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Phloem Mobility of Xenobiotics

I. MATHEMATICAL MODEL UNIFYING THE WEAK ACID AND INTERMEDIATE PERMEABILITY THEORIES

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ABSTRACT

A passive diffusion model has been developed which simultaneously accounts for the dependence of phloem mobility on permeability and acid dissociation. The model is consistent with the observation that the addition of an acid moiety to an otherwise phloem immobile compound may enhance that compound's ability to move in the phloem. However, acid trapping in the basic phloem is not the only enhancement factor. Acid functionalization also lowers the effective permeability usually towards its optimum value. The unified theory predicts that for a given acid dissociation constant there is an optimum permeability and conversely for a given permeability there is an optimum dissociation constant.

According to one theory, the phloem mobility of a compound depends upon the presence of a weak acid functionality within that compound (2). Another theory deals with compounds which are nonelectrolytes at physiological pH and ascribes efficient phloem mobility to compounds whose membrane permeabilities fall within some optimum range (6, 8). The optimum range is determined by attributes such as plant length, leaf size, phloem sap velocity, etc. The latter theory has been developed into a mathematical model (8). Neither of these theories invokes a carrier mechanism and the two theories are not necessarily in opposition. This paper describes an extension of the mathematical model (8) that unifies the two theories. The extended model explains in a straightforward fashion the enhanced phloem mobility of weakly acidic compounds without invoking a carrier mechanism. While the model provides for acid trapping within the sieve tubes, the mobility of weak acids is in large part due to their intermediate permeability.

Table I. *Abbreviations and Symbols Used in the Text*

L:	Length of plant in m
l:	Length of leaf in m
l^*:	Length of leaf in m over which compound is applied
r:	Radius of sieve tube in m
v:	Maximum velocity of phloem sap in m/s
s:	Distance from leaf tip in m
HA:	An undissociated acid
A^-:	Conjugate base of HA
$[\mathrm{HA}]_o$:	Concentration of HA (M) in apoplast
$[\mathrm{HA}]_s$:	Concentration of HA (M) within sieve tube at a distance s from leaf tip
$[A^-]_o$:	Concentration of A^- (M) in apoplast
$[A^-]_s$:	Concentration of A^- (M) within sieve tube at a distance s from leaf tip
$C_{t,o}$:	Total concentration of xenobiotic (M) in leaf apoplast; total of $[\mathrm{HA}]_o$ and $[A^-]_o$
$C_t(s)$:	Concentration of xenobiotic (M) within the sieve tube at a distance s from the leaf tip; total of $[\mathrm{HA}]_s$ and $[A^-]_s$
C_f:	Concentration factor (unitless); the ratio of C_t (0.9 L) to $C_{t,o}$
$[\mathrm{H}^+]_i$:	Hydrogen ion concentration (M) within sieve tube
$[\mathrm{H}^+]_o$:	Hydrogen ion concentration (M) within apoplast
P_{HA}:	Permeability of HA in m/s
P_A:	Permeability of A^- in m/s
K_a:	Acid dissociation constant of HA (M)
pK_a:	Log $(1/K_a)$
K_{ow}:	Octanol-water partition coefficient
n_{HA}:	Number of moles of HA
$n_A{}^-$:	Number of moles of A^-
Q:	Area of cylindrical sieve tube element (m^2)
v_s:	Flow velocity (m/s) of phloem sap at a distance s from leaf tip

THEORY

The model used is an extension of that of Tyree *et al.* (8). It consists of a linear plant of length L[1] (Fig. 1). A xenobiotic is assumed to have been applied over a length l^* of the leaf whose length is l. The length of the leaf, petiole, and stem is $0.5L$, while the root system accounts for the other half of the plant's length. Phloem sap is assumed to flow through a sieve tube of radius r. The velocity of the phloem sap is assumed to rise linearly from near zero at the leaf tip until it reaches a maximum value of v which is maintained throughout the petiole and stem. Xenobiotic is assumed to enter the sieve tubes in the leaf zone by passive diffusion driven by a concentration gradient. For an acidic substance, HA, the total concentration of xenobiotic in the leaf apoplast, $C_{t,o}$, is defined as the sum of the concentrations of HA and A^- where A^- is the conjugate base of HA. All concentrations may be assumed to be in mol/L. Analogously, $C_t(s)$ is defined as the total concentration of xenobiotic at point s in the leaf sieve tube. Generally, $C_{t,o}$ will exceed $C_t(s)$ for $s < l$, that is within the leaf. Hence, within the leaf portion of the plant there is a net flow of xenobiotic into the sieve tube.

In the stem and petiole, the concentration of xenobiotic in the apoplast surrounding the sieve tube (including the xylem) is assumed to be zero. Hence, some of the xenobiotic leaks into the apoplast as the phloem sap carries the remaining portion towards the root. The xenobiotic which leaks into the apoplast is assumed

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[1] A complete list of abbreviations and symbols appears in Table I.

