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Kinetics of Nonionic Diffusion of Hydrogen Fluoride in Plants

II. Model estimations on uptake, distribution, and translocation of F in higher plants[1])

By

Winfried KRONBERGER *)

With 2 Figures

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Summary

KRONBERGER W. 1988. Kinetics of nonionic diffusion of hydrogen fluoride in plants. II. Model estimations on uptake, distribution, and translocation of F in higher plants. – Phyton (Austria) 28 (1): 27–49, with 2 figures, – English with German summary.

By means of model tissues and organs of plants it was tested, whether the concept of nonionic diffusion of HF together with an F^- ion trap can explain already known data on uptake, distribution and translocation of F. From the estimations the following picture arises which does not contradict the known data:

F^- content increases with the pH of a compartment; for one unit of pH the F^- content increases 10-fold. Thus, neutral and slightly alkaline compartments reach higher F concentrations and are more stressed than acid ones. Diffusion of HF from the atmosphere into a leaf is determined essentially by air phase resistances (boundary layer, stomata, intercellular spaces), whereas diffusion of HF from an aqueous solution into the xylem of a root is limited mainly by the resistances of the plasmalemmata (endodermis, pericycle, stelar parenchyma). It takes from 200 to 800 days to reach half the equilibrium concentration for a leaf, for the central stele of a root it takes around one day. F may be translocated within both the xylem and the phloem. A fraction of the F applied to a leaf will be exported via the phloem. However, it is partly stored in tissues along the phloem pathway and part of it is swept back to the leaf via the xylem. F taken up into a root will be exported via the xylem, however, it

[1]) To Ophelia, Eliza, Julia, and the maiden with the lucifers.

*) Univ.-Doz. Dr. W. KRONBERGER, Botanisches Institut der Universität für Bodenkultur, Gregor Mendel-Straße 33, A-1180 Wien (Austria)

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partly is stored in tissues along the xylem pathway and partly is transported back toward the root via the phloem.

The concept of F uptake by diffusion of HF may account for already known facts and thus it could contribute to clarify unresolved questions.

Zusammenfassung

KRONBERGER W. 1988. Die Kinetik der Diffusion von undissoziiertem Fluorwasserstoff in Pflanzen. II. Modell-Abschätzungen der Aufnahme, Verteilung und Translokation von F in höheren Pflanzen. – Phyton (Austria) 28 (1): 27–49, mit 2 Figuren. – Englisch mit deutscher Zusammenfassung.

An pflanzlichen Modellgeweben und -organen wurde überprüft, ob das Konzept der HF-Diffusion und der F^--Ionenfalle mit bekannten Daten über Aufnahme, Verteilung und Translokation von F im Einklang steht. Aus den Abschätzungen ergibt sich folgendes, den bekannten Daten nicht widersprechendes Bild:

F^- reichert sich entsprechend dem pH eines Kompartments an; mit der Zunahme um eine pH Einheit steigt der F^--Gehalt um das 10fache, sodaß neutrale und schwach alkalische Kompartimente höhere F-Konzentrationen aufweisen und somit stärker belastet sind als saure. Die Diffusion von HF aus der Atmosphäre in ein Blatt wird wesentlich durch Widerstände in der Gasphase bestimmt (Grenzschicht, Stomata, Interzellularen), während die Diffusion von HF aus einer wäßrigen Lösung in das Xylem der Wurzel vor allem durch den Widerstand der Plasmalemmata (Endodermis, Perizykel, Stelarparenchym) begrenzt wird. Für ein Blatt beträgt die Dauer zur Einstellung der halben Gleichgewichtskonzentration 200–800 Tage, während dazu für den Zentralzylinder einer Wurzel die Dauer in der Größenordnung eines Tages liegt. F kann sowohl im Xylem als auch im Phloem verlagert werden. Aus dem Blatt wird F zwar über das Phloem exportiert, teilweise aber in Geweben entlang des Phloems gespeichert und teilweise über das Xylem wieder zurückgeschwemmt. In die Wurzel aufgenommenes F wird im Xylem exportiert, teilweise in den Geweben entlang des Xylems gespeichert und teilweise über das Phloem in die Wurzel zurücktransportiert.

Das Konzept der F-Aufnahme durch Diffusion von HF eignet sich zur Erklärung bereits bekannter Fakten und könnte somit zur Klärung noch offener Fragen beitragen.

Introduction

In part I of this paper (KRONBERGER 1987) nonionic diffusion of HF was confirmed to be an important uptake mechanism also for higher plants. Although there exists an abundance of information about the toxic effects of inorganic fluorides on vegetation, obtained mainly from air pollution studies, this mechanism was not taken into account so far. However, such a basic concept should contribute to a better understanding of F toxicity. Furthermore, as some other gaseous air pollutants as well as many biologically important metabolites are weak acids (or bases), nonionic diffusion may be of general significance.

In the second part of this paper it will be examined whether already known facts on uptake, distribution and translocation of F could be explained as a consequence of purely diffusive HF uptake. For the present this

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can only be done by an analysis of model tissues and organs. However, it can be done now with the knowledge of the permeability coefficient for HF. For the purpose of model estimations a value of 2.10^{-7} m s^{-1} or its reciprocal, the plasmalemma resistance to HF of 5.10^{6} s m^{-1} is assumed. But it should be kept in mind that these absolute values can only be regarded as the first ones available and that they could vary with a greater variety of plant species, and, as has been shown in part I, that they even vary with pH within one species.

Abbreviations and Symbols

A list of symbols has been presented in part I of this paper. In order of better legibility the symbols used in this paper are recapitulated below, completed with symbols used in this paper only.

HF = indication of hydrogen fluoride (nonionic form), also amount of HF (mol)
F^- = indication of fluoride ion (HF, dissocoated form), also amount of F^- (mol)
F = indication of fluorine, sum of HF and F^-, also amount of F (mol)
c, [] = concentration (mol m^{-3})
Δc = concentration difference, driving force (mol m^{-3})
V = volume (m^3)
t = time (s)
$t_{(0,5)}$ = equilibrium half time (s)
A = area (m^2)
P = permeability coefficient (m s^{-1})
R = resistance (s m^{-1})
K = partition coefficient
D = diffusion coefficient (m^2 s^{-1})
Δd = thickness of a barrier (m)
subscript i refers to inside of a volume specified
subscript o refers to outside of a volume specified
subscript (g) refers to gas or air phase
subscript (l) refers to liquid water phase
subscript cw refers to cell wall
subscript pm refers to plasmalemma

superscript mes refers to mesophyll
superscript rh refers to root hair
superscript c refers to cortex
superscript e refers to endodermis
superscript pc refers to pericycle
superscript sp refers to stelar parenchyma

Symbols of substances are used also as superscripts.

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F Distribution in cell compartments

It follows from the ion trap concept that accumulation of F^- ions is strongly pH-dependent: at equilibrium for the permeable HF the concentration of F^- in a comprtment will increase 10-fold with each pH unit. According to the quite different pH values of the compartments within a plant tissue, a quite unequal F distribution should occur. A vacuole with an acid cell sap will contain much less F^- than the slightly alkaline cytoplasm.

