Diagnosing Vegetation Injury Caused By Air Pollution

ASA

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Chapter 5

FLUORIDES

Introduction

Fluorine is a relatively common and abundant element of the earth's crust. It is present in soils as fluoride, and in minerals, such as fluorspar, biotite, apatite, hornblende, and muscovite. In one ton of soil, on the average, there is about four-tenths of a pound of fluoride or 190 parts per million (ppm). It has been estimated that about 30 million tons of soil enter the atmosphere of the United States each year and this is equivalent to about 6,000 tons of fluoride per year as the rate of emission for one natural source. By comparison, it was estimated that industrial emissions in the United States totaled 119,000 tons of fluoride for 1968.

Atmospheric fluoride had adverse effects on agriculture as a natural pollutant long before it became a man-made one. Air-borne fluoride sometimes affected agriculture adversely without directly affecting plants. Livestock in parts of North Africa developed an illness called "darmous" when prevailing winds carried a relatively fluoride-rich fluoroapatite dust onto vegetation. This illness was due to fluorosis that occurred when the vegetation was consumed by the animals. Volcanoes and fumaroles are another natural source of gaseous and particulate atmospheric fluoride. Roholm has written, "In the Icelandic literature from round about the year 1000 up to recent times we find accounts of how the domestic animals turned sick and died when there were volcanic eruptions . . . the disease attacked animals which ate the grass contaminated with the fallen ash, which means sheep especially, as cattle and horses were kept stabled as much as possible and so escaped [illness] . . ."

It is not known exactly when man's activities first generated atmospheric fluoride to the extent that it adversely and directly affected plants. Reports of fluoride-induced injury to vegetation began to appear in the late 19th century with the advent of certain industrial processes and became more frequent as new processes developed and others expanded. In general, man's activities can be viewed as gradually augmenting and changing the natural rates at which fluoride is transferred among earth, air, water, and organisms; a composite picture of environmental fluoride is given in Figure 5-1.

Sources

Atmospheric fluoride reaches the plant in the form of a gas, particulate matter, or gaseous fluoride adsorbed to particles. The most phytotoxic and best studied form of atmospheric fluoride is gaseous hydrogen fluoride (HF). Al-

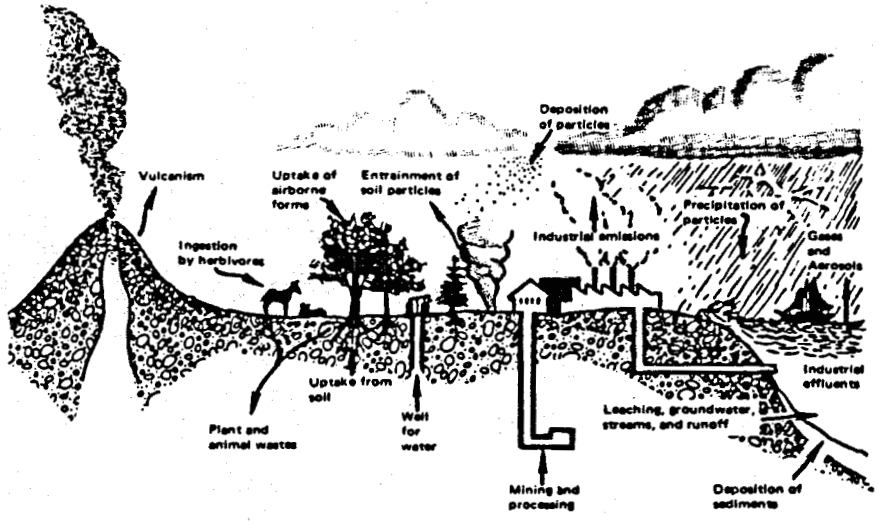

Figure 5-1. *Composite Picture of Environmental Fluoride*

Source: *Fluorides.* Washington, D.C.: Committee on Biological Effects of Atmospheric Pollutants, National Academy of Sciences, Publication ISBN O-309-01922-2, 1971.

though silicon tetrafluoride (SiF_4) may be evolved, atmospheric reactions probably convert it to HF before it reaches the plant. The particulate forms of fluoride have not been so extensively studied as the gaseous forms with respect to their effects on plants. In general, they exist as salts and their toxicity may be determined by the characteristics of the particles and the environmental conditions that affect their collection and retention by foliage and the subsequent penetration of fluoride into the foliar tissue. However, when forage crops or vegetation that is eaten by wildlife is of concern, the presence of particulate material on the foliage must also be considered.

