear shielding, and experience a high effective nuclear charge of 9 - 2 = 7; this affects the atom's physical properties. Fluorine atoms have a small covalent radius of around 60 picometers, similar to those of its period neighbors oxygen and neon (Jaccaud et al., 2000).

Fluorine occurs as a diatomic molecule, F_2, in its elemental form. The bond energy of difluorine is much lower than that of either Cl_2 or Br_2 and similar to the easily cleaved peroxide bond; this accounts for fluorine's easy dissociation, high reactivity, and strong bonds to non-fluorine atoms. Conversely, bonds to other atoms are very strong because of fluorine's high electronegativity (Greenwood and Earnshaw, 1998; Macomber, 1996). It reacts at room temperature or elevated temperatures with all elements other than nitrogen, oxygen, and the lighter noble gases (US DHHS, 2003). Due to its notably small size, large numbers of fluorine atoms fit around atoms of another element. This allows the formation of many simple and complex fluorides in which the other element is in its highest oxidation date.

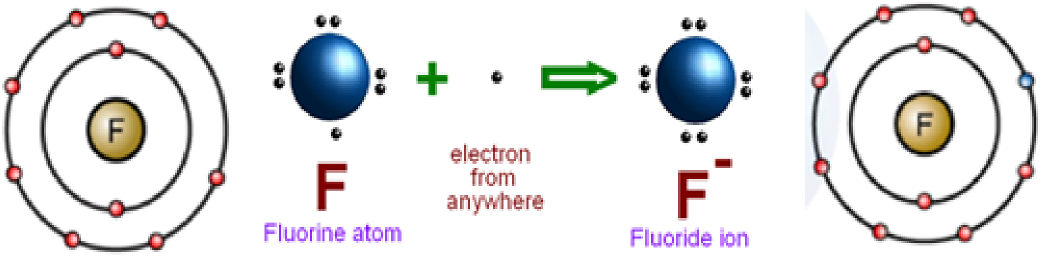

Fig. 1. Electron configuration of fluorine atom and fluoride ion.

Fluorine has a rich chemistry, encompassing organic and inorganic domains. It combines with metals, nonmetals, metalloids, and most noble gases, and usually assumes an oxidation state of -1 (Riedel and Kaupp, 2009). Hydrogen and fluorine combine to yield hydrogen fluoride, in which discrete molecules form clusters by hydrogen bonding, resembling water more than hydrogen chloride (Pauling, 1960; Atkins et al., 2007). It boils at a much higher temperature than heavier hydrogen halides and unlike them is fully miscible with water (Greenwood and Earnshaw, 1998). Hydrogen fluoride readily hydrates on contact with water to form aqueous hydrogen fluoride, also known as hydrofluoric acid. Unlike the other hydrohalic acids, which are strong, hydrofluoric acid is a weak acid at low concentrations (Wiberg et al., 2001). Fluorine's high electron affinity results in a preference for ionic bonding; when it forms covalent bonds, these are polar, and almost always single (Harbison, 2002; Edwards, 1994). Fluorine occurs in ionic forms, or combined with other chemicals in minerals like fluorspar, fluorapatite, and cryolite, and other compounds (Jaccaud et al., 2000). Ions are atoms, collections of atoms, or molecules containing a positive or negative electric charge. Fluorine gas reacts with most organic and inorganic substances; with metals, it forms fluorides and with water, it forms hydrofluoric acid. In aqueous solution, fluorine commonly occurs as the fluoride ion F-. Fluorine readily forms compounds with most other elements, even with the noble gases krypton, xenon and radon. It is so reactive that glass, metals, and even water, as well as other substances, burn with a bright flame in a jet of fluorine gas. About 30% of agrichemicals contain fluorine, most of them herbicides and fungicides with a few crop regulators (Theodoridis, 2006).