To further illustrate this, F amounts and F concentrations in only 3 compartments of a simplified tissue are calculated and shown in Table 1. Let us consider 4 different tissues with increasing vacuolar pH values, with the pH of the apoplast and the cytoplasm the same in each tissue. Volume fractions of the compartments are assumed to represent a fully developed tissue, e. g. of a mesophytic leaf.

Tissues with a cell sap pH below 5 contain most of the F in the cytoplasm. Vacuolar pH values higher than 6 cause an increasingly higher percentage of F to be stored in the vacuole. At pH 7.1 nearly 90% is found there. In treating F concentrations instead of amounts, 2 variants are choosen. In variant (1) all the compartments of the different tissues are assumed to have equilibrated with 10^{-6} mol HF/l (1 μM). Each compartment's F concentration increases 10-fold with each pH unit (irrespective of volume fractions). Therefore, in tissues with higher vacuolar pH the average F concentration of the tissue increases, too.

In variant (2) the 4 different tissues are assumed to have the same average F concentration of 10^{-3} mol F/l (1 mM). With increasing vacuolar pH, apoplastic and cytoplasmatic F concentration decreases, as well as HF concentrations of all compartments. This decrease is caused by increasing vacuolar F concentrations (i. e. increasing storage of F), due to the high volume fraction of the vacuole and its increasing pH. So the neutral vacuole would be able to detoxicate the cytoplasm. However, plant species containing a cell sap more acid than pH 6 do not have this ability, and most of the F is concentrated within the living part of a cell. This might be one of the reasons of the high phytotoxicity of fluoride, as most plant species contain rather acid cell saps. Since fluoride toxicity has not been seen in the light of the ion trap concept so far, correlations between F sensitivity and vacuolar pH were not established. A cell sap of pH 6 to pH 7 should be considered to act as a mechanism of F tolerance. The pH and volume fractions of compartments should therefore be kept in mind when relating F concentrations (e. g. obtained by chemical analysis) of F-contaminated tissues to a certain effect. The 4 tissues given in variant (2) will have about 100 ppm F on a dry weight basis, assuming about 20% dry matter content for a mesophytic leaf. The tissue with a cell sap pH of 4.1 will have a cytoplasmatic c^F of 9 mM, whereas with an increase in vacuolar pH from 6.1 to 7.1 cytoplasmic c^F drops from 5.3 to 1.1 mM.

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Table 1

Calculated F amounts and F concentrations at equilibrium for the permeable HF in compartments of 4 tissues as a function of vacuolar pH. Average F concentrations are given for each of the two variants selected. Variant 1: the compartments of each tissue are assumed to have equilibrated with 1 μ*M* HF. Variant 2: each tissue is assumed to have the same average F concentration of 1 m*M*.

compartment	volume fraction	F amounts (% of total) in compartments at a vacuolar pH of			
		4.1	5.1	6.1	7.1
vacuole	0.80	0.8	6.8	42.1	87.9
apoplast, pH 6.1	0.10	9.0	8.5	5.3	1.1
cytoplasm, pH 7.1	0.10	90.2	84.7	52.6	11.0
		F concentrations (m*M*) in compartments at a vacuolar pH given on top; *variant 1*			
vacuole	0.80	0.011	0.1	1.0	10.0
apoplast, pH 6.1	0.10	1.0	1.0	1.0	1.0
cytoplasm, pH 7.1	0.10	10.0	10.0	10.0	10.0
c^F, tissue average (m*M*)		1.11	1.18	1.90	9.10
c^{HF}, all compartments (μ*M*)		1	1	1	1
		F concentrations (m*M*) in comprtments at a vacuolar pH given on top; *variant 2*			
vacuole	0.80	0.010	0.086	0.53	1.1
apoplast, pH 6.1	0.10	0.90	0.85	0.53	0.11
cytoplasm, pH 7.1	0.10	9.0	8.5	5.3	1.1
c^F, tissue average (m*M*)		1	1	1	1
c^{HF}, all compartments (μ*M*)		0.90	0.85	0.53	0.11
overall pH*)		6.14	6.17	6.38	7.06

*) As would be obtained from weak acid distribution with HF.

It may further be mentioned that other mechanisms also could lead to F accumulation, even in an acid compartment, as for instance complex formation with aluminium. This seems to be true for the tea plant and many other Al accumulating plant species as shown by DAVISON (1983). This mechanism can be considered to detoxicate in two means. Because of the toxic property of free Al, one can say that F^- and Al^{3+} detoxicate each other. Such an effect

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was shown by KONISHI & al. (1983) in an investigation of pollen tube growth in the tea plant. In addition see also WEINSTEIN & ALSCHER-HERMAN (1982) discussing hormoligosis.

As outlined in Table 1, the highest F concentrations are to be expected in the most alkaline compartments. These are the content of the sieve tubes with pH values of up to 8 or even higher (ZIEGLER 1975) and the chloroplast stroma at light exposure (HELDT & al. 1973) with a pH near 8. Mitochondria, the cytosol, and the chloroplast stroma (in the dark) are reported to have pH values from 7 to 7.6 (RAVEN & SMITH 1977, HELDT & al. 1973). The high F accumulation postulated for chloroplasts, mitochondria and the cytosol implies that photosynthesis and respiration should be quite susceptible processes; there are numerous reports that they are in fact primary targets of fluoride toxicity (see BOREI, 1945, CHANG 1975, MILLER & al. 1983). Furthermore, CHANG & THOMPSON (1966) found in F-exposed *Citrus sinensis* leaves that the chloroplasts contained the major amount of F when corrected for cross contamination during the nonaqueous homogenization in hexane-CCl_4; with aqueous homogenization the major amount of F appeared in the supernatant.

However, as will be shown in the next sections high equilibrium concentrations per se are not overly relevant in reality, because they often are reached only after long periods in the case of F uptake.

Fluoride and Translocation

There exists only scarce information about (a) fluoride effects on phloem transport in general, and (b) translocation of fluoride in the phloem. Both processes should be influenced by the high F^- accumulating potency of the alkaline sieve tubes.

(a) Phloem transport: WILLENBRINK (1957) found some inhibition of fluorescein, nitrogen, and phosphorus transport by applying NaF to isolated strands of *Pelargonium zonale* petioles. GARDNER & PEEL (1972), tracing aphid stylet exudate from bark strips of *Salix viminalis* could detect a decrease of ATP in phloem sap after NaF treatment due to inhibition of glycolysis. Inhibitors of oxidative phosphorylation failed to decrease ATP. However, both types of inhibitors are able to stop stylet exudate flow. In a study with ^{14}C-labelled photosynthates MADKOUR & WEINSTEIN (1987) found a reduced export rate out of the source leaf of soybean plants *(Glycine max)* when they were fumigated with 1 or 5 μg HF/m³ for 8–10 days. All experiments cited show inhibitory effects of fluoride either on the source or on the pathway site of translocation. However, they do not indicate such drastic effects as expected from the high equilibrium concentrations in sieve tubes. The possible reason will be shown.

