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THE UPTAKE OF HYDROGEN FLUORIDE BY A FOREST*

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ABSTRACT

Murphy, Charles E., Jr. and Ares, Jorge. The uptake of hydrogen fluoride by a forest.

A mathematical model of hydrogen fluoride (HF) deposition and accumulation of fluoride in a *Eucalyptus rostrata* forest has been developed. The model is based on tree physiology and meteorological principles. The data base for the model was derived from a literature survey of the physiological characteristics of *E. rostrata* and similar eucalyptus species and from current knowledge of meteorological processes in plant canopies.

Comparison of the mathematical simulations with measurements in the vicinity of a source of HF (an aluminum reduction plant) shows that (1) the pattern of seasonal fluoride accumulation in leaves agrees with that seen in the field, and (2) the vertical pattern of accumulation inside tree leaves agrees with field observations. The simulations indicate that 50% of the released HF was deposited within 81 km of the source and that the concentration of HF in the air 81 km from the source was reduced to 2% of the concentration 1 km from the source. However, a very large forest area (20,600 km^2) was required to achieve these reductions.

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INTRODUCTION

As a consequence of the combined operation of passive and active ecophysiological processes, plants absorb and incorporate into their structures large amounts of gaseous substances from the atmosphere. Passive processes (those not demanding metabolic energy) include turbulent diffusion in the atmosphere, molecular diffusion near and inside the plant, and solution in the cell protoplasm. Active processes include mediation of diffusion by changes in stomatal aperture, and metabolically mediated chemical absorption of the gas. The transfer of a gaseous substance from the atmosphere to some organic structure within a leaf can be described in terms of a flow which is regulated by concentration gradients and resistances along the flow path (Bennett and Hill, 1973).

Atmospheric pollutants can enter the leaves through the stomata along with other gases. Pollutants can also flow directly through the epidermis and cuticle, or they can be adsorbed on dust on the surface and be leached to the inner tissues of leaves (Ares et al., 1980). When a sufficient amount of a pollutant that has a deleterious action reaches an active metabolic site within a tissue, some damage occurs. The damage can be visible, as in wilting or markings of leaf tissue, or hidden, as in subtle modifications of shape, size, rate of growth, etc.

Studies of the effectiveness of vegetation as a pollutant sorber have necessarily centered on laboratory and some limited field work, under controlled environments (Spedding, 1969; Roberts, 1974; Martin and Barber, 1971). In a number of cases, plants have accumulated large amounts of pollutants without showing any damage, probably because of the accumulation of the pollutant in inactive or even external sites of leaves, such as the cuticle, cell walls, etc. (Weinstein, 1977).

When the absorption of pollutants does not damage the plants, it might be feasible to manipulate the living biomass so as to improve the quality of the air in the vicinity of the canopy. Such.manipulation, which would utilize energy produced by photosynthesis to remove air pollutants, has received increasing attention because of its implications for industrial activities that emit atmospheric pollutants (Bennett and Hill, 1975). Under favorable meteorological conditions, a pine forest can absorb quantities of SO_2 from the atmosphere in quantities comparable to those released by big power plants (Murphy et al., 1977). The absorption of SO_2 by vegetation represents an initial step in a cycle by which sulfur is delivered to various environmental compartments (Shriner and Henderson, 1978). This removal mechanism probably applies to other industrial pollutants, like fluorine (Ares, 1978).

Considerable information is available on uptake of fluoride by vegetation. Plants take up fluorides primarily through the leaves (Ledbetter et al., 1960). Most of the fluoride adsorbed by xerophytic plants is deposited on the external surface of the leaves (Ares et al., 1980). These plants normally have high stomatal resistances. Fluoride is found internally in mesophytic plants, often concentrated near the substomatic chamber (Bligny et al., 1973; Garrec et al., 1974). The fate of fluoride within the leaf has been the subject of a considerable amount of research (Ledbetter et al., loc. cit.; Jacobson et al., 1966; Keller, 1974; Hitchcock et al., 1971; McCune et al., 1976; Ares et al., loc. cit., 1980). Research to date suggests that the mechanism of fluoride uptake and subsequent distribution consists of dissolution in the leaf's aqueous free space from which fluoride is further transported to the mesophyll inner space. While in the aqueous free space, fluoride moves along with the transpirational stream and accumulates near the margin of leaves, because of decreased aerodynamic resistance to water flow at those sites. While in this phase, fluoride is in diffusional equilibrium with fluoride in the atmosphere. Under the conditions prevailing near an emission source, where periods of exposure to high concentrations of airborne fluoride may be followed by periods of exposure to very low concentrations, the possibility that fluoride may flow back from the leaves to the atmosphere cannot be ruled out. This flux is probably small in semi-arid environments, as suggested by the distribution pattern of fluoride within the canopy of xerophytic shrubs (Ares, 1978).

Fluorides can be translocated, usually in small amounts, from the leaves to different organs of the plant. The distribution pattern of fluoride within a plant depends on the entrance site and on the physiological and environmental conditions regulating the transfer of fluoride from the aqueous free space to the inner space. Thus, fluoride absorbed by a leaf can be translocated both to stems and to neighboring leaves, following a pattern that suggests some limited transport through the phloem (Keller, 1974).

The simulation and validation described in this paper was aimed at determining the effectiveness of a forest for absorption of HF released to the atmosphere from a single industrial source. The results obtained during the simulation are compared with field data obtained by sampling an experimental planting of E. rostrata located near an aluminum reduction plant* which started operations in 1974.