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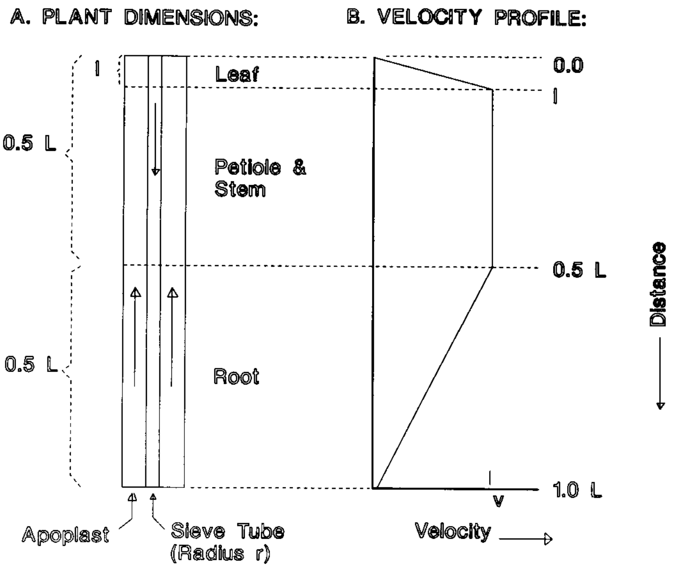

FIG. 1. Definition of plant parameters. A, plant dimensions. L is the total length of the plant. The length of the leaf, petiole and stem taken together is 0.5 L. The length of the root is 0.5 L; l is the length of the leaf. The radius of the sieve tube is r. B, Velocity profile assumed for this model. The velocity rises linearly from near zero at the leaf tip to a value of v at the base of the leaf. The phloem sap velocity is maintained at the constant value of v throughout the petiole and stem. At the base of the stem the sap velocity begins to fall linearly towards a value of near zero at the bottom of the root.

to return quickly to the leaf through the transpiration stream. As the mathematical elaboration of the model will confirm (Appendix A), what is needed to concentrate the xenobiotic in the root zone is a compound that is permeable enough to penetrate into the sieve tubes within the leaf zone but is not so permeable as to leak back into the apoplast during its passage to the root zone. For an acidic substance, both the neutral and anionic species are assumed capable of permeating the sieve tube membrane, but the neutral species is assumed to have a permeability that is approximately 4 orders of magnitude greater than that of the anionic species. This assumption follows from the observation that the ionized form of a carboxylic acid lowers the octanol-water partition coefficient by 3.7 orders of magnitude relative to the undissociated form (3). Acid-base equilibrium is assumed to be maintained at all times and at all points in both the apoplast and in the phloem sap within the sieve tubes. Furthermore, the fluids in the apoplast and phloem are assumed to be buffered. Once in the root zone, the phloem velocity is assumed to decrease linearly with distance until reaching a value of nearly zero at the root tip.

Using the above assumptions, differential equations governing the rate of flow of xenobiotic through sieve tube elements of the leaf, stem, and root are derived. A steady state is then assumed so that the amount of xenobiotic entering a sieve tube element in a given period of time is just balanced by the amount leaving. The resultant steady state equations for both the neutral and anionic species are similar in form to those derived by Tyree *et al.* (8). They are thus solved in an analogous fashion. Details of the derivation are given in Appendix A. If the concentration factor C_f is defined as the ratio of total concentrations, $C_t(0.9L)/C_{t,o}$, where $C_t(0.9L)$ is the total concentration of xenobiotic within the phloem sap at a point deep in the root zone and $C_{t,o}$ is the total concentration at the point of application in the leaf apoplast, then the following equation may be derived:

$$
\begin{aligned}
C_f &= C_t(0.9L)/C_{t,o} \\
&= \{([H^+]_i + K_a)/([H^+]_o + K_a)\} \qquad (1) \\
&\quad \times \left[\frac{(a)([H^+]_o P_{HA} + P_A K_a)}{[H^+]_i(P_{HA} + b) + K_a(P_A + b)} \right] \\
&\quad \times \exp\{-c([H^+]_i P_{HA} + P_A K_a)/([H^+]_i + K_a)\}
\end{aligned}
$$

In this formula, K_a is the acid dissociation constant, $[H^+]_i$ and $[H^+]_o$ are the hydrogen ion concentrations inside and outside the sieve tube respectively, P_{HA} and P_A are the permeabilities of the undissociated acid and conjugate base respectively, in m/s, and a, b, and c are parameters which characterize the linear plant:

$$a = 5.0\, l^*/l$$
$$b = rv/2l$$
$$c = 2.609L - 2\,l(1 - \ln(l/l^*))/rv$$

Here L is the length of the plant, l is the length of the leaf, l^* is the length of the leaf over which xenobiotic has been applied, r is the sieve tube radius (all in m), and v is phloem sap velocity (m/s) in the petiole and stem.

We note that Eq. 1 passes smoothly into equation 14 of Tyree *et al.* (8) in the limits when $K_a = 0$ and when K_a is very large. In the former case the permeability appearing in the limiting equation is that of the undissociated species HA, and in the latter case the permeability appearing in the limiting equation is that of the anion, A^-. Also observe that Eq. 1 passes smoothly into Eq. 14 of Tyree *et al.* when $[H^+] = [H^+]_i = [H^+]_o$. In this instance the permeability appearing in the limiting equation is

$$P_{ave} = ([H^+]P_{HA} + K_a P_A)/([H^+] + K_a)$$

which is the average permeability of HA and A^- at the prevailing pH.

Since experimental values for permeabilities are not readily available, an empirical relationship was sought between permeability P and the more easily measured or estimated octanol-water partition coefficient K_{ow}. The octanol-water partition coefficient of a substance is the concentration of the substance in the octanol phase of a two phase octanol-water system divided by the concentration in the water. The following linear relationship between permeability and octanol-water partition coefficient was derived from data found in the literature (1) for the permeation of 70 compounds through *Nitella* cell membranes:

$$\log P = 1.20 \log(K_{ow}) - 5.85 \qquad (2)$$
$$r = 0.85$$

In this equation P has the units m/s and r is the correlation coefficient for the least squares fit. Using Eq. 2 the expression for the concentration factor C_f was recast in terms of the $\log(K_{ow})$ of the xenobiotic.