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(b) Fluoride translocation: There exists experimental evidence that F is translocated only to a small amount out of a source leaf by the phloem, and that it is rather xylem mobile (WEINSTEIN & ALSCHER-HERMAN 1982, DAVISON 1983). This seems to be not in accordance with a high ionic accumulation within sieve tubes, too.

Let us first consider the potential transport capacity for F of both xylem and phloem. A useful value to compare volume flow in xylem and phloem is the water use efficiency, i. e. the transpirational water demand to produce 1 g dry matter. Assume a plant which demands 500 ml water, all entering the leaves via xylem. At the same time 1 g photosynthates are exported from the leaf via phloem (neglecting losses by respiration). With a phloem sap containing 20% dry matter, about 5 ml of sap are needed to export 1 g of photosynthates. Thus, phloem to xylem volume flow ratio approximates 1 to 100. To estimate F flow rates, concentrations have to be known: at equilibrium, phloem to xylem F concentrations relate 100 to 1 with a phloem sap of pH 8 and a xylem sap of pH 6. Thus, F flow rates relate 100 to 100, i. e. phloem and xylem would have about the same F transport capacity at equilibrium conditions.

Therefore, and since xylem and phloem strands are in intimate contact to each other virtually on their full path length (PATE 1975), circulation of F could be considered: F containing phloem sap moving out from a source leaf, will reach petiole and stem tissue, where HF is absent or much lower in concentration than in the sieve tubes. HF will permeate out, reach the xylem vessels and be swept back into the source leaf together with dissociating F^- according to the pH along that path. Some HF will permeate into the surrounding tissue acting as a storage pool. The part swept back into the leaf will equilibrate again with the phloem. In this way circulation of F could prevent an effective long distance transport out of a source leaf.

Such a translocation pattern of a solute is called pseudoapoplastic (PETERSON & EDINGTON 1976). Although phloem mobile, the solute accumulates in margins and tips of leaves, which is typical for purely apoplastic translocation (but here a solute is not able to enter the phloem). Pseudoapoplastic behavior is found with solutes at very high plasmalemma permeabilities. As P_{pm} becomes smaller, equilibration times between phloem and xylem will rise. Thus, a solute can move out for increasingly longer distances from the source, i. e. the solute increasingly shows ambimobile behavior (xylem and phloem mobility). With a further decrease in P_{pm}, at first optimum ambimobility is reached and afterwards apoplastic behavior increases.

TYREE & al. (1979) have given a theory to quantify these various translocation patterns for a nonelectrolyte. However, it should be possible to apply criteria of their theory to an electrolyte to estimate at least the quality of the F translocation pattern.

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In a model translocation path they found optimum ambimobility when a nonelectrolytic solute, supplied to the apoplast of a leaf, reaches about $^1/_{10}$ of the equilibrium concentration in the phloem sap at its egrees from the source leaf. This corresponds to an optimum plasmalemma permeability of 2.10^{-9} m s^{-1}. With a greater P_{pm}, a solute reaches $^1/_{10}$ equilibrium more quickly and will pass the petiole with a concentration nearer to equilibrium, but will evade also more quickly from sieve tubes as already outlined.

Let us compare now $^1/_{10}$ equilibrium times, $t_{(0.1)}$, of a nonelectrolyte with F. For a nonelectrolyte $t_{(0.1)}$ will amount to $\frac{V_i}{A\,P}$ ln 1.11 (see Table 1 in Part I of this paper). With an average sieve tube diameter of 11 µm given by TYREE et al. (1979), a V_i/A ratio of half the radius of the sieve tube and optimum $P_{pm} = 2.10^{-9}$ m s^{-1} this time amounts to 2.4 min.

To estimate $t_{(0.1)}$ for F in the same leaf, an apoplastic pH of 6.1 and a pH of 8.1 in the phloem sap is assumed. At a ΔpH of 2, F^- accumulates in the phloem sap 100 times more compared with a nonelectrolyte. It is therefore not necessary to reach $^1/_{10}$ of HF equilibrium, but only $^1/_{1000}$. For HF in this case $t_{(0.001)} = \frac{V_i\,x_i}{A\,P}$ ln 1.001. With the same sieve tubes as above, $x_i = 10^5$ according to pH 8.1 in the phloem, and a P of 2.10^{-7} m s^{-1} for HF, $t_{(0.001)}$ amounts to 23 min.

That is, F equilibrates between xylem and phloem too slowly for optimum ambimobility. F therefore may be considered to show an apoplastic transport pattern and not a pseudoapoplastic one. However, dependent on factors influencing optimum ambimobility (see TYREE & al. 1979), F may be more or less ambimobile, and so F will be exported more or less via phloem. This quality agrees with experimental data. For a quantitative evaluation it should be attempted to adapt TYREE's theory to electrolytes.

It further becames obvious that F equilibrates rather slowly into sieve tubes. This will be more apparent when calculating $t_{(0.5)}$ instead of $t_{(0.001)}$. For sieve tubes 11 µm in diameter it would take 11 days to half equilibrate from the apoplast, provided apoplastic F concentration does not drop during uptake. This may be realistic when a leaf is fumigated continously. Allowing for the F concentration in the apoplast to drop, $t_{(0.5)}$ will decrease, but equilibrium concentration decreases, too.

The rather slow equilibration of sieve tubes seems also to be the reason why drastic effects on translocation of assimilates caused by F where not observed, as mentioned in section (a).

It should be noted that equilibrium times are of general importance for fluoride toxicity. They may vary in a very wide range, dependent from the factors given in the equations for $t_{(0.5)}$ for an electrolyte. With rising pH of both the receiver and the donor volume (represented by x_i and x_o), $t_{(0.5)}$ increases. Therefore, more alkaline compartments will reach higher F equilibrium concentrations, but it takes longer. When various weak acids

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are considered for comparison, pH – pK of the compartments is of importance; with increasing pH – pK, half equilibrium times increase, that is, at a given pH $t_{(0.5)}$ increases for stronger acids. The second important factor is the V/A ratio of the compartment considered. For a spherical compartment V/A = r/3, for a cylindrical one V/A = r/2. So $t_{(0.5)}$ increases with radius. Smaller and more acid compartments will therefore equilibrate sooner than larger and more alkaline compartments. Any receiver volume will equilibrate sooner from smaller and more acid donor volumes, however at decreasing equilibrium concentrations. It is therefore not possible to relate fluoride effects solely to the F concentration of the bathing medium. It is necessary to know of the pH of the medium and the compartments, the ratio of volume to surface area of the compartments, and the duration of uptake.

Xylem translocation will be delt with in the root uptake section.

HF uptake from air into leaves

When HF at a given atmospheric concentration equilibrates via open stomata with the water in cell walls (the apoplast water), the resulting HF concentration depends on the partition coefficient of HF between the gaseous and the liquid water phase, $K^{HF} = c^{HF}_{(g)} / c^{HF}_{(l)}$. Unfortunately, K-values are reported only for relatively high HF concentrations (for technical purposes) and are not fully relevant to air pollution. However, some of the data are given in Figure 1 as a function of temperature, together with values of H_2O and CO_2 for comparison.