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A forest was chosen for evaluation of pollution absorption capacity because the turbulent mixing above and inside forest canopies is greater than for shorter vegetation. This mixing allows the pollutant to reach the absorbing surfaces more efficiently. Furthermore, some types of trees are evergreen, and thus absorb pollutants during the entire year.

An additional characteristic of forests, which may be desirable, is the ability to sequester some of the absorbed fluoride in the non-living wood. The fluoride in the wood is stored for the life of the tree. The wood fluoride could be removed in forests products; but since forest products are not usually eaten, the presence of fluoride in the wood would not normally be a problem. Therefore, absorption and storage of atmospheric fluoride in forests may be a reasonable alternative to control at the source if absorption rates are high enough.

METHODS

Field measurements of fluoride in vegetation

Fluoride levels in the canopy of E. rostrata stands were evaluated by sampling different parts of the trees and analyzing for their fluoride content. Sampling was stratified by levels of 1 m within the canopy and by orientation with respect to the emission source (windward-leeward). The samples from the field were sorted into leaves, terminal branches, and lateral branches. After oven-drying at 70°C, leaf samples were further separated into two subsamples; one was washed with distilled water for one minute and oven-dried, the other was untreated before oven-drying. Fluoride concentrations in leaves and branches were determined by extraction with perchloric acid followed by emf measurements with a fluoride-specific electrode (Villa, 1979).

Leaf area at each height was estimated by clipping combined with visual estimation. Clipped leaves were counted. The leaf area of a subsample was determined with millimeter graph paper. Allometric relations of leaves were determined from a number of samples of 100 leaves each, taken from several trees. To obtain representative samples, both old and young branches were sampled, because this species shows a certain degree of foliar dimorphism with age.

Estimation of fluoride concentration in the air

Air concentrations of fluoride around the emission source were estimated by direct sampling and by modelling. A plume dispersion model developed by Bastianon et al. (1975) was used to compute maximum likely concentrations of fluoride in the air. Estimates obtained with this model agree with estimates based on an alternative model developed by Barros et al. (1975) to describe the same situation.

The model of Bastianon et al. was run with boundary conditions imposed by the dimensions of the boundary layer and topography. While this model allows estimation of maximum possible concentrations along the main axis of a dispersion plume, computation of average concentrations over the area surrounding the emission source requires a probability density function of the occurrence of various concentrations at a given point.

Probability density functions associated with fluoride concentrations at various sampling points near a number of emitting sources have been compiled and reported by McCune et al. (loc. cit.). These functions differ in scatter by as much as 400%. Estimates based on extremes and on one standard deviation were tested with the models described in this paper.

A limited number of air samples at several points in the vicinity of the fluoride source were analyzed. Air, which contained both particulate and gaseous fluoride, was pumped through a solution of sodium hydroxide for 24 hours; the fluoride concentration of the solution was then measured with a fluoride-specific electrode. Soil in the region near the fluoride source, which is resuspended by the wind and collected by the samplers, contained fluoride in adsorption equilibrium (Ares, 1978). Because of these limitations, field samples of air were used only for the purpose of qualitative validation of the estimates obtained by using Bastianon's model and McCune's density functions. The air concentrations obtained from these calculations were used to estimate the air concentration range in which the model must operate.

Modelling fluoride deposition on a forest

Modelling leaf absorption

The model that describes uptake of gaseous pollutants by a leaf is based on the equation developed by Bennett et al. (1973), which is an extension of the work by Waggoner (1969). In this model, the flux of fluoride (as HF) from the air near the leaf to the sinks for fluoride at the leaf surface and in the leaf mesophyll is described by Eq. 1:

$$F = \frac{sC_a}{s(r_a + r_s) + r_i} + \frac{C_a}{r_a + r_s + r_c} \qquad (1)$$

where F is the flux density of hydrogen fluoride to the leaf surface, s is the solubility of hydrogen fluoride, r_a is the aerodynamic boundary layer resistance, r_s is the stomatal resistance, r_i is the internal resistance (mesophyll and cell wall), r_c is the surface cuticular resistance, and C_a is the air concentration of hydrogen fluoride. The success of the leaf model depends on reasonable estimates of the resistances.

For many broad leaf species, the aerodynamic boundary layer resistance can be estimated by the equation (Murphy and Knoerr, 1977):

$$r_a = 1.6 \left(\frac{d}{u}\right)^{0.5} \left(\frac{D_{HF}}{D_h}\right)^{0.33} \tag{2}$$

where d is the average leaf length, u is the wind speed, D_{HF} is the molecular diffusion coefficient of hydrogen fluoride in air, and D_h is the thermometric diffusivity of heat in air.

Stomatal resistance can often be described as a function of light intensity, temperature, atmospheric water stress, and soil water stress. However, porometer measurements also show that sensitive species close their stomata soon after being exposed to air containing 15 g m^{-3} of gaseous fluoride. McCune et al. (1976) showed that exposure to from 0.7 to 3.5 g m^{-3} of gaseous fluoride depresses CO_2 uptake by milo. The depressed uptake is maintained during the exposure period. These results indicate that fluoride affects either the stomata or the internal resistance to CO_2 flux. Woltz (1964) reported stomatal opening in detached leaves of gladiolus (var. Orange Gold and Friendship) after imbibing fluorides from solution. Doley and Johnston (1977) reported various responses ranging from low depression to low stimulation of stomatal opening, which they attributed to modifications of CO_2 concentrations within the leaves. In milo, these authors report a 100-fold increase in internal resistance, compared with a six-fold increase in stomatal resistance. Since these experiments are at air concentrations of fluoride higher than those near the Chubut plant, the effect of air concentration on stomatal closure has not been included in the model.