The coefficients on the right hand side of Eq. 2 may be considered as plant parameters. These coefficients will depend upon the thickness and viscosity of the sieve tube membranes, and ultimately upon the chemical composition of the membranes. Plant cell membranes may differ from *Nitella* membranes in a significant way. In fact, a relationship consistent with tighter membranes has been determined for potato tuber discs (5). Thus, the permeability values predicted by Eq. 2 may in fact be too high. This point is worthy of further investigation.

RESULTS

Phloem sap is maintained at a pH more basic than that of the surrounding apoplast. Thus, in order to model the phloem mobility of acids, we have taken the pH of the phloem sap to be 8.0 and that of the apoplast to be 6.0 (9). For our standard long plant we have taken a length of 1.0 m, a leaf length of 0.05 m,

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sieve tube radius of 5.0 μm, and a phloem transport velocity 0.1 mm/s. These parameters are characteristic of potato plants (8). The xenobiotic was assumed to be spread over the entire leaf ($l = l^* = 0.05$ m).

The calculated log C_f values as a function of pK_a and $\log(K_{ow})$ are provided in Table II and plotted in Figures 2 and 3. It is to be noted that we usually take $\log(K_{ow})$ for the undissociated acid (HA) to be 3.7 greater than that of the conjugate base (A^-). For a given pK_a, Figure 2 demonstrates that these is an optimum $\log(K_{ow})$ which represents a balance between the high permeability required for the xenobiotic to permeate the sieve tube membranes within the leaf and the low permeability required for the compound to remain largely entrapped on its path to the root zone. The improvement in phloem mobility to be expected from acid functionalization is evident when the curves labeled $pK_a = 14$ and $pK_a = 4$ are compared.

Just as there is an optimum $\log(K_{ow})$ for a given pK_a, there is an optimum pK_a for a given $\log(K_{ow})$. An oily acid with a high pK_a favors rapid entry into the phloem within the source leaf but makes for a leaky passage through the stem and petiole. A low pK_a enhances the ability of the xenobiotic to remain in the phloem en route to the root zone but slows entry into the phloem at the source. Again, the optimum pK_a represents a balance between these opposing considerations.

From this model it is clear (Fig. 3) that a xenobiotic which is both nonacidic and highly permeable (high $\log[K_{ow}]$) represents a very poor candidate for phloem mobility. Such a substance would fall into the deep well of the depicted surface. It would readily enter the sieve tubes of the treated leaf, but would just as readily be lost from the symplast as the compound moved down through the petiole and stem. Such compounds have been termed pseudoapoplastic (7). However, one way of drawing a compound out of the well is to functionalize it with an acidic substituent. This will have the effect of simultaneously lowering the permeability of the parent and decreasing the pK_a, both changes tending to move the compound up and perhaps over the lip of the abyss. Thus, the weak acid theory and the intermediate permeability theory of phloem mobility are seen to be incorporated into a single model. It should be noted, however, that the model, while incorporating an acid trapping factor in the presence of a pH differential, predicts improved mobility for an acid functionalized compound even when the pH differential is zero (Table III). Thus, acid trapping usually improves the mobility of weakly acidic compounds, but much of the improvement is simply due to reduction of the effective permeability upon acid functionalization.

In order to provide a feeling for the effect of plant parameters on phloem translocation, we have also calculated the phloem mobility of a series of compounds as a function of pK_a and $\log(K_{ow})$ for a shorter plant (Table IV). Our standard short plant is identical to the standard long plant except that its length is 15 cm and the sap velocity is taken as 0.3 mm/s. As expected, the calculated C_f values are generally much larger for the short plant than for the long plant. This is due to the much shorter transit distance through regions of the plant where the xenobiotic can leak back into the surrounding apoplast.

As specific examples, we note that benzoic acid with a pK_a of 4.2 and a $\log(K_{ow})$ of 1.87 should fall near the maximum on the right forward edge of the surface depicted in Figure 3. On the other hand, a nonacidic compound such as *N*-methylpyridinium chloride with a pK_a nominally of 14 and a $\log(K_{ow})$ of −3.3 should fall near the maximum on the back edge of the surface depicted in Figure 3. Modest structural modifications of these parent compounds may have significant effects on phloem mobility. In order to test the model, we have performed a systematic study of the effect of structural modifications of benzoic acids and *N*-alkylpyridiniums on phloem mobility. In the case of the benzoic acids we have attempted to vary the pK_a while maintaining a roughly constant $\log(K_{ow})$. In the case of the *N*-alkylpyridiniums we have varied the length of the alkyl chain in order to study the effect of changing the $\log(K_{ow})$ while maintaining a constant pK_a. The results of these systematic studies are reported in a companion paper (4).

APPENDIX

Mathematical Elaboration of the Model. Consider a cylindrical sieve tube element of length ds and radius r located at a distance s from the leaf tip (Fig. 4). Let n_{HA} and n_{A^-} represent the number of moles of undissociated acid HA and conjugate base A^-, respectively. The steady state condition requires that the number of moles of a given species entering the sieve tube element equal the number of moles leaving so that

$$dn_{\mathrm{HA}}/dt = dn_{A^-}/dt = 0 \qquad \text{(A1)}$$

for every element along the length of the plant. For each such element there are three distinguishable surfaces through which xenobiotic may enter or exit. If phloem sap flow is from top to bottom (Fig. 4), xenobiotic may enter through the top circular face and exit through the bottom circular face. Additionally, it may permeate through the cylindrically shaped plasma membrane separating the apoplast from the living tissue of the sieve tubes.

Consider first the permeation of the membrane. We assume that once a given amount of either HA or A^- penetrates the lipid membrane, dissociation or association occurs instantaneously to the degree required to maintain the prevailing equilibrium in its environment (apoplast or sieve tube).