Any process that utilizes fluorine-containing material can be a potential source of atmospheric fluoride. Fluorides may be emitted when fluorine-containing material is ground, crushed, or pulverized; treated with strong acids; heated; or used in some process in a gaseous or volatile form. The magnitude of the source depends upon the kind of process, kind of material, volume of material processed, and degree of emission control. An estimate of the quantities of fluorides emitted by different industries is given in Table 5-1.

The emission of fluorides can result from the manufacture of phosphate fertilizers and feeds, phosphoric acid, or elemental phosphorus. The phosphate rock used as a raw material in these industries contains 3 to 4% fluorine. Dust can be produced in the grinding and drying of the rock, and gaseous fluoride can be produced (as HF or SiF_4) when the rock is treated with sulfuric acid to produce phosphates or is heated in electric furnaces for the production of elemental phosphorus. The ponds that contain waste process water may also be significant sources of atmospheric fluoride.

Table 5-1

Estimated Total Fluoride Emissions from Major Industrial Sources in the United States in 1968

Source	*Atmospheric Emissions, tons/year*
Manufacture of brick and tile products	18,500
Manufacture of steel (open-hearth furnace)	16,800
Manufacture of aluminum	16,000
Combustion of coal	16,000
Manufacture of steel (electric furnace)	14,900
Manufacture of normal superphosphate fertilizer	9,700
Manufacture of steel (basic-oxygen furnace)	8,400
Manufacture of elemental phosphorus	5,500
Nonferrous-metal foundries	4,000
Manufacture of wet-process phosphoric acid	3,000
Manufacture of glass and frit	2,700
Welding operations	2,700
Manufacture of triple superphosphate fertilizer	300
Manufacture of diammonium phosphate fertilizer	100
Manufacture of phosphate animal feed	100
TOTAL	118,700

Source:
Fluorides. Washington, D.C.: Committee on Biological Effects of Atmospheric Pollutants, National Academy of Sciences, Publication ISBN O-309-01922-2, 1971.

In the manufacture of aluminum, alumina is dissolved in molten cryolite and reduced electrolytically. Both cryolite and fluorite, which is also present in the process, contain fluoride, and in the electrolyte cell fluorine is evolved in gases such as hydrogen fluoride, or as particulate matter such as fluoride salts. In steel-making, fluorspar is used as a flux from which hydrogen fluoride may be generated. The combustion of coal can be another source of atmospheric fluoride because coal contains an average of 0.008% fluoride. The clays used for the manufacture of bricks, pottery, and cement contains fluorine, and gaseous fluorides may be emitted from the kilns. In the manufacture of glass and enamel, fluoride-containing materials that are heated evolve gaseous and particulate fluorides. Other sources of fluorides are industries that produce hydrogen fluoride and those that use it for petroleum refining or the production of fluoro-carbons.

Atmospheric Chemistry

There is no general set of concentrations that can be expected for all fluoride sources. The extent and magnitude of atmospheric concentrations over the area affected will depend upon the rate of emissions. Most major sources are char-

acterized by a relatively constant rate of emission. Therefore, pattern of dispersion, in time and space, will be determined by the combination of source, topography, and meteorology. Diurnal and seasonal fluctuations can be expected to follow the changes in those climatic and meteorological factors that determine dispersion. Occasional high concentrations (relative to the mean or median) may occur due to failure of controls, accidental spills, or unusual meteorological conditions.