Stomatal resistance in _E. rostrata_ was assumed to be a function of light intensity and atmospheric water stress as estimated by the equations below:

$$r_s = r_{mn} + \frac{(r_{mx} - r_{mn})}{(1 + L/L_{0.5})} \tag{3}$$

$$r_{mn} = r_{mnm} \text{ for } \delta < \delta_{cr} \tag{4}$$

$$r_{mn} = r_{mnm} + a(\delta - \delta_{cr}) \text{ for } \delta > \delta_{cr} \tag{5}$$

where r_{mn} is the minimum stomatal resistance, r_{mx} is the maximum stomatal resistance, L is the light intensity, $L_{0.5}$ is the light intensity at half saturation, r_{mnm} is the minimum stomatal resistance possible as limited by leaf structure, δ is the vapor density deficit of air, $_{cr}$ is the critical vapor density deficit when stoma begin to close from atmospheric water stress, and "a" is an adjustable constant to fit the model to the measurements.

Values of r_{mn} and r_{mx} were estimated from observations of stomatal resistances in *E. regnans* by Connor et al. (1977). These authors indicated that no stomatal closure occurs in this species under soil water tensions as low as -24 bar. Therefore, it is unnecessary to introduce the effect of soil-water stress on stomatal resistance of the *E. rostrata* forest in this study, which is under irrigation. However, Slatyer and Ferrar (1977) reported data on *E. pauciflora* which strongly suggest that high vapor-density deficits cause stomatal closure. The slope, a, in Eq. 5 was estimated from their data.

McCune and Hitchcock (1970) proposed that the concentration of fluoride in forage crops exposed to abnormal concentrations of airborne fluoride were proportional to the dosage:

$$F = KCT \tag{6}$$

where F is the tissue fluoride concentration corrected for background level, C is the atmospheric concentration of fluoride, T is the length of exposure, and K is a coefficient of fluoride accumulation. Doley and Johnston (1977) reported values of K in the vicinity of 3 for *Eucalyptus crebra* and *E. tereticornis*; they observed that accumulation is usually high at the beginning of the exposure to the pollutant, and decreases after a couple of days under continuous exposure. This slow decrease of accumulation coefficients suggests that the uptake rate depends on the internal resistance of the leaf mesophyll. These observations are consistent with biochemical evidences about the subcellular effects of fluoride, as will be discussed later.

Equation 7 incorporates these ideas into the simulation of the internal resistance r_i to fluoride flux:

$$r_i = b[C_{max}/(C_{max} - C) -1] + r_i \tag{7}$$

where C_{max} is the maximum concentration of fluoride which does not produce injury in *E. rostrata*, b is a shape parameter, and r_{im} is the value of r_i at background levels of fluoride concentration.

Values of C_{max} for this equation were estimated from observations at experimental plantings of E. rostrata. The shape parameter, b, was estimated by trial-error iteration to obtain accumulation rates similar to those reported by Doley and Johnston (1977) for similar species.

The surface resistance in Eq. 1 can also be described by an equation like Eq. 7. McCune and Hitchcock (1970) showed that surface absorption can be important for short exposures; however, internal absorption is more important than surface absorption for longer, chronic exposures. Therefore, values of the parameters in the surface resistance equation are specified to yield a surface resistance that rapidly reaches a high value and limits surface absorption.

The solution of Eq. 1 requires estimation of the solubility of hydrogen fluoride in water as a function of temperature and pressure. The $HF-H_2O$ system was studied extensively by Brosheer et al. (1947) and Munter et al. (1949). On the basis of their results, Eq. 8

$$s = 446 \exp 550 \left[1/(273 + T_L) - 1/293\right] \qquad (8)$$

was developed to estimate Henry's Law solubilities of fluoride as a function of T_L, the leaf temperature. Leaf temperature was estimated from stomatal resistance, solar radiation, air temperature, and air humidity by the energy-balance equation of Gates (1962).

Values of the parameters in Eqs. 1 through 8 used to model the absorption of HF by E. rostrata leaves are listed in Table I. The leaf model was used as the basis of the forest absorption model.

Modelling transport in the surface boundary layer and the canopy

A model which synthesizes the effects of leaf physiology and boundary layer theory has been developed for the estimation of sulfur dioxide uptake by vegetation (Murphy et al., 1977). The general form of this one-dimensional, steady-state model can represent transport of any pollutant that is moved vertically from the atmosphere into a vegetation canopy. The processes of vertical diffusion and absorption are described by the equation

$$\frac{d}{dz}\left(K \frac{dC_a}{dz}\right) + S = 0 \qquad (9)$$

where K is the turbulent diffusivity for mass in the atmosphere, z is the height, and S is the sink strength for the pollutant, equal to the flux defined by Eq. 1 multiplied by the leaf area per increment of height.

The turbulent diffusivity for mass is a function of the state of the atmosphere. The following equations describe the effect of environment on diffusivity in the canopy:

$$\frac{d\tau}{dz} = C_D A u^2 \qquad (10)$$

$$\frac{du}{dz} = \sqrt{\frac{\tau/\rho}{\ell}} \qquad (11)$$

$$K = \ell\sqrt{\tau/\rho} \qquad (12)$$

In these equations, τ is the shearing stress of wind on the surface of the canopy, C_D is the drag coefficient for the canopy elements, A is the leaf area, u is the wind speed, ℓ is the mixing length (analogous to mean free path in molecular diffusion), and ρ is the air density.