HF is highly soluble in H_2O, and its solubility shows a great dependency on temperature. It can be taken as a rule of thumb that at a given temperature atmospheric HF partitions into liquid water 10-fold more than water vapor into liquid water.

An atmospheric HF concentration of 1 µg/m³ air equilibrated with the apoplast water should yield the 10^6-fold higher concentration of about 1 mg HF/l (at 15° C). According to the pH of the water phase HF dissociates and the following concentrations (mg/l) of HF, F^- and their sum are present:

pH	c^{HF}	c^{F^-}	c^F
3.1	1	1	2
4.1	1	10	11
5.1	1	100	101
6.1	1	1000	1001
7.1	1	10 000	10 001

Therefore, at equilibrium apoplastic water with a pH around 6 will contain 1 g F/l (nearly all in ionic form). Thus, a further increase of concentration (with respect to c^{F^-}) by a factor of 10^3 is caused by the action of the

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ionic trap. As becomes evident, the ionic trap concept can be extended to a gaseous-aqueous phase border (instead of a membrane), because of its impermeability to ions.

Considering also cytoplasm to be equilibrated with atmospheric and apoplastic HF, this compartment with a pH around 7 should contain 10 g F/l. On a dry weight basis a total leaf F-concentration of 5000 ppm would result, assuming 20% dry matter and an overall leaf tissue pH of about 6. These are concentrations never found in leaves after exposure to 1 μg HF/m³ air.

What is the reason for this discrepancy? It can be argued that HF from the air does not fully equilibrate with vegetation, even after prolonged periods of exposure. We should ask where the main diffusive resistances are situated and how long it would take to reach half the equilibrium concentration in a leaf. HF diffusion from bulk atmosphere into leaf cells is impeded by a series of air phase resistances, R_{air}, (boundary layer, stomata, intercellular air spaces) plus the resistance in the aqueous phase of the cell walls, R_{cw}, plus the resistance in the lipid phase of the plasmalemma membrane, R_{pm}, and so on into all compartments.

As HF and water vapor has nearly the same diffusion coefficient in air, their resistances are rather similar, too. To estimate the cell wall resistance let us adapt to HF the equation given for CO_2 by NOBEL (1983, p. 423):

$$R_{CW} = \frac{A\ \Delta d\ K^{HF}}{A^{mes}\ D^{HF}}$$

where A is the abaxial leaf surface area, A^{mes} the cell wall area available for diffusion in the mesophyll, Δd the cell wall thickness, K the partition coefficient as defined above, and D the diffusion coefficient of HF within the cell wall water. With a Δd of 1 μm, $A^{mes}/A = 20$, $K^{HF} = 10^{-6}$, and $D^{HF} = 5.10^{-10}\ m^2\ s^{-1}$ (assumed to be lower compared with D in free water because of the tortuous path through cell wall interstices), $R_{cw} = 10^{-4}\ s\ m^{-1}$ related to the abaxial leaf area.

However, this resistance would apply if HF were a nonelectrolyte. Since immediately behind the phase border HF dissociates, its concentration decreases very rapidly and an enhancement of diffusion has to be considered. LISS (1971) has discussed this enhancement factor for SO_2 diffusion

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Fig. 1. Partition coefficients of HF, H_2O and CO_2 between air (g) and water (l) phase versus temperature.

HF, curve a: after vapor pressure data from VIEWEG (1963), $c_{(l)} = 5$ wt. % HF; curve b: after data from KÖTHE & MÜLLER (1973), $c_{(l)} = 1$–2.5 g F/1; round symbol: $K = 3.1\ 10^{-6}$, $c^{HF} \rightarrow 0$, given by FREDENHAGEN & al. (1932); square symbol: $K = 2.1\ 10^{-6}$, $c^{HF} \rightarrow 0$, transformed from Henry's law constant ($K^{-1} = 0.46\ Torr^{-1}$) given by VDOVENKO & al. (1965). H_2O: after vapor pressure data from D'ANS-LAX (1967). CO_2: after NOBEL (1983).

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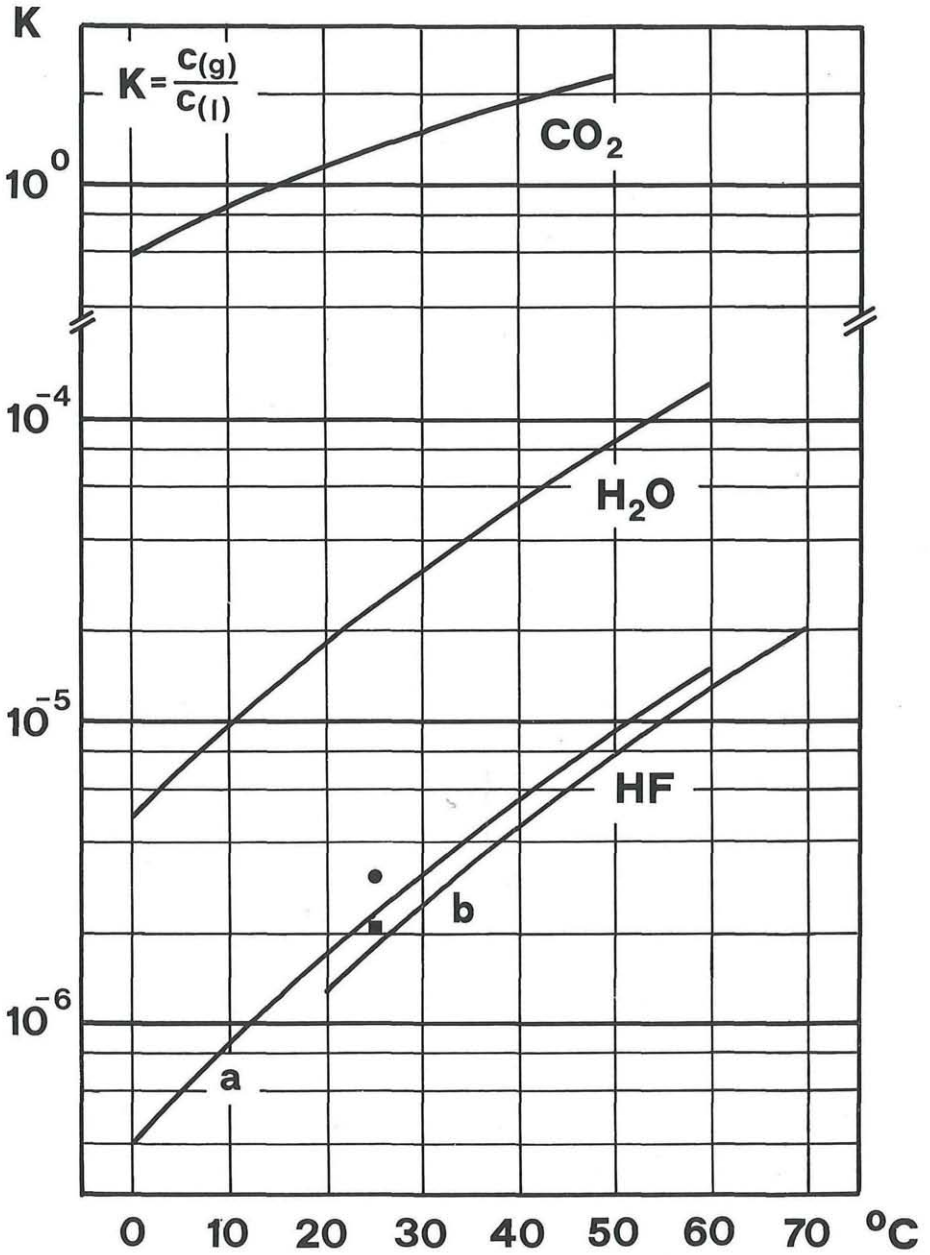