Permeation of neutral HA takes place under the influence of a concentration gradient, ($[\mathrm{HA}]_o - [HA]_s$), across the plasma membrane. Similarly, permeation of A^- is assumed to take place under the influence of a concentration gradient ($[A^-]_o - [A^-]_s$). $[\mathrm{HA}]_s$ and $[A^-]_s$ are concentrations at point s in the sieve tube, while $[\mathrm{HA}]_o$ and $[A^-]_o$ are concentrations in the surrounding apoplast. The concentrations $[\mathrm{HA}]_o$ and $[A^-]_o$ are assumed to be uniform within the application zone (*i.e.* within a distance l^* from the tip of the leaf). $[\mathrm{HA}]_o$ and $[A^-]_o$ are approximated as zero below the application zone. The rate of permeation of HA through the membrane is assumed to be proportional to the product of the concentration difference and the surface area Q of the cylinder surrounding the element:

$$(dn_{\mathrm{HA}}/dt)_{\mathrm{perm}} = P_{\mathrm{HA}}Q([\mathrm{HA}]_o - [\mathrm{HA}]_s) \qquad \text{(A2)}$$

The constant of proportionality P_{HA} is by definition the permeability of the membrane for the undissociated species HA and has the dimension of velocity. A similar equation can be written for the anion A^- with a permeability constant P_A. We usually take the permeability constant of the anion to be 3 to 4 orders of magnitude less than that of the undissociated conjugate acid. We do not explicitly take into account the effect of electric fields on the permeation of the charged species.

In order to maintain acid-base equilibrium within that portion of the sieve tube located in the leaf, only a certain fraction of the xenobiotic transported across the membrane into the sieve tube as HA can remain associated there and only a certain fraction of the xenobiotic transported as A^- can remain dissociated upon arrival. Similarly, in those regions of the plant below the point of application where the sieve tube is expected to leak xenobiotic, only a certain fraction of the xenobiotic transported across the membrane as HA can originate from undissociated HA, the remainder must arise from A^- which associates immediately before entering the membrane, and only a certain fraction of the xenobiotic transported across the membrane as A^- can originate from A^-, the remainder must arise from undissociated HA which dissociates immediately before entering.

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Table II. *Log C_f Values for a Standard Long Plant*[a]

C_f is defined as the total concentration of xenobiotic in the phloem at a point $0.9L$(L is the total length of the plant) divided by the total concentration in the apoplast at the point of application. A standard long plant is 1.0 m long, has a leaf length of 0.05 m, a sieve tube radius of 5.0e–06 m, and a maximum phloem sap velocity of 1.0e–04 m/s. The pH of the phloem is taken as 8.0 and that of the surrounding apoplast as 6.0. K_{ow} is the octanol-water partition coefficient of the undissociated acid.

Log K_{ow}	pK_a = 10	pK_a = 9	pK_a = 8	pK_a = 7	pK_a = 6	pK_a = 5	pK_a = 4	pK_a = 3	pK_a = 2	pK_a = 1
5.00	−2.97e + 09	−2.73e + 09	−1.50e + 09	−2.73e + 08	−2.98e + 07	−3.11e + 06	−4.09e + 05	−1.39e + 05	−1.12e + 05	−1.09e + 05
4.00	−1.87e + 08	−1.72e + 08	−9.48e + 07	−1.72e + 07	−1.88e + 06	−1.96e + 05	−2.58e + 04	−8.78e + 03	−7.07e + 03	−6.90e + 03
3.00	−1.18e + 07	−1.08e + 07	−5.98e + 06	−1.08e + 06	−1.18e + 05	−1.23e + 04	−1.62e + 03	−5.52e + 02	−4.45e + 02	−4.35e + 02
2.00	−7.48e + 05	−6.86e + 05	−3.77e + 05	−6.87e + 04	−7.50e + 03	−7.79e + 02	−1.00e + 02	−3.30e + 01	−2.70e + 01	−2.68e + 01
1.00	−4.71e + 04	−4.33e + 04	−2.38e + 04	−4.33e + 03	−4.71e + 02	−4.67e + 01	−4.36e + 00	−9.32e + 01	−1.36e + 00	−1.79e + 00
0.00	−2.97e + 03	−2.73e + 03	−1.50e + 03	−2.71e + 02	−2.76e + 01	−1.12e + 00	7.11e − 01	1.02e − 02	−8.42e − 01	−1.30e + 00
−1.00	−1.87e + 02	−1.71e + 02	−9.39e + 01	−1.57e + 01	−3.16e − 01	6.94e − 01	−8.96e − 02	−1.05e + 00	−1.93e + 00	−2.40e + 00
−2.00	−1.14e + 01	−1.04e + 01	−5.44e + 00	−4.31e − 01	3.15e − 01	−3.14e − 01	−1.26e + 00	−2.24e + 00	−3.12e + 00	−3.59e + 00
−3.00	−1.23e + 00	−1.17e + 00	−8.56e − 01	−5.72e − 01	−7.68e − 01	−1.50e + 00	−2.46e + 00	−3.44e + 00	−4.32e + 00	−4.79e + 00
−4.00	−1.70e + 00	−1.70e + 00	−1.68e + 00	−1.70e + 00	−1.96e + 00	−2.70e + 00	−3.66e + 00	−4.64e + 00	−5.52e + 00	−5.99e + 00
−5.00	−2.86e + 00	−2.86e + 00	−2.86e + 00	−2.90e + 00	−3.16e + 00	−3.90e + 00	−4.86e + 00	−5.84e + 00	−6.72e + 00	−7.19e + 00

[a] The notation e ± n means × $10^{\pm n}$. Thus, 5.06 e-06 means 5.06 × 10^{-6}.