Fluorides

Fluorides which occur in the earth’s crust where they are found in rocks, coal, clay, and soil are released into the environment naturally through the weathering of minerals, in emissions from volcanic ash and in marine aerosols (Tylenda, 2011). Estimates of the annual global release of hydrogen fluoride from volcanic sources through passive degassing and eruptions range from 60 to 6,000 kilo tons, of which approximately 10% may be introduced directly into the stratosphere (Symonds et al., 1988). Fluoride can also be deposited into soil from several anthropogenic sources, both directly through phosphate fertilizers or indirectly through atmospheric pollution from industrial activities and burning of fossil fuels (Elloumi et al., 2005). According to Bhat et al. (2015), it was observed that mean fluoride concentration was significantly highest at 0 km from smelter in upper soil layer and deeper soil layer. Moreover, upper soil layer revealed significantly greater mean F concentration than deeper soil layers at all distances (Table 1).

Fluorides are normally found in very small amounts in the air. Levels of fluoride measured in areas around cities are usually less than 1 $\mu g m^{-3}$ of air. The fluorides released into air will eventually fall on land or water.

Fluoride, the simplest anion of fluorine, is properly defined as binary compounds or salts of fluorine and another element. Fluorides are compounds that combine fluoride with some positively charged counterpart. It is the most chemically reactive and electronegative of all the elements. Fluoride can act as a base. It can combine with a proton (H^+) as following equation below:

$$F^- + H^+ \rightarrow HF$$

This neutralization reaction forms hydrogen fluoride (HF), the conjugate acid of fluoride. In aqueous solution, fluoride has a pK_b value of 10.8. It is therefore a weak base, and tends to remain as the fluoride ion rather than generating a substantial amount of hydrogen fluoride. That is, the following equilibrium favors the left-hand side in water:

Table 1. Comparative assessment of Fluoride concentration in vegetables and soils at various distances from Zinc Smelter (Bhat et al., 2015).

Distance (km)	Fconc. in vegetables (ppm, Mean ± SD)	Fconc. in soil (ppm, Mean ± SD)		p-value
		Upper layer	Deeper layer	
0	0.71 ± 0.90	189 ± 1	139 ± 1	0.001
1	0.66 ± 0.84	179 ± 1	128 ± 1	0.001
2	0.56 ± 0.71	168.3 ± 0.58	108 ± 0	0.001
5	0.39 ± 0.53	101.67 ± 0.58	97.3 ± 0.58	0.001
10	0.36 ± 0.69	101.67 ± 0.58	98 ± 0.02	0.001
p-value	0.79	0.001	0.001	

$$F^- + H_2O \rightleftarrows HF + HO^-$$

In terms of charge and size, the fluoride ion, the most electronegative element in halogen family, resembles the hydroxide ion and occurs in ionic forms or combined with other chemicals in minerals like fluorspar, fluorapatite, and cryolite and other compounds (Prystupa, 2011). It forms inorganic and organic compounds called fluorides (Greenfacts, 2002). Examples of fluorides include sodium fluoride and calcium fluoride.

In water, fluorides associate with various elements present in the water, mainly with aluminum in freshwater and calcium and magnesium in seawater, and settle into the sediment where they are strongly attached to sediment particles (Tylenda, 2011). Fluorides which are strongly retained by soil are in the form of cryolite (Na_3AlF_6), flurapatite ($Ca_5(PO_4)_3F$) and other phosphate rocks (Begum, 2012). Leaching removes only a small amount of fluorides from soils (Tylenda, 2011). Soluble fluoride is distributed over the earth's surface and atmosphere as a result of natural processes such as erosion, hydraulic leaching, volcanic activity, and to a lesser extent by mining and manufacturing processes. The hazards of solutions of fluoride salts that release hydrogen fluoride in the presence of strong acids depend on the concentration (Nakagawa et al., 1999). However, upon prolonged contact with moisture, soluble fluoride salts will decompose to their respective hydroxides or oxides, as the hydrogen fluoride escapes. Fluoride is distinct in this regard among the halides.