Within the canopy, the mixing length is determined by the space between the crowns and the scale of the eddies shed by the canopy elements. This relationship is modelled with the equation:

$$\ell = \ell_c X_s + S_p(1 - X_s) \qquad (13)$$

where ℓ_c is the mixing length of eddies shed by the canopy, X_s is a horizontal average of the relative cross-sectional crown area for each height in the stand, and S_p is the average distance between crowns.

In the boundary layer above the canopy, there are no surfaces for drag to take place, and the shearing stress is nearly independent of height. In this region of boundary layer flows, the mixing length is proportional to the height from the surface less the displacement height, d, of the profile caused by the presence of the forest; thus

$$\frac{du}{dz} = \frac{\phi\sqrt{\tau/\rho}}{k(z-d)} \qquad (14)$$

$$K = \phi k(z-d)\sqrt{\tau/\rho} \qquad (15)$$

where k is von Karman's constant ($\sim$0.4), and ϕ is a correction for atmospheric stability (Businger et al, 1971).

Eqs. 12 through 15 were solved numerically using the upper boundary condition of wind speed and a displacement height equal to 75% of the average height of the trees. Table II lists the climatic data used for simulations of the whole-canopy model by Eqs. 12 through 15.

The local climate was simulated by a climate generator which uses air temperature, air dew-point temperature, solar radiation, and incoming terrestrial radiation as functions of the annual and diurnal cycles and an observed nine-day synoptic cycle. The simulated climate is more regular than the true climate but is not expected to cause large deviations in average deposition over long periods of time. The climate generator provides a means of simulating environments with a minimum input to the computer code.

Modelling growth and development of the forest canopy

The models incorporate the available physiological knowledge of Eucalyptus rostrata and similar species as well as meteorological turbulent boundary-layer theory. The various parameters in Eqs. 1 through 15 indicate that knowledge of the structure of the forest is necessary to determine absorption rates. Furthermore, the forest is not a static system during the period in which pollutants such as fluoride are being removed from the atmosphere. The leaf area will change seasonally even in evergreen species such as eucalyptus. The trees will grow, increasing in height and leaf surface area. There will be a turnover in leaf mass, causing a renewal of leaf capacity for absorbing pollutants.

In constructing a model of growth and development of E. rostrata, the observations of Jacobs (1955) have been used. Jacobs reported that eucalyptus foliage is relatively short-lived for an evergreen species, averaging about 18 months in longevity. Leaves grow most rapidly during the warmer part of the year, and the canopy thins greatly during the winter. Fig. 1 shows the cumulative growth and death of a flush of leaves as used in the simulations. Classes of leaves were initiated during the spring and summer and kept track of separately in the simulations.

Leaf growth was distributed vertically in the stand as a normal distribution around the maximum growth at a point 60% of the height of the tree. The resultant leaf-age distribution at any height in the tree could be used to determine the average leaf concentration of fluoride as a function of depth in the canopy and length of exposure to HF.

The tree height was adjusted continuously, beginning in the spring and stopping in the fall. A sigmoid growth pattern of tree height was assumed during the growing season. The average leaf area was assumed to be constant over the period of the simulation.

Implementation of model

The HF absorption model described above was implemented in several separate stages. First, the leaf submodel was run separately to determine by trial and error the values of the parameters that best duplicated the data of Doley and Johnston (1977).

After setting the values of the leaf parameters, the model was run with the canopy meteorological and tree growth submodels. This allowed the simulation of HF absorption for a particular atmospheric concentration of HF above the forest. The seasonal dynamics and vertical distribution of absorption could be evaluated with these simulations.

The forest canopy model was then used to calculate the relationship between the HF concentration in the atmosphere above the forest and the deposition velocity for HF (the flux density divided by the atmospheric concentration) to the *E. rostrata* forest. The deposition velocity varies with meteorological conditions, i.e., the season of the year, as well as with the HF concentration. The deposition velocity relationships were used to calculate the forest area necessary to absorb a desired fraction of the release or to decrease the concentration by a desired amount. The area and concentration calculations were done with a Gaussian diffusion model which incorporates a deposition velocity.

The forest canopy deposition model was coded in the simulation language CSMP. CSMP is a preprocessor for FORTRAN, and a FORTRAN deck can be produced. The diffusion code is a FORTRAN code. The compatibility of CSMP with FORTRAN may allow future combination of a simplified forest canopy code with an atmospheric dispersion code.

RESULTS

Leaf absorption

Fig. 2 illustrates the simulated response of an individual leaf exposed to two different levels of HF, based on the parameters listed in Table I. These parameters were selected to duplicate the leaf absorption curve of Doley and Johnston (1977). The environmental conditions during these simulations were selected for a clear, midsummer day in the vicinity of Chubut.

Canopy absorption

Fig. 3 illustrates the simulated response of an *E. rostrata* canopy over a three-year period. The simulation was parameterized with initial conditions of no fluoride in the forest vegetation.

From the beginning of the simulation, the air concentration of HF was specified as the constant value of 0.001 g m^{-3}. Total leaf area index and deposition velocity are also presented to indicate the relationship between deposition rate, leaf growth, and leaf concentration. Despite high deposition rates, leaf concentration falls in the spring, because rapid leaf growth produces new leaves with low fluoride content. The highest leaf concentrations are found in the winter when the leaves that remain have had a longer exposure and no new growth is taking place. This pattern of seasonal variation has been observed near the aluminum plant at Chubut.