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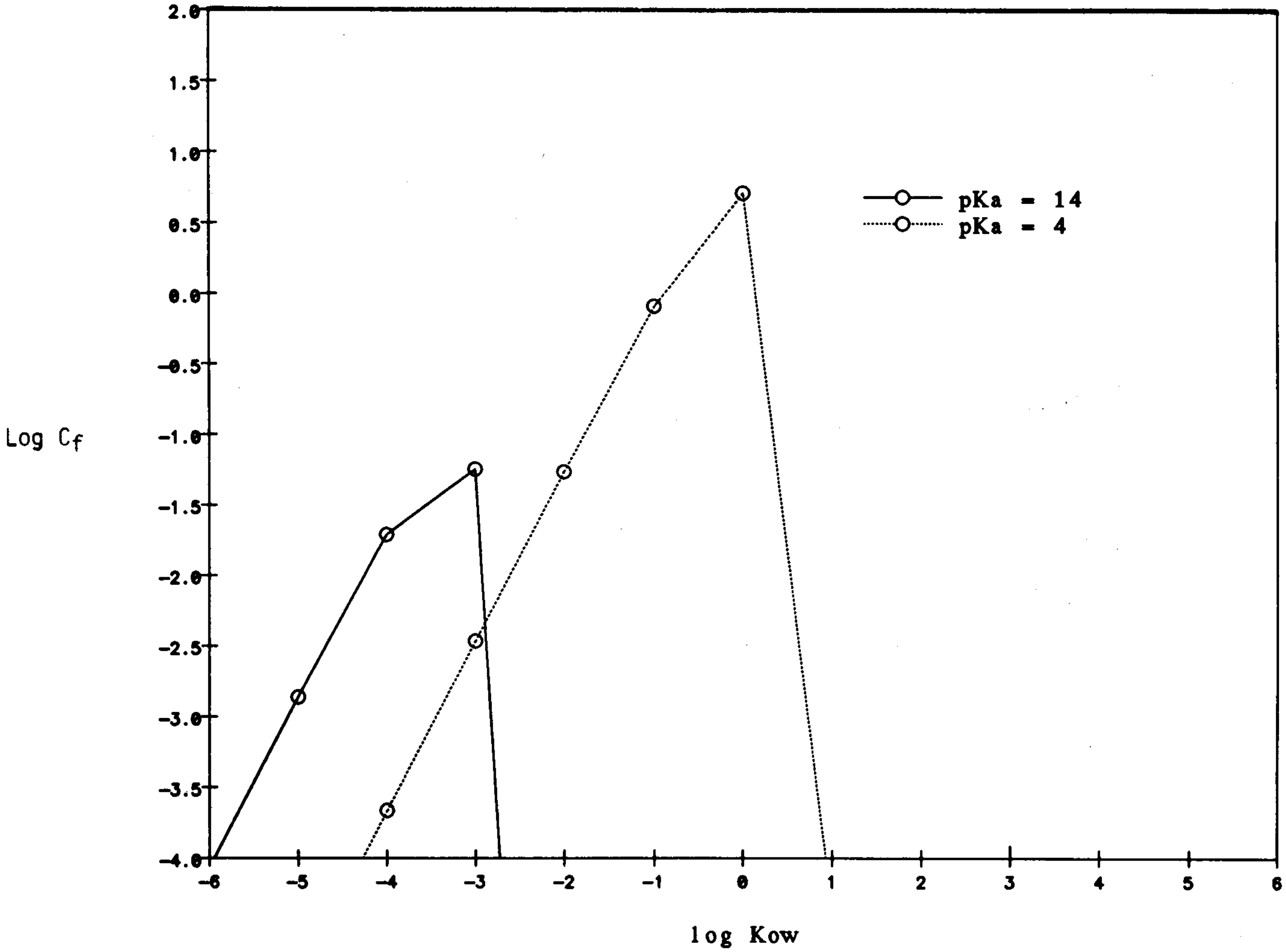

FIG. 2. Plot of the log C_f *versus* log K_{ow} for two values of the pK_a. C_f is the concentration factor (see text for definition). High values of C_f imply good mobility. K_{ow} is the octanol-water partition coefficient of the undissociated acid and K_a is the acid dissociation constant. These curves have been determined for a standard long plant with a length of 1.0 m, leaf length of 0.05 m, and phloem sap velocity of 0.0001 m/s. The pH of the phloem sap was taken as 8.0 and that of the surrounding tissue as 6.0.

Since the phloem is assumed to be buffered, these fractions are determined by the requirement that $[\mathrm{HA}]_s/[A^-]_s = [\mathrm{H}^+]_s/K_a$ remain unchanged after transport of an aliquot of xenobiotic. Thus, the effective rate of transport of neutral HA due to permeation of both HA and A^- is given by

$$(dn_{\mathrm{HA}}/dt)_{\mathrm{perm}} =$$
$$P_{\mathrm{HA}}Q([\mathrm{HA}]_o - [\mathrm{HA}]_s) \times \{[\mathrm{HA}]_s/([\mathrm{HA}]_s + [A^-]_s)\}$$
$$+ P_AQ([A^-]_o - [\mathrm{A}^-]_s) \times \{[\mathrm{HA}]_s/([\mathrm{HA}]_s + [A^-]_s)\}$$

The first term accounts for the rate change of n_{HA} due to permeation of *HA* while the second term accounts for the rate change of n_{HA} due to permeation of A^-. Within the application zone the factor in braces in the first term represents the fraction of HA which remains associated after permeation into the sieve tube and the factor in braces in the second term represents the fraction of A^- which associates after permeation into the sieve tube. Below the application zone the factor in braces in the first term represents the fraction of outward permeating HA which originates from associated *HA* and the factor in braces in the second term represents the fraction of outward permeating A^- which originates from associated HA.