2. Transition of fluoride into plants from soil

Plants are exposed to fluoride through the air, soil, and water (Anshumali, 2014). Plants can also incorporate F from contaminated soils (Arnesen, 1997). 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 (Anshumali, 2014). The route of exposure to fluoride is through uptake through the plant's roots. The amount of fluoride taken up by plants depends on the type of plant, the nature of the soil, and the amount and form of fluoride in the soil (Tylenda. 2001). Uptake of F by roots is passive (Garrec and Letourneur, 1981; Venkateswarlu et al., 1965) and is dependent on several parameters such as soil pH and activity and composition of fluoride (Mackowiak et al., 2003). Bioaccumulation of fluoride in different plant parts vary depending on its transfer from soil solution to roots and translocation from root to shoot (Agarwal and Chauhan, 2014).

From the soil, F is absorbed by plant roots and can then be transported by the symplastic or apoplastic pathway in the roots or via xylematic flow to the transpiratory organs, mainly the leaves (Elloumi et al., 2005; Punita et al., 2015). Stevens et al. (1997) also recorded that ionic species of fluoride in solution had a marked influence on the uptake of fluoride by plant roots with complexes species being more readily taken up by the roots than the free fluoride ions. In acidic soil fluoride showed highest solubility due to its complexation with aluminum, but in alkaline condition, desorption of free fluoride due to repulsion by negatively charged surfaces. However, in neutral pH, fluoride readily bound to soil surface and is not available to plants (Mondal and George, 2015). Most of the soluble F added to soils is converted into insoluble chemical forms which are not available to plants whereas addition of soluble F to soils of low pH can result in serious damage to vegetation (Elrashidi et al., 1998). Venkateswarlu et al. (1965) found that almost 99% of the F absorbed by roots of Hordeum vulgare was desorbed in water, indicating that most of it was retained in the apoplast. Jha et al. (2009) reported that the order of retention of fluoride in onion found to be roots > shoot > bulb. Therefore, it can be said that fluoride accumulation in the roots is higher than in leaves, stems and seeds. This might be due to high affinity of fluoride at the surface of roots and relatively low permeability through the endodermis (Takmaz and Davison, 1988). The concentration of fluoride in food products is not significantly increased by the addition of superphosphate fertilizers, which contain significant concentrations of fluoride from 1 to 3% as impurities, to agricultural soil, due to the generally low transfer coefficient from soil to plant material (Anshumali, 2014).

3. Fluoride in soil

Fluorine is unique chemical element which occurs naturally, but is not an essential nutrient for plants (Mackowiak, et al., 2003). 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. More than 90 percent of the natural fluoride content of soils is insoluble, or tightly bound to soil particles (Marier and Rose, 1971). In most soils fluoride is associated with micas and other clay minerals (Tylenda, 2011). Total fluoride concentrations in soils range from 20 to 1,000 $\mu g\ g^{-1}$ in areas without natural phosphate or fluoride deposits, whereas the organic soils are usually lower (Davison A, 1983; US NAS, 1971). Higher levels of the fluoride may also occur where phosphate fertilizers are used, where coal-fired power plants or fluoride-releasing industries are located, or in the vicinity of hazardous waste sites (Tylenda, 2011).

Fluoride in soil is primarily associated with the soil colloid or clay fraction and its mobility in soil is highly dependent on the soil’s sorption capacity, which varies with pH, the types of sorbents present, and soil salinity. The clay and organic carbon content as well as the pH of soil are primarily responsible for the retention of fluoride in soils. In soils, fluoride is predominantly combined with aluminum or calcium and soils of silt and clay loam soils had higher fluoride content than sandy soils (Tylenda, 2011; Greenfacts, 2002). Fluoride forms its most stable bonds with Fe, Al, and Ca, and labile F is held by soil components that contain these elements, including clay minerals, calcium and magnesium compounds, and iron and aluminum compounds (Omueti and Jones 1977). Elrashidi et al. (1998) indicated that F forms Al and Fe complexes which disrupt the mineral surfaces. Barrow and Ellis (1986) later predicted that at low pH, complexes between Al and F formed in soil solution and that little was present as free F^-. Macintire (1950) also reported that some soils, especially those with relatively high calcium content, were very effective in fixing fluoride. The electronegative fluoride ion replaces $-OH/H_2O$ groups bound to surficial Al atoms as ligand exchange, loosens other $Al-OH$ bonds (Vasudevan et al., 2003).

