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AIR POLLUTION IMPACTS ON FOREST TREES: EFFECTS OF FLUORIDES

Abstract. Gaseous fluorides, in the form of hydrofluoric acid (HF) or hydrofluorsilicic acid (H_2SiF_4), have injured trees in forests, fruit orchards, and ornamental plantings in many countries of the world. These injuries can lead to reductions in the value and function of trees in forestry, horticulture, arboriculture, and ecology. Fluorides are among the most phytotoxic air pollutants and an important cause of this toxicity may be the reduction in availability of calcium or magnesium for physiological processes. Several procedures are used to identify injury to vegetation by fluorides and to determine the area affected. Harmful effects on the use and function of trees can be avoided by judicious siting of fluoride sources, minimizing fluoride emissions, and planting plant species that are resistant to injury.

Key words: air pollution, forest trees, fluorides.

Introduction

The pattern of air pollution effects on vegetation has undergone a change in the USA during the last several decades. Originally, site-specific pollutants (fluorides, sulfur oxides, heavy metals) were the most serious problem and identification of effects of these pollutants was relatively simple. The area affected was usually well-defined, near isolated emission sources, and the effects on vegetation were acute and obvious within hours or days after an air pollution episode occurred. Improved emission controls have reduced the frequency and severity of these problems, but they still occur at specific locations. Presently, air pollutants such as ozone and acidic rain, which are regional and international in scope, are the most serious on a nationwide basis. Their effects on the environment are more difficult to assess because they are cumulative and subtle. The occurrence of long-range transported pollutants also raises the possibility of interactions between ozone and acidic rain and the effects of localized pollutant emissions. This paper deals with the impact of site-specific pollutants, atmospheric fluorides, one of the earliest pollutants to be recognized as phytotoxic (Polomski et al., 1982).

Fluorides have special importance in air pollution for several reasons. Although the element fluorine is naturally present in ample quantities in soils, the background level in vegetation is quite low. Atmospheric fluorides are usually avidly accumulated by vegetation, and they are highly reactive and potent toxicants for certain metabolic reactions. Finally, fluorides are readily transmitted through the food chain from organisms that may not be susceptible to organisms that may be highly susceptible to injury. Although the distribution of atmospheric fluorides is usually localized, the impact can be severe and persistent even after emissions have been reduced.

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Form and Sources of Atmospheric Fluorides

The most important toxic forms of atmospheric fluorides are hydrofluoric and hydrofluorsilicic acids (HF and H_2SiF_4). Fluorine gas (F_2) also is highly toxic, but it is rarely emitted to the atmosphere and reacts to form HF with moisture. Fluorides in particulate matter may be toxic, especially if they are water-soluble, but their toxicity to vegetation is usually considerably less than that of the aforementioned gaseous fluorides (Fluorides, 1971).

There are many natural sources of fluorides in the environment including the lithosphere (average of 0.07% fluorine in upper layers of rock), soils (up to several thousand micrograms fluoride per gram), natural waters (up to 20 micrograms fluoride per milliliter or more), and emissions from volcanoes. Fluorides from industrial sources are emitted during the production of aluminum, fertilizers, phosphorous and phosphoric acids, steel, brick and tile, glass, and electricity from the combustion of coal. Frequently, other pollutants are emitted simultaneously with fluorides such as sulfur dioxide, nitrogen oxides, and/or particulate matter containing heavy metals. Fluorides accumulate in soils and, if deposition of fluorides to soils is sufficiently great, important chemical and biological processes may be altered (McGlenahen, 1976; Polomski et al., 1982; Sidhu, 1979; Temple et al., 1978; Thompson et al., 1979).

Effects of Fluorides on Trees

Fluorides have decreased the productivity of forests and orchards and altered the ecological functions of native trees in many parts of the world (Amundson and Weinstein, 1980; Bunce, 1979; Guderian, 1977; MacLean, 1982; Weinstein and Bunce, 1982). Many coniferous and fruit trees are susceptible to fluorides whereas the majority of broad-leaved deciduous trees and shrubs appear to be relatively tolerant, at least for those species that have been tested. There are particularly susceptible species within the following genera: *Larix*, *Picea*, *Pinus*, and *Prunus*. Susceptibility has been evaluated according to the development of foliar symptoms. Other criteria, interference with physiological processes, growth, or productivity for example, may give different interpretations of susceptibility to fluorides. Furthermore, biological and environmental factors along with pollutant characteristics influence the susceptibility of trees to fluorides. Consequently, injury will not necessarily be the same from year to year or from location to location even when fluoride concentrations in the atmosphere are similar. Factors controlling response to fluorides include: genetic characteristics; age and stage of development; rates of accumulation, distribution, and loss of fluoride from vegetative tissues; light intensity and photoperiod; soil moisture and nutrient supply; temperature, humidity, and wind speed; and the presence of pathogens, insects, and other air or soil pollutants (Amundson and Weinstein, 1980; Bunce, 1979; Guderian, 1977; MacLean, 1982; Weinstein and Bunce, 1982).