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across an air-water interface. An analogous calculation for HF (not shown here) yields an enhancement of about 250-fold in a 1 μm thick unstirred (cell wall) layer of pH 6. This enhancement is much higher when compared with that of SO_2 (80-fold) or CO_2 (below 2-fold) across the same cell wall.

Thus, with an enhancement factor of 250, R_{cw} decreases to 4.10^{-7} s m^{-1}. This rather small R_{cw} can be neglected in comparison with R_{air}, which ranges from 125 to 500 s m^{-1} for HF related to the total leaf area (compiled by DAVISON 1983) or from 100 to 2000 s m^{-1} for water vapor related to the abaxial leaf area (NOBEL 1983).

Now converting plasmalemma permeability to suit a measure of resistance ($R = K/P$) the value for P_{pm} amounts to $10^{-6}/2.10^{-7}$ s m^{-1} = 5 s m^{-1} related to the plasmalemma area and 0.25 s m^{-1} related to the abaxial leaf area (with $A^{mes}/A = 20$).

It should be noted that R_{air}, R_{cw} and R_{pm}, all are expressed on an air phase basis to be directly comparable. In this system $\triangle c^{HF}$ is expressed in air phase concentrations (although R_{cw} and R_{pm} are not located in the air phase), thus the ratios $\triangle c^{HF}/R$ yield also directly comparable flux densities; to convert R values on an air phase basis to R values on a water phase basis they have to be divided by K^{HF}.

Resistances outlined above are now listed on an air phase basis and are related to the abaxial leaf area:

$$R_{air} = 250 - 1000 \text{ s m}^{-1}$$
$$R_{cw} = 4.10^{-7} \text{ s m}^{-1}$$
$$R_{pm} = 0.25 \text{ s m}^{-1}$$

That means that HF diffusion into the cytoplasm is determined nearly entirely by air phase resistances and not by water or lipid membrane resistances. This is a picture often assumed by previous workers; however, first quantitative estimations are now possible.

To calculate the time necessary for half equilibrium, $t_{(0,5)}$, of a leaf exposed to atmospheric HF the equation

$$t_{(0.5)} = \frac{V_i\, x_i}{A\, P} \ln 2$$

from Table 1 (in part I of this paper) is adapted: V_i can be taken as the fresh water volume of the leaf and A as the abaxial leaf area; x_i represents the overall leaf pH (by $x_i = 1 + 10^{pH_i - pK_i}$). The volume of the bulk atmosphere (V_o), is considered not to decrease in c^{HF}. P transferred to an air phase ($\triangle c^{HF}$) basis equals K/R, therefore

$$t_{(0.5)} = \frac{V_i\, x_i\, R}{A\, K} \ln 2$$

Taking a leaf with a fresh water volume of 100 ml/m^2 abaxial leaf area and an overall pH of 6.1, and assuming the dominant air phase resistances just

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given, $t_{(0.5)}$ ranges from 200 to 800 days. It would, therefore, exceed the lifetime of many leaves to reach half equilibrium. However, in longlived leaves or needles concentrations not even half that high were found; the question remains, why.

There are several reasons. For example, F causes partial closure of stomata and so R_{air} further increases; some F can be lost from leaves by translocation to other plant organs. Under field conditions, F may be leached by rain. See also DAVISON (1983) for further reasons of F loss.

Considering the specific properties of HF, the following aspect should be kept in mind, too: HF is a gas which highly partitions into water and which can be ion-trapped in water directly from air, as well as after diffusion through biological membranes. For such a gas any liquid water (free or membrane surrounded) represents a strong sink in the biogeosphere, much more than for nonelectrolyte gases and for electrolyte gases less soluble in water, or with higher pK. A dense plant canopy, therefore, is a far stronger sink (related to the ground area) than a single model leaf. This sink is to be filled up with HF from an imaginary air column above the canopy ground area which will be depleted from HF more easily than from nonelectrolytes or from electrolytes less soluble in water. Thus, the HF concentration adjacent to the boundary layer will be lower compared to a given reference height above ground. Therefore, an additional resistance in the turbulent air has to be taken into account (see NOBEL 1983, for a discussion of turbulent air resistances of H_2O and CO_2), which should become much more dominant for HF than for H_2O or CO_2. Summing up, the high equilibrium concentrations stated above but never found do not contradict an ion trap mechanism, and vegetation in fact does not equilibrate with HF in real times.

Until now only the pathway through stomata was considered. A second path normally considered to be of minor importance is the cuticle. CHAMEL & GARREC (1977) investigated $^{18}F^-$ penetration through isolated, astomatous pear leaf cuticles. From their data a P value of 1.1 10^{-8} m s^{-1} (on a water phase Δc^{F^-} basis) results for the F^- ion. In a study with isolated cuticles from *Monstera deliciosa* leaves with closed stomata (adaxial leaf side: 3 stomata/mm^2, abaxial leaf side: 44 stomata/mm^2) GARREC & PLEBIN (1986) found a P^{F^-} of 0.19 10^{-8} and 2.3 10^{-8} m s^{-1} for the adaxial and abaxial side respectively. These authors investigated also P^{HF} of *Monstera* cuticles: considering only the P values of 1.3 10^{-4} and 4.9^{-4} m s^{-1} (which contain the lowest boundary layer resistance applied) for the adaxial and abaxial side respectively, and converting them to a water phase (Δc^{HF}) basis, P^{HF} would amount to 1.3–4.9 10^{-10} m s^{-1} (with a K = 10^{-6}). Thus P^{HF} would even be lower than P^{F^-} and would also range lower than P for water vapour (around 10^{-9} m s^{-1}, SCHÖNHERR 1982) of isolated cuticles.

These first data available suggest that P^{F^-} and P^{HF} of cuticles do not

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differ exceptionally. A cuticle, therefore, would not allow an ion trap to operate in contrast to a plasmalemma or to an air-water interface.

If the data are more widely applicable, cuticular uptake of HF indeed is of minor importance, but cuticular uptake of F^- could contribute eventually under certain conditions. We may consider the leaf surface as an outer compartment of a leaf (phylloplane) with a poorly defined and variable volume. A wetted leaf has a large phylloplane volume, a dry one nearly zero. The phylloplane may contain up to 50% of the total F of a leaf, some of it easily removable by short washing. It seems that phylloplane F occurs in many and quite different states: e. g. solved in water (if present), adherent to or embedded in waxes (in particulate form), or fixed to adsorptive binding sites.