Use of the equilibrium relationship, $K_a = [\mathrm{H}^+]_s[A^-]_s/[\mathrm{HA}]_s = [\mathrm{H}^+]_o[A^-]_o/[\mathrm{HA}]_o$, division by the volume of the sieve tube element, $V = \pi r^2 ds$, and use of the expression $Q = 2\pi r ds$, for the surface area of the cylinder surrounding the element then yields the following equation for the permeation rate:

$$(d[\mathrm{HA}]_s/dt)_{\mathrm{perm}} = \{(P_{\mathrm{HA}} + (P_AK_a/[H^+]_o))[HA]_o - (P_{\mathrm{HA}} + (P_AK_a/[\mathrm{H}^+]_s))[\mathrm{HA}]_s\} \times (2/r)/\{1 + (K_a/[\mathrm{H}^+]_s)\} \quad \text{(A3)}$$

The rate change in concentration due to entry of xenobiotic from the top face of the element and exit from the bottom face is given by:

$$d[\mathrm{HA}]_s/dt = -v_s(d[\mathrm{HA}]_s/ds) - [\mathrm{HA}]_s(dv_s/ds) \quad \text{(A4)}$$

Here V_s is the flow velocity of the phloem sap at point s in the sieve tube. Combining Eqs. A3 and A4 and using the steady state assumption $d[\mathrm{HA}]_s/dt = 0$ yields the following differential equation:

$$\{(P_{\mathrm{HA}} + (P_AK_a/[\mathrm{H}^+]_o))[\mathrm{HA}]_o - (P_{\mathrm{HA}} + (P_AK_a/[\mathrm{H}^+]_s))[\mathrm{HA}]_s\} \times (2/r)/\{1 + (K_a/[\mathrm{H}^+]_s)\} - v_s(d[\mathrm{HA}]_s/ds) - [\mathrm{HA}]_s(dv_s/\mathrm{ds}) = 0 \quad \text{(A5)}$$

Multiplying Eq. A5 by minus one and using the following symbols

$$K_i = 1/\{1 + K_a/[\mathrm{H}^+]_s\}$$
$$P_o = P_{\mathrm{HA}} + (P_AK_a/[\mathrm{H}^+]_o)$$
$$P_s = P_{\mathrm{HA}} + (P_AK_a/[\mathrm{H}^+]_s)$$

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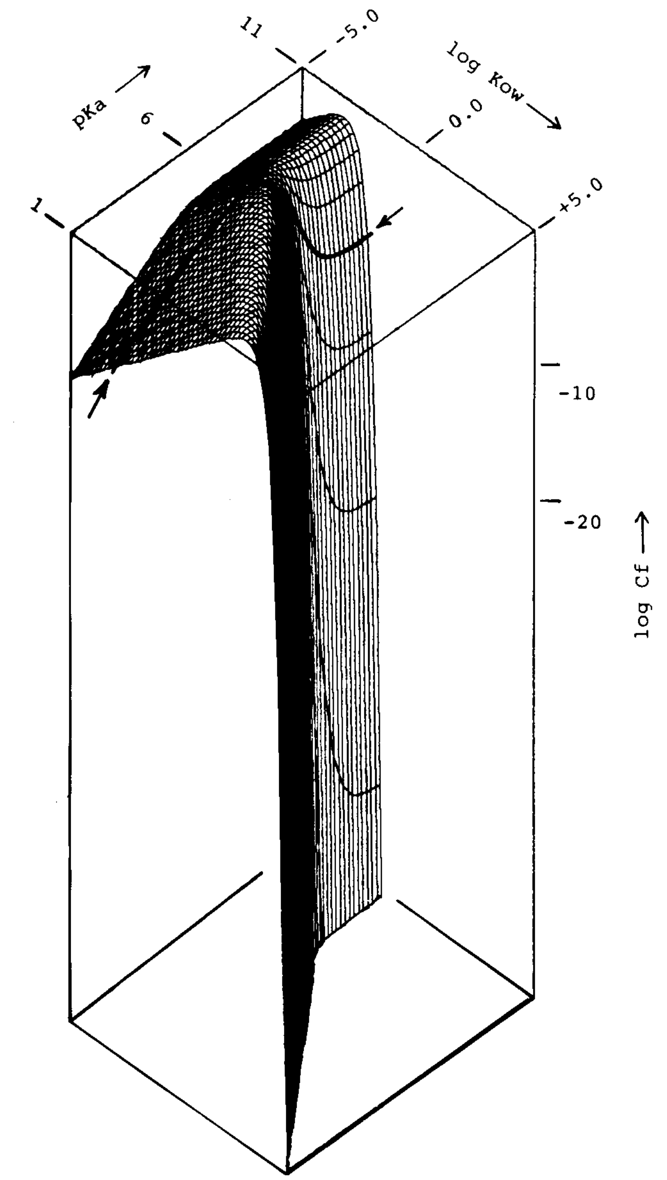