The foliage of trees accumulates fluorides obtained both from the soil and from the atmosphere (Davison, 1982; Garrec et al., 1977; Sidhu, 1979; Treshow et al., 1967). A few species are avid accumulators of fluorides from the soil, and many species rapidly accumulate fluorides from the atmosphere. Rates of accumulation are dependent on the physical form, chemical properties, and concentrations of atmospheric fluoride; characteristics of the foliage and forest canopy; and meteorological conditions. The fluoride content of vegetation is determined by rates of removal and accumulation. Abscission of leaves, ingestion by herbivorous insects and mammals, weathering of leaf surfaces, and leaching by rain will remove fluorides from trees. Volatilization of fluorides from vegetation also may occur but it has not been proven conclusively. Once fluorides have accumulated in foliage, they do not seem to be readily redistributed to new leaves or other portions of the plant.

Exposure to persistent or recurring fluoride concentrations in the range of 1 $\mu g/m^3$ or more may result in substantial accumulation of fluoride in foliage. Injury to leaves may occur for the more susceptible species, and injury, discoloration, and morphological abnormalities may also occur with fruits such as peaches, cherries, apricots, plums, and pears (Bonte, 1982). A critical factor is the susceptibility of the foliage and/or fruit at the time of exposure to fluorides (Laurence, 1981).

Fluorides influence all levels of biological organization from the cell to the ecosystem as do other air pollutants (Amundson and Weinstein, 1980; Ares, 1978; Guderian, 1977; Guderian and Kueppers, 1980; Weinstein and Alscher-Herman, 1982). At the subcellular level, rates of enzyme reactions are altered, levels of metabolites are changed, and membranes and organelles may be disrupted. At the organ level, rates of photosynthesis and respiration may be altered, lesions may occur, growth and development may be delayed, and leaves may abscise. At the level of the whole organism, growth and development may be decreased, senescence may occur prematurely, and reproduction may be affected. At the community level, structure and succession may be altered, species diversity reduced, productivity decreased, and tolerance to environmental stress diminished. Finally, at the ecosystem level, rates of elemental cycling may be changed, fertility and water retention of soil decreased, erosion increased, and meteorological and climatological conditions changed. In addition, herbivores may be affected by the transfer of fluorides through the food chain.

It has been difficult to determine which physiological effects are primary and which are secondary consequences of fluoride pollution in vegetation. However, it appears that calcium and magnesium metabolism are associated with each of the sensitive processes: respiration (oxidative phosphorylation and metabolic pathways); photosynthesis (biosynthesis of pigments, development of chloroplasts, electron transport); transport of nutrients (plasmalemma ATPases, immobilization of calcium); fertilization and fruit development (pollen germination and growth, ovule development, and seed formation); morphogenesis (suture red spot of peaches, misshapen fruit, premature abscission of leaves); seed germination (capacity to germinate); and nucleic acid metabolism (transcription and translation) (Amundson and Weinstein, 1980; Bonte, 1982; Garrec et al., 1977; Horsman and Wellburn, 1976; Weinstein and Alscher-Herman, 1982).

Diagnosis of Fluoride Injury to Trees

Identification of fluoride injury to trees can be very difficult and many techniques have been developed to aid in the recognition of fluoride symptoms (Malhotra and Blauel, 1980; McClenahen and Weidensaul, 1977). Symptoms on foliage or fruit must be carefully observed and described, the affected and unaffected species identified, and the existence of insects and diseases and unusual climatological conditions reported. The geographical area affected is usually mapped and the relationship to known sources of pollutants is determined. Knowledge of prevailing wind and meteorological conditions is useful. The disruption, treatment, or management of land should be known. If chemical analysis of the air is available, information should be compiled on the nature of pollutants, their concentrations, durations, and dates of occurrence. Data on the types and amounts of pollutants emitted to the atmosphere are useful especially when air monitoring information is not available. Chemical analysis of samples of vegetation is particularly valuable when fluorides are suspected. It is necessary to take samples by systematic, prescribed techniques that are appropriate for the circumstances, and to employ standardized, reliable methods for the analysis of fluorides (Jacobson and Weinstein, 1977).