Monitoring Data

In contrast to the better studied urban and industrial air pollutants – photochemical oxidants and sulfur dioxide – there is no extensive compilation of ambient levels of atmospheric fluoride. The lower limit of detection may range from 0.01 to 0.05 $\mu g/m^3$ (about .012 to .06 ppb)* in a 24-hour sample depending upon the methods used. The lower limits for shorter sampling periods are higher.

The analysis of more than 7,700 air samples for total water-soluble fluoride by the National Air Pollution Control Administration over the years 1966 and 1967 showed that 97% of the samples from non-urban areas had no detectable fluoride. The highest concentration was 0.16 $\mu g/m^3$ (.195 ppb). In urban areas the corresponding values were 87% and 1.89 $\mu g/m^3$ (2.306 ppb). In the heavily industrialized Ruhr area of Germany, samples in the city of Duisburg during 1965 and 1966 showed a mean of 1.3 $\mu g/m^3$ (1.586 ppb).

Symptomatology

The HF-induced symptoms that appear on the foliage of plants result from a series of complex events: the interaction of fluoride and metabolic processes in the leaf and the action of environmental factors upon it. Some general aspects of symptom development will be considered here so that the symptoms and their variations can be more easily described and understood. Specific guidelines for diagnosing fluoride-induced symptoms are presented in Chapter 10.

Of what do symptoms consist? First, there is a change in the color of a portion of the leaf due to a loss of chlorophyll in the affected area. When the amount of this pigment is reduced, the yellow pigments that remain are unmasked and a condition of chlorosis, which may range from a slight paling of the green to an appearance of a yellow color in the affected area, appears. Second, a color change may be due to death of the tissue and the formation of brown pigments as the affected area dies. To a certain extent, the coloration of this necrotic area depends upon the species and how rapidly the necrosis develops. Third, symptoms may consist of deformation as well as discoloration of the foliage. These deformations occur usually on broad-leaved plants as a result of

*ppb = parts per billion, in which "billion" means "thousand-million" or 10^9 and not 10^{12} as in British and German usage. American and French usage agree however. See Appendix A for methods of conversion between ppm and $\mu g/m^3$. One ppb is 10^{-3} ppm. Atmospheric concentrations for HF use ppb to avoid awkward numbers. The unit ppb refers only to atmospheric concentration and is v/v.

necrosis which occurs as the leaf is expanding. The tip of the leaf may become necrotic and the rest of the leaf may become cupped as it expands, or the tissue between the veins may expand more rapidly than the veins, giving the leaf a savoyed appearance. Sometimes the edges of the leaf take on a ragged appearance owing to the loss of necrotic marginal tissue.

Where do symptoms occur? The distribution of the affected areas, or lesions, on the leaf is usually determined by two factors: (1) the species of plant, which determines the morphology of the leaf; (2) the severity of the exposure, which determines the response of the leaf. Of these two factors, species as related to leaf morphology is probably the more important. Generally, the lesions induced by fluoride appear first or are more intense in the apical and marginal areas of the leaf. Young expanding leaves are most likely to be injured by an exposure. Exceptions to these generalizations occur and will be discussed later.

How does fluoride produce these symptoms? The mode of action of fluoride is imperfectly understood, but fluoride is known to act as an inhibitor of plant metabolism. As fluoride accumulates in the leaf, it causes an increased inhibition of metabolism, and chlorosis appears as the first visible sign of this metabolic disruption. With further increases in the concentration of fluoride in the tissue, the cells die and necrosis is observed. When the leaf is exposed to relatively high concentrations of HF for short periods of time, local concentrations of fluoride in the leaf may rapidly exceed the toxic threshold, and irregular patches of necrosis may occur in the intercostal areas. But more often, the leaf is exposed over a longer period of time, constantly or periodically, to relatively low concentrations. Under these conditions, the fluoride absorbed by the leaf is translocated to and accumulates in the apical or marginal tissues where the more characteristic symptoms of fluoride toxicity appear.