Fig. 4 shows the vertical profile of HF concentration in leaves as a percent of the maximum concentration in washed leaves. These profiles result from the interaction of several simultaneous dynamic processes: the deposition of gaseous and particulate fractions of fumes, the absorption of these fractions within the leaf tissues, the translocation of these fractions from the leaves to other organs of the plant, the washout by precipitation of fluoride retained externally on the leaves and redeposition on leaves at lower levels, and the growth of leaves. The dynamic balance among these processes determines the concentration of fluoride in any leaf at a particular time.

Differences between windward and leeward exposures (Fig. 4) probably reflect the influence of the canopy boundary-layer resistance on the deposition flux. Differences between the washed and unwashed leaf samples reflect the partition of the fluoride contained by leaves into (1) an internal, metabolic fraction, and (2) external fractions that are retained mainly by adsorption mechanisms (Ares, 1980).

Several factors might account for the observed increase in fluoride concentrations at lower levels of the canopy. Top soil blown by the wind in this region carries a considerable amount of fluoride (Ares, 1978b), particularly to lower branches. Lower leaves are older and may have accumulated more fluoride. Upper leaves, however, are old enough to have attained high concentration levels, as indicated by uptake rhythms observed for similar species of Eucalyptus (Doley and Johnston, 1977); furthermore, the fact that leaves of both young and old stands show similar concentrations at a same height indicates that the observed profiles are caused by some process independent of the age of the leaf, but dependent on its height within the canopy.

The uptake of fluoride has been shown to be regulated by the leaf water potential in species living in this same environment (Ares et al, 1980). Water stress in leaves of Eucalyptus regnans varies with height according to the expected static-head gradient of 0.1 bar/m (Conner et al., 1977). Also, since higher leaves are more exposed than lower leaves to direct radiation, the evaporative demand is greater in the upper part of the canopy. Accordingly, the higher water stresses prevailing at elevated branches of the canopy could be responsible for lower fluxes of cuticular transport to inner tissues of leaves.

The sharp decrease in concentrations along the path from the leaves to other parts of the plant indicate that fluoride is very slowly translocated from leaves. Fast downward transport through the xylem is unlikely in this kind of vegetation because of the expected direction of the bulk fluid flow under irrigation conditions. Also, long-distance transport through the phloem should be detectable by sampling branches, because of the slow speeds involved in the transport through this tissue.

The objective of the modelling effort was not to simulate the profiles of fluoride concentration observed in the field, but rather to reproduce the mean values, thus minimizing the computational complexity. Nevertheless, the profiles of fluoride concentration predicted by the model (Fig. 5) agree reasonably well with the profiles of internal fluoride concentration (fluoride after washing). It is to be expected that the model will not predict the external fluoride concentration as well because it simulates only absorption of HF and does not take into account deposition of particulate fluoride, which would be on the outer surface of the leaves.

Fig. 6 illustrates the variation in deposition velocity simulated for the E. rostrata forest as a function of season and concentration of HF in the air. The values in Fig. 6 are those reached during the third year after the start of the exposures, when steady state had been reached. These values were used in the calculation of HF absorption around the aluminum plant near Chubut.

Calculation of deposition in the vicinity of the Chubut aluminum plant

The model used for calculation of deposition and ground-level concentration was developed at the Savannah River Laboratory (Garrett, 1980). It compares favorably with other dispersion-deposition models of the same type (Horst, 1976). This model has the advantage of being able to handle fairly complex surface conditions, such as those posed in this paper. It is a Gaussian-plume model with a source-depletion term that can be modified with distance from the source.

Transport of HF after release at the aluminum plant was simulated by assuming an extensive E. rostrata forest surrounding the plant and a ground-level release point. The distance at which

50% of the fluoride would have been deposited was estimated as 81 km from the plant. The concentration in the atmosphere at this point would have decreased to 2.0% of the concentration at 1 km. These results are independent of the source strength.

The area needed to accumulate 50% of the released fluoride would be 20,600 km^2 (circular area of radius 81 km). This is a very large area to use for pollution control. The reasons for such a large area are the high wind speeds in the Chubut area and the rapid decrease in concentration with distance due to horizontal dispersion. It appears that an effective control strategy must supply the forest with hydrogen fluoride at a high enough level to ensure rapid uptake. Calculations (Murphy et al., 1977) indicate that this might be done by releasing the HF beneath the vegetation, where atmospheric mixing and wind speed are lower. Design and construction of a system to do this would entail some expense, but might still be cost-effective compared to other pollution control systems.

DISCUSSION

As is often the case, the data are not available to test the predictions of the model. However, the approach of the modelling effort has been to base the model structure on submodels that can be compared to available data. First, the leaf submodel was constructed on the basis of data gathered for eucalyptus species similar to E. rostrata. The canopy diffusion model is based on current understanding of forest meteorology. The tree growth and development submodel is based on data gathered over a long period on eucalyptus growth patterns. Finally, the atmospheric dispersion-deposition model is "state of the art," given the available meteorologic data. The results of the simulations do agree reasonably well with available data.

The deposition rates indicate that forests are major sinks for HF. However, large land areas may be necessary to remove a significant fraction of the HF from a point source. Even where it might be practical to use forests as sinks for HF, it would be necessary to investigate recycling of fluoride in vegetation and soil accumulation of fluoride in the environment over long periods of time, and ultimate dispersal by soil erosion, removal of forest products, and water movement. These factors are the subject of continuing research at the ALUAR plant site.