Biological indicators can be helpful in identifying the cause of injury to vegetation and the area affected (Amundson and Weinstein, 1980; Brenner and Skye, 1976; Manning and Feder, 1980; Posthumus, 1976). Plants of known susceptibility to different pollutants that exhibit characteristic symptoms are exposed at different locations and observed for injury. Two types of indicator plants have been used for fluorides. Bulb plants, such as gladiolus and tulip, respond to concentrations of 1 $\mu g/m^3$ or less with obvious discolored lesions on the distal portion of leaves. Certain species of weeds also are highly susceptible and may be used as indicators (Amundson and Weinstein, 1980). Grasses, such as ryegrass, accumulate fluorides rapidly and their tissues can be analyzed to estimate the geographical distribution of fluoride. In cases where facilities and equipment are available, experimental studies can be performed on-site. Exposure of plants to pollutants in chambers is a powerful tool for determining cause and effect relationships in a quantitative manner. Experimental chambers may utilize filtered and unfiltered air or suspected pollutants can be added to the air flowing through chambers where plants are grown.

Each of the procedures that aid diagnosis of a problem has advantages and limitations (Guderian, 1977; McCune et al., 1976; Fluorides, 1971). Foliar symptoms that are similar to those caused by fluorides can be produced by a variety of causes including drought, winter injury, nutrient deficiencies, and diseases. Foliar fluoride content may not correlate well with foliar injury, growth, productivity, or with atmospheric fluoride concentrations. The relationship between susceptibility of bio-indicators and injury to trees is usually not known and these relationships may differ under different growing conditions. Plant growth and productivity can be measured at different distances from an emission source, but relative susceptibility of species may be different under different soil and climatic conditions. Filtration of pollutants from air flowing through an exposure chamber seldom removes only one pollutant and conditions in chambers may alter the growth and susceptibility of vegetation to pollutants.

Prevention and Amelioration of Effects of Fluorides

Damage to forests and orchards can be avoided by careful planning before emission sources are constructed. Correct siting to avoid locations upwind of susceptible species and regions with poor atmospheric dispersion during the growing season are among the most effective ways of avoiding later problems. With existing emission sources, reduction or elimination of pollutant emissions at the source is the most effective cure. Where this procedure is too difficult or expensive, stack heights can be increased to emit pollutants above the inversion layer to avoid ground-level concentrations. Alternatively, emissions can be timed to avoid periods of poor atmospheric dispersion and high tree susceptibility. Improvements in the efficiency of industrial production and use of combinations of control procedures also are useful strategies. Changes at the receptor are usually difficult or impossible with indigenous, unmanaged forests. When land is reclaimed or trees used for their aesthetic or ecological value, species tolerant to fluorides should be planted in areas with known fluoride emissions. Maintenance of optimum plant vigor will help vegetation to recover from injury by fluorides. Protective chemicals have been applied to orchards exposed to fluorides on a limited basis (Guderian, 1977). Application of existing knowledge can offer protection of forests, orchards, and other botanical resources from fluorides but several important research needs still exist.

Research Needs

The susceptibility to fluorides of many species of plants is unknown and primary mechanisms of action of fluorides in vegetation have not been completely clarified. The relationship between the occurrence of foliar symptoms, accumulation of fluoride in vegetative tissues, and reductions in tree growth and productivity is uncertain. There still is controversy over the maximum allowable exposure of vegetation to atmospheric fluorides and the maximum allowable ingestion of fluoride-containing vegetation for grazing animals (Davison, 1982; MacLean, 1982). Recently, research has been summarized on the effects of combinations of fluorides and sulfur dioxide, nitrogen dioxide, and ozone, but the effects of combinations of pollutants need further exploration (McCune, 1981). Field observations suggest that there are relationships between insect infestations and the occurrence of fluorides in forests, but the exact nature of these relationships is unknown (Bunce, 1979; Laurence, 1981; McCune, et al., 1976). The impact of fluorides on the geochemical cycling of elements in ecosystems has not been clarified (Amundson and Weinstein, 1980). However, theoretical considerations suggest that fluorides should have a profound effect on geochemical weathering processes. Experimental research on these problems would be aided by the development of: (a) a reliable, fast-response instrument for the measurement of atmospheric fluorides, (b) more accurate methods for the measurement of fluorides in vegetation, and (c) exposure chamber techniques more closely simulating ambient environmental conditions (McCune et al., 1976).

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