FIG. 3. Plot of log C_f *versus* log K_{ow} and pK_a. This surface has been calculated for a standard long plant with a length of 1.0 m, leaf length of 0.05 m, and phloem sap velocity of 0.0001 m/s. The pH of the phloem sap was taken as 8.0 and that of the surrounding tissue as 6.0. For this plot the permeability of the conjugate base A^- was assumed to be zero. K_{ow} is the partition coefficient for the undissociated acid. The surface is reminiscent of a waterfall viewed from above and to the side. Nonacidic compounds (follow curve on back edge for $pK_a = 11$) with log K_{ow} values close to -3 are near the lip of the falls. Increasing log K_{ow} beyond -3.0 sends the predicted log C_f value plunging over the lip of the falls and into the abyss of neoapoplastic compounds. The arrows point to the ends of a curve on the surface with a constant log K_{ow} value of -2.0. Moving from the front edge ($pK_a = 1.0$) to the back edge ($pK_a = 11$) along this curve involves slowly climbing to higher log C_f values, reaching the lip at a pK_a value of approximately 6.0, then plunging into the abyss for pK_a values greater than 6.0. Following this curve in the direction described is equivalent to following the row of Table II labeled log $K_{ow} = -2$ from right to left.

yields an equation very similar to Eq. 1 of Tyree *et al.* (8):

$$(2K_i/r)(P_s[HA]_s - P_o[HA]_o) + v_s(d[HA]_s/ds) + [HA]_s(dv_s/ds) = 0 \quad (A6)$$

Eq. A6 is the working differential equation of this model. Solution of this equation following Tyree yields the following expression for the concentration of HA at point $s = 0.9L$ which is 90% of the length of the plant from the leaf tip:

$$[HA]_{0.9L}/[HA]_o = \{aK_iP_o/(K_iP_s + b)\} \times \exp(-cK_iP_s) \quad (A7)$$

where *a, b,* and *c* are defined in the Theory section above.

The equilibrium condition requires $[A^-]_{0.9L} = K_a[HA]_{0.9L}/[H^+]_{0.9L}$. Thus,

$$[A^-]_{0.9L}/[HA]_o = \{K_a/[H^+]_{0.9L}\} \times \{aK_iP_o/(K_iP_s + b)\} \times \exp(-cK_iP_s) \quad (A8)$$

If we define the concentration factor C_f as the ratio of xenobiotic in the sieve tube at $s = 0.9L$ to that of the xenobiotic in the apoplast of the leaf, we obtain

$$\begin{aligned} C_f &= ([HA]_{0.9L} + [A^-]_{0.9L})/([HA]_o + [A^-]_o) \\ &= \{[H^+]_o/([H^+]_o + K_a)\} \quad (A9) \\ &\quad \times \{([HA]_{0.9L} + [A^-]_{0.9L})/[HA]_o\} \end{aligned}$$

where we have used $[A^-]_o = K_a[HA]_o/[H^+]_o$. Substituting Eqs. A7 and A8 into Eq. A9 and replacing K_i, P_s, and P_o with their definitions gives Eq. 1.

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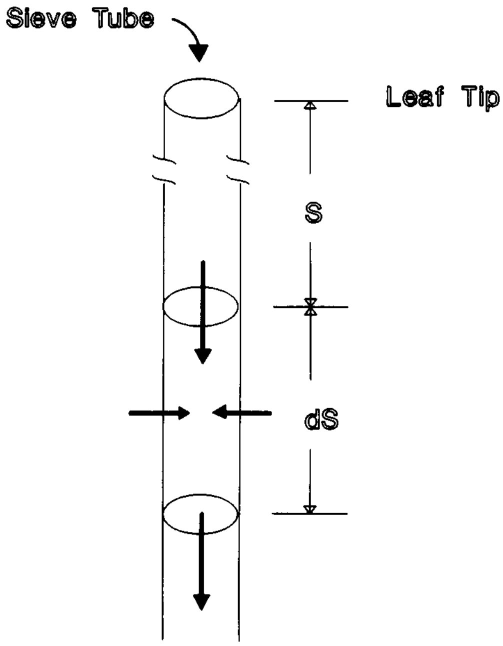

FIG. 4. A sieve tube element within the leaf. The sieve tube element has a length *ds* and is located at a distance *s* from the leaf tip. Xenobiotic which has been applied to the leaf is carried into the sieve tube element by mass flow of the sap from above and by permeation through the cylindrical walls. Xenobiotic leaves the sieve tube element from the bottom by mass flow. In the steady state the amount entering the sieve tube from above by mass flow and through the walls by permeation is equal to the amount leaving the sieve tube from below by mass flow.

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Table III. *Log C_f Values for a Standard Long Plant*[a]

C_f is defined as the total concentration of xenobiotic in the phloem at a point 0.9*L* (*L* is the total length of the plant) divided by the total concentration in the apoplast at the point of application. A standard long plant is 1.0 m long, has a leaf length of 0.05 m, a sieve tube radius of 5.0e–06m, and a maximum phloem sap velocity of 1.0e–04 m/s. The pH of both the phloem sap and the surrounding apoplast is taken as 7.0. K_{ow} is the partition coefficient for the undissociated acid.