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TABLE I

Values of parameters used in simulations

Type	Parameter		Value
Forest stand	Height		7 to 12 m
	Maximum leaf area index		6
Physiological	Stomatal resistance:	minimum	300 s m^{-1}
		maximum	4×10^{3} s m^{-1}
		half-light saturation	2×10^{-3} cal cm^{-2} min^{-1}
	Internal resistance:	saturation concentration	3×10^{-3} g g^{-1}
		minimum resistance	1×10^{4} s m^{-1}
		half-saturation resistance	1×10^{5} s m^{-1}

TABLE II

Mean monthly values of agrometeorological variables recorded at the station of the National Institute of Agricultural Technology, Trelew, Chubut. Values are based on tridiurnal observations, period 1971-1975 (MacKarthy, 1977).

Atmospheric Conditions	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec
Temperature (°C)	19.8	18.2	16.2	12.6	8.7	4.8	5.3	7.7	12.8	12.9	15.4	18.0
Temperature Amplitude[a] (°C)	15.3	16.9	14.4	11.9	12.5	11.4	11.4	11.0	14.9	16.0	15.0	15.6
Dew point (°C)	9.9	10.3	10.1	8.1	7.1	6.6	5.1	7.8	6.7	5.1	6.9	8.3
Relative humidity (%)	46	51	59	60	69	73	68	60	51	51	50	47
Wind velocity (m s^{-1})	11.7	7.8	6.4	5.1	5.8	6.0	6.2	8.1	9.1	8.0	8.2	8.3
Precipitation (mm)	14.2	7.2	19.2	7.4	20.5	16.7	12.2	12.6	2.1	4.3	11.0	14.1

a. i.e., maximum deviation around mean value.

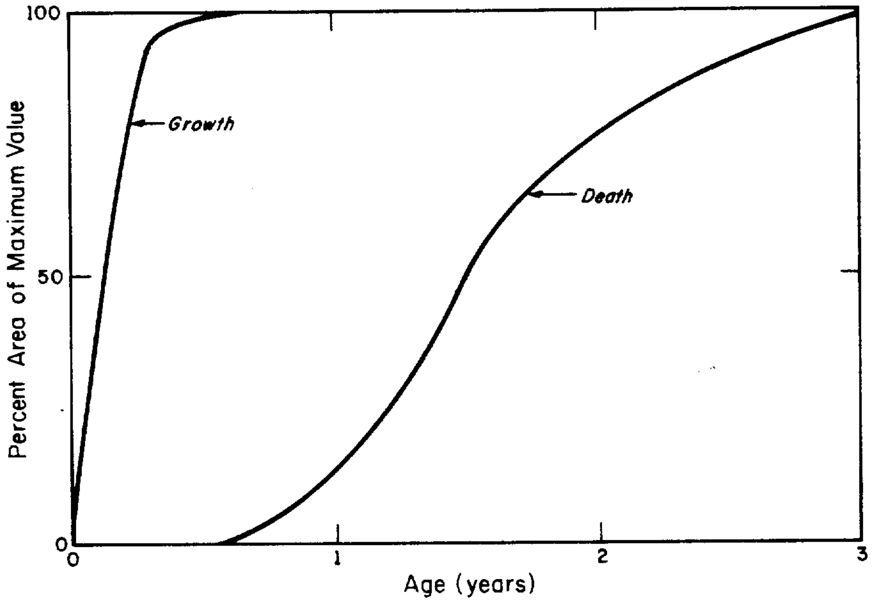

Fig. 1. The relationship between the increase in leaf area due to growth and decrease due to death of leaves initiated at the same time as a function of length of time after initiation.