It has been shown that in field exposed spruce needles absolute and relative amounts of F removable by short washing decrease with increasing needle age, probably due to degradation of waxes; on the other hand older needles showed a greater permeability to surface-applied as well as to internal F than younger ones (KRONBERGER 1981).

As regards the ion trap mechanism, only a wet phylloplane will be considered, which is wetted by dew or mist not dropping from leaves. A water surface outside the leaf represents a far better possibility for HF absorption than apoplastic water, as it is separated from the bulk of air by the boundary layer resistance only. This resistance should nearly equal that for water vapour, namely 13–130 s m^{-1} (NOBEL 1983), which is much lower than the resistance between apoplast and atmosphere, even when stomata are open.

As a consequence, half equilibrium time will be much lower, too, provided volume to surface area ratio and pH of the water are similar to the apoplast. Furthermore, small (and nowadays often more acid) mist droplets with an extreme V/A ratio may equilibrate far quicker and already arrive F-loaded on the leaf surface. When phylloplane water evaporates after a wet period, further concentration takes place and leads to a very high driving force ($\triangle c^{F^-}$) across the cuticle. During that time cuticular F^- uptake may be rather high and compare with stomatal uptake. Under changed conditions, such as clean air and clean rain water dropping from leaves, the driving force will be reversed after the removal of previous phylloplane F, and internal fluoride can move across the cuticle into the phylloplane.

Accumulation of F via the cuticle may highly depend on environmental factors and on the plant species considered. So the pH of rain or fog water is reported to further decrease when evaporating (FREVERT & KLEMM 1984). Thus, from an extreme acid phylloplane, such as from conifers HF would degas back into the atmosphere. On the other hand, members of the *Malvaceae* are found to have an extreme alkaline phylloplane (up to pH 11) due to secretion of Mg- and K-carbonates (HARR & al. 1984). In this case the

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phylloplane provides a very effective ion trap to F^-. However, cuticular uptake will be limited when Ca^{++} is present in the phylloplane, since F^- concentration is restricted to a value determined by the solubility product of CaF_2. A last example may demonstrate the practical relevance of cuticular uptake: in a field study performed in Logan, Utah, WALLENDER & KELLER (1984) have shown that bush bean plants accumulate F when sprinkler irrigated. Accumulation increased with the F^- concentration of the applied water, the sprinkler set time, the evaporative demand, and the sprinkler rotation speed.

HF uptake from soil solution into roots

Diffusion from soil solution across a root into the central xylem may follow several paths interconnected to form a resistance network (see Fig. 2), namely: (1) across cell walls and plasmalemmata of root hairs into the root hair symplast; (2) along cell walls and across plasmalemmata of cortex parenchyma cells into the cortex symplast; (3) from cortex cell walls across the outer plasmalemma of the endodermis into the plasma of endodermis; (4) along the symplasts of root hairs, cortex and endodermis *via* plasmodesmata into the symplast of the stele (pericycle and stelar parenchyma); (5) across plasmalemmata of the inner side of endodermis, the pericycle and stelar parenchyma through stelar apoplast into xylem vessels.

Diffusion within aqueous phase paths (apoplast, symplast) is possible for HF and F^-, whereas diffusion of F^- is prevented by lipid membranes and diffusion of both species by the Casparian strip.

To roughly estimate the rate-limiting steps across a root let us consider some selected resistances of a model root with the following dimensions: root diameter 1.4 mm (radius of the stele 200 μm, thickness of the cortex 500 μm), diameter of cortex parenchyma cells 40 μm, of stelar parenchyma cells 20 μm, and of root hairs 12 μm, thickness of parenchyma and root hair cell walls 1 μm.

Let us relate estimated resistances to a reference area (A), namely to the part of the endodermal plasmalemma facing the inner, stelar side of the root, $A^e_{pm,i}$ = (A). It also would be possible to choose the outer side facing the cortex, $A^e_{pm,o}$, or any other tangential layer as a reference area. This cross sectional area for the HF flow in radial direction into a cylindrical body may serve as a reference to other cross sectional areas.

Consider the radial path tortuosly along the cortex cell walls, then the cross sectional cell wall area, A^c_{cw} will amount to 5% of each tangential layer area. As the area of each cortex layer increases toward the rhizodermis from (A) to 3.5 (A), also A^c_{cw} becomes larger. Thus, the cell wall resistance per layer (all together connected in series) will decrease toward the rhizodermis with respect to (A). Consider now the path across the cortex parenchyma plasmalemmata, where diffusion of HF from cell walls into the

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symplast occurs from all directions. Here the single cell resistances are connected in parallel. As the total plasmalemma area of the cortex, A^c_{pm} is assumed to be 50 (A), the total plasmalemma resistance, R^c_{pm} will be 50 times lower with respect to (A).

Resistances are now estimated on a water phase ($\triangle c^{HF}$) basis: from a plasmalemma permeability of 2.10^{-7} m s^{-1} the plasmalemma resistance of the inner endodermis side, $R^e_{pm,i}$ amounts to 5.10^6 s m^{-1} with respect to its area (A). About the same value may be taken for the outer endodermis side. As just outlined, R^c_{pm} is 50-fold lower when related to (A), thus 1.10^5 s m^{-1}. Root hair plasmalemma surface are, A^{rh}_{pm} may also be assumed 50 (A), so R^{rh}_{pm} = 1.10^5 s m^{-1}, too. Plasmalemma resistance of the pericycle, R^{pc}_{pm} will be near 2.5 10^6 s m^{-1} because of a near 2-fold membrane area compared with (A). The resistance of each tangential layer of stelar parenchyma will increase stepwise, as the membrane area decreases stepwise toward the centre.

All the membrane resistances given are for HF only. In order to compare them with water phase resistances it is necessary to stay within a system where $\triangle c$ is expressed in HF concentrations. However, resistances in the water phase of apoplast and symplast discussed now are concerned with both HF and F^-. As the diffusion coefficients for both species are rather similar, their resistances will be also similar. On the other hand the driving force for HF and F^- might be quite different, depending on the pH of the water phase. E. g. at a homogeneous pH of 6.1 throughout the pathway a 1000-fold higher $\triangle c$ for F^- exists compared with $\triangle c$ for HF. This causes also a 1000-fold higher flux density of F^- across a similar resistance. HF is accompanied by diffusive flow of F^- (in this example the joint flow is almost completely governed by F^-). Thus a hypothetical "joint resistance" with respect to HF as the species considered is 1000-fold lower in the example given. Expressed in a general form, the "joint resistance" equals $R/x = R/(1 + 10^{pH-pK})$, where pH denotes the pH of the aqueous phase path and pK is the pK of the weak acid (here of HF).