Fluoride is relatively immobile and is not easily leached in soil because most of the fluoride was not readily soluble or exchangeable (Gilpin and Johnson, 1980; Greenfacts, 2002). Calcium fluoride can be formed in soils irrigated with fluoride solutions or when the fluoride adsorption capacity is exceeded and the fluoride and calcium ion activities exceed the ion activity product of calcium fluoride (Tracy et al., 1984). However, fluoride is a mobile ion and its retention in the soil depends on the amount and rate of water percolating into the soil zone which depends on the permeability of the soil (Abugri, 2010). There was a sharp increase of the soluble F with the added F up to 200 mg NaF kg^{-1} soil and then increased steadily with the increase of the added F which may be mainly due to the release of OH^- during the adsorption process (Bower and Hatcher, 1967). This release of OH^- in turn might have increased the pH and hence more F leached out in the soil solution due to high alkalinity, which is in agreement with earlier findings (Stevens et al., 1997). In some cases F retention was greatest near pH 5.5 and decreased at both lower and higher pH levels (Omueti and Jones 1977). At high pH an increasingly unfavorable electrostatic potential decreases retention of F on the soil and increases the F- concentration in soil solution. It is also due to displacement of adsorbed F- by the increased concentration of OH^- in soil solution at the higher pH (Larsen and Widdowson 1971). At higher F dose, soil pH changes to alkaline which support to release higher fluoride from soil surface and subsequently plant availability increased (Saxena and Rani, 2012).

For all soils, the soluble F content is biologically important to plants and animals (Davison, 1983). Fluoride solubility in soil is complex and may be controlled by solid phases related to the solubility of Al or other ionic species with which it forms complexes (Arnesen, 1997). The solubility of F in soil is controlled mainly through F adsorption by inorganic constituents of the soil and soil pH (McLaughlin et al., 2001; Loganathan et al., 2003). The greater solubility of F under acidic conditions was explained by the formation of AlF_x complexes, whereas under alkaline conditions by desorption of free F as a result of repulsion by the negatively charged surfaces (Wenzel and Blum, 1992). In sandy acidic soils, fluoride tends to be present in water-soluble forms (Shacklette et al., 1974). 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 (Brewer, 1966a). Fluoride binds to clay by displacing hydroxide from the surface of the clay (Bower and Hatcher, 1967; Huang and Jackson, 1965; Meeussen et al., 1996).

Early studies concluded that F is retained by finer textured soils, particularly those with a significant clay component (Brewer, 1966b). Later work revealed that the sorption of F also depended strongly on soil pH. The degree of F adsorption is also controlled by soil pH and is greatest in non-calcareous soils, which generally contain higher Al levels (Omueti and Jones 1977; Barrow and Ellis, 1986). Adsorption to the soil solid phase is stronger at slightly acidic pH values from 5.5 to 6.5. (WHO, 2002). Bower and Hatcher (1967) concluded that F adsorption occurs primarily by exchange with OH groups from $Al(OH)_3$ and basic Al polymers adsorbed on mineral surfaces, rather than by exchange with crystal lattice OH groups of clay minerals. This indicates that adsorption of F^- released only a fraction of OH^- from the mineral phase, discounting ligand exchange as an important F binding mechanism (Wehr, 2014). At low concentrations, iron and aluminum oxides and hydroxides have the greatest ability to adsorb F and, among the layer-lattice clay minerals, kaolinite and halloysite have the greatest capacity for adsorption (Bower and Hatcher 1967; Omueti and Jones 1977).