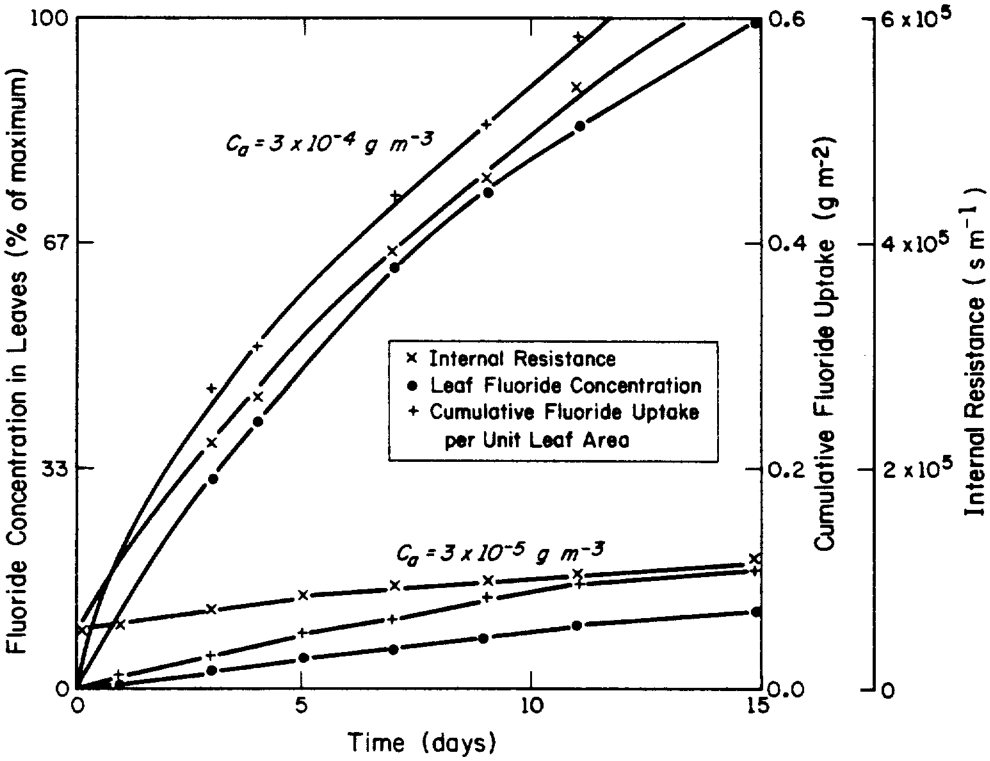

Fig. 2. Simulation of leaf absorption of hydrogen fluoride in eucalyptus leaves at two different air concentrations.

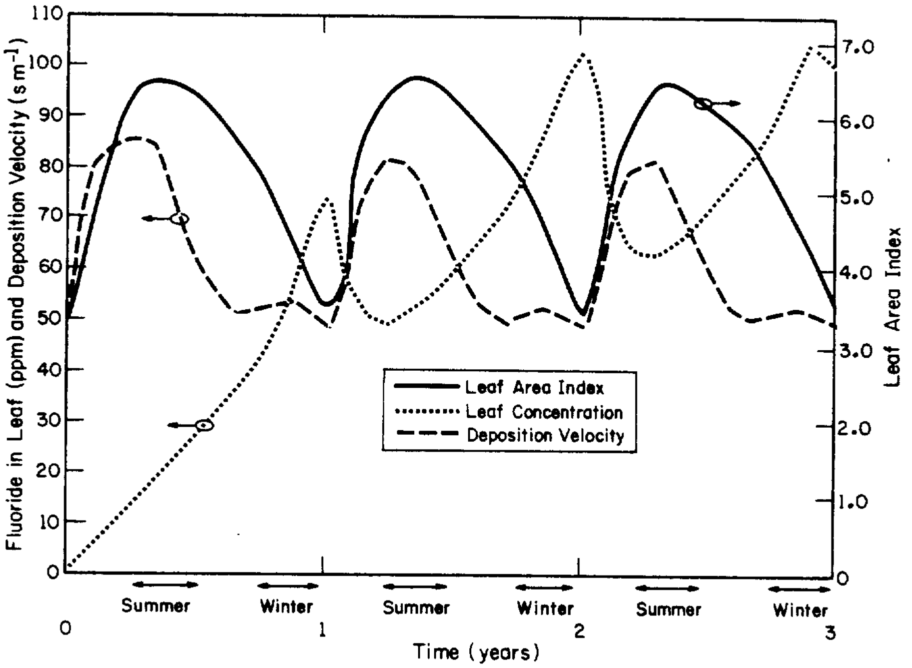

Fig. 3. Simulation of deposition velocity and leaf fluoride concentration for a *Eucalyptus rostrata* forest.

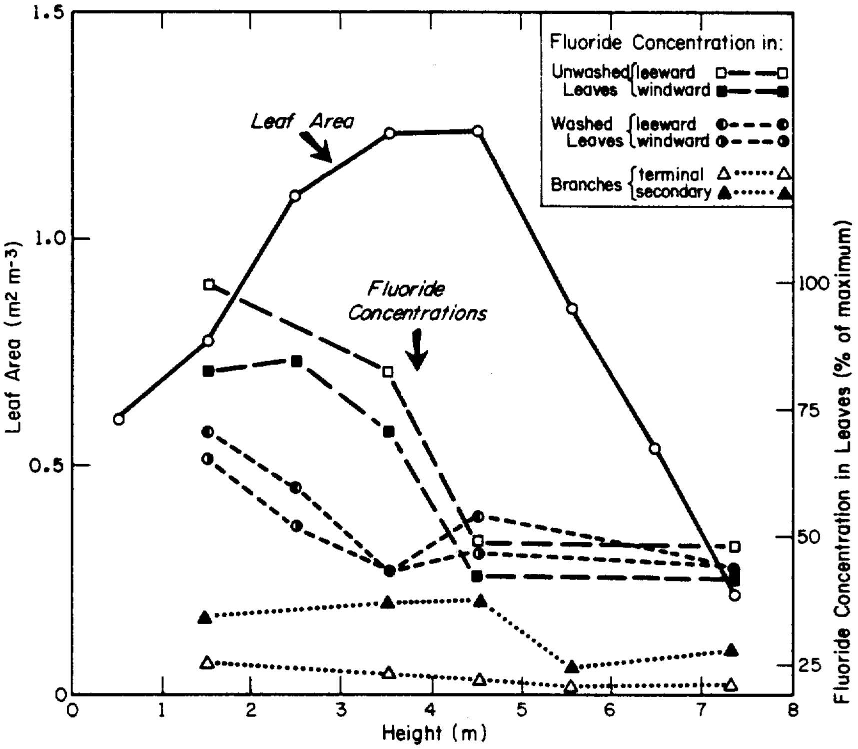

Fig. 4. Vertical profiles of relative fluoride concentration in branches and in leaves before and after washing.