It may be remarked that this discussion leads to the same result as derived by WALTER & al. (1982) for the resistance of an unstirred and sufficiently buffered layer to a weak acid. Their expression $1/P([HA] + [A^-])$ corresponds to R/x when [HA] is unity. In analogy, $P([HA] + [A^-])$ could be defined as a "joint conductance".

In part I of this paper R/x values were used to correct the measured P values obtained from the turion experiments.

Now the resistance across the cell walls of root hairs (1 μm path length) can be calculated to be $R^{rh}_{cw} = \triangle d/D = 1.10^{-6}/5.10^{-10} = 2.10^3$ s m^{-1} related to A^{rh}_{cw}. Related to (A) it is 50 times lower, and assuming a homogenous pH of 6.1, R^{rh}_{cw}/x decreases 1000 times to 4.10^{-2} s m^{-1}.

The radial path length along the cell walls of the cortex (500 μm thick) with a tortuosity of 1.6 amounts to 800 μm. Therefore, R^c_{cw} = 1.6 10^6 s m^{-1} related to the cross sectional area A^c_{cw}, and because $A^c_{cw}/(A) = 0.05$, R^c_{cw} =

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Table 2

Resistances to diffusion of HF through selected pathways in a model root. Details of derivation see text.

	R in s m^{-1}	R related to	F species considered
R_{pm}	$5 . 10^6$	A_{pm}	HF
R^{rh}_{pm}	$1 . 10^5$ *	(A)	HF
R^{c}_{pm}	$1 . 10^5$ *	(A)	HF
$R^{e}_{pm,i,o}$	$5 . 10^6$ *	(A)	HF
R^{pc}_{pm}	$2.7 . 10^6$ *	(A)	HF
R^{sp}_{pm}	$3.0 . 10^6$ *	(A)	HF
R^{rh}_{cw}	$2 . 10^3$	A^{rh}_{cw}	HF, F^-
R^{rh}_{cw}	$4 . 10^1$	(A)	HF, F^-
R^{rh}_{cw}/x	$4 . 10^{-2}$ *	(A)	HF (+ F^-), pH 6.1
R^{c}_{cw}	$8 . 10^5$	A^{c}_{cw}	HF, F^-
R^{c}_{cw}	$1.6 . 10^7$	(A)	HF, F^-
R^{c}_{cw}/x	$1.6 . 10^4$ *	(A)	HF (+ F^-), pH 6.1
R^{sp}_{cw}	$4 . 10^5$	A^{sp}_{cw}	HF, F^-
R^{sp}_{cw}	$4 . 10^6$	(A)	HF, F^-
R^{sp}_{cw}/x	$4 . 10^3$ *	(A)	HF (+ F^-), pH 6.1
R_{pd}	$5 . 10^2$	A_{pd}	HF, F^-
R_{pd}	$2.5 . 10^6$	A_{pm}	HF, F^-
R^{rh}_{pd}	$7 . 10^5$	(A)	HF, F^-
R^{rh}_{pd}/x	$7 . 10^1$ *	(A)	HF (+ F^-), pH 7.1
R^{c}_{pd}	$1.3 . 10^7$	(A)	HF, F^-
R^{c}_{pd}/x	$1.3 . 10^3$ *	(A)	HF (+ F^-), pH 7.1
R^{e}_{pd}	$2.5 . 10^6$	(A)	HF, F^-
R^{e}_{pd}/x	$2.5 . 10^2$ *	(A)	HF (+ F^-), pH 7.1
R^{pc}_{pd}	$2.8 . 10^6$	(A)	HF, F^-
R^{pc}_{pd}/x	$2.8 . 10^2$ *	(A)	HF (+ F^-), pH 7.1

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3.2 10^7 m^{-1} related to (A). This would apply if A^c_{cw} were a plane, but in the cylindrical cortex A^c_{cw} increases toward the rhizodermis 3.5-fold as already discussed. Related to (A) a larger area than 5% is to be taken, namely 2-fold more in a cylindrical body with the dimensions assumed. Thus, R^c_{cw} equals 1.6 10^7 s m^{-1} with respect to (A). At a pH of 6.1 R^c_{cw}/x will be 1.6 10^4 s m^{-1}. In analogy, cell wall resistance of stelar parenchyma, R^{sp}_{cw} , can be estimated and is listed in Table 2.

To estimate the resistance of the plasmodesmata, R_{pd}, it is assumed that they occupy 0.2% of a plasmalemma area and that only 10% of their pores are open aqueous channels with a path length of 1 μm (NOBEL 1983). The resistance of the pores amounts to $\Delta d/D = 1.10^{-6}/2.10^{-9} = 5.10^2$ s m^{-1}. Related to the plasmalemma area R_{pd} increases by $1/0.002 \cdot 0.1 = 5.10^3$, thus R_{pd} = 2.5 10^6 s m^{-1}. Plasmodesmata from root hairs to cortex cross the inner rhizodermal cell walls, an area about 3.5 times larger than (A). R^{rh}_{pd} related to (A) will therefore amount to 7.10^5 s m^{-1}, and assuming a cytoplasmatic pH of 7.1, $R^{rh}_{pd}/x = 7.10^4$ s m^{-1}. In the cortex plasmodesmata can be considered connected in series, tangential cell layer by tangential cell layer. In the radial direction 12 layers are to be crossed, the area of each layer decreasing stepwise from 3.5 (A) to (A). Therefore, the resistance per layer increases stepwise. The sum of these 12 resistances in series, R^c_{pd}, is listed below. Plasmodesmatal resistances from endodermis to pericycle (R^e_{pd}) and from pericycle to the first stelar parenchyma layer (R^{pc}_{pd}) are given separately.

All values listed in Table 2 are on a water phase (△c HF) basis and those indicated by an asterisk are relevant for comparison in the resistance network in Figure 2.

The total resistance across the symplast caused by plasmodesmata adds up to about 2.10^3 s m^{-1}, which is rather small compared with membrane resistances. Cytoplasmic resistance will be even lower, because of enhancement of diffusion in the unstirred layer behind a plasmalemma in the same way as behind a phase border (LISS 1971), of the larger cross sectional area and of cytoplasmic streaming. Therefore, the symplast may be considered as a fairly good path for the diffusion of HF (together with F^-). Resistance across root hairs can be neglected, whereas the resistance along the cortex cell walls is higher compared with the symplast.

The main resistance outside the endodermis is situated in the plasmalemmata. Connected in parallel, R_{pm} of cortex and root hairs amounts to 5.10^4 s m^{-1} (from soil solution into symplast). However, the rate limiting resistances across the whole root are given by the plasmalemmata of the inner side of the endodermis, the pericycle and the stelar parenchyma. On the path from symplast to xylem these membrane resistances are connected in parallel.