The short-term, high-level and the long-term, low-level exposures are commonly referred to as acute and chronic, respectively. Whereas acute exposures usually produce necrotic lesions, chronic exposures may produce either necrosis or chlorosis depending upon the species and tolerance of the plant. Therefore, it matters not so much whether a symptom be classified as acute or chronic but what the severity of the symptom, its distribution on the plant, and its occurrence on different species tell about the kind of exposure that has occurred.

Broad-leaved Plants

Within this group of plants, symptoms consist of chlorosis of varying intensity, or necrosis, or both. The affected areas are initially located at the tips or margins of leaves and, with increasing severity, extend toward the base of the leaf from the tip or toward the middle of the leaf from the margins.

Citrus. In naval orange, irregular chlorotic patches appear in the intercostal areas of the leaf near the margin and tip. With prolonged exposure, these patches extend further towards the midrib and base and increase in intensity until the midrib and venation appear as a green-arborescent figure on a pale chlorotic field (sometimes called the "Christmas tree" pattern of chlorosis). Necrosis occurs principally at the tips of nearly mature leaves with a chlorosis and mottling which affect the remaining portion but decrease in intensity toward the base of

the leaf. In lemon, chlorosis develops also along the margins and tips of leaves and with increasing severity involves the intercostal areas to give the "Christmas tree" pattern of chlorosis. In grapefruit, symptoms may first appear as irregular, ill-defined chlorotic blotches in the intercostal areas or as a thin marginal area of chlorosis. With increasing severity the marginal and interveinal chlorosis intensifies and the affected areas merge (Plate 5-1). This pattern is most common on older leaves.

Some of the chlorotic and necrotic symptoms of citrus foliage resemble injury from excessive boron, but a gumming of the undersurface of the leaf is found when boron toxicity is responsible. The "Christmas tree" pattern of chlorosis also resembles that induced by manganese deficiency.

Other fruit crops. On grape (European) necrosis may appear along the margins of the leaf and extend irregularly into the intercostal areas, with some zonation or banding of the necrotic areas.

On blueberry (Plate 5-2) necrosis of the apical and marginal portions of the leaf can develop under chronic exposure. With low bush blueberry, a reddening of the tip and apical margins of the leaf can precede the development of necrosis in chronic exposures. However, this reddening can also be induced by other conditions.

Apple leaves show a very dark-reddish brown coloration at the tip and margin of the leaf with very little necrotic flecking of the interveinal areas. Grape leaves (Plate 5-3) show necrosis of both the marginal and intercostal tissues after more acute exposure. Injured areas are initially dull or pale green, then change to buff or light tan with death and desiccation. Frequently, these dry, brittle portions fall away from the uninjured portion of the leaf, leaving an irregular margin. Prune foliage shows about the same pattern of injury as apricot, but the necrotic areas may be colored a much darker brown. If recurrent injuries occur, the necrotic areas show zonation or bands of darker necrotic tissue within the paler necrotic areas. On peach and sour cherry foliage, necrosis in trace amounts will appear at the tip of the leaf. The damaged area may fall from the leaf leaving a notched leaf tip. If this kind of injury occurs before the leaf has completed expansion, a cupping of the leaf may occur. On the foliage of apple, sour cherry, and peach, chlorosis may appear on the tips and margins of the leaf after chronic exposures. Intensification of this symptom results in more pronounced chlorosis and an expansion of the chlorosis into the intercostal areas.

As with citrus, certain nutrient deficiencies, such as zinc or manganese, can also induce the "Christmas tree" pattern typical of chlorosis. Low temperature and drought injury, oil sprays, and virus diseases can induce fluoride-like symptoms.

Other Deciduous Trees and Shrubs. The range of symptoms seen on deciduous trees follows the same patterns seen on other broad-leaved plants (Plate 5-4). Acute exposures may cause necrosis of the tips and margins and sometimes of intercostal areas of leaves with irregular but distinct demarcation between dead and live tissue. Chronic exposure will tend to cause chlorosis, first of the tips or serrations, then of the apical and marginal areas, and finally of the intercostal areas. The venation of damaged intercostal tissue is a darker green than the

laminar tissue. Sometimes chronic injury may appear only as a necrosis of the tips of lanceolate leaves or tips of lobes of palmate leaves, such as maple. On some species, such as poplar, intercostal chlorosis may accompany marginal necrosis.