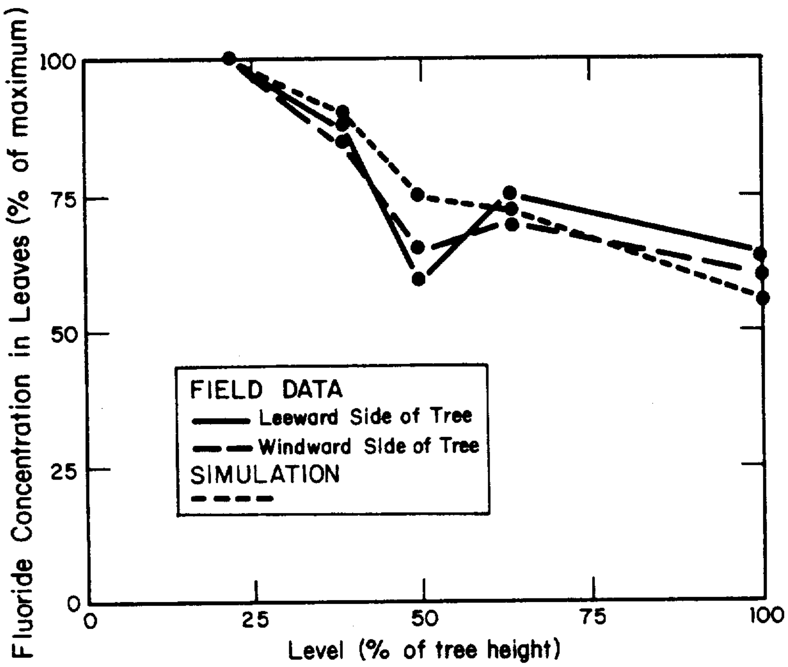

Fig. 5. Simulation of fluoride concentration in leaves of Eucalyptus rostrata after washing. The concentrations are given as a percent of the maximum internal concentration.

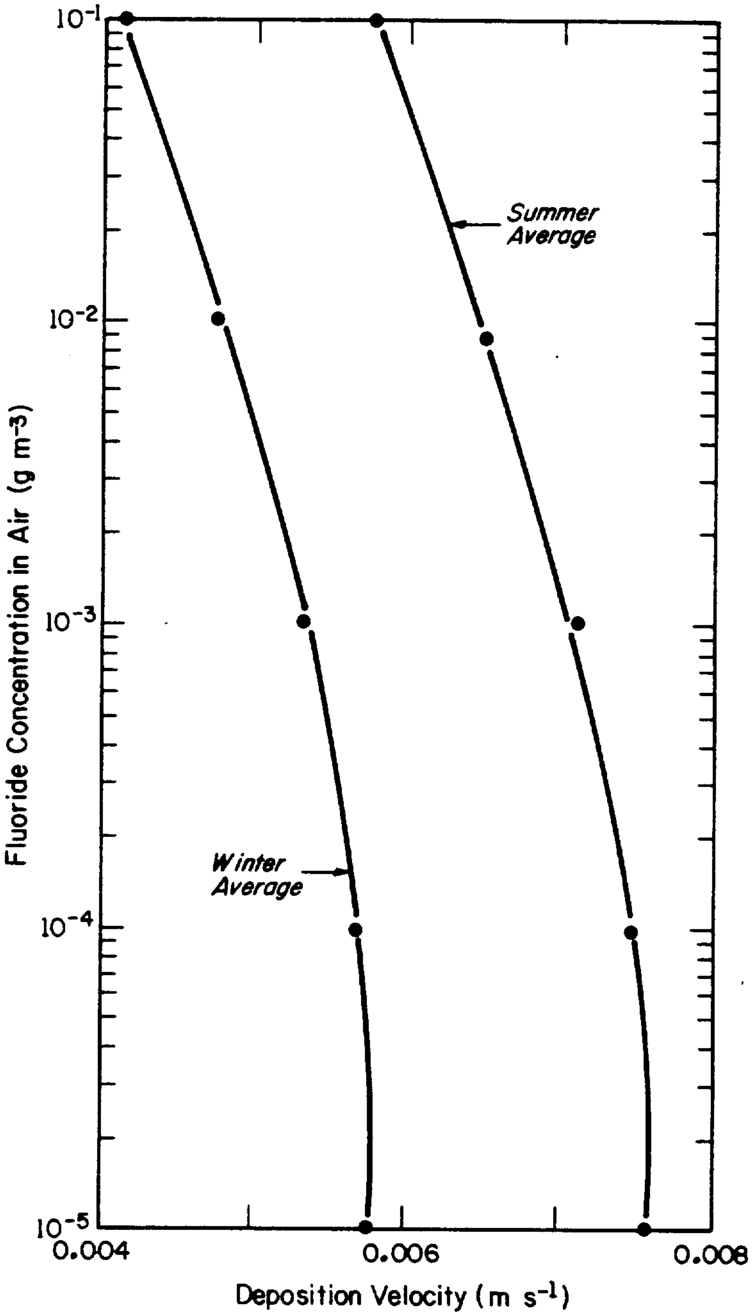

Fig. 6. Simulated deposition velocity of hydrogen fluoride as a function of air air concentration and time of year.

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TIS File

December 5, 1980

TO DISTRIBUTION

Attached is a copy of the following:

DP-MS-80-108, "The Uptake of Hydrogen Fluoride by a Forest" by C. E. Murphy and J. Ares.

This paper is proposed for publication in *Ecological Modelling.*

If there are comments about its release, notify the TIS office within 14 days (Ext. 3598).

For any technical clarification, we suggest you call:

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Savannah River Laboratory