4. Fluorides on plants

Many investigations have been conducted on the effects of fluorides such as hydrogen fluoride on a wide variety of plants. A classified bibliography of the early publications concerning the' effects of fluorides on plant and other forms of life was prepared by Campbell (1950). A review of the literature relating to gas damage to plants was prepared by Thomas (1951, 1955). The effects of fluorine compounds on plants have been summarized by Daines et al. (1952), Griffin and Bayles (1952), Miller (1952), and Zimmerman (1952).

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 (Fig. 2). Some plants accumulate F and even at higher concentration up to 4,000 μg g^{-1} F do not show sign of toxicity (Jacobson et al., 1966; Sheldrake et al., 1978) but most other plants show sign of toxicity at much lower concentration less than 20 μg g^{-1} (Brewer, 1966a; Jacobson et al., 1966; Istas and Alaerts, 1974). Many plants are sensitive to fluoride. To most plants, fluoride (F) is phytotoxic through altering a series of metabolic pathways (Elloumi et al., 2005). Fluoride negatively affects germination, growth, reproduction, yield of crops, respiration, the metabolism of amino acids and proteins, and photosynthesis by acting on the membranes and the stromal enzymes associated with carbon dioxide fixation and resulting in lowered chlorophyll concentrations (Garrec et al., 1981). Fluoride often inhibits enzymes that require such cofactors as Ca^{2+}, Mg^{2+}, and Mn^{2+} ions. (Panda, 2015). Seeds and seedlings appear to be potentially more susceptible to fluorides than whole plants. The excess accumulation of fluorides in vegetation leads to visible leaf injury, damage to fruits, changes in the yield (Ando, 1998). As observed by Mezghani et al. (2005) the leaf concentration of F varied from 30 μg/g dry weight in the rosebush to 420 μg/g dry weight in the olive tree ($p < 0.05$). On the other hand, large increases in the foliar F concentration during the exposure periods were detected each month in all species, increasing significantly from May through October. However, the plants in the control area 30 km SW of the pollution source did not show significant changes in their levels of foliar F as shown in Fig. 3.

Fig. 2. Leaf spots due to fluorine toxicity (Neil Bell, 2009).

The onset of symptoms observed in plants following exposure to hydrogen fluoride depends upon a number of factors such as the concentration, time of exposure, type and age of plant, temperature, type of light and intensity, composition of the air, and its rate of circulation. The exposure of sensitive green plants to elevated concentrations of the gas for an appropriate time interval under controlled environmental conditions may produce one or more of the following manifestations: slight paling of normal green pigment at the tips or margins of the leaves which may spread to other portions of the leaf, a pale green area at the margins which may gradually turn into a light buff color and finally a reddish brown. Varying degrees of injury to leaf tissues may occur until the entire leaf is affected and it falls from the plant. Vital plant processes such as respiration and photosynthesis may be influenced. Marked differences in the ability of plants to absorb and tolerate fluorides have been observed by different investigators (Greenwood, 1956).

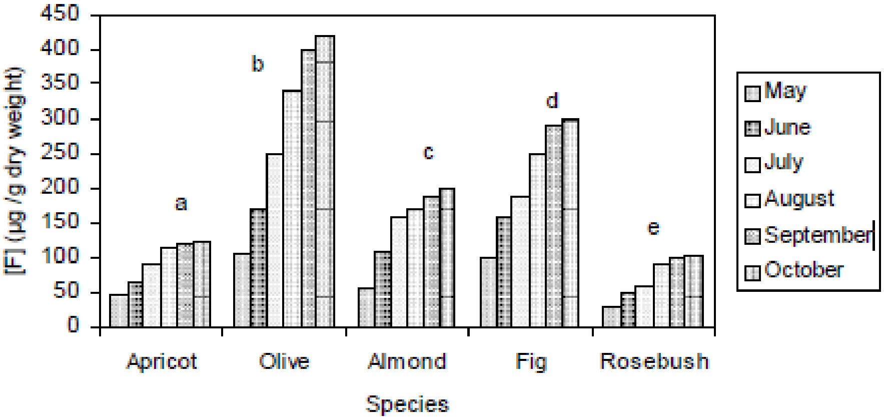

Fig. 3. Foliar F content of cultivated species growing 1 km SW of the fertilizer plant during the year 2000. Means with different letters reflect significant differences (p = 0.05) using the Tukey test.