In the arrangement given in Figure 2 (with only one stelar parenchyma layer) the total resistance will amount to 1.11 10^6 s m^{-1}. With each additional stelar parenchyma layer along the path to the xylem this resistance will

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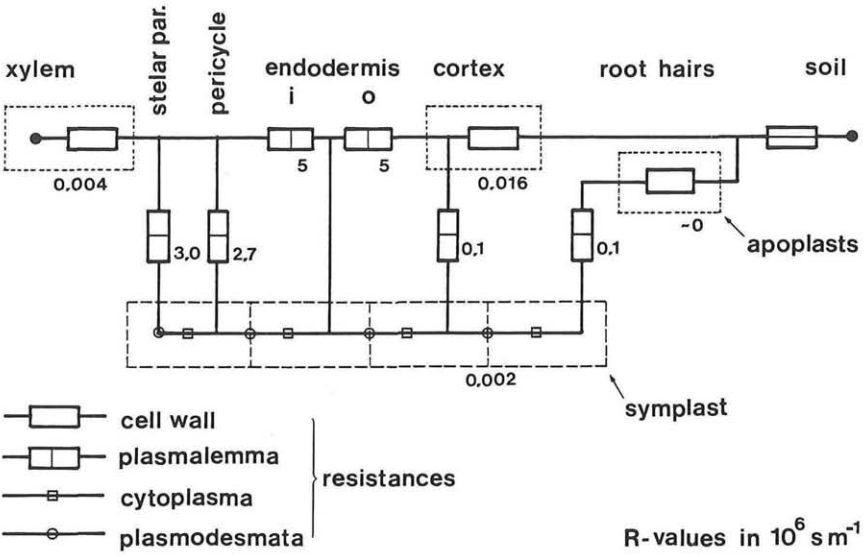

Fig. 2. Resistance network for diffusion of F across a root in the region of cell differentiation. For explanation see text.

decrease, provided there are plasmodesmatal connections between the parenchyma cells. Although such connections were reported (ROBARDS 1975) to exist normally, ANDERSON & HOUSE (1967) could not find them in *Zea mays* stelar parenchyma.

So the total resistance to HF across a root will depend on the distribution of plasmodesmata within the stele and may vary with the plant species considered; it will not be very sensitive to variation of single path resistances outside the endodermis.

As a first rough estimate let us assume therefore the total resistance to HF diffusion across the whole root to range from 0.7 to 1.8 10^6 s m^{-1} on a water phase basis and related to (A).

It should be noted that the ratio of apoplastic or symplastic to membrane resistance is valid only for an electrolyte of a pK near 3. With electrolytes of a higher pK and nonelectrolytes, showing the same plasma membrane permeability, this ratio may decrease or even reverse.

To further illustrate the kinetics of HF diffusion half equilibrium times for selected compartments are listed in Table 3. Each donor volume (V_o) is considered not to decrease essentially in HF concentration during diffusion. Resistances and root dimensions are taken as given above. Apoplast pH and overall pH_i of living cells are assumed to be 6.1 (x and $x_i = 10^3$).

If receiver volumes (V_i) are filled via plasmalemma resistances $t_{(0.5)}$ is calculated by $\frac{V_i\, x_i\, R}{A} \ln 2$. If V_i is filled via aqueous phase resistances (e. g.

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the cortex apoplast via its own resistance from soil solution) R/x has to be used instead of R. Thus at a homogenous pH along the path, x_i and x cancels out and $t_{(0.5)}$ equals $\frac{V_i R}{A}$ ln 2, the same as for a nonelectrolyte.

Data in Table 3 indicate that apoplastic volumes in contact with the soil solution equilibrate rather quickly. To fill up the symplast it takes far longer, and to reach the stelar apoplast with the xylem vessels a further increase of $t_{(0.5)}$ is seen. This last step shows a marked dependency on the distribution of plasmodesmata within the stele, as has been already discussed for resistances.

Overall, half equilibration time from soil solution to xylem may be assumed to be longer than $t_{(0.5)}$ from symplast to stele. This is the case especially with variant (c), as the symplast does not equilibrate quickly enough with the apoplast to maintain a constant HF concentration as a donor volume (which was assumed for calculation).

On the other hand, mass flow of water into the root caused by the transpiration stream will support the transport by diffusion. Along aqueous pathways this support also shortens $t_{(0.5)}$, especially for long distances (as $t_{(0.5)}$ raises with the second power of path length). However, aqueous paths into a root are not rate-limiting for HF diiffusion. Therefore, this support will not contribute essentially, but it will be dominant in the long axial pathway of the xylem vessels. Whether there exists such a support for HF across the rate-limiting plasmalemma resistances due to "solvent drag" (STEIN 1967) remains open until experimental data are available. The possibility should be kept in mind.

Let us now compare the leaf with the root in HF uptake from their environment: in the leaf, 200 to 800 days are necessary for half equilibration with atmospheric HF, whereas in the root half equilibrium time for HF from

Table 3

Half equilibrium times, $t_{(0.5)}$ for diffusion of HF into selected compartments of a model root. Plasmodesmata considered to reach up (a) into the pericycle, (b) into the first, and (c) into the third stelar layer. Variant (b) corresponds to Figure 2.

$t_{(0.5)}$	from (V_o)	into (V_i)
0.001 seconds	soil solution	root hair apoplast
3 minutes	soil solution	cortex apoplast
2.9 hours	root hair apoplast	root hair symplast
6.4 hours	cortex apoplast	cortex symplast
31 hours	symplast	stele (a)
17 hours	symplast	stele (b)
8 hours	symplast	stele (c)

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the soil solution range around 1 day. The main resistance is given by the air phase in the leaf, whereas by the lipid membrane pathways in the root.

Furthermore, one may consider the central stele of a root as a compartment in which also apoplastic regions of a tissue are able to trap ions. From this it follows that a loading of the xylem sap by nonionic diffusion of permeable electrolytes can take place in the stele. A relatively high accumulation can be achieved by an ionic trap mechanism, and therefore this may cause also an increase in osmotic pressure and, thus an additional driving force for the uptake of water.

F translocation to the shoot. F in the apoplast of the stele will be carried away by mass flow with water within the xylem vessels. When the xylem sap passes through older parts of the root and through the stem, HF will diffuse into the cells surrounding the xylem and F will accumulate there. Some of the F diffusing out of the xylem will accumulate also in sieve tubes and be swept back towards the root tip. Thus, with an increasing distance from the uptake zone of the root, F concentration in the xylem sap will decrease and only a minor amount of F will reach the leaves.

When comparing F taken up by a leaf with F taken up by a root, a common property becomes apparent: in both organs F is more or less retained. F uptake by a root, assumed to be a purely diffusive process in the model given above, will therefore depend on the driving force, namely the $\triangle c^{HF}$ between the soil solution and the xylem, and the resistance across this pathway. With a given root surrounded by a soil solution of a given F concentration, diffusion will increase with increasing $\triangle c^{HF}$. This should occur with a decreasing pH of the soil (or of a nutrient) solution. A higher F uptake from acid soils has been observed repeatedly (see DAVISON 1983) and compares well with the model.

On the other hand, translocation from root to shoot will depend on the volume flow of the xylem sap (i. e. on transpiration), on the F storage capacity of the cells surrounding the xylem vessels and from the exchange rate between the xylem vessels and these cells (specially the phloem). This picture compares also well with data obtained from field grown or experimentally treated plants.

However, as the single steps were not studied so far in detail, quantitative relations remain to be established.

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