To the same extent as with other groups of plants, the kind of exposure, kind of leaf, and tolerance of the plant will determine the kinds of symptoms. Moreover, natural or other kinds of stresses can induce symptoms that mimic those induced by atmospheric fluoride (Plate 5-5).

Herbaceous Weeds. St. John's wort is one of the more ubiquitous and sensitive species of herbaceous weed. Fluoride-induced injury appears on it as a red-brown necrosis of the apical portion of the leaf. Chronic exposure produces a light-green flecking and then chlorosis on the younger, expanding leaves of lamb's-quarters (Plate 5-6). More intense symptoms appear as an increase in the intensity of chlorosis, chlorosis of the intercostal areas, and a cupping and puckering of the leaves.

In chronic exposures, chlorosis develops at the tips and margins of the expanding leaves of night-shade, knotweed, mares tail, and crab grass. When necrosis of leaf tips occurs, relatively little chlorosis precedes it. Pigweed, smartweed, ragweed, golden rod, and oxalis also show these kinds of symptoms. In acute exposures, apical markings are more common on chickweed, nettle-leaf goosefoot, and blue grass; marginal markings are more common on mustard, sunflower, dandelion, and cheeseweed; and both kinds of markings appear on pigweed.

Narrow-leaved Plants

There is probably no single type of symptom that would apply to all monocots, but there are certain kinds of symptoms that are typical for many species.

Grains and Cane. Sweet corn is a reasonably ubiquitous and sensitive indicator of atmospheric fluoride, although sensitivity depends upon the cultivar (Plate 5-7). Fluoride-induced symptoms usually can be distinguished from those caused by disease, insect injury, mineral deficiencies, or other pollutants by appearance, pattern, and development. At the lowest exposures that produce symptoms, there are scattered chlorotic flecks or stipples near the tip of the leaf and along the apical margins of the leaf. With an increase in exposure, the area affected by stippling extends down toward the base of the leaf along the margins and inward on the leaf toward the midrib. The intensity of the stipple diminishes toward the basal or medial areas of the leaf. Also, with an increase in severity, the stippling along the apical margins will increase and coalesce to give a chlorotic band of tissue at the tip and along the margins. As with the stipple, this band of chlorosis decreases in width toward the base of the leaf. With a further increase in severity, necrosis appears at the tip and then spreads along the margins of the leaf toward the base and inward toward the midrib.

The symptoms produced by fluoride in milo maize (sorghum) are similar to those of corn. The effect starts at the tip and the immediately adjacent margins of the leaf. As the effect increases, the affected area enlarges by an extension of