The symptoms of fluoride toxicity in plants are necrotic regions, especially at the tips and along margins of leaves. Some plants that are more susceptible to fluoride toxicity are monocots, including spider plant, lilies, spikes and dracaena. Furthermore, some of these crops also have long cropping times and therefore will be irrigated with fluorinated water by growers for months, increasing the risk of developing fluoride toxicity (Wollaeger, 2015; Krupa, 2001). In most plant species there was a rapid translocation of absorbed fluoride to the tips or margins of the leaves, where toxic concentrations accumulated, causing necrotic areas. Photosynthesis was reduced by the extent of the injured areas, but the green portions of the leaf remained fully functional. The range of "sub-lethal" concentrations with different species was marked. Recovery from this inhibition of photosynthesis was relatively slow. The exact mechanism of injury to plants by fluorides is unknown. It has been postulated that they interfere with the functioning of certain enzymes such as enolase and phosphatases (Greenwood, 1956).

Fluoride is an accumulative poison in plant foliage. When fluoride has entered the plants and is dissolved in the water, it is transported via the vascular tissue to the leaf edges where it is accumulated (Threshow, 1970). Thus, fluoride absorbed is translocated to the shoots, causing physiological, biochemical and structural damage and even cell death depending on the concentration in the cell sap (Miller, 1993). Histochemical studies of fluoride-injured plants have indicated that the damage to leaves first occurs in the spongy mesophyll and lower epidermis followed by distortion and disruption of chloroplast in the palisade cells. The upper epidermis is last to exhibit any distortion or collapse (Panda, 2015). The fluoride may affect the early stages or pigment synthesis or induce the degradation of chloroplast structure (Kumar et al., 2013). The concentrations at the leaf tips can thus reach quite high concentrations why the first signs of fluoride toxicity are often observed at the leaf edges (Threshow, 1970). Fluoride strongly inhibits photosynthesis and other processes. Some of the visible evidences of toxic effects of fluorides to plants are necrosis and chlorosis (Landis et al., 2011). Chlorosis is related to the plants partial failure to produce chlorophyll due to lack of nutrition or pathogenic attacks. Due to reduced chlorophyll content chlorosis leads to yellowing of the attacked plant tissue. Necrosis occurs when plant tissue start to die (Landis et al., 2011). Both necrosis and chlorosis eventually lead to plant death. Kumar et al. (2013) studied that the concentration of ‘F’ ions in 200 mg kg^{-1} reduced chlorophyll content in green leaves of wheat which caused chlorosis and necrosis. Jha (2009) reported that the visible symptoms of F toxicity in terms of tip burning and death of the plant was noticed in highly contaminated soils with 400 mg kg^{-1} or greater of NaF in soil.

Fluoride reduces germination by lowering the enzymatic activity and growth by slow the rate of cellular division and expansion (Chang and Thompson, 1966). During germination, phytin is broken down by the activity of the enzyme phytase to supply the young seedling with inorganic phosphate. Fluoride is known to prevent the dephosphorylation of phytin compound in the tissues by inhibiting phytase enzyme and retards the rate of seedling root growth during germination. Limited supply of phytin may possibly be one of the factors which inhibit the growth rate of fluoride treated seedlings (Chang, 1967). Holub and Navara (1966) found that a culture solution of only 100 mg kg^{-1}, fluoride caused total inhibition of germination of *Pisum sativum* (pea) seeds and Purohit and Sharma (1985) reported germination inhibition of *Brassica campestris* (field cabbage) by only 2.5 mg kg^{-1}.