Log K_{ow}	$pK_a = 10$	$pK_a = 9$	$pK_a = 8$	$pK_a = 7$	$pK_a = 6$	$pK_a = 5$	$pK_a = 4$	$pK_a = 3$	$pK_a = 2$	$pK_a = 1$
5.00	−3.00e + 09	−2.97e + 09	−2.73e + 09	−1.50e + 09	−2.73e + 08	−2.98e + 07	−3.11e + 06	−4.09e + 05	−1.39e + 05	−1.12e + 05
4.00	−1.89e + 08	−1.87e + 08	−1.72e + 08	−9.48e + 07	−1.72e + 07	−1.88e + 06	−1.96e + 05	−2.58e + 04	−8.78e + 03	−7.07e + 03
3.00	−1.19e + 07	−1.18e + 07	−1.08e + 07	−5.98e + 06	−1.08e + 06	−1.18e + 05	−1.23e + 04	−1.63e + 03	−5.53e + 02	−4.46e + 02
2.00	−7.54e + 05	−7.48e + 05	−6.86e + 05	−3.77e + 05	−6.87e + 04	−7.50e + 03	−7.81e + 02	−1.02e + 02	−3.44e + 01	−2.76e + 01
1.00	−4.76e + 04	−4.71e + 04	−4.33e + 04	−2.38e + 04	−4.33e + 03	−4.72e + 02	−4.87e + 01	−6.22e + 00	−2.28e + 00	−1.93e + 00
0.00	−3.00e + 03	−2.97e + 03	−2.73e + 03	−1.50e + 03	−2.72e + 02	−2.93e + 01	−3.06e + 00	−1.15e + 00	−1.33e + 00	−1.40e + 00
−1.00	−1.88e + 02	−1.87e + 02	−1.71e + 02	−9.42e + 01	−1.67e + 01	−2.01e + 00	−1.24e + 00	−1.95e + 00	−2.40e + 00	−2.49e + 00
−2.00	−1.15e + 01	−1.14e + 01	−1.04e + 01	−5.73e + 00	−1.43e + 00	−1.38e + 00	−2.25e + 00	−3.12e + 00	−3.59e + 00	−3.68e + 00
−3.00	−1.24e + 00	−1.24e + 00	−1.21e + 00	−1.15e + 00	−1.57e + 00	−2.47e + 00	−3.44e + 00	−4.32e + 00	−4.79e + 00	−4.88e + 00
−4.00	−1.70e + 00	−1.71e + 00	−1.74e + 00	−1.98e + 00	−2.70e + 00	−3.66e + 00	−4.64e + 00	−5.52e + 00	−5.99e + 00	−6.08e + 00
−5.00	−2.86e + 00	−2.86e + 00	−2.90e + 00	−3.16e + 00	−3.90e + 00	−4.86e + 00	−5.84e + 00	−6.72e + 00	−7.19e + 00	−7.28e + 00

[a] The notation e ± *n* means × $10^{\pm n}$. Thus, 5.0 e − 06 means 5.0 × 10^{-6}.

Table IV. *Log C_f Values for a Standard Short Plant*[a]

C_f is defined as the total concentration of xenobiotic in the phloem at a point 0.9*L* (*L* is the total length of the plant) divided by the total concentration in the apoplast at the point of application. A standard short plant is 0.15 m long, has a leaf length of 0.05 m, a sieve tube radius of 5.0e–06 m, and a maximum phloem sap velocity of 3.0e–04 m/s. The pH of the phloem sap is taken as 8.0 and that of the surrounding apoplast is taken as 6.0. K_{ow} is the partition coefficient of the undissociated acid.

Log K_{ow}	$pK_a = 10$	$pK_a = 9$	$pK_a = 8$	$pK_a = 7$	$pK_a = 6$	$pK_a = 5$	$pK_a = 4$	$pK_a = 3$	$pK_a = 2$	$pK_a = 1$
5.00	−1.15e + 08	−1.05e + 08	−5.82e + 07	−1.05e + 07	−1.15e + 06	−1.20e + 05	−1.58e + 04	−5.38e + 03	−4.34e + 03	−4.23e + 03
4.00	−7.27e + 06	−6.67e + 06	−3.67e + 06	−6.68e + 05	−7.29e + 04	−7.60e + 03	−9.98e + 02	−3.38e + 02	−2.72e + 02	−2.66e + 02
3.00	−4.58e + 05	−4.21e + 05	−2.31e + 05	−4.21e + 04	−4.60e + 03	−4.77e + 02	−6.06e + 01	−1.94e + 01	−1.60e + 01	−1.61e + 01
2.00	−2.89e + 04	−2.65e + 04	−1.46e + 04	−2.65e + 03	−2.88e + 02	−2.76e + 01	−1.54e + 00	4.07e − 01	−1.63e − 01	−6.01e − 01
1.00	−1.82e + 03	−1.67e + 03	−9.21e + 02	−1.66e + 02	−1.59e + 01	5.11e − 01	1.52e + 00	7.64e − 01	−9.44e − 02	−5.61e − 01
0.00	−1.14e + 02	−1.05e + 02	−5.72e + 01	−8.93e + 00	9.22e − 01	1.46e + 00	6.38e − 01	−3.29e − 01	−1.20e + 00	−1.67e + 00
−1.00	−6.63e + 00	−6.01e + 00	−2.80e + 00	5.69e − 01	1.06e + 00	4.11e − 01	−5.41e − 01	−1.52e + 00	−2.40e + 00	−2.87e + 00
−2.00	−3.30e − 01	−2.83e − 01	−4.62e − 02	1.65e − 01	−4.43e − 02	−7.79e − 01	−1.73e + 00	−2.72e + 00	−3.60e + 00	−4.07e + 00
−3.00	−9.75e − 01	−9.73e − 01	−9.61e − 01	−9.82e − 01	−1.23e + 00	−1.97e + 00	−2.93e + 00	−3.92e + 00	−4.80e + 00	−5.27e + 00
−4.00	−2.13e + 00	−2.13e + 00	−2.14e + 00	−2.17e + 00	−2.43e + 00	−3.17e + 00	−4.13e + 00	−5.12e + 00	−6.00e + 00	−6.47e + 00
−5.00	−3.33e + 00	−3.33e + 00	−3.34e + 00	−3.37e + 00	−3.63e + 00	−4.37e + 00	−5.33e + 00	−6.32e + 00	−7.20e + 00	−7.67e + 00

[a] The notation e ± *n* means × $10^{\pm n}$. Thus, 5.0 e − 06 means 5.0 × 10^{-6}.

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