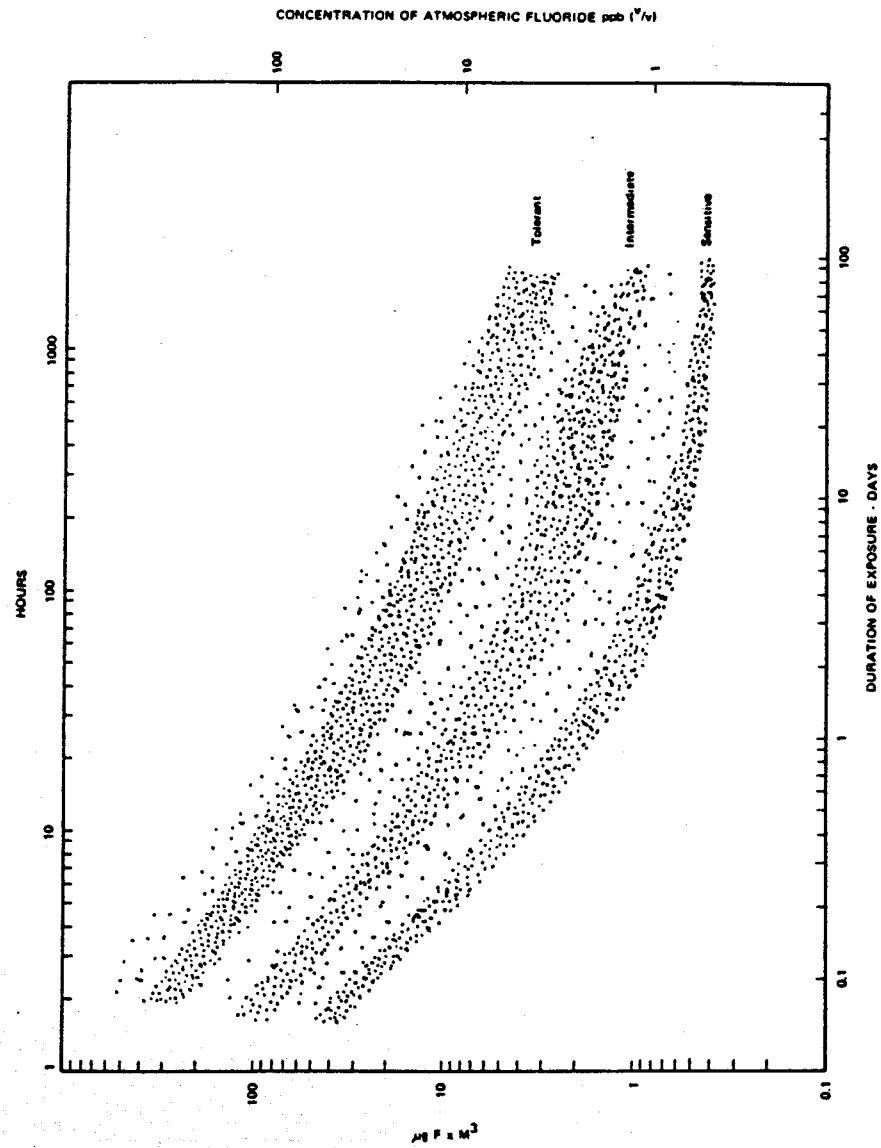

Figure 5-2. *The Relationship of Concentration of Atmospheric Fluoride (Vertical Axis) and Duration of Exposure (Horizontal Axis) to the Threshold for Foliar Symptoms for Sensitive, Intermediate, and Tolerant Species of Plants*

Table 5-2

Relative Sensitivity of Various Plants to F

Flowering Shrubs and Ornamental Plants

Sensitive	*Intermediate*	*Tolerant*
Gladiolus	Azalea	Mock-orange
Jerusalem cherry	Rose	Bridalwreath
Tulip	Narcissus	Firethorn
Iris	Dahlia	Chrysanthemum
	Lilac	Camellia
	Rhododendron	Petunia
	Aster	Privet
	Violet	
	Geranium	
	Peony	
	Sweet William	
	Flowering cherry	
	Flowering plum	
	Jerusalem cherry	

Weeds

Sensitive	*Intermediate*	*Tolerant*
St. John's Wort	Johnson grass	Burdock
Crabgrass	Nettle-leaf goosefoot	Nightshade
Smartweed	Goldenrod	Dock
Chickweed	Sunflower	Plantain
Lamb's quarters		Purslane
Pigweed		
Johnson grass		

Conifers

Sensitive	*Intermediate*	*Tolerant*
Pine, Ponderosa, Scotch (young needles)	Grand fir	Pine, Lodgepole, Mugo (mature needles)
Western larch	White spruce (young needles)	Arborvitae
Douglas fir	Spreading Japanese yew	Juniper
Blue spruce		

Broad-leaved Trees and Shrubs

Sensitive	*Intermediate*	*Tolerant*
Oregon grape	Serviceberry	Sycamore
Boxelder	Quaking aspen	American linden
Serviceberry	Red mulberry	Currant
	Black walnut	London planetree
	English walnut	Sweetgum
	European mountain ash	Birch, white
	Silver maple	Birch, cutleaf
	Common chokecherry	Mountain laurel
		Dogwood