Fluoride causes reduction in root length and shoot length due to unbalanced nutrient uptake by seedlings in presence of fluoride (Sabal et al., 2006). Mondal and George (2015) studied that shoot length decreased gradually with increasing the F concentration and that maximum reduction of root biomass uo to 82.5 % at the fluoride dose 95 mg NaF kg-1 soil. Similar results was demonstrated by Pant et al. (2008) for wheat (*Triticum aestivum*), Bengal gram (*Cicer arietinum* L.), mustard (*Brassica juncea*) and tomato (*Lycopersicon esculentum*). Saini et al. (2008) also reported that both root and shoot growth decreased with increasing accumulation of NaF for *Prosopis juliflora*. Agarwal and Chauhan (2014) reported that there were the necrosis and chlorosis in the plant, reduction in growth of shoot and root and ultimately reduced the yield of *Triticum aestivum* var. due to this high concentration of fluoride.

Fresh weight, dry weight and percent of seedlings decreased monotonically with increasing fluoride concentration due to reduction of metabolic activity in presence of fluoride (Gupta et al., 2009). Maize and chilli are more sensitive to fluoride contamination than other crops such as tomato, mung, mustard, ladies finger). Bustingorri et al. (2015) reported that yield loss of soybean reached 30% at F levels 375 mg kg^{-1} or greater. Singh et al. (1979) studied that increasing F above 50 mg L^{-1} decreased the yield of rice. Among crops, vegetables and fruits normally contain fluoride though at low concentration between 0.1 and 0.4 mg kg^{-1} while Higher levels up to 2 mg kg^{-1} of fluoride have been found in cereals (Jolly et al., 1974).

Total soluble sugar and proline content in leaves initially decreased but increased with increasing fluoride concentration because there was gradual accumulation of proline during the germination period, with increasing fluoride concentration due to fresh synthesis or breakdown of proline rich proteins during stress. This might have contributed towards increase in the level of sugar and proline content for enhancing the tolerance capacity of plant under stress condition (Yang and Miller, 1963; Greenway and Munns, 1980). Yu (1996) reported that total soluble sugars of mung bean (Vigna *radiata*) seedlings and, particularly, reducing sugars, decreased with increase in F concentration. Elloumi et al. (2005) reported that the chlorophyll, calcium, magnesium, starch and sugar content of the leaves showed a significant decrease. In case of protein content in leaves of seedlings showed gradual decrease with increasing fluoride concentration due to stress condition which was formed under fluoride treatment (Singh et al.,1985).

Summary

Fluoride is 13th most abundant element of the earth crust and represents about 0.3 g/kg of earth's crust, mainly found as sodium fluoride or hydrogen fluoride which are present in minerals fluorspar, fluorapatite, topaz and cryolite. The F content of soils which is inherited from parent material to through atmospheric pollution and phosphatise fertilizers including industrial deposit shows relatively close positive relationship in slow increase of fluoride concentrations in topsoil. The onset of symptoms following exposure to fluoride depends on a number of factors such as the concentration, time of exposure, type and age of plant, temperature, type of light and intensity, composition of the air, and its rate of circulation. Exposure of sensitive green plants to elevated concentrations of F for appropriate time intervals under controlled environmental conditions may produce one or more of the following: slight paling of the normal green pigment at the tips or margins of leaves which may spread to other parts of the leaf, a pale green area at the margins may tum into a light buff color, and finally a reddish brown sometimes called leaf scorch. A correct positive diagnosis of injury to plants by fluorides requires that a complete history of the plants and their environment be known and adequate chemical tests for fluorides in the atmosphere, soil, water, and plant tissues reveal the presence of toxic amounts of the element. Still, data on the critical soil F concentration affecting soil biota and plant growth is scarce and inconclusive. Additional information is required for adequate recommendations to mitigate the risks of increasing F levels in soils that are sustainable in